Chapter 5

Hydrogeologic Investigations of Groundwater Contamination

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CHAPTER OVERVIEW

This chapter describes the current status of hydrogeologic investigations. The first section, The *Conduct of Hydrogeologic Investigations,* summarizes the general approach used for investigations, describes the two primary driving forces of investigations (i. e., site conditions and objectives), and discusses the design of investigations in terms of information requirements, techniques, and monitoring networks. (This section is based on GeoTrans, Inc., 1983a, unless otherwise indicated.) The second section, *Approaches for Minimizing Difficulties With Groundwater Contamination Investigations,* discusses reliability of data collection and interpretation.

The conclusions that follow are based on this information.

Hydrogeologic investigations play an integral role in understanding and evaluating groundwater contamination regardless of the policy objective (i.e., whether to detect, correct, or prevent contamination). The techniques for obtaining information on hydrogeologic conditions and groundwater quality are now generally available.

Because of the inherent difficulties in dealing with the subsurface (e. g., its inaccessibility to direct observation), there will always be some degree of uncertainty about contaminants—which substances are present and at what concentrations, where they are going, and how fast they are moving. The nature and degree of the uncertainty vary according to such factors as the hydrogeologic environment, types of contaminants, the number and history of the sources involved, and the type of techniques used. Under most circumstances, the uncertainties can be reduced, although not eliminated, to obtain reliable results. The uncertainties are most often reduced by combining complementary techniques and/or collecting increasingly detailed site information. These strategies, however, usually increase the costs of and/or time for an investigation. The impacts of uncertainties on decisionmaking can be minimized by making conservative assumptions and conducting sensitivity analyses.

Design and implementation of investigations are highly dependent both on site-specific conditions and on the specific objective to be achieved at a site (i.e., detection, correction, or prevention). The site- and objective-specific nature of groundwater contamination problems requires that investigations be tailored to each individual problem. It is thus impractical to standardize requirements for hydrogeologic investigations (e. g., with respect to the number or location of monitoring wells). The burden of performing reliable hydrogeologic investigations falls on those responsible for obtaining, interpreting, and applying results; and the required skilled personnel are in short supply.

Many techniques are available for analyzing contaminants once a groundwater sample has been obtained. Generally, the techniques *identify contaminants* and *quantify their concentrations,* but they also introduce a bias in terms of which of the contaminants present are detected. *Behavioral properties* of contaminants (e. g., mobility and toxicity), on the other hand, cannot be measured directly and thus must be deduced from indirect information, experience, and judgment. Understanding the behavior of contaminants is important for detection, correction, and prevention of problems.

THE CONDUCT OF HYDROGEOLOGIC INVESTIGATIONS

General Approach of Investigations

Hydrogeologic investigations are the process for collecting and analyzing information on the presence and behavior of contaminants in the subsurface. This knowledge is obtained primarily by collecting and analyzing data on the *hydrogeologic environment* (to ascertain the rate and direction of groundwater flow and help predict contaminant behavior) and on *groundwater quality* (to ascertain the presence and concentrations of contaminants). Investigations are simplified if information about the nature and location of *sources of contamination* is known and if information is available on the *properties of contaminants* likely to be found. Knowledge of contaminant properties is helpful, for example, in determining how fast contaminants move relative to groundwater flow or if they move independently of flow.

Hydrogeologic investigations usually involve the design and operation of a groundwater quality monitoring network to collect data on the behavior of contaminants in the subsurface in order to satisfy detection, correction, or prevention objectives.[1] For example, to detect contamination from a potential source, understanding the behavior of expected contaminants is required to determine where contamination is most likely to be found. To correct a problem, understanding contaminant behavior is necessary to determine the nature and extent of the problem and to predict responses to alternative corrective measures. To prevent contamination, understanding contaminant behavior is necessary to select, design, and evaluate preventive measures.

Key issues in the design of monitoring systems are: what information is required, what techniques are applicable for obtaining this information, what should be the number and location of measuring points, and how frequently should samples be collected. Answers to these questions depend on conditions at the site and the objectives to be achieved.

Hydrogeologic investigations of groundwater contamination problems rely on many of the same techniques (e. g., groundwater exploration, aquifer testing, geochemistry, and mathematical modeling of groundwater flow) developed in the past 60 years to evaluate groundwater resources for supply purposes. These hydrogeologic techniques were developed primarily to evaluate permeable and saturated geologic units (e. g., aquifers) covering extensive areas, most often at the county or regional scale. For investigations of contamination, the scale is usually much smaller; and low permeability units, which can act as a barrier to contaminant migration, and the unsaturated zone, which can retain contaminants for long periods, can be very significant. Data that were historically collected and analyzed only in special research studies must be obtained routinely in investigations of contamination.

Many simplifying assumptions often used in groundwater supply investigations (e. g., that the vertical component of flow is not significant; that flow in fractured media can be approximated by an equivalent porous media; and that the unsaturated zone is of minor importance) are often not applicable in groundwater contamination investigations. As a result, the costs and time required for these hydrogeologic investigations are higher than those for water supply investigations. In addition, the investigation of contamination requires more precise well drilling and water quality sampling.

Site Conditions

There are inherent difficulties in obtaining information on an environment that not only is mostly inaccessible to direct observation but is also extremely variable in both space (i. e., the hydrogeology at a single site may be complex and non-uniform) and time (i. e., the rate and direction of groundwater flow and groundwater quality are not constant). Each site will have a unique combination of characteristics including:[2]

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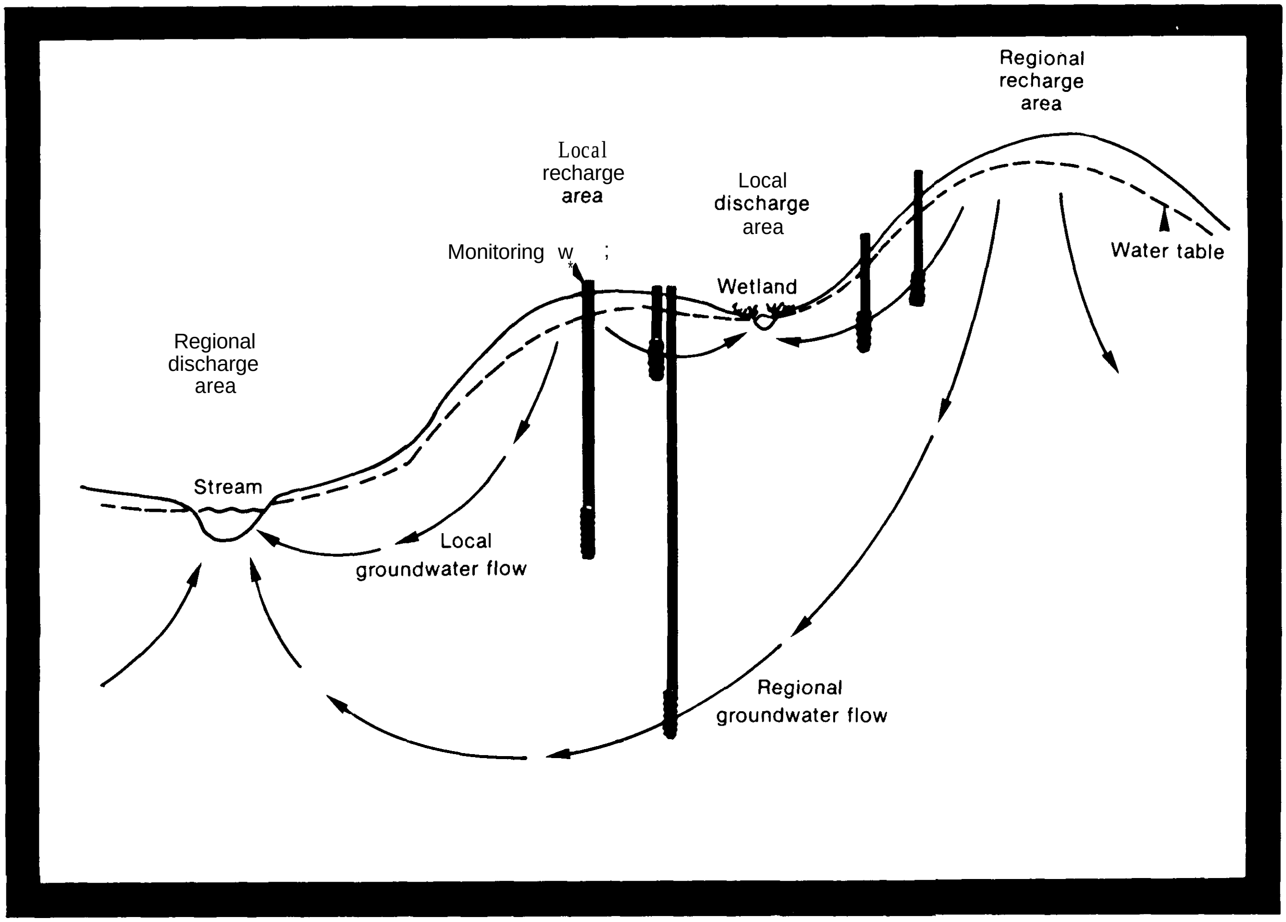
[1] For sample discussions of methodologies for hydrogeologic investigations, see Todd, et al., 1976; Wood, et al., 1984; and GeoTrans, Inc., 1983b.

[2] Listing is based on discussion by Keith, et al., 1982a.



Credit: Geraghty & Miller, 1983

Regional groundwater flow is of primary interest in evaluating the water supply potential of an aquifer; local groundwater flow is of primary concern in investigations of contamination.

- sources of contaminants (e. g., associated types of contaminants and release patterns);
- the hydrogeologic environment (e. g., topography, vegetation, climate, geology, surface and subsurface hydrology, unsaturated zone, and contaminant transport parameters); and
- groundwater use (e. g., effects of pumping rates and schedules on groundwater flow).

To have confidence that the interpretation of information in hydrogeologic investigations reflects actual conditions in the subsurface, some investigations require more detailed information than others on the hydrogeologic environment and groundwater quality, More detailed information is required at sites where: the hydrogeologic environment is very complex (e. g., heterogeneous or fractured aquifers v. uniform or simple aquifers), the contaminants present do not move with groundwater flow (e. g., the presence of immiscible v. miscible contaminants), and information is limited about which contaminants are present, contaminant properties, and sources and their contaminant release characteristics.

Objectives

The different purposes of hydrogeologic investigations—detection, correction, and prevention—are presented in table 24. As shown, the design and operation of a monitoring effort will vary according to the objective to be achieved, the steps to be taken to meet the objective, and the type of pro-

Table 24.—Elements of Groundwater Protection and Topics for Hydrogeologic Investigations

Detection	Correction	Prevention
Objectives		
Identify/quantify existing contamination	Characterize nature and extent of contamination	Identify potential for future contamination
Characterize nature and extent of contamination	Reduce/eliminate existing groundwater contamination	Hinder/prohibit contaminants from entering subsurface
Assess impacts	Assess/reduce/eliminate impacts of groundwater contamination	Assess/reduce/eliminate impacts of future contamination
Steps in meeting objectives		
Evaluate detection options—assess their applicability and potential impacts	Evaluate both technology- and management-based corrective action options — assess their applicability and potential impacts	Evaluate preventive action measures — assess their applicability and potential impacts
Select detection measures and design system	Select and design corrective action measures	Select and design preventive measures
Implement detection system	Implement corrective action stragtegy	Implement preventive measures
Evaluate performance	Evaluate performance	Evaluate performance
Programs		
Monitor sources	Correct sources that are causing contamination	Prevent sources from causing contamination
Monitor supplies	Correct supplies (uses) that are contaminated	Prevent supplies from becoming contaminated
Monitor groundwater resources (e.g., ambient quality)	Correct groundwater resources that are contaminated	Prevent groundwater resources from becoming contaminated
Inventory sources		

SOURCE: Office of Technology Assessment

gram to be implemented.[3] Examples of how these three elements influence the need for information about the hydrogeologic environment and water quality in a hydrogeologic investigation is described below.

Objective. At a given site, an objective to detect contamination will generally require less detailed water quality information than an investigation to correct contamination. For example, in a detection investigation it may be sufficient to define the boundaries of a contaminated area; in a correction investigation, more detailed information about variations in contaminant concentrations within the area may be necessary to evaluate correction alternatives.

Steps. Steps in meeting an objective also influence the level of detail to be obtained about water quality and the hydrogeologic environment. Investigations to evaluate the feasibility of options generally require less detailed information than investigations to select and design the action.

Program. Different kinds of programs may require different kinds of information. A detection program for water supplies may be limited to identification and quantification of contaminants in public water supplies, as required under the Safe Drinking Water Act. Monitoring under such a program is relatively straightforward because the measuring points are defined as the existing water supply wells, and the type of information required is water quality data. There is no need to evaluate the hydrogeologic environment to determine where to collect samples. However, samples taken without information about the hydrogeologic environment and associated flow system provide only a single snapshot of water quality-at the place and at the time the sample is collected; they cannot be used either to predict whether water quality is likely to change or to indicate the location of the source of contamination. Alternatively, a detection program

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[3] Other factors, such as different motivations for conducting investigations (e. g., a State environmental program investigating threats to public health; an industry complying with regulatory requirements; and an industry investigating potential liabilities associated with known contamination), also influence the nature of the investigation in terms of funds, time, and expertise that are devoted to the task.

to determine whether a source is in fact contaminating groundwater requires information on the hydrogeologic environment near the source—in addition to the collection and analysis of water quality samples —in order to identify areas that are most likely to show evidence of contamination.

Design of Hydrogeologic Investigations of Groundwater Contamination

Information Requirements

Contamination investigations require information on the hydrogeologic environment, water quality, sources of contamination, and properties of contaminants, as shown in table 25.[4] The importance of this information in understanding the behavior of subsurface contaminants is also presented in table 25. The major points of the table are summarized below:

- The *primary purposes* for collecting hydrogeologic data are to determine the rate and direction of groundwater flow, evaluate the types of contaminants likely to be found, and determine whether the contaminants and the groundwater are likely to be moving at the same rate and direction.
- *Information on the hydrogeologic environment* (i. e., surface conditions—topography, vegetation, climate and surface water hydrology; geology; and subsurface hydrology—unsaturated zone, groundwater hydrology, contaminant transport parameters, and groundwater use) is obtained primarily to describe the flow of groundwater. Evaluating flow involves the collection of data on the quantity, timing, rate, direction, and pathways of water moving from the surface through the unsaturated zone and into and through the saturated zone.

  Information about the hydrogeologic environment is important in understanding whether contaminants will move at the same rate as groundwater or if physical, chemical, and/or biological processes are likely to occur that will cause them to move at different rates.[5] Analysis of the physical, chemical, and biological properties of the hydrogeologic environment, along with information on the properties of contaminants, is needed to evaluate the behavior of contaminants in the subsurface.

  The hydrogeologic environment is dynamic, and information on spatial and temporal variations is also important to assess contamination problems accurately. Some human activities can influence the flow of groundwater (e. g., pumping groundwater for use can alter the direction of flow, and modifications to the land surface can alter the amount of water infiltrating to the groundwater system).
- *Information on water quality is* collected primarily to determine the nature and/or verify the extent of contamination. Water quality information also contributes to knowledge of the nature and rate of chemical and biological reactions that influence contaminant behavior.
- *Information on sources* of contamination is useful in predicting the types of contaminants likely to be present, their locations, and their concentrations. When interpreted along with data on groundwater flow and associated contaminant behavior, source data can be used to predict the location, rate, and direction of contaminant movement. Knowledge of sources aids in determining the area to be in-

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[4] Hydrogeologic terms are defined in app. D.

[5] Chemical and biological processes can alter the rate of contaminant movement, change contaminant concentrations, and transform the contaminants that are present. These processes are a function of both the properties and concentrations of the contaminants present and the properties of the hydrogeologic environment (i. e., the unsaturated and saturated zones). Chemical processes include: adsorption-desorption, oxidation-reduction, acid-base, solution-precipitation, ion pairing or complexation reactions; and radioactive decay. Chemical processes are least significant in clean sand aquifers and some crystalline environments. Biological processes may be direct (e. g., enzyme activity) or indirect (e. g., production of metabolizes; alteration of pH and Eh conditions; and provision of a surface for the accumulation and concentration of contaminants). Biological processes may result in the uptake, decay, or transformation of organic materials or the generation of additional contaminants. These processes can be particularly confusing in investigations of a source when information is available on the original contaminants but not on their altered states. For example, biological processes can transform trichloroethylene (TCE) to vinyl chloride, tetrachloroethylene to trichloroethylene, and heptachlor to heptachlor epoxide (McCarty, 1984). Biological processes are most significant in zones of higher oxygen availability and larger pore spaces, such as the unsaturated zone.

Physical processes include dispersion, whereby dissolved contaminants spread in ways that would not be predicted if the contaminants were moving only with the groundwater. Dispersion is a function of the hydrogeologic environment. It is independent of the properties of the contaminant. Dispersion results in an apparent faster movement of contaminants, relative to the average groundwater flow, at lower concentrations. Dispersion is especially important in fractured systems.

Table 25.—importance of Information Used in Hydrogeologic Investigations[a]

Information obtained for hydrogeologic investigations[b]	Importance of information for understanding contaminant behavior in subsurface
L information on the hydrogeologic environment	
A. Topographic data	Provide partial information on flow (i.e., rate, directions, and pathways of unsaturated zone and groundwater flow and relationship of groundwater to surface water including: relative position of water levels in wells, locations of possible discharge and recharge areas, rates of infiltration and surface runoff, and general direction of groundwater flow).
B. Vegetative data	Provide partial information on flow (i.e., rate and pathways of water movement into and out of the subsurface). Also vegetation type and condition may reflect the quality of groundwater and be used to identify areas of contamination. Used to estimate depth to water table and identify possible discharge and recharge areas.
C. Climatic data (precipitation; evapotranspiration; site temperature)	Provide partial information on flow (i.e., the quantity, timing, and rate of movement of water and contaminants into the subsurface). Provide basic information to assess rate of reactions and biodegradation of contaminants.
D. Geologic data (surficial deposits; subsurface stratigraphy; lithology; structural geology)	Provide partial information on flow (i.e., location and volumes of potential groundwater supplies, pathways for water and contaminant movement into and out of underlying formations, and direction and rate of groundwater movement) and are used to identify possible recharge and discharge areas. Also, provide partial information on mechanical dispersion (mixing) and attenuation reactions of contaminants.
E. Surface hydrology data (overland flow; stream discharge; stage; recurrence interval; baseflow discharge)	Provide partial information on flow (i.e., quantity, rate, and timing of water movement into and out of subsurface). Used to identify and quantify possible discharge and recharge areas, and to identify potential conduits for contamination. Surface water may affect concentrations of contamination at discharge points.
F. Unsaturated zone data (water table; geometry; hydraulic properties: effective porosity, effective permeability, relative permeability, permeability, specific storage; flow parameters: pressure head, hydraulic gradient, fluid saturation; recharge/discharge: surface water characteristics, precipitation/evapotranspiration)	Provide partial information on flow (i.e., on the flow regime which influences the rate, direction, and quantity of water and contaminants moving from the surface into the saturated zone). Usually relatively unimportant in the humid areas such as the Eastern United States.
G. Groundwater hydrology (Saturated Zone) data (aquifer characterization: confined aquifers, unconfined aquifers, leaky aquifers; hydraulic parameters of aquifers: storativity, transmissivity, primary permeability, secondary permeability, primary porosity, secondary porosity; confining unit geometry; hydraulic parameters of confining units: hydraulic conductivity, specific storage; flow parameters: water levels, hydraulic gradient, flow velocity; recharge/discharge: surface water characteristics, precipitation contributions, confining layer leakage, fracture/matrix flux)	Provide partial information on flow (i.e., the rate, direction, and quantity, of groundwater and contaminant flow). Also, provide partial information on recharge and discharge characteristics.
H. Contaminant transport parameters (distribution coefficient; dispersivity coefficient; flow velocities; relative saturations; cation exchange capacity; subsurface mineralogy; ambient water chemistry; microbiology)	Provide partial information on properties of the hydrogeologic environment that influence the potential for physical, chemical, and biological reactions that result in contaminants moving at different rates than water through the groundwater flow system.

Table 25.—importance of Information Used in Hydrogeologic Investigations[a]—continued

Information obtained for hydrogeologic investigations[b]	Importance of information for understanding contaminant behavior in subsurface
1. Groundwater use (current usage; projected usage)	Provides partial information on flow (i.e., the influence of groundwater pumping on the rate and direction of groundwater and contaminant flow). Also provides information on impacts of contamination.
II. Information on water quality (contaminants present; concentrations)	Provides data on concentrations and distribution of contaminants.
III. Information on sources of contamination (location; contaminants; release characteristics: location, volumes, contaminants, concentrations, timing) timing)	Provides data on types of contaminants that are likely to be present, requirements for collecting and analyzing samples, and suitability of different types of corrective action. Also provides data on flow (i.e., used to describe and predict the rate and direction of contaminant movement and the location of contaminants).
Iv. Information on properties of contaminants	
A. **Molecular-based properties**	Provide information to identify which contaminants are present and at what concentrations.
B. Media-based properties	Provide information used as a basis for deducing contaminant behavior (e.g., persistence and mobility).

[a] Based on GeoTrans, Inc., 1983b

b Hydrogeologic terms are defined In app D 1

SOURCE Off Ice of Technology Assessment

vestigated, the sites for collecting water quality samples, and sampling and analysis procedures.

- *Information on properties of contaminants* is important in understanding the rate and direction of contaminant movement, the location of contaminants relative to the water table and less permeable units, the persistence of the contaminants in the subsurface, and the types of techniques that can be used to detect, correct, and prevent contamination.

  The properties of contaminants that are most important for their detection in the subsurface relate to volubility. Hydrogeologic investigations of contaminants that are only slightly soluble (immiscible) require more information on the hydrogeologic environment and water quality than may be needed to describe contaminants that move with groundwater flow, Immiscible fluids that are also more dense than groundwater (e. g., many industrial solvents) may move in a different direction than groundwater flow. Immiscible fluids that are less dense than water (e. g., many petroleum products) tend to float on top of the water table and may require water quality sampling in the unsaturated zone.

Although all the hydrogeologic information shown in table 25 is useful for accomplishing investigation objectives for most site conditions, the **amount and types of information collected in practice is limited because of the time and costs of obtaining and analyzing data. The information collected varies, depending on site conditions and study objectives.** Examples of different information needs according to objectives were discussed in the preceding section on *Objectives.* The major site conditions that determine the information to be collected relate to the complexity of the hydrogeologic environment, the climate, the number of potential contamination sources, and knowledge of the behavior of the contaminants.[c]

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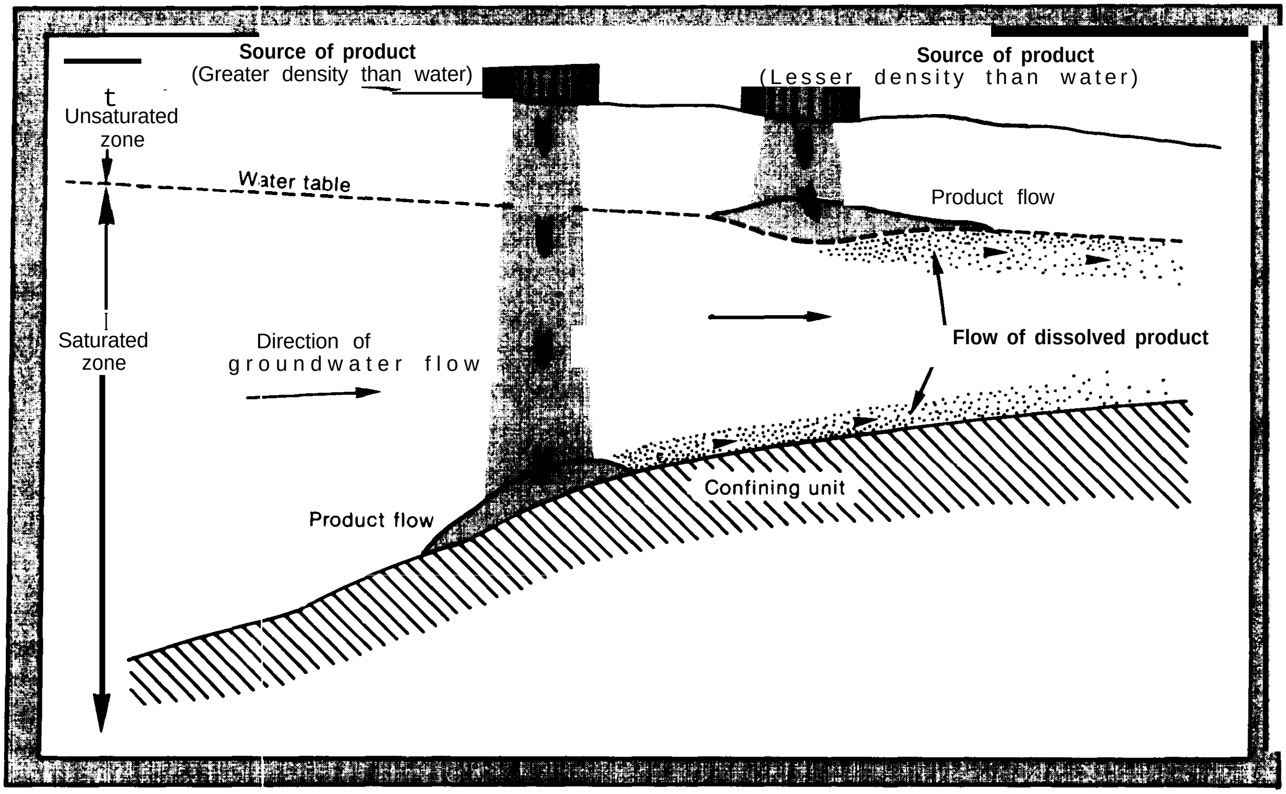
[c] Examples of variations in information collected under different site conditions are described below:

- In fractured (as opposed to unfractured) aquifers, information is needed on fracture patterns, joint patterns and spacings, and possibly dual porosity properties (i. e., primary and secondary permeability and porosity).
- In semi-arid (as opposed to humid) climates where the water table is deep, information on the properties of the unsaturated zone (e. g., moisture content and relationships between relative permeabilities and capillary pressure) is very important for defining groundwater flow and determining the potential for contamination.
- Where multiple sources (rather than a single source) of contamination are **suspected, water quality** sampling and analysis may be directed more to contaminants that are unique to a particular source, perhaps at very low concentrations, than to contaminants that are likely to be found at the highest concentrations.
- Where the behavior of contaminants can be readily described-for example, by having knowledge that the contaminant is quickly degraded or strongly retarded in groundwater—collection of data on water quality can be concentrated in areas near the source rather than over a wider area.



Credit: Geraghty & Miller, 1983

Immiscible contaminants that are more dense than water may not move in the same direction as groundwater flow. Immiscible contaminants that are less dense than water tend to float on top of the water table.

Techniques for Obtaining Information About the Hydrogeologic Environment

The presence and concentrations of most contaminants are determined from groundwater quality samples. Techniques for sample collection are discussed in this section on the hydrogeologic environment, and the analytical techniques for measuring the contaminants in a water quality sample are discussed in the next section on contaminants.

Techniques used to describe the hydrogeologic environment and to collect groundwater quality samples are organized into 12 major categories in table 26. The table outlines the general types of information obtained from the techniques and the limitations of the techniques under different conditions.

In general, some information on the behavior of subsurface contaminants can be obtained and interpreted with greater reliability than others. Groundwater flow can be readily described in most environments; however, information cannot be readily obtained on the physical, chemical, and biological processes that may cause contaminant attenuation. This difference reflects both the state of scientific understanding and available technology. For example, groundwater flow is better understood and mathematical modeling of flow is more highly developed than for contaminant behavior; thus data can be interpreted more reliably, and more accurate predictions can be made for groundwater flow than for contaminant behavior.[7] Summary points and findings from table 26 are highlighted below:

- Techniques. There are many techniques for obtaining information about groundwater flow and the movement of contaminants.

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[7] For a more detailed discussion of differences in models for groundwater flow and contaminant behavior, see OTA, 1982.

Table 26.—Techniques for Hydrogeologic Investigations: Information Obtained and Principal Constraints on Application[a]

Techniques	Information	Major site constraints				Other constraints
		Subsurface geology	Subsurface hydrology	Water quality	Surface conditions	
published information	10 identity geologic, nydrologic, hydrogeologic, water-quality, topographic, and climatic conditions.	type of geologic formation: May not be sufficiently detailed for complex geologic settings.	Complexity of subsurface conditions: Usually data are unavailable for specific sites, but some regional hydrogeologic information may be useful, particularly in simple, uniform hydrogeologic settings.	Not a constraint.	Not a constraint.	Proprietary data may limit availability.
2. Mapping	To delineate surface geologic, soil, or topographic conditions.	Not a constraint.	Not a constraint.	Not a constraint.	Site access: Inaccessible terrain may be problematic during ground surveys.	Nonsite-specific information often adequate; represents separate cost. May require a relatively long time to complete (days to months).
3. Remote sensing (aerial photography and thermal, infrared, and radar satellite imagery)	To assess indirectly geologic, hydrologic, hydrogeologic, or water quality characteristics of the earth's surface. A reconnaissance tool to optimize surface field studies.	Depth: Techniques generally provide information on only face features but some techniques may provide some information on shallow groundwater flow and/or contaminant seepage within 10 feet of the land surface. Type of geologic formation: Some techniques can penetrate the surface and provide information on contaminants if under thin alluvium or sand.	Saturation conditions: Some techniques (e.g., radar) to detect presence of contamination are applicable only in unsaturated areas where there is a moisture difference between contaminated and uncontaminated areas. Flow system: Detectable contamination limited to discharge areas with techniques other than radar.	Nature of Chemical Compounds: Contaminant distribution can be detected by various techniques if chemicals stress vegetation, cause tonal changes in surface water, or thermal anomalies.	Climate: Some techniques are weather dependent; cloud cover interferes with all techniques except radar. Timing: Some techniques are accomplished best at different times of day (e.g., predawn or midday) and seasons.	Nonsite-specific information often adequate; represents separate cost.
4. Excavations and drilling	To access directly the subsurface environment for the purpose of geologic sampling, geophysical logging, water quality sampling, and fluid potential measurements.	Depth: Excavations generally only done at less than 20 feet. Applicability of different drilling techniques varies with depth; however, with use of proper equipment, holes can be drilled to virtually any depth. Type of geologic formation: Some drilling techniques can be used in only certain types of materials (soil versus rock, consolidated versus unconsolidated, prone to caving versus non-caving).	Not a constraint.	Nature of chemical compounds: Presence of certain contaminants may limit use of some drilling fluids to avoid sample contamination. Variations in contamination with depth may limit use of certain techniques to avoid cross-contamination.	Scale: Excavations can cover larger areas than drilling. Site access: H may be difficult to reach some sites (e.g., steep or marshy) with steep or marshy) with some types of equipment.	Property access: May require a relatively long time to complete (days to months). Relatively high cost to implement.

Table 26.-Techniques for Hydrogeologic Investigations: Information Obtained and Principal Constraints on Application[a]—continued

		Major site constraints				
Techniques	Information	Subsurface geology	Subsurface hydrology	Water quality	Surface conditions	Other constraints
5. Geologic sampling	To identify directly stratigraphy and geologic structure and to obtain geologic samples for laboratory testing of hydraulic and soil characteristics.	Depth: Type of sample that can be obtained depends on the depth and penetration capability of drill rig and/or sampling equipment. Depth is not a limiting factor for obtaining either undisturbed samples from some unconsolidated materials, or representative and non-representative samples from any type of materials.[b] Type of geologic formation: Some limitations depending on whether consolidated or unconsolidated. See Depth.	Not a constraint.	Not a constraint.	Not a constraint.	May require a relatively long time to complete (days to months).
6. Hydrometeorological measurements	To quantify temperature, precipitation, evapotranspiration, and infiltration at the earth's surface.	Not a constraint.	Not a constraint.	Not a constraint.	Not a constraint.	Field techniques to measure transpiration are difficult to apply, so estimates are usually made. Nonsite-specific information often adequate; represents separate cost.
7. Surface hydrology (hydraulic measurements; surface water sampling)	To identify flow and water quality characteristics of surface water.	Not a constraint.	Not a constraint.	Nature of chemical compounds: Difficult to obtain samples of many organic compounds that are only slightly water-soluble.	Not a constraint.	Nonsite-specific information often adequate; represents separate cost.
8. Subsurface Hydrology a. Potential measurements	To measure subsurface water level or pressure for evaluating direction of flow and to calculate flow rates within and between hydrologic units in both the unsaturated and saturated zones.	Depth: Depth is a limiting factor for some techniques (e.g., some tensiometers and drill stem tests). However, techniques are available to obtain measurements at any depth, provided specially designed wells are drilled. Type of geologic formation: Fine-grained, low permeability material limits the use of certain techniques (e.g., standpipes). However,	Saturation conditions: Choice of techniques depends on whether measurement is required for the saturated or unsaturated zone.	Not a constraint.	Not a constraint.	Not a constraint.

Table 26.--Techniques for Hydrogeologic Investigations: Information Obtained and Principal Constraints on Application[a]—continued

Techniques	Information	Major site contraints				Other constraints
		Subsurface geology	Subsurface hydrology	Water quality	Surface conditions	
a. Potential measurements (cent'd)		techniques are available to obtain measurements in any type of formation provided specially designed wells are drilled.				
b. Hydraulic testing	To determine the hydraulic properties of in-situ subsurface materials needed for calculations of flow rates in the unsaturated zones or directly measure groundwater flow velocities and to determine contaminant transport parameters.	Type of geologic formation: Some unsaturated zone techniques (e.g., infiltration tests) are impractical in coarse-grained soils due to the amount of water required. Choice of techniques (e.g., slug test, pressure injection test, and pump test) for saturated zone dependent on permeability of formation.	Complexity of subsurface conditions: Some techniques (e.g., slug tests and flow meters) measure conditions only at or near the point of measurement, and do not account for spatial heterogeneities. Saturation conditions: Some techniques are applicable in either saturated or unsaturated zones.	Not a constraint.	Not a constraint.	Relatively high equipment cost; intensive manpower requirements; and need for skilled personnel. May cause short-term changes in water levels. Tracers may have adverse environmental effects.
c. Laboratory testing (hydraulic, geologic)	To measure the hydraulic properties of samples of subsurface materials needed for groundwater flow calculations of variably saturated materials (e.g., porosity) and selected contaminant transport parameters (e.g., adsorption).	Depth: Testing dependent on obtaining appropriate type of sample (i.e., undisturbed, representative, or non-representative). Type of geologic formation: Depends on whether consolidated or unconsolidated. See Depth. Provides good method of measuring permeability of fine-grained unconsolidated materials. Choice of geologic sampling technique (hydrometer v. sieve tests) depends on grain size.	Complexity of subsurface conditions: Superior to field measurements of vertical permeability of fine-grained unconsolidated materials. Major limitation is small sample size and the applicability of extrapolating point information to the three-dimensional space being assessed.	Not a constraint.	Not a constraint.	Not a constraint.
d. Water quality sampling	To obtain a subsurface water sample representative of in-situ water quality for analyses of the presence and concentrations of chemicals and other substances in unsaturated and saturated zones.	Depth: Some pumps to evacuate wells and obtain samples have depth limitations. Type of geologic formation: In high permeability formations, evacuation of sampling wells to ensure sample is not affected by the well is problematic. However, techniques are available to minimize the amount of pumpage required	Complexity of subsurface conditions: Multiple completion wells to characterize vertical distribution of water quality are limited due to concerns about the effectiveness of sealing to prevent hydraulic connections and the ability to obtain representative samples from different sampling zones. Saturation conditions: Different techniques are used to obtain samples in the unsaturated zone	Nature of chemical compounds: Casing, well materials, and pumps must be selected both to resist deterioration from long-term exposure to natural chemicals or contaminants and to minimize interference with the measurement of specific constituents. Current knowledge of sampling interferences is limited for most well materials.	Not a constraint.	Not a constraint

Table 26.—Techniques for Hydrogeologic Investigations: Information Obtained and Principal Constraints on Application[a]—continued

Techniques	Information	Major site contraints				Other constraints
		Subsurface geology	Subsurface hydrology	Water quality	Surface conditions	
d. Water quality sampling (cent'd)		before sample collection, which may in turn limit selection of the most effective sampling equipment for particular constituents.		Design constraints of multiple completion wells (e.g., small diameter) may may limit use of most effective sampling equipment for some chemical parameters. Proper disposal of evacuation water prior to sampling is dependent on its quality. Techniques used to evacuate wells and obtain samples may result in incorrect measures of some compounds (especially dissolved gases and volatile organics). Also, the presence of some constituents (e.g., sediment) may damage some types of equipment. Some techniques allow excessive exposure to the atmosphere or other gases that might influence the measurement of specific parameters.		
9. Hydrogeologic system analysis (modeling; geostatistics)	To simulate or predict the behavior of subsurface hydrogeologic units, including groundwater flow and solute transport; or to estimate the values of hydrogeologic phenomena at unmeasured points.	Not a constraint	Complexity of subsurface conditions: choice of modeling technique (i.e., analytic or numeric) depends on complexity of problem. Modeling complex systems limited by cost of obtaining data. Most geostatistical methods require that the sample population be normally distributed; thus if data represent complex subsurface conditions, geostatistical methods may be difficult or impossible to apply.	Not a constraint.	Not a constraint.	Relatively high cost to implement. May require a relatively long time to complete (weeks to months). Specialized skills required. Requires a clear definition of the hydrogeologic parameters used, including their variability in time and space.
10. Surface geophysics (electrical resistivity and electromagnetic conductivity; ground-penetrating radar; seismic refraction; shallow geothermic method)	To assess indirectly stratigraphy and extent of subsurface contamination to aid in placement of monitoring well sand to reduce number of wells.	Depth: Depth limitations are dependent on technique. Generally, techniques cannot be applied at depths greater than 500 feet. Type of geologic formation: Minimum detecta-	Complexity of subsurface conditions: Techniques applicable only in relatively simple stratigraphic conditions. Natural subsurface properties must be sufficiently uniform so as not to confuse or mask the effects of chemicals. Natural	Nature of chemical compounds: Chemicals of interest must be capable of both inducing a change in the subsurface parameter measured by the method and showing a different response than	Climate: Some techniques requiring electrode contact not applicable in frozen soils or in dry sandy areas (e.g., electrical conductivity). However, other techniques are applicable in these	Relatively high equipment cost; need for skilled personnel; may require a relatively long time to complete (weeks to months).

Table 26.—Techniques for Hydrogeologic Investigations: Information Obtained and principal Constraints on Application[a]—continued

		Major site contraints				
Techniques	Information	Subsurface geology	Subsurface hydrology	Water quality	Surface conditions	Other constraints
10 Surface geophysics (cent'd)		ble concentration strongly Influenced by properties of subsurface materials. Conditions that may prevent good results include: naturally conductive brackish water, steep water table, crystalline rock, and karst or other environs where groundwater flow is concentrated along Interconnected fractures in massive bedrock.	conditions that may be responsible for false detection or nondetection Include: discontinous, thick layers of clay; hydrogeologic heterogeneity; variations in natural groundwater chemistry due to changes in geologic materials; and variations in surface topography. Some methods are more effective than others for detecting small fracture zones containing high contaminant concentrations (e.g., electromagnetic conductivity is better than electrical resistivity). Homogeneous subsurface environments having layers of increasing densities present interpretative difficulties for some techniques (e.g., seismic refraction). All techniques generally require subsurface drilling or monitoring for verification of results. Saturation conditions: Some techniques can be used to obtain some types of information only in the unsaturated zone (e.g., electrical resistivity can track contaminant movement in only the unsaturated zone).	surrounding subsurface conditions, Many techniques (e.g., resistivity and conductivity methods) generally are ineffective for defining organic contaminant plumes. However, the presence of organic chemicals and petroleum products may be delineated in sand or gravel aquifers at depths generally less than 25 feet with ground penetrating radar. Relatively high concentrations required by techniques for detection of contaminants. Techniques only provide gross information on concentrations of some individual constituents. Some techniques can be effective in delineating extent of high concentrations of inorganic contamination in suitable geologic environments.	conditions (e.g., electromagnetic conductivity). Nature of surface: Conductors (e.g., metal fences, overhead power lines, paved areas, buildings, storage tanks, and buried pipelines or wires) may impair use of some techniques. Sensitivity of different techniques to these features is variable. Bare rock, wetlands, shallow lakes, and dry sandy areas prevent use of techniques requiring electrode contact.	
11. Subsurface (borehole) geophysics (acoustical; electrical-magnetic; nuclear; flow; thermal; geochemical)	To measure direct physical properties of subsurface materials to evaluated lithology, geologic structure, hydraulic properties, water quality, and flow.	Depth: Not a limiting factor for most techniques provided an uncased borehole can be drilled. Type of geologic formation: Most techniques can be used only in uncased boreholes, and thus cannot be used in geologic formations that cave in when drilled. Exceptions include nuclear logs which can be used in cased boreholes. Some tech-	Saturation conditions: Some techniques (e.g., electrical-magnetic logging techniques) are applicable only in saturated zone. Some techniques can be used to provide certain types of information in the unsaturated zone, and other types of information in the saturated zone (e.g., neutron logs).	Nature of chemical compounds: Some techniques applicable only if constituents in groundwater have properties that will induce response from instruments (e.g., spontaneous potential logs). Some techniques can be used to detect particular contaminants (e.g., Draeger tubes can detect over 140 in-situ soil gases).	Not a constraint.	Relatively high cost to implement.

Table 26.—Techniques for Hydrogeologic Investigations: Information Obtained and Principal Constraints on Application[a]-continued

		Major site constraints				
Techniques	Information	Subsurface geology	Subsurface hydrology	Water quality	Surface conditions	Other constraints
11. Subsurface (cent'd)		niques more suitable for obtaining information on particular types of geologic materials (e.g., natural gamma logs for obtaining clay unit properties).				
12. Hydrogeochemistry	To perform field testing of water samples to determine need for further laboratory chemical analysis and to analyze for unstable constituents.	Not a constraint.	Not a constraint.	Nature of chemical compounds: Field techniques available to obtain information on conductance, organic vapors, alkalinity, pH, Eh, DO, iron, and hydrocarbons. (See Subsurface Hydrology — Groundwater quality sampling, for additional constraints.)	Not a constraint.	Not a constraint.

[a] Based on Geotrans, Inc., 1983b.

[b] *Undisturbed sample*—An in-place specimen in which features such as structure, density, and moisture content are essentially preserved. Suitable for laboratory testing of pr
Representative sample—A disturbed sample in which some features do not survive but grain size and gradation are preserved. Suitable for grain size gradation analyses and obta
Nonrepresentative sample—A sample that may consist only of drill cuttings or other incomplete or contaminated portions of subsurface materials. Generally not suitable for testin
face stratigraphy.

SOURCES: Office of Technology Assessment; Geotrans, Inc., 1983b.

Photo credit: U.S. Geological Survey

Techniques are available for the direct sampling of groundwater quality.

- Information Obtained. Regardless of what techniques are used, which parameters are measured, and whether the measurements are taken directly or indirectly, all measurements must be interpreted in conjunction with other data to determine groundwater flow and the behavior of contaminants. Interpretation of data is uncertain because of factors relating to: the precision, accuracy, or detection limits of the equipment; lack of a unique measurement (e.g., geophysical response) for particular subsurface conditions; the degree to which averaging of conditions masks actual conditions; and the degree to which the sample or the measurement represents in-situ phenomena.

  Some techniques are useful in obtaining general information; others are used to obtain site-specific information. Some techniques (e.g., excavation and drilling) are not used to provide information per se, but their use is a necessary step before other techniques can be applied. Other techniques (e. g., mathematical modeling) are not used to measure properties of the hydrogeologic environment but can be used to simulate conditions and predict groundwater flow and movement of contaminants.

  Techniques are generally available to collect data on the unsaturated zone, groundwater hydrology, sources, and contaminants; this information is necessary to make reliable predictions of groundwater flow and estimate current and future water quality in most environments. However, historic data and data reflecting changes with time (e. g., groundwater use and the contaminant release characteristics of sources) are usually not available for a specific site, which diminishes the reliability of some investigations.

- **Constraints.** Factors that can limit the use of different techniques are related primarily to site conditions, costs, and the availability of skilled personnel. Additional constraints include problems with property access and the potential for adverse effects.

  Site conditions that can limit the use of hydrogeologic techniques include: subsurface geology (e. g., depth and type of geologic formation); subsurface hydrogeology (e. g., complexity of subsurface conditions, saturation conditions, and flow system); water quality (e. g., nature of the contaminants), and surface conditions (e. g., presence of buildings, pavement, power lines, vegetative cover, and other features; site accessibility; climatic factors; time of day; and size of the area).

  As shown in table 26, site constraints on obtaining information vary for different categories of hydrogeologic techniques as well as for specific techniques within each category (e. g., climate is a constraint only on certain remote sensing and surface geophysical techniques). Some techniques are limited to particular subsurface conditions (e. g., different techniques are used for the saturated zone than for the unsaturated zone). In addition, the site constraints that apply to a particular technique vary, depending on the purpose for which the technique is used (e. g., subsurface geology constraints on geologic sampling depend on the type of sample that is needed).

  There are a few types of information that cannot be obtained reliably using any technique including: chemical reactions in fluids containing multiple contaminants, properties characterizing in detail groundwater flow and chemical transport in fractured media, certain hydraulic properties of very low permeability media, in-situ determinations of hydraulic properties in the unsaturated zone when immiscible contaminants are present, and history of the contaminating source.[8]

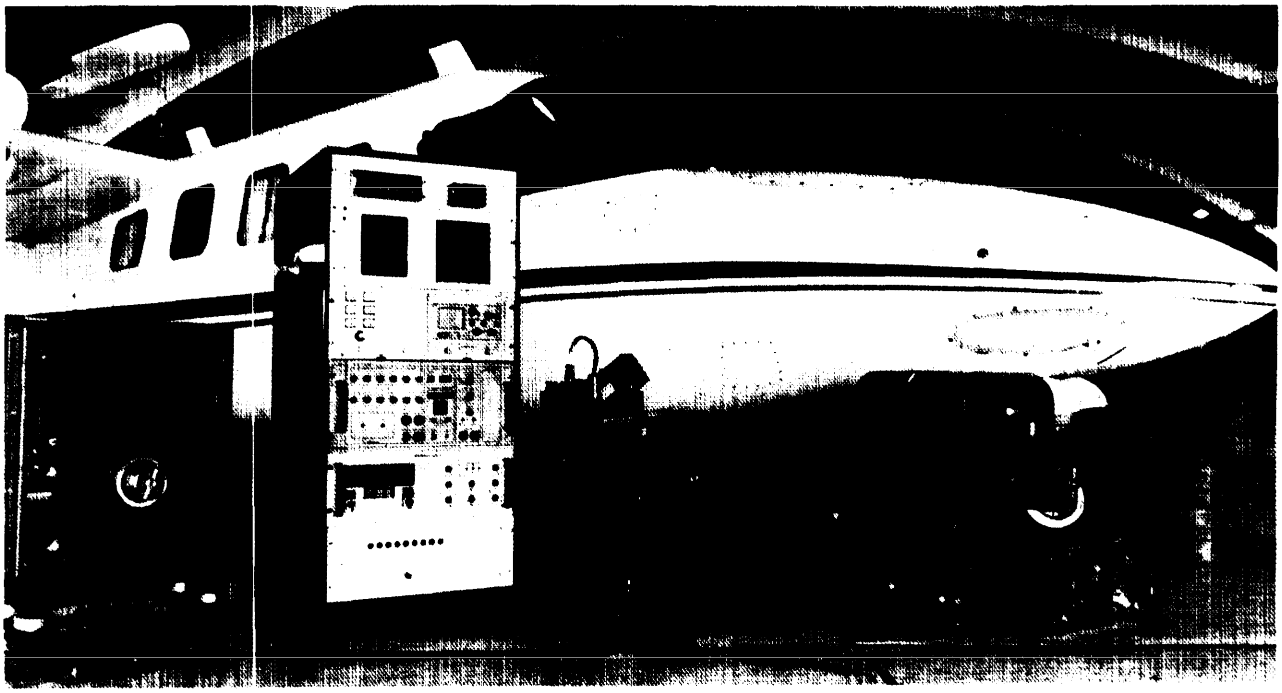

Photo credit: U.S. Environmental Protection Agency

Remote sensing equipment can be used to identify, document, and evaluate groundwater quality problems. The data acquisition system, which is mounted on the aircraft and operates 500-10,000 ft above ground level, includes (from left to right): an instrument logger for recording location, time, and altitude; a control console; a multispectral scanner; and an aerial mapping camera.

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[8] See ch. 2 for discussion of the problems associated with determining the contribution of a source to groundwater contamination.

The *costs* of applying hydrogeologic techniques depend primarily on site conditions and the objectives to be achieved. Costs of hydrogeologic investigations to define contamination problems can range from $25,000 to $250,000, and litigation can double the figure (Miller, D., 1982). Many factors determine costs: the complexity of surface and subsurface conditions, areal extent of the study area, number and frequency of measurements, availability and quality of existing information, site access, experience and training of personnel, reliability and capability of equipment, availability of equipment, geology, weather, and the need for site-specific v. regional data. These same factors also determine the amount of time required, and they affect the choice of equipment and the number and locations of measurements to be taken.

Equipment costs limit the use of certain techniques (e. g., hydraulic testing, hydrogeologic systems analysis, surface geophysics, and subsurface geophysics). Either less costly or less sophisticated techniques are used. The costs of applying certain techniques (e.g. geologic sampling, potential measurements, water quality sampling, and subsurface geophysics) are reduced if a well or borehole can be used for more than one purpose. However, the information required to meet particular objectives will influence the decision on whether to use a single well or borehole for several techniques. Investigation costs can also be reduced by using indirect or field screening techniques to provide reconnaissance level information for selection of direct measurement locations.

Availability of reliable equipment capable of operating efficiently under the site conditions is an important factor in determining costs (e. g., choice of drilling methods and pumping equipment depends on site conditions). Capital expenditures for major equipment and materials vary, depending on the purpose and technical sophistication of the equipment. Certain types of equipment are more readily available in some areas of the country than others because of their other uses (e.g., subsurface geophysics equipment is used extensively for petroleum and mineral exploration).

The experience and training of personnel affect costs in terms of the level of skills needed to design an investigation and collect and interpret data. Highly specialized skills are required for some techniques, and skilled people are in short supply. The result is relatively high costs to obtain their services.

Property access may limit the use of drilling and associated techniques. Permission to drill wells is often not readily granted on private property because of the inconvenience and disruption created by the drill rig. Interest in drilling beyond property boundaries is often quite low because whoever finances the drilling must usually assume liability for damages.

The potential for short- or long-term *adverse effects* limits the use of some techniques. For example, short-term changes in water levels during hydraulic pump tests may limit their use in some environments (e. g., where there are water supply wells). Use of tracer tests is unacceptable to many regulatory authorities because tracers (some of which maybe radioactive) may remain as a potential contaminant in the environment.

Techniques for Obtaining Information About Contaminants

Advances during the last decade in techniques for analyzing water quality samples—for identifying increasing numbers of specific substances, for detecting substances at progressively smaller concentrations, and for increasing the automation of instrumentation—have been major driving forces behind the detection of contaminants in groundwater. Continued improvement is expected; not only will previously undetected substances be found but more will be detected at increasingly small concentrations.

Not all contaminants, however, can be detected at low concentrations using routinely available techniques. Further, the fact that certain substances *can* be measured at increasingly small concentrations does not mean that they need to be. Rather, analysis should be guided by the levels at which substances may cause adverse impacts (Environ Corp. , 1983). Major unresolved issues concern which substances and concentrations to measure, given limited resources, in order to evaluate the risks to public health and to provide the public with confidence that it is being protected.

At present, techniques for measuring substances in groundwater are not being used consistently, and they introduce a bias in terms of which of the substances present are detected. In addition, analytical accuracy becomes increasingly difficult to achieve as concentrations become very small and mixtures become more complex (Woodward-Clyde Consultants, 1983; Shifrin, 1984).

Properties of Substances. —Analyzing contaminants in a groundwater sample is based on the capability of instrumentation to discern certain properties of substances. These properties are important in contamination studies because they are characteristic of either individual substances or groups of substances and because they determine the nature, behavior, and response of substances under various conditions.

In the context of groundwater contamination, a distinction can be made between two types of properties, molecular-based and media-based (Woodward-Clyde Consultants, 1983).[9] Measurement of these two types of properties is based on different principles. In addition, the two relate to different objectives. For example, the detection of contaminants in a groundwater quality sample (e. g., determining the general presence of substances or identifying and/or quantifying the concentrations of specific substances) is based principally on the measurement of molecular-based properties. Molecular-based properties are derived solely from the basic construction of the substance: 1) elemental composition (i. e., elements and their frequency of occurrence in a molecule); 2) structure (i. e., spatial arrangement of elements); and 3) functional group (i.e., arrangement of elements into stable combinations). In contrast, media-based properties are the principal basis for characterizing the *behavior* of contaminants. Understanding behavior is necessary for designing hydrogeologic investigations including: evaluating the applicability of corrective actions, assessing the vulnerability of an aquifer to contamination, and assessing health and environmental impacts. Media-based properties are derived not only from the basic construction of a substance but also from its concentration in solution (in this case, in groundwater) and its interaction with the surrounding (e. g., hydrogeologic) environment. Although molecular-based and media-based properties are interrelated by molecular composition, this interrelationship is not well understood.

Information examined as part of this study, about the current status of the techniques for analyzing substances that are found in groundwater, is summarized below.

Measuring Molecular-Based Properties. —Many analysis techniques are available for measuring the molecular-based properties of substaces in groundwater, as shown in tables 27 and 28 (Woodward-Clyde Consultants, 1983). Many of these techniques are routinely available and have been standardized—i. e., they are ' 'referenced' and published by the scientific community. Many standardized techniques have also been sanctioned by EPA—i.e., protocols have been established to ensure that the regulated community applies techniques consistently and to facilitate enforcement. 10

With *general (also* known as non-specific, surrogate, or indicator) *methods,* it is possible to discern molecular-based properties that are common to, and hence can be used to determine the presence of, groups or classes of molecules. The major advantages of general methods are that they are relatively inexpensive in terms of both capital costs and costs per sample, and their use requires neither sophisticated equipment nor highly skilled technical personnel. The shortcomings include that many general methods can neither measure low concentration levels (i. e., several parts per billion or less)

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[9] For the purposes of this study, substances have been organized into nine groupings (see ch. 2, footnote 7 and table 6).

[10] Standardized methods have been subjected to statistical tests of precision (i. e., the reproducibility of results) and accuracy (i, e., the proximity of the measured results to the actual value) when used to detect substances in a representative group of samples. Detection using standardized methods therefore is not to depend on the specific nature of the sample.

Development of analytical methods for measuring substances in water has intensified since the passage of the Federal Water Pollution Control Act Amendments of 1972. The act's requirements triggered widespread analysis of surface water as well as municipal and industrial effluents for biochemical oxygen demand (BOD), chemical oxygen demand (COD), and other general parameters. Enforcement of regulations developed pursuant to the 1972 Amendments led to the need for a high degree of uniformity in the conduct of analytical programs to ensure consistency and equity within the regulated community. EPA first sanctioned the use of methods for measuring both general parameters and specific parameters in EPA, 1974 (revised 1979).

Table 27.—Analytical Methods for Measuring the Molecular-Based Properties of Groundwater Contaminants[a]

Methods	Contaminants measured	Routinely[b] Available
Organics		
General methods		
TOC (total organic carbon)	Carbon-containing	Yes
UV (ultra-violet spectroscopy)	Aromatic hydrocarbons	No
FLUOR (fluorescence)	Polynuclear hydrocarbons	No
RI (refractive index)	Soluble organics	No
4AAP (4-aminoantipyrene)	Phenols	Yes
TKN (total Kjeldahl nitrogen)	Nitrogen-containing	Yes
MBAS (methylene blue active substance)	Sulfonate detergents	Yes
TOX (total organic halogen)	Halogenated organics	Yes
O&G (oil and grease)	Oil and grease in solution	Yes
TP (total phosphorus)	Phosphorus-containing (both for organics and inorganics)	Yes
Contaminant-specific methods[c]		
Isolation systems		
Separaton systems		
GC (gas chromatography, both gas-liquid and gas-solid)	Organics	Yes[d]
HPLC (high performance liquid chromatography)	Polynuclear aromatics	Yes
Detection systems		
CD (conventional detectors)	Organics	Yes
MS (mass spectrometry)	Organics	Yes
Inorganic		
General methods		
Eh (Oxidation potential)	Oxidizing metals	Yes
Specific conductance	Ionized species	Yes
pH/acidity	Mineral acids	Yes
Contaminant-specific methods		
AA (atomic absorption spectrometry)	Metals/cat ions	Yes
ICAP (induction-coupled argon plasma)	Metals	Yes
Wet chemistry		Yes
Colorimetry	Non-metals/anions	
Gravimetry	Metals	
Titrimetry	Acids	
Radionuclides		
General methods		Yes
Gross emission		
Contaminant-specific methods		Yes[e]
Concentration/identification		
Microorganisms		
General methods		Yes
Standard plate count	Aerobic and facultative anaeorbic, heterotrophic bacteria	
Multitube fermentation	Coliform bacteria	
Membrane filtration	Coliform bacteria, pathogens, parasites	
Contaminant-specific methods		Yes[e]
Culturing	Pathogens	
Morphology	Parasites, fungi	
Concentration/Identification		

[a] Based on Woodward-Clyde Consultants, Inc., 1983.

[b] Methods examined for this study are those that are "referenced," or published, and commercially available. Less common techniques include innovative (R&D) methods such as "triple quadrupole mass spectrometry" and "tandem mass spectrometry" (as reported in *Environ. Sci. Tech.* Vol. 15, No. 6, 1982) and special methods such as ion chromatography, size exclusion *chromatography, and infrared spectroscopy.*

[c] There are typically three stages in this analysis; isolation of the contaminant (e.g., via headspace analysis, purge-and-trap, or liquid-liquid extraction), separation (e.g., via gas chromatography or high performance liquid chromatography), and detection (e.g., via conventional detectors such as flame ionizaton, electron capture, or via mass spectrometry).

[d] GS/MS is standardized for chemical subgroups, specific members of which are on the Priority Pollutant List, and for pesticides *regulated under the CWA.*

[e] These contaminant-specific methods are time-consuming, costly, and tend to be reserved for research and specialty applications.

SOURCE: Office of Technology Assessment.

Table 28.—Costs and Detection Limits of Methods for Measuring the Molecular-Based Properties of Contaminants[a]

	Costs[b] ($)		Detection limits[c]	
Method	Per sample	Capital	(ppm)	(ppb)
Methods for measuring organics				
General methods				
TOC	15-30	9,000-15,000	1	1,000
UV	30-60	12,000-30,000	**(0.1)**[d]	(loo)
FLUOR	20-40	5,000-16,000	(1)	(1,000)
RI	10-30	5,000-12,000		—
4AAP	30-60	4,000-6,000	0.002	2
TKN	20-30	4,000-6,000	0.002	2
MBAS	20-40	1000-2,000	0.025	25
TOX	60-100	8,000-10,000	0.01	10
O&G	20-30	500-1,500	0.2	200
TP	30-70	1,000-2,500	0.01	10
Contaminant-specific methods				
GC/CD	30-500	8,000-30,000	<0.001-01	<1-1oo
GC/MS	100-1,500	55,000-220,000	<0.001-0.01	<l–lo
HPLC	40-500	8,000-40,000	0.000001	0.001
Methods for measuring inorganics				
General methods				
Eh[e]	10-15	1,000-1,500	N/A	
Specific conductance	3-5	1,000-1,500	N/A	
pH	3-5	1,000-1,500	±0.1 pH unit	
Acidity	10-15	500-1,000	±0.1 mg $CaC0_3$/l	
Contaminant-specific methods				
AA	150	12,000-20,000	<0.001–0.2	<1-200
ICAP	125-200	125,000-175,000	<0.001-0.2	<1-200
Wet chemistry	10-35	2,000-5,000	01-1	100-1,000
Methods for measuring micro-organisms				
General methods	75/group	2,500-4,000	N/A	
Contaminant-specific	1,000/strain	2,500-4,000	N/A	
Methods for measuring radionuclides				
General methods	40-75	5,000-7,000	l-2pCi/l	
Contaminant-specific	1,000-1,500	30,000-60,000	l-loo pCi/l[f] 0.05-1 pCi/l[g]	

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[a] Based on Woodward-Clyde Consultants, Inc., 1983; additional information in Brass, 1982, and Vicory, et al., 1982.

[b] Approximate cost ranges are presented only for general comparison. In practice, costs will depend on many factors including the level of automation of the equipment, the need for auxiliary apparatus, the sophistication of the data system, and the work load of the laboratory (e.g. number of analyses to be performed, lead-time available, and required turn-around time).

[c] Detection limits are not absolute and will depend on such factors as the contaminant to be measured, interference among contaminants contained within the sample, sample size, methodology, and skill and experience of the analyst. In practice, levels of accuracy and precision would need to be specified in order to interpret the data. Detection limits are generally presented with the following units:

1 mg/l (milligrams per liter) = 1 ppm (parts per million)
1 ug/l (nanograms per liter) = 1 ppb (parts per billion)
1 ppb = 1,000 ppT (parts per trillion)
1 ppm = 1,000 ppb

[d] Detection limits in parentheses are presented only as examples for non-standardized methods.

[e] Some contaminants, such as oxidizing metals, are unstable and need to be measured in the field.

[f] For alpha, beta emitters.

[g] For gamma emitters.

SOURCE: Office of Technology Assessment.

nor identify individual substances of a group or class. Individual substances would be of concern if they were expected to vary in terms of their potential impacts. In addition, data from general methods can be difficult to interpret, especially when interferences arise from the presence of several different types of substances in the sample. These interferences are known to give misleading results ('false positives' (Davis, 1984).

With *contaminant-specific methods,* it is possible both to identify individual substances and to quantify their concentrations at extremely low levels. The disadvantages of contaminant-specific methods are that they are more costly than general methods, and they require the use of relatively sophisticated equipment. These methods, as well as general methods, are also subject to quality control problems with analysis procedures, and data can be difficult to interpret (e. g,, there will always be some degree of uncertainty about how well data represent in-situ conditions).

Three important points about measuring molecular-based properties are discussed below related to: 1) which substances can be measured, 2) the extensive use of gas chromatography/mass spectrometry (GC/MS), and 3) the ' 'standardized' concept as it relates to groundwater contamination (see Woodward-Clyde Consultants, 1983).

Substances Measured. —Not all known or potential substances can be detected at trace levels using routinely available standardized methods. Some of these substances have been, or may be, associated with toxic effects in either clinical or laboratory studies.

Organic chemicals:

- There are no routinely available general methods for measuring trace levels of some organic chemicals known to occur in groundwater, including aromatic and polynuclear hydrocarbons. There are no general methods for measuring trace levels of some substances that have the potential to be found in groundwater—e. g, glycols and oxygenated hydrocarbons such as aldehydes, ethers, esters, ketones, and alcohols,
- Standardized contaminant-specific methods —namely gas chromatography/mass spectrometry, GC/MS—tend to be available for only selected organics (i. e., 129 "Priority Pollutants' and pesticides regulated under CWA).[11]
- There are no cost-effective methods for measuring many **''exotic'' chemicals,** including some pharmaceuticals, specialty chemicals, and chemical products of research and development efforts (e.g., for new pesticides). These chemicals are generally not manufactured in large quantities or widely dispersed but still may be of concern in selected locations. Their detection will depend on factors related to available analytic equipment, available time, laboratory skills, cost, and knowledge about their manufacture, use, and disposal (Davis, 1984).

Inorganic chemicals, micro-organisms, and radionuclides:

- Inorganic chemicals, micro-organisms, and radionuclides can be measured with standardized general and contaminant-specific methods. There are no standardized methods, however, for measuring viruses.

Use of GC/MS.—The contaminant-specific methods sanctioned by EPA favor the use of GC/MS (e.g., GC/MS is required during the permit application process under the NPDES program [40 CFR 136]). GC/MS has gained in popularity in recent years, both to detect known or suspected substances in groundwater and to scan a sample of unknown composition. GC/MS has regulatory advantages (e.g., protocols have been established to ensure uniformity of application and to facilitate enforcement), and it produces data about specific chemicals.

Reliance by EPA on standardized GC/MS methods is limited in three major ways:

1. **Some substances cannot be detected with these methods,** including substances of high

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[11] A 1976 consent decree settling lawsuits brought by a number of environmental organizations against EPA for failure to implement certain requirements of the 1972 Act and the 1977 Amendments to the Act (the Clean Water Act) focused attention on the control of toxic pollutants. (See *Natural Resources Defense Council, et al.* v. *Train*, June 8, 1976, 8 ERC 2120. Several provisions of the consent decree were incorporated into the 1977 Amendments.) EPA was required to establish technology-based effluent standards for 65 classes of toxic pollutants (129 "Priority Pollutants") in 21 major industrial categories. Methodology for the analysis of the Priority Pollutants was proposed in December 1979 (44 FR 69464). Specific chromatographic methods for pesticides are described in EPA, 1983.

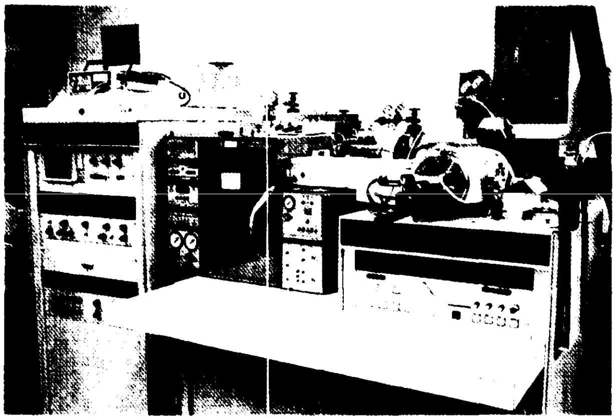

Photo credit: U.S. Environmental Protec(/on Agency

Gas chromatography/mass spectrometry equipment is used for the qualitative identification and quantitative measurement of individual organic chemicals.

molecular weight, substances that are unstable at high temperatures, and substances that are highly soluble in water. In many of these cases, relatively simple, modified versions of some standardized GC/MS procedures are adequate (e. g., for malathion); in other cases, entirely different methods, such as High Performance Liquid Chromatography (HPLC), may be required (Davis, 1984). Specialized modifications of standardized GC/MS methods may also be possible for additional substances such as dioxin (2,3,7,8 -TCDD); dioxin is difficult to detect because it is relatively insoluble in water and often present at concentrations of only parts per trillion. In general, none of these other techniques have been standardized and used routinely.

2. Standardized GC/MS methods could be applied directly (i. e., without modification) to substances in addition to the Priority Pollutants (e. g., xylenes and aniline). Although EPA has made significant research and development commitments to improve the basic instrumentation of GC/MS and associated data processing systems, less attention has been given to widening the routine use of standardized GC/MS methods for additional substances (e. g., by expanding the list of Priority Pollutant organics).
3. While contaminant-specific techniques, such as standardized GC/MS methods, are cost-effective for identifying substances in a sample of *unknown* composition *if* the substances are amenable to analysis by the methods, the methods may be otherwise inefficient (i. e., very costly) for unknown samples. Little research attention has been given to developing techniques for substances not amenable to analysis by GC/MS or to developing reliable and inexpensive screening techniques (e.g., alternative types of analytical and physical/chemical testing methods) for narrowing the universe of potential substances that might be present in a sample and therefore for efficiently determining which contaminant-specific techniques are most applicable (Davis, 1984; Woodward-Clyde Consultants, 1983).[12]

***Standardized** Methods.* -Central to the standardization of methods is the concept of a representative sample (refer to footnote 10). This is a difficult concept to apply to groundwater samples because groundwater contamination is site-specific, and the ' 'representative samples' used to standardize a method may not represent the universe of groundwater samples to which the method might be applied. Thus the use of a standardized, routinely available method does not guarantee that substances in groundwater can be detected with the precision and accuracy indicated by following the standard procedures.

Measuring Media-Based Properties. —Once substances in groundwater have been identified by measuring their molecular-based properties, it is often essential to understand their behavior. Behavioral characteristics—e. g., persistence and mobility-determine, for example, the extent of the contamination problem and likely impacts. However, with present techniques, behavioral characteristics of a substance cannot be measured directly. Rather, the characteristics are deduced from the media-based properties of the substance. These properties are determined by the nature of the sub-

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[12] ''The issues of the presence of groundwater contamination and its extent are not resolved economically or universally by the extensive use of GC/MS . . . The failings of the GC/MS protocol are not, in fact, limitations of the protocol itself. They are, rather, instances where the protocol can be either erroneously assumed to be a complete assessment of groundwater contamination, or erroneously determined to be (either) the optimum means of determining a contaminant's identity and concentration in groundwater, or the most cost effective means of gathering data to achieve one of the identified objectives'' (Woodward-Clyde Consultants, Inc., 1983, ch. 5, pp. 6, 33).

stance in relation to its surrounding environment. Each behavioral characteristic typically requires information on a *combination* of media-based properties.[13]

Standardized analytical methods are generally available for measuring individual media-based properties (see table 29). However, because media-based properties are site-specific and because numerous media-based properties are often of interest, determining the behavior of substances is a technically complex and time-consuming process that theoretically must be performed at each site. In practice, information about media-based properties is obtained primarily from physical and chemical measurements (taken both during the hydrogeologic investigation and in the laboratory) and from published data.[14] Behavior of a substance is then deduced using this information together with professional judgment and experience (e. g., to perform correlation analyses).

Approaches for the Measurement of Substances in Groundwater.—Techniques for measuring substances in groundwater are not now being selected and used consistently to ensure that all potential contaminants at a given site are being addressed, that substances are being detected efficiently given time and financial constraints, and that information obtained can be meaningfully interpreted,

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[13] For example, the mobility of a substance cannot be measured directly, but mobility can be deduced from a combination of media-based properties, including adsorption, volatility (e.g., Henry's Law Constant), solubility, and chemical/biological reactivity; persistence can be deduced from such media-based properties as adsorption, bioaccumulation, partition coefficient, chemical/biological reactivity, and degradability.

[14] All sources of technical information have limitations in assessing the behavior of substances. Physical/chemical measurements are time-consuming and costly; high-quality data required for correlations are often not available; and published data are often incomplete, inconsistent, or imprecise. For example, published data are found in such references as Weast, 1978-1979; Perry, et al., 1973; EPA, 1981; Windholz, et al., 1983; and Sax, 1979. Data tend to be limited to such properties as density, viscosity, ignitability, corrosivity, miscibility, volubility, and vapor pressure. Information is not available for all substances and is often not sufficiently accurate for analysis of tram levels. Moreover, while some of these properties, such as ignitability and corrosiveness, are used for classifying wastes as hazardous (under RCRA), they contribute little information about the behavior of such substances in groundwater. Other properties that are of interest to groundwater contamination studies, such as adsorption, bioaccumulation, and the partition coefficient (i. e., the tendency of a substance to partition between soil and water) are not generally available and must be measured using groundwater samples.

Table 29.—Techniques Commonly Used To Measure Media-Based Properties of Contaminants

Media-based property	Techniques employed
Density	Measure forces transmitted by a mass of the substance being analyzed as in viscous-drag, gas-density meter.
Viscosity	Measure fluid friction by either mechanical drag between driven and free members immersed in the sample or resistance to flow.
Adsorption	Use batch test or leaching columns.
Volubility	Dissolve measured amount of contaminant in a given volume of water at room temperature.
Volatility	Estimate quantity of contaminant vaporized from water by use of an Organic Vapor Analyzer (OVA).
Immiscibility	Shake contaminants in water and observe if there is complete mixing.
Bioaccumulation	Determine concentration of contaminant in sample (e.g., via fish) and compare with background level.
Reactivity	Observe violent reaction of contaminant and/or generation of toxic gases, vapors or fumes when mixed with water.
Degradability	Measure CO_2 evolution, or determine rate of disappearance of parent compound over time.
Stability	Observe disappearance of parent compounds or generation of daughter products.
Oxygen uptake	Determine biochemical oxygen demand (600) or chemical oxygen demand (COD).
Partition coefficient	Measure concentration of contaminant in soil relative to concentration of contaminant in water.

SOURCE: Woodward-Clyde Consultants, Inc., 1983.

given the objective (detection, correction, or prevention) of the measurement program. A coherent approach would consider measuring molecular-based properties with both general methods (e. g., as screening tools to narrow the choice of possible substances present) and contaminant-specific methods (e. g., to identify individual substances and determine their concentrations).[15]

EPA has made efforts in the direction of a master scheme for measuring substances (e. g., EPA Method 8600 is being developed as a comprehensive analytical scheme to determine the presence of chemicals listed in Appendix VIII of RCRA, Part 261). Agency efforts are not yet coordinated in a way that responds fully to the spectrum of substances found in groundwater and possibly at extremely low concentrations.

For example, the groundwater indicator parameters to be measured at both interim status facilities (40 CFR 265) and permitted facilities under the detection monitoring system (40 CFR 264) are delineated as pH, Specific Conductance, Total Organic Carbon (TOC), and Total Organic Halogens (TOX). Some substances known to cause adverse health impacts are not detectable using the indicator parameters. TOC and TOX measurements have the disadvantages of general methods discussed above (e. g., subject to interference effects). In addition, there are categories of contaminants that are neither halogenated, acidic, nor conducting and that may be toxic at less than 1 part per million (ppm, the detection limit of TOC) including pesticides and pesticide byproducts (e. g., dioxin and 2,4,5-T, both of which are known to occur in groundwater; see ch. 2) (Woodward-Clyde Consultants, 1983). "To a great extent, because of an overreliance on indicator parameters, we don't know much more now about which sites are 'clean' or 'potentially dirty' than we did before EPA started using the indicator monitoring approach 3 years ago" (Davis, 1984).

Monitoring Networks

Hydrogeologic investigations involve collecting information about the hydrogeologic environment and water quality at selected locations and then making assumptions about what is likely to be occurring between sampling points. In general, the more the sampling points, the less uncertainty is associated with interpretation of what is taking place in the subsurface. But practical considerations limit the number of measurements taken. The number of measuring points (for direct techniques), the density of measurements (for indirect techniques), and the verification that is required to obtain a satisfactory level of confidence in the results depend on site conditions and the objective of the investigation.

To account for horizontal and vertical variations in the hydrogeologic environment and in water quality, both the location *of sampling points* and *sampling frequency will vary* depending on site conditions and objectives. For example, measuring points could be located at random or in an evenly spaced pattern, or in relation either to the pathways of substances (i. e., measuring points are located where substances are either expected and/or not expected to be found) or to concentrations (i.e., measuring points are located where concentrations are highest and/or lowest). Sampling could be conducted once, annually, seasonally, or more frequently, depending, for example, on whether groundwater flow patterns change periodically.

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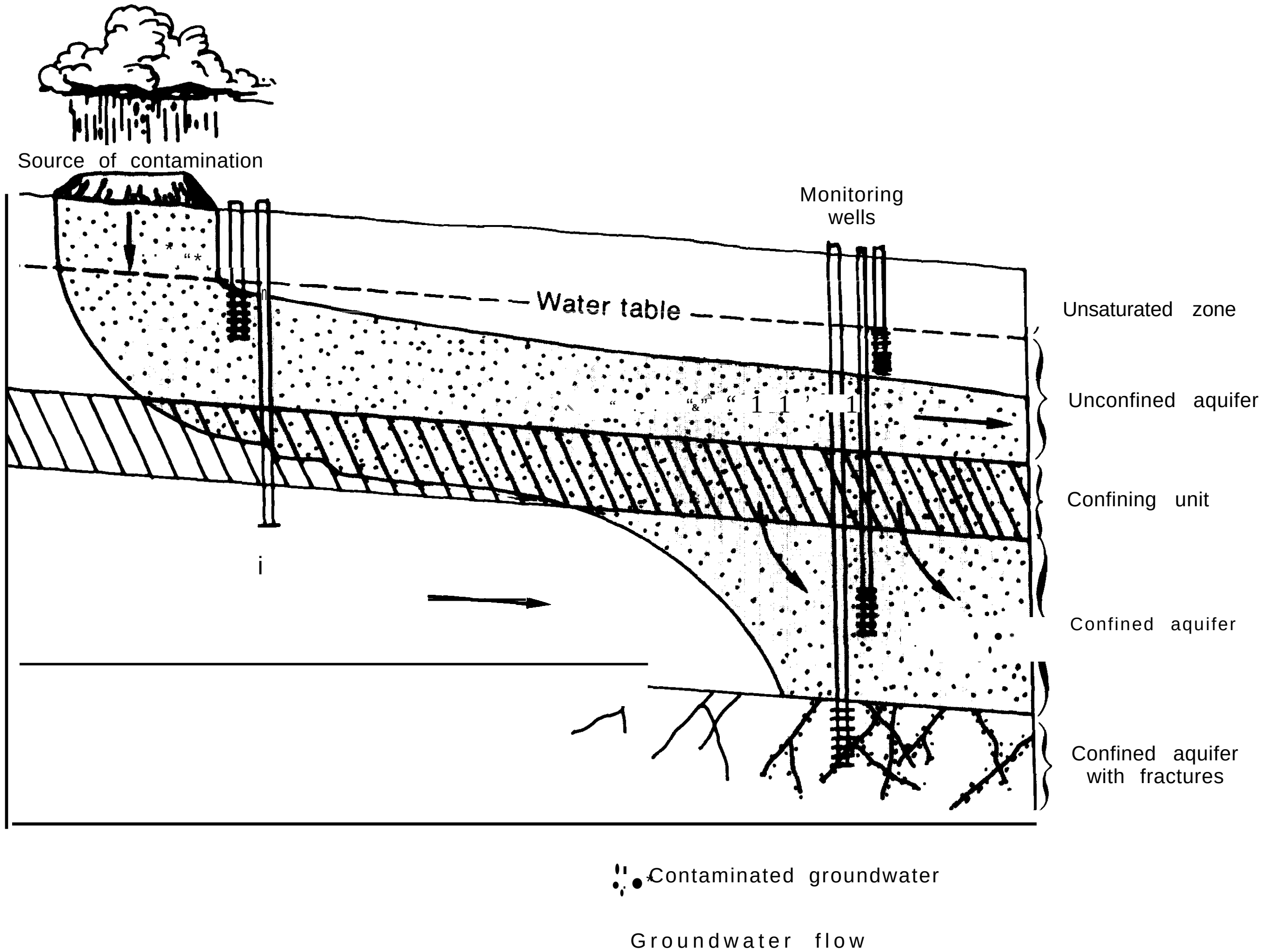
[15] Additional information about contaminant measurement can be found in EPA, 1979, 1981, 1982, 1983; Chapman, et al., 1982; Neal, 1983; and USGS, 1979.



Credit: Geraghty & Miller, 1983

In order to detect contamination, sampling wells need to be located at varying depths and distances from the source.

APPROACHES FOR MINIMIZING DIFFICULTIES WITH GROUNDWATER CONTAMINATION INVESTIGATIONS

Ensuring the Reliability of Hydrogeologic Investigations

As described in the previous sections, investigations of groundwater contamination are very complex and uncertain because the hydrogeologic environment is not easily observed, and hydrogeology varies both spatially and temporally. Hydrogeologists cannot describe and predict with absolute confidence the rate, direction, and pathways of contaminant movement in groundwater. Estimates can be made and ranges of values given but there will always be some degree of uncertainty about which contaminants are present, where they are moving, how fast they are moving, and their concentrations as they move.

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. Given the nature of such decisions—e.g., regarding public health and the dollars involved-decisionmakers and the public need some assurance that certain elements of uncertainty are minimized and that hydrogeologic investigations provide reliable results.

Factors that tend to increase uncertainty in investigations of groundwater contamination include: complex hydrogeologic environments; lack of historic information about sources of contamination; substances that do not move with groundwater (because they are immiscible, or due to physical, chemical, and biological processes that alter their nature or retard their movement); changing patterns of groundwater use; and inexperienced or untrained individuals designing investigations and collecting and analyzing hydrogeologic information.

All of these factors reflect conditions at the site and are beyond the direct control of decisionmakers, except the choice of personnel. Most of the site-related factors that contribute to uncertainty can be overcome by an experienced hydrogeologist, provided sufficient time and funds are available. That is, steps can be taken such that the uncertainties do not undermine ability to make reliable predictions about the response of contamination to various corrective or preventive measures. For example, by collecting more information over a longer period on the presence of substances and the rate and direction of groundwater flow, investigators can reduce many uncertainties about complex hydrogeologic environments, sources of contamination, and changing patterns of water use. The one major exception, where reliable predictions are unlikely, is in fractured environments (e. g., karst regions of the southeastern United States).

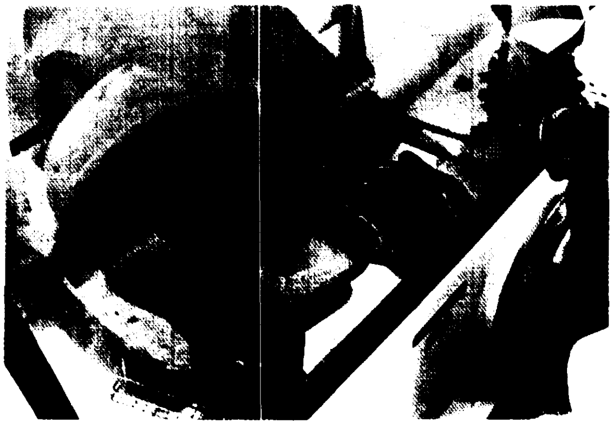


Photo (<redlt: U.S. Environmental Protection Agency

Special precautions must be taken to ensure that samples are not contaminated by the sampling equipment. This photo shows aquifer material being extruded from a core sampling tube while a sterile shaving device removes material that has been in contact with the inside of the sampler.

Uncertainties about immiscible substances that do not move with groundwater can be reduced with the collection of more information, especially about the hydrogeologic factors that control the movement of such substances. The uncertainty associated with the behavior of substances that do not move with groundwater flow due to physical, chemical, and biological processes cannot be reduced significantly, given technical limitations in understanding these processes. However, precautionary steps can be taken to minimize the impact of this and any other remaining uncertainties, including: using sensitivity analyses to test the significance of varying assumptions about groundwater flow and the behavior of substances; using conservative or worst-case assumptions about groundwater flow as the basis for designing corrective or preventive measures; and continuing the monitoring of groundwater flow and water quality as part of the implementation of any program to corrector prevent contamination so that any errors in predictions about the response of contaminants can be recognized early and compensating actions can be undertaken.

These precautionary steps may lead to overdesign and higher costs for corrective or preventive measures. However, overdesign may be the only way to limit risks associated with the lack of precise knowledge about the concentration and location of substances and the rate and direction of their movement.

An additional step that can be taken to improve reliability, and perhaps to reduce future costs and time required, is to keep records on the use of groundwater and the location of potential sources and their associated substances, With these records the hydrogeologist will have a better idea about which substances are of concern at a site and where to look for them.

Approaches for Minimizing Difficulties in Measuring Substances

Analysis of water quality samples is a technically complex process, and the difficulties associated with accurate measurement and interpretation of data are discussed in the literature (e. g., Keith, et al., 1982b, 1983; Miller, S., 1982). Uncertainties can be introduced at many steps—including when the sample is collected, handled, transferred, stored, prepared for analysis, as well as analyzed (Shifrin, 1984). Thus, detection limits (as presented in table 28) are not absolute; they depend on many factors, including the skill and experience of the analyst, the combinations and concentrations of the substances present, and the equipment used. For example, acceptable ranges for precision and accuracy, used for EPA-sanctioned methods by contract laboratories, range from 15 to 50 percent and 15 to 200 percent, respectively, depending on the organic classes measured (Keith, et al., 1983).[16]

In all cases, uncertainties in the analytical results need to be defined if the data are to be correctly interpreted. This need is especially important for the types of groundwater samples for which a high degree of accuracy is ***not*** now attainable—samples in which there are complex mixtures of substances, samples in which substances are present at trace concentrations, and samples being analyzed with relatively new analytical methods.

Some uncertainties can at least be defined, if not reduced, through quality assurance/quality control programs. QA/QC programs, which are part of EPA's contract analysis program, need to consider sample handling and storage procedures, sample preparation, care of equipment, methods for assessing data for completeness, and record-keeping and documentation (ACS, 1980, 1982). Analysis of several samples is also important for obtaining statistically significant results. Other factors important for obtaining meaningful analytical results in groundwater contamination studies concern: the laboratory certification process,[17] laboratory selection, availability of background information (e.g. about sources and users), availability of information about the nature and history of the sample, independent confirmation of the quality of laboratory data, and guidance on the selection of appropriate measurement methods (Woodward-Clyde Consultants, 1983; Keith, et al., 1983).

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[16] With respect to precision, if acceptable precision is, say, 50 percent, then only those samples with concentration differences *greater* than 50 percent actually represent samples with differing concentrations. With respect to accuracy, an acceptable accuracy range of, for example, 75 to 115 percent implies that the observed concentration of a substance would have to be either: 1) lower than the true value by one-fourth, or 2) greater than the true value by 15 percent for the data to indicate that the substance was *not* present at the actual concentration.

[17] While the laboratory certification process is meant to promote the reliable generation and documentation of data, certification has certain limitations which should be examined on a laboratory-specific basis. For example, specific requirements for certification may vary by State or by region; certification status can change over time; certification usually is issued on a substance-by-substance basis and only at specified concentration levels (e.g., laboratory certification for compliance purposes under SDWA is issued only for substances covered by NIPDWR and for those concentration levels expected to be found in drinking water); and certification may apply either to individual personnel or to the entire laboratory.

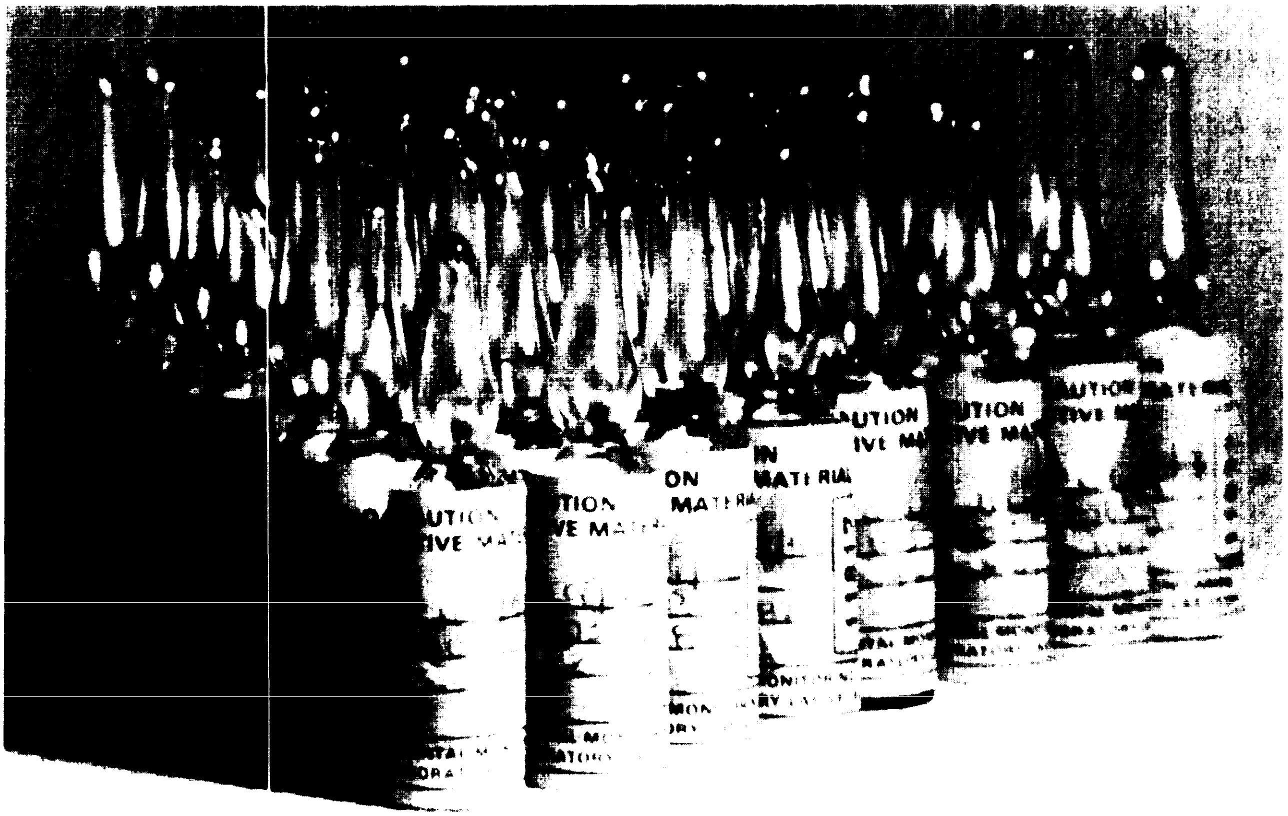

Photo credit: U.S. Environment/ Protectlon Agency

Standard reference materials are provided by EPA's Environmental Monitoring Laboratory to laboratories for instrument calibration and internal checks in order to evaluate performance.

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