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Technology Transfer

# EPA Seminar Publication

# Site Characterization for Subsurface Remediation

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# Site Characterization for Subsurface Remediation

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
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# Notice

# Preface

Site characterization of contaminated sites has become an increasingly complex process as a result of rapid developments in (1) methods for observing the physical, chemical, and biological characteristics of the subsurface, and (2) methods for remediation of soil and ground water. Consideration of the possible methods that may be used to clean up contaminated soils or ground water early in the site characterization process can ensure that data collected are appropriate and possibly reduce the time it takes to initiate clean-up efforts.

This seminar publication provides a comprehensive approach to site characterization for subsurface remediation. Chapter 1 describes a methodology for integrating site characterization with subsurface remediation. This introductory chapter of the handbook also provides a guide for quickly and efficiently accessing information in the rest of the document for specific remediation applications through the use of summary tables, checklists, figures, and flow charts.

The rest of the handbook is divided into three parts. Part I covers methods for subsurface characterization, Part II covers physical and chemical processes in the subsurface that relate to the selection of remediation methods, and Part III covers methods for soil and ground-water remediation.

In Part I, Chapter 2 provides an overview of the site characterization process. The next four chapters cover physical aspects of site characterization: geologic and hydrogeologic aspects (Chapter 3), characterization of water movement in the unsaturated zone (Chapter 4), characterization of the vadose zone (Chapter 5), and characterization of water movement in saturated fractured media (Chapter 6). The remaining three chapters in Part I cover geochemical aspects of site characterization: basic analytical and statistical concepts (Chapter 7), the geochemical variability of the natural and contaminated subsurface (Chapter 8), and geochemical sampling of soil and ground water (Chapter 9).

Part II contains three chapters on physiochemical processes affecting the transport of major types of contaminants: organics in liquid and solid phases in the subsurface (Chapter 10), organic volatilization and gas-phase transport (Chapter 11), and inorganic contaminants (Chapter 12). Chapter 13 focuses on abiotic and microbiological degradation and transformation processes in the subsurface.

Part III contains three chapters on remediation. Chapter 14 outlines basis approaches to remediation of contaminated soil and ground water. The concluding chapters provide more detailed information on specific techniques for cleaning up contaminated soil (Chapter 15) and ground water (Chapter 16).

# Contents

**Part I: Methods for Subsurface Characterization**

# Contents (continued)

# Contents (continued)

**Part II: Physical and Chemical Processes in the Subsurface**

# Contents (continued)

**Part III: Soil and Ground-Water Remediation**

# Contents (continued)

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# Chapter 1
# Integrating Site Characterization with Subsurface Remediation

Ronald C. Sims and Judith L. Sims

This handbook on site characterization for subsurface remediation emphasizes processes and concepts (Parts I and II), characterization tools and analyses of data (Part I), and remediation decisions (Part III). Chapter 1 relates subsurface site characterization activities to the selection of subsurface remediation technologies. Chapters 2 through 16 each address a specific aspect of site characterization or remediation technology (e.g., geologic aspects, saturated zone, unsaturated zone, remediation techniques for contaminated soils).

## 1.1 Approach for Integration of Site Characterization with Subsurface Remediation

Chapter 1 integrates the information presented in Chapters 2 through 16 so that the reader is guided through the Handbook and may access necessary interdisciplinary information quickly and efficiently for specific remediation applications. The tables, checklists, figures, and flow charts in this chapter synthesize relevant terms, parameters, and concepts relating site characterization to specific subsurface remediation techniques. Using this information to select subsurface treatment technologies requires specific information that is interdisciplinary, thereby cutting across areas of specialization, i.e., chapters. Therefore, this chapter not only provides an index to the Handbook, but also provides comments and guidance about the relationship between characterization parameters and technology selection.

This chapter also discusses the importance of understanding the surface physical layout of a site, including cultural features and industrial structures (e.g., buildings, lots, production units) and the evaluation of historical records of production and waste management within the context of site characterization for subsurface remediation. Activities such as making site visits and obtaining historical records of site and waste management are an integral part of site characterization. Information from these activities, which can provide valuable insights concerning limitations as well as applications of remediation technologies at field scale, is referred to collectively as site reconnaissance information.

## 1.2 Subsurface Site Characterization for Remediation Technology Selection

A methodology for integrating site characterization with subsurface remediation is shown in Figure 1-1. The development of information for a specific site progresses from characterization through monitoring (left to right as illustrated across Figure l-l). The figure presents characterization needs in terms of waste interaction with unsaturated soil in the vadose zone or sediment or aquifer material in the saturated zone as influenced by site factors such as climate, topography, surface slope, etc. Information from site characterization is used to formulate, in qualitative and quantitative terms, the problem(s) in terms of pathways of migration, escape, and/or exposure at a contaminated site (problem assessment). This information is used for subsurface treatment technique evaluation, elimination of unsuitable technique(s), and selection of an appropriate treatment (train). Monitoring provides feedback on rate and extent of remediation at field scale as well as information for modification of site management. Sections 14.1 and 14.2 present this methodology in more detail.

Table 1-1 lists specific aspects of each step of the methodology, presents relevant concepts, and indicates references in the Handbook for additional information on each step of the methodology. Specific characterization parameters are related to problem assessment, treatment, and monitoring. For example, the distribution coefficient, $K_d$, will allow evaluation of the problem at a site with regard to migration. If soil flushing is selected as a treatment technique, it may be monitored effectively through pore-liquid phase sampling. Information on each aspect can be found in the sections in the Handbook listed under Text Reference (Section) on the table.

Subsurface-based waste characterization information needs are summarized in Table 1-2. Potential impacts of waste on ground-water, vadose-zone, atmosphere, and surface-water resources depend upon properties of the waste chemicals and properties of the affected matrix. Information on these properties is necessary to adequately assess the problem at a specific site, as described above. Table 1-2 presents individual parameters and text references for describing those parameters.

Figure 1-2 illustrates problem assessment in terms of compartments as well as pathways of migration for chemical migration, escape, and/or exposure. A mass balance conceptual approach to the subsurface identifies chemicals that will (1) migrate upward (volatilization); (2) migrate downward (leaching, pure product); (3) migrate laterally (aqueous plume and pure product); and (4) remain in place as persistent chemicals. A nonaqueous phase liquid (NAPL) may be further classified as a light NAPL (LNAPL) if the density of the

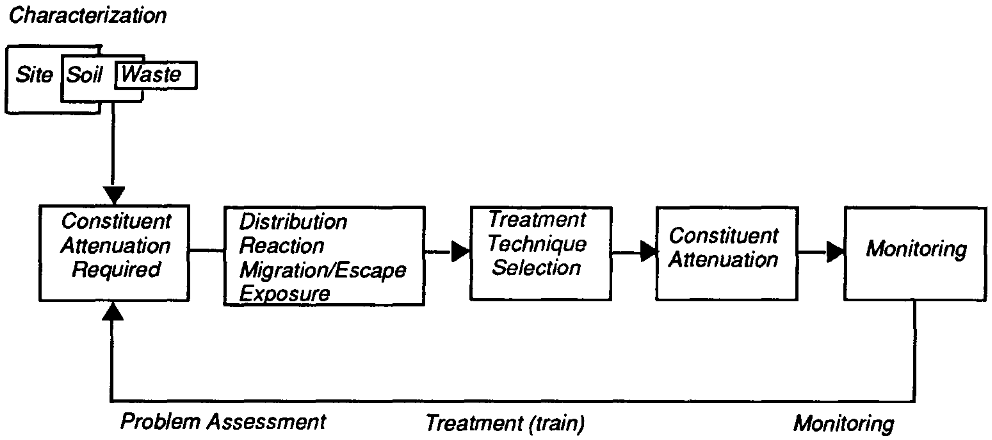


**Figure 1-1.** **Methodology for integrating site characterization with subsurface remediation.**

*Table 1-1.* *Methodology for Relating Site Characterization to Subsurface Remediation*

| *Characterization* | *Problem Assessment* | *Treatment* | *Monitoring*[a] | *Text Reference (Section)* |
|---|---|---|---|---|
| *Distribution* | | | | |
| $K_d$ | *persistence* | *biodegradability* | *c* | *(10.3.1) (12.1.4) (14) (15.2.3) (16.2)* |
| | *migration* | *soil flushing* | *l* | *(10.3.2) (12.2) (14.1) (14.2) (14.3) (15.2.4) (16.2)* |
| $K_h$ | *loss in air* | *vacuum extraction* | *g* | *(5.2.5) (11) (14.1) (14) (15.2.1)* |
| $K_o$ | *residential saturation* | *soil flushing* | *l* | *(102.) (12.3) (14) (15.2.4) (16.2)* |
| | | *biodegradation* | *c* | *(13.3) (14) (15.2.2) (16.3)* |
| *species*[b] | *phase(s) of occurrence* | *immobilization flushing, volatilizing* | *c, l, g* | *(8.1) (12.1.1) (12.4) (15.2.3) (15.2.4)* |
| *Degradation* | | | | |
| *chemical* | *rate/extent intermediates* | *chemical destruction and detoxification* | *c, l* | *(12.1) (13.1) (14) (15.1) (15.2.3)* |
| *biological* | *rate/extent intermediates* | *biological destruction and detoxification* | *c, l* | *(13.2) (13.3) (14) (15.1) (15.2.2) (15.3) (16.3)* |
| *Transport* | | | | |
| *advection* | *extent/rate of escape/ exposure* | *containment, removal destruction* | *l, g* | *(2.2) (3) (4.1) (5.2) (6.1) (10.1) (11.2) (12.2) (12.4.4) (14) (15) (16)* |
| *diffusion* | *slow release* | *containment, removal destruction* | *c, l, g* | *(8.1) (8.3) (11.2.1) (12.4.3) (14) (16.2)* |
| *Sampling* | | | | |
| *physical environment* | *extent of contamination* | *accurate evaluation of any technology* | *c* | *(2.5) (3.1) (3.2) (3.3) (6.2) (7.3) (9.2)* |
| *aqueous environment* | *extent of contamination* | *accurate evaluation of any technology* | *l* | *(2.5) (3.4) (4.2) (5.2) (7.3) (8.1) (8.3) (9.2) (9.3)* |
| *Modeling* | | | | |
| *vadose zone* | *identify problem for any treatment* | | *c, l, g* | *(5.3) (10.1) (10.2) (10.3.1) (10.3.2) (11.2) (12.4) (13.2.4) (14.2.1) (14.2.2) (14.3.1)* |
| *saturated zone* | *identify problem for any treatment* | | *c, l, g* | *(2.2) (3.5.2) (4.3) (4.5) (6.3) (10.1) (10.2) (10.3.1) (10.3.2) (12.4) (13.2.4) (14.2.1) (14.2.2) (16.3)* |

[a] (c) = core material; (1) = pore liquid phase; (g) = gas phase.

[b] Species are determined primarily for inorganics (metals) and affect metal phase (aqueous, solid, gas).

liquid is less than water, or as a dense NAPL (DNAPL) if the density of the liquid is greater than water. Additional information on the compartments comprising the subsurface is presented in Section 14.1. Figure 1-2 also indicates references for additional information on each topic.

Subsurface remediation techniques that may be evaluated based upon site characterization and problem assessment, as outlined above, are summarized in Table 1-3 and presented for each technology-and-environment combination in Tables 1-4 through 1-9. The tables are organized according to treatment category (biological, physical/chemical, and containment) and environment (vadose zone and saturated zone). Each table also is organized according to characterization parameters, comments, and text reference by sections in the Handbook. These tables can be used to quickly locate information within the Handbook that relates treatment technologies to specific site characterization parameters.

## 1.3 Site Reconnaissance

Site reconnaissance activities include gathering information on site layout, history, and records of management. Aboveground natural and cultural features and industrial processes are important aspects of a site that may affect subsurface processes and the application of subsurface remediation technologies. Table 1-10 lists important site conditions that can be used as part of site characterization for subsurface remediation. Identification of these features and processes provides critical information concerning potential vadose-zone and ground-water quality as well as limitations for the application of subsurface remediation technologies. A site visit may reveal the industrial processes or waste sources that contribute to contamination at a site. Observations of topography, buildings, parking lots, and waste facilities provide valuable information on accessibility for sampling, culturally induced flow of gases (e.g., beneath buildings), and limitations or constraints to the application of subsurface treatment technologies (e.g., site size constraints or natural boundaries).

Information on past waste management practices that documents conditions under which hazardous waste has been managed is important to site characterization. Table 1-11 lists important waste management data and records that can be used in planning a site characterization effort. These records may include available history of waste disposal and waste composition. This information may be used in conjunction with subsurface core and pore-liquid characterization data to determine areas of contamination and areas of nonhomogeneity, to evaluate the areal and depth extent of contamination, and to modify a site characterization plan.

Figure 1-3 presents a flow chart demonstrating an iterative approach for data collection from site characterization activities for subsurface remediation evaluation and selection, as well as field optimization of remediation technologies. This approaches combines site reconnaissance information with site characterization and sampling, utilizing the methodology presented in Figure 1-1, for selecting, evaluating, and applying the subsurface remediation techniques addressed in Tables 1-4 through 1-9.

*Table 1-2. Subsurface-Baaed Waste Characterization*

| *Parameter* | *Text Reference (Section)* |
|---|---|
| *Chemical class*[a] | *(7.4.2) (8.1.2) (8.3) (9.1.4) (9.3.1) (9.3.3) (9.3.4) (12) (14.1) (14.2)* |
| *Chemical properties*[b] | *(8.1) (8.3) (10.2) (10.4) (14.1)* |
| *Chemical reactivity*[c] | *(2.2) (7.4.2) (8.1) (8.3) (8.4) (12.1.2) (12.1.3) (14.1)* |
| *Sorption*[d] | *(2.2) (8.1.2) (10.3) (12.1.4) (14.1) (15.2.3 (15.2.4)* |
| *Degradation*[e] | *(2.2) (8.1) (8.3) (13) (15.2.2) (14.1) (16.3* |
| *Volatilization*[f] | *(5.2.5) (5.4) (9.1.6) (9.2) (11) (14.1) (15.2* |
| *Interphase phase potential*[g] | *(5.2.5) (14.1) (14.4)* |

[a] Organic (acid, base, polar neutral, nonpolar neutral), and inorganic.

[b] Molecular weight, melting point, specific gravity, structure, volubility, ionization, cosolvation.

[c] Oxidation, reduction, hydrolysis, precipitation, dissolution, polymerization.

[d] Adsorption, desorption, ion exchange.

[e] Biotic, abiotic.

[f] Henry's Law partitioning, soil gas analysis, vacuum extraction.

[g] Includes gas, inorganic mineral solid, organic matter solid, water, and nonaqueous phases.

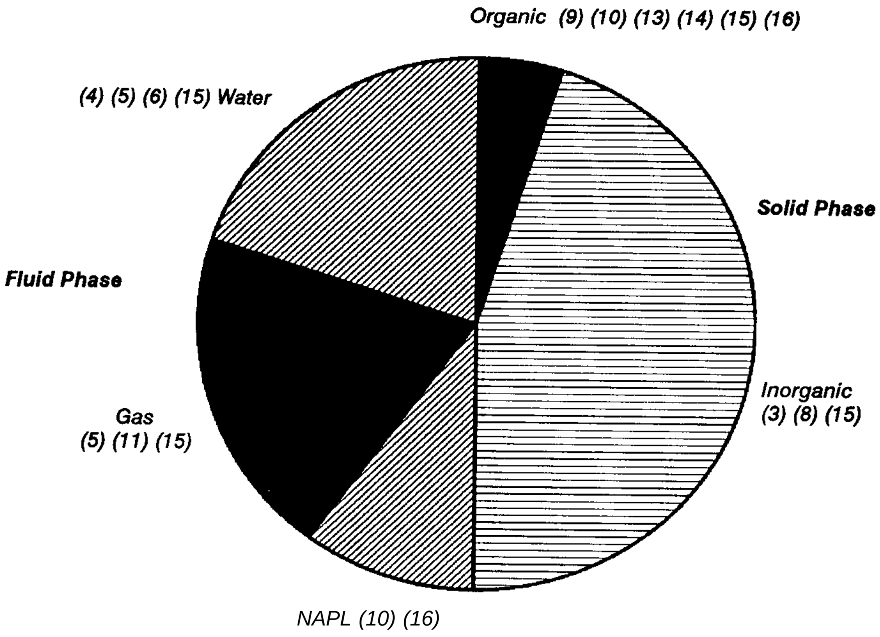
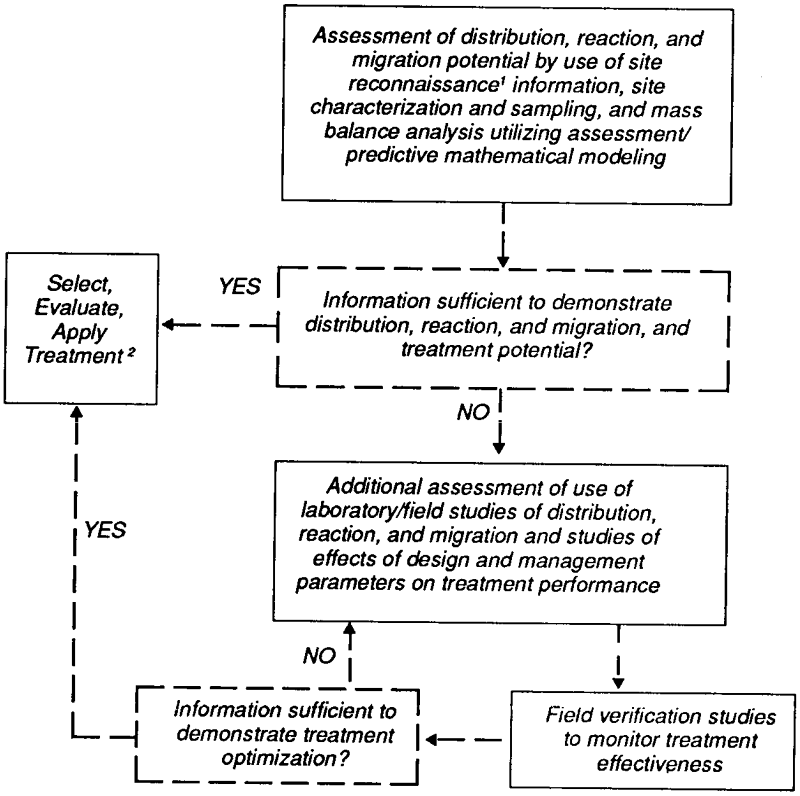


**Figure 1-2.** **Problem assessment for site characterization baaed on mass balance approach (Chapters 2, 12, and 14).**



[1] Site reconnaissance activities at a site include gathering information such as site layout, history, and records of management.

[2] Treatment = biological, physical/chemical, or containment (Table 1-3).

**Figure 1-3.** **Flow chart for evaluation of site characterization for subsurface remediation.**

*Table 1-3. Summary of Tables of Characterization Parameters for Subsurface Remediation Technologies*

| | *Treatment Technology Category* | | |
|---|---|---|---|
| *Subsurface Environment* | *Biological* | *Physical/ Chemical* | *Containment* |
| | *[Text Reference (Table Number)]* | | |
| *Vadose zone* | *1-4* | *1-6* | *1-8* |
| *Saturated zone* | *1-5* | *1-7* | *1-9* |

*Table 1-4. Characterization for Biological Treatment of Soil in the Vadose Zone**

| *Parameter* | *Comments* | *Text Reference (Section)* |
|---|---|---|
| Physical | | |
| *moisture* | *affects microbial activity/kinetics* | *(4.2.2) (5.2.3) (5.2.4) (5.2.5) (9.2.2) (13.2.2) (14.2.1) (14.3.2) (15.2.1) (15.2.2) (15.3)* |
| *temperature* | *affects microbial activity/kinetics* | *(13.2.2) (14.2.1) (14.3.2) (15.2.2)* |
| *permeability* | *affects nutrient supply and gas exchange* | *(5.2.4) (13.3.1) (14)* |
| *pH* | *affects chemical form and microbial activity* | *(13.2.2) (8.1.2) (12.2.2) (14.2.1) (14.3.2)* |
| *oxygen availability* | *affects aerobic/anaerobic metabolism, activity/kinetics* | *(5.2.5) (11) (12.1.3) (13.2) (13.3) (14.2.1) (14.3.2) (15.2.2)* |
| *interphase transfer potential* | *used in mass balance to determine abiotic removal* | *(56.2.5) (14.1) (14.4)* |
| Chemical | | |
| *individual chemicals* | *affects rate and extent of degradation* | *(8.1.2) (13.2.1) (13.3.2) (14.2.2) (15.2.2)* |
| *redox potential* | *often controlled by microorganisms and related to aerobic/anaerobic pathway* | *(8.1.2) (13.2.2)* |
| *C:N:P ratio/ nutrient* | *affects microbial growth* | *(13.2.2) (13.3.1)* |
| Biological | | |
| *kinetics/activity* | *affects rate of degradation* | *(13.2.4) (13.3.1) (15.2.2)* |
| *enumeration* | *related to population or mass of microorganisms* | *(13.2.1) (13.3.1)* |
| *toxicity* | *affects rate and extent of degradation* | *(13.3.1) (15.2.2)* |
| *metabolism* | *influences production of (toxic) intermediates and indicates mechanism(s) of biodegradation* | *(13.2.3) (15.2.2)* |
| *treatability studies* | *can indicate potential for degradation and important factors controlling rate and extent* | *(14.3.2)* |
| *adaptation* | *ability of system to acclimate, indicated by increase in rate and extent of degradation with incubation time and with repeated applications of contaminated material* | *(13.2.3) (15.2.2)* |

**Approaches and specific techniques for treatment are addressed in Chapters 14 and 15 and listed in Tables 15-3 and 15.4.*

***Table 1-5. Characterization for Biological Treatment of Aquifer Material in the Saturated Zone****

| *Parameter* | *Comments* | *Text Reference (Section)* |
|---|---|---|
| Physical | | |
| *temperature* | *affects microbial activity/kinetics* | ***(13.2.2) (14.2.1) (14.3.2) (15.2.2)*** |
| *permeability* | *affects nutrient supply and gas exchange* | ***(4.2.3) (13.3.1) (14)*** |
| *geology* | *influences heterogeneity, clay lenses influences waste distribution* | ***(3.1) (3.2) (3.3) (3.4)*** |
| *geochemistry* | *influences microbial activity* | ***(8.1.2) (8.3)*** |
| *pH* | *affects chemical form (mobility) and microbial activity* | ***(13.2.2) (8.1.2) (12.2.2) (14.2.1) (14.3.2)*** |
| *oxygen availability* | *affects aerobic/anaerobic metabolism, and activity kinetics* | ***(11) (12.1.3) (13.2) (13.3) (14.2.1) (14.3.2) (15.2.2)*** |
| *interphase transfer potential* | *used in mass balance to determine abiotic removal* | ***(5.2.5) (14.1) (14.4)*** |
| Chemical | | |
| *individual chemicals* | *affects rate and extent of degradation* | ***(8.1.2) (8.3) (13.2.1) (13.3.2) (14.2.2) (15.2.2)*** |
| *redox potential* | *often controlled by microorganisms and related to aerobic/anaerobic pathway* | ***(8.1.2) (13.2.2)*** |
| *C:N:P ratio/nutrient* | *affects microbial growth* | ***(13.2.2) (13.3.1)*** |
| Biological | | |
| *kinetics/activity* | *affects rate of degradation* | ***(8.1.2) (13.2.4) (13.3.1) (15.2.2)*** |
| *enumeration* | *related to population or mass of microorganisms* | ***(13.2.1) (13.3.1)*** |
| *toxicity* | *affects rate and extent of degradation* | ***(13.3.1) (15.2.2)*** |
| *metabolism* | *influences production of (toxic) intermediates and indicates mechanism(s) of biodegradation* | ***(9.3.1) (13.2.3) (15.2.2)*** |
| *treatability studies* | *can indicate potential for degradation and important factors controlling rate and extent* | ***(14.3.2)*** |
| *adaptation* | *ability of system to acclimate, indicated by increase in rate and extent of degradation with incubation time and with repeated exposure* | ***(13.2.3) (15.2.2)*** |

** Approaches and specific techniques for treatment are addressed in Chapters 14 and 16.*

**Table 1-6. Characterization Parameters for Physical/Chemical Treatment of the Vadose Zone***

| Technique | Parameter | Comments | Text **Reference (Section)** |
|---|---|---|---|
| Extraction | | | (15) (15.2.4) |
| | **physical** | | |
| | particle size distribution | affects volume reduction, sorption, extraction difficulty | (3.2) |
| | conductivity/permeability | affects flow velocity (time) for extraction | (5.2.4) (15.2.4) |
| | organic matter | affects distribution and sorption of chemicals | (3.2) |
| | moisture content | affects conductivity of air through soil for vacuum extraction | (4.2.2) (5.1) (5.2.3) |
| | heterogeneity/layering | affects relative rates of extraction for different layers | (3.1) (3.3) |
| | depth | along with area, determines volume of contaminated material and engineering strategies for extraction | (3.5.1) (5.1) |
| | soil gas | used along with soil core analysis to monitor extent and rate of vacuum extraction | (5.2.5) |
| | interphase transfer potential | used in mass balance to determine treatment effectiveness | (5.2.5) (14.1) (14.4) |
| | **chemical** | | |
| | individual chemicals | examples of chemicals that have been treated | (5.4) (15) |
| | pH changes | may indicate precipitation or dissolution that affects ease of extraction (permeability) | (8.1.2) |
| | chemical characteristics[c] | aids in selection of extraction fluid | (5.1.5) (5.4) (7.4.2) (8.2) (10.3.1) (10.4) (11.1) (11.2.3) (12. 1) (12.3) |
| | cation exchange capacity | determine cation sorption potential, related to clay content | |
| | organic and metal content | determine target and/or interfering constituents, pretreatment needs, extraction fluid | |
| | redox potential | indicates mobile and immobile forms of chemicals | |
| Oxidation/ Reduction | | | |
| | individual chemicals | examples of chemicals that have been treated | |
| | redox potential | status of the system before treatment | |
| Solidification/ Stabilization | | | |
| | individual chemicals/sites | examples of chemcals/sites that have been treated | |
| | porosity/permeability | affects delivery and mixing of chemicals | |

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[a] Approaches and specific techniques for treatment are addressed in Chapters 14 and 15 and are listed in Tables 15-1, 15-2, 15-3, and 15-4.

[b] Extraction techniques include aqueous, solvent, critical fluid, vacuum (air/steam), and low temperature thermal stripping.

[c] Chemical characteristics include vapor pressure, solubility, Henry's Law constant, partition coefficient, boiling point, and specific gravity.

**Table 1-7. Characterization Parameters for Physical/Chemical Treatment of the Saturated Zone**

| Technique | Parameter | Comments | Text Reference (Section) |
|---|---|---|---|
| Product Removal | | | (16)(16.1) |
| | **physical** | | |
| | particle size distribution in vadose zone | affects amount of contaminant stored in capillary fringe for LNAPL | (3.2)(10.2) |
| | particle size distribution in saturated zone | affects permeability and product retention | (3.2)(8.1.2) |
| | flow characterization | affects direction, location, and extent of LNAPL | (2.2)(2.4)(10.2) |
| | geology | influences distribution of DNAPL and LNAPL | (3)(6.1) |
| | organic matter | affects distribution and sorption | (3.2)(10.3.2) |
| | interphase transfer potential | assists in determining phase(s) where more than one phase is involved | (5.2.5)(14.1)(14.4) |
| | **chemical** | | |
| | individual chemicals, contaminants | examples of contaminants that have been treated | (3.5.2)(4.4)(11.3)(14.3) |
| | redox | temporal and spatial variation may influence permeability | (8.1.2)(8.3.3)(8.4)(9.1.3)(13.2.2) |
| | soil gas analysis | assist in locating contamination (area) | (5.2.5)(9.2.1) |
| | properties[b] | assist in locating contamination (depth) | (10.2)(10.4)(11.1)(11.2) |
| Pump-and-Treat | | | (16)(16.2) |
| | **physical** | | |
| | particle size distribution in saturated zone | affects pumping (recovery) rate of water and contaminant | |
| | flow characterization | affects direction, location, and extent of contamination | (2.2)(2.3)(2.4)(4.1)(4.2.2)(4.2.3)(6.1) |
| | geology | influences distribution of contaminants | (3)(6.4) |
| | organic matter | affects distribution and sorption | (3.2)(10.3.2.) |
| | interphase transfer potential | assists in determining phase(s) where contaminant is found | (14.1)(14.4) |
| | **chemical** | | |
| | individual chemicals, contaminants | examples of contaminants that have been treated | (3.5.2)(4.4)(4.5) |
| | redox | temporal and spatial variation may influence permeability | (8.1.2)(8.3.3)(8.4)(9.1.3)(13.2.2) |
| | soil gas analysis | assist in locating contamination (area) | (5.2.5)(9.2.1) |
| | propertied | assist in locating contamination (depth) | (10.2)(10.4)(11.1)(11.2)(12.1)(12.2) |
| | organic-inorganic interactions | affects design of systems | (12.3) |

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[a] Approaches and specific techniques for treatment are addressed in Chapters 14 and 16, Section 16.1.

[b] Properties include molecular weight, specific gravity, volubility, melting point, structure, ionization, and cosolvation.

***Table 1-8. Characterization Parameters for Immobilization[a]/Containment[b] Techniques in the Vadose Zone[c]***

| *Technique* | *Parameter* | *Comments* | *Text Reference (Section)* |
|---|---|---|---|
| *Immobilization* | | | *(15)(15.2.3)* |
| | **physical** | | |
| | *particle size distribution* | *affects sorption, ion exchange* | *(3.2)* |
| | *moisture content* | *affects efficiency, energy requirements, and sorption* | *(5.1)(5.2.3)(14.1)(15)(15.2.3)* |
| | *permeability* | *affects delivery of chemicals* | *(5.2.4)(15.2.3)* |
| | *organic matter* | *affects distribution and sorption* | *(3.2)(10.3.1)(14.1)* |
| | *depth* | *along with area, determines volume of contaminated material and engineering strategies* | *(3.5.1)(5.1)* |
| | *lithology* | *affects extent of sorption and ion exchange* | *(3.2)* |
| | *interphase transfer potential* | *used in mass balance to evaluate solution to solidphase transfer for immobilization* | *(5.2.5)(14.1)(14.2.2)(14.4)* |
| | **chemical** | | |
| | *individual chemicals contaminants* | *examples of contaminants that have been treated* | *(5.5)* |
| | *redox potential* | *affects chemical speciation and thus immobilization* | *(8.1.2)* |
| | *pH* | *affects chemical speciation and thus immobilization* | *(8.1.2)* |
| | *cation exchange capacity* | *affects ion exchange* | *(8.1.2)* |
| | *properties* | *affects affinity of chemicals for surfaces and for precipitation* | *(8.1)(8.3)(10.3.1)(10.3.2)(10.4)<br>(11.1)(12.1)(14.1)(14.2.1)* |
| *Containment* | | | |
| | **physical** | | |
| | *stratigraphy* | *identify path ways and extent of chemical migration* | *(3.1)* |
| | *interphase transfer potential* | *used in mass balance to evaluate success of containment* | *(5.2.5)(14.1)(14.2.2)(14.2.3)(14.4)* |
| | *containment requirements* | *evaluate containment of gas, liquid, and solid phases* | *(14.2.3)* |

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[a] *immobilization techniques include sorption, ion exchange, precipitation, stabilization/solidification, and vitrification.*
[b] *Containment techniques include physical stuctures.*
[c] *Approaches and specific techniques for treatment are addressed in Chapters 14 and 15, Section 15.2.3.*
[d] *Properties include molecular weight, melting point, specific gravity, structure, ionization, solubility, and cosolvation.*

**Table 1-9. Characterization Parameters for Containment Technlques[a] in the Saturated Zone [b]**

| Technique | Parameter | Comments | Text Reference (Section) |
|---|---|---|---|
| Hydraulic | | | |
| | **physical** | | |
| | flow system characterization | determine area and depth for containment | (2.2) |
| | permeability | affects rate of movement and rate of pumping | (4.4) |
| | geology | assists with flow system characterization | (3) |
| | advection | generally primary transport (escape) path | (4.1) |
| | interphase transfer potential | used in mass balance to assess and evaluate containment | (5.2.5)(14.1)(14.2.2)(14.4) |
| | fracture flow | may exercise control on ground-water flow | (6.1) |
| | physical gradients | affects geochemistry, which may affect permeability | (8.3.2) |
| | **chemical** | | |
| | contaminants present | identify chemicals of concern that might escape | (2.3) |
| | individual chemicals/ contaminants | examples of contaminants that have been contained | (3.5.2)(4.4)(4.5) |
| | environmental parameters[c] | may change with pumping and affect recovery and permeability | (8.1.2) |
| | chemical gradients | may affect geochemistry if reinfected and affect permeability | (8.3.3) |
| | propeties[d] | affects affinity of chemicals for surfaces and for precipitation, as well as interphase transfer | (10.2)(10.3.1)(10.3.2) |
| | reactions[e] | may affect treatment/permeability while pumping | (13.1)(13.2) |
| Physical Structuresf | | | |
| | **physical** | | |
| | flow system characterization | determine area and depth for containment | (2.2) |
| | geology | assists with flow system characterization | (3) |
| | fracture flow | may exercise control on ground-water flow | (6.1) |
| | **chemical** | | |
| | contaminants present | identify chemicals of concern that might escape | (2.3) |
| | individual chemicals/ contaminants | examples of contaminants that have been contained | (3.5.2) |

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[a] Containment techniques may be temporary and used as part of a treatment train that includes product removal, pump-and-treat, pumping and reinjection, and bioremediation.

[b] Approaches and specific techniques are addressed in Chapters 4 (section 4.4), 14 and 16 (Section 16.2).

[c] Environmental parameters include pH, alkalinity, redox potential, salinity, temperature, and pressure.

[d] Properties include molecular weight, melting point, specific gravity, structure, solubility, ionization, and cosolvation.

[e] Reactions include hydrolysis, substitution, elimination, oxidation-reduction, and biodegradation.

[d] Physical structures often are used in conjunction with hydraulic containment and withdrawal (e.g., clay cap to reduce recharge combined with extraction wells to remove chemical) (refer to Section 3.5.2).

**Table 1-10. Aboveground Features for Site Characterization**

| Item | Specific Information |
|---|---|
| Site location | Topographic map, including contours, map scale and date, floodplain areas, surface waters, springs and intermittent streams, and site legal boundaries. |
| | Site map, including injection and withdrawal wells on site and off site; buildings and recreation areas, access and internal roads; storm, sanitary, and process sewerage systems; loading and unloading areas; and fire control facilities. |
| | Location of past ano/or present operation units and equipment cleaning areas, ground-water monitoring wells, delineation of waste management units, and site modifications. |
| | Surrounding area land use patterns. |
| | Vegetation (trees, shrubs, grasses). |
| Climatological data | Precipitation/evaporation/humidity. |
| | Site water budget. |
| | Temperature (averages and extremes) |
| | Wind rose. |
| | Predicted storm events (e.g., 24-hour, 25-year, average number of days of rain and snow). |
| | Frost action potential |

**Table 1-11. Waste Management Information for Site Characterization**

| Category | Item | Specific Information |
|---|---|---|
| History of waste application | Years in operation and annual quantity of waste generated and/or disposed. | Records of measured annual waste quantity (weight/volume) over life of site. Include hazardous and nonhazardous managed at same site. |
| | Placement of waste. | Records of quantity (weight/volume), and location of each waste disposal action. |
| | Size of waste unit(s) | Area and depth. |
| History of waste quality | Waste analyses. | Periodic analyses of hazardous. wastes. |
| | Unit processes. | History of unit processes employed in the generation and treatment of wastes. |
| | Disposal areas. | Pits, ponds, lagoons, landfills, storage tanks, wastewater treatment plant locations (present and historical). |

# PART I: METHODS FOR SUBSURFACE CHARACTERIZATION

## Chapter 2

## Site Characterization Overview

James W. Mercer and Charles P. Spalding

### 2.1 Introduction

Characterization of a hazardous waste site involves gathering and analyzing data to describe the processes controlling the transport of wastes from the site. It provides the understanding to predict future site behavior based on past site behavior. It can encompass the characterization of the waste itself as well as that of various transport pathways such as air, surface water, biota, and ground water. Ground water, the focus of this discussion, is often the most significant and least apparent transport pathway.

Site characterization follows the scientific method and is performed in phases (see Figure 2-l). First, a hypothesis is made concerning site or system behavior. Based on this hypothesis, a data collection program is designed, data are collected, and an analysis or assessment is made. Using the results of the analysis, the hypothesis is refined and additional data may be collected. As the knowledge of the site becomes more detailed, the working hypothesis may take the form of either a numerical or analytical model. Data collection continues until the hypothesis is proven sufficiently to form the basis for decision making.

Because the ultimate goal of site characterization is to make informed decisions, the first step is to define study objectives. A possible list of objectives, provided by Cartwright and Shafer (1987), includes the following: (1) assess the background or "ambient" water quality (how was the water before contamination?); (2) establish the impacts of certain facilities, practices, or natural phenomena on water quality (what is the extent of contamination?); and (3) predict future ground-water quality trends under a variety of conditions (what would be the impact of various remedial actions?).

Whatever the objectives, ground-water site characterization has two major components: assessment of the ground-water flow system and assessment of the contamination in the ground water. All too often, emphasis is placed on the latter component, which involves ground-water quality monitoring, Everett (1980) defines monitoring as a scientifically designed surveillance system of continuing measurement and observations. At many waste sites, ground-water quality data are abundant; however, water-level data used to determine advective transport are limited. This is unfortunate because water-level data are equally important, and they are easier and less expensive to collect than water-quality data.

This chapter provides an overview of Part I of the Handbook, which focuses on methods of site characterization. This chapter covers the following topics (1) flow system characterization, (2) contamination characterization, (3) techniques for characterization, and (4) analysis of data.

### 2.2 Flow System Characterization

Flow system characterization begins with an understanding of controlling processes and of the data required to define those processes (Table 2-l). Ground water is always in motion from areas of natural and artificial recharge to areas of natural and artificial discharge. Natural recharge occurs from precipitation and surface water bodies; artificial recharge results from human-induced actions such as irrigation and well injection. Ground water discharges naturally to springs and other surface water bodies, e.g., rivers, lakes, and oceans. Under natural conditions, ground water moves very slowly, its flow velocity ranging from a fraction of a foot per year to several feet per day. In most cases, flow obeys Darcy's law, which states that the velocity is proportional to both the hydraulic conductivity of the formation and the hydraulic gradient.. The term hydraulic conductivity is used to express the water-conducting capacity of the formation material. The hydraulic gradient is an expression of the slope of the ground-water surface.

Shallow aquifers are usually important sources of ground water. These upper aquifers are also the most susceptible to contamination. Contaminants may enter an upper aquifer in one of the following ways: (1) artificial recharge or leakage through wells; (2) infiltration from precipitation or irrigation

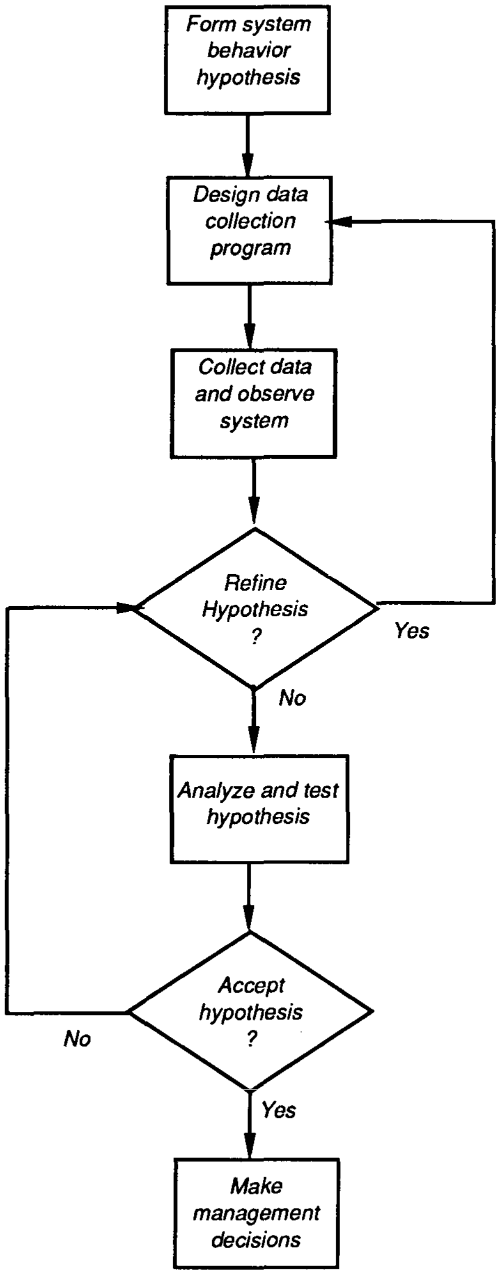


**Figure 2-1.** **Site characterization phasea (from Bouwer et al., 1988).**

return flow through the vadose zone above the water table; (3) induced recharge from influent streams and lakes or other surface water bodies; (4) inflow through aquifer boundaries and leakage from overlying or underlying formations; and (5) leakage or seepage from impoundments, landfills, or miscellaneous spills.

Water and contaminants carried with it may leave an aquifer in the following ways: (1) ground-water leakage from the aquifer into adjacent strata, (2) ground-water withdrawal by pumping and drainage, (3) seepage into effluent streams and lakes, (4) spring discharge, and (5) evapotranspiration. Data required to assess these processes are shown in Table 2-2. In general, these data requirements include a geometric description of the site (layering and hydraulic boundaries); storage and transmissive properties; and source/sink information. such as wells. More specific lists of data with ranges of values are provided in Mercer et al. (1982). For any particular site, it is rare to have all this information. Data gaps can be addressed by a field collection program, but to some extent must be filled based on experience. In addition to physical and chemical data, other factors listed in Table 2-2 include regulatory and legal issues such as water rights and future land use.

The first step in designing a field program is to review existing data for the site or nearby locations. Sources of information include the U.S. Geological Survey (USGS) (Mercer and Morgan, 1981); state geologic and water agencies; local water districts; and city, county, and state health departments. Other federal agencies that may provide data include the U.S. Environmental Protection Agency (EPA) (e.g., the STORET computerized information storage system); U.S. Bureau of Reclamation; U.S. Army Corps of Engineers; and U.S. Soil Conservation Service. Additional inforation may be available from consultants and universities. Several data sources are discussed below.

The U.S. Department of Agriculture, Soil Conservation Service, has three soil geographic data bases the Soil Survey Geographic Data Base (SSURGO), the State Soil Geographic Data Base (STATSGO), and the National Soil Geographic Data Base (NATSGO). Components of map units in each geographic data base are generally phases of soil series. The Soil Conservation Service also maintains a soil interpretations record data base, which encompasses more than 25 soil, physical, and chemical properties for the 15,300-plus soil series recognized in the United States. Interpretations are displayed differently for each geographic data base to be consistent with the level of detail expressed. Particle size distribution, bulk density, available water capacity, soil reaction, salinity, and organic matter are included for each major layer of the soil profile. Data on flooding, water table, bedrock, and subsidence characteristics of the soil; and interpretations for erosion potential, septic tank limitations, engineering, building and recreation development, and cropland, woodland, wildlife habitat, and rangelands management also are included.

The U.S. Department of Interior Geological Survey created and maintains a central storage facility for water resources data, known as the National Water Data Storage and Retrieval System (WATSTORE), at its National Headquarters in Reston, Virginia. Included in this computerized storage facility are representative ground-water data collected throughout the United States, This ground-water information resides in a computer data file, which is maintained by a database management system (DBMS) called SYSTEM 2000. The name and acronym given this data base is the Ground-Water Site-Inventory (GWSI) file. Although several field-collected parameters of water-quality data (including temperature, conductance, and pH) are stored in the GWSI, the bulk of water-quality data reside in a nationwide file called Storage and Retrieval (STORET), a file maintained by EPA. The National

*Table 2-1. A Summary of the Processes Associated with Dissolved Solute Transport and Their Impact*

| *Process* | *Definition* | *Impact on Transport* |
|---|---|---|
| Solute Transport | | |
| *Advection* | *Movement of solute as a consequence of ground-water flow.* | *Most important way of transporting solute away from source.* |
| *Diffusion* | *Solute spreading due to molecular diffusion in response to concentration gradients.* | *An attenuation mechanism of second order in most flow systems where advection and dispersion dominate.* |
| *Dispersion* | *Fluid mixing due to effects of unresolved heterogeneities in the permeability distribution.* | *An attenuation mechanism that reduces solute concentration in the plume. However, it spreads to a greater extent than a plume moving by advection alone.* |
| Solute Transfer | | |
| *Radioactive decay* | *Irreversible decline in the activity of a radionuclide through a nuclear reaction.* | *An important mechanism for attenuation when the half-life for decay is comparable* to *or less than the residence time of the flow system.*<br>*Also adds complexity in production of daughter products.* |
| *Sorption* | *Partitioning of a solute between the ground water and mineral or organic* solids *in the aquifer.* | *An important mechanism that reduces the rate at which the solute is apparently moving. Makes it more difficult to remove solute at a site.* |
| *Dissolution precipitation* | *The process of adding solutes to or removing them from solution by reactions dissolving or creating various solids.* | *Precipitation is an important attenuation mechanism that can control the concentration in solution. Solution concentration is mainly controlled either at the source or at a reaction front.* |
| *Acid-base reactions* | *Reactions involving a transfer of protons (I-P).* | *Mainly an indirect control on solute transport by controlling the pH of ground water.* |
| *Complexation* | *Combination of cations and anions to form more complexion.* | *An important mechanism resulting in increased volubility of metals in ground* water, *if adsorption is not enhanced. Major ion complexation will increase the quantify of a solid dissolved in solution.* |
| *Hydrolysis/ substitution* | *Reaction of a halogenated organic compound with water or a component ion of water (hydrolysis) or with another anion (substitution).* | *Often hydrolysis/substitution reactions make an organic compound more susceptible to biodegradation and more soluble.* |
| *Redox reactions (biodegradation)* | *Reactions that involve a transfer of electrons and include elements with more than one oxidation state.* | *An extremely important family of reactions in retarding solute spread through precipitation of metals.* |
| Biologically Mediated Mass Transfer | | |
| *Biological transformations* | *Reactions involving the degradation of organic compounds and whose rate is controlled by the availability of nutrients to adapted microorganisms and redox conditions.* | *Important mechanism for solute reduction, but can lead to undesirable daughter products.* |

*From NRC, 1990*

Water Data Exchange (NAWDEX) Local Assistance Centers are authorized users of the STORET file and may retrieve ground-water quaIity data for subscribers.

A field program usually follows a data review of hydrogeologic investigation techniques (U.S. EPA, 1986 and Sisk, 1981). Summaries of procedures for well installation and aquifer testing are described in Ford et al. (1984) and Aller et al. (1989). Kruseman and de Ridder (1976), Lawrence Berkeley Laboratory (1977, 1978) discuss methods of analysis of aquifer and slug tests. In general, as the scale of the observation increases, the range of measured properties, such as hydraulic conductivity, tends to change because of the heterogeneous nature of geologic materials. Particularly, ground-water flow rates estimated from measurements on cores may underestimate ground-water flow rates in the area if flow is in fractures or in other more permeable layers.

Because of seasonal changes in ground water, a minimum of one year should be devoted to characterization. As the site complexity increases, this period will increase proportionately. Several factors influence the number of boreholes required, the most important being heterogeneities in the aquifer materials. Methods of quantifying ground-water networks are not widely used but do exist. For example, van Geer (1987) shows how Kalman filters are used to design ground-water monitoring networks. Another technique used to evaluate ground-water networks is kriging (e.g., Olea, 1982); this technique is discussed further in Section 2.5 and in Chapter 7 (Section 7.3.2).

*Table 2-2. Data Pertinent to the Prediction of Ground-Water Flow*

*I. Physical Framework*
  - *1. Hydrogeologic map showing areal extent and boundaries of aquifer.*
  - *2. Topographic map showing surface-water bodies.*
  - *3. Water-table, bedrock-configuration, and saturated-thickness maps.*
  - *4. Hydraulic conductivity map showing aquifer and boundaries.*
  - *5. Hydraulic conductivity and specific storage map of confining bed.*
  - *6. Map showing variation in storage coefficient of aquifer.*
  - *7. Relation of stream and aquifer (hydraulic connection).*

*II. Stresses on System*
  - *1. Type and extent of recharge areas (irrigated areas. recharge basins, recharge wells, impoundments, spills, tank leaks, etc.).*
  - *2. Surface water diversions.*
  - *3. Ground-water pumpage (distributed in time and space).*
  - *4. Stream flow (distributed in time and space).*
  - *5. Precipitation and evapotranspiration.*

*III. Observable Responses*
  - *1. Water levels as a function of time and position.*

*IV. Other Factors*
  - *1. Economic information about water supply.*
  - *2. Legal and administrative rules.*
  - *3. Environmental factors.*
  - *4. Planned changes in water and land use.*

*After Moore, 1979*

## 2.3 Contamination Characterization

As with flow system characterization, contamination characterization begins with understanding the processes controlling transport and degradation (Table 2-1) and the data required to define those processes. These processes determine minimum data requirements needed to characterize a site. Nonreactive (conservative) dissolved contaminants in saturated porous media are controlled by the following factors:

1. *Advection:* This mechanism causes contaminants to be transferred by the bulk motion of the ground water. The term convection is sometimes used in place of advection.

2. *Mechanical (or kinematic) dispersion:* This process involves mechanical mixing caused by three mechanisms. The first mechanism occurs in individual pore channels because molecules travel at different velocities depending on whether they are near the edge or in the center of the channel. The second mechanism is triggered by differences in surface area and roughness relative to the volume of water in individual pore channels, causing different bulk fluid velocities in different pore channels. The third mechanism is related to the tortuosity, branching, and interfingering of pore channels, causing the streamlines to fluctuate with respect to the average flow direction. Mechanical dispersion occurs in the direction of the average flow velocity and in the plane orthogonal to the average flow direction, These effects are called longitudinal dispersion and transverse dispersion, respectively, Longitudinal dispersion is due to variations of the velocity component along the average flow direction, whereas transverse dispersion is due to variations of the velocity components in the normal plane.

3. *Molecular diffusion:* Fickian diffusion causes the contaminant molecules or ions to move from high concentrations to lower concentrations. Movement also is caused by the random kinetic motion of the ions or molecules (Brownian diffusion).

The combined effect of mechanical dispersion and molecular diffusion is known as hydrodynamic dispersion. Dispersion causes the zone of contaminated ground water to occupy a greater volume than if the contaminant distribution were influenced only by advection. If a slug of contaminant enters the ground-water system, advection causes the slug to move in the direction of ground-water flow. Hydrodynamic dispersion causes the volume of the contaminated zone to increase and the maximum concentration in the slug to decrease. Transverse dispersion may expand a contaminant plume 10 to 20 percent beyond the width defined by convective transport (Lehr, 1988). Macroscopic variations in hydraulic conductivity and porosity are probably more significant factors affecting solute transport than hydrodynamic 1 dispersion changes (Wheatcraft, 1989).

Additional processes affect transport for reactive contaminants. In addition to advection and hydrodynamic dispersion, the migration of reactive contaminants is further controlled by adsorption, desorption, chemical reactions, and biological transformation.

1. *Adsorption or desorption:* These processes involve mass transfer of contaminants. Adsorption is the transfer of contaminants from the ground water to the soil. Resorption is transfer of contaminants from the soil to the ground water.

2. *Chemical reactions:* These processes involve mass transfer of contaminants caused by various chemical reactions (e.g., precipitation and dissolution, oxidation and reduction). For some contaminants, degradation is also an important process that may need to be characterized.

3. *Biological Transformation:* These processes may remove contaminants from the system by biological degradation, or transform contaminants to other toxic compounds that are subject to mass transfer by the other processes discussed above.

The processes of adsorption-desorption, chemical reactions, and biological transformation play important roles in controlling the migration rate as well as concentration distributions. These processes tend to retard the rate of contaminant migration and act as mechanisms to reduce concentrations. Because of their effects, the plume of a reactive contaminant expands and the concentration changes more slowly than those of an equivalent nonreactive contaminant (see Figure 2-2). As discussed in subsequent chapters, however, resorption can require longer time periods to reach concentration cleanup standards.

Table 2-3 shows data requirements for contamination characterization, in addition to the requirements shown in Table 2-2. For example, to characterize advective transport, the flow system must first be understood. More specific lists of data with ranges of values are provided in Mercer et al. (1982). These data requirements provide a broad view of the factors affecting contaminant transport from a site.

## 2.4 Techniques for Characterization

For site characterization, it is important to understand the transport mechanisms and ground-water flow system at a site. Once these mechanisms and systems are understood, ground-water monitoring data can be interpreted to obtain information far more useful than simple information on contaminant levels at specific points and times. The procedures used to obtain water-quality data are of critical importance. Procedures for drilling monitoring wells, taking samples, and having samples analyzed by a laboratory are discussed in this section.

Table 2-4 shows actions that were typically taken at hazardous waste sites in the early 1980s. Two data gaps are the vertical distribution of hydraulic head, as measured by water levels in adjacent wells cased to different depths, and hydraulic conductivity values. Therefore, most guidance documents now recommend the actions shown in Table 2-5. At sites where conditions warrant (e.g., fractured media), additional actions may be necessary to fully characterize the site (see Table 2-6).

A variety of common well drilling methods maybe used to install monitoring wells at hazardous waste sites. These methods include solid stem continuous flight and hollow stem continuous flight augering, cable tool drilling, mud and air rotary drilling, jetting, and driving well points. Detailed discussions of the principles of operation of each of these methods are available from numerous sources including Scalf et al. (1981), Driscoll (1986), and Campbell and Lehr (1973). A summary of the advantages and disadvantages of various drilling methods relative to monitoring well construction is provided in Scalf et al. (1981) and Larson (1981), as well as in Chapter 4 of this Handbook (Section 4.2.1).

A variety of materials are available for use in casing, screening, and other structural and sampling components of monitoring wells. The most commonly used are mild steel, stainless steel, polyvinyl chloride (PVC), polypropylene, polyethylene, and Teflon®. Barcelona et al. (1983) summarizes the characteristics of several of these materials. These materials have substantially different properties relative to strength, corrosion resistance, interference with specific contaminant measurements, expense, and availability. Consequently, they must be selected carefully and demonstrated to be the most appropriate for the particular monitoring program. Considerations should include all pertinent, site-specific factors such as well installation method, depth, geochemical environment, and probable contaminants to be monitored. Well casing materials are discussed further in Section 4.2.1 (see especially Table 4-3) and Section 9.3.4.

Construction details for individual wells should be documented and verifiable through the use of drilling logs. The drilling log should contain information about the texture, color, size, and hardness of the geologic materials encountered during the drilling (Barcelona et al., 1985). Any use of drilling fluids, grouts, and seals also should be noted in the record of well construction. Well casing materials should be documented because the type of well casing may have an effect on the quality of the water samples (Barcelona et al., 1983). The same considerations that apply to well casing materials for newly constructed monitoring wells apply to evaluating the suitability of existing wells for ground-water quality monitoring.

Guidance documents on ground-water monitoring emphasize the need for depth-discrete data to determine the three-dimensional flow field and chemical distribution (Barcelona et al., 1983; Barcelona et al., 1985; and U.S. EPA, 1986). Shorter well screens and more nested wells are recommended where immiscible liquids (liquids that tend to float above water or sink to the bottom), heterogeneous conditions, or a thick flow zone are present (U.S. EPA, 1986). Barcelona et al. (1983) recommend installing nested wells with short well screens (less than 5 ft long) where the potential flow zone is more than 10 ft thick.

Once the wells are designed and drilled, accepted practice is to remove fluid from the formation, with subsequent laboratory analysis of the sample (Morrison, 1983; de Vera, 1980; USATHAMA, 1982 Guswa et al., 1984; and Everett et al., 1984). This approach results in a set of point data that represent (depending on the type of well construction, the sampling

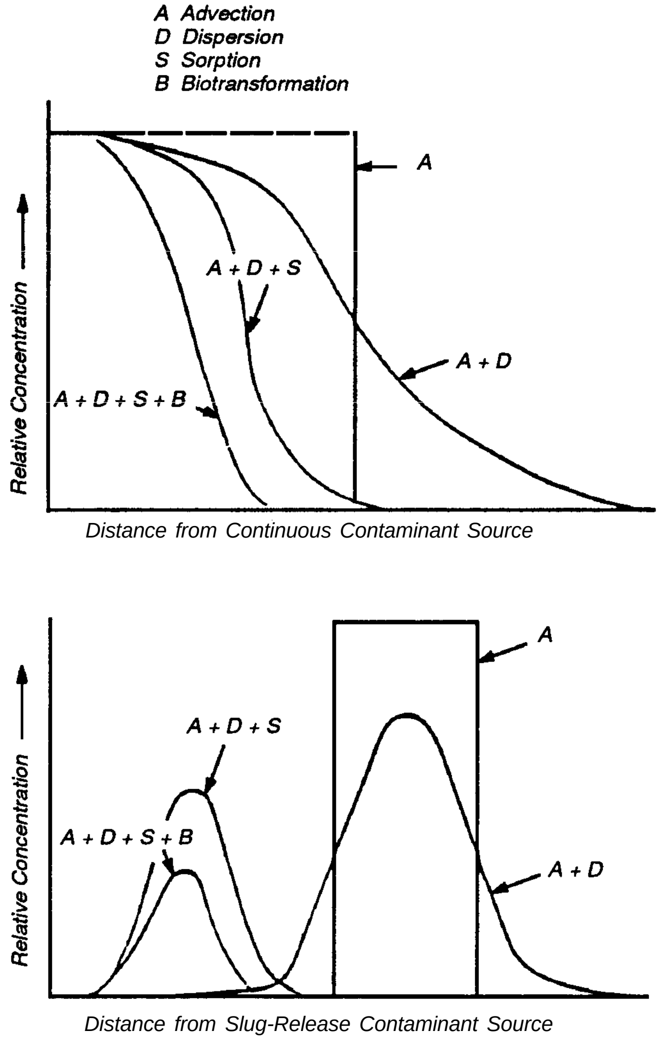


**Figure 2-2.** **The influence of natural processes on levels of contaminants downgradient from continuous and slug-release sources (from Keety et al., 1986).**

***Table 2-3. Data Pertinent to Prediction of the Pollutants in Ground Water (in addition to those in Table 2-2)***

*I. Physical Framework*
  1. *Estimates of the parameters that comprise hydrodynamic dispersion.*
  2. *Effective porosity distribution.*
  3. *information on natural (background) concentration distribution (water quality) in the aquifer.*
  4. *Estimates of fluid density variations and relationship of density to concentration (most important where contaminant is salt water or results in significantly higher concentration of total dissolved solids compared to the natural aquifer or where there are significant temperature differences between the contaminant plume and the natural aquifer).*

*II. Stresses on System*
  1. *Sources and strengths of pollutants,*

*III. Chemical/Biological Framework*
  1. *Mineralogy media matrix.*
  2. *Organic content of media matrix.*
  3. *Ground-water temperature.*
  4. *Solute properties.*
  5. *Major ion chemistry.*
  6. *Minor ion chemistry.*
  7. *Eh-pH environment.*

*IV. Observable Responses*
  1. *Areal and tamporal distribution of water quality in the aquifer.*
  2. *Stream flow quality (distribution in time and space)*

mechanism, laboratory procedure, and hydrodynamics of the ground-water system), particular aspects of the in situ water quality at a specific time. Much work (Gibb et al., 1981; Gillham et al., 1983; Keith et al., 1983; Nacht, 1983; Barcelona et al., 1984; Olea, 1984; Barcelona et al., 1985) has focused on improving this process (i.e., providing greater quality control and quality assurance). Chapter 9 discusses sampling of subsurface solids and ground water in more detail.

## 2.5 Analysis of Data

Although this section emphasizes network design and sampling considerations, no section on data analysis would be complete without a discussion of database management systems (DBMS) and geographic information systems (GIS). At hazardous waste sites, large amounts of data are generated. To take full advantage of these data in the interpretation stage, they should be in electronic/magnetic format for use in a DBMS and/or GIS. Both systems can be used to manipulate, correlate, and display data, and this method of organizing large amounts of data facilitates the interpretation process.

The assessment of ground-water quality on any scale involves the estimation of chemical variables distributed in three-dimensional space. A key consideration in establishing an effective and efficient ground-water quality monitoring program is the spatial distribution of sampling locations. Care must be taken in designing monitoring well networks to avoid biasing any inferences made from the resulting data.

As pointed out, knowledge of the hydrodynamics of the ground-water system(s) being monitored is also of critical importance for the design of monitoring networks. For certain ground-water monitoring program objectives, an optimum monitoring network for a relatively homogeneous porous flow environment is different from that for a discretely fractured hydrogeologic medium. For other monitoring objectives, however, the fundamental differences between flow regimes may have very little impact on the design of an optimum sampling network.

Proper ground-water sampling and analysis are equally important for assuring effective ground-water monitoring. A quality assurance program composed of well-conceived and effectively implemented quality control procedures should be followed (Cartwright and Shafer, 1987). Strict adherence to

*Table 2-4. Acthons Typically Taken*

1. *Install shallow monitoring wells.*
2. *Sample ground water numerous times for a range of pollutants such as those constituents contained in the RCRA Appendix IX ground-water monitoring list.*
3. *Define geology primarily by drillers' logs and drill cuttings.*
4. *Evaluate local hytrology with water level contour maps of shallow wells.*
5. *Possibly obtain soil and core samples for chemical analyses.*

**Benefits**

1. *Screening of the site problems is rapid.*
2. *Costs of investigation are moderate to low.*
3. *Field and laboratory techniques used are standard.*
4. *Data analysis/interpretation is straightforward.*
5. *Tentative identification of remedial alternatives is possible.*

**Shortcomings**

1. *True extent of site problems may be misunderstood.*
2. *Selected remedial alternatives may not be appropriate.*
3. *Optimization of final remediation design may not be possible.*
4. *Cleanup costs remain unpredictable, tend to excessive levels.*
5. *Verification of compliance is uncertain and difficult.*

*Modified from Keely et al., 1986*

*Table 2-5. Recommended Actions*

1. *Install depth-specific clusters of monitoring wells.*
2. *Initially sample for a range of pollutants, but subsequently, become more selective.*
3. *Define geology by extensive coring/sediment samplings.*
4. *Evaluate local hydrology wth well clusters and geohydraulic tests.*
5. *Perform limited tests on sediment samples (grain size, clay content, etc.).*
6. *Conduct surface geophysical surveys (resistivity, EM, ground-penetrating radar).*

**Benefits**

1. *Conceptual understanding of site problems is more complete.*
2. *Prospects are improved for optimization of remedial actions.*
3. *Predictability of remediation effectiveness is increased.*
4. *Cleanup costs are lowered, estimates are more reliable.*
5. *Verification of compliance is more soundly based.*

**Shortcomings**

1. *Characterization costs are somewhat higher.*
2. *Detailed understanding of site problems is still difficult.*
3. *Full optimization of remediation is still not likely.*
4. *Field tests may create secondary problems (disposal of pumped waters).*
5. *Demand for specialists is increased, shortage is a key limiting factor.*

*Modified from Keely et al., 1986*

*Table 2-6. Additional Actions Where Conditions Warrant Them*

1. *Assume Table 2.5 as starting point.*
2. *Conduct soil vapor surveys for volatiles and fuels.*
3. *Conduct tracer tests and borehole geophysical surveys (neutron and gamma).*
4. *Conduct karst stream tracing and recharge studies, if appropriate to the setting.*
5. *Conduct bedrock fracture orientation and interconnectivity studies, if appropriate.*
6. *Determine the percent organic carbon and cation exchange capacity of solids.*
7. *Measure redox potential, pH, and dissolved oxygen levels of subsurface.*
8. *Evaluate sorption-desorption behavior by laboratory column and batch studies.*
9. *Assess the potential for biotransformation of specific compounds.*

**Benefits**

1. *Thorough conceptual understandings of site problems are obtained.*
2. *Full optimization of the remediation is possible.*
3. *Predictability of the effectiveness of remediation is maximized.*
4. *Cleanup costs maybe lowered significantly, estimates are reliable.*
5. *Verification of compliance is assured.*

**Shortcomings**

1. *Characterization costs may be much higher.*
2. *Few previous applications of advanced theories and methods have been completed.*
3. *Field and laboratory techniques are specialized and are not easily mastered.*
4. *Availability of specialized equipment is low.*
5. *Need for specialists is greatly increased (it may be the key limitation overall).*

*Keely et al., 1986*

quality assurance programs minimizes both systematic and random errors, and maximizes the likelihood of collecting ground-water samples in a manner that ensures the reliability of analytical determinations. As with monitoring network design, a detailed understanding of the overall objectives of the monitoring program is a key factor in determining sampling and analysis requirements. See Chapter 7 for further discussion of sources of error in sampling and considerations in the development of quality assurance programs.

The results of laboratory analyses are only as reliable as the samples, field standards, and blanks received (Cartwright and Shafer, 1987). Therefore, to assure that representative samples are provided to the laboratory, careful thought and practice must be part of any sampling program. A representative sample accurately reflects in situ conditions in proximity to the sample point at the time the sample was collected. Maintaining representative samples requires consideration of well purging, sample collection, and sample preservation. Barcelona et al. (1985) have prepared an extensive guide to the practical aspects of ground-water sampling. (See also Chapters 7, 8, and 9 of this Handbook.)

Parameter selection is an important aspect of the design of a sampling program. The types of hydrochemical measurements to be made affect the choice of sampling equipment and the sampling methodology. Barcelona et al. (1985) state that it is often wise to obtain slightly more chemical and hydrologic data than immediately required in order to aid subsequent interpretation. Sections 9.2.1 and 9.3.1 discuss further selection of analytes for the vadose and saturated zones.

The frequency of sample collection is important in the design of an optimum ground-water quality monitoring program (Cartwright and Shafer, 1987). Sampling frequency affects the cost of the monitoring program and the appropriateness of any inference(s) made from the resulting data. Sample collection and analysis should not occur so often as to result in redundant information that would increase costs with no marginal gain in useful information. Conversely, sample collection should not be so infrequent as to detract from the ability to accurately forecast trends in ground-water quality. Ground-water sampling frequency should be based on the objectives of the monitoring program and the hydrodynamics of the ground-water system being monitored. As discussed, since ground-water movement is relatively slow, there is little need to sample every few meters of the flow path. Sampling frequency is discussed further in Section 9.1.4.

During the past decade, the use of geostatistical principles (i.e., structural analysis, kriging, and conditional simulation) to interpret ground-water data has increased. Geostatistical techniques are used to evaluate the spatial variability of ground-water flow parameters, particularly hydraulic head and transmissivity. However, less work has been conducted on the application of geostatistics to interpret hydrochemical data and ground-water quality monitoring network design. Samper and Neuman (1985), who performed a geostatistical analysis of selected chemical variables, showed that geostatistical approaches may be valid to evaluate ground-water chemical data, particularly on a regional scale (Cartwnght and Shafer, 1987).

The principles of geostatistics may be appropriate for interpolation of point data to estimate the spatial distribution of certain aspects of ground-water quality (Englund and Sparks, 1988). Kriging measures the error of estimation, which can be mapped and used to select locations for additional sampling points. These error maps show where the interpolated values deviated from the expected statistical structure, thus indicating the best locations to place additional wells (Virdee and Kottegoda, 1984). However, this information can only serve as a guide because of other constraints on well location such as environmental concerns, political issues, and economic limitations (see Table 2-2). Nevertheless, a near-optimal monitoring network can be developed for a predetermined level of reliability.

The use of geostatistics to design monitoring networks and interpolate data has limitations. Using kriging for ground-water investigations often may have a limited effectiveness because of lack of sufficient data to perform the structural analysis. Hughes and Lettenmaier (1981) suggest that a minimum sample size of 50 is required before kriging is superior to more traditional interpolation schemes (e.g., the least squares method). Even with sufficient data and suitable statistical support, structural analysis is highly subjective. Further, the theoretical basis for the application of geostatistics is the concept of a regionalized variable, which is defined as a spatially correlated random variable. To date, there have been no definitive studies of the validity of assuming that hydrochemical properties of ground water behave as regionalizcd phenomena (Cartwright and Shafer, 1987). For a further discussion of geostatistical methods, see Section 7.3.2.

## 2.6 References

Aller, L., T.W. Bennett G. Hackett, Rebecca J. Petty, J.H. Lehr, H. Sedoris, D.M. Nielsen. 1989. Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells. EPA/600/4-89/034 (NTIS PB90-159807). Also published in NWWA/EPA series, National Water Well Association, Dublin, OH.

Barcelona, M.J., J.P. Gibb, and R.A. Miller. 1983. A Guide to the Selection of Materials for Monitoring Well Construction and Ground Water Sampling. ISWS Contract Report 327. Illinois State Water Survey, Champaign, IL.

Barcelona, MJ., J.A. Helfrich, E.E. Garske, and J.P. Gibb. 1984. A Laboratory Evaluation of Ground Water Sampling Mechanisms. Ground Water Monitoring Review 4(2):32-41.

Barcelona, MJ., J.P. Gibb, J.A. Helfrich, and E.E. Garske. 1985. Practical Guide for Ground-Water Sampling. EPA 600/2-85/104 (NTIS PB86-137304). Also published as ISWS Contract Report 374, Illinois State Water Survey, Champaign, IL.

Bouwer, E., J.W. Mercer, M. Kavanaugh, and F. DiGiano, 1988. Coping with Groundwater Contamination. J. Water Pollution Control Federation 60(8): 1414-1428.

Campbell, M.D. and J.H. Lehr. 1973. Water Well Technology. McGraw-Hill, New York, NY.

Cartwright, K. and J.M. Shafer. 1987. Selected Technical Considerations for Data Collection and Intepretation-Ground Water. In: National Water Quality Monitoring and Assessment, National Academy Press, Washington, DC, pp. 33-56.

de Vera, E.R. 1980. Samplers and Sampling Procedures for Hazardous Waste Streams. EPA-600/2-80-018 (NTIS PB80-135353).

Driscoll, F.G. 1986. Groundwater and Wells, 2nd ed. Johnson Division, UOP, Inc., St. Paul, MN.

Englund, E. and A. Sparks. 1988 GEO-EAS (Geostatistical Environmental Assessment Software) User's Guide. EPA/600/4-88/033a (Guide NTIS PB89-151252; Software: NTIS PB89-151245).

Everett, L.G. 1980. Ground Water Monitoring. Technology Marketing Operation, General Electric Co., Schenectady, NY.

Everett, L.G., L.G. Wilson, and E.W. Hoylman. 1984. Vadose Zone Monitoring for Hazardous Waste Sites. Noyes Data Corp., Park Ridge, NJ.

Ford, P.J., P.J. Turina, and D.E. Seely. 1984. Characterization of Hazardous Waste Sites - A Methods Manual, II, Available Sampling Methods, 2nd ed. EPA 600/4-84-076 (NTIS PB85-521596). [The first edition was published in 1983 as EPA/600/4-83-040 (NTIS PB84-126920)].

Gibb, J.P., R.M. Schuller, and R.A. Griffin. 1981. Procedures for the Collection of Representative Water Quality Data from Monitoring Wells. Cooperative Groundwater Report 7. Illinois State Water Survey and Illinois State Geological Survey, Champaign, IL.

Gillham, R.W., M.J.L. Robin, J.F. Barker and J.A. Cherry. 1983. Groundwater Monitoring and Sample Bias. API Publication 4367. American Petroleum Institute, Washington, DC.

Guswa, J.H., WJ. Lyman, A.S. Donigan, Jr., T.Y.R. Lo, and E.W. Shanahan. 1984. Groundwater Contamination and Emergency Response Guide. Noyes Publication, Park Ridge, NJ.

Hughes, J.P. and D.P. Lettenmaier. 1981. Data Requirements for Kriging: Estimation and Network Design. Water Resources Research 17(6): 1641-1650.

Keely, J.F., M.D. Piwoni, and J.T. Wilson. 1986. Evolving Concepts of Subsurface Contaminant Transport. J. Water Pollution Control Federation 58(5):349-357.

Keith, S.J., M.T. Frank, G. McCarty, and G. Mossman. 1983. Dealing with the Problem of Obtaining Accurate Groundwater Quality Analytical Results. In: Proc. Third Nat. Symp. on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, Dublin, OH, pp. 272-283.

Kruseman, G.P. and N.A. de Ridder. 1976. Analysis and Evaluation of Pumping Test Data. International Institute for Land Reclamation and Improvement, Bulletin 11. Wageningen, The Netherlands.

Larson, D. 1981. Materials Selection for Ground Water Monitoring. Presented at the National Water Well Association Short Course entitled practical Considerations in the Design and Installation of Monitoring Wells, Columbus, OH, December 16-17.

Lawrence Berkeley Laboratory. 1977. Invitational Well-Testing Symposium Proceedings. LBL-7027. Lawrence Berkeley Laboratory, Berkeley, CA.

Lawrence Berkeley Laboratory. 1978. Second Invitational Well-Testing Symposium Proceedings. LBL-8883. Lawrence Berkeley Laboratory, Berkeley, CA.

Lehr, J. H. 1988. An Irreverent View of Contaminant Dispersion. Ground Water Monitoring Review 8(4):4-6.

Mercer, J.W., S.D. Thomas, and B. Ross. 1982. Parameters and Variables Appearing in Repository Siting Models. NUREG/CR-3066. U.S. Nuclear Regulatory Commission, Washington, DC.

Mercer, M.W. and C.O. Morgan. 1981. Storage and Retrieval of Ground-Water Data at the U.S. Geological Survey. Ground Water 19(5):543-551.

Moore, J.E. 1979. Contribution of Ground-Water Modeling to Planning. J. Hydrology 43:121-128.

Morrison, R.D. 1983. Ground Water Monitoring Technology, Procedures, Equipment and Applications. TIMCO Manufacturing, Inc., Prairie du Sac, WI.

Nacht, SJ. 1983. Monitoring Sampling Protocol Considerations. Ground Water Monitoring Review 3(3):23-29.

National Research Council (NRC). 1990. Ground Water Models: Scientific and Regulatory Applications. National Academy Press, Washington, DC.

Olea, R.A. 1982. Optimization of the High Plains Aquifer Observation Network, Kansas. Groundwater Series 7. Kansas Geological Survey, Lawrence, KS.

Olea, R.A. 1984. Systematic Sampling of Spatial Functions. Series on Spatial Analysis No. 7. Kansas Geological Survey, Lawrence, KS.

Samper, F.J. and S.P. Neuman. 1985. Gcostatistical Analysis of Hydrochemical Data from the Madrid Basin, Spain (Abstract). Eos (Trans. Am. Geophysical Union) 66(46):905.

Scalf, M.R., J.F. McNabb, W.J. Dunlap, R.L. Cosby, and J. Fryberger. 1981. Manual of Ground-Water Quality Sampling Procedures. EPA/600/2-81/160, (NTIS PB82-103045). Also published in NWWA/EPA Series, National Water Well Association, Dublin OH.

Sisk, S.W. 1981. NEIC Manual for Groundwater/Subsurface Investigations at Hazardous Waste Sites. EPA/330/9-81-002 (NTIS PB82-103755).

USATHAMA. 1982. Sampling and Chemical Analysis Quality Assurance Program for U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD.

U.S. Environmental Protection Agency (EPA). 1986. RCRA Ground Water Monitoring Technical Enforcement Guidance Document. EPA OSWER-9950.1. Also published in NWWA/EPA Series, National Water Well Association, Dublin, OH.

van Geer, F.C. 1987. Applications of Kalman Filtering in the Analysis and Design of Groundwater Monitoring Networks. TNO Institute of Applied Geoscience, Delft, The Netherlands.

Virdee, T.S. and N.T. Kottegoda. 1984. A Brief Review of Kriging and its Application to Optimal Interpolation and Observation Well Selection. Journal des Sciences Hydrologiques 29(4):367-387.

Wheatcraft, S.W. 1989. An Altemate View of Contaminant Dispersion. Ground Water Monitoring Review 9(3): 11-12.

# Chapter 3
# Geologic Aspects of Site Remediation

James W. Mercer and Charles P. Spalding

This chapter addresses the geologic aspects of remediation: (1) What geologic factors are significant? (2) How are geologic data collected? and (3) How are geologic data interpreted? To help answer these questions, this chapter includes information on stratigraphy, lithology, structural geology, and hydrogeology. However, this chapter does not include information on basic geology, but the reader may consult any of numerous textbooks on the subject. There is also a concise review of basic geology in U.S. EPA (1987).

To support discussions of the geologic factors, means of collecting geologic data are also included. See Chapter 4 for specific, detailed information on wells. This chapter covers soil and rock coring, as well as various surface and borehole geophysical techniques. A case history on the Hyde Park landfill concludes the chapter.

## 3.1 Stratigraphy

Stratigraphy is the study of the formation, composition, sequence, and correlation of stratified rocks and unconsolidated materials (e.g., clays, sands, silts, and gravels). Stratigraphic data include formational designations, age, thickness, areal extent, composition, sequence, and correlations. In a stratigraphic investigation, aquifers and confining formations are identified so that units likely to transport pollutants can be delineated, and lateral changes in formations (facies changes) are noted if present. In effect, the stratigraphy of a site defines the geometry and framework of the ground-water flow system. Therefore, knowledge of the stratigraphy is necessary in order to identify pathways of chemical migration, to estimate extent of migration, and to define the hydrogeologic framework.

The first step in conceptualizing a site is to study driller's logs, well cuttings, and/or corings. While observations made during drilling activities can provide additional information such as drilling rates and water losses, the primary goal of these observations is to characterize layers of like material. This layering can be differentiated based on material type, but a major consideration for characterization should be how well the material transmits water. The primary differentiation should be based on whether the material has properties of an aquifer and readily transmits water or has properties of a confining bed, prohibiting the movement of water.

Once the layering has been determined at each well, the next task is to plot the wells at their relative locations to each other and attempt to correlate the layers among the wells. This correlation involves interpreting well-log data and requires knowledge of geological processes. At some sites, the correlation will be straightforward; at others, correlation may be impossible, The ability to correlate also will depend on the scale of the correlation. To understand the stratigraphic controls of flow and chemical migration, only larger scale features may need to be correlated. The completed correlation results in a figure called a fence diagram (see Figure 3-1). As shown in the figure, a fence diagram is composed of intersecting geological cross-sections.

The elevations of where the layers connect can be contoured to form structural maps representing either the top or bottom surface of various layers. Where dense immiscible fluids are a concern, structural maps on top of confining layers are valuable because such fluids will flow via gravity on top of the confining layer toward the lower elevations. Structural maps for adjacent units can be subtracted from each other to yield thickness or isopach maps. An isopach map may be used, for example, to show the overburden thickness of unconsolidated material overlying bedrock. Once completed, these maps, along with the fence diagram, will provide a three-dimensional picture of the subsurface system through which the ground water and chemicals are moving.

In addition to wells and well cuttings, other means to obtain stratigraphic data include hand augers, split-spoon samplers, shelby tubes, and rock-coring equipment. Hand augers are useful, particularly in sandy materials, for examining soil profiles to shallow depths (a few meters) and for installing monitoring devices. Many types of hand augers are available, but all are limited to use in unconsolidated geologic materials and tend to be impractical in dense clays or stony materials (Gillham, 1988).

A split-spoon sampler consists of a metal cylinder that is split longitudinally and threaded on both ends. A cutting head is threaded onto the lower end and a drill-rod attachment threaded onto the upper end. The sampler is driven into the formation at the bottom of an augered borehole, using a drilling rig with a 140-pound weight (ASTM, 1990a). The number of blows required to penetrate a soil is a function of the compactability of the soil; thus, blow count can be used to characterize soil types. When withdrawn and opened,. the

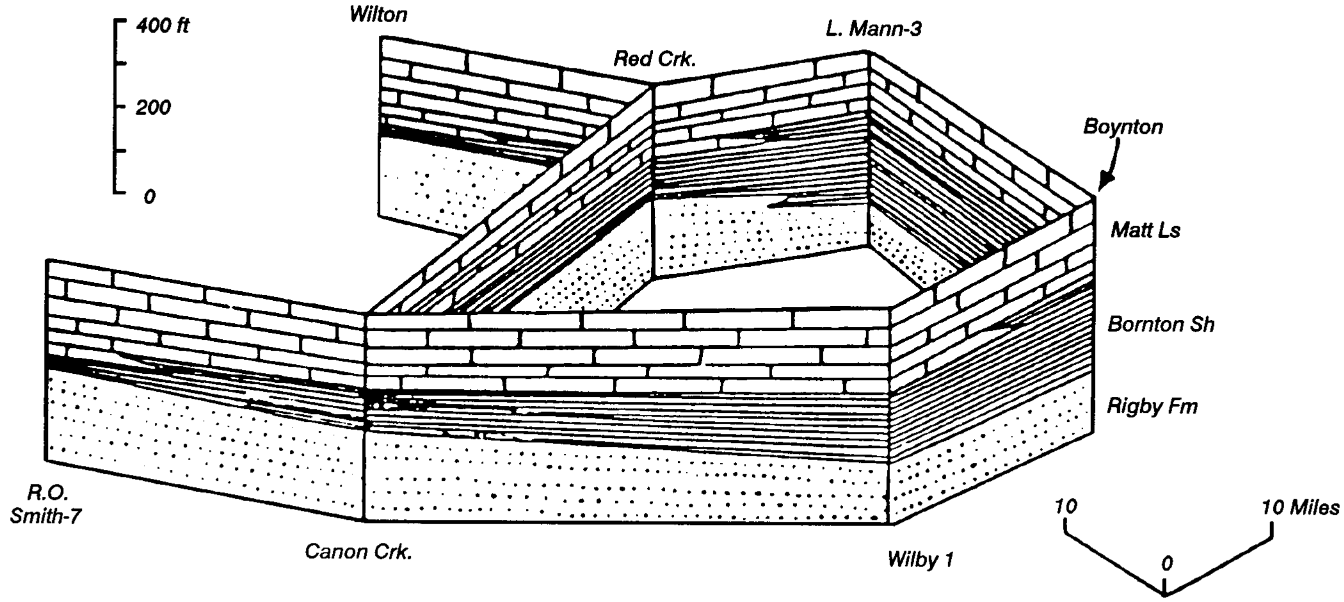


**Figure 3-1. Sample fence diagram construction (from Compton, 1962).**

sample is relatively undisturbed and shows the natural stratification of the geologic material. Shelby tubes are thin-walled metal tubes that are attached to drill rods and are driven into the formation (Gillham, 1988). Samples can be sealed and stored in the tubes and later extruded for examination. However, both shelby tubes and split-spoon samplers are limited to sampling of unconsolidated materials.

When formations are too hard to be sampled by soil sampling methods, core drilling can be used (ASTM, 1990b). The simplest core barrel consists of a hollow steel tube with a core catcher and a diamond or tungsten carbide core bit. Other core barrels have a dual wall system with a floating inner sleeve that remains stationary while the outer barrel rotates and cuts the core. A wireline system is available that eliminates pulling the drill pipe from the hole to recover each core (Landau, 1987). In this system, the core material is retrieved through the annulus of the drill rods.

Analysis of cores is performed both in the field and in the laboratory. Laboratory analysis includes determination of porosity; permeability; and saturation with respect to a specific fluid component e.g., nonaqueous phase liquids (NAPL); and lithology studies (Keelan, 1987). Field studies of cores include determination of rock quality designation (RQD), core recovery rate, fracture nature and frequency, presence of chemical odors, and general core lithology. RQD represents the amount of core greater than 4 in. in length divided by the length of core run attempted. This parameter is related to the competence of the material core and the fracture density of the core run, Because RQD often can be correlated to permeability, it is useful in characterization studies. Often cores are broken during transport so all fracture-related analyses should be performed as soon as possible after the core has been retrieved,

Coring also provides opportunities to monitor drilling return fluids for both color changes related to lithology and visual and olfactory evidence of contaminants. As coring proceeds, net drilling fluid loss or gain to the cored formation can be determined by maintaining an accurate balance of drilling fluids used. Fluid losses to an interval may be the result of fractures or solutioning within the rock matrix. As rock of varying competence is encountered, drilling rate also varies and for a given drilling system, drilling rate can be characteristic of the material penetrated.

Because the conceptualization of site conditions is based on roughly correlated parameters of subsurface and unseen conditions, it is useful to construct a correlation chart of selected parameters versus depth (see Figure 3-2). Additional parameters that may have been included in this figure are permeability, drilling rate per foot, water loss or gain, and presence and type of contamination.

## 3.2 Lithology

Lithology is the study of the physical character and composition of unconsolidated deposits or rocks. As discussed in the Handbook, it includes (1) mineralogy, (2) organic carbon content, (3) grain size, (4) grain shape, and (5) packing. The first two items affect sorption, whereas the last three items affect water storage and flow. Additiomlly, compaction and cementation will reduce permeability based on primary porosity, whereas solution channels will increase permeability (Levorsen, 1967).

The mineral composition of rocks and unconsolidated deposits can be used to determine the chemical composition. The chemical composition of the media affects chemical transport in ground water via a variety of chemical reactions. Such interactions primarily involve inorganics and include

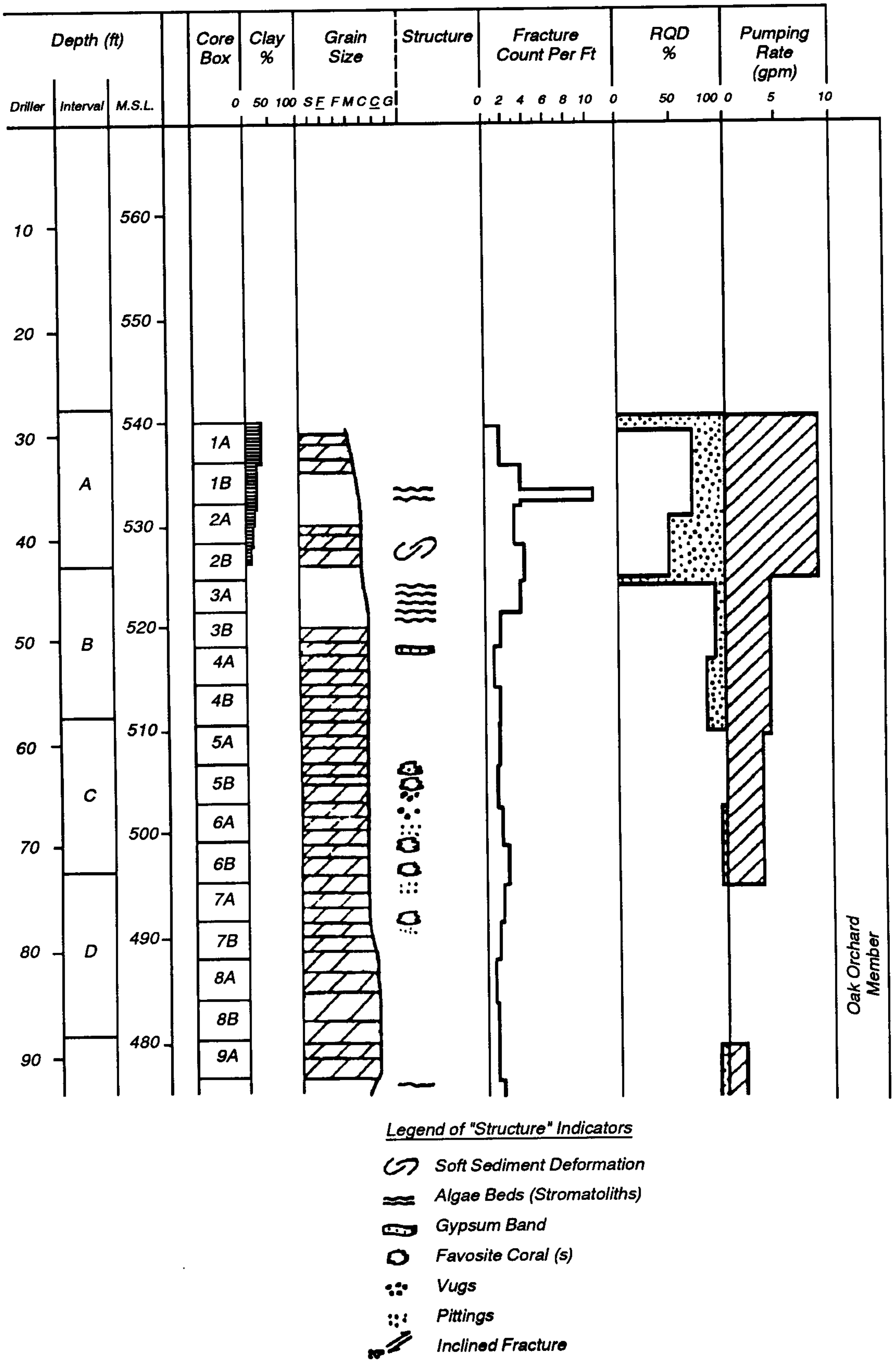


**Figure 3-2.** Correlation chart of hydrogeologic features (from GeoTrans, 1989).

sorption, precipitation and dissolution, acid-base reactions, complexation, and redox reactions. Examples of chemicals that could be reduced to lower concentrations in ground water through the formation of precipitates include arsenic (by reaction with iron, aluminum, or calcium), lead (by reaction with sulfide or carbonate), and silver (by reaction with sulfide or chloride). Hydrolysis can lead to the precipitation of iron, manganese, copper, chromium, and zinc contaminants. Oxidation or reduction could favor the precipitation of chromium, arsenic, and selenium.

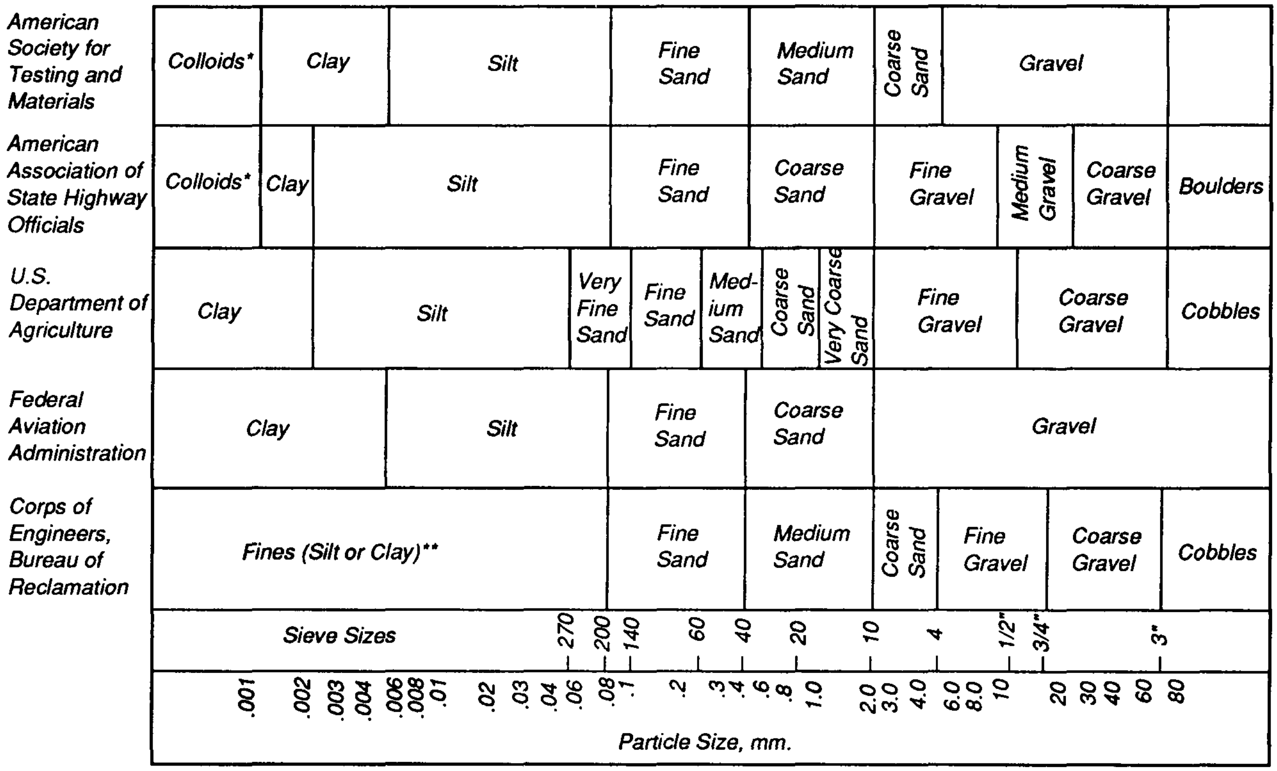
The tendency of an organic chemical to sorb is directly related to the fraction of total organic carbon content in terms of grams of organic carbon per gram of soil. A typical value of organic matter in mineral soils is 3.25 percent (Brady, 1974). The amount of organic matter is approximately 1.9 times the amount of organic carbon; therefore, a typical value for organic carbon content is 1.7 percent. However, data will vary from site to site.

Although variation in sorption between different grain-size fractions is mostly a reflection of their organic carbon content, other factors such as surface area have an effect. In general, the fine silt and clay fractions of soils have the greatest tendency to sorb chemicals. Grain size also influences water storage and movement. The amount of soil in each of various size groups is one of the major factors used in analyzing and classifying a soil. Various agencies define soil groups in slightly different ways (see Figure 3-3). In general, coarser grained soil is more transmissive and has less storage capacity than finer grained soil.

Grain shape also influences water storage and porosity because grain shape affects the manner in which grains are arranged. Highly angular and irregularly shaped, noncemented grains tend to result in a greater porosity than smooth, regularly shaped grains, although the difference may be slight

Grain-size analysis, conducted on samples from unconsolidated formations, yields the proportion of material in each specified size range. Range distributions can be used to estimate permeabilities, design monitoring wells, and enable better stratigraphic interpretation. The results of a grain-size analysis usually are plotted as shown in Figure 3-4. The sieve-opening size retaining 90 percent of the soil is called the effective particle size ($D_{90\%}$), whereas the sieve-opening size retaining 50 percent is called the average particle size ($D_{50\%}$). Uniform soils consist of grains of predominantly one size yielding curves with steep slopes. Well-graded soils have grains of many different sizes and, therefore, are characterized by more gently sloping curves.

Soils composed of grains of nearly uniform particle size have a larger porosity than a well-graded soil because, in the well-graded soil, small particles occupy a portion of the volume between the larger particles. In the vadose zone,



** Colloids included in clay fraction in test reports.*

*** The LL and PI of "Silt" plot below the "A" line of the plasticity chart, Table 4, and the LL and PI for "Clay" plot above the "A" line.*

**Figure 3-3. Soil-group size limits of ASTM, AASHO, USDA, FAA, Corps of Engineers, and USBR (from Portland Cement Association, 1973).**

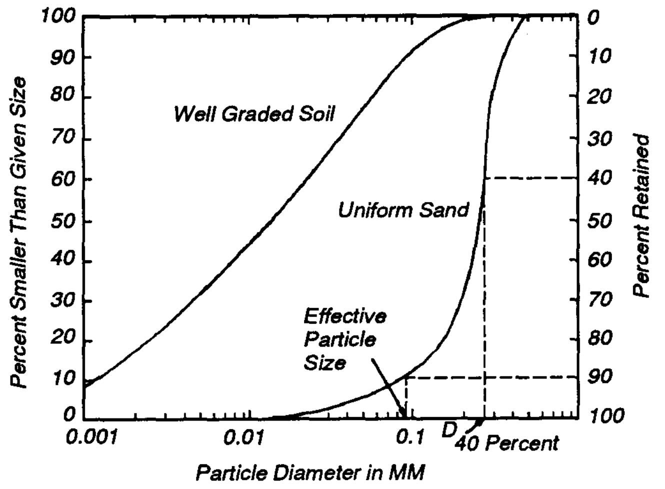


Figure 3-4. Particle-size distribution for a uniform sand and a well-graded soil (from Bouwer, 1978).

uniform soils develop a well-defined capillary fringe, whereas well-graded soils tend to have a higher, but less distinct capillary fringe.

In summary, much qualitative information concerning properties that affect flow and transport can be gained from lithology. At many hazardous waste sites, this type of information may be all that is available in the early stages of field study. Thus, it may be used to help guide subsequent phases of the field work, such as well screen design. This type of qualitative information may be very helpful in characterizing vadose-zone properties, where hydrologic testing is more difficult to conduct and interpret.

## 3.3 Structural Geology

Structural geology includes studying and mapping features produced by movement after deposition. Structural features include folds, faults, joints/fractures, and interconnected voids (i.e., caves and lava tubes). Highly vesicular tops and bottoms of basalt flows, for example, are often cited as sources of significant permeability. Just as important to the definition of structural features is the more rapid cooling and more intense fracturing of the top and bottom of flows (Huntley, 1987). Deformed, inclined, or broken rock formations can control topography, surface drainage, and ground-water recharge and flow. Joints and fractures are commonly major avenues of water transport (preferential pathways) and usually occur in parallel sets.

*Most* fractures can be attributed to one of three causes (Lcworsen, 1967). Some fractures format depth as a result of an increase in rock volume from the folding and bending of strata. Others are caused by the removal of overburden by erosion in the zone of weathering. As sediments are unloaded through erosion, the upper parts expand, and incipient weaknesses in the rocks become joints, fractures, and fissures. Therefore, an increase of fracturing below an unconformity is to be expected. Probably much of the initial solution channeling through which surface waters percolate results from the gradual increase in jointing and fracturing that accompanies weathering. The third cause of fracturing is a reduction in the volume of shales in the ground, due to diagenetic mineral changes coupled with a loss of water during compaction.

Solution features, such as enlarged joints, sinkholes and caves are common in limestone rocks and promote rapid ground-water movement. Pertinent data on structural features necessary to study and understand solution features include type, compass orientation, dip direction and angle, and stratigraphy. Chapter 6 discusses the influence of fractured media on ground-water flow and how it is characterized.

## 3.4 Hydrogeology

Hydrogeology concerns the relationship of the movement of subsurface waters with geology, and ties stratigraphy, lithology, and structural geology to the theory of ground-water hydraulics. The main goal in studying hydrogeology is to determine directions and rates of ground-water flow. This information is essential to any ground-water remediation or ground-water monitoring program. Although this topic is introduced in this section, it is discussed in more detail in Chapter 4.

Hydrologic factors that are important to hydrogedogy include surface drainage and surface water/ground-water relationships. Surface drainage information includes tributary relationships, stream widths, depths, channel elevations, and flow data. In a hydrogeologic investigation, the nearest permanent gaging station and period of record should be determined. A U.S. Geologic Survey (USGS) 7 1/2-minute topographic map will show some of the necessary information. Gaging stations and flow data can be identified and obtained through USGS data bases. Streams either can receive ground-water inflow or lose water by channel exfiltration. As part of the investigation, hydrologic literature should be reviewed to determine if local streams are “gaining” or “losing.” Losing streams are common in areas of limestone bedrock and those with arid climates and coarse-grained channel substrates. Potential ground-water recharge areas, sometimes indicated by flat areas or depressions noted on the landscape, also should be identified. Stereo-pair aerial photographs can also be useful in these determinations (Ray, 1960). Irrigated fields detected in aerial photographs suggest ground-water recharge areas; swampy, wet areas suggest areas of ground-water discharge.

Other important factors include aquifer delineation, background water quality, and depth to ground water. As used in this Handbook, depth to ground water refers to the vertical distance from the ground surface to the standing water level in a well. In a confined aquifer, the depth to water represents a point on a “piezometric” surface. The depths will limit the equipment that can be used for purging and sampling. Information should be collected to delineate aquifer type (unconfined, confined, or perched); composition; boundaries; hydraulic properties (permeability, porosity, transmissivity, etc.); and interconnection with other aquifers (direction of leakage). These data are generally available through geological survey publications.

Probable ground-water flow directions (both horizontal and vertical) are determined by comparing the elevation of water levels in different wells. The quality of ground and surface water in an area should define, to a large extent, potential uses. Knowledge of natural or background water quality and water uses is required to assess contaminant impacts. The quality of surface waters is usually available from U.S. EPA, USGS, and state records. Ground-water data will probably be limited for any given area, but may be discussed through USGS Water Resources Division offices, state geological surveys, and county health departments.

## 3.5 Hydrogeologic Investigations

Much of the data needed to understand site-specific ground-water movement will be determined via hydrogeologic investigations. The purpose of these investigations is to determine flow directions, pathways and rates of ground-water flow, potential receptors of ground water, potential contaminants, and the extent of contamination in the subsurface. This information is required for selecting from alternative remedial strategies, and it provides the framework for design of a ground-water remedial program, if needed.

Some of the field methods used to obtain this information include borehole exploration (including coring), mapping surface features, and geophysical methods (both surface and downhole techniques). Much of the information gained from these methods will be helpful in interpreting the geology. For ground-water flow information, additional field methods include (1) monitoring water elevations in wells and adjacent surface waters, (2) performing aquifer tests (pumping and/or slug tests), and (3) using special methods such as laboratory analysis of cores and borehole flowmeters. For subsurface chemistry, soil sample analysis must be performed, as well as sampling and analysis of ground water. A typical monitoring well for ground-water sampling is shown in Figure 3-5. If nonaqueous phase liquid (NAPL) is present, any free product thickness must be measured and sampling performed.

### *3.5.1 Geophysical Techniques*

Geophysical techniques are used to better understand subsurface conditions arid to delineate the extent of contamination. Common surface techniques used at hazardous waste sites include surface resistivity, electromagnetic surveys, seismic reflection method, ground-penetrating radar, and magnetometer surveys (see Table 3-1).

In *surface resistivity* methods (Zohdy et al., 1974; Stewart et al., 1983), the geologic materials act as part of a direct current circuit. In general, there are two current electrodes and two electrodes for measuring voltage differences. The electrical potential measured between the electrodes depends on the electrical properties of the geologic materials which, in turn, depend upon the resistivity of the pore water and the amount of pore water. Most soil and rock materials are highly resistive, while water is highly conductive. Porosity and local stratigraphy, therefore, can be deduced from the measurements. Because of the concentrations of some solutes, contaminant plumes frequently appear as a highly conductive layer. Resistivity methods, therefore, can be useful in identifying and mapping certain plumes (Wish, 1983).

*Electromagnetic instruments* used in hydrogeologic investigations consist of a transmitter and receiver (Stewart, 1982). The transmitter produces an alternating magnetic field that induces electrical currents within the ground. The induced currents vary with the electrical conductivity of the geological materials and alter the magnetic field of the transmitter. This alteration is detected by a receiver. Generally, these devices are carried by one person, and do not require the installation of electrodes or geophones. They are likely to be more cost-effective than resistivity methods because field work can be completed more rapidly. They can be used to detect changes in subsurface conductivity related to contaminant plumes or buried metallic waste such as drums (Greenhouse and Slaine, 1983).

In *surjace seismic methods* (Sverdrup, 1986), an impact is made at a particular point on the ground surface using a mechanical hammer or an explosive device. The resulting sound waves are monitored by sensing devices (geophones) positioned at various distances from the impact. The time of arrival of the sonic waves depends on velocity and density contrasts that occur as the wave passes through different stratigraphic layers. By interpreting the sigml, the investigation determines the geologic layering in the area.

In *ground-penetrating radar* (Koemer et al., 1981), radio waves are transmitted into the ground and the reflected waves are monitored and analyzed. Reflections occur as a result of geologic variations in porosity and water content. The method is useful for determining stratigraphic variations and for locating buried objects such as steel drums.

*Magnetometer surveys* (Gilkeson et al., 1986) measure the strength of the earth's magnetic field. A proton nuclear magnetic resonance magnetometer is frequently used. One person can rapidly perform a survey over a site of a few acres by using this hand-held instrument. The surveyor sets up a grid system and measures the magnetic field at each intersection of the grid. Areas with large amounts of buried metal, such as steel drums, will have magnetic anomalies associated with them. The strength of the anomaly will vary with the amount and depth of the buried metal.

*Borehole logging* (Keys and MacCary, 1971; Keys, 1988) includes a variety of methods involving lowering a tool into the borehole (see Table 3-2). The tool measures the physical properties of the geologic materials, or, alternatively, provides an impulse or disturbance to the natural system, and measures the response of the system to the disturbance. Common logging tools include caliper, resistivity, neutron, gamma, and sonic tools. Logging can proceed in both cased or uncased boreholes, though most measurements can be made only when the hole has not been cased. Most of the logging methods are effective in distinguishing between sand and clay and are, therefore, useful in locating zones of high permeability (Kwader, 1986),

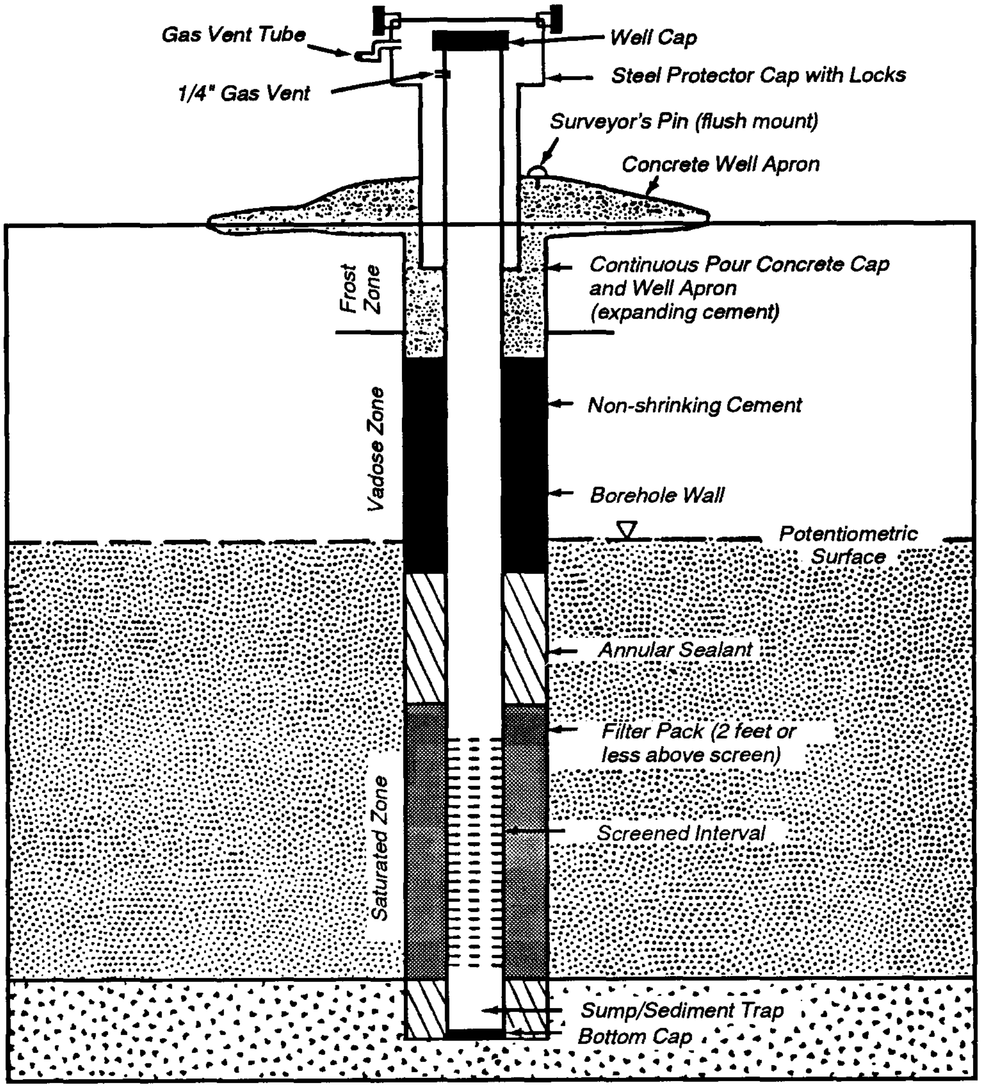


**Figure 3-5. A typical monitoring well design (from GeoTrans, 1989).**

*Induction logging* can be used to identify soil and rock types, geologic correlations, soil and rock porosity, and pore fluid conductivity. Resistivity logging is effective in identifying soil and rock types, geologic correlations, soil and rock porosity, pore fluid resistivity, and secondary permeability such as the locations of fractures and solution openings. Natural gamma logging can assist in positioning wells and casings, by providing information on clay or shale content, grain size, pore fluid resistivity, and soil and rock identification. Gamma-gamma logging will help to position cementing for the well casings and to determine total porosity or bulk density. Neutron logs can provide estimates of moisture content above the water table, total porosity below the water table, specific yield of confined aquifers, the location of the water table outside the casing, chemical and physical properties of the water, and the rate of moisture infiltration. Temperature logs help provide the chemical and physical characteristics of the water source and movement of the water in the well; and dilution, dispersion, and movement of the waste.

*Video cameras* also have been developed that can be lowered down a 4-in. (l0-cm) diameter borehole. They can be used for visual inspection and to provide a visual record of the wall of the borehole. They are particularly useful for inspecting the casing for corrosion, damage, or leaks, and also are

*Table 3-1. Summary of Surface Geophysical Methods*

| *Surface Geophysical Survey Method* | *Applications* | *Advantages* | *Limitations* |
|---|---|---|---|
| *SEISMIC REFRACTION AND REFLECTION* | | | |
| *Determines lithological changes in subsurface* | *- Ground-water resource evaluations*<br>*- Geotechnical profiling*<br>*- Subsurface stratigraphic profiling including top of bedrock* | *- Relatively easy accessibility*<br>*- High depth of penetration dependent on source of vibration*<br>*- Rapid areal coverage* | *- Resolution can be obscured in layered sequences*<br>*- Susceptibility to noise from urban development*<br>*- Difficult penetration in cold weather (depending on instrumentation)*<br>*- Operation restricted during wet weather* |
| *ELECTRICAL RESISTIVITY* | | | |
| *Delineates subsurface resistivity contrasts due to lithology, ground water, and changes in ground-water qualify* | *- Depth to water table estimates*<br>*- Subsurface stratigraphic profiling*<br>*- Ground-water resource evaluations*<br>*- High ionic strength contaminated ground-water studies* | *- Rapid areal coverage*<br>*- High depth of penetration possible (400-800 ft)*<br>*- High mobility*<br>*- Results can be approximated in the field* | *- Susceptibility to natural and artificial electrical interference*<br>*- Limited use in wet weather*<br>*- Limited utility in urban areas*<br>*- Interpretation that assumes a layered subsurface*<br>*- Lateral heterogeneity not easily accounted for* |
| *ELECTROMAGNETIC CONDUCTIVITY* | | | |
| *Delineates subsurface conductivity contrasts due to changes in ground-water quality and lithology* | *- Subsurface stratigraphic profiling*<br>*- Ground-water contamination studies*<br>*- Landfill studies*<br>*- Ground-water resource evaluations*<br>*- Locating buried utilities, tanks, and drums* | *- High mobility*<br>*- Rapid resolution and data interpretation*<br>*- High accessibility*<br>*- Effectiveness in analysis of very high resistivity*<br>*- Equipment readily accessible* | *- Data reduction less refined than with resistivity*<br>*- Use unsuitable in areas with surface or subsurface power sources, pipelines, utilities*<br>*- Less vertical resolution than with other methods*<br>*- Limited use in wet weather* |
| *GROUND PENETRATING RADAR* | | | |
| *Provides continuous visual profile of shallow subsurface objects, structure, and lithology* | *- Locating buried objects*<br>*- Delineation of bedrock subsurface and structure*<br>*- Delineation of karst features*<br>*- Delineation of physical integrity of manmade earthen structures* | *- Great areal coverage*<br>*- High vertical resolution in suitable terrain*<br>*- Visual picture of data* | *- Limited depth of penetration (a meter or less in wet, clayey soils; up to 25 meters in dry, sandy soils)*<br>*- Accessibility limited due to bulkiness of equipment and nature of survey*<br>*- Interpretation of data qualitative*<br>*- Limited use in wet weather* |
| *MAGNETICS* | | | |
| *Detects presence of buried metallic objects* | *- Location of buried ferrous objects*<br>*- Detection of boundaries of landfills containing ferrous objects*<br>*- Location of iron-bearing rock* | *- High mobility*<br>*- Data resolution possible in field*<br>*- Rapid areal coverage* | *- Detection dependent on size and ferrous content of buried object*<br>*- Difficult data resolution in urban areas*<br>*- Limited use in wet weather*<br>*- Data interpretation complicated in areas of natural magnetic drift* |

*Source: Modified after O'Brien and Gere (1988)*

*Table 3-2.* ***Summary of Borehole Log Applications***

| *Required information on the Properties of Rocks, Fluid Wells, or the Ground-Water System* | *Widely Available Logging Techniques That Might Be Utilized* |
|---|---|
| *Lithology and stratigraphic correlation of aquifers and associated rocks* | *Electric, sonic, or caliper logs made in open holes. Nuclear logs made in open or cased holes.* |
| *Total porosity or bulk density or gamma-gamma* | *Calibrated sonic logs in open holes, calibrated neutron logs in open or cased holes.* |
| *Effective porosity or true resistivity* | *Calibratad long-normal resistivity logs.* |
| *Clay or shale content* | *Gamma logs.* |
| *Permeability* | *No direct measurement by logging. Maybe related to porosity, injectivity, sonic amplitude.* |
| *Secondary permeability - fractures, solution openings* | *Caliper, sonic, or borehole televiewer or television logs.* |
| *Specific yield of unconfined aquifers* | *Calibrated neutron logs.* |
| *Grain size* | *Possible relation to formation factor derived from electric logs.* |
| *Location of water level or saturated zones* | *Electric, temperature, or fluid conductivity in open hole or inside casing. Neutron or gamma-gamma logs in open hole or outside casing.* |
| *Moisture content* | *Calibrated neutron logs* |
| *infiltration* | *Time-interval neutron logs under special circumstances or radioactive tracers.* |
| *Direction, velocity, and path of ground-water flow* | *Single-well tracer techniques - point dilution and single-well pulse. Multiwell tracer techniques.* |
| *Dispersion, dilution, and movement of waste* | *Fluid conductivity and temperature logs gamma logs for some radioactive wastes, fluid sampler.* |
| *Source and movement of water in a well* | *infectivity profile. Flowmeter or tracer logging during pumping or injection. Temperature logs* |
| *Chemical and physical characteristics of water, including salinity, temperature, density, and viscosity* | *Calibrated fluid conductivity and temperature in the well Neutron chloride logging outside casing. Multielectrode resistivity.* |
| *Determining construction of existing wells, diameter and position of casing, perforations, screens* | *Gamma-gamma, caliper, collar, and perforation locator, borehole television.* |
| *Guide to screen setting* | *All logs providing data on the lithology, water-bearing characteristics, and correlation and thickness of aquifers.* |
| *Cementing* | *Caliper, temperature, gamma-gamma. Acoustic for cement bond.* |
| *Casing corrosion* | *Under some conditions caliper or collar locator.* |
| *Casing leaks and/or plugged screen* | *Tracer and flowmeter.* |

*Source: Keys and MacCary (1971)*

used in uncased rock holes for locating fractures and fracture zones (Gillharn, 1988).

### 3.5.2 *Example-Hyde Park Landfill*

This example, discussed in detail in Cohen et al. (1987), concerns the Hyde Park landfill in Niagara Falls, New York (see Figure 3-6). Ground-water studies were initiated at the site in 1978 when a shallow tile drain and clay cover were installed at the landfill. Remedial investigations (RI), required by a settlement agreement, were conducted from 1982 to 1984. A major component of the RI was a drilling program designed to determine the extent of chemical contamination in the overburden and bedrock. Borings were cored and tested in 15-ft sections to the top of the Rochester Shale along 10 vectors radiating out from the landfill. Ground-water samples were taken for analysis from those 15-ft sections that yielded significant amounts of water. If chemicals were present above specified levels, a new hole was drilled about 800 ft away along the vector. Some of these holes were used as observation wells during aquifer tests prior to being grouted.

As a result of the drilling programs, the local geology is fairly well known. Approximately 15 to 30 ft of waste at the landfill are underlain by 0 to 10 ft of silty clay sediments. At Hyde Park, the overburden lies unconformably on the Lockport Dolomite. Undulations in the bedrock surface were carved by previous glaciation. The Lockport Dolomite ranges in thickness from 130 ft (200 ft southeast of the landfdl) to 65 ft at the Niagara Gorge. The Lockport Dolomite overlies the Rochester Shale and several lower units in a layer-cake sequence.

The hydrogeology of the Hyde Park area is unique because of the Niagara River Gorge and the human-induced channels associated with a nearby pump storage reservoir (see Figure 3-6). The Niagara Gorge (about 2,000 ft to the west), the forebay canal (about 4,000 ft to the north), and the buried conduits (about 3,000 ft to the east) control ground-water movement in the Hyde Park area.

The ground-water system can be conceptualized as a series of slightly dipping, permeable zones sandwiched between aquitards, all of which are bounded on three sides by drains. Precipitation infiltrates the wastes and the low-permeability overburden before recharging the highly fractured upper layer of the Lockport Dolomite. Where glacial sediments are present beneath the landfill, downward ground-water flow and chemical migration are retarded. In areas

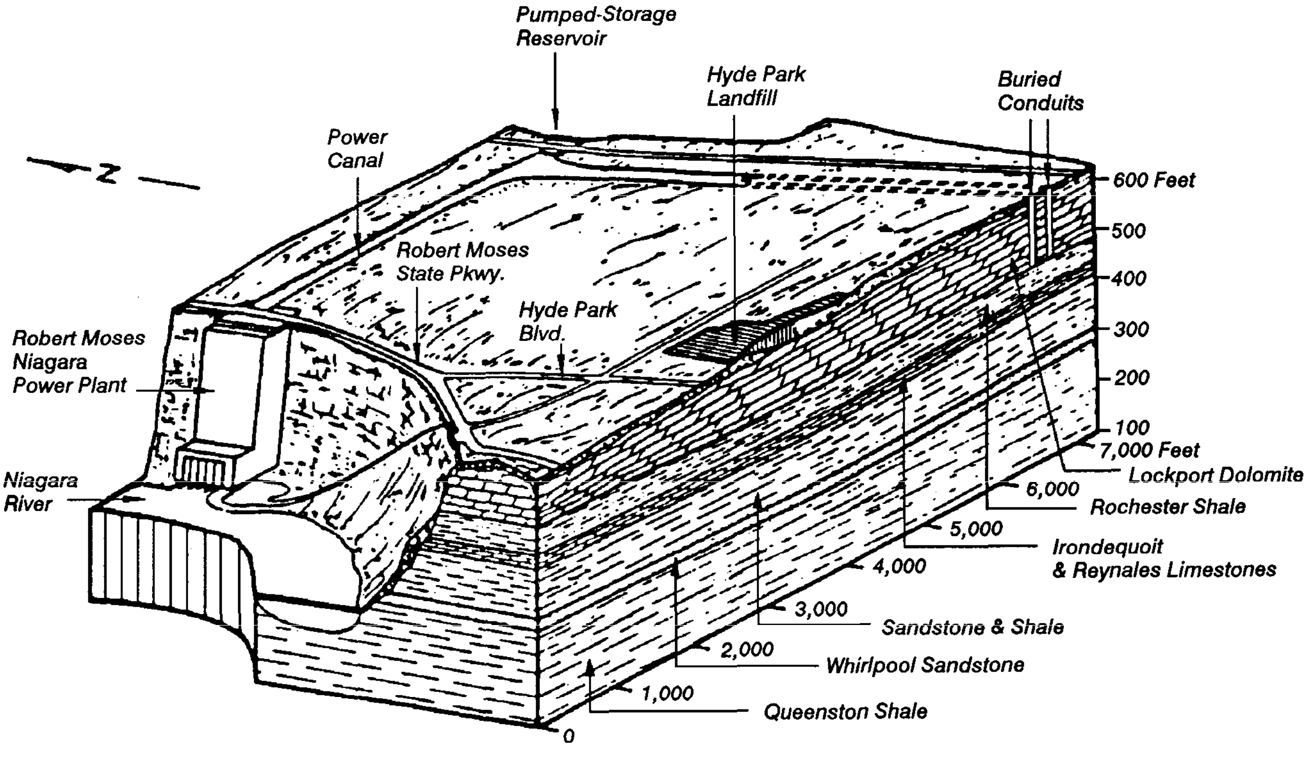


**Figure 3-6.** A generalized diagram showing the geologic formation and topographic features in the vicinity of the Hyde Park landfiii (from Faust, 1985).

where these sediments are thin and/or absent, ground water and chemicals move freely into the underlying rock. In the permeable bedrock zones, much of the ground water flows laterally toward the three boundaries. Between these zones, ground water moves slowly downward to the next lower permeable layer. Pumping tests suggest an anisotropic system where hydraulic conductivities are greatly affected by preferential flow along fractures (Figure 3-7). This conceptualization is supported by the alignment and dip of joint systems expressed at nearby outcrops.

Analyses of ground-water samples taken during the vector well survey revealed that contamination had migrated much further than previously thought. In fact, Hyde Park chemicals were found in seeps emanating from the Lockport Dolomite along the Niagara Gorge in July 1984. Dissolved chemical and NAPL plumes in the overburden and in the Lockport Dolomite were delineated during the RI as shown in Figure 3-8. Although the areal extent of contamination has been defined, the depth of chemical migration was unknown because at many locations dissolved chemicals and NAPL were observed all the way to the base of the Lockport Dolomite.

The distribution of chemicals in the overburden reflects the downward migration of contaminated surface runoff from the Hyde Park landfill, which is elevated relative to surrounding properties. Lateral chemical transport through the overburden has been limited because the potential for downward flow to bedrock exceeds that for outward flow through the low-permeability glacial sediments.

The contamination observed in the Lockport Dolomite reflects variations in the directions of ground-water flow that have occurred since waste disposal began at Hyde Park and, to a lesser extent, at the dipping beds of the Lockport Dolomite. Chemical analyses indicate the past migration of chemicals through the upper Lockport Dolomite in all directions. Present ground-water flow is primarily to the northwest, but the southern and eastern areas of contamination suggest that at one time ground water moved toward those areas. Ground-water flow prior to the construction of the forebay canal and buried conduits (from 1958 to 1962) was inferred to be toward the southwest. Similarly, dewatering during the construction of these conduits could have drawn contaminated ground water toward the east. Chemicals have moved downward to the base of the Lockport Dolomite by dissolution in ground water and by dense NAPL flow.

The Hyde Park Stipulation requires several remedial actions, focusing on source control, overburden remedies, bedrock remedies, and control of seeps at the Niagara Gorge face. The application of a series of numerical models of ground-water flow and chemical transport facilitated these remedies.

The source control program is designed to reduce the amount of chemicals migrating from the landfill into the overburden and bedrock. This reduction will be achieved by a synthetic cap to reduce recharge and by extraction wells to remove chemicals. During the prototype phase of the program, two large-diameter extraction wells will be installed in the landfill. Exploratory boreholes were completed in the landfill to characterize the overburden stratigraphy of the landfill and to help determine stratigraphic controls on NAPL movement. All exploratory boreholes were then converted to NAPL monitoring wells. The success of the prototype extraction wells depends in part on the compatibility of the sandpack with landfill materials. To test the selection of the well sandpack, two sandpack materials were selected based on known landfill constituents. If a reasonable amount of NAPL can be removed with this method, an operational network of six extraction wells will be installed.

The remedial program specified for the overburden is designed to laterally contain the dissolved chemicals and NAPL and to maximize collection of NAPL. Mobile NAPL not removed from the overburden will tend to sink downward to the bedrock and will be addressed by the bedrock remedy. The overall approach of the program is to further define the boundary of the overburden NAPL plume with a series of borings and then install a tile drain to collect mobile NAPL. The location and depth of the drain will be determined after the overburden plume boundaries have been refined by a series of 44 overburden borings around the landfill. As the drain is installed, additional stratigraphic information will be added as soil is removed. The performance criteria for the overburden system are:

- An inward hydraulic gradient must be maintained toward the drain *or* downward into the bedrock.

- There must be no expansion of the NAPL plume toward the drain or downward.

Remedial systems planned for the Lockport Dolomite are designed to contain both the NAPL and APL plumes. Specific objectives of the bedrock remedial system are to contain dissolved chemicals and NAPL within the NAPL plume, contain dissolved chemicals in the area near the gorge face that is designated the remediated APL plume, and eliminate the seepage of chemicals at the gorge face. However, portions of the APL plume will not be remediated. As with the source control system, a prototype system will be implemented first and later refined into an operational system. The system will use extraction and injection wells to maximize the collection of both dissolved chemicals and NAPL. The locations of purge, injection, and monitoring wells, and a schematic cross-section of the containment concept, are shown in Figures 3-9 and 3-10, respectively. The recirculation wells are added to the NAPL plume containment system to speed up the recovery of contaminants and to maintain higher water levels for the flushing of chemicals in the upper bedrock.

All prototype bedrock extraction/injection wells and related Lockport monitoring wells will be completed in three separate hydrogeologic zones. The separation of the Lockport into three zones allows optimization of the remedial system through better characterization, monitoring, and pumping schemes for the selected zones.

The main performance criteria for the bedrock system is the maintenance of an inward hydraulic gradient at the NAPL plume boundary. In addition, the flux of certain chemicals to

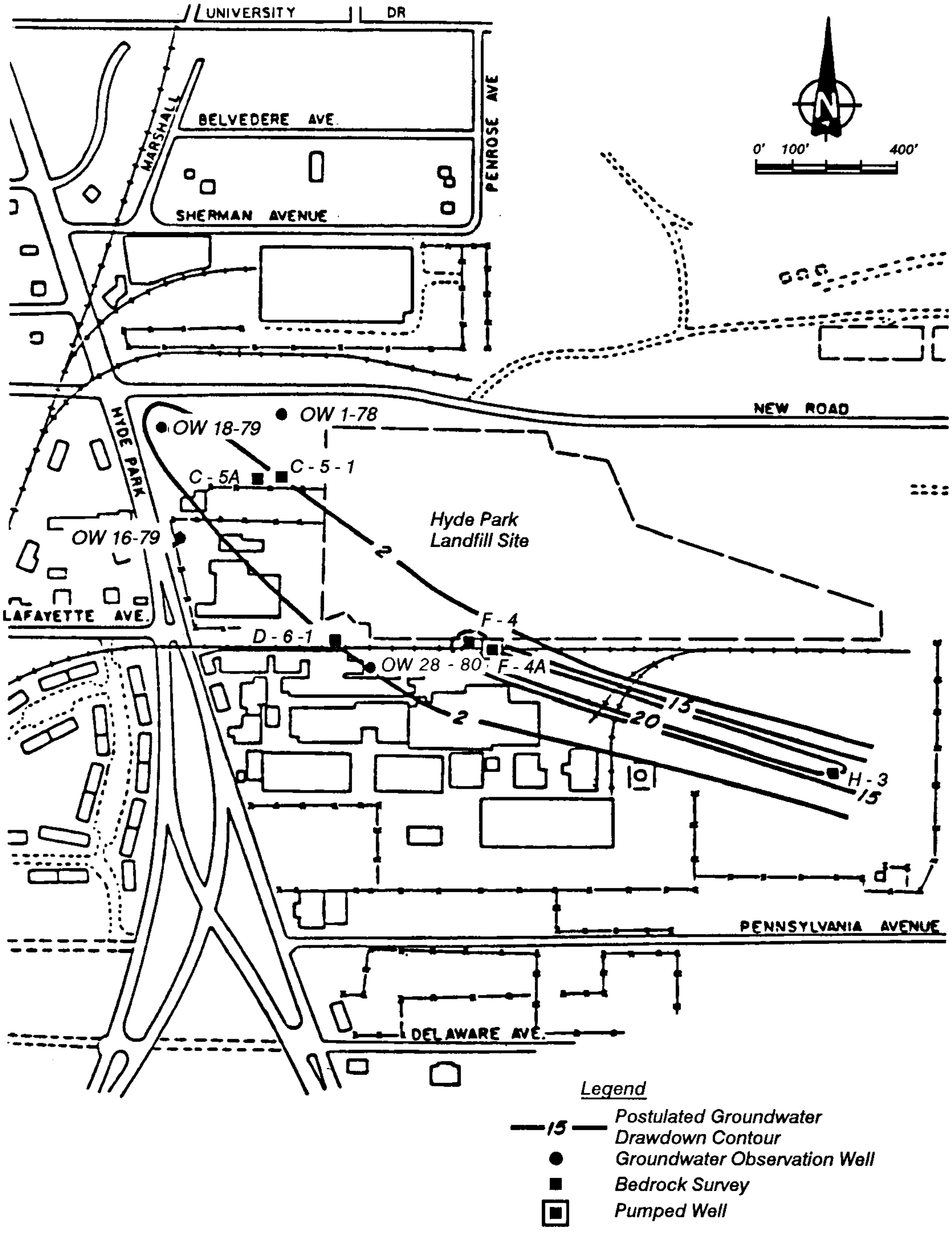


**Figure 3-7.** **Postulated ground-water drawdown contours during Hyde Park landfill pump test (from Conestoga-Rovers & Associates Limited, 1984).**

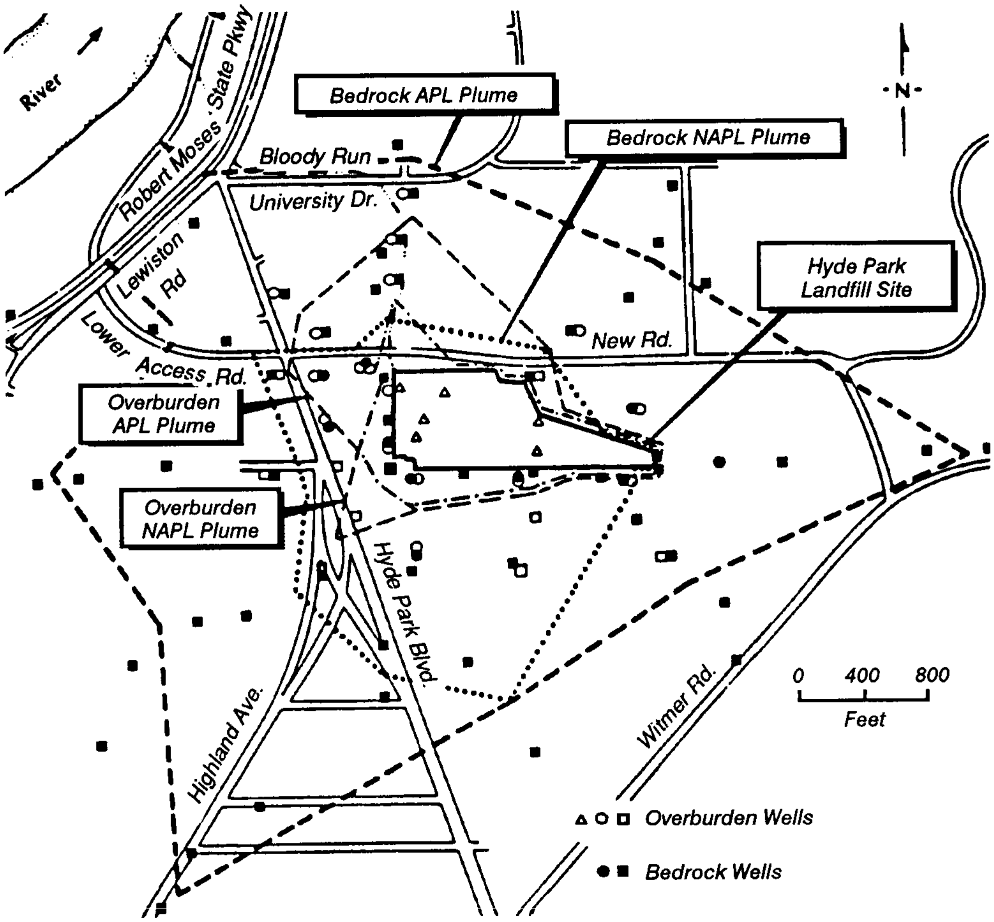


**Figure 3-8. Boundaries of dissolved chemical (APL) and NAPL plumes of contaminated ground water emanating from the Hyde Park landfill through the overburden and Lockport Dolomite (from Faust, 1985).**

the Niagara River must be below specified limits. The interim flux level for 2,3,7,8-TCDD is 0.5 g/yr. This level will be modified based on a future study of TCDD in the Niagara River and Lake Ontario.

Hyde Park is an excellent example of a remediation that both allows for better site characterization and does not make itself obsolete as more data become available. The remedies described in the stipulation include extensive monitoring programs that both ensure that performance goals are achieved and enhance the understanding of site hydrogeology. The phased approach with initial prototype remedies allows for better initial site characterization that will ultimately lead to the optimal remediation approach. The program is not limited to current technologies, but can be modified should new innovations be found. This flexibility is important because of the long cleanup times expected.

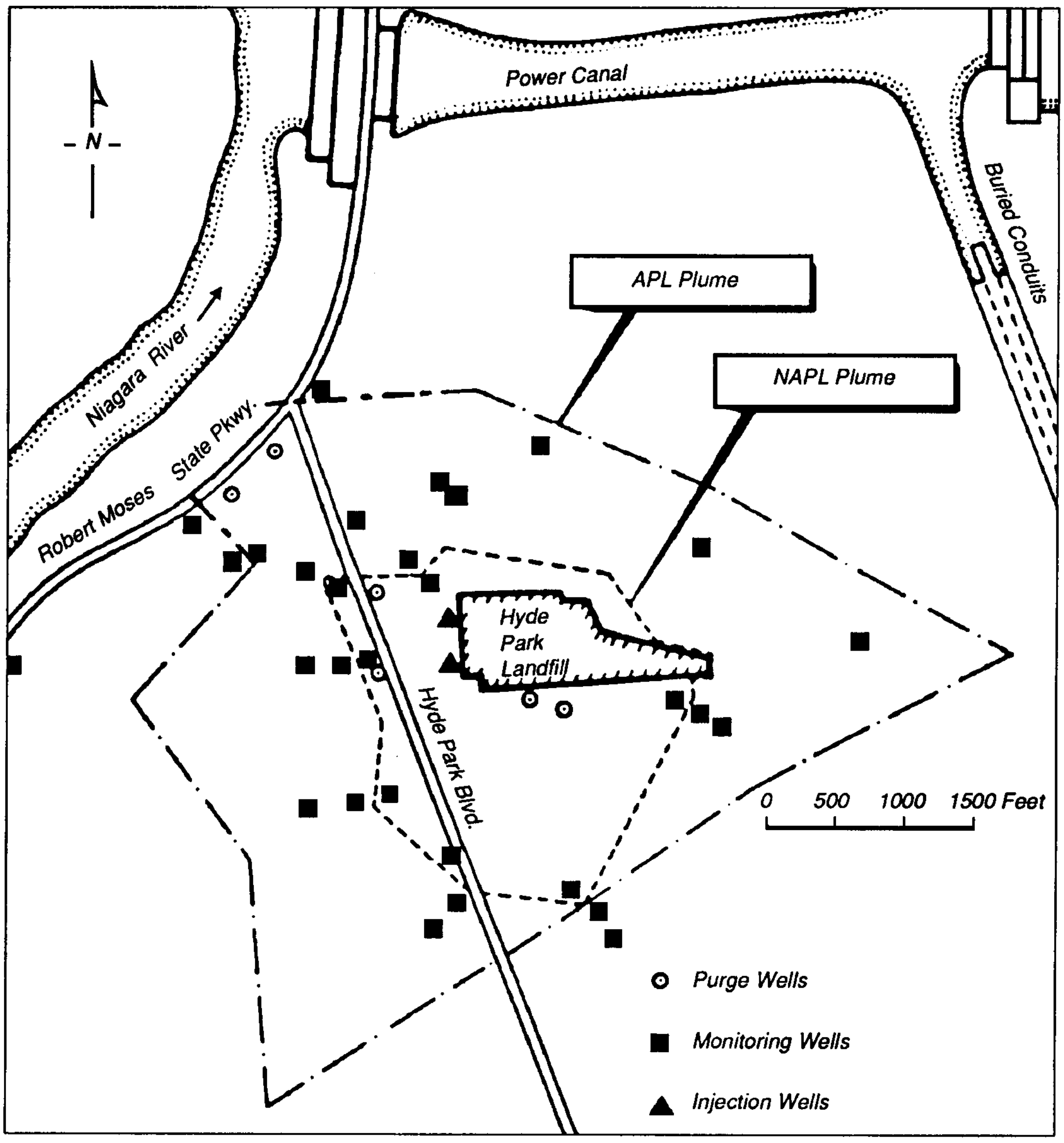


**Figure 3-9.** Locations of purge, injection, and monitoring wells to be installed for the prototype Lockport Dolomite hydraulic containment system at the Hyde Park site (from Faust, 1985).

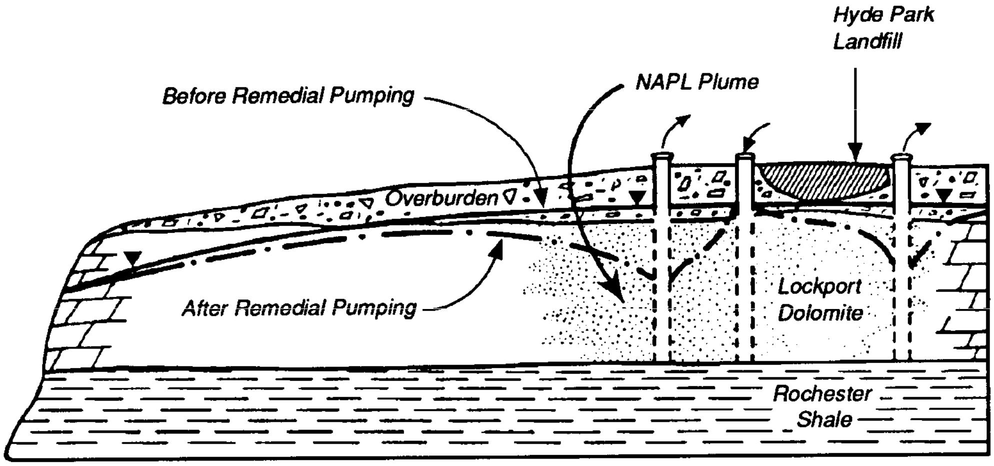


Figure 3-10. A conceptual cross-section of the Lockport Dolomite hydraulic containment system at the Hyde Park site (from Faust, 1985).

## 3.6 References

American Society for Testing and Materials (ASTM). 1990a. Standard Method for Diamond Core Drilling for Site Investigation. In: Annual Book of ASTM Standards, Vol. 04.08, D2113-83. ASTM, Philadelphia, PA.

American Society for Testing and Materials (ASTM). 1990b. Standard Method for Penetration Test and Split-Barrel Sampling of Soils. In: Annual Book of ASTM Standards, Vol. 04.08, D 1586-84.

Bouwer, H. 1978. Ground-Water Hydrology. McGraw-Hill, New York.

Brady, N.C. 1974. The Nature and Properties of Soils, 8th ed. MacMillan, New York.

Cohen, R.M., R.R. Rabold, C.R. Faust, J.O. Rumbaugh III, and J.R. Bridge. 1987. Investigation and Hydraulic Containment of Chemical Migration: Four Landfills in Niagara Falls. Civil Engineering Practice 2(1):33-58.

Compton, R.R. 1962. Manual of Field Geology. John Wiley & Sons, New York.

Conestoga-Rovers & Associates Limited. 1984. Requisite Remedial Technology Study, Overburden & Bedrock, Hyde Park Remedial Program. Prepared for Occidental Chemical Corporation, Ref. No. 1069.

Faust C.R. 1985. Affidavit re: Hyde Park. U.S., N.Y. v. Hooker Chemicals and Plastics Corp. et al., Civil Action No. 79-989.

GeoTrans. 1989. Progress Report - Hydrogeological Characterization of the Bedrock Near the S-Area Landfill (Niagara Falls, NY) in Support of Requisite Remedial Technology (RRT) Evaluation. GeoTrans, Inc., Hemdon, VA.

Gilkeson, R.H., P.C. Heigold, and D.E. Laymen. 1986. Practical Application of Theoretical Models to Magnetometer Surveys of Hazardous Waste Disposal Sites—A Case History. Ground Water Monitoring Review 6(1):54-61.

Gillham, R.W. 1988. Glossary of Ground Water Monitoring Terms. Water Well Journal 42(5):67-71.

Greenhouse, J.P. and D.J. Slaine. 1983. The Use of Reconnaissance Electromagnetic Methods to Map Contaminant Migration. Ground Water Monitoring Review 3(2):47-59.

Huntley, D. 1987. Some Fundamentals of Hydrogeology, 5th ed. In: Subsurface Geology, L.W. LeRoy, D.O. LeRoy, S.D. Schwochow, and J.W. Raese (eds.), Colorado School of Mines, Golden, CO, pp. 746-755.

Keelan, D.K. 1987. Core Analysis. In: Subsurface Geology, 5th d., L.W. LeRoy, D.O. LeRoy, S.D. Schwochow, and J.W. Raese (eds.), Colorado School of Mines, Golden, CO, pp. 35-47.

Keys, W.S. and L.M. MacCay. 1971. Application of Borehole Geophysics to Water-Resources Investigations. U.S. Geological Survey Techniques of Water-Resources Investigations TWI-2E1.

Keys, W.S. 1988. Borehole Geophysics Applied to Ground-Water Investigations. U.S. Geological Survey Open-File Report 87-539,303 pp. [Published in 1989 with the same title by National Water Well Association, Dublin, OH.]

Koemer, R.M., A.E. Lord, Jr., and J.J. Bowders. 1981. Utilization and Assessment of a Pulsed RF System to Monitor Subsurface Liquids. In: National Conference on Management of Uncontrolled Hazardous Waste Sites, Hazardous Materials Control Research Institute, Silver Spring, LD, pp. 165-170.

Kwader, T. 1986. The Use of Geophysical Logs for Determining Formation Water Quality. Ground Water 24:11-15.

Landau, H.L. 1987. Coring Techniques and Applications. In: Subsurface Geology, 5th cd., L.W. LeRoy, D.O. LeRoy, S.D. Schwochow, and J.W. Raese, (eds.), Colorado School of Mines, Golden, CO, pp. 395-398.

Levorsen, A.I. 1967. The Reservoir Pore Space. In: Geology of Petroleum, 2nd ed, W.H. Freeman and Company, San Francisco, CA, Chapter 4, pp. 115, 119, 120.

O’Brien and Gere Engineers, Inc. 1988. Hazardous Waste Site Remediation. Van Nostrand Reinhold, New York, 422 pp.

Portland Cement Association. 1973. PCA Soil Primer. Engineering Bulletin EBO07.045, Portland Cement Association, Skokie, IL, 39 pp.

Ray, R.G. 1960. Aerial Photographs in Geologic Interpretation and Mapping. U.S. Geological Survey Professional Paper 373,230 pp.

Stewart, M., M. Layton, and T. Lizanec. 1983. Application of Surface Resistivity Surveys to Regional Hydrogeologic Reconnaissance. Ground Water 21:42-48.

Stewart, N.T. 1982. Evaluation of Electromagnetic Methods for Rapid Mapping of Salt-Water Interfaces in Coastal Aquifers. Ground Water 20:538-545.

Sverdrup, K.A. 1986. Shallow Seismic Refraction Survey of Near-Surface Ground Water Flow. Ground Water Monitoring Review 6(1):80-83.

Urish, D.W. 1983. The Practical Application of Surface Electrical Resistivity to Detection of Ground-Water Pollution. Ground Water 21:144-152.

U.S. Environmental Protection Agency (EPA). 1987. Handbook Ground Water. EPA/625/6-87/016, 212 pp.

Zohdy, A.A.R, G.P. Eaton, and D.R. Mabey. 1974. Application of Surface Geophysics to Ground-Water Investigations. U.S. Geological Survey Techniques of Water-Resources Investigations TWI-2D1.

# Chapter 4
# Characterization of Water Movement in the Saturated Zone

James W. Mercer and Charles P. Spalding

Advection is the primary transport mechanism for conservative chemicals and for many nonconservative chemicals. It is the controlling process for chemicals moving away from a source area (e.g., a landfill or a spill) and for removing chemicals from the subsurface (e.g., pump-and-treat systems). Therefore, understanding advection is important to both site characterization and remediation.

An understanding of the factors that control ground-water movement is needed to understand advection. This chapter reviews concepts needed to determine and understand ground-water flow. This review is followed by a discussion of field techniques used to obtain the data needed to characterize ground-water flow. As important as it is to collect data, it is just as important to analyze and interpret the data. Therefore, this chapter also discusses different analysis techniques and ground-water remedial actions. Finally, an example ties the discussion together and illustrates the important points of the chapter.

Both general data requirements and characterization techniques are presented throughout this chapter. Each application of these techniques is unique and site specific. No subsurface characterization tool provides perfect information; several techniques (e.g., geophysical and geochemical) should be combined, such that different types of data support the same conclusion. Because the field work is completed in phases, remediation decisions often involve some uncertainty; therefore, the importance of monitoring is stressed.

## 4.1 Review of Concepts

There are numerous books that characterize and present the principles and concepts of ground-water hydrology (e.g., Bear, 1979; Bouwer, 1978; Davis and DeWiest, 1966; DeWiest, 1969; Domenico, 1972; Freeze and Cherry, 1979; Todd, 1980 and Walton, 1970). Other general references have been published by the U.S. Environmental Protection Agency (e.g., U.S. EPA, 1987). This section specifically discusses contaminant hydrology and will not cover many of the general topics included in these references.

At hazardous waste sites, the following questions need to be addressed with respect to ground-water hydrology: (1) where is the water coming from? (2) where is the water going? and (3) what are the rates of movement? Answering these questions requires information on the local water balance, the transmissive properties of the media, and the hydraulic head distribution.

Hydraulic head is rhe elevation to which water rises in a well that is open to the surface (Figure 4-l). It is composed of two parts: (1) the pressure head that produces the column of water above the open interval; and (2) the elevation head, which is the elevation of the open interval relative to a datum, usually mean sea level. Depth to water normally is measured from a reference point (e.g., top of the casing) that has been surveyed. This information is used to compute water-level

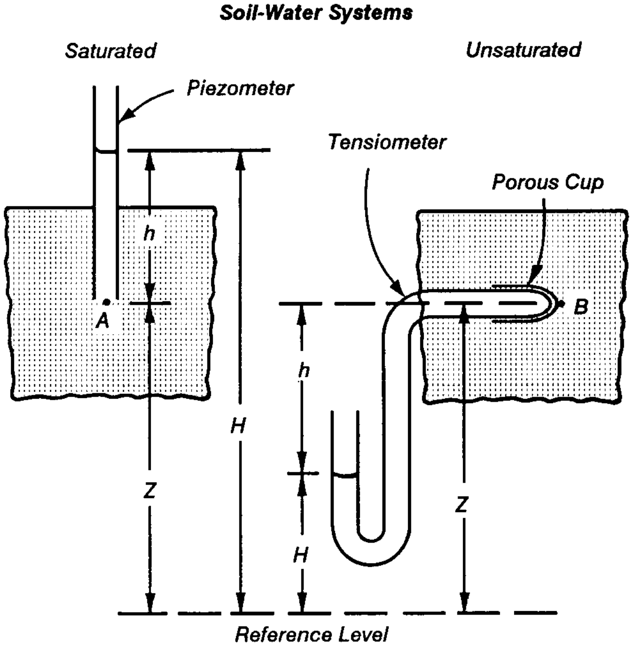


Figure 4-1. A diagram of the relationships between hydraulic head, H, pressure head, h, and gravitatlonal head, Z. The pressure head is measured from the level of termination of the piezometer or tensiometer in the soil to the water level in the manometer and is negative in the unsaturated soil.

elevations. Although depth to water is useful to know, without converting it to a water-level elevation (i.e., hydraulic head), directions and rates of ground-water movement cannot be determined.

Hydraulic head data m often displayed in two dimensions as a potentiometric surface map (Figure 4-2). Such a map represents the elevation to which water would rise in an open well placed in the interval of interest. It is analogous to a topographic map with the direction of water flow from higher to lower elevations and generally running perpendicular to the contours. However, ground-water flow directions may diverge from the direction predicted by potentiometric contours when the aquifer is anisotropic (hydraulic conductivity is not the same in all directions). Fetter (1981) describes techniques for determining the direction of ground-water flow in anisotropic aquifers. Again, using the analogy of the topographic map, behavior of ground-water flow is similar to how surface

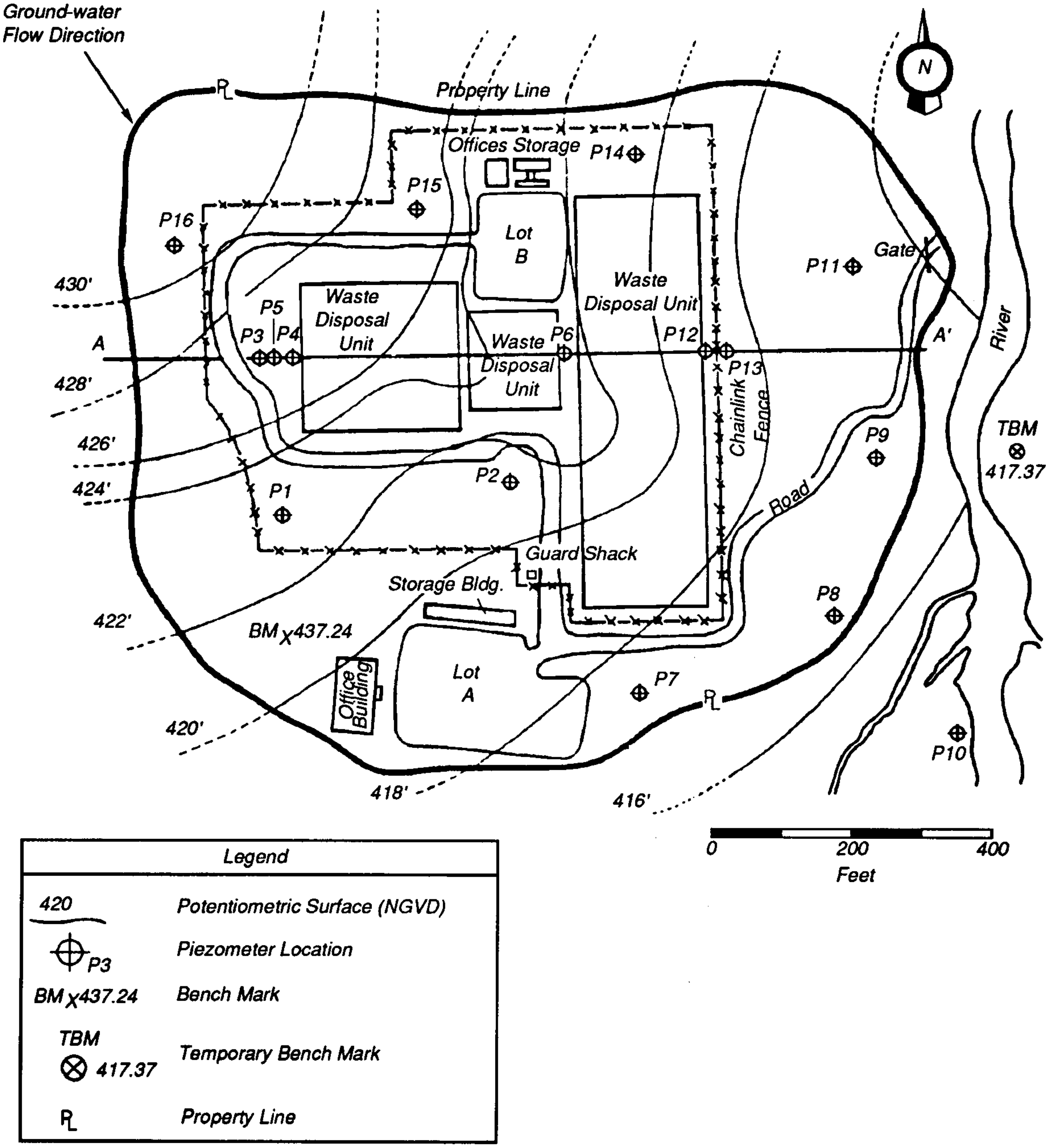


Figure 4.2. Potentiometric surface map (from EPA, 1988).

water runoff occurs via overland flow. Different subsurface units or intervals may have different potentiometric surface maps. The uppermost potentiometric surface map, which is in contact with the atmosphere through the vadose zone (Chapter 5), is the water table.

Although displayed on a two-dimensional surface, the hydraulic head distribution is generally a three-dimensional phenomena that is, hydraulic head varies vertically as well as areally. To determine the vertical distribution of hydraulic head, wells must be drilled in the same vicinity, but must be open to different depths (elevations). If hydraulic head increases with increasing depth, ground-water flow is upward; in general, this results in an area of discharge. If hydraulic head decreases with increasing depth, ground-water flow is downward this is an area of ground-water recharge.

Often the stratigraphy supports multiple aquifers that are separated by confining beds. In these cases, the aquifers are dominated by horizontal flow and the confining layers are dominated by vertical flow, i.e., leakage between adjacent aquifers. At hazardous waste sites, it is important to determine how many aquifers are contaminated. As part of this determination, the direction of leakage and the direction of flow in the affected aquifers must be assessed. It is possible that flow direction in one aquifer could differ from flow in an adjacent aquifer. The difference in hydraulic head over a given distance is known as the hydraulic gradient. Hydraulic gradients must be known to determine rates and directions of groundwater movement.

Often, topographic highs are recharge areas and topographic lows are discharge areas. For this reason, surface water bodies (such as lakes, rivers, springs, and seeps) are often surface expressions of the water table. Therefore, these surface water bodies are useful for inferring watertable elevation data where no wells exist.

As indicated, ground water generally flows from potentiometric highs to potentiometric lows, following a trace that is perpendicular to the potentiometric contours. This trace is sometimes referred to as a flow line. Unlike surface water, however, ground-water flow is resisted by the rock and soil through which it flows. This resistance is quantified by the transmissive properties of the media. As these transmissive properties vary at different locations in the aquifer and in different directions from a given point, they cause the flow lines to change directions such that they may no longer be perpendicular to the apparent potentiometric contours. Therefore, in addition to hydraulic gradients, the transmissive properties of the media must be known in order to determine rates and directions of ground-water flow.

The transmissive properties of the media have been given different but related terms, including intrinsic permeability, hydraulic conductivity, and transmissivity. Intrinsic permeability is a property of the porous medium and has dimensions of length squared. It is a measure of the resistance to fluid flow through the medium; the greater the permeability, the less the resistance. Hydraulic conductivity is defined as the volume of water that will move in unit time under a unit hydraulic gradient through a unit area measured at right angles to the direction of flow. It is a property of the fluid and medium with dimensions of length per time. It is equal to the product of intrinsic permeability, density of water, and the gravitational acceleration constant divided by the dynamic viscosity of water. Finally, transmissivity is the rate of water flow through a vertical strip of aquifer one unit wide, extending the full saturated thickness of the aquifer, under a unit hydraulic gradient. It is equal to the product of hydraulic conductivity and the aquifer thickness. Consequently, it has dimensions of length squared per time.

All these properties can vary spatially and directionally at a given point. If the medium is homogeneous, the transmissive properties do not vary spatially. If the medium is isotropic, they do not vary when measured in different directions from a given point. Most geologic materials are heterogeneous and anisotropic.

The final information that is needed to answer the questions about ground-water hydrology that were posed earlier concerns the local water balance. At hazardous waste sites, it is generally not possible to accurately quantify the local water balance, primarily because of data limitations. One of the main goals at a hazardous waste site investigation is to define the extent of contamination. Consequently, monitoring wells are clustered near potential sources. Ground-water hydrologists look at the bigger picture to determine what hydraulic boundaries control or influence flow at the site. Data covering the larger area are rarely available for hazardous waste sites. Regardless, it is important to attempt the mass balance and to estimate what regional factors control the local flow system. This exercise, while not highly quantitative, will provide a valuable qualitative understanding of the flow system controlling contaminant migration.

## 4.2 Field Techniques

Ground water is generally below the land surface and, therefore, difficult to observe. One of the most effective techniques for observing ground water is to use point measurements made in wells. Wells must be designed, drilled, and developed in order to measure water levels and to take water quality samples. Tests are conducted to determine transmissive and storage properties. The following section discusses methods used to drill wells, measure water levels, and determine subsurface properties.

### *4.2.1 Drilling Techniques*

Table 4-1 summarizes the advantages and disadvantages of various drilling methods used for monitoring well construction. In shallow unconsolidated deposits, a hollow stem continuous flight auger is the preferred method. The use of hollow stem augers (Figure 4-3) requires no fluid in the borehole and allows for installation of the casing and screens prior to removal of the augers, thereby eliminating problems associated with caving of the borehole. However, it may be difficult to seal the annular space in wells constructed in this manner, and other construction techniques may be more suitable. In situations where borehole caving is not a problem, the use of solid stem or bucket augers is equally suitable. Unfortunately, the use of augers becomes impractical when drilling

***Table 4-1. Auger, Rotary, and Cable-Tool Drilling Techniques-Advantages and Disadvantages for Construction of Monitoring Wells***

| *Type* | *Advantages* | *Disadvantages* |
|---|---|---|
| *Auger* | •*Minimal damage to aquifer*<br>•*No drilling fluids required*<br>•*Auger flights act as temporary casing, stabilizing hole for well construction*<br>•*Good technique for unconsolidated deposits*<br>•*Continuous core can be collected by wireline method* | •*Cannot be used in consolidated deposits*<br>•*Limited to wells less than 150 feet in depth*<br>•*May have to abandon holes if boulders are encountered* |
| *Rotary* | •*Quick and efficient method*<br>•*Excellent for large and small diameter holes*<br>•*No depth limitations*<br>•*Can be used in consolidated and unconsolidated deposits*<br>•*Continuous core can be collected by wireline method* | •*Required drilling fluids which alter water chemistry*<br>•*Results in a mud cake on the borehole wall, requiring additional well devopment, and potentially causing changes in chemistry*<br>•*Loss of circulation can develop in fractured and high-permeability material* |
| *Cable tool* | •*No limitation on well depth*<br>•*Limited amount of drilling fluid required*<br>•*Can be used in both consolidated and unconsolidated deposits*<br>•*Can be used in areas where lost circulation is a problem*<br>•*Good lithologic control*<br>•*Effective technique in boulder environments* | •*Limited rigs and experienced personnel available*<br>•*Slow and ineffcient*<br>•*Difficult to collect core* |

*From GeoTrans, 1989*

deeper wells (100 to 150 ft) or when hard unconsolidated deposits are encountered. Thick clay deposits that tend to bind augers also may make the use of augers impractical. When drilling beneath the water table where cross-contamination between water-bearing strata is considered problematic, augers may not be the optimum technique. If auger techniques are used, it may not be possible to prevent fluid flow in the borehole between formations.

When drilling in deeper consolidated deposits, air rotary drilling (Figure 4-3) is frequently the preferred method because no drilling fluids are employed. However, oil from air compressors may contaminate the borehole, and special filters are required to minimize this effect. In some cases, drillers may use foams to help lift cuttings to the surface and increase the speed of drilling. Caving of unconsolidated material overlying consolidated material can frequently limit the use of air rotary drilling. However, some air rotary rigs are equipped with casing hammers that can drive a casing as drilling proceeds, similar to cable tool drilling techniques (see discussion below). Mud rotary techniques also can be used to drill through unconsolidated material, a casing can be set to hold these deposits open, and the hole can be continued with air rotary.

Cable tool drilling methods (Figure 4-3) may be used for constructing monitoring wells. However, cable tool drilling through unconsolidated material, particularly below the water table, will probably require the simultaneous driving of a casing to prevent caving. Because casing driven in this manner may seal strata through which it is driven, this method may be used at sites when cross-contamination of water bearing zones could be a problem. Completing a well cased during drilling will probably require that the casing be pulled back to expose the formation before setting the screens. An advantage of cable tool drilling is that it can be used to drill to great depths, although a minimum borehole diameter of 3 in. is required. Another advantage is that it can penetrate through consolidated material, although frequently at a slow pace.

During drilling for any ground-water contamination investigation, precautions must be taken to prevent cross-contamination of boreholes. Thoroughly cleaning the drilling rig and tools initially and after each borehole is drilled are examples of specific precautions that should be taken. No uniform procedure has been developed for all sites, but a soap wash followed by solvent and distilled water rinse is commonly used. Proper drilling plans also can minimize potential cross-contamination. If possible, drilling should progress from the least to most contaminated areas (Sisk, 1981).

Upon completion, the monitoring well must be developed. Any contamination or formation damage from well drilling and any fines from the natural formation must be removed to provide a particulate-free discharge. A variety of techniques are available to remove such contamination and develop a well (Table 4-2). To be effective, all these techniques require reversals or surges in flow to avoid bridging by particles, which is common when flow is continuous in one direction. These reversals or surges can be created by using surge blocks, air lifts, bailers, or pumps (see Scalf et al., 1981). Natural formation water should be used; use of other water is not recommended. The discharge from the well should be continuously monitored and development should be continued until the discharge is particulate-free. Ideally, the well should be developed so as to minimize the creation of water requiring disposal.

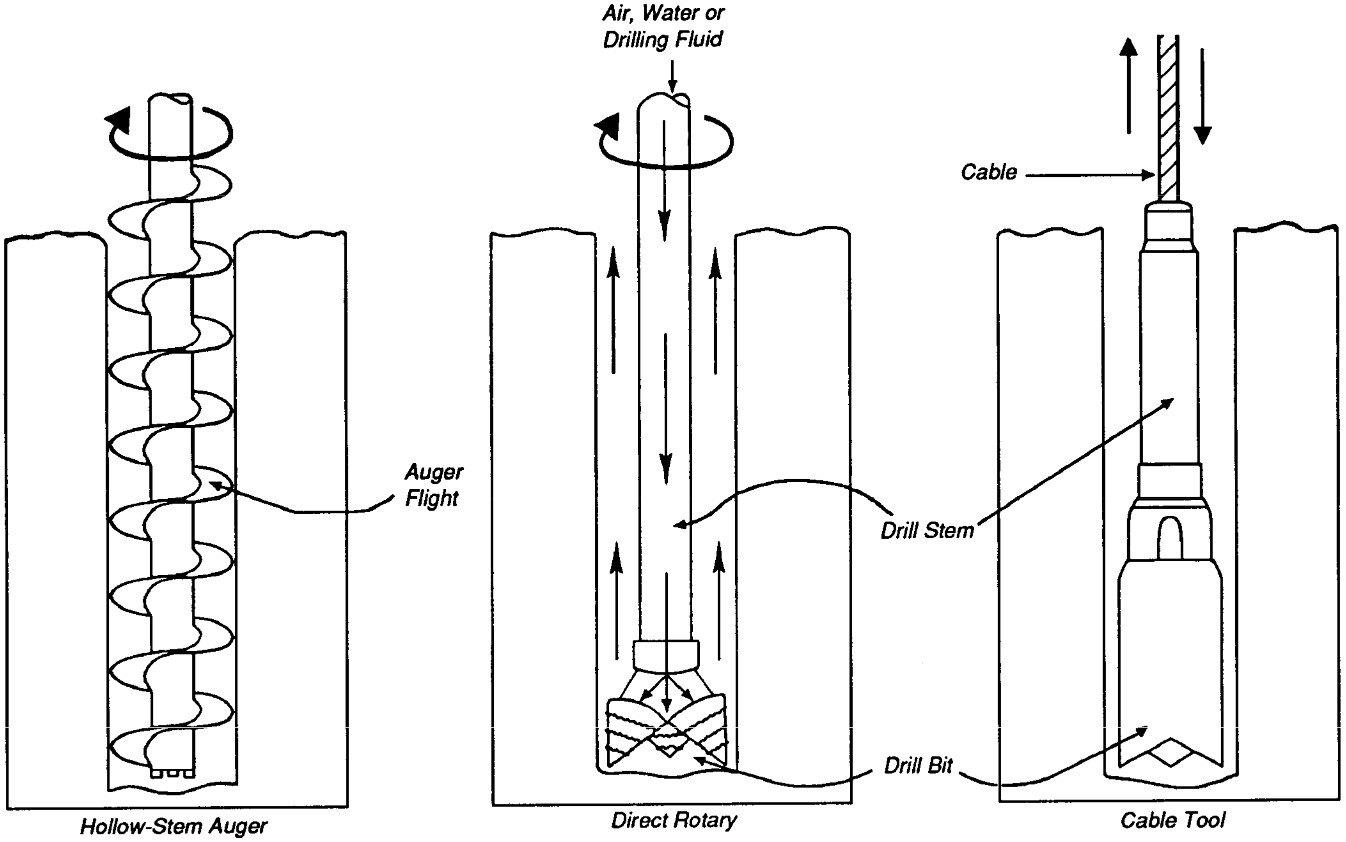


**Figure 4-3. A conceptual comparison of the hollow-stem auger, the direct-rotary, and the cable-tool drilling methods (from GeoTrans, 1989).**

*Table 4-2. Well Development Techniques-Advantages and Disadvantages*

| *Technique* | *Advantages* | *Disadvantages* |
|---|---|---|
| *Overpumping* | *•Minimal time and effort required*<br>*•No new fluids introduced*<br>*•Remove fluids introduced during drilling* | *•Does not effectively remove fine-granted sediments*<br>*•Can leave the lower portion of large screen intervals undeveloped*<br>*•Can result in a large volume of water to be contained and disposed.* |
| *Backwashing* | *•Effectively rearranges filter pack*<br>*•Breaks down bridging in filter pack*<br>*•No new fluids introduced* | *•Tends to push fine-grained sediments into filter pack*<br>*•Potential for air entrapment if air is used*<br>*•Unless combined with pumping or bailing, does not remove drilling fluids* |
| *Mechanical surging* | *•Effectively rearranges filter pack*<br>*•Greater suction action and surging than backwashing*<br>*•Breaks down bridging in filter pack*<br>*•No new fluids introduced* | *•Tends to push fine-grained sediments into filter pack*<br>*•Unless combined with pumping or bailing, does not remove drilling fluids* |
| *High velocity jetting* | *•Effectively rearranges filter pack*<br>*•Breaks down bridging in filter pack*<br>*•Effectively removes the mud cake around screen* | *•Foreign water and contaminants introduced*<br>*•Air blockage can develop with air jetting*<br>*•Air can change water chemistry and biology (iron bacteria) near well*<br>*•Unless combined with pumping or bailing, does not remove drilling fluids* |

*From GeoTrans, 1989*

A variety of materials are available for use in casing, screenings and other structural and sampling components of monitoring wells (Table 4-3). Well materials must have sufficient strength to ensure the structural integrity of the well during installation and during protracted periods of monitoring. The materials should sufficiently resist deterioration that may result from long-term exposure to natural chemical or pollutant constituents in the ground water at each site. The materials also must be selected to minimize their interference with the measurement of specific constituents. The most commonly used materials are mild steel, stainless steel, polyvinyl chloride (PVC), polypropylene, polyethylene, and Teflon®. These materials have substantially different properties relative to strength, corrosion resistance, interference with specific constituent measurements expense, and availability. Consequently, materials should be selected only after consideration of all pertinent, site-specific factors such as well installation method, depth, geochemical environment, and probable contaminants to be monitored. Larson (1981) and Barcelona et al. (1983) have summarized the chemical resistance of various casings and well materials to differing environments. These topics also are discussed in more detail in subsequent chapters of this Handbook.

There are three basic categories of monitoring well designs that are used to monitor vertical distribution of contaminants at a specific location (Figure 4-4). The first type of nested-sampler design consists of a series of multiple-port samplers installed in a single borehole. The sampling ports are isolated from each other by inflatable packers or by other annular seals. In some systems, a special tool is lowered into the well to open ports at the specific location when a water level or water quality sample is desired. In others, different plastic (such as nylon) tubings are used for sampling each zone where a vacuum is used to bring the sample to the

***Table 4-3. Well Casing and Screen Material—Advantages and Disadvantages in Monitoring Wells***

| *Type* | *Advantages* | *Disadvantages* |
|---|---|---|
| *Fluorinated ethylene propylene (FEP)* | *Good chemical resistance to volatile organics*<br>*Good chemical resistance to corrosive environments* | *Lower strength than steel and iron* |
| *Polytetrafluoroethylene (PTFE) or Teflon®* | *Lightweight*<br>*High-impact strength*<br>*Resistant to most chemicals* | *Weaker than most plastic material* |
| *Polyvinylchloride (PVC)* | *Lightweight*<br>*Resistant to weak alkalis, alcohols, aliphatic hydrocarbons, and oils*<br>*Moderately resistant to strong acids and alkalis* | *Weaker than steel and iron*<br>*More reactive than PTFE*<br>*Deteriorates when in contact with ketones, esters, and aromatic hydrocarbons* |
| *Polyethylene* | *Lightweight* | *Low strength*<br>*More reactive than PTFE, but less reactive than PVC*<br>*Not commonly available* |
| *Polypropylene* | *Lightweight*<br>*Resistant to mineral acids*<br>*Moderately resistant to alkalis, alcohols, ketones, and esters* | *Low strength*<br>*Deteriorates when in contact with oxidizing acids, aliphatic hydrocarbons, and aromatic hydrocarbons*<br>*More reactive than PTFE, but less reactive than PVC*<br>*Not commonly available* |
| *Kynar* | *High strength*<br>*Resistant to most chemicals and solvents* | *Poor chemical resistance to ketones, acetone*<br>*Not commonly available* |
| *Stainless steel* | *High strength*<br>*Good chemical resistance to volatile organics* | *May be a source of chromium in low pH environments*<br>*May catalyze some organic reactions* |
| *Cast iron and low-carbon steel* | *High strength* | *Rusts easily, providing highly sorptive surface for many metals*<br>*Deteriorates in corrosive environments* |
| *Galvanized steel* | *High strength* | *May be a source of zinc*<br>*If coating is scratched, will rust, providing **a** highly sorptive surface for many metals* |

*From GeoTrans, 1989*

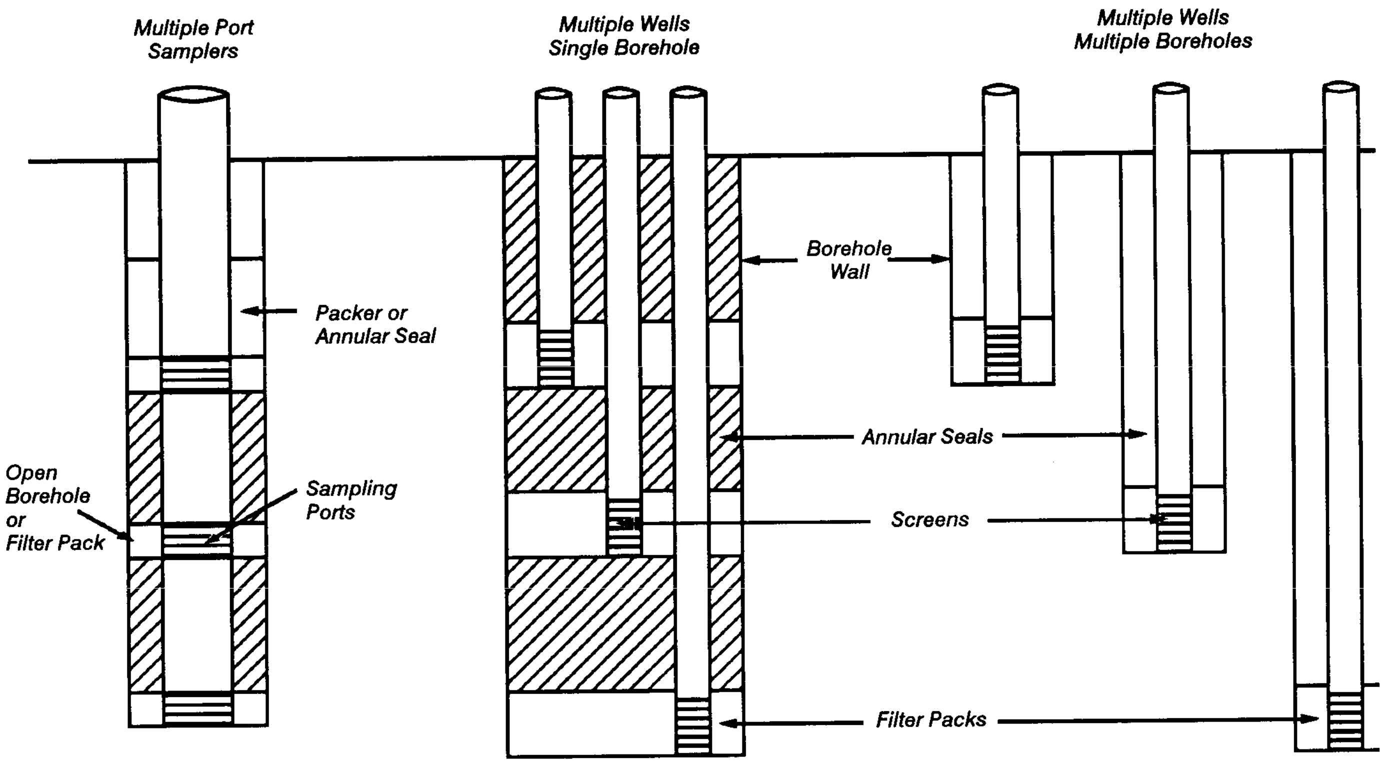


**Figure 4-4.** **A conceptual comparison of three multilevel sampling designs (from GeoTrans, 1989).**

surface. However, for deep wells and volatile organic chemicals, the vacuum may result in unacceptable chemical losses from volatilization. The second configuration for nested-samplers consists of multiple well stings installed in one large borehole (Figure 4-4). Individual zones are isolated from each other using a low permeability material. Seals between zones may be difficult to obtain and maintain.

Finally, the third type of nested-sampler design consists of drilling a separate borehole for each monitoring well (Figure 4-4). This system is superior to the two previous systems because the potential for cross- contamination from faulty seals is minimized, and smaller diameter holes can be drilled, thereby reducing the volume of water that needs to be pumped prior to sampling. The additional costs associated with drilling multiple boreholes often is offset by technical problems associated with the installation of the two previous systems. Use of multiple piezometers and ports in a single borehole should be avoided according to U.S. EPA (1986), because the potential for erroneous data is increased. (A piezometer is a small-diameter well open to a point in the subsurface.) Table 4-4 summarizes the advantages and disadvantages of these three multilevel sampling designs.

### *4.2.2 Methods to Measure Hydraulic Head*

There are a number of ways to measure hydraulic head in the saturated or vadose zones (see Table 4-5). For convenience, both zones are discussed in the following section. The accuracy of depth-to-water measurements is discussed in a Superfund ground-water issue paper (Thornhill, 1989). When comparing various methods of measurements, as indicated in Table 4-5, the steel tape method is the most precise. Although less precise, the air line method is useful in pumped wells where water turbulence exists. Pressure transducers can be used in either the saturated or vadose zones. They are useful for making frequent measurements, such as during a slug test.

In a saturated zone, the hydraulic head, H, is measured at a point using a piezometer (see Figure 4- 1) and is defined as the elevation (pressure head) at which the water surface stands in an open piezometer tube terminated at a given point in the porous medium. Hydraulic head is a combination of pressure head and elevation head (distance of the measuring point above a reference level [datum]). The reference level chosen for measurement of H is arbitrary. The hydraulic head is a potential function, the potential energy per unit weight of the ground water.

*Table 4-4. Multilevel Monitoring Well Design-Advantages and Disadvantages in Monitoring Wells*

| *Type* | *Advantages* | *Disadvantages* |
|---|---|---|
| *Multiple-port sampler* | *•Large number of sampling zones per borehole*<br>*•Smaller volume of water required for purging than nested sampler/single borehole and multiple boreholes*<br>*•Lower drilling costs than nested sampler/multiple boreholes* | *•Potential for cross-contamination among ports*<br>*•Potential sampling ports becoming plugged*<br>*•Special sampiing tools required* |
| *Nested sampler/ single borehole* | *•Lower drilling costs than multiple boreholes*<br>*•Low potential for screens becoming plugged* | *•Potential for cross-contamination among screen intervals*<br>*•Number of sampling intervals limited to three or four*<br>*•Larger volume of water required for purging than multiple-port campier or nested sampler/ multiple boreholes*<br>*•Higher installation costs* |
| *Nested sampler/ multiple boreholes* | *•Potential for cross-contamination minimized*<br>*•Voliume of water required for purging smaller than nested sampler/single borehole*<br>*•Low installation costs*<br>*•Low potential for screens becoming plugged* | *•Higher drilling costs* |

*From GeoTrans, 1989*

*Table 4-5. Summary of Methods to Measure Hydraulic Head*

| *Method* | *Application* | *Reference* |
|---|---|---|
| *Steel tape* | *Saturated zone. Most precise method. Noncontinuous measurements. Slow* | *Garber and Koopman (1968)* |
| *Electric probe* | *Saturated zone. Frequent measurements possible. Simple to use. Adequate precision* | *Driscoll (1986)* |
| *Air line* | *saturated zone. Continuous measurements. Useful for pumping tests. Limited accuracy* | *Driscoll (1986)* |
| *Mechanical float recorder* | *Saturated zone. Continuous measurements. Useful for long-term measurements. Permanent record can be delicate* | *USGS (1977)* |
| *Pressure transducer* | *saturated or vadose zone. Continuous or frequent measurements. Rapid response to changing pressure. Permanent record. Expensive* | *Gerber and Koopman (1986)* |
| *Acoustic sounder* | *Saturated zone. Fast; permanent record. Imprecise* | *Davis and DeWiest (1966)* |
| *Tensiometry* | *Saturated or vadose zone. Laboratory or field method. Useful range is 0 to 0.85 bars capillary pressure. Direct measurement. A widely used method* | *Cassei and Klute (1986): Stannard (1986)* |
| *Electrical resistivity* | *Vadose zone. Laboratory or field method. Useful range is 0 to 15 bars capillary pressure. indirect measurement. Prone to variable and erratic readings* | *Campbell and Gee (1986); Rehm et al. (1987)* |
| *Thermocouple psychrometry* | *Vadose zone. Laboratory or field method. Useful range 10 to 70 bars capillary pressure. interference from dissolved solutes likely in calcium-rich waste* | *Rawlins and Campbell (1986)* |
| *Thermal diffusivity* | *Vadose zone. Laboratory or field method. Useful range O to 2.0 bars capillary pressure. indirect measurement* | *Phene and Beale (1976)* |

*Modified from Thompson et al., 1989*

These same concepts of hydraulic head, pressure head, and gravitational (or elevation) head may be applied to the vadose zone (Chapter 5). A common device used to measure the hydraulic head in the vadose zone is a tensiometer. It is terminated in the soil by a porous cup permeable to water, but impermeable to air, when the pores of the cup are filled with water. The porous cup is necessary to establish hydraulic contact between the water in the tensiometer and the soil water. For the vadose zone, the pressure head is inherently negative, i.e., the free water surface in the open arm of the manometer will stand below the point of termination in the soil.

Mercury often is used in the manometer, reducing manometer size (Figure 4-5). Other measuring devices include vacuum gauges and pressure transducers. In areas subject to freezing, a 40 percent ethylene-glycol solution can be used in the tensiometer in place of water (Stephens and Knowlton, 1986).

The effective pressure range of a standard tensiometer, O to about -0.08 megapascals (MPa), is limited by the fact that negative pressures are measured with reference to atmo spheric pressure. Peck and Rabbidge (1966; 1969) developed an osmotic tensiometer for field use that expands the effective measurement range from O to as low as -1.5 MPa. Another instrument that has a wide range of pressure measurements is the thermocouple psychrometer (Table 4-5).

Hydraulic head can vary temporally at any given well. The variation may be the result of an aquifer's response to a known stress (e.g., a pumping well or seasonal changes in recharge) and may demonstrate a temporal relationship between hydraulic head and contamination concentrations. For example, an observation well, located adjacent to a ditch that only contains water during the growing season, exhibits changes in hydraulic head that cause seasonal changes in uranium concentrations (Figure 4-6). This change highlights the importance of a sampling frequency sufficient to monitor

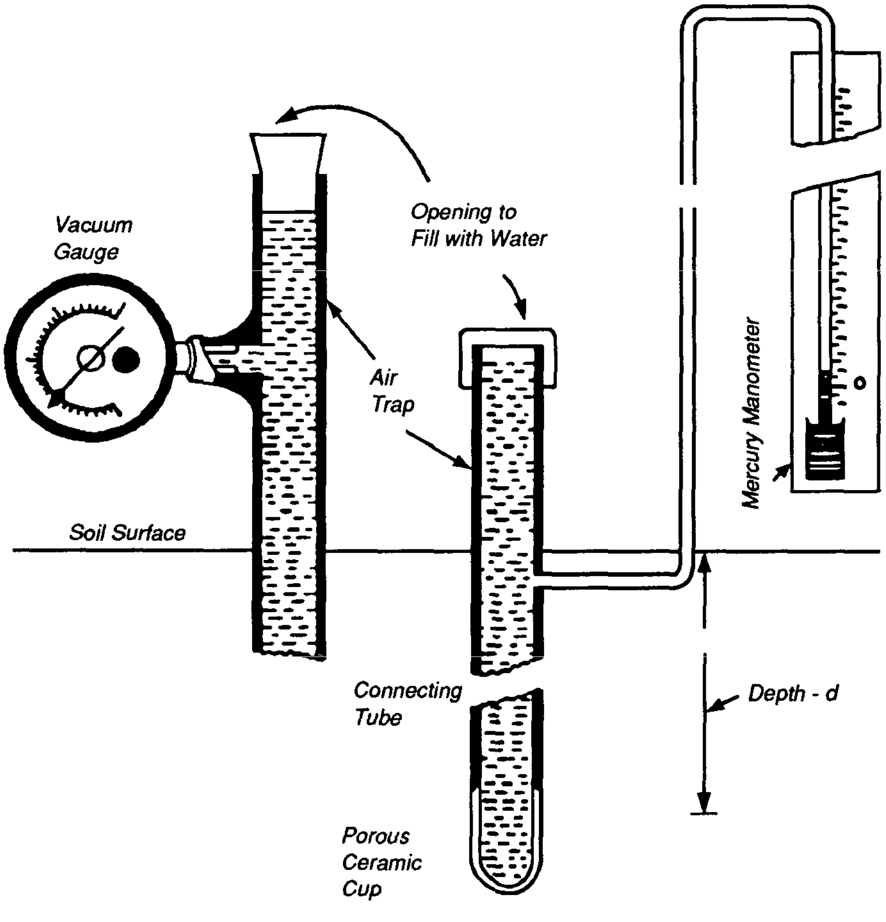


**Figure 4-5. Schematic illustration of the essential parts of a tensiometer (from Hillel, 1980).**

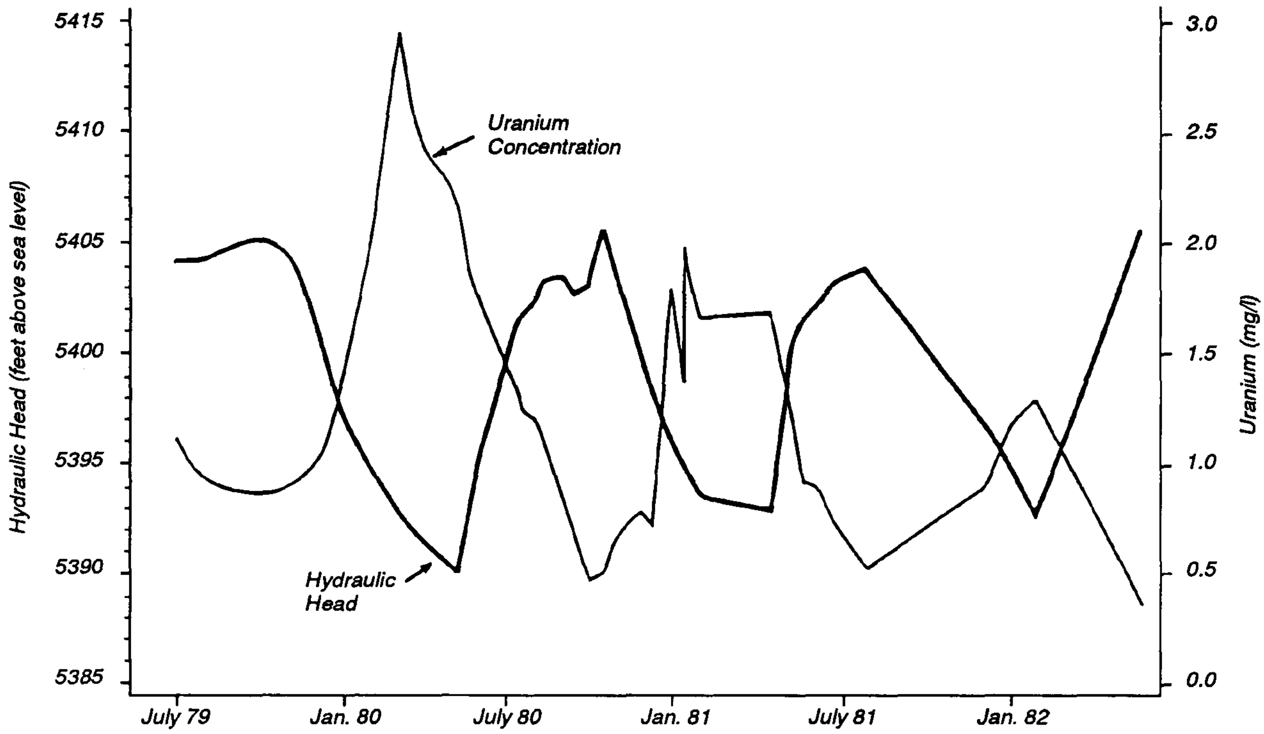


**Figure 4-8.** **Hydrography versus uranium concentrations (modified from Goode and Wilder, 1987).**

the range of contaminant concentrations that may occur at a site. At many sites, the seasonal variation of hydraulic head already may be known from existing regional studies. At sites where these type of data do not exist, it may be necessary to monitor water levels on a continuous basis to determine the measurement frequency.

### 4.2.3 Methods to Determine Aquifer Properties

The aquifer properties considered here include storage properties and hydraulic conductivity. In addition, methods are considered for estimating the spatial variability of hydraulic conductivity. The methods used to measure or estimate storage properties are listed in Table 4-6; methods to measure or estimate hydraulic conductivity are listed in Table 4-7; and methods to measure or estimate spatial variability are listed in Table 4-8.

Determination of aquifer properties begins with identifying a known stress to the ground-water system, and then measuring the response to that stress over space and/or time. Given the system geometry and boundary conditions representing the stress, a mathematical description and corresponding solution (computed response) can be determined for a range of parameters. The observed aquifer response is matched to a computed response, and the corresponding parameters are determined. Thus, aquifer properties are not measured directly, but instead are determined through this curve-matching process. Using more than one method to determine aquifer properties is recommended. Results then can be weighted toward the best performed tests with the greatest stress to the aquifer system.

Stress on the ground-water system can result from tidal or river stage fluctuations, from pumping, or from displacing the water in a well by a known volume. According to Walton (1987), a pumping tests defined as a field in situ study aimed at obtaining controlled aquifer system response data. Usually, a well is pumped at several fractions of full capacity and/or at a constant rate, and water levels are measured at frequent intervals in the pumped well and nearby observation wells. Measurement of hydraulic head can be important in establishing equilibrium water-level conditions prior to pump tests. The influence of ground-water fluctuations external to a pump test often can be eliminated prior to pump test analyses by this process. Shallow watertable aquifers can exhibit centimeter-range changes in daily ground-water levels due to evaporation. Increases in barometric pressure can cause centimeter-range declines in hydraulic head in a well. Water levels in wells near coastal areas often respond to ocean tides. Centimeter-range changes in hydraulic head are typical for earth tide responses.

***Table 4-6. Summary of Methods to Measure Storage Properties***

| ***Method*** | ***Application*** | ***Reference*** |
|---|---|---|
| *Pumping test* | *Can be used to measure storage values for unconfined or confined aquifers. Multiple-well tests are more accurate than single-well tests. Tests a relatively large volume of the aquifer.* | *Bureau of Reclamation (1985); Stallman (1971); Driscoll (1986); Lehman (1972)* |
| *Slug test* | *Single-well tests for confined or unconfined aquifers. Test highly influenced by well construction and borehole conditions.* | *Hvorslev (1951); Bouwer and Rice (1976); Bouwer (1989): Lehman (1972); Cooper et al. (1967)* |
| *Water-balance* | *Measures specific yield only. Requires several observation wells around pumping well to accurately determine the cone of depression. Tests a relatively large volume of the aquifer.* | *Nwankwor et al. (1984); Neuman (1972)* |
| *Laboratory* | *Obtain a maximum long-term value. Fractures, macropores, and heterogeneities of geologic material may not be represented. Only specific yield can be determined.* | *Nwankwor et al. (1984)* |

*From Thompson et al., 1989*

***Table 4-7. Summary of Methods to Measure Saturated Hydraulic-Conductivity Values in the Field and Laboratory (modified from Thompson et al, 1989)***

| *Method* | *Application* | *Reference* |
|---|---|---|
| *Slug test* | *Confined aquifers with fully penetrating wells screened along the entire aquifer thickness. Single-well test for wells.* | *Hvorslev (1951); Bouwer and Rice (1976); Lehman (1972)* |
| *Pumping test* | *Complex multiple-well tests for confined or unconfined aquifers with fully or partially penetrating wells. Used for wide range of aquifer permeabilities. Test wells can be used for sampling. Tests a relatively large volume of the aquifer.* | *Bureau of Reclamation (1985); Stallman (1971); Driscoll (1986): Lehman (1972);* |
| *Steady-state permaemeter* | *Laboratory method to determine sample hydraulic conductivity within a range from 1.0 cm/sec to $10^{-5}$ crn/sec.* | *Klute and Dirksen (1986)* |
| *Falling-head permeameter* | *Laboratory method to determine sample hydraulic conductivity within a range from $10^{-3}$ cm/sec to $10^{-9}$ cm/sec.* | *Klute and Dirksen (1986)* |

Drawdown is defined as the drop in water level from static-water level conditions as a result of pumping stress. Time-drawdown and distance-drawdown data are analyzed with model equations and type-curve matching, straight-line matching, or inflection-point selection techniques. For examples, see Bentall (1963); Ferns et al. (1962); Kruseman and De Ridder (1976); Lehman (1972); Neuman (1974); Reed (1980); Stallman (1971); Walton (1962); and Walton (1970). One disadvantage of conducting pumping tests at hazardous waste sites is the disposal of contaminated water. Pumping tests are valuable, however, because a relatively large portion of the aquifer is stressed. Therefore, the hydraulic conductivity determined from an aquifer test is more representative of spatially averaged conditions. These type of data are required for final design considerations of a pump-and-treat system.

The slug test method consists of causing a water-level change within a well and measuring the rate at which the water level in the well returns to its initial level. The water-level change can be caused either by injecting or withdrawing a volume of water or weighted float in the well. The rate of recovery then can be related to the hydraulic conductivity of the surrounding aquifer material. For further information, see Cooper et al. (1967) or Bredehoeft and Papadopulos (1980).

As indicated in Table 4-7, a disadvantage of slug tests is that only a small volume of aquifer material is tested. If the

*Table 4-8.* ***Summary of Methods to Measure Spatial Variability of Hydrogeologic Parameters***

| *Method* | *Application* | *Reference* |
|---|---|---|
| *Piezometer slug tests* | *Localized measurement, influenced by well disturbed zone. Efficient and easy to conduct.* | *Hvorslev (1951); Bouwer and Rice (1976);<br>Lehman (1972)* |
| *Hydraulic conductivity from grain size* | *Samples of aquifer material required. Empirical and poor accuracy, especially for silt and day fractions.* | *Hazen (1982): Krumbein and Monk (1942); Masch and Denny (1966)* |
| *Surface geophysics* | *Direct current resistivity, electromagnetic induction, streaming potential. Difficult to interpret and poor accuracy.* | *Zohdy et al. (1974); Sendlein and Yazicigal (1981);<br>Yazicigal and Sandlein (1982)* |
| *Borehole geophysics* | *Natural gamma, gamma-gamma density, single-point resistance, neutron. K= (Ø), Accuracy?* | *Serra (1984); Wheatcraft et al. (1986); Wyllie (1963);<br>Patten and Bennett (1963)* |
| *Large-scale aquifer tests (pumping tests)* | *Provides bulk parameters over relatively large region.* | *Bureau of Reclamation (1985);<br>Stallman (1971);<br>Driscoll (1986);<br>Lehman (1972)* |
| *Geological mapping of sedimentological facies* | *Problems with extrapolation-geological sections above water table and away from site.* | *Willis (1989); Leeder (1973);<br>Matthews (1974);<br>Turnbull et al. (1950)* |
| *Continuous core* | *Split-spoon sampler, samples are disturbed. Grain size analysis, laboratory K.* | *Wolf (1988)* |
| *Borehole flowmeter* | *Most promising. Equipment difficult to obtain.* | *Rehfeldt et al. (1988);<br>Hufschmied (1986);<br>Guthrie (1986);<br>Kerfoot (1964)* |

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well has been damaged (such as from a skin effect from drilling mud), then the test may only determine the hydraulic conductivity of the skin (Faust and Mercer, 1984). However, at hazardous waste sites, slug tests offer many advantages, includlng (1) there are no contaminated water disposal problems when a slug rod is used to displace the water, (2) a pressure transducer can be used to measure the pressure response in wells so that data can be collected even in fairly permeable material, and (3) decontamination is relatively simple, allowing as many as a dozen wells to be slug tested in a day. The slug test method is very inexpensive and provides a considerable amount of data on the flow characteristics of the subsurface.

One method to determine hydraulic conductivity that is listed in Table 4-8 is grain size analysis. Since Hazen (1892), a number of formulas have been proposed that relate some measure of grain size to hydraulic conductivity (for example, Fair and Hatch, 1933; Krumbein and Monk, 1942; Masch and Denny, 1966; and Er-Hui, 1989). These formulas are empirical with hydraulic conductivity proportional to a function of representative grain diameters. However, these formulas are not very accurate, and the accuracy decreases when the samples are predominantly silt or clay. In the early stages of a field investigation they may be very useful. They also may be helpful in estimating hydraulic conductivity in the vadose zone, which can be a difficult task (see Chapter 5).

Twenty years ago, when hydrologists were mainly interested in water supply, one or two pumping tests were often sufficient to design an adequate water supply system. With the advent of contaminant hydrology, more information is required to understand and remediate contamination distributions in the subsurface. In general, the more detailed the investigation, the more heterogeneous the subsurface was observed to be. Recently, much research has focused on an improved capability to better define spatial variability and its impact on chemical transport. Methods used to determine spatial variability as depicted in Table 4-8 were developed from information in Waldrop et al. (1989). Another recent reference on this subject is Taylor et al. (1990), in which six borehole methods are evaluated for determining the vertical distribution of hydraulic conductivity.

Most of this discussion has focused on hydraulic conductivity; however, many of the methods for determining hydraulic conductivity also give an estimate of storage properties (Table 4-6). Hydraulic conductivity is needed to calculate ground-water velocities and chemical travel times. Storage properties are also important for the following reasons: (1) porosity is used in chemical travel-time calculations, (2) porosity is used to estimate mass in place, and (3) the storage properties determine how rapidly the flow system will respond to pumpage. This latter factor is important for pump and-treat systems where pulsed pumping is used because the storage properties can be used to help determine the cycle duration of pumping.

## 4.3 Analysis of Data

Once ground-water data are collected, they must be analyzed and interpreted. Numerous analysis tools are available, including graphical methods, mathematical modeling, and geostatistical techniques. Graphical methods have been used for years. However, with the increased use of microcomputers and software such as geographical information systems (GIS), database management systems (DBMS) and plotting packages, it is now easy to view data via a variety of graphical techniques. The key is to have field data readily transferred or directly recorded on electronic/magnetic format instead of paper.

Mathematical models have been used extensively for ground-water analysis since the mid-1960s. Models test hypothesized conceptualizations of site conditions. They often are enhanced by data acquisition and can test the relative importance of some information. Knowledge of the varying importance of data can help direct the data collection. Thus, where appropriate, using models in unison with active field investigations can aid in characterization efficiency. Once a model has been properly calibrated, it can make limited predictions about future ground-water flow, contaminant transport, or the effectiveness of remedial activities. A large number of models are available and are listed in van der Heijde et al. (1988). NRC (1990) also provides an overview of modeling.

During the past decade, applying geostatistical principles (i.e., structural analysis, kriging, and conditional simulation) to interpret ground-water data has increased. Geostatistical techniques are used to evaluate the spatial variability of ground-water flow parameters, particularly hydraulic head and transmissivity. A code for performing geostatistical assessments is provided in Englund and Sparks (1988). The principles of geostatistics may be appropriate for interpolating point data to estimate the spatial distribution of certain aspects of ground-water quality. Kriging provides a measure of the error of estimation, which can be mapped and used to select locations for additional sampling points. Using this approach, a near-optimal monitoring network can be developed for a predetermined level of reliability.

## 4.4 Remedial Actions

Pumping wells are part of a ground-water flow system. In many cases, ground-water contamination is discovered because a water-supply well has become affected. These wells create cones of depression in the potentiometric surface that cause water to flow toward them. If that water is carrying contaminants, they, too, will flow toward the well. When contamination is discovered, the immediate response is to shut the well down. This is the correct response, but doing so changes the ground-water flow system. The potentiometric surface adjusts to the change in source/sink term, usually within a few days, and chemicals begin to slowly migrate to portions of the aquifer that perhaps were previously uncontaminated. Therefore, an interim remedial action that should be considered at such sites is well-head treatment. Such treatment will bring the well back into production, minimizing the disruption to the water supply. It also will prevent the further spread of contamimnts within the aquifer, which, hopefully, will be consistent with any final remediation that is conducted at the site.

Final remedial actions at hazardous waste sites are discussed in OTA (1984) and EPA (1988). Ground-water containment/cleanup options include physical containment (e.g., construction of low-permeability walls and caps/covers), in situ treatment (e.g., bioreclamation), and hydraulic containment/cleanup (e.g., extraction wells and intercept trenches/drains). To effect complete cleanup, a treatment train combining several methods may be formed.

When a pump-and-treat system is used for cleanup, contaminated ground-water or mobile nonaqueous phase liquids (NAPLs) are captured and pumped to the surface for treatment. This process requires locating the ground-water contaminant plume or NAPLs in three-dimensional space, determining aquifer and chemical properties, designing a capture system, and installing extraction (and in some cases injection) wells. Monitoring wells/piezometers, used to check the effectiveness of the pump-and-treat system, are an integral component of the system. Injection wells are used to enhance the extraction system by flushing contaminants (including some in the vadose zone) toward extraction wells or drains. A pump-and-treat system may be used in combination with other remedial actions, such as low-permeability walls, to limit the amount of clean water flowing to the extraction wells, thus reducing the volume of water to be treated. Pump and-treat technology also can be used as a hydraulic barrier to prevent offsite migration of contaminant plumes from landfills or residual NAPLs. The basic principle of a barrier well system is to lower ground-water levels near a line of wells, thus diverting ground-water flow toward the pumping wells.

Whether the objective of the pump-and-treat system is to reduce concentrations of contaminants to an acceptable level (cleanup) or to protect the subsurface from further contamination (containment), the system components are

- A set of goals or objectives.
- Engineered components such as wells, pumps, and a treatment facility.
- Performance criteria and monitoring.
- Termination criteria.

Each of these components must be a part of the design and evaluation of a pump-and-treat technology.

Pump-and-treat technology is appropriate for many ground-water contamination problems (Ziegler, 1989). For this technology to be effective, the physical-chemical subsurface system Must allow the contaminants to flow to the extraction wells. The subsurface must have sufficient hydraulic conductivity to allow fluid to flow readily and the chemicals must be transportable by the fluid. These requirements make the sure of pump-and-treat systems highly site specific. Cases in which contaminants cannot readily flow to pumping wells include

- Heterogeneous aquifer conditions where low-permeability zones restrict contaminant flow toward extinction wells.
- Presence of chemicals that are sorbed or precipitated on the soil and slowly desorb or dissolve back into the ground water as chemical equilibrium changes in response to the extraction process.
- Presence of immobile NAPMs that may contribute to a miscible contaminant plume by prolonged dissolution (e.g., a separate phase gasoline at residual saturation).

In these cases modifications to pump-and-treat technology, such as pulsed pumping, maybe appropriate. Pump-and-treat technology also may be used in combination (treatment train) with other remedial alternatives, such as vacuum extraction and/or bioremediation. Under complex conditions, no single technology is a panacea for subsurface remediation.

The main limitation of pump-and-treat technology is the long time that may be required to achieve an acceptable level of cleanup. The length of time results from the “tailing” effect often observed with this remedial action. Tailing is the asymptotic decrease of contaminant concentration in water that is removed in the cleanup process (Figure 4-7). Other potential limitations include (1) a design that fails to contain the contaminant plume and allows continued migration of contamimnts either horizontally or vertically or, (2) operational failures that allow the loss of containment. Typical operational problems stem from the failure(s) of surface equipment or electrical and mechanical control systems; and chemical precipitation causing plugging of wells, pumps, and surface plumbing. Limitations are discussed further in Mackay and Cherry (1989).

Physical containment involves low-permeability barriers such as slurry walls. Problems associated with slurry walls may involve a difficulty with achieving design permeability and underflow; such problems lead to loss of containment. Slurry walls also may be used to prevent the movement of clean water into an area being remediated by a pump-and-treat system, thereby reducing the amount of water that needs treatment. Slurry walls also reduce the amount of fresh ground water that is contaminated in a pump-and-treat system. Drains also can be used to create a hydraulic barrier. Factors that must be considered in drain construction include health and safety during construction, maintenance access, disposal of excavated soils, and expected volume of water produced. Generally, drains are used in shallow applications where low-permeability material discourages the use of wells. Using drains for deeper applications usually is not cost effective. Other ground-water remedial actions are discussed in subsequent chapters.

## 4.5 Example-Conservation Chemical Company Site

The Conservation Chemical Company (CCC) site is located over an alluvial aquifer about 1,000 ft from the Missouri River in Kansas City, Missouri (Figure 4-8). Formerly the site was used to treat, store, and dispose of hazardous waste. As may be seen, the Missouri River Valley is underlain by deposits of alluvium with an average thickness of 90 to 95 ft. The alluvial sediments contain interbedded clays, silts, sands, and gravels. Although the composition varies locally, there me some typical characteristics. Grain size increases with depth, which reflects the depositional history of the Missouri River. In many locations, the increasing grain size creates three layers: (1) the uppermost layer is composed of silts and clays; (2) the intermediate layer includes fine to medium sands, and (3) the lowest layer is sands and gravels. The upper layer is approximately 20-ft thick; the intermediate layer 40 to 60-ft thick; and the lower layer 30-ft thick. These alluvial deposits overlie interlayered shales and limestones.

The alluvial aquifer is highly productive and supplies about 500,000 gpd to a well located less than 2,000 ft from the site. The aquifer is generally unconfined; however, short-term responses to pumping tests and river-level variation indicate semiconfined conditions. Various hydraulic tests conducted on and near the site indicate that hydraulic conductivity increases with depth, as can be expected from the grain size distribution. Crabtree and Malone (1984) obtained hydraulic conductivity estimates from 0.51 to 2.35 ft/d for the shallow alluvium. Pumping tests at a nearby production well indicated an overall transmissivity of the aquifer between 4,000 and 16,700 $ft^2$/d and a specific yield between 0.15 to 0.27. Slug tests were attempted but proved unsatisfactory because of large oscillations (see Chapter 6). Analysis of the response of the aquifer to changes in river levels suggests that the ratio of horizontal to vertical hydraulic conductivity is about 100:1 for the site vicinity.

Water levels are from 5 to 15 ft below land surface (Crabtree and Malone, 1984). Water-level data indicate that for the area south of the river, ground-water discharges to the river; however, during periods when the river is high, ground water flows from the river into the aquifer. This variability is indicated in Figure 4-9 where the vector direction indicates the flow direction and its length indicates the gradient magnitude. These data were collected over a l-year period. Cluster wells indicate a very small vertical hydraulic gradient.

The site was contaminated with metals and organic compounds. The spatial distribution of concentrations for specific contaminants did not define a meaningful “plume.” However, concentration of all contaminants tends to decrease with distance from the site. Also, organic contaminants are generally located directly under, northeast, and southeast of

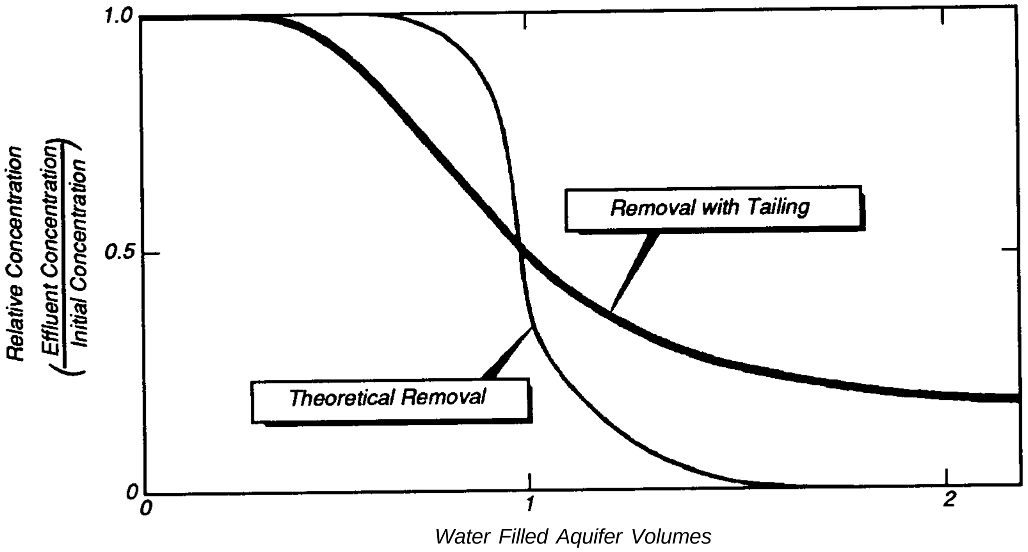
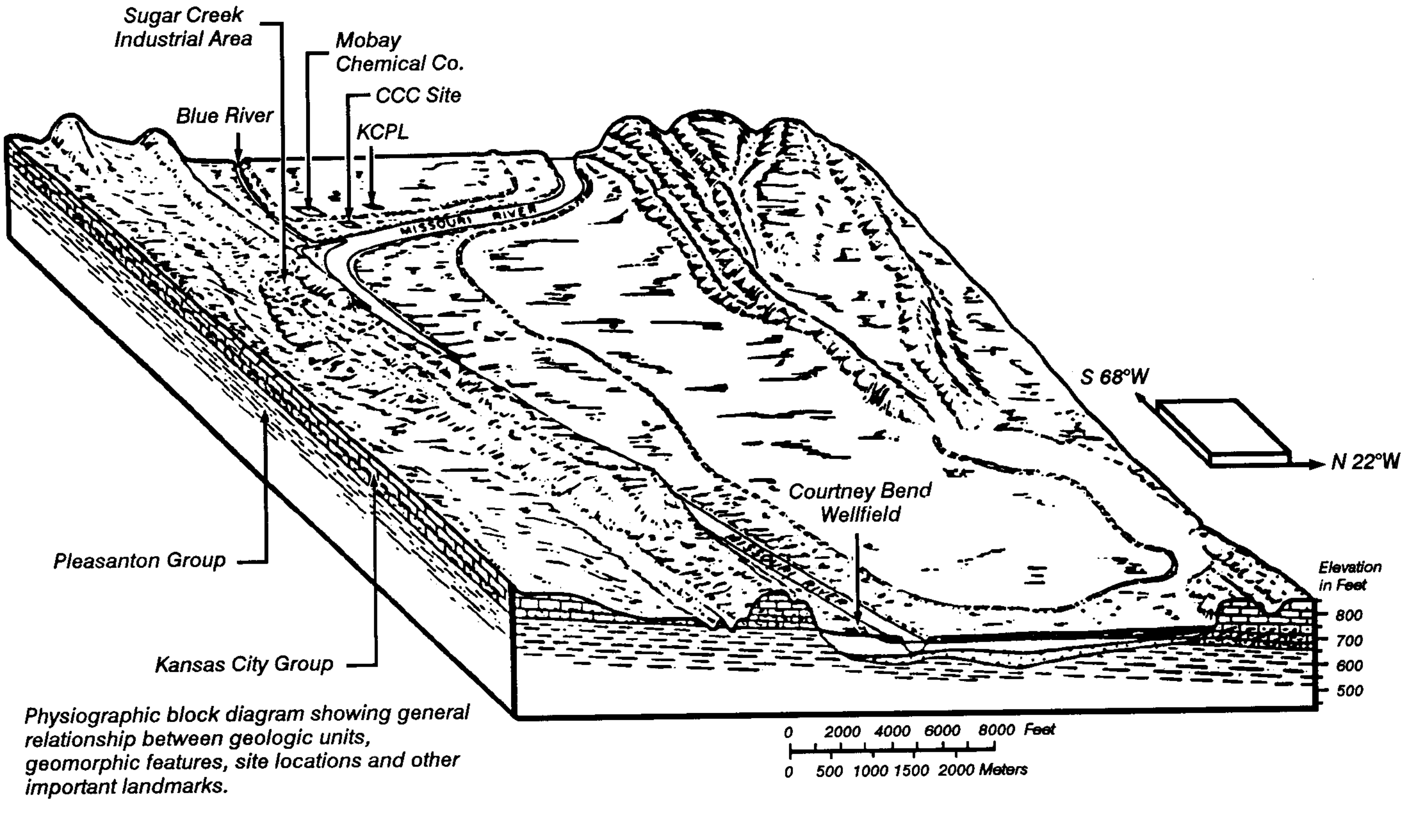


Figure 4-7. Effects of tailing on pumping time (from Keeley et al., 1989).



*Physiographic block diagram showing general relationship between geologic units, geomorphic features, site locations and other important landmarks.*

Figure 4-8. Bock diagram showing the location of the CCC site and generalized geology.

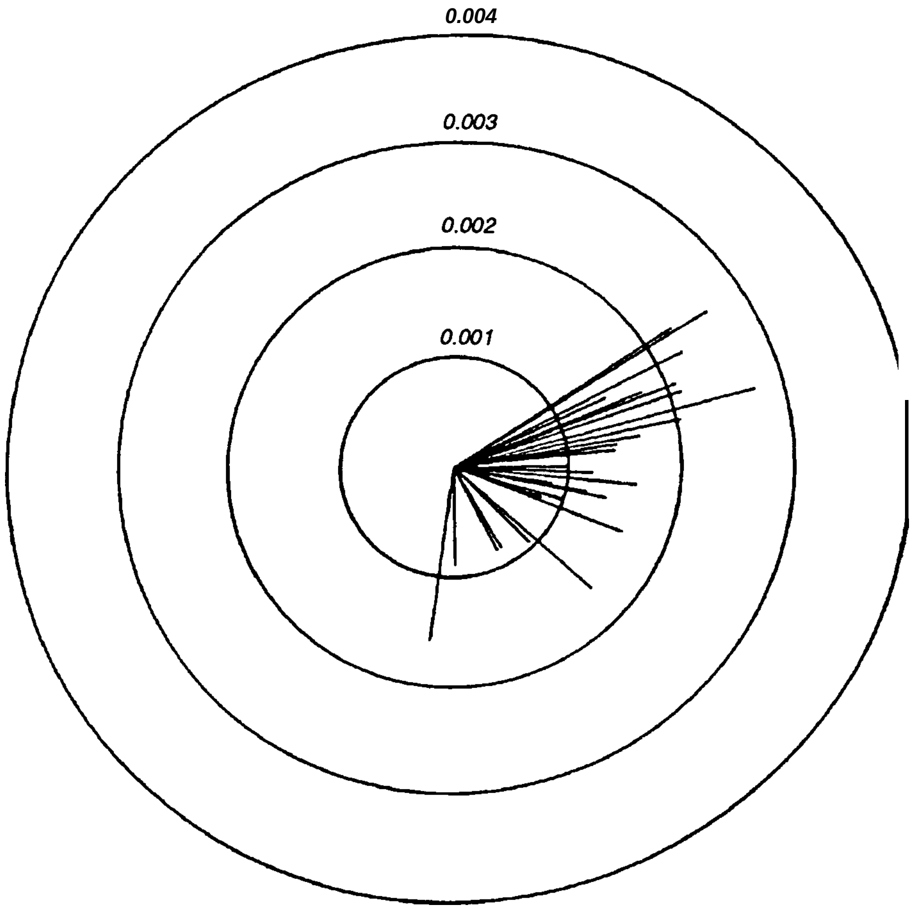


Figure 4-9. Ground-water flow directions and gradients observed in various piezometers (from Larson, 1986).

the site; concentrations of metals are found north and west of the site. For the nearby offsite wells, the highest concentration of organics generally are found in the deeper wells.

The design of a remedial pumping system at the CCC site was complicated by two factors-the impact of the Missouri River and the high productivity of the aquifer below the site. Changes in river stage cause significant variations in ground-water flow rates and directions. Consequently, the operating system must be flexible enough to track these changes and to modify pumping as necessary to meet design objectives. Pumping rates required to achieve design goals are relatively high for all the alternatives considered because of the high productivity of the aquifer. Even with high pumping rates, the area of influence or control is difficult to verify because the changes in water-level elevation, normally used to determine flow direction, are small and difficult to measure.

To evaluate optimal pumping and monitoring strategies, an analytical approach was embedded in a linear program. This approach accounts for variations in flow directions and provides an analysis of pumping requirements under alternative performance criteria. Hydraulic gradients are of particular interest because performance monitoring of site pumping is based on the measurement of water-level elevation differences between piezometer pairs. The amount of water pumped has been minimized while performance requirements continue to be met. For a site pumping remedy, the quantifiable performance requirement is a minimum inward hydraulic gradient at paired piezometers.

Numerous simulations were performed using gradient data provided in Figure 4-9. These simulations were performed on both regional and local scales. The regional analysis was performed to study the influence of offsite pumping centers. Based on these simulations, a recovery system that met all the requirements is currently being implemented.

## 4.6 References

Barcelona, MJ., J.P. Gibb, and R.A. Miller. 1983. A Guide to the Selection of Materials for Monitoring Well Construction and Ground-Water Sampling. ISWS Contract Report 327. Illinois State Water Survey, Champaign, IL.

Bear, J. 1979. Hydraulics of Ground-water. McGraw-Hill, New York.

Bentall, R. (Compiler). 1963. Shortcuts and Special Problems in Aquifer Tests. U.S. Geological Survey Water Supply Paper 1545-C.

Bouwer, H. 1978. Ground-Water Hydrology. McGraw-Hill, New York.

Bouwer, H. 1989. The Bouwer and Rice Slug Test—An Update. Ground Water 27(3):304309.

Bouwer, H. and P.C. Rice. 1976. A Slug Pest for Determining Hydraulic Conductivity of Unconfined Aquifers with Completely or Partially Penetrating Wells. Water Resources Research 12(3):423-428.

Bredehoeft, J.D. and S.S. Papadopulos. 1980. A Method for Determining the Hydraulic Properties of Tight Formations. Water Resources Research 16(1):233-238.

Bureau of Reclamation. 1985. Ground-Water Manual-A Water Resources Technical Publication, 2nd ed. U.S. Department of the Interior, Bureau of Reclamation, Denver, CO.

Campbell, G.S. and G.W. Gee. 1986. Water Potential: Miscellaneous Methods. In: Methods of Soil Analysis, Part 1, 2nd ed., A. Klute (ed.), Agronomy Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 619-633.

Cassel, D.K. and A. Klute. 1986. Water Potential: Tensiometry. In: Methods of Soil Analysis, Part 1, 2nd ed., A. Klute (ed.), Agronomy Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 563-596.

Cooper, H. H., Jr., J.D. Bredehoeft, and I.S. Papadopulos. 1967. Response of a Finite-Diameter Well to an Instantaneous Charge of Water. Water Resources Research 3(1):263-269

Crabtree, J.E. and P.G. Malone. 1984. Hydrogeologic Characterization Conservation Chemical Company Site, Kansas City, Missouri. U.S. Army Corps of Engineers Waterways Experiment Station, Vicksburg, MS.

Davis, S .N. and R.J. DeWiest. 1966. Hydrogeology. John Wiley & Sons, New York, 463 pp.

DeWiest, R.J.M. 1969. Flow through Porous Media. Academic Press, New York.

Domenico, P.A. 1972. Concepts and Models in Ground-water Hydrology. McGraw-Hill, New York.

Driscoll, F.G. 1986. Ground-water and Wells, 2nd ed. Johnson Division, St. Paul, MN, 1089 pp.

Englund, E. and A. Sparks. 1988. GEO-EAS (Geostatistical Environmental Assessment Software) User's Guide. EPA/600/4-88/033a (Guide: NTIS PB89-151252, Software: NTIS PB89-151245).

Er-Hui, Z. 1989. Experimental Research on Permeability of Granular Media. Ground-Water, 27(6):848-854.

Fair, G.M. and L.P. Hatch. 1933. Fundamental Factors Governing the Streamline Flow of Water through Sand. J. Am. Water Works Ass. 25:1551-1565.

Faust, C.R. and J.W. Mercer. 1984. Evaluation of Slug Tests in Wells Containing a Finite-Thickness Skin. Water Resources Research 20(4):504-506.

Ferris, J.G., D.B. Knowles, R.H. Brown, and R.W. Stallman. 1962. Theory of Aquifer Tests. U.S. Geological Survey Water Supply Paper 1536-E, 174 pp.

Fetter, Jr., C.W. 1981. Determination of the Direction of Ground-Water Flow. Ground-Water Monitoring Review 1 (3):28-31.

Freeze, R.A. and J.A. Cherry. 1979. Ground-water. Prentice-Hall, Englewood Cliffs, NJ.

Garber, M.S. and F.C. Koopman. 1968. Methods of Measuring Water Levels in Deep Wells. U.S. Geological Survey Techniques of Water-Resources Investigations TWI 8-A1.

GeoTrans, 1989. Ground-water Monitoring Manual for the Electric Utility Industry. Edison Electric Institute, Washington, DC.

Goode, D.J. and R.J. Wilder. 1987. Ground-water Contamination Near a Uranium Tailing Disposal Site in Colorado. Ground-Water 25(5):545-554

Guthrie, M. 1986. Use of a Geoflowmeter for the Determination of Ground-Water Flow Direction. Ground-Water Monitoring Review 6(1):81.

Hazen, A. 1892. Experiments upon the Purification of Sewage and Water at the Lawrence Experiment Station. In: 23rd Annual Report, Massachusetts State Board of Health.

Hillel, D. 1980. Fundamentals of Soil Physics. Academic Press, New York.

Hufschmied, P. 1986. Estimation of Three-Dimensional Statistically Anisotropic Hydraulic Conductivity Field by Means of Single Well Pumping Tests Combined with Flowmeter Measurements. Hydrogeologic 1986(2):163-174.

Hvorslev, M.J. 1951. Time Lag and Soil Permeability in Ground-water Observations. U.S. Army Corps of Engineers Waterways Experiment Station, Bull. 36, Vicksburg, MS.

Keeley, J.W., D.C. Bouchard, M.R. Scalf, and C.G. Enfield. 1989. Practical Limits to Pump and Treat Technology for Aquifer Remediation. Submitted to Ground-Water Monitoring Review.

Kerfoot, W.B. 1984. Darcian Flow Characteristics Upgradient of a Kettle Pond Determined by Direct Ground-Water Flow Measurement. Ground-Water Monitoring Review 4(4):188-192.

Klute, A. and C. Dirksen. 1986. Hydraulic Conductivity and Diffusivity: Laboratory Methods. In: Methods of Soil Analysis, Part 1, 2nd ed., A. Klute (ed.), Agronomy Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 687-734.

Krumbein, W.C. and G.D. Monk. 1942. Permeability as a Function of the Size Parameters of Unconsolidated Sand. AIMME Petroleum Division Technical Pub. No. 1492 (published in Petroleum Technology Vol. 5, No. 4).

Kruseman, G.P. and N.A. De Ridder. 1976. Analysis and Evaluation of Pumping Test Data. International Institute for Land Reclamation and Improvement, Wageningen, The Netherlands, 200 pp.

Larson, D. 1981. Materials Selection for Ground-Water Monitoring. Paper Presented at the National Water Well Association Short Course entitled Practical Considerations in the Design and Installation of Monitoring Wells, Columbus, OH, December 16-17.

Larson, S.P. 1986. Notes from November Meeting between Settling Defendants and EPA, Washington, DC.

Leeder, M.R 1973. Fluviatile Fining-Upward Cycles and the Magnitude of Paleochannels. Geology Magazine 110(3):265-276.

Lohman, S.W. 1972. Ground-water Hydraulics. U.S. Geological Survey Professional Paper 708.

Mackay, D.M. and J.A. Cherry. 1989. Ground-Water Contamination: Pump-and-Treat Remediation. Environ. Sci. Technol. 23(6):630-636.

Masch, F. and K. Denny. 1966. Grain Size Distribution and Its Effect on the Permeability of Unconsolidated Sands. Water Resources Research 2(4):665-577.

Matthews, R.K. 1974. Dynamic Stratigraphy. Prentice Hall, Englewood Cliffs, NJ, Chapter 10, pp. 137-172.

National Research Council (NRQ. 1990. Ground-Water Models Scientific and Regulatory Applications. National Academy Press, Washington, DC, 303 pp.

Neuman, S.P. 1972. Theory of Flow in Unconfined Aquifers Considering Delayed Response of the Water Table. Water Resources Research 8(4): 1031-1045.

Neuman, S.P. 1974. Effect of Partial Penetration on Flow in Unconfined Aquifers Considering Delayed Gravity Response. Water Resources Research 10(2):303-312.

Nwankwor, G. I., J.A. Cherry, and R.W. Gillman. 1984. A Comparative Study of Specific Yield Determinations for a Shallow Sand Aquifer. Ground-Water 22(6):764-772.

Office of Technology Assessment (OTA). 1984. Protecting the Nation’s Ground-water from Contamination. OTA-O-233. U.S. Office of Technology Assessment, Washington, DC.

Patten, Jr., E.P. and G.D. Bennett. 1963. Application of Electrical and Radioactive Well Logging to Ground-Water Hydrology. U.S. Geological Survey Water Supply Paper 1544-D, 60 pp.

Peck, A.J. and R.M. Rabbidge. 1966. Soil Water Potential: Direct Measurements by a New Technique. Science 151:1385-1386.

Peck, AJ. and R.M. Rabbidge. 1969. Design and Performance of an Osmotic Tensiometer for Measuring Capillary Potential. Soil Sci. Soc. Am. Proc. 33:196-202.

Phene, CJ. and D.W. Beale. 1976. High-Frequency Irrigation for Water-Nutrient Management in Humid Regions. Soil Sci. Soc. Am. J. 40:430-436.

Rawlins, S.L. and G.S. Campbell. 1986. Water Potential: Thermocouple Psychrometry. In: Methods of Soil Amlysis, Part 1, 2nd ed., A. Klute (ed.), Agronomy Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 597-618.

Reed, J.E. 1980. Type Curves for Selected Problems of Flow to Wells in Confined Aquifers. U.S. Geological Survey Techniques of Water-Resources Investigations TWI 3-B3.

Rehfeldt, K.R., P. Hufschmied, L.W. Gelhar, and M.E. Schaefer. 1988. The Borehole Flowmeter Technique for Measuring Hydraulic Conductivity Variability. Draft topical report prepared by MIT for Electric Power Research Institute, Research Project 2485-5.

Rehm, B. W., B.J. Christel, T.R. Stolzenburg, D.G. Nichols, B. Lowery, and B.J. Andraki. 1987. Field Evaluation of Instruments for the Measurement of Unsaturated Hydraulic Properties of Fly Ash. EPRI EA-5011. Electric Power Research Institute, Palo Alto, CA.

Scalf, M.R., J.F. McNabb, W.J. Dunlap, R.L. Cosby, and J. Fryberger. 1981. Manual of Ground-Water Quality Sampling Procedures. EPA/600/2-81/160, (NTIS PB82-103045). Also published in NWWA/EPA Series, National Water Well Association, Dublin OH.

Sendlein, L.V.A. and H. Yazicigal. 1981. Surface Geophysical Techniques in Ground-Water Monitoring, Part 1. Ground-Water Monitoring Review 1(4):42-46.

Serra, O. 1984. Fundamentals of Well-Log Interpretation, 1: The Acquisition of Logging Data. In: Developments in Petroleum Science, Vol. 15A. Elsevier, New York, 423 PP.

Sisk, S.W. 1981. NEIC Manual for Ground-water/Subsurface Investigations at Hazardous Waste Sites. EPA/330/9-81-002 (NTIS PB82-103755).

Stallman, R.W. 1971. Aquifer-Test Design, Observation, and Data Analysis. U.S. Geological Survey Techniques of Water-Resources Investigations TWI 8-B1.

Stannard, D.I. 1986. Theory, Construction and Operation of Simple Tensiometers. Ground-Water Monitoring Review 6(3):70-78.

Stephens, D.B. and R. Knowlton, Jr. 1986. Soil Water Movement and Recharge through Sand at a Semiarid Site in New Mexico. Water Resources Research 22(6):881-889.

Taylor, K., S. Wheatcraft, J. Hess, J. Hayworth, and F. Molz. 1990. Evaluation of Methods for Determining the Vertical Distribution of Hydraulic Conductivity. Ground-Water 28(1):88-98.

Thompson, C.M., et al. 1989. Techniques to Develop Data for Hydrogeochemical Models. EPRI EN-6637. Electric Power Research Institute, Palo Alto, CA.

Thomhill, J.T. 1989. Accuracy of Depth to Water Measurements. EPA Superfund Ground-Water Issue Paper. EPA/540/4-89/002.

Todd, D.K. 1980. Ground-water Hydrology. John Wiley & Sons, New York.

Tumbull, W.J., E.S. Krinitsky, and L.J. Johnson. 1950. Sedimentary Geology of the Alluvial Valley of the Mississippi River and its Bearing on Foundation Problems. In: Applied Sedimentation, P.D. Trask, (ed.), John Wiley & Sons, New York, pp. 210-226.

U.S. Environmental Protection Agency (EPA). 1986. RCRA Ground-Water Monitoring Technical Enforcement Guidance Document. EPA OSWER-9950. 1. Also published in NWWA/EPA Series, National Water Well Association, Dublin, OH.

U.S. Environmental Protection Agency (EPA). 1987. Handbook Ground-water. EPA/625/6-87/016.

U.S. Environmental Protection Agency (EPA). 1988. Guidance on Remedial Actions for Contaminated Ground-Water at Superfund Sites. Advance Copy, OSWER Directive No. 9283.1-2.

U.S. Geological Survey (USGS). 1977. National Handbook of Recommended Methods for Water Data Acquisition (Chapter 2-Ground-Water, updated January 1980). USGS Office of Water Data Coordination, Reston, VA.

van der Heijde, P.K M., A.I. E1-Kadi, and S.A. Williams. 1988. Ground-water Modeling An Overview and Status Report. EPA/600/2-89/028.

Waldrop, W.R., K.R. Rehfeldt, L.W. Gelhar, J.B. Southard, and A.M. Dasinger. 1989. Estimates of Macrodispersivity Based on Analyses of Hydraulic Conductivity Variability at the MADE Site. EPRI EN-6405. Electric Power Research Institute, Palo Alto, CA.

Walton, W.C. 1962. Selected Analytical Methods for Well and Aquifer Evaluation. ISWS Bulletin 49. Illinois State Water Survey, Champaign, IL.

Walton, W.C. 1970. Ground-water Resource Evaluation. McGraw-Hill, New York.

Walton, W.C. 1987. Ground-water Pumping Tests Design and Analysis. Lewis Publishers, Chelsea, MI, 201 pp.

Wheatcraft, S.W., K.C. Taylor, J.W. Hess, and T.M. Morris. 1986. Borehole Sensing Methods for Ground-Water Investigations at Hazardous Waste Sites. EPA/6OO/2-86/l1 (NTIS PB87-132783).

Willis, B J. 1989. Paleochannel Reconstruction from Pointbar Deposits: A Three-Dimensional Perspective. Sedimentology 36:757-766.

Wolf, S. 1988. Spatial Variability of Hydraulic Conductivity in a Sand and Gravel Aquifer. Master of Science Thesis, Department of Civil Engineering, MIT, Cambridge, MA.

Wyllie, M.R.J. 1963. The Fundamentals of Well Log Interpretation. Academic Press, New York, 238 pp.

Yazicigal, H. and L.V.A. Sendlein. 1982. Surface Geophysical Techniques in Ground-Water Monitoring, Part II. Ground-Water Monitoring Review 2(1):56-62.

Ziegler, G.J. 1989. Remediation through Ground-Water Recovery and Treatment. Pollution Engineering 22(7):75-79.

Zohdy, A.A.R., G.P. Eaton, and D.R. Mabey. 1974. Application of Surface Geophysics to Ground-Water Investigations. U.S. Geological Survey Techniques of Water-Resources Investigations TWI 2-DI.

# Chapter 5
# Characterization of the Vadose Zone

James W. Mercer and Charles P. Spalding

The vadose zone is the subsurface extending from land surface to the water table. It also is called the zone of aeration, variably saturated zone, or the unsaturated zone. Use of this latter term is discouraged, however, because since the vadose zone contains moisture up to 100 percent saturation, the term unsaturated could be misleading. Depth of the vadose zone can vary greatly depending on the region of the site. For example, in the humid eastern portion of the United States, the vadose zone can be only a few feet thick, disappearing during times of the year when the water table is high. In the arid west, the vadose zone can be several hundred feet thick.

Because the vadose zone overlies the saturated zone, chemical releases at or near the land surface must pass through the vadose zone before reaching the water table. Therefore, at many contaminated sites, often both the vadose zone and the saturated zone need to be characterized and remediated (i.e., treatment trains must be applied). As discussed later in this chapter, the vadose zone can have more complex flow conditions than the saturated zone. These conditions can be difficult to characterize. On the other hand, because the vadose zone is nearer to the land surface, for remedial actions, the flow system may not need to be completely characterized under certain site conditions and contaminants.

The main difference between the saturated and vadose zones is the presence of air/gas in the pore spaces of the vadose zone. The amount of water and air varies both spatially and temporally, which contributes to the complex nature of the vadose-zone flow system. However, the presence of soil gas also provides a valuable screening tool for locating volatile organic compounds (VOCs) In addition, there is the potential for significant biological activity. The advantages and disadvantages of characterizing and remediating the vadose zone are discussed in the following sections: (1) Review of Concepts, (2) Field Techniques, (3) Analysis of Data, and (4) Remedial Actions. An example of the application of techniques as discussed in the chapter follows these sections.

## 5.1 Review of Concepts

The vadose zone can be divided into (1) the belt of soil water, (2) the intermediate belt, and (3) the capillary fringe. The belt of soil water is the uppermost zone extending from the land surface to a depth where soil moisture changes are minimal. It contains the root zone of plants, and is the site of many active processes. Precipitation, for example, falls to the land surface and runs off via overland flow or infiltrates into the ground. Working against the infiltrating water are evaporation and transpiration. Evaporation is the process that converts the water at or near land surface to vapor. Transpiration is the process by which plant roots absorb water and release water vapor back to the atmosphere through their leaves and stems. Hydrologists combine these two processes into the term evapotranspiration. Much of the infiltrating water is consumed by evapotranspiration. The water that is not consumed and eventually makes it to the water table is recharge. It is important to understand and characterize these processes for hazardous waste sites (1) to help understand recharge events and how contaminants may move through the vadose zone, and (2) to help design caps used to limit infiltration and recharge to a contaminant source area.

The capillary fringe (at the base of the vadose zone) extends upward from the water table until there is a decrease in soil moisture. Portions of this zone can be at 100 percent saturation. This zone also will change as recharge/discharge causes the water table to fluctuate. The capillary fringe is formed due to a capillary rise caused by the surface tension between air and water. Hydraulic head is made up of an elevation head and a pressure head. At the water table, the pressure head is zero. It increases below the water table and decreases above the water table. That is, pressure head is negative in the vadose zone, a phenomenon sometimes referred to as soil tension or suction. The latter term refers to the effect of water being sucked into a dry soil. The negative pressure head will pull water upward from the saturated zone, forming the capillary fringe. The height of the capillary fringe depends on the pore size of the soil (e.g., the capillary rise is greater for smaller pores). Unfortunately, pore size is difficult to determine and is not directly related to grain size.

Hydraulic head in the vadose zone is defined the same way as it is in the saturated zone-the sum of pressure head and elevation head. In the vadose zone, however, pressure head is used for the saturation-dependent relationships. Capillary pressure, defined as the difference between the nonwetting fluid pressure and the wetting fluid pressure, also is used. For an air-water system, the air pressure is assumed to be negligible, and capillary pressure is essentially equal to the negative of the pressure head.

The moisture present in the vadose zone is quantified by a term called the volumetric water content or degree of

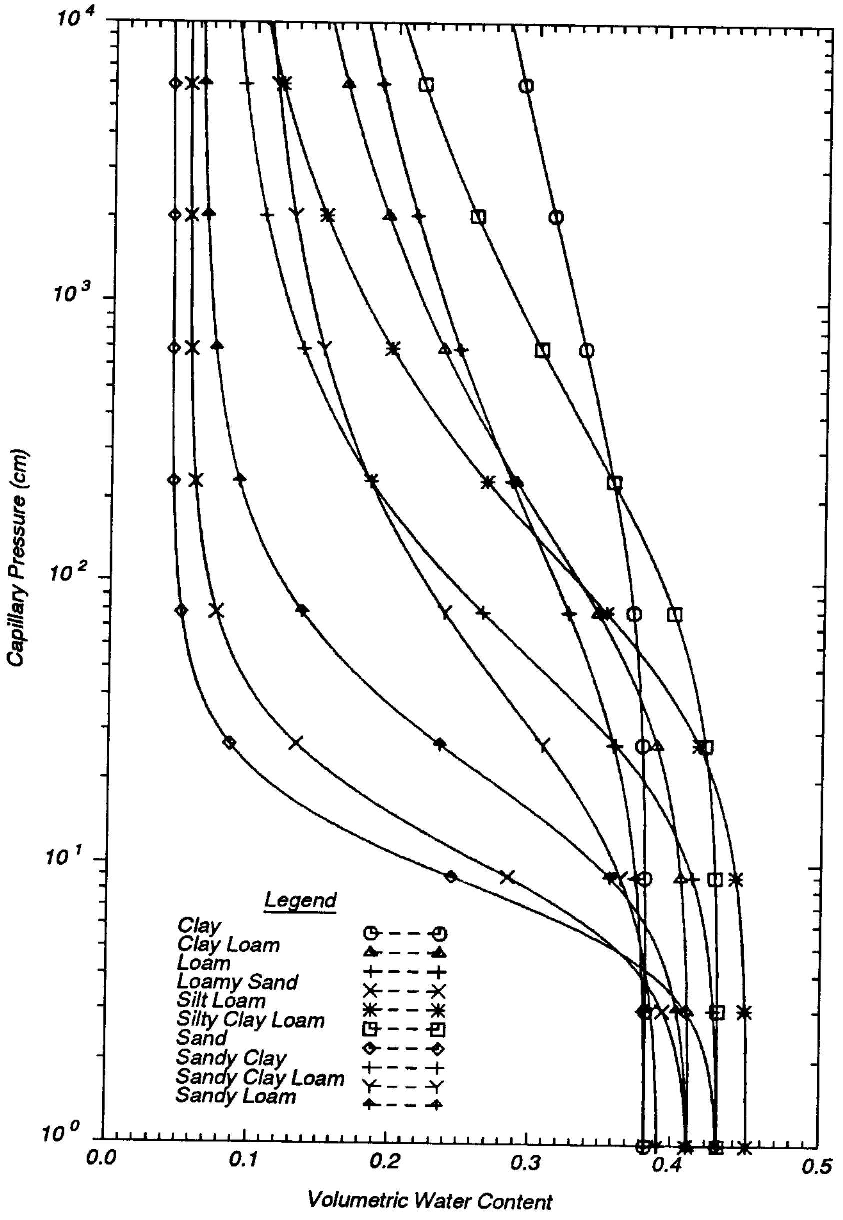


**Figure 5-1.** Moisture characteristic or specific retention curves for various soil types.

saturation. Saturation varies from zero to one and refers to the amount of volume of pore space filled with water. Volumetric water content varies between zero and the porosity value. For complete saturation, the volumetric water content is equal to porosity, and the degree of saturation is 100 percent or 1.0. If the pore space is only half filled with water, then the saturation is 50 percent or 0.5 and volumetric water content is half the porosity.

In the vadose zone, a relationship called the moisture characteristic curve exists between volumetric water content and pressure head (Figure 5-1). As the figure shows, this curve is nonlinear and generally is not a single-valued-function relationship. That is, a different curve is used to describe the pressure-head-volumetric-water-content relationship depending on whether the soil is filling or draining. Depending on the wetting history, an entire set of curves is needed. This phenomenon is called hysteresis, and is due in part to entrapped air in the soil after wetting. This set of curves is necessary to fully describe the flow conditions in the vadose zone.

Flow in the vadose zone is complicated further by the presence of air. Because both air and water are in the pore space, each resists the flow of the other. This results in a decrease in fluid mobility, characterized by the term relative permeability. Relative permeability varies between zero and one. It is a nonlinear function of saturation that also can exhibit hysteresis. Thus, to fully characterize flow in the vadose zone, the relative permeability function must be known, in addition to the saturated hydraulic conductivity.

## 5.2 Field Techniques

Based on the review of concepts, near-surface processes, as well as other parameters that are functions of moisture content, need to be characterized. For hazardous waste remediation, vadose zone processes must be understood to design caps and covers to minimize infiltration. Methods to measure or estimate these processes/parameters are discussed in this section. Reviews of vadose zone monitoring are discussed in Wilson (1980, 1981, 1982, 1983). Section 9.2 further discusses sampling of subsurface solids and vadose zone water, and Table 9-5-identifies additional references focusing on characterization of the vadose zone.

### 5.2.1 Precipitation and Infiltration

Precipitation is defined as the total amount of water that reaches land surface, and is measured with gauges as a depth of water (see Table 5-l). Because weather stations are not generally set up at hazardous waste sites, precipitation information is obtained from nearby airports. Another source of precipitation data is the National Climatic Data Center in Asheville, North Carolina. Wind velocity and air temperature also are studied for remediation.

The maximum rate at which water can enter a soil is the infiltration capacity or potential infiltration rate. The maximum rate occurs when the water supply at the surface is unlimited. During precipitation events, all the water will infiltrate if the rainfall intensity is less than the infiltration capacity. If this capacity is exceeded, the excess rain cannot infiltrate and will produce surface runoff. Although this discussion concerns water infiltration, it also applies to a chemical spill infiltrating the subsurface. Infiltration capacity varies with time; it is highest at the begiming of a precipitation event and decreases as the soil becomes saturated. Table 5-2 lists methods to measure or estimate infiltration rates. These methods are discussed in Thompson et al. (1989) and in the references provided in the table.

Spatial variability is present in the vadose zone as well as the saturated zone. Spatial variability produces a fingering of flow as it moves downward from the surface. This means that the wetting front does not move as a sharp front, but instead moves downward with an irregular shape where some zones (fingers) move more rapidly than other zones. Laboratory studies by Stephens and Heermann (1988) suggest that this variability increases with decreasing soil moisture content.

### 5.2.2 Evaporation and Evapotranspiration

Evaporation is the loss of water from the soil into the atmosphere. In the absence of vegetative cover, the bare soil surface is subject to radiation and wind effects, and soil water evaporates directly from the soil surface. An associated proccss is evaporation of water from plants, or transpiration. For evaporation to occur (1) a continual supply of heat must meet the latent heat requirements, (2) a vapor pressure gradient must exist between the soil surface and the atmosphere, and (3) there must be a continual supply of water from and/or through the soil layers. The first two conditions determine the evaporative demand (Table 5-3) and are controlled by micrometeorological factors such as air temperature, humidity,

*Table 5-1.* ***Summary of Methods to Measure Precipitation***

| *Method* | *Application* | *Reference* |
|---|---|---|
| *Sacramento gage* | *Accumulated precipitation. Manual recording.* | *Finkelstein et al. (1989);*<br>*National Weather Service (972)* |
| *Weighing gage* | *Continuous measurement on precipitation. Mechanical recording.* | *Finkelstein et al. (1989)* |
| *Tipping-bucket gage* | *Continuous measurement of precipitation. Electronic recording. Recommended.* | *Finkelstein et al. (1989)* |

*From Thompson et al., 1989*

*Table 5-2* ***Summary of Methods to Measure or Estimate infiltration Rates***

| *Method* | *Application* | *Reference* |
|---|---|---|
| *Infiltrometers* | *Measures the maximum infiltration rate of surface soils. Useful for determining relative infiltration rates of different soil types: however, infiltration rates determined by this method tend to overestimate actual rates.* | *Dunne and Leopold (1978);<br>Bouwer (1986)* |
| *Sprinkler infiltrometer* | *Measures the potential range of infiltration rates under various precipitation conditions. Tends to be expensive and non-portable. Sprinkler infiltrometers have typically been used for long duration research studies.* | *Dunne and Leopold (1978);<br>Peterson and Bubenzer (1986)* |
| *Average infiltration method* | *Method for estimating the average infiltration rate for small watersheds. Provides an approximate estimate of infiltration for specific precipitation events and antecedent moisture conditions.* | *Dunne and Leopold (1978)* |
| *Empirical relations* | *Methods to approximate the infiltration for large watersheds. These methods can be useful when combined with limited infiltrometer measurements to obtain a gross approximation of infiltration.* | *Musgrave and Holtan (1964)* |
| *infiltration equations* | *Analyticai equations for calculating infiltration rates. Parameters required in the equations can be readily measured in the field or obtained from the literature. Probably the least expensive and most efficient method for estimating infiltration.* | *Bouwer (1986);<br>Green and Ampt (1911);<br>Philip (1957)* |

*From Thompson et al., 1989*

***Table 5-3. Summary of Methods to Measure Evaporation***

| *Method* | *Application* | *Reference* |
|---|---|---|
| *Class-A pan* | *Evaporation from surface of free liquid.* | *Veihmeyer (1964);<br>National Weather Service (1972)* |
| *Weighing lysimeter* | *Direct measure of bare soil evaporation.* | *USGS (1977) (updated 1982)* |
| *Remote sensing* | *Currently in development. Useful for large areas.* | *USGS (1977) (updated 1982)* |

*Modified from Thompson et al., 1989*

wind velocity, radiation, and crop cover. The third condition, which determines the rate of water supply to the evaporative site (soil surface), is controlled by soil-water content, pressure potential, and relative permeability of the soil. Thus, the actual evaporation rate is determined by evaporative demand and soil hydraulic properties.

Transpiration occurs in response to a vapor pressure deficit between leaves and the atmosphere. To meet this demand, plants must extinct water from the root zone. Combined losses due to evaporation and transpiration are commonly referred to as evapotranspimtion. When the soil surface is covered completely by a crop canopy, evaporation losses are negligible, and transpiration is the principal process by which water is lost from the root zone. The same environmental factors that control evaporation also control the potential transpiration. Table 5-4 summarizes methods to measure or estimate evapotranspiration.

### 5.2.3 Moisture Content and Moisture Characteristic Curves

In the vadose zone, the void space is partly filled by air and partly by water. The moisture content or volumetric water content represents the quantity of water present at a certain time at a point in the porous media. The maximum value of volumetric water content occurs when all voids are filled; the minimum value occurs when all voids are empty (filled with air). Thus, moisture content varies between O to the value of the soil porosity.

Changes in moisture content are important to detect. For example, under a cap/cover, changes in moisture content could indicate leaks in the cover. By determining moisture content with depth, perched water zones can be located for use in water quality sampling. Several methods are used to measure moisture content (see Table 5-5), but the recommended techniques are gravimetric and neutron scattering. Gravimetric moisture content measurements are made by weighing soils before and after drying. The neutron scatter method lowers the moisture meter, which contains a source of fast neutrons and a slow neutron detector, into the soil through an access tube (Figure 5-2). Neutrons are emitted by the source (e.g., radium or americium-beryllium) at a very high speed. When these neutrons collide with a small atom, such as hydrogen contained in soil water, their direction of movement is changed and they lose part of their energy. These “slowed” neutrons are measured by a detector tube and a scalar. This

**Table 5-4. Summary of Methods to Measure or Estimate Evapotranspiration**

| Method | Application | Reference |
|---|---|---|
| WATER BALANCE METHODS | | |
| Pan lysimeter | Direct field method; accurate; moderate to low cost. | Veihmeyer (1964);<br>Sharma (1985) |
| Soil moisture sampling | Direct field method; accurate; moderate to low cost. | Veihmeyer (1984) |
| Potential evapotranspirometers | Direct field method of PET Moderately accurate and low cost. | Thornthwaite and Mather (1955) |
| Cl tracer | Indirect combined field and laboratory method; moderate to high cost. | Sharma (1985) |
| Water-budget analysis | Indirect field estimate of ET; manageable to difficult; moderate to low cost. | Davis and DeWiest (1966) |
| Ground-water fluctuation | Indirect field method; moderate to low cost. | Davis and DeWiest (1966) |
| MICROMETEOROLOGICAL METHODS | | |
| Profile method | Indirect field method. | Sharma (1985) |
| Energy budget/ Bowen ratio | Indirect field method; difficult; costly; requires data which is often unobtainable; research oriented. | Veihmeyer (1964);<br>Shamra (1985) |
| Eddy covariance method | Indirect field method; costly measures water-vapor flux directly; highly accurate; well accepted; research oriented. | Veihmeyer (1964); Sharma (1985) |
| Penman equation | Indirect field method; ditficult; costly; very accurate; eliminates need for surface temperature measurements; research oriented. | Veihmeyer (1964); Sharma (1985) |
| Thornthwaite equation | Empirical equation; most accepted for calculating PET: uses average monthly sunlight: moderate to low cost. | Veihmeyer (1964); Sharma (1985) |
| Blaney-Criddle equation | Empirical equation; widely used; moderate to high accuracy; low cost; adjusts for certain crops and vegetation. | Stephens and Stewart (1964) |

From Thompson et al., 1989

**Table 5-5. Summary of Methods for Measuring Moisture Content**

| Method | Application | Reference |
|---|---|---|
| Gravimetric | Laboratory measurements of soils which should be dried at 110°C. The standard method for moisture content determination. Recommended. | Gardner (1986):<br>Radian Corporation (1988) |
| Neutron scattering | In situ measurements via installed access tubes. Widely used. Requires calibration curves. Recommened. | van Bavel (1963) |
| Gamma ray attenuation | In situ measurements via installed access tubes. Difficult to use. Not recommended for routine use. | Gardner (1986) |
| Electromagnetic | In situ measurements from implanted sensors. Not widely used. Not recommended for routine use. | Schmugge et al. (1980) |
| Tensiometry | In situ measurements inferred from moisture-matric potential relationship. Prone to error resulting from uncertainty of moisture-matric potential relationship. Not recommended. | Gardner (1986) |

From Thompson et al., 1989

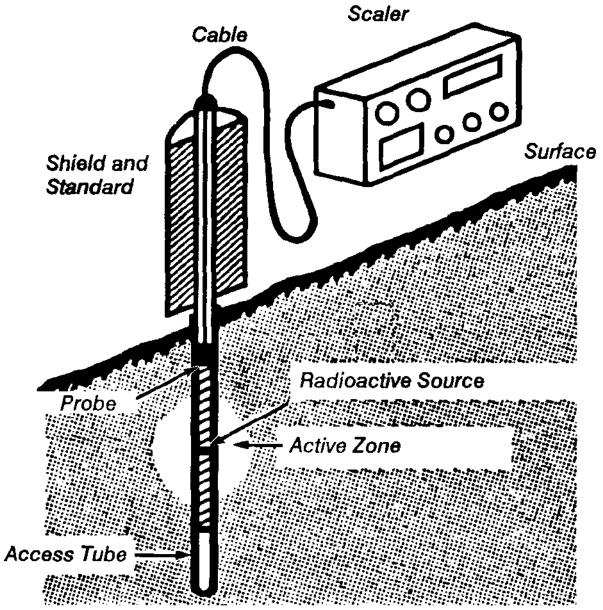


**Figure 5-2.** **Components of the neutron moisture meter (from Hillet, 1980).**

reading is then related to the soil moisture content in the vadose zone and porosity in the saturated zone. These measurements are good indicators of relative changes in moisture content; absolute values of moisture content are difficult to determine.

If the moisture characteristic curve is known (Figure 5-2), then pressure head can be measured using, for example, a tensiometer, and then converted to moisture content using the characteristic curve. Because of the uncertainty involved, however, this approach is not recommended.

In a saturated soil at equilibrium with free water at the same elevation, the matric potential or negative pressure potential is atmospheric and hence equal to zero. Subatmospheric pressure (suction or tension) applied to soil draws water out of the soil, as the voids cannot retain water against the applied suction. Thus, increasing matric potential is associated with decreasing volumetric water content. The soil-water retention curve, also known as the soil-water characteristic curve, expresses this relationship. In most soils, drainage (drying) and infiltration (wetting) produce different water retention curves (Figure 5-3). This is because air that is trapped in the pores upon wetting decreases the water content. In this case, the soil-water characteristic curve is said to display hysteresis. Table 5-6 lists methods for determining moisture characteristic curves.

### 5.2.4 Vadose-Zone Hydraulic Conductivity

The hydraulic conductivity of a porous medium is largest at saturation and decreases as the water content decreases. The saturated hydraulic conductivity in the vadose zone, as well as the relationship between water content and hydraulic conductivity, must be determined. At relatively low water contents, the hydraulic conductivity decreases primarily because air occupies more of the pore space, leaving less cross-sectional area available for water transport. The film of water covering the soil particles becomes thinner and thinner, until at low water contents, it becomes thin enough that attractive forces between the water molecules and the soil particles become stronger than other forces that might be acting to make water move; at this point, the hydraulic conductivity approaches zero. Hence, in the vadose zone, hydraulic conductivity is expressed as a function of moisture content or pressure head.

Measuring vadose-zone hydraulic conductivity values is difficult because head gradients, flow rates, and moisture content or pressure head also must be measured. Factors that influence these measurements include soil texture, soil structure, initial water content, depth of water table, water temperature, entrapped air, biological activity, entrained sediment in the applied water, and chemistry of the applied water (Wilson, 1982).

Relative permeability also must be determined. The relative permeability is a normalized coefficient, which when multiplied by the saturated hydraulic conductivity, yields the vadose-zone hydraulic conductivity. It is typically presented as either a function of capillary pressure or saturation. Relative permeability ranges from one at 100 percent saturation to zero at residual saturation, the water saturation where the water phase becomes disconnected and ceases to flow.

A number of empirical equations have been developed for approximating the vadose-zone permeability of isotropic porous media. Three commonly used equations for estimating the vadose-zone hydraulic conductivity are those by Brooks and Corey (1964), Mualem (1976), and van Genuchten (1980). Methods to determine the vadose-zone hydraulic conductivity are listed in Table 5-7 and discussed in Thompson et al. (1989). Figure 5-4 shows typical relative permeability curves computed using van Genuchten (1980).

### 5.2.5 Soil Gas Analysis

Although not strictly flow related, soil gas analysis is an important remote sensing tool for locating areas contaminated by VOCs in the vadose zone. This method requires the drilling of a shallow hole or the injection of a sample tube into the soil. Volumes of soil gas are evacuated to the surface for collection and analysis at a remote lab or measured on site by a lab-quality vapor analyzer. This method also can be used to analyze cuttings from well drilling operations or in cases where installed wells yield no water. Soil gas analysis is dependent upon the pore spacing within the soil and is less reliable in tightly packed soils such as clay. It also cannot be used to detect nonvolatile organic compounds and inorganic compounds (see Table 5-8). Section 9.2.2 provides some further discussion of soil gas sampling techniques.

Using soil vapor monitoring wells to detect plumes of ground water contaminated with VOCs has been suggested as a cost-effective means of tracing ground-water contamination (e.g., Marrin and Kerfoot, 1988). Indeed, some success in using this technique has been reported (Marrin and Thomp-

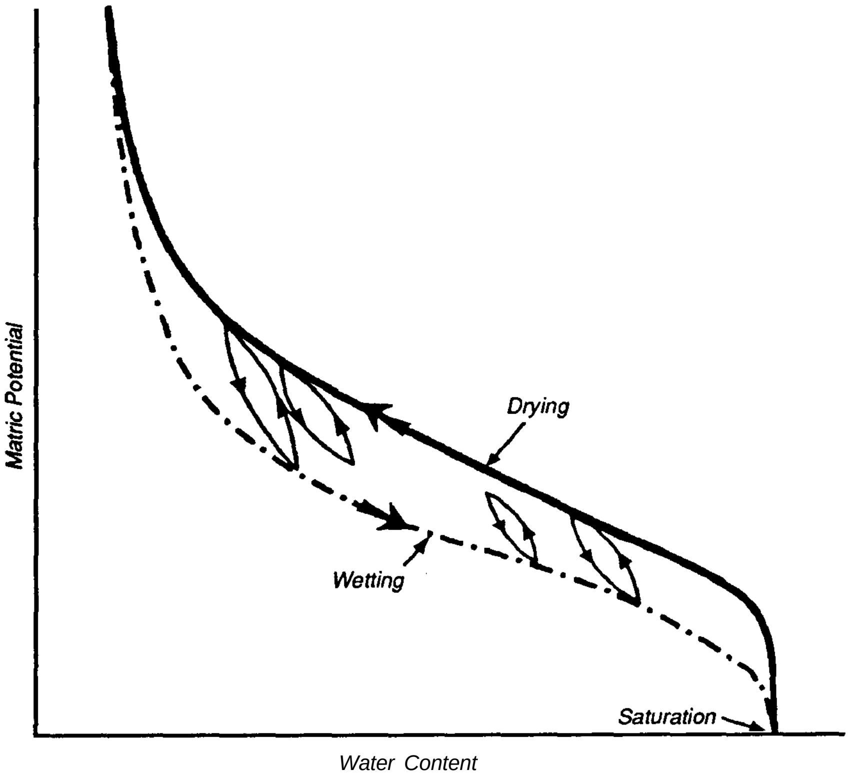


**Figure 5-3. Soil-water characteristic curve displaying hysteresis (modified from Hillei, 1980).**

***Table 5-6. Summary of Methods for Determining Moisture Characteristic Curves***

| *Method* | *Application* | *Reference* |
|---|---|---|
| *Porous plate* | *Standard laboratory method for measurement of soils. Can be used to characterize both wetting and drying behavior.* | *Klute (1986)* |
| *Vapor equilibration* | *8est suited for matric potentials less than -15 bars.* | *Klute (1986)* |
| *Osmotic* | *Similar to porous plate method. Requires long equilibration times. Not recommend.* | *Klute (1986)* |

*From Thompson et al., 1989*

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son, 1987; Marrin and Kerfoot 1988). See, also, the soil gas sampling case studies summarized in Table 9-6.

If the source of the VOCs is below the water table, then the maximum concentration of the organics in the unsaturated zone is the top of the capillary fringe. Once the contaminants have reached the top of the capillary fringe they should diffuse very rapidly because of the large gas-phase diffusion coefficients in the unsaturated zone. This rapid mass transfer from the water in capillary fringe to the soil air just above it should deplete the capillary fringe of the volatile contaminant. The concentrations in the unsaturated zone, therefore, are more controlled by the rate of mass transfer from the ground water to the top of the capillary fringe, a process controlled by the very low solute diffusion coefficients. Laboratory studies of mass transfer across the capillary fringe substantiate these ideas. With the additional loss of mass by mass transfer across the atmosphere-soil boundary and by biodegradation that also may be occurring (e.g., Huh et al., 1987), concentrations in the unsaturated zone are expected to be very low. The best opportunity for detecting VOC contaminants under these conditions is to use soil-gas monitoring wells installed just above the capillary fringe.

There are, of course, exceptions to this scenario. If there is residual nonaqueous phase liquid (NAPL) in the unsaturated zone or product floating on the water table, then soil gas monitoring would detect the volatiles. In the absence of any NAPL, VOCs may be detected by soil-gas monitoring if the water table fluctuates enough to bring the contaminated water up into the unsaturated zone and leave it there as part of the residual phase. The VOCs would then partition from the

*Table 5-7.* ***Summary of Methods to Measure Vadose-Zona Hydraulic-Conductivity Values in the Field and Laboratory***

| *Method* | *Application* | *Reference* |
|---|---|---|
| *Constant-head borehole infiltration* | *Field method in open or partially cased borehole. Most commonly used method. Includes a relatively large volume of porous media in test. Amoozegar and Warrick (1986)* | *Bouwer (1978);*<br>*Stephens and Neuman (1982 a,b,c);* |
| *Guelph permeameter* | *Field method in open, small-diameter borehole (> 5cm). Relatively fast method (5 to 60 minutes) requiring small volume of water. $K_s$, K ( and sorptivity are measured simultaneously. Many boreholes and tests may be required to fully represent heterogeneities of porous media.* | *Reynolds and Elrick (1986)* |
| *Air-entry permeameter* | *Field method. Test performed in cylinder which is driven into porous media. Small volume of material tested; hence, many tests maybe needed. Fast, simple method requiring little water (-10 L).* | *Bouwer (1966)* |
| *Instantaneous profile* | *Field or lab method. Field method measures vertical during drainage. Measurement of moisture content and hydraulic head needs to be rapid and nondestructive to sample. Commonly used method, reasonably accurate.* | *Bouma et al. (1974):*<br>*Klute and Dirksen, (1986)* |
| *Crust-imposed steady flux* | *Field method. Measures vertical K( ) during wetting portion of hysteresis loop. Labor and time intensive.* | *Green, et al. (1986)* |
| *Sprinkler-imposed steady flux* | *Field method. Larger sample area than for crust method. Useful only for relatively high moisture contents.* | *Green, Ahuja, and Chong (1986)* |
| *Parameter identification* | *Results of one field or lab test are used by a numerical approximation method to develop* $K(\theta)$, $K(\psi)$, **and** $\psi(\theta)$ *over a wide range of* $\theta$ **and** $\psi$. *Relatively fast method; however, unique solutions are not usually attained.* | *Zachmann et al. (198la,b, 1982);*<br>*Kool et al. (1985)* |
| *Empirical equations* | *Each empirical equation has its own application based upon the assumptions of the equation. Relatively fast technique.* | *Brooks and Corey (1964);*<br>*van Genuchten (1980); Mualem (1976)* |

*From Thompson et al, 1989*

residual phase into the gas phase where they could be detected.

Given the current understanding of the magnitude of the processes controlling the rate of migration of organic contaminants in the gas phase, it may be more reasonable to reverse the argument. If there is some NAPL in the unsaturated zone, VOCs can travel significant distances in the gas phase. Provided that the Henry's constants for these organic contaminants are sufficiently small, these volatiles can partition into the infiltrating water and be carried to the subsurface to form a shallow contaminant plume. So, the ground-water contaminant plume results from the soil-gas contamination rather than from the ground water.

If this describes the interaction between contaminated soil gas and contaminated ground water, then the greatest use of shallow soil-gas monitoring surveys is for locating potential residuals of NAPL in the subsurface. The areas with the highest gas-phase concentrations are most likely to be those closest to any residual product. Thus, such a survey could be an effective guide for determining the optimal locations for soil-gas extraction wells.

## 5.3 Analysis of Data

There are several programs used to evaluate flow in the vadose zone, many of which are discussed in van der Heijde et al. (1988). Because of the nonlinear and hysteretic behavior of various parameters, modeling vadose-zone flow is more difficult than modeling saturated flow. There are additional problems because of the atmospheric boundary conditions associated with seepage faces, infiltration, and evapotranspiration. Because of the research associated with pesticides, several programs that analyze the vadose zone are available through the Center for Exposure Assessment Modeling in Athens, Georgia. Other vadose-zone programs are available from the Robert S. Kerr Environmental Research Laboratory in Ada, Oklahoma, and the International Ground Water Modeling Center, Holcomb Research Institute, Butler University, Indianapolis, Indiana.

## 5.4 Remedial Actions

When the vadose zone is shallow, excavation as a remedial action is commonly considered. (An example of excavation with fixation is given in Section 5.5.). For volatile chemicals near or above the water table, vacuum extinction is another technique that can remove contaminants from the residual phase. During vacuum extraction, air is pulled through

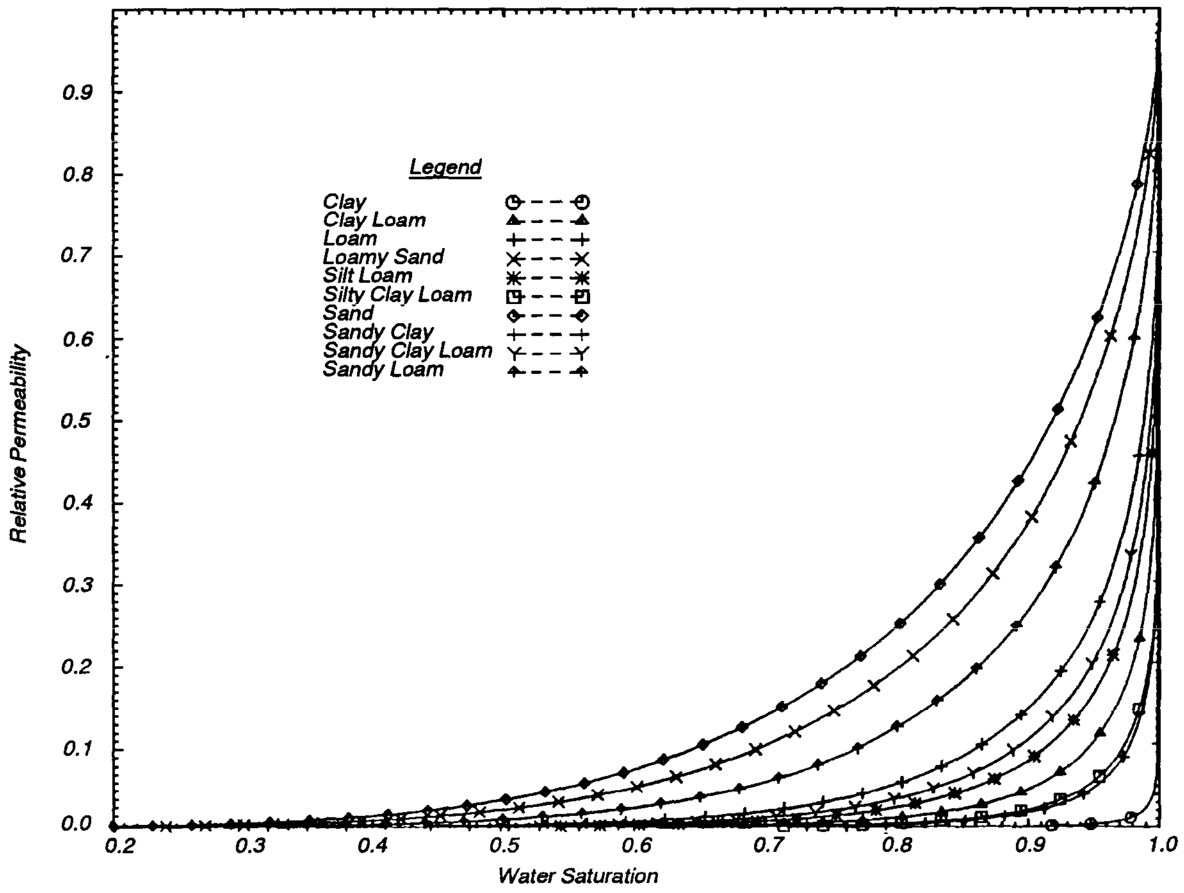


**Figure 5-4.** **Relative permeability curves for various soil types.**

soils contaminated with VOCs. The resulting vapors move through the soil and are collected at extraction wells. Simple techniques that have been developed to control subsurface hydrocarbon vapors are discussed in O'Connor et al, (1984), Dunlap (1984), and Marley and Hoag (1984). In general, two principal types of vapor management systems are available. The frost type, a positive differential pressure system, induces vapor flow away from the control points, while the second type, a negative differential pressure system, induces vapor flow toward the control points. The vapor management methods may be either passive or active. Passive methods use naturally occurring differences in vapor pressures to induce the required flow regime. Active methods require the artificial generation of differential vapor pressures to accomplish the same flow pattern. Practical experience demonstrates that active generation of negative differential vapor pressures typically provides the most favorable field results.

The air flow generates advective vapor fluxes that change the vapor-liquid equilibrium, inducing volatilization of contaminants. This method is advantageous because it is implemented in place, and, therefore, causes minimum disruption. This is especially important at active facilities or sites where investigations are hindered by physical obstacles. Vacuum extraction laboratory studies are descriked in Marley and Hoag (1984), Thornton and Wootan (1982), and Texas Research Institute (1984). Crow et al. (1985, 1987) discusses a field-scale experiment. Agrelot et al. (1985), Regalbuto et al. (1988), Connor (1988), and Hutzler et al. (1989) show applications to hazardous waste sites.

Vacuum extraction can effectively remove chemicals from the vadose zone. According to Hutzler et al. (1989), most chemicals successfully extracted have a low molecular weight and high volatility. Most of the compounds have values of Henry's Law constants water than 0.01. If the water table is lowered, vacuum extraction also can be used to remove residual NAPL from below the original water table elevation. For example, ground-water pumping and vacuum extraction are being used together to clean up DNAPL contamination at the Tyson's Superfund site (Wassersug, 1989). Vacuum extraction also can increase natural biodegradation processes by introducing additional oxygen into the subsurface. Finally, vacuum extraction generally is used in conjunction with other remedial methods.

*Table 5-8.* ***Characteristics of Contaminants in Relatlon to Soil Gas Surveying***

| *Group/Contaminants* | *Applicability of Soil-Gas Survey Techniques* |
|---|---|
| *Group A: Halogenated Methanes, Ethanes, and Ethenes* | |
| *chloroform, vinyl chloride, carbon tetrachloride, trichlorofluoromethane, TCA, EDB, TCE* | *Detectable in soil gas over a wide range of environmental conditions. Dense non-aqueous phase liquid (DNAPL), wi// sink in aquifer if present as pure liquid.* |
| *Group B: Halogenated Propanes, Propenes and Benzenes* | |
| *chlorobenzene, trichlorobenzene, 1,2-dichloropropane* | *Limited value; detectable by soil-gas techniques oniy where probes can sample near contaminated soil or ground water. DNAPL.* |
| *Group C: Halogenated Polycyclic Aromatics* | |
| *aldrin, DDT chlordane, heptachlor, PCBs* | *Do not partition into the gas phase adequate!v to be detected in soil gas under normal circumstances. DNAPL.* |
| *Group D: $C_1$ - $C_8$ Petroleum Hydrocarbons* | |
| *benzene, toluene, xylene isomers, methane, ethane, cyclohexane, gasoline, JP-4* | *Most predictably detected in shallow aquifers or leaking underground storage tanks where probes can be driven near the source of contamination. Light nonaqueous phase liquids (LNAPLs), float as thin film on the water table. Can act as a solvent for DNAPLs, keeping them nearer the ground surface.* |
| *Group E: $C_9$ - $C_{12}$ Petroleum Hydrocarbons* | |
| *trimelhylbenzene, naphthalene, decane, diesel and jet A fuels* | *Limited value; detectable by soil gas techniques only where probes can sample near contaminated soil or ground water. DNAPL.* |
| *Group F: Polycylic Aromatic Hydrocarbons* | |
| *anthracene, benzopyrene, fluoranthene, chrysene, motor oils, coal tars* | *Do not partition adequately into the gas phase to be detected in soil gas under normal circumstances. DNAPL.* |
| *Group G: Low Molecular Weight Oxygenated Compounds* | |
| *acetone, ethanol, formaldehyde, methylethylketone* | *LNAPLs, but dissolve readily in ground water. May be detected in soil gas if they result from a leak or spill in relatively dry soil.* |

*Source: Adapted from Marrin (1987)*

## *5.5 Example-Pepper's Steel Site*

Fixation technology is demonstrated in a case study of the 30-acre Pepper's Steel cleanup site, located near Miami and Medley, Florida, where the Miami Canal borders the site (Figure 5-5). Ground water in the Biscayne aquifer is about 5 to 6 ft below land surface. Soils above the aquifer were contaminated as a result of prior business operations at the site, and polychlorinated biphenyls (PCBs) and heavy metals (lead, arsenic) were found in concentrations significant to warrant action.

The two primary goals of site cleanup were

- Collect and dispose of oils containing PCBs that are uncovered during site excavations.
- Treat or dispose of soils that are contaminated with PCBs and heavy metals.

After reviewing several remedial options, investigators selected solidification/stabilization. In accordance with regulations, PCB-contaminated oils were removed and disposed of at an approved facility off site. All the contaminated soils were solidified on site with a proportioned mix of fly ash and cement. Solidification changes the physical characteristics of the waste and decreases the surface area of pollutants available for leaching. Through stabilization, the wastes become less water soluble and less toxic. The PCBs are trapped in the cement mixture and the heavy metals (arsenic and lead) become insoluble metal silicates.

The amount of soil excavated for fixation was minimized by using kriging on soil chemistry data. The kriged results indicated zones of contamination as well as a measure of the error of estimation. Some details of the cleanup include (U.S. EPA, 1987):

- Approximately 60,000 cubic yards of contaminated soils were excavated.

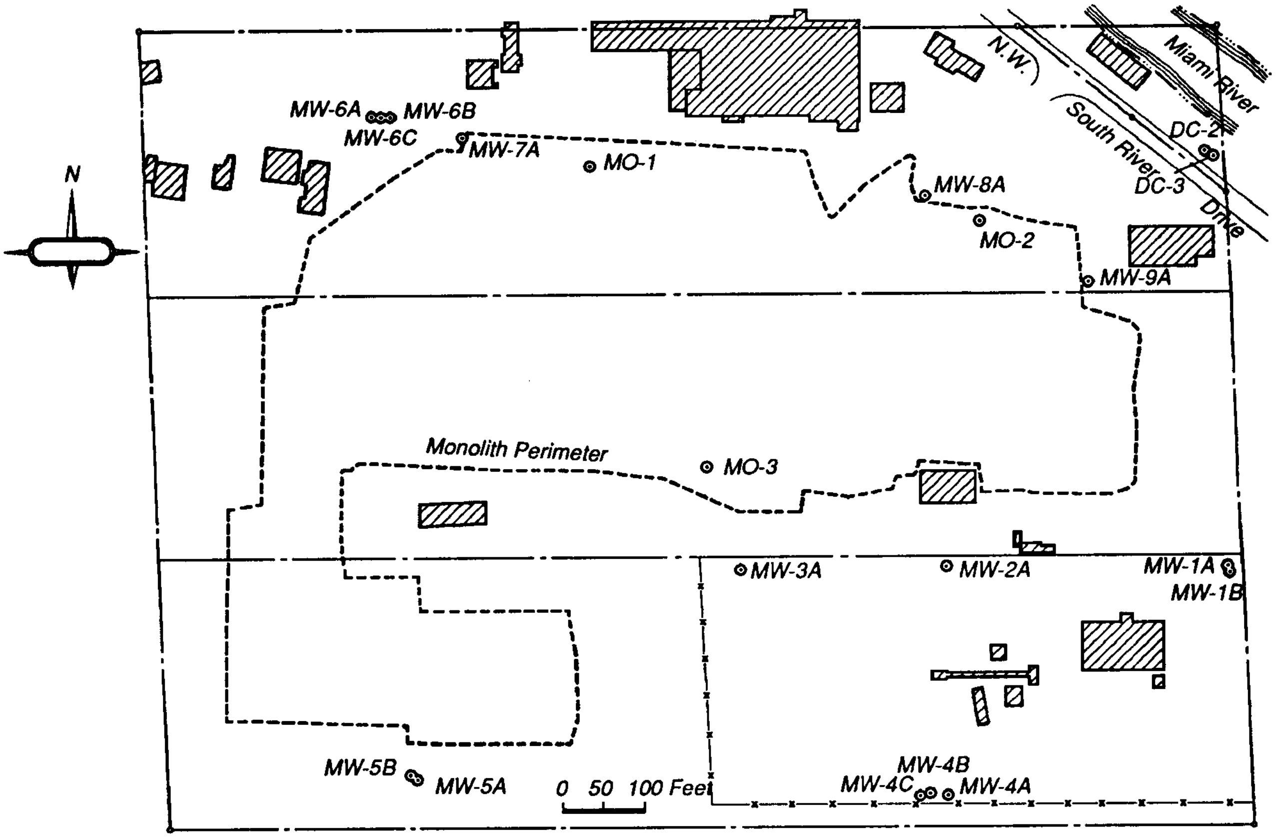


**Figure 5-5. Location of Pepper's Steel and Alloy site monitoring wells.**

- All free oil uncovered during excavation was collected and sent for treatment or disposal.
- Soils contaminated with PCBs and heavy metals were stabilized solidified with a cement mixture.
- Solidified materials were placed back on the Pepper's Steel site and covered with 12 in. of crushed limestone.
- Surface water was controlled by grading the site and placing drains around the solidified material.

Ground water is monitored annually.

## 5.6 References

Agrelot, J.C., J.J. Malot, and M.J. Visser. 1985. Vacuum: Defense System for Ground Water VOC Contamination. In: Fifth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, Dublin, OH, pp. 485-494.

Amoozegar, A. and A.W. Warrick. 1986. Hydraulic Conductivity of Saturated Soils: Field Methods. In: Methods of Soil Analysis, Part 1, 2nd ed., A. Klute (ed.), Agronomy Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 735-770.

Bouma, J., F.G. Baker, and P.L.M. Veneman. 1974. Measurement of Water Movement in Soil Pedons above the Water Table. University of Wisconsin-Extension, Geological and Natural History Survey, Information Circular No. 27.

Bouwer, H. 1966. Rapid Field Measurement Air Entry Value and Hydraulic Conductivity of Soil as Significant Parameters in Flow System Analysis. Water Resources Research 2(4):729-738.

Bouwer, H. 1978. Ground-Water Hydrology. McGraw-Hill, New York.

Bouwer, H. 1986. Intake Rate: Cylinder Infiltrometer. In: Methods of Soil Analysis, Part 1, 2nd ed., A. Klute (ed.), Agronomy Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 825-844.

Brooks, R.H. and A.T. Corey. 1964. Hydraulic Properties of Porous Media. Hydrology Paper No. 3. Colorado State University, Fort Collins, CO.

Conner, J.R. 1988. Case Study of Soil Venting. Pollution Engineering 20(7):75-78.

Crow, W.L., E.P. Anderson, and E.M. Minugh. 1985. Subsurface Venting of Hydrocarbon Vapors from an Underground Aquifer. In: Proc. NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water-prevention, Detection and Restoration, National Water Well Association, Dublin, OH, pp. 536-554.

Crow, W.L., E.R. Anderson, and E. Minugh. 1987. Subsurface Venting of Hydrocarbons Emanating from Hydrocarbon Product on Groundwater. Ground Water Monitoring Review 7(1}51-57.

Davis, S.N. and R.J.M. DeWiest. 1966. Hydrogeology. John Wiley & Sons, New York.

Dunlap, L.E. 1984. Abatement of Hydrocarbon Vapors in Buildings. In: Proc. NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water—prevention, Detection and Restoration, National Water Well Association, Dublin, OH, pp. 504-518.

Dunne, T. and L.B. Leopold. 1978. Water in Environmental Planning. W.H. Freeman, San Francisco,818 pp.

Finkelstein, P.L., D.A. Mozzarella, T.A. Lockhart, WJ. King, and J.H. White. 1989. Quality Assurance Handbook for Air Pollution Measurement Systems, IV: Meteorological Measurements, revised. EPA/600/4-90-O03.

Gardner, W.H. 1986. Water Content. In: Methods of Soil Analysis, Part 1, 2nd ed., A. Klute (ed.), Agronomy Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 493-544.

Green, R.E., L.R. Ahuja, and S.K. Chong. 1986. Hydraulic Conductivity, Diffusivity, and Sorptivity of Unsaturated Soils: Field Methods. In: Methods of Soil Analysis, Part 1, 2nd ed., A. Klute (ed.), Agronomy Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 771-798.

Green, W.H. and C.A. Ampt. 1911. Studies on Soil Physics, I: Flow of Air and Water through Soils. J. Agricultural Science 4:1-24.

Hillel, D. 1980. Fundamentals of Soil Physics. Academic Press, New York, 413 pp.

Hult, M.F. and R.R. Grabbe. 1985. Permanent Gases and Hydrocarbon Vapors in the Unsaturated Zone. In: Proceedings, U.S. Geological Survey Second Toxic Waste Technical Meeting, Cape Cod, MA, October 1985.

Hutzler, N.F., B.E. Murphy, and J.S. Gierke. 1989. State of Technology Review Soil Vapor Extraction Systems. U.S. EPA Cooperative Agreement CR-8143 19-01-1 (NTIS PB89-195184), 36 pp.

Klute, A. 1986. Water Retention: Laboratory Methods. In: Methods of Soil Analysis, Part 1, 2nd ed., A. Klute (ed.), Agronomy Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 635-662.

Klute, A. and C. Dirksen. 1986. Hydraulic Conductivity and Diffusivity: Laboratory Methods. In: Methods of Soil Analysis, Part 1, 2nd ed., A. Klute (ed.), Agronomy Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 687-734.

Kool, J.B., J.C. Parker, and M.T. van Genuchten. 1985. Determining Soil Hydraulic Properties from One-Step Outflow Experiments by Parameter Estimation: I. Theory and Numerical Studies. Soil Sci. Soc. Am. J. 49:1348-1354.

Marley, M.C. and G.E. Hoag. 1984. Induced Soil Venting for Recovery/ Restoration of Gasoline Hydrocarbons in the Vadose Zone. In: Proc. NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water—prevention, Detection and Restoration, National Water Well Association, Dublin, OH, pp. 473-503.

Marrin, D.L. 1987. Soil Gas Sampling Strategies: Deep vs. Shallow Aquifers. In: Proc. 1st Nat. Outdoor Action Conf. on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, National Water Well Association, Dublin, OH, pp. 437-454.

Marrin, D.L. and H.B. Kerfoot. 1988. Soil-gas Surveying Techniques. Environ. Sci. Technol. 22(7):740-745.

Marrin, D.L. and G.M. Thompson. 1987. Gaseous Behavior of TCE Overlying a Contaminated Aquifer. Groundwater 25:21-27.

Mualem, Y. 1976. A New Model for Predicting the Hydraulic Conductivity of Unsaturated Porous Media. Water Resources Research 12:593-622.

Musgrave, G.W. and H.N. Holtan. 1964. Infiltration. In: Handbook of Applied Hydrology, V.T. Chow (ed.), McGraw-Hill, New York, pp. 12-1 to 12-30.

National Weather Service. 1972. Observing Handbook No. 2. Data Acquisition Division, Office of Meteorological Op emtions, Silver Spring, MD.

O'Connor, M.J., J.G. Agar, and R.D. King. 1984. Practical Experience in the Management of Hydrocarbon Vapors in the Subsurface. In: Proc. NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water-Prevention, Detection and Restoration, National Water Well Association, Dublin, OH, pp. 519-533.

Peterson, A.E. and G.D. Bubenzer. 1986. Intake Rate Sprinkler Infiltrometer. In: Methods of Soil Analysis, Part 1, 2nd ed., A. Klute (ed.), Agronomy Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 845-870.

Philip, J.R. 1957. The Theory of Infiltration, I: The Infiltration Equation and its Solution. J. Soil Science 83:345-357.

Radian Corporation. 1988. FGD Chemistry and Analytical Methods Handbook, 2 Chemical and Physical Test Methods, Revision 1. EPRI CS-3612. Electric Power Research Institute, Palo Alto, CA. [Originally published in 1984].

Regalbuto, D.P., J.A. Barrera, and J.B. Lisiecki. 1988. In-situ Removal of VOCs by Means of Enhanced Volatilization. In: Proc. NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water-Prevention, Detection and Restoration, National Water Well Association, Dublin, OH, pp. 571-590.

Reynolds, W.D. and D.E. Elrick. 1986. A Method for Simultaneous In Situ Measurement in the Vadose Zone of Field Saturated Hydraulic Conductivity, Sorptivity and the Conductivity-pressure Head Relationship. Ground Water Monitoring Review 6(4):84-95.

Schmugge, T.J., T.J. Jackson, and H.L. McKim. 1980. Survey of Methods for Soil Moisture Determination. Water Resources Research 16(6):961-979.

Sharma, M.L. 1985. Estimating Evapotranspiration. In: Advances in Irrigation, 3. Academic Press, New York.

Stephens, D.B. and S.P. Neuman. 1982a. Vadose Zone Permeability Tests: Summary. J. Hydraulics Division ASCE 198(HY5):623-639.

Stephens, D.B. and S.P. Neuman. 1982b. Vadose Zone Permeability: Steady State Results. J. Hydraulics Division ASCE 198(HY5):640-659.

Stephens, D.B. and S.P. Neuman. 1982c. Vadose Zone Permeability Unsteady Flow. J. Hydraulics Division ASCE 198(HY5):660-677.

Stephens, D.B. and S. Heermann. 1988. Dependence of Anisotropy on Saturation in a Stratified Sand. Water Resources Research 24(5):770-778.

Stephens, J.C. and E.H. Stewart. 1964. A Comparison of Procedures for Computing Evaporation and Evapotranspiration. Agricultural Research Service, Ft. Lauderdale, FL.

Texas Research Institute. 1984. Forced Venting to Remove Gasoline Vapors from a Large-Scale Model Aquifer. American Petroleum Institute, Washington, DC, 60 pp.

Thompson, C.M., et al. 1989. Techniques to Develop Data for Hydrogeochemical Models. EPRI EN-6637. Electric Power Research Institute, Palo Alto, CA.

Thomthwaite, C.W. and J.R. Mather. 1957. Instructions and Tables for Computing Potential Evapotranspiration and Water Balance. Drexel Institute of Technology, Laboratory of Climatology, X(3).

Thornton, J.S. and W.L. Wootan. 1982. Venting for the Removal of Hydrocarbon Vapors from Gasoline Contaminated Soil. J. Environmental Science and Health A17(1):31-44.

U.S. Environmental Protection Agency. 1987. Protecting the Biscayne Aquifers: Actions to be Taken at the Pepper's Steel and Alloy Site. Prepared by $CH_2M$ Hill.

U.S. Geological Survey. 1977. National Handbook of Recommended Methods for Water Data Acquisition (Chapter 8—Evaporation and Transpiration, updated June 1982). USGS Office of Water Data Coordination, Reston, VA.

van Bavel, C.H.M. 1963. Soil Moisture Measurement with the Neutron Method. USDA-ARS, ARS-41-70, U.S. Government Printing Office, Washington, DC.

van Genuchten, M.T. 1980. A Closed Form Equation for Predicting the Hydraulic Conductivity of Unsaturated Soils. Soil Sci. Soc. Am. J. 44:892-898.

van der Heijde, P. K. M., A.I. E1-Kadi, and S.A. Williams. 1988. Groundwater Modeling: An Overview and Status Report. EPA/600/2-89/028 (NTIS PB89-224497). Also available from International Ground Water Modeling Center, Butler University, Indianapolis, IN.

Veihmeyer, F.J. 1964. Evapotranspiration. In: Handbook of Applied Hydrology, V.T. Chow (ed.), McGraw-Hill, New York, pp. 11-1 to 11-38.

Wassersug, S.R. 1989. Policy Aspects of Current Practices and Applications. In: Remediating Groundwater and Soil Contamination, Report on a Colloquium, Water Science and Technology Board, National Academy Press, Washington, DC.

Wilson, L.G. 1980. Monitoring in the Vadose Zone: A Review of Technical Elements and Methods. EPA/600/7-80-134 (NTIS PB81-125817), 168 pp.

Wilson, L.G. 1981. Monitoring in the Vadose Zone, Part I: Storage Changes. Ground Water Monitoring Review 1 (3):32-41.

Wilson, L.G. 1982. Monitoring in the Vadose Zone, Part II: Ground Water Monitoring Review 2(4):31-42.

Wilson, L.G. 1983. Monitoring in the Vadose Zone, Part III: Ground Water Monitoring Review 3(4):155-166.

Zachmann, D.W., P.C. DuChateau, and A. Klute. 1981a. The Calibration of the Richards Flow Equation for a Draining Column by Parameter Identification. Soil Sci. Soc. Am. J. 45:1012-1015.

Zachmann, D.W., P.C. DuChateau, and A. Klute. 1981b. The Estimation of Soil Hydraulic properties from Inflow Data. In: Proceedings, Symposium on Rainfall-Runoff Modeling, V.V. Singh (ed.), Water Resources Publications, Littleton, CO, pp. 173-180.

Zachmarm, D.W., P.C. DuChateau, and A. Klute. 1982. Simultaneous Approximation of Water Capacity and Soil Conductivity by Parameter Identification. Soil Science 134:157-163.

# Chapter 6
# Characterization of Water Movement in Saturated Fractured Media

James W. Mercer and Charles P. Spalding

Characterizing heterogeneity and anisotropy in the subsurface is important, especially in fractured or karst media. Fracturing or caverns provide preferential flow paths for ground water. Many of the characterization tools and techniques discussed for porous media also may be used for fractured media, if care is used to interpret the data. Techniques that are particularly helpful in understanding fractured/cavernous media include coring, aquifer tests, tracer tests, geophysical tools, geochemical techniques, and fracture trace analysis. Most of these techniques are discussed in this chapter.

As in the preceding chapters, the discussion begins with a review of concepts. This review is followed by sections on field techniques, analysis of data, and a case study. This chapter draws freely upon material contained in a recent EPA Superfund ground water-issue paper on contaminant transport in fractured media (Schmelling and Ross, 1989).

## 6.1 Review of Concepts

Most fractured bedrock systems consist of rock bounded by discrete discontinuities composed of fractures, joints, and shear zones, usually occurring in sets with similar geometries (Witherspoon et al., 1987). Figure 6-1 illustrates this type of system, referred to as a dual-porosity system. In addition to the discontinuities shown in the figure, bedding planes also can behave as discontinuities. Fractures may be open, mineral-filled, deformed, or any combination thereof (Nelson, 1985).

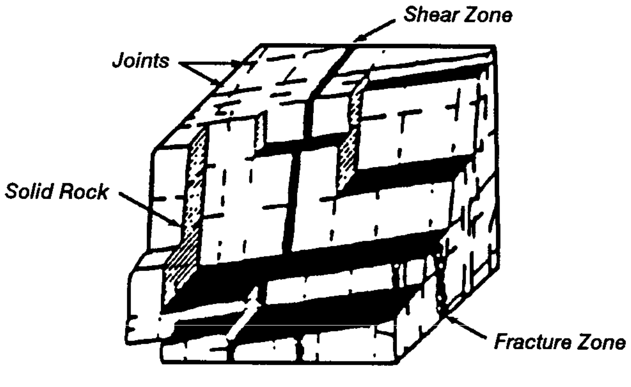


**Figure 6-1. Conceptualization of discontinuities in a fractured medium (from Gale, 1982).**

Open fractures may provide conduits for ground-water and contaminant movement through a rock mass that is otherwise relatively impermeable. Fractures may be filled either partially or completely by secondary cementing materials. such as quartz or carbonate minerals, which reduce or eliminate fracture porosity and permeability. The permeability of deformed fractures also may be reduced by gouge, a finely abraded material produced by the cataclasis of grains in contact across a fault plane during displacement of the rock masses. Slickensides, striated surfaces formed by frictional sliding along a fault plane, also are a deformed-fracture feature. Slickensides reduce permeability perpendicular to the fracture plane, but the mismatch of fracture surfaces may increase permeability along the fracture plane. Very little displacement is necessary to produce gouge or slickensides. Another factor that may reduce permeability is the deposition of a thin layer of low- permeability material called a fracture skin. This skin prevents the free exchange of fluids between the rock matrix and the fracture (Moench, 1984).

The concept of fracturing presented so far is one element of a more complicated hierarchy of multiple-porosity systems. In soluble bedrock like limestone, dolostone, or evaporates, conduit flow can develop as original fracture systems are enlarged by solution. The important feature of conduit flow, when it is able to develop, is the integration of the drainage network (Quinlan and Ewers, 1985). In many ways, the network is analogous to a river system with smaller tributaries supplying water to a succession of larger and larger conduits. As a result of the integration, both the conduit system and the individual conduits can become large. For example, the karst system at Mammoth Cave, Kentucky, has over 330 miles of connected passages.

Major factors affecting ground-water flow through fractured rock include (1) fracture density, (2) orientation, (3) effective aperture width, and (4) the nature of the rock matrix. Fracture density (number of fractures per unit volume of rock) and orientation are important determinants of the degree of interconnection of fracture sets, which is a critical feature contributing to the hydraulic conductivity of a fractured rock system (Witherspoon et al., 1987). Only interconnected fractures provide pathways for ground-water flow and contaminant transport, although the flow network may be a subset of the fracture network. Fractures oriented parallel to the hydraulic gradient are more likely to provide effective pathways than fractures oriented perpendicular to the hydraulic gradient. Flow in fractured rock systems can be similar to flow in porous media when (1) the fracture apertures are constant, (2) the fracture orientations are randomly distributed, and (3) the fracture spacing is small relative to the scale of the system (Long et al., 1982).

The cross-sectional area of a fracture will have an important effect on flow through the fracture. Under certain conditions, fracture-flux is generally proportional to the cube of the fracture aperture (distance between rock blocks) when apertures exceed 10 microns (Witherspoon et al., 1987). Fracture apertures and, therefore, flow through fractures are highly stress-dependent and generally decrease with depth (Gale, 1982).

The nature of the rock matrix affects the movement of water and contaminants through fractured rock systems. Metamorphic and igneous rocks generally have very low primary porosity and permeability. Fractures may account for most of the permeability in such systems, and the movement of water and contaminants into and out of the rock matrix may be minimal. On the other hand, sedimentary rocks generally have higher primary porosity and varying permeability. Examples include coarse-grained materials, such as sandstone, which have relatively high primary porosity and significant matrix permeability, and fine-grained materials, such as shale, which have high primary porosity and low permeability.

Fractures may enhance the permeability of all types of materials. High porosity allows significant storage of water and contaminants in the rock matrix. Authigenic clays formed during the weathering on certain rock-forming minerals may significantly reduce the porosity and permeability of the fractures and rock matrix. Rates of contaminant migration into and out of the rock matrix will depend on the permeability of the matrix, the presence of low-permeability fracture skins, and the matrix diffusion coefficient of the contaminant (Figure 6-2).

A complete description of a contaminated fractured rock system would include data on (1) the dimensions of the system; (2) individual fracture length, aperture width, location, and orientation; (3) the hydraulic head throughout the system; (4) the porosity and permeability of the rock matrix; (5) the sources of water and contaminants; (6) the nature and concentrations of the contaminants throughout the system; and (7) the chemical interactions between the contaminants and rock matrix. Presently, collection of such detailed information is neither technically possible nor economically feasible at the scale of most contaminated sites.

## 6.2 Field Techniques

Hydrogeologic characterization methods usually are most successful when used in conjunction with one another. These methods may include coring, aquifer tests, tracer tests, surface and borehole geophysical techniques, and use of borehole flowmeters, or other tools. Important information may be gathered before, during, and after drilling operations.

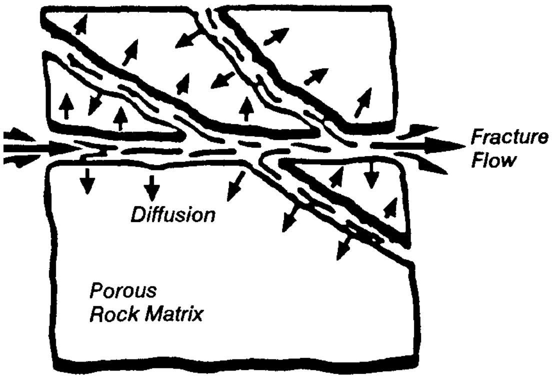


**Figure 6-2.** **Flow through fractures and diffusion of contaminants from fractures into the rock matrix of a dual-porosity medium (from Anderson, 1984).**

### *6.2.1 Fracture Trace Analysis*

Ground-water flow in bedrock is generally concentrated in the upper weathered zone of the rock and in fractures at depth. A well penetrating a zone of subsurface fractures, therefore will yield more water than a well drilled in an area with relatively few fractures. Such zones are also pathways for contaminant migration. Selecting drill sites by examining aerial photographs stereoscopically for surficial expressions of linear zones of subsurface fractures will increase the probability of high yields and locating contaminants. This type of study is known as fracture trace analysis (Ray, 1960; Fetter, 1980). Figure 6-3 shows the relationship between fracture traces and zones of fractures. In general, higher yields can be expected in topographic low areas because (1) swales and valleys tend to be cut into less-resistant, more highly fractured and more-permeable rock; and (2) ground-water flow usually converges in stream valleys.

Although fracture traces, fault planes, and other lineaments are often identifiable on aerial photographs, they must be field-verified to distinguish anthropogenic features such as fences and buried pipelines from geologic features. The orientation of all fractures (e.g., outcrops and excavations) identified from aerial photographs and field observations should be measured and plotted on maps as well as on rose diagrams (where the frequency of fracture orientation is plotted) to identify major fracture trends. Such trends are usually related to the geologic (tectonic) history of a site. A basic understanding of a site's tectonic history and subsequent fracture orientation allows a better understanding of potentiaI contaminant pathways.

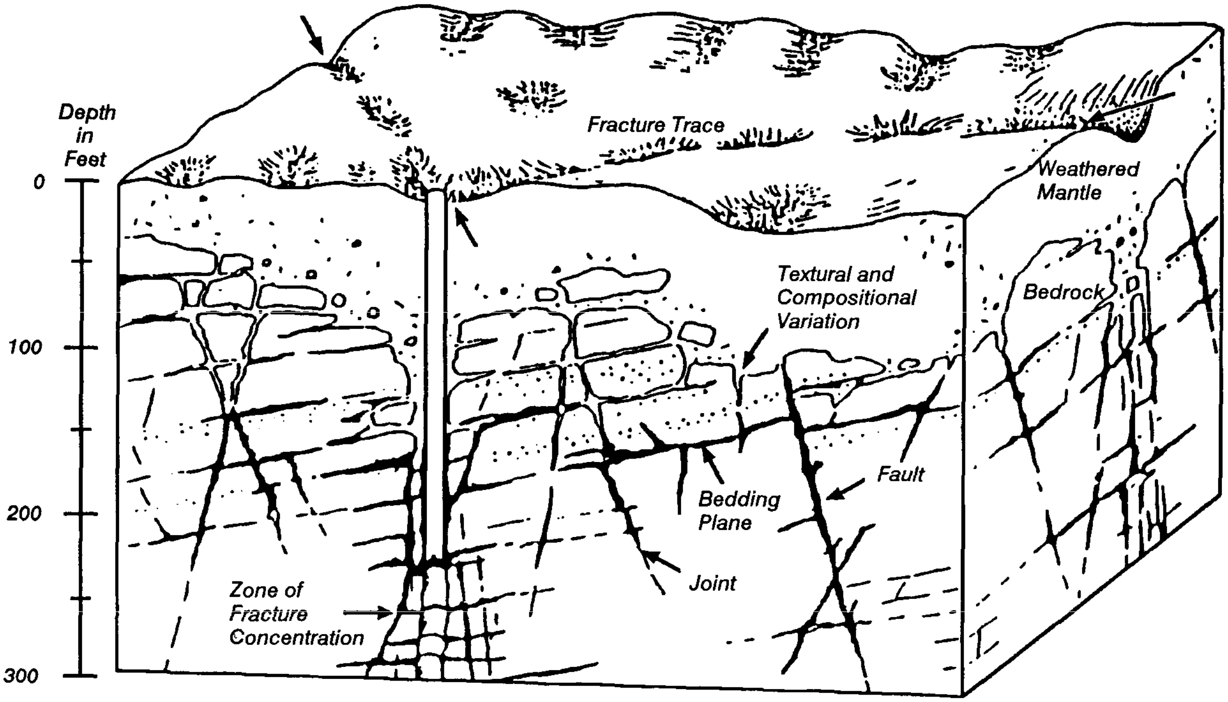


**Figure 6-3.** **Relationship between fracture traces end zones of fracture concentration (after Lattman and Parizek, 1964).**

## *6.2.2 Coring*

Core material obtained during drilling operations can yield information on the density, location, and orientation of fractures and provide samples for physical and chemical testing. Core samples also may provide information concerning fracture roughness and mineral precipitation on fracture surfaces. Information collected during coring operations with open hole completions should include (1) the location of major water-bearing fractures, (2) changes in hydraulic head with depth, and (3) changes in the ground-water geochemistry, Water loss to a fracture zone, drilling rates, and the presence of contaminants also are useful active drilling data (this information is discussed in detail in Chapter 4). In certain instances, cores may be taken diagonally to intercept near vertical fractures and determine fracture azimuth. While a major drawback of coring can be the relatively high cost, the information obtained often makes this characterization technique cost effective.

## *6.2.3 Aquifer Tests*

Aquifer tests, including constant rate pumping tests and slug tests, can provide hydraulic conductivity and information on anisotropy for fractured formations. These tests also allow the estimation of average fracture apertures of a medium. The same tests commonly used for unconsolidated porous media can be used for fractured media, but the test results will generally be more difficult to interpret. Barker and Black (1983) note that transmissivity values will always be overestimated by applying standard type curve analysis to fissured aquifers.

Other more complex tests, such as cross-hole packer tests, are particularly applicable to fractured media. For example, Hsieh and Neuman (1985) and Hsieh et al. (1985) describe a method of determining the three-dimensional hydraulic conductivity tensor. The method consists of injecting fluid into, or withdrawing fluid out of, selected intervals isolated by inflatable packers and monitoring the transient response in isolated intervals of neighboring wells.

This method is applicable to situations where the principal directions of the hydraulic conductivity tensor are not necessarily vertical and horizontal. A minimum of six cross-hole tests is required to determine the six independent comp nents of the hydraulic conductivity tensor. In practice, scatter in the data is likely to be such that more than six cross-hole tests will be required. Hsieh and his coworkers concluded that failure to fit data to an ellipsoidal representation indicated that the rock under study could not be represented by an equivalent, continuous, uniform, anisotropic medium the scale of the test. Depending on the application to be made, the test may be repeated on a larger scale or the data may be interpreted in terms of discrete fractures of the system.

While aquifer tests can provide information on aquifer anisotropy, heterogeneity, and boundary conditions, they do not provide information on the range of fracture apertures or surface roughness. One of the major drawbacks associated with long-term aquifer testing is the necessity to store and treat the large volume of water discharged during the test.

Results of aquifer tests in fractured media often demonstrate S-shaped response curves. Early in the pumping test, the fractures control the yield to the well; therefore, the fracture properties control the aquifer response. Once the fractures drain, there is a transition period followed by a time period during which the porous block properties control the aquifer response (see Streltsova, 1988).

### 6.2.4 *Tracer Tests*

Tracer tests can provide information on effective porosity, dispersion, and matrix diffusion generally unobtainable from other hydrogeologic methods. Tracer tests either can be conducted under natural-gradient or forced-gradient conditions. The primary disadvantages of tracer tests are the time, expense, number of necessary sampling points, and difficulties associated with data interpretation. However, the important information provided by tracer tests is difficult to obtain by any other means. Davis et al. (1985) provide an introduction to the use of tracers in ground-water investigations (see also discussion of this report by Quinlan, 1986, and reply by Davis, 1986). Tracers, most commonly fluorescent dyes, also are used to help map karst areas (LaMoreaux et al., 1989; Mull et al., 1988; Quinlan, 1986, 1989).

Graphical geochemical techniques commonly used in porous media may provide valuable information at fractured rock sites. Hem (1985) and Lloyd and Heathcote (1985) provide overviews of methods used to identify the sources and extent of ground-water mixing. Environmental isotopes, such as tritium, also are used to interpret pathways and travel times (LaMoreaux et al., 1989).

### 6.2.5 *Geophysical Tools*

Both surface and borehole geophysical methods can be used to characterize fractured rock systems. Application of surface geophysical methods such as direct current electrical resistivity, electromagnetic induction methods, ground-penetrating radar, magnetometer surveys, and seismic and remote sensing techniques should be evaluated before a drilling program is initiated. These techniques may provide insight for locating potential monitoring wells by identifying the location of contaminant plumes or the orientation of major fracture systems. However, the correlation of major surface geophysical features with contaminant transport processes in fractured media has yet to be thoroughly characterized.

Borehole walls are usually less susceptible than cores to fractures induced during drilling operations. Borehole geophysical techniques can usually provide a more reliable estimate of fracture density than can cores. However, as indicated by Nelson (1985) in a review of down-hole techniques, responses used to detect fractures on well logs are nonunique and require detailed knowledge of the tool and the various rock property effects that could cause fracture-like responses. Borehole geophysical methods include acoustic, electrical resistivity, caliper, gamma, and other high-energy logging techniques. The acoustic televiewer presents a continuous image of the acoustic response of the borehole face and can detect fracture apertures as small as one millimeter. This oriented tool also allows the determination of fracture orientations. Caliper logs are best suited for determining relative fracture intensity in continuous, competent rock. Advances in electronic miniaturization have led to the development of down-hole cameras, capable of providing in situ viewing of fractures in the subsurface (Morahan and Dorrier, 1984).

### 6.2.6 *Borehole Flowmeters*

Flowmeters have been used for many years in industry. Only recently, however, has instrumentation been developed that can accurately measure very low flow rates. Borehole flowmeters measure the incremental discharge along screened or open-hole portions of wells during small-scale pumping tests. The three major types of flowmeters currently being developed are impeller, heat-pulse, and electromagnetic. Heat-pulse and electromagnetic flowmeters have no moving parts that may deteriorate over time; they also are more sensitive than impeller flowmeters (Young and Waldrop, 1989). This greater sensitivity may allow the detection of the vertical movement of water within the borehole under nonpumping conditions. Under pumping conditions, fracture zones contributing ground water to a borehole may be identified.

## 6.3 Analysis of Data

Flow in fractured media has been modeled using one of three possible conceptualizations: (1) an equivalent porous continuum, (2) a discrete fracture network, and (3) a dual-porosity medium (National Research Council, 1990). The first of these approaches assumes that the medium is fractured to the extent that it behaves hydraulically as a porous medium. The actual existence of fractures is reflected in the choice of values for the material coefficients (e.g., hydraulic conductivity, storativity, or relative permeability). Often these parameters take on values significantly different from those used for modeling a porous medium (Shapiro, 1987). Examples of this approach as cited by Shapiro (1987) are presented in Elkins (1953), Elkins and Skov (1960), and Grisak and Cherry (1975).

With the discrete fracture approach, most or all of the ground water moves through a network of fractures. This approach assumes that the geometric character of each fracture (e.g., position in space, length, width, and aperture) as well as the pattern of connection among fractures are known exactly. In the simplest theoretical treatment, the blocks are considered to be impermeable. Figure 6-4a is an idealization of a two-dimensional network of fractures consisting of two different sets. Note how each fracture, represented on the figure by a line segment, has a definite position in space, length, and aperture. The hydraulic characteristics of the fracture system develop as a consequence of the intersection of the individual fractures. In three dimensions, the network can be described in terms of intersecting planes that could be rectangular (Figure 6-4b) or circular (Figure 6-4c). Examples of the discrete fracture treatment of flow in networks are included in Long et al. (1982), Long (1985), Robinson (1984), Schwartz et al. (1983), and Smith and Schwartz (1984).

The dual-porosity conceptualization of a fractured medium considers the fluid in the fractures and the fluid in the blocks as separate continua. Unlike in the discrete approaches, no account is taken of the specific arrangement of fractures with respect to each other-there is simply a mixing of fluids in interacting continua (Shapiro, 1987). In the most general formulation of the dual-porosity model, the possibility exists for flow through both the blocks and the fractures, with a transfer function describing the exchange between the two continua. Thus, a loss in fluid from the fracture represents a gain in fluid in the blocks (Shapiro, 1987).

Although modeling tools exist to deal with fractured media, at present, results should be interpreted with caution. Systems are often complex and extraordinarily difficult to characterize, especially with the level of effort considered normal for most site investigations. The state of the art in field testing provides a relatively rudimentary estimate of values for some parameters like hydraulic conductivity, while other parameters, like storativity, must be established through fitting simple theoretical models (usually of the porous medium type).

## 6.4 Remedial Actions

In principle, the remedial actions discussed for porous media apply to fractured media. However, the remediation for fractured media is usually more difficult to design and implement. For example, there are two major problems associated with pump-and-treat technologies: (1) hydraulic conductivity reduction with stress; and (2) matrix diffusion.

Fractures are difficult to work with because apertures and, hence, hydraulic conductivity, depend on the stress within the medium. A fracture can be opened or closed simply by reducing or increasing the forces applied to it, For example, pumping a well in a fractured medium reduces the pore pressure, effectively decreasing the fracture aperture. Gale (1982) describes a number of empirical-theoretical approaches designed to model the stress coupling to hydraulic conductivity.

For heterogeneous conditions such as fractured media, advected water will sweep through the higher permeable zones (fractures), removing contamination from those zones. Movement of contaminants out of the less-permeable zones is a slower process than advective transport in the higher permeability zones. The contaminants either are slowly exchanged by diffusion with the flow water present in the larger pores or move at relatively slower velocities in the smaller pores. A rule of thumb is that the longer the site has been contaminated and the more lenticular (layered) the geologic material, the longer will be the tailing effect. The water and contaminants residing in the more permeable zones are those first mobilized during pumping. Thus, pump-and-treat technologies work in heterogeneous media, but cleanup times will be longer and more difficult to estimate than for similar systems in more homogeneous media.

## 6.5 Example-Marion County, Florida

This example involves site characterization in Marion County, Florida, at a site located approximately 10 mi west of

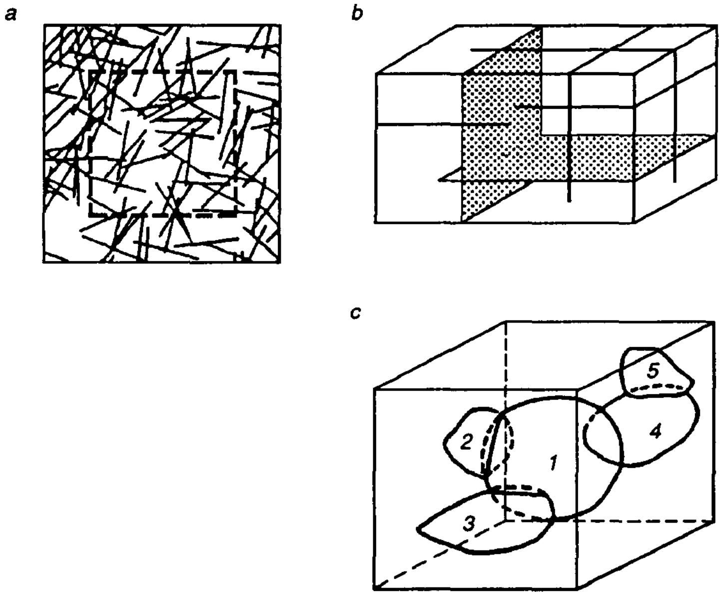


**Figure 6-4,** **Three different conceptualizations of fracture networks: (a) a two-dimensional system of line segments (from Shimo and Long, 1987); (b) a three-dimensional system of rectangular fractures (from Smith et al., 1985); and (c) a three. dimensional system of "penny-shaped" cracks (from Long, 1986).**

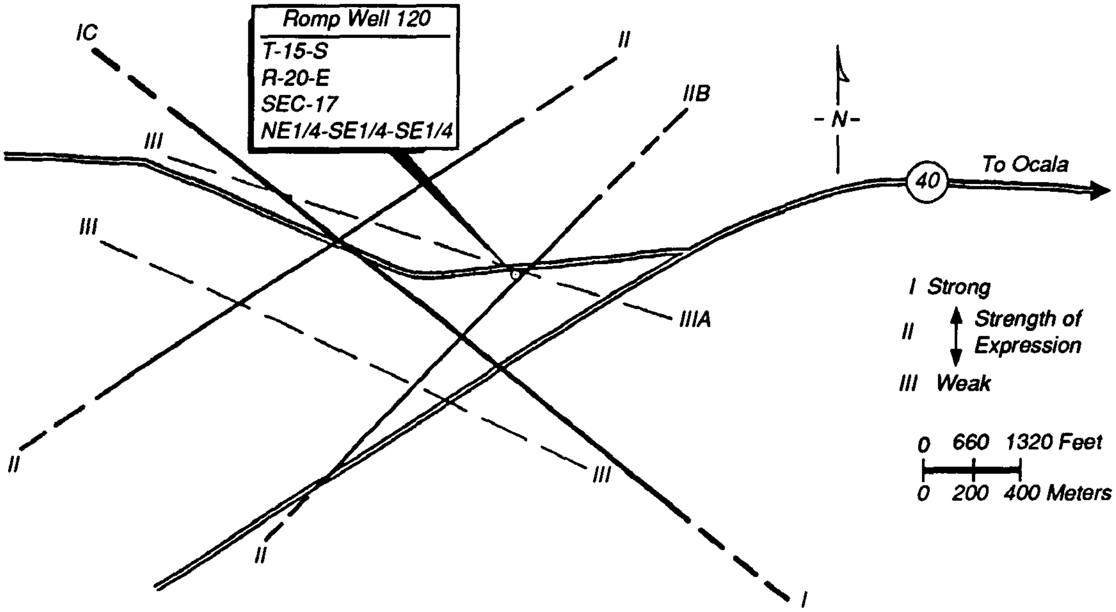


**Figure 6-5.** **Fracture-trace expreasions based on photo interpretation.**

Ocala. The work, performed for the Southwest Florida Water Management District (Ward et al., 1989), concerned water resource assessment of the Floridan aquifer however, many of the steps and techniques used to characterize the site are similar to those that would be used at a hazardous waste facility overlying fractured media. Some of the work is described in Giffin and Ward (1989).

The first step of the assessment was to perform a fracture-trace analysis using aerial photographs. Photolinears were classified as I, II, or III depending on the strength and continuity of their linear patterns on the photo. Class I photolinears have the strongest, most continuous expression; Class III have the weakest. Figure 6-5 shows the fmcture-trace map and the location of Regional Observation Monitoring Program (ROMP) Well 120.

After field checking the mapped fractures, the next step was to confirm them using surface geophysics. The tri-potential method was used (Ogden and Eddy, 1984; Habberjam, 1969), and the results of this geophysical survey were used to pinpoint two lineaments within a few hundred feet of a site where aquifer testing would be performed.

To help locate monitoring wells for the aquifer testing, numerical modeling was performed using a fracture flow code. Data typical for that part of Florida were used to estimate the response to pumping. Based on the field work and the modeling, the wells were located as shown in Figure 6-6. The locations of some wells were modified due to access difficulties; three wells were located to penetrate fracture or solution channel zones; and one well was sited within the limestone matrix.

After drilling the wells, the investigators performed borehole geophysics tests including caliper, gamma-gamma, and neutron. In general, cavernous zones are located using the caliper log, whereas shalely zones that are less likely to form cavernous zones are located using the gamma-gamma log. The neutron log is used to indicate porous zones, which should correspond to caverns. Unfortunately, the geophysical logs were not useful in differentiating between areas of solution features (OW1, 0W2, and 0W3) and rock matrix (OW4).

The final step in the characterization of this site was to perform hydraulic testing. Both slug tests and an aquifer test performed at the site demonstrated an underdamped response (see Figure 6-7). In this type of response, the water level in the well oscillates due to inertial effects, which are common in highly permeable aquifers. Vart der Kamp (1976) presents a method for analyzing underdamped responses to slug tests. Pumping tests were analyzed using classical Theis analysis and anew approach based on early-time deviations (Ward and Giffin, 1989, and Shapiro, 1989).

As a result of site data analysis, dual-porosity conceptualization, thought to be appropriate for this site, did not need to be observed in the field testing. The site was used to develop a regional dual-porosity and discrete fracture model, which was then calibrated with transient response at wells and major spring discharges. A conceptual composite of the site and model response (Figure 6-8) demonstrates the dramatic difference in the site-scale storage as compared to the regional-scale matrix response. This difference is evidenced by a four order of magnitude shift in time forming the dual-porosity envelope.

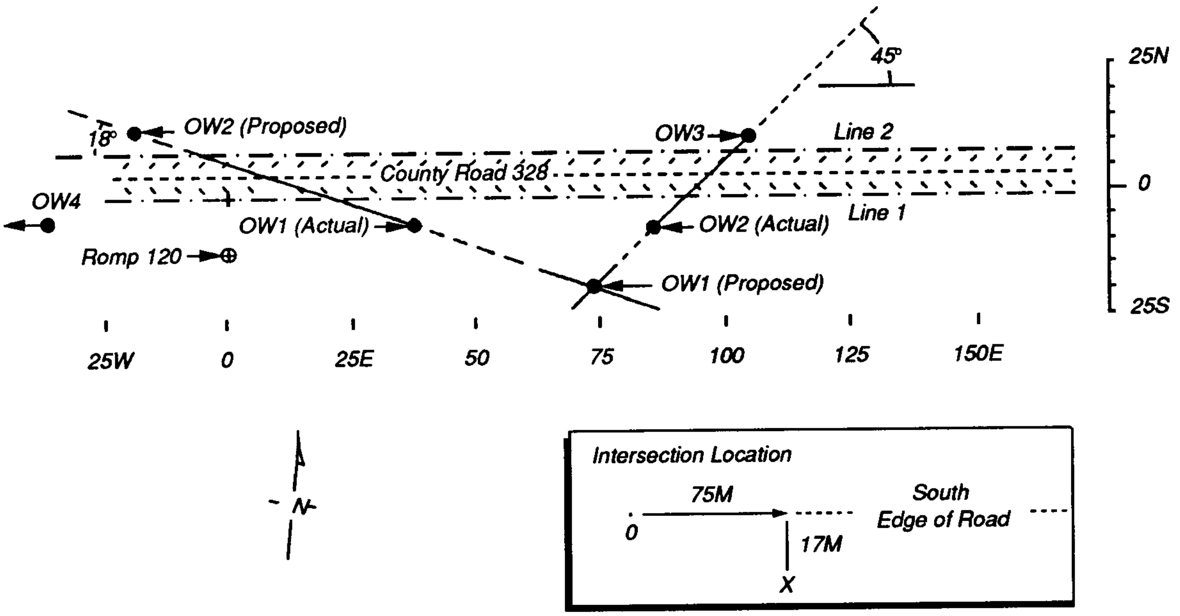
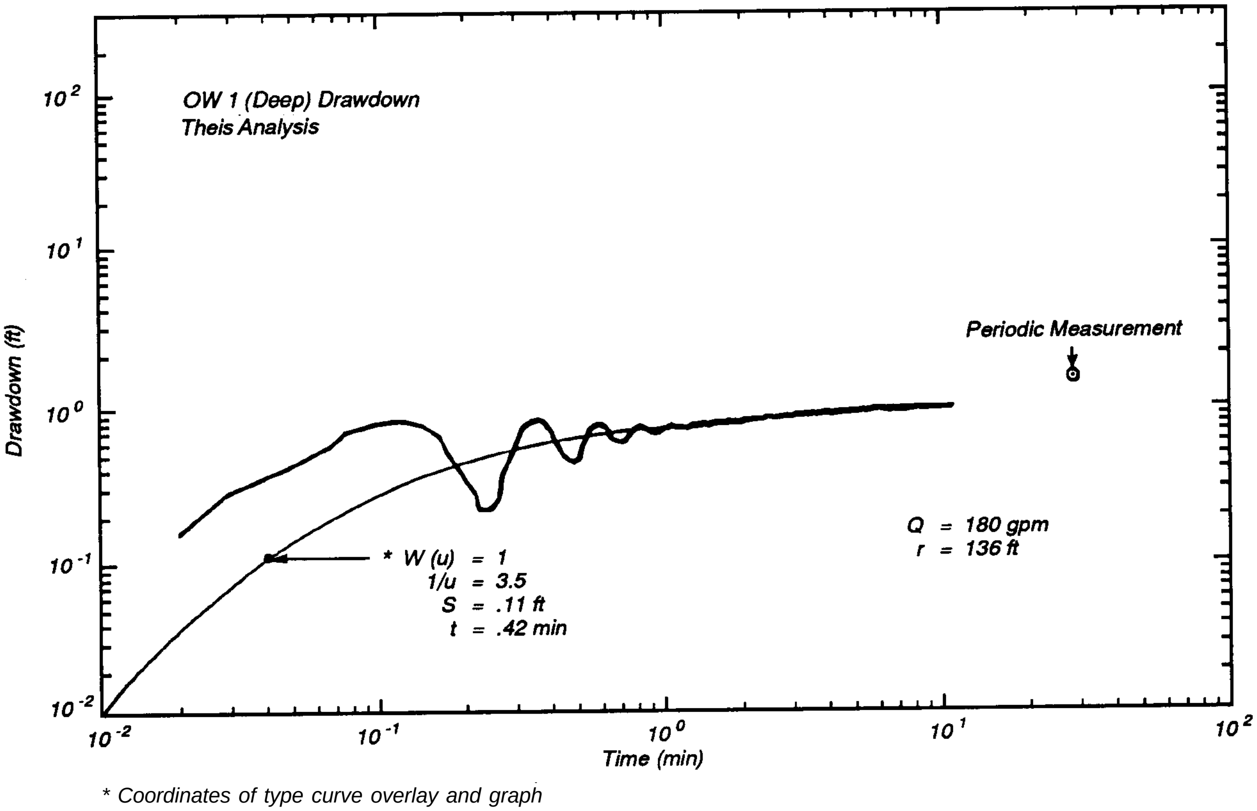


**Figure 6-6.** **Location of four observation wells in the vicinity of ROMP 120.**



* Coordinates of type curve overlay and graph

**Figure 6-7.** **Pump test Interpretation using the deep transducer at monitor well OW1 using Theis method.**

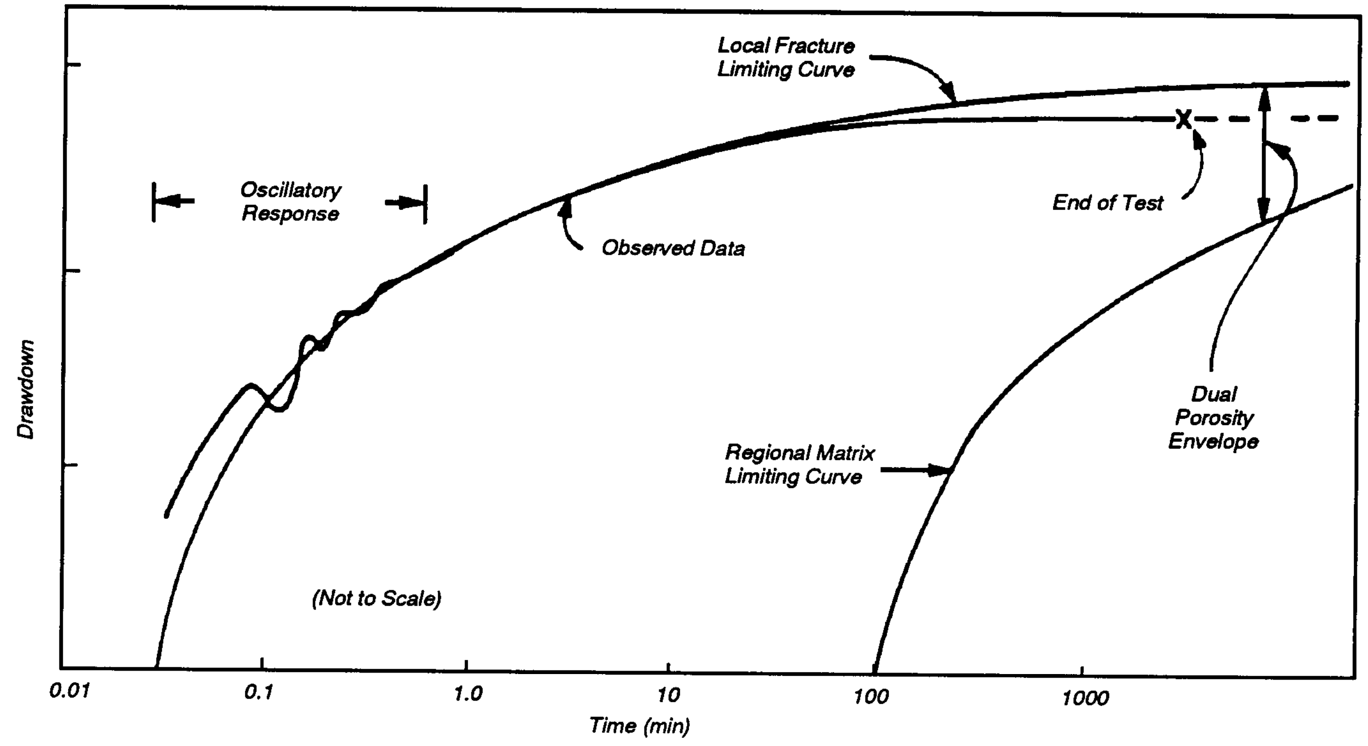


Figure 6-6. Conceptual composite of aquifer test and dual-porosity model response.

## 6.6 References

Anderson, M.P. 1984. Movement of Contaminants in Ground Water Ground Water Transport-Advection and Dispersion. In: Ground-Water Contamination, National Academy Press, Washington, DC, pp. 37-45.

Barker, J.A. and J.H. Black. 1983. Slug Tests in Fissured Aquifers. Water Resources Research 19:1558-1564.

Davis, S.N. 1986. Reply to the Discussion by James F. Quinlan of Ground-Water Tracers. Ground Water 24(3):398-399.

Davis, S.N., D.J. Campbell, H.W. Bentley, and T.J. Flynn. 1985. Introduction to Ground-Water Tracers. EPA 600/2-85/022 (NTIS PB86-100591). Also published under the title Ground-Water Tracers in NWWA/EPA Series, National Water Well Association, Dublin, OH.

Elkins, L.F. 1953. Reservoir Performance and Well Spacing, Spraberry Trend Area Field of West Texas. Trans. American Institute of Mining Engineers 198:177-196.

Elkins, L.F. and A.M. Skov. 1960. Determination of Fracture Orientation from Pressure Interference. Trans. American Institute of Mining Engineers 219:301-304.

Fetter, Jr., C.W. 1980. Applied Hydrogeology. Charles E. Merrill, Columbus, OH, pp. 406-411.

Gale, J.E. 1982. Assessing the Permeability Characteristics of Fractured Rock. GSA Special Paper 189. Geological Society of America, Boulder, CO, pp. 163-181.

Giffin, D.A. and D.S. Ward. 1989. Analysis of Early-Time Oscillatory Aquifer Response. In: Proc. Conf. on New Field Techniques for Quantifying the Physical and Chemical Properties of Heterogeneous Aquifers (Dallas, TX), National Water Well Association, Dublin, OH, pp. 187-211.

Grisak, G.E. and J.A. Cherry. 1975. Hydrologic Characteristics and Responses of Fractured Till and Clay Confining a Shallow Aquifer. Canadian Geotechnical Journal 12:23-43.

Habberjam, G.M. 1969. The Location of Spherical Cavities Using a Tri-Potential Technique. Geophysics 34(5):780-784.

Hem, J.D. 1985. Study and Interpretation of the Chemical Characteristics of Natural Water, 3rd ed. U.S. Geological Survey Water-Supply Paper 2254,263 pp.

Hsieh, P.A. and S.P. Neuman. 1985. Field Determination of the Three-Dimensional Hydraulic Conductivity Tensor of Anisotropic Media, 1. Theory. Water Resources Research 21:1655-1665.

Hsieh, P.A., S.P. Neuman, G.K. Stiles, and E.S. Simpson. 1985. Field Determination of the Three-Dimensional Hydraulic Conductivity Tensor of Anisotropic Media, 2. Methodology and Application to Fractured Rocks. Water Resources Research 21:1667-1676.

LaMoreaux, P.E., E. Prohic, J. Zoetl, J.M. Tanner, and B.N. Roche. 1989. Hydrology of Limestone Terranes Annotated Bibliography of Carbonate Rocks, Volume 4. International Association of Hydrogeologists, International Contributions to Hydrogeology, Vol. 10, Verlag Heinz Heise GmbH, Hannover, Germany, 267 pp.

Lattman, L. H., and R.R. Parizek. 1964. Relationship between Fracture Traces and the Occurrence of Ground Water in Carbonate Rocks. J. Hydrology, 2:73-91.

Lloyd, J.W. and J.A. Heathcote. 1985. Natural Inorganic Hydrochemistry in Relation to Ground Water. Clarendon Press, Oxford, 296 pp.

Long, J. C. S., J.S. Remer, C.R. Wilson, and P.A. Witherspoon. 1982. Porous Media Equivalents for Networks of Discontinuous Fractures. Water Resources Research 18:645-658.

Long, J.C.S. 1985. Verification and Characterization of Fractured Rock at AECL Underground Research Laboratory. BMI/OCRD- 17. Office of Crystalline Repository Development, Battelle Memorial Institute, 239 pp.

Long, J. C. S., P. Gilmour, and P.A. Witherspoon. 1985. A Model for Steady Fluid Flow in Random Three-Dimensional Networks of Disc-Shaped Fractures. Water Resources Research 21:1105-1115.

Moench, A.F. 1984. Double-Porosity Models for a Fissured Ground Water Reservoir with Fracture Skin. Water Resources Research 20831-846.

Morahan, T. and R.C. Dorrier. 1984. The Application of Television Borehole Logging to Ground-Water Monitoring Programs. Ground-Water Monitoring Review 4(4): 172-175.

Mull, D.S., T.D. Lieberman, J.L. Smoot, and L.H. Woosely, Jr. 1988. Application of Dye-Tracing Techniques for Determining Solute-Transport Characteristics of Ground Water in Karst Terranes. EPA 904/6-88-001, Region 4, Atlanta, GA.

National Research Council. 1990. Ground-Water Models: Scientific and Regulatory Applications. National Academy Press, Washington, DC, 303 pp.

Nelson, R.A. 1985. Geologic Analysis of Naturally Fractured Reservoirs. Contributions in Petroleum Geology and Engineering, Vol. 1. Gulf Publishing Company, Houston, TX, 320 pp.

Ogden, A. and P.S. Eddy, Jr. 1984. The Use of Tri-Potential Resistivity to Locate Fractures and Caves for High Yield Water Wells. In: NWWA/EPA Conf. on Surface and Borehole Geophysical Methods in Ground Water Investigations (San Antonio, TX), National Water Well Association, Dublin, OH, pp. 130-149.

Quinlan, J.F. 1986. Discussion of "Ground Water Tracers" by Davis et al. (1985) with Emphasis on Dye Tracing, Especially in Karst Terranes. Ground Water 24(2):253-259 and 24(3):396-397 (References).

Quinlan, J.F. 1989. Ground-Water Monitoring in Karst Terranes: Recommended Protocols and Implicit Assumptions. EPA 600/X-89/050, EMSL, Las Vegas, NV.

Quinlan, J.F. and R.O. Ewers. 1985. Ground Water Flow in Limestone Terrains: Strategy Rationale and Procedure for Reliable, Efficient Monitoring of Ground Water Quality in Karst Areas. In: Proc. Fifth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, Dublin, OH, pp. 197-234.

Ray, R.G. 1960. Aerial Photographs in Geologic Interpretation and Mapping. Geological Survey Professional Paper 373, 230 pp.

Robinson, P.C. 1984. Connectivity Flow and Transport in Network Models of Fractured Media. DP 1072. Theoretical Physics Division, AERE, Harwell, U.K.

Schmelling, S.G. and R.R. Ross. 1989. Contaminant Transport in Fractured Media Models for Decision Makers. EPA Superfund Ground Water Issue Paper. EPA/540/4-89/004.

Schwartz, F.W., L. Smith, and A.S. Crowe. 1983. A Stochastic Analysis of Macroscopic Dispersion in Fractured Media. Water Resources Research 19:1253-1265.

Shapiro, A.M. 1987. Transport Equations for Fractured Porous Media. In: Advances in Transport Phenomena in Porous Media, J. Bear and M.Y. Corapcioglu (eds.), NATO Advanced Study Institutes Series E, Vol. 128, Martinus Nijhoff Publishers, Dordrecht, The Netherlands, pp. 407-471.

Shapiro, A.M. 1989. Interpretation of Oscillatory Water-Level Responses in Observation Wells During Aquifer Tests in Fracture Rock. Water Resources Research 25(10>2129-2138.

Shimo, M. and J.C.S. Long. 1987. A Numerical Study of Transport Parameters in Fracture Networks. In: Flow and Transport through Unsaturated Fractured Rock, D.D. Evans and T.J. Nicholson (eds.), AGU Monograph 42, American Geophysical Union, Washington, DC, pp. 121-131.

Smith, L. and F.W. Schwartz. 1984. An Analysis of Fracture Geometry on Mass Transport in Fractured Media. Water Resources Research 20:1241-1252.

Smith, L., C.W. Mase, and F.W. Schwartz. 1985. A Stochastic Model for Transport in Networks of Planar Fractures. In: Greco 35 Hydrogeologie, Ministere de la Recherche et la Technologies Centre Nationale de la Recherche Scientifique, Paris.

Streltsova, T.D. 1988. Well Testing in Heterogeneous Formations. John Wiley & Sons, New York, 413 pp.

van der Kamp, G. 1976. Determining Aquifer Transmisivity by Means of Well Response Tests: The Underdampened Case. Water Resources Research 12(1):71-77.

Ward, D.S., D.C. Skipp, D.A. Giffin, and M.D. Barcelo. 1989. Dual-Porosity and Discrete Fracture Simulation of Ground Water Flow in West-Central Florida. In: NWWA Conference on Solving Ground Water Problems with Models (Indianapolis, IN), National Water Well Association, Dublin, OH, pp. 385-408.

Witherspoon, P.A., J.C.S. Long, E.L. Majer, and L.R. Myer. 1987. A New Seismic Hydraulic Approach to Modeling Flow in Fractured Rocks. In: Proceedings, NWWA/IGWMC Conference on Solving Ground-Water Problems with Models (Denver, CO), National Water Well Association, Dublin, OH, pp. 793-826.

Young, S.C. and W.R. Waldrop. 1989. An Electromagnetic Borehole Flowmeter for Measuring Hydraulic Conductivity Variability. In: Proc. Conf. on New Field Techniques for Quantifying the Physical and Chemical Properties of Heterogeneous Aquifers (Dallas, TX), National Water Well Association, Dublin, OH, pp. 463-474.

# Chapter 7
# Geochemical Characterization of the Subsurface: Basic Analytical and Statistical Concepts

J. Russell Boulding and Michael J. Barcelona

This chapter presents basic analytical and statistical concepts related to the measurement and interpretation of geochemical data on the natural and contaminated subsurface environment. Many expensive geochemical investigations suffer because analytical and statistical variability may have been ignored or not fully appreciated in the sample design and collection phase. Consequently, these analytical and statistical concepts are covered here before the chapters on the subsurface geochemical variability (Chapter 8), and the best methods for sampling the subsurface to characterize this variability (Chapter 9). In the normal sequence of events, laboratory amlysis and data interpretation come after sample collection. However, because they should be carefully considered in the design of geochemical investigations they are presented here first.

## 7.1 Data Measurement and Reliability

### *7.1.1 Deterministic versus Random Geochemical Data*

Observation or measurement of physical phenomena can be broadly classified as either deterministic or nondeterministic. Deterministic data can be described by an explicit mathematical relationship. Nondeterministic or random data, must be described in terms of probability statements and statistical averages rather than by the use of explicit equations. Figure 7-1 summarizes a classification scheme for deterministic and random data from Bendat and Piersol (1986). The classification of physical data as deterministic or nondeterministic is not always clear-cut in the real world. In fact, most geochemical data probably fail in a gray area between the two types of data. For example, the total dissolved solids in an aquifer is a function of the chemical composition of the aquifer solids and residence time of the flowing ground water. Consequently, the distribution of sample values over space and time will not be completely random. On the other hand, the factors that determine the precise value of a given sample are sufficiently complex and variable that the distribution often cannot be predicted by an explicit mathematical equation.

The transient, nonperiodic data box in Figure 7-la is a residual category that includes all data not included in the other boxes, This nonperiodic characteristic of geochemical data allows modeling of the distribution of geochemical species using thermodynamic principles. Essentially all geochemical modeling of the subsurface is done deterministitally. The difficulty in accurately modeling the geochemistry of the subsurface can, however, be attributed to large random elements (see Figure 7-lb). Depending on the geochemical parameter, and the time frame of sampling, data may be stationary, where characteristics of the population being sampled do not vary over time, or nonstationary, where the random process varies with time. Typically, geochemical subsurface data invoIving contamination are nonstationary, but are not fully random (i.e., the value of one sample may show some correlation with the value of an adjacent sample). This creates special considerations in statistical analysis that are discussed in Section 7.3. Subsurface physical parameters such as hydraulic conductivity, porosity, and soil particle size distribution do not typically change with time, at least not on a time scale of human concern. These parameters, however, are not fully random.

### *7.1.2 Data Representativeness*

In measuring environmental parameters, there is no “true” value, but rather a distribution of values. A representative unit or sample is one selected for measurement from a target population so that it, in combination with other representative samples, will give an accurate picture of the phenomena being studied (Gilbert, 1987). Failure to take samples from locations and to use methods that yield samples that are “representative” of a site will result in the collection, at some expense, of analytical data that may be worthless. Representativeness determines whether accurate analysis of the samples will yield results that are close to actual conditions. Quality assurancd quality control systems (QA/QC) in the laboratory or field may be useless if even greater emphasis isn’t placed on QA/QC in selecting locations and procedures for sampling.

Thorough site characterization of soils, hydrology, and geology, as described in the previous chapters, is an essential prerequisite to geochemical sampling. This information provides the basis for developing sampling strategies that will provide some assurance that geochemical samples accurately reflect what is happening in the field. Sample representativeness is essentially knowledge-based. For example, sampling locations selected by someone with a rudimentary understanding of sampling theory may yield less accurate results

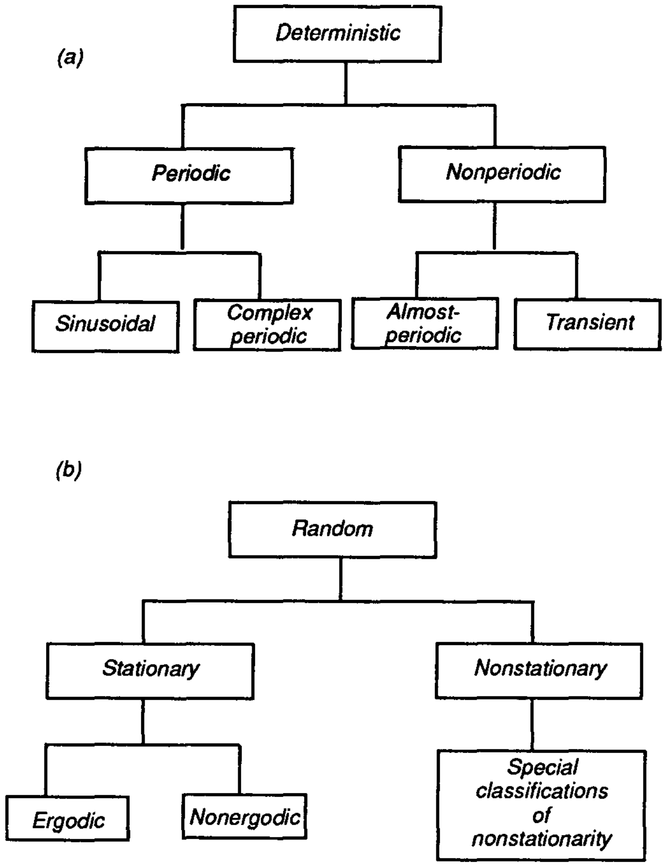


**Figure 7-1.** Classifications of (a) deterministic and (b) random data (from Bendat and Piersol, 1986).

than locations chosen by an individual thoroughly grounded in this theory. At the same time, sampling locations selected without careful site characterization will yield less representative samples than locations selected with thorough site characterization even with equally sophisticated application of sampling theory. See Section 9.1 for general considerations in designing sampling plans.

In contamination investigations, obtaining samples that can be considered representative for assessing one or more particular kinds of environmental exposure is a primary objective. This requires selecting not only the right place, but the right type of sample (see discussions of analyte selection in Sections 9.2.1 and 9.3.1).

### *7.1.3 Measurement Bias, Precision, and Accuracy*

A measured value that is close to the estimate of the true average value is an unbiased or accurate value. This average or mean can only be estimated by a number of repeat determinations. Biased measurements will consistently under- or overestimate the true values in sampled population units. Precision is a measure of how closely individual measurements agree and is influenced principally by random measurement uncertainties. Both bias and precision influence accuracy as illustrated in Figure 7-2. The center of each target in the figure represents that true value. Both low bias and high precision are required for high accuracy.

Accuracy is largely technologically based. In other words, accuracy can be improved by better drilling and monitoring well installation procedures and better sampling devices and procedures. Pennino (1988) has suggested that "there is no such thing as a representative ground water sample" because of geochemical biases inherent in well installation, purging, and sample collection. However, a good understanding of both potential sources of error (see next section) and the way alternative sampling methods may bias results (see Section 9.3) minimizes sample disturbance. The final evaluation of the results should be done with full consideration of the unavoidable disturbances involved in subsurface investigations.

### *7.1.4 Sources of Error*

Random error results from slight differences in the execution of the same sampling procedure. Systematic error results from procedures that alter the properties of the sample. Random error is unavoidable, but must be evaluated to determine its effect on accuracy. For example, Figure 7-2b shows data with no systematic bias, but accuracy is low because random error is high. Systematic errors can be minimized by careful selection and conduct of sampling techniques.

Figure 7-3 illustrates five possible sources of error in ground-water sampling: (1) site selection, (2) sampling,

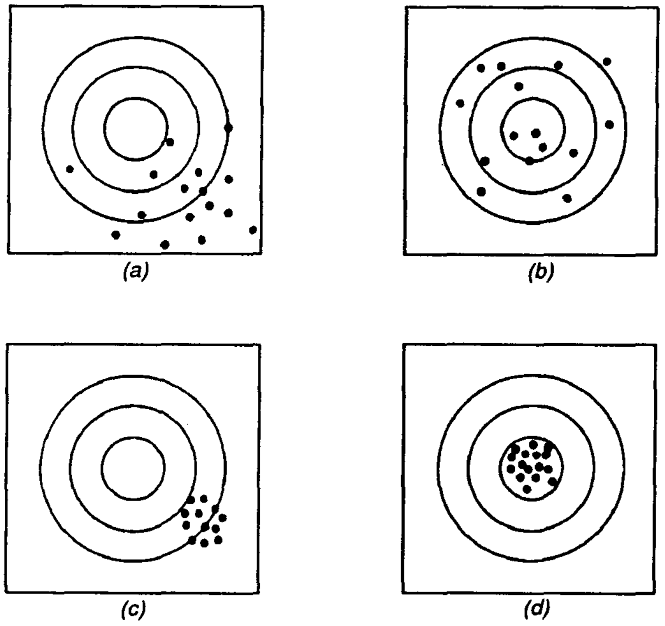
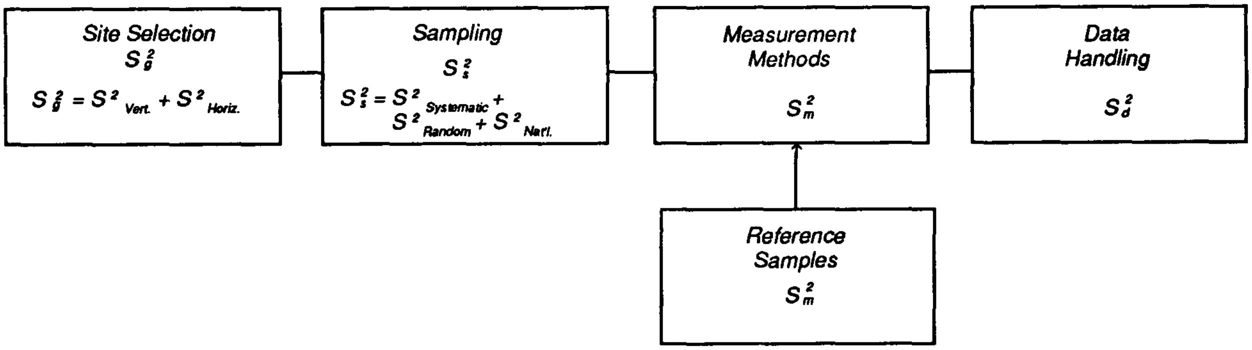


**Figure 7-2.** Shots on a target analogy for illustrating influence of bias and precision on accuracy (after Jessen, 1978).
(a): high bias + low precision= low accuracy; (b): low bias + low precision = low accuracy; (c): high bias + high precision = low accuracy; (d) low bias + high precision = high accuracy.



*Thus the overall variance* $= S^2 = S_g^2 + S_s^2 + S_m^2 + S_r^2 + S_d^2$

**Figure 7-3. Sources of error involved in ground-water monitoring programs contributing to total variance (from Barcelona et al., 1983).**

(3) measurement methods, (4) reference samples for calibration, and (5) data handling. Both random and systematic errors may be involved in each stage. Errors at each stage are cumulative, but are not of equal significance or magnitude. Total variance in geochemical data results from the combination of natural geochemical variability and the cumulative error. The percentage of variance attributable to natural variability may often be greater than either field or laboratory error. Natural variance cannot be reduced; however, variance resulting from field and laboratory error can be reduced so that the actual variance closely approximates the natural variance.

Table 7-1 shows estimates of the relative contribution of natural variability, field error, and laboratory error to total variance at three sites of ground-water investigations. For most chemical constituents, at the three sites, natural variability accounted for more than 90 percent of the variance. For most inorganic constituents where field and laboratory error could be estimated, field error contributed a larger percentage of total variance. Table 7-1 also shows that organic contaminant indicators (TOC and TOX) showed typically much higher percentages of variance due to field and laboratory error than did the inorganic indicators. Both field sampling and laboratory analyses were subject to strict QA/QC procedures at the sites shown in Table 7-1, so variance due to field and laboratory error during routine ground-water investigations will commonly be greater than shown in the table.

*Field Error.* Figure 7-4 identifies specific possible sources of error at various steps in ground-water sampling. The largest sources of error are unrepresentative sample locations (hence the importance of hydrogeologic site characterization prior to geochemical sampling design) and disturbances caused by drilling and well construction. Sample collection is the next largest source of error. Major sources of systematic sampling error include (1) well construction and screen design preventing representative samples, and (2) improper purging. All of these large sources of systematic error are related to the hydrology of the site over which there is often little QA/QC.

Table 7-2 lists potential contributions of sampling methods and materials to error in ground-water chemical results. This table shows that well purging procedures can result in large variations in pH, TOC, Fe(II), and VOCs (also see Table 9-11 for variations in other constituents). Table 7-2 shows well casing to be the next largest source of error, followed by sampling mechanisms and grouting/sealing. Poorly grouted or cemented wells can greatly alter the pH of water (as much as pH 12). Sampling tubing can result in errors in VOC measurement. Sections 9.3.3 (Purging) and 9.3.4 (Well Construction and Sampling Devices) discuss selection criteria for minimizing error from these sources.

Other possible sources of systematic error in sampling include (1) changing sampling procedures, (2) changing sampling personnel without a strictly defined sampling protocol, and (3) failure to document unavoidable deviations from the sampling protocols, such as no water in the well. Another source of water quality error is mixing from multiple aquifers. Mixing is most common with public water supply wells that penetrate several hydrological unconnected aquifers. Improper sealing of ground-water monitor wells also may bias results by mixing water from distinct subsurface formations.

*Analytical Error.* Figure 7-5 identifies possible sources of error during water sample analysis. Analysis, including measurement methods and reference samples, is typically subject to the most stringent QA/QC procedures, and consequently analytical errors tend to be relatively minor components of total error (see Table 7-l). Failure to analyze blanks, standards, and samples by exactly the same procedures may result in either a biased blank correction or a biased calibration (Kirchmer, 1983). Porter (1986) examined in detail the sources of random analytical error for measurement near the limit of detection and how to incorporate this observation error into data analysis procedures. Sources of analytical error are discussed further in Section 7.3.

Einarson and Pei (1988) and Rice et al, (1988), in separate studies of laboratory performance, concluded that the reliability of laboratory analyses should not be taken for granted. Both studies also concluded that the cost of analysis did not necessarily correlate with analytical accuracy. The most expensive of the 10 laboratories evaluated by Einarson

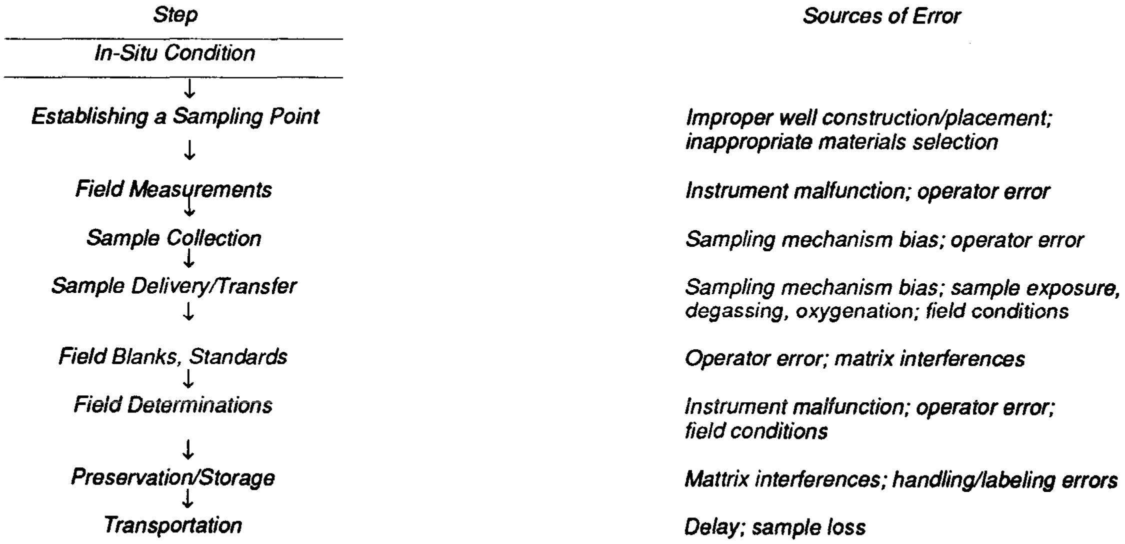
*Table 7-1. Percentage of Variance Attributable to Laboratory Error, Field Error, and Natural Variability by Chemical and Site*

| Type of parameter | Sand Ridge |  |  | Beardstown (upgradient) |  |  | Beardstown (downgradient) |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | lab | field | nat | lab | field | nat | lab | field | nat |
| **Water quality** |  |  |  |  |  |  |  |  |  |
| $NO_3^-$ | 0.0 | 00.0 | 100.0 | 0.1 | NA[a] | 99.9 | 0.2 | NA | 99.8 |
| $SO_4^=$ | 0.0 | 0.0 | 100.0 | 0.2 | NA | 99.8 | 1.4 | 0.1 | 98.6 |
| $SiO_2$ | 0.0 | NA | 100.0 | 0.0 | 20.0 | 80.0 | 0.0 | 6.8 | 93.2 |
| $o\text{-}PO_4^=$ | 1.2 | 1.2 | 97.6 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 | 100.0 |
| $T\text{-}PO_4^=$ | 0.0 | NA | 100.0 | 2.8 | NA | 97.8 | 0.9 | NA | 99.1 |
| $Cl^-$ | 7.2 | NA | 92.8 | 0.0 | 3.3 | 96.7 | 0.0 | 17.2 | 82.8 |
| Ca | 0.0 | 45.7 | 54.3 | 0.0 | 2.3 | 97.7 | 0.0 | 3.6 | 96.4 |
| Mg | 0.0 | 20.0 | 80.0 | 0.0 | 2.2 | 97.8 | 0.0 | 2.8 | 97.2 |
| Na | 0.0 | NA | 100.0 | 0.0 | 0.3 | 99.7 | 0.0 | 7.1 | 92.9 |
| K | 0.0 | NA | 100.0 | 33.9 | NA | 66.1 | 87.1 | NA | 12.9 |
| **Geochemical** |  |  |  |  |  |  |  |  |  |
| $NH_3$ | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | 0.0 | 100.0 |
| $NO_2^-$ | NA | NA | NA | 0.1 | NA | 99.9 | 0.3 | NA | 99.7 |
| $S^=$ | NA | NA | NA | NA | NA | NA | NA | NA | NA |
| $Fe^{+2}$ | NA | NA | NA | 0.0 | 0.1 | 99.9 | 0.0 | 5.9 | 94.1 |
| $Fe_T$ | 0.0 | NA | 100.0 | 0.0 | 0.0 | 100.0 | 0.0 | NA | 100.0 |
| $Mn_T$ | 0.0 | NA | 100.0 | 0.0 | 40.1 | 59.9 | 0.0 | 73.6 | 26.4 |
|  | lab + field[b] |  |  | lab + field |  |  | lab + field |  |  |
| **Contaminant indicator** |  |  |  |  |  |  |  |  |  |
| TOC | 15.4 |  | 84.6 | 29.9 |  | 70.1 | 40.6 |  | 59.5 |
| TOX | 0.0 |  | 100.0 | 12.5 |  | 87.5 | 24.6 |  | 75.4 |

[a] NA indicated that the number of observations on which the estimated variance was based was less than 5, or the estimated variance was negative.

[b] True field spiked standards not available for these costituents demanding combined estimates of laboratory and field variability.

Source: Barcelona et al. 1989



| Step | Sources of Error |
|---|---|
| In-Situ Condition |  |
| Establishing a Sampling Point | Improper well construction/placement; inappropriate materials selection |
| Field Measurements | Instrument malfunction; operator error |
| Sample Collection | Sampling mechanism bias; operator error |
| Sample Delivery/Transfer | Sampling mechanism bias; sample exposure, degassing, oxygenation; field conditions |
| Field Blanks, Standards | Operator error; matrix interferences |
| Field Determinations | Instrument malfunction; operator error; field conditions |
| Preservation/Storage | Mattrix interferences; handling/labeling errors |
| Transportation | Delay; sample loss |

**Figure 7-4. Steps in ground-water sampling and sources of error (from Barcelona et al., 1985).**

*Table 7-2. Potential Contributions of Sampling Methods and Materials to Error” in Ground-Water Chemicail Results*

| | | Chemical Parameter | | |
|---|---|---|---|---|
| *Sampling method/ material* | *pH* | *TOC (mg C/L)* | *Fe(II) (mg/L)* | *VOC (µg/L)* |
| *Range of concentration* | *5-9* | *0.5-25* | *0.01-10* | *0.15-8000* |
| *Drilling muds* | --- | *+, 300%* | --- | --- |
| *Grouts, seals* | *+, 4 to 5 units (cement)* | --- | *-,[b] 500% cement* | --- |
| *Well purging* | *±, 0.1 to 5 units* | *±, 500%* | *-,[b] 1000%* | *±, 10 to 1000%[c]* |
| *Well casing* | --- | *±, 200%* | *+, 1000% iron, galvanized steel* | *±, 200%[c]* |
| *Sampling mechanism* | *gas lift +, 0.1 to 3 units* | *bailer +, 150%* | *gas lift -,[b] 500%* | *suction -,[b] 1 to 15%[d]* |
| *Sampling tubing* | --- | --- | --- | *-10 to 75%[d]* |
| *References* | *1,5,7* | *1,4* | *1,2,5,7* | *1,3,6* |

[a] *Bias values exceeding >± 100% denoted as gross errors (+ or -): other values expressed as percent of reported mean.*
[b] *No data available on the type and extent of error for this parameter.*
[c] *Concentration range 0.5-15 µg/L (from Barcelona and Helfrich, 1984).*
[d] *Concentration range 80-8000 µg/L (from Barcelona et al., 1984; Ho, 1983).*

1 *Barcelona and Helfrich (1984)*
2 *Barcelona et al. (1983)*
3 *Barcelona et al. (1984)*
4 *Barcelona et al. (1988)*
5 *Gibbet al. (1981)*
6 *Ho (1983)*
7 *Schuller et al. (1981)*

*Source: Adapted from Barcelona et al. (1988)*

and Pei (1988) tied for the worst ranking, while the four least expensive laboratories included the top ranked and other bottom ranked laboratory. Both studies describe criteria and procedures for choosing laboratories that will provide good analytical results. Section 7.3 discusses analytical and QA/QC concepts further.

*Data Handling Error.* There is probably no large body of scientific records free from human or machine errors. Faulty recording of observations in field or laboratory notebooks or incorrect coding for computer analysis are examples of data handling errors. Misrecorded values that are much larger or smaller than the range of the actual population are called outliers and may distort the results of statistical analysis. Statistical techniques are available for analyzing such data sets (Gilbert, 1987), but prevention of data handling error is always better than a cure. Censoring of analytical measurements below the limit of detection (see Section 7.4.1) is another serious error introduced by data handling.

Webster (1977) suggests some of the following methods to reduce data handling errors: (1) write neatly, forming characters well; (2) distinguish ambiguous digits and letters by a firm convention; (3) restrict the digit O to mean zero and use other notations for “missing” or “inapplicable”; (4) eliminate or minimize transcription of field notes (5) record data on forms designed for the purpose of the investigation with clear headings and ample space; and (6) double-check any transcribed data against the original

## 7.2 Analytical and QA/QC Concepts

Quality assurance and quality control are accomplished by (1) selecting the best methods for the program purpose, (2) clearly defining protocols or procedures to be followed, and (3) carefully documenting adherence or departures from the protocols. Figure 7-6 shows the relationship of program purpose and protocols to the scientific method. Both field sampling and laboratory analyses require protocols for good QA/QC. Campbell and Mabey (1985) have summarized key ele-

| *Step* | *Sources of Error* |
|---|---|
| *Samples, from Storage Field Blanks and Standards* | *"Aged" samples; loss of analyties; contamination* |
| *Subsampling* | *Sample aging/contamination in lab; cross-contamination; mishandling/labeling* |
| *Procedural Standards* | *"Aged" standards; analyst error* |
| *Analytical Separation* | *Matrix interferences; inappropriate/ invalid methodology; instrumental malfunction/analyst error* |
| *Analysis* | *Matrix interferences; inappropriate/ invalid methodology; instrumental malfunction/analyst error* |
| *Reference Standards* | *"Aged" standards* |
| *Calculations* | *Transcription/machine errors; sample loss in tracking system; improper extrapolation/ interpolation; over-reporting/ under-reporting errors* |
| *Results* | |

**Figure 7-5.** **Steps in water sample analysis and sources of error (from Barcelona et al., 1985).**

ments of data evaluation systems applicable to both field and laboratory measurements. Provost and Elder (1985) have provided guidance for choosing cost-effective QA/QC programs for chemical laboratories. Evans (1986) reviews data quality objectives for remedial site investigations, and Starks and Flatman (1991) discuss the use of industrial quality control methods as a model for evaluating RCRA ground-water monitoring decision procedures.

### *7.2.1 Instrumentation and Analytical Methods*

A bewildering array of methods are available for analyzing geochemical constituents. Table 7-3 lists the major signals and analytical methods based on signal measurement. Most methods used for geochemical analysis involve either emission or adsorption of radiation. The fine points of instrumentation and analysis are the province of the analytical chemist, but the field scientist can benefit from a general understanding. Skoog (1985) and Willard et al. (1988) are two good general references on this topic. Analytical techniques for specific constituents of geochemical interest may be specified by regulation or, if not so specified, determined by the instrumentation that is most readily available. Table 7-4 lists seven major sources of information describing analytical techniques for specific chemical constituents.

### *7.2.2 Limit of Detection*

Ground-water detection monitoring commonly involves measurement of contaminants that are either at or below the detection limit of analytical procedures. The statistical concept of detection limit includes accurately reporting and analvzing data including measurement near or below the detection limit (McNichols and Davis, 1988).

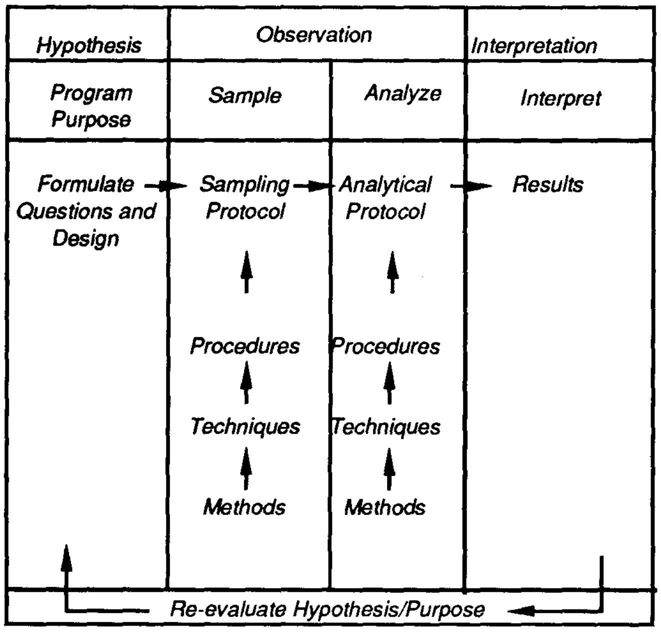


**Figure 7-6.** **Relationship of program purpose and protocols to the scientific method (from Barcelona, 1988).**

**Table 7-3. Major Analytical Signals and Methods**

| *Signal* | *Analytical Methods Based on Measurement of Signal* |
|---|---|
| *Emission of radiation* | *Emission spectroscopy (X-ray, UV, visible electron auger); fluorescence and phosphorescence spectroscopy (X-ray, UV, visible); radiochemistry* |
| *Absorption of radiation* | *Spectrophotometry (X-ray, UV, visible, IR); photoacoustic spectroscopy; nuclear magnetic resonance and electron spin resonance spectroscopy* |
| *Scattering of radiation* | *Turbidimetry; nephelometry; Raman Spactroscopy* |
| *Refraction of radiation* | *Refractometry; interferometry* |
| *Rotation of radiation* | *Polarimetry; optical rotatory dispersion; circular dichroism* |
| *Electrical potential* | *Potentiometry; chronopotentiometry* |
| *Electrical current* | *Polarography; amperometty; coulometty* |
| *Mass-to-charge ratio* | *Mass Spectrometry* |
| *Rate of reaction* | *Kinetic methods* |
| *Thermal properties* | *Thermal conductivity and enthalpy methods* |
| *Mass* | *Gravimetric analysis* |
| *Volume* | *Volumetric analysis* |

[a] *Source: Skoog (1985)*

Figure 7-7 and Table 7-5 illustrate the definitions of limit of detection and regions of analyte measurement recommended by the Subcommittee on Environmental Analytical Chemistry of the American Chemical Society's (ACS) Committee on Environmental Improvement (1980). The zero analyte signal for measuring the limit of detection comes from the field blank (see Section 7.2.3). If the actual field blank measurement gives a positive signal, this means that analytical measurements on other samples with a lower signal will be recorded as a negative concentration. For example, a low concentration standard (typically 1 part per billion (ppb) for organic constituents) is made in the laboratory for the contaminant of interest. The standard deviation for analytical measurement of the 1 ppb standard is commonly plus or minus 100 percent or 1 µg/L. The detection limit for a contaminated sample is defined as three standard deviations (3 µg/L) above the mean for the standard, or six standard deviations above the zero point defined by the field blank (see Figure 7-7). The limit of detection should be defined every day of analysis. The detection limit is probably the most important kind of laboratory quality assurance data and should be reported with the analytical results for each constituent.

Table 7-5 lists the regions of analyte measurement. Following the above example, signals below three standard deviations are considered below the limit of detection. The region of detection is between 3 and 10 standard deviations (5 standard deviations by some rules) and is where the constituent can be said to be present but the precise concentration cannot be stated with certainty. Analyte signals above the limit of quantification (plus 10 standard deviations) can be interpreted quantitatively.

The above-described definition reaffirms the model for limit of detection calculations adopted by the International Union of Pure and Applied Chemistry (IUPAC) in 1975 (IUPAC, 1978). However, considerable confusion still surrounds the definition of the limit of detection. This is because (1) acceptance of the above definition by the general analytical community has been slow, and (2) different statistical approaches to calculating limits of detection for constituents can easily vary by an order of magnitude (Long and Winefordner, 1983). This is particularly true for chemical constituents at the ppb level.

A major problem with failure to understand the statistical nature of the limit of detection is negative censoring of data. Negative censoring involves reporting analyte concentrations that are below the limit of detection as zero, "less than" values, or "not detected." Since 1983 the American Society for Testing and Materials (ASTM) has recommended that data should not be routinely censored by laboratories (ASTM, 1983). Nevertheless, censoring of water quality analytical data remains a problem (Porter et al., 1988). Section 7.4.1 examines this issue further.

Laboratories should be asked to provide uncensored data on all water samples with measurements near or below the limit of detection. Measurement data should not be discarded unless the lack of statistical control in the measurement process is clearly demonstrated. The general public, and even the uninformed scientist, may find the concept of a negative concentration difficult to understand, so it is prudent to report less than zero values as "trace." Remediation decisions, however, should be based on concentrations at or above the limit of quantification, not the limit of detection.

The limit of detection is both a site- (as a result of the field blank) and instrument/operator-specific value. Consequently, the precision and accuracy for low standards must be reported on the analytical report forms. The instrument manufacturer's definition of detection is based normally on carefully controlled conditions (e.g., distilled water solutions) that may not be achievable in routine analyses of complex samples. Consequently, actual limits of detection in contaminated ground water are often higher.

### *7.2.3 Types of Samples*

Field scientists tend to consider QA/QC requirements and procedures to be primarily the responsibility of the laboratory. However, QA/QC procedures are equally, if not more important in the field. Chapter 8 examines methods to minimize error in selecting sample location and collecting samples. Field personnel also should be familiar with the different types of samples that may be taken, and their importance for interpreting the analytical results.

***Table 7-4. Major Compilations* of *Analytical Procedures for Constituents of Geochemical interest***

| *Reference* | *Description* |
|---|---|
| *American Public Health Association (1990)* | Comprehensive compilation of analytical methods for measurement of metals, inorganic nonmetallic, and organic constituents in water samples. |
| *ASTM, annual* | Published annually by the American Society for Testing and Materials, Water and Environmental Technology Volumes 11.01and 11.02 cover analytic methods for water. |
| *Fresenius et al. (1988)* | A guide to physico-chemical, chemicaland microbiological analysis of water and qualify assurance procedures. |
| *Klute (1986), Page et al. (1982)* | Part 1 (Klute, 1986) contains 50 chapters covering a range of physical and mineralogical methods and Part 2 (Page et al., 1982) contains 54 chapters covering methods for analyzing chemical and microbiological properties of soils. |
| *Kopp and McKee (1983)* | This third edition contains the chemical analytical procedures used in U.S. EPA laboratories for examining ground and surface water, domestic and industrial waste effluents and treatment process samples. |
| *Longbottom and Lichtenberg (1982)* | Describes tests for 15 groups of organic chemicals and includes an appendix defining procedures for determining the detection limit of an analytic method. The test procedures in this manual are cited in Table IC (organic chemical parameters) and ID (pesticide parameters) in 40 CFR 136.3(a). |
| *Mueller et al. (1991)* | Compilation of summary information on more than 150 EPA-approved, and a total of 650, sampling and analysis methods for industrial chemicals, pesticides, elements, and water quality parameters. Associated data base is available on diskette. |
| *Noblett and Burke (1990) Radian Corporation (1988)* | Handbook on flue gas desulfurization (FGD) chemistry and analytical methods. Volume 1 (Noblett and Burke, 1980) covers sampling, measurement, laboratory, and process performance guidelines. Volume 2 (Radian Corporation, 1988) presents 54 physical-testing and chemical-analysis methods for FGD reagents, slurries, and solids. |
| *Rainwater and Thatcher (1960)* | Describes types of methods, choice of analytical methods for water samples, and specific analytical procedures for over 40 inorganic water parameters. |
| *Smith (1991)* | Edited volume with 14 chapters on instrumental techniques for soil analysis. |
| *Thompson et al. (1989)* | Contains summary description of methods for elemental analysis, analysis of anionic species, inorganic and organic carbon, redox sensitive species and other chemical parameters along with recommendations for methods best suited for obtaining data for hydrochemical modeling. |
| *U.S. EPA (1988)* | *Guide for selection of instrumental methods for field screening of inorganic and organic contaminants. Covers 26 specific field screening methods. Also available as a computerized information retrieval system.* |
| *U.S. Geological Survey Techniques of Water-Resource Investgations* | *USGS's TWI series includes manuals describing procedures for planning and conducting specialized work in water-resources investigations. Wood (1976) covers field analysis of unstable constituents; Skougstad et al. (1979) cover methods for analyzing inorganic constituents in water and fluvial sediment; Barnett and Mallory (1971) describe determination of minor elements in water by emission spectroscopy: Wershaw et al (1987) cover methods for determination of organic substances in water and fluvial sediments (revision of Goerlitz et al., 1972).* |
| *Westerman (1990)* | *Edited volume on methods for analysis of soil and plants focussing on use for assessing nutritional requirements of crops, efficient fertilizer use, saline-sodic conditions, and toxicity of metals.* |

A *field blank is* a sample of distilled or deionized water taken from the laboratory out into the field, poured into a sampling vial at the site, closed, and returned as if it were a sample. The level of contamination of the field blank is the zero analyte signal for determining the limit of detection,

A *rinse or cleaning blank* is a sample of the final rinse of a sampling mechanism before it is put in a new well. This type of sample is used to evaluate whether a sample may have been contaminated from material taken in the previous sample.

*Field samples* are those samples that are taken in the field as "representative" of conditions at the site and analyzed in the laboratory for constituents of interest. If sampling points or locations are unrepresentative, or biased sampling procedures are used, no amount of care in QA/QC in subsequent stages will salvage an accurate picture of actual field conditions.

*Duplicate samples* are collected and not analyzed unless it is later determined that they contain additional useful information. Soil samples are commonly duplicated.

*Replicate samples* are subsamples of the same sample that are labeled separately to estimate the precision of laboratory analytical results.

*Split samples are* field samples that are split between two storage vessels or cut in half in the field. One subsample may be analyzed by one laboratory and the other subsample may be archived or given to another laboratory,

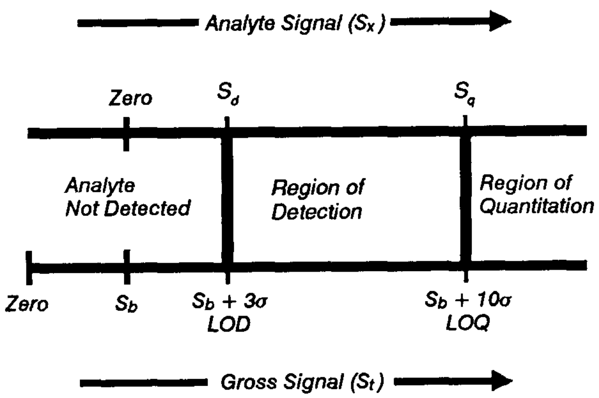


**Figure 7-7. The ACS recommended definition of limit of detection (from ACS Committee on Environmental Improvement, 1980).**

*Spiked samples* are field samples that may be split with one aliquot receiving a spike volume of a reference standard to estimate the recovery of the analyte in the laboratory. Spiked samples allow estimates of accuracy and detect possible matrix interference problems.

*Laboratory blanks* are similar to field blanks except that the distilled deionized water used in the laboratory at the time each batch of samples is received is analyzed in the same manner as other samples. This type of sampling may detect contamination that occurs in the laboratory.

*Standard reference samples* have been analyzed previously by outside laboratories. These samples are available from the National Institute of Standards and Technology or the EPA to detect either instrument calibration error or the use of inappropriate laboratory analytical methods (Keith et al., 1983).

## 7.3 Statistical Techniques

### 7.3.1 Statistical Approaches to Geochemical Variability

Virtually all soil sampling and most ground-water sampling that has been done at a high enough level of resolution have shown that chemical constituent concentrations are neither normally distributed nor independent (i.e., noncorrelated). This creates special challenges for statistical analysis of geochemical sampling data because many of the traditional statistical techniques for analyzing sample data, such as linear regression and t-testing, assume that the population sampled has the symmetric, bell-shaped Gaussian (normal) distribution. Linear regression is probably the most frequently misused statistical technique in this context (Mann, 1987; Kite, 1989).

*Table 7-5. Regions of Analyte Measurement*

| *Analyte Signal (standard deviations in µg/L)* | *Recommended Inference* |
|---|---|
| *<3* | *Analyte not detected* |
| *3 to 10* | *Region of detection* |
| *>10* | *Region of quantitation* |

*Source: ACS Committee on Environmental Improvement (1980)*

The first step in analyzing geochemical data is to determine whether they are normally distributed. If they are, traditional techniques described in standard textbooks on statistics can be used. If not, one or more of the following methods must be used (1) data transformations such as logarithmic conversions to create data sets that are normally distributed and hence amenable for analysis by conventional methods (Wilson et al., 1990, discuss how to evaluate bias that may be introduced by this manipulation); (2) nonparametric or distribution-free statistical techniques that do not require independent data observations and (3) geostatistical techniques that facilitate differentiation of correlated and noncorrelated data sets and interpolation of values between sample points. The technique of “fuzzy” linear regression maybe useful in hydrologic situations where the relationship between variables is imprecise, data are inaccurate, and/or sample sizes are insufficient (Bardossy et al., 1990). Subsurface contamination investigations typically involve measurements of concentration changes in geochemical parameters over time. Consequently, statistical techniques designed specifically for analysis of trends in time-series data are important (Harris et al., 1987; Montgomery et al., 1987).

Alhajjar et al. (1990) describe use of the median-polish statistical methods of exploratory data analysis developed by Tukey (1977) for analyzing highly variable geochemical data collected during a study of chemical pollution from septic systems. This technique is especially well suited for analyzing data in two-way tables (multiple rows and columns) in which each data value is related simultaneously to two factors.

### 7.3.2 Geostatistics

Geostatistical techniques such as use of correlograms, semivariograms, and kriging have gained increasing popularity in evaluating spatially distributed hydrologic and geochemical data in the last 10 years. Using empirical gold-ore evaluation techniques developed by D.C. Krige in South Africa (hence the term kriging), the French mathematician G. Matheron developed the theory of regionalized variables in the late 1960s (Matheron, 1971). This general theory of sampling and estimating spatially dependent (autocorrelated) variables is well suited to analysis of hydrologic and geochemical parameters, which tend to be nonrandom in the classical Gaussian statistical sense.

Geostatistical techniques have three main applications for characterization of subsurface variability: (1) they can assist in reducing spatial sampling intensity, and hence reduce sampling and analytical costs; (2) they can be used to differentiate sample data that are autccorrelated or noncorrelated, elucidating trends for selecting the appropriate statistical analysis of sampling analytical results; and (3) they can be used to interpolate values at locations where measurements have not been made. The last application is done by kriging, a weighted moving-averaging technique, that in most situations will pro vide the most accurate way of contouring data on physical and geochemical parameters. Furthermore, a kriging standard deviation map that provides a clear indication of the reliability of contours can be readily created from kriged contour data.

One of the first steps in geostatistical analysis is to calculate the nonsampling variance (gamma) of samples at different distance spacings. Gamma is a statistical measure of the difference between sample values. For example, if samples were taken from a 50-m grid, gamma would be calculated for the samples spaced at 50 m, 100 m, 150 m, 200 m, and so on. Next, a semivariogram is plotted on a XY plot, where X is distance and Y is the nonsampling variance. Figure 7-8 shows an "ideal" semivariogram. Samples within a certain range of influence, also called the range of correlation (distance *a* in Figure 7-8), show an approximately linear correlation (are autocorrelated). At some spacing distance, if there is no trend in the data, a sill *(C* on Figure 7-8) marks a plateau that limits the range of correlation. The nonsampling variance between samples will equal *C* as long as the distance is greater than *a.*

From a sampling perspective, samples spaced closer than distance *a* in Figure 7-8 will yield redundant, correlated data, which results in both unnecessary expense and complications in statistical analysis. The minimum distance at which samples are independent (distance *a* in Figure 7-8) is the optimum sampling distance.

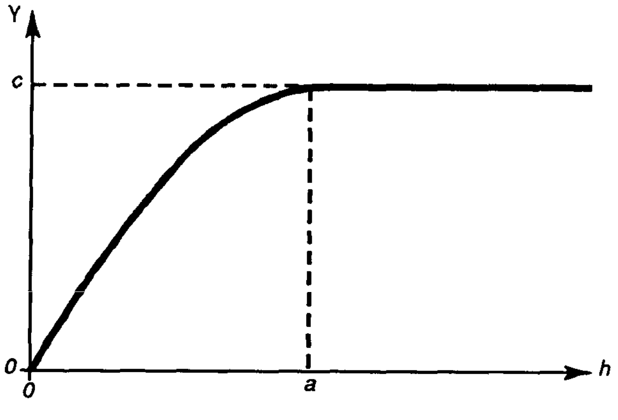


Figure 7-8. The '"ideal" shape for a semivariogram-spherical model (from Clark, 1979).

Figure 7-9 shows a semivariogram of lead values in soil sampled by Flatman (1986) on a systematic 750-ft grid. The diagram shows that samples for lead that are closer to each other than about 1,200 ft are correlated. In other words, the same information could be obtained by cutting the number of samples almost in half. Figure 7-10 shows a kriged contour map of lead concentrations in the vicinity of the smelter, and Figure 7-11 shows contours of the standard deviations of the lead concentrations.

Table 7-6 summarizes ranges of influence (in meters) that have been estimated for a variety of soil physical and chemical parameters. Direct comparisons between different studies are difficult, however, because definitions and the methodologies for determining the range vary somewhat. Commonly, however, the range is scale-dependent, i.e., as the sample area increases, the range increases. For example, at the same site Gajem et al. (1981) found ranges of 1.5,21, and 260 m for pH values of 100-member transects spaced at 0.2, 2, and 20 m.

Semivariograms may exhibit a variety of correlation structures other than the one shown in Figure 7-8, and correct interpretation requires an understanding of the various models that are available for describing semivariogram plots. When data are not normally distributed, such as when a spatial trend is present, estimating the correlation structure is difficult. In these cases, some of the techniques for transforming lognormal data for conventional statistical analysis can be used (Gilbert, 1987).

Most basic texts on geostatistics are still oriented towards mining. Clark (1979) provides a good introduction to geostatistics and kriging, while more comprehensive treatments (all oriented toward mining) can be found in the following sources: David (1977), Isaaks and Srivastava (1989), Matheron (1971), and Journal and Huijbregts (1978). Olea (1974, 1975) provide a good introduction to the use of geostatistics in contour mapping of data. Gilbert and Simpson (1985) provide a good review of potentials and problems with using kriging for estimating spatial pattern of contaminants

Trangmar et al. (1985) and Warrick et al. (1986) reviewed specific geostatistical methods applied to spatial studies of soil properties. Use of geostatistics in sampling for soil contaminants is discussed by Flatman (1984), Flatman and Yfantis (1984), and Flatman (1986). Delhomme (1978, 1979) reviewed the use of geostatistics in the characterization of ground-water variability, and Hughes and Lettenmaier (1981) and Sophocleous et al. (1982) discuss applications for groundwater monitoring network design.

## 7.4 Interpretation of Geochemical and Water Chemistry Data

Table 7-7 indexes some sources of information on (1) basic statistical approaches to data analysis, (2) methods for analysis of soil data, and (3) methods for analysis of water quality data. The general references on soil and water chemistry listed in Table 7-1 provide a framework for interpreting

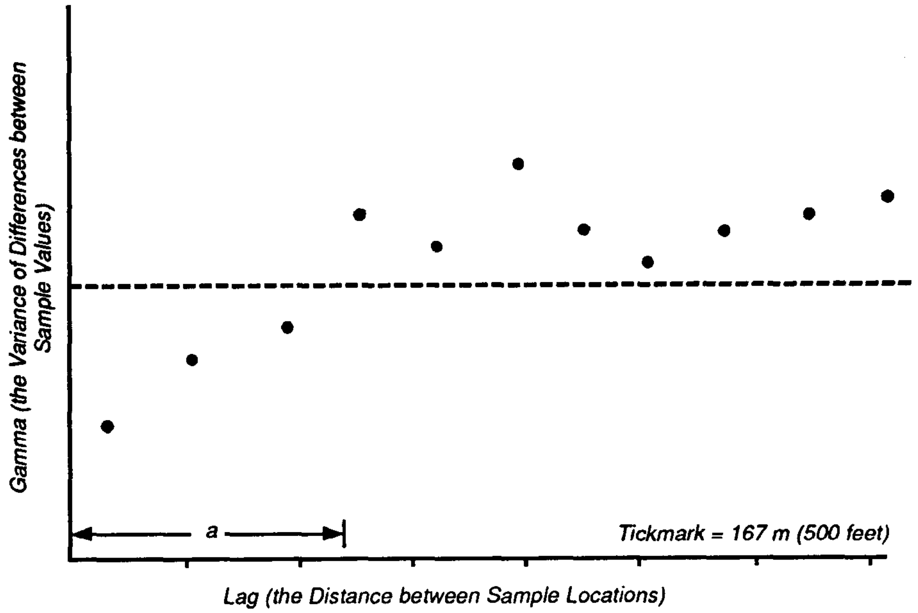


**Figure 7-9.** **A semivariogram of lead samples taken systematically on a 230-m (750-foot) grid (from Flatman, 1986).**

background geochemistry. Hem (1985) is an especially good source for the interpretation of water quality data.

Gilbert (1987) presented probably the best systematic treatment of statistical methods for environmental pollution monitoring. Bury (1975) provides a comprehensive treatment of basic statistical concepts and models oriented toward the applied scientist. Hollander and Wolfe (1973), Lehmann and D'Abrera (1975), and Seigel (1956) offer more in-depth discussion of nonparrametric statistical methods. Bury (1975) presents a table that is a useful guide for finding the appropriate nonparametric procedure for particular topics or problems. Chatfield (1984) is a good source on techniques for analysis of time series.

### *7.4.1 Analysis of Censored Data*

Table 7-8 illustrates the effect of two types of censoring of analytical results near and below the limit of detection. Data reported as less than the limit of detection are heavily censored and yield an average concentration of 3.5 µg/L since only two values are quantified. Reporting of negative concentrations as zero is called negative censoring; in Pable 7-8 negative censoring yields an average of 1.2 µg/L. The uncensored data average 0.5 µg/L. The averages of the heavily and negatively censored data would appear to indicate contamination, but the 95 percent confidence interval for the uncensored data is at best equivocal.

Gilliom et al. (1984) found that any censoring of trace-level water quality data, even when the censored data were highly unreliable, reduced the ability to detect trends in the data. Unfortunately, censored data continues to be routinely reported by laboratories. The following references contain discussions of statistical techniques for analyzing censored data: Gilbert (1987), Gilliom and Helsel (1986), Gilliom et al. (1984), Helsel and Gilliom (1986), McBean and Rovers (1984) and Porter et al. (1988).

### *7.4.2 Contaminant Levels versus Background Conditions*

Numbers on a standard list from an analytical laboratory arc useful only to the extent that they can be compared to known or estimated background conditions before contamination. Using such numbers effectively requires both data on background conditions and the use of appropriate techniques to detect statistically significant departures from background levels. An analytical result from a rinse or cleaning blank between the limit of detection and the limit of quantification may indicate that more careful decontamination procedures should be followed, but does not add to the information on which to base remediation decisions.

Crustal and natural background abundances of metallic elements must be considered when evaluating analyses for inorganic contaminants. See the listing under "background" for soil chemical parameters and water chemistry in Table 8-1, which identifies some sources of background data on minor and trace elements in the United States. For organics, there is always some background of total inorganic carbon and organic carbon, which should be determined in some samples to identify natural background levels. The amount of organic matter may vary considerably in soil, but dissolved organic

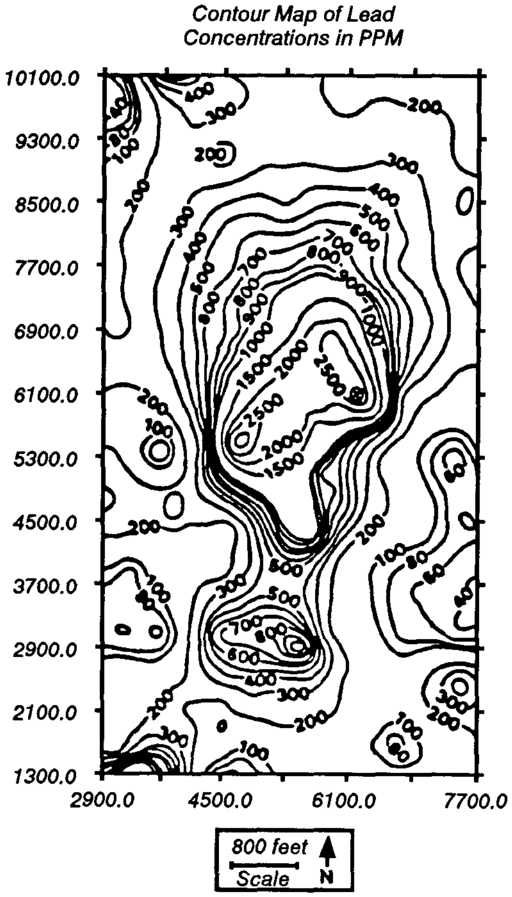


Figure 7-10. Kriged contour map of lead concentration in ppm around a smelter (from Flatman, 1988).

carbon in ground water does not vary greatly. There are definite analytical difficulties in achieving reliable analyses in the range of 0.1 to 0.5 percent organic carbon in the solid fraction.

Equilibrium calculations based on thorough chemical analysis may be useful for interpreting water quality data (Jenne, 1979; Melchior and Bassett 1990 Summers et al., 1985). For example, reducing or suboxic conditions, indicated by low Eh (i.e., measured oxidation-reduction potential), lack of detectable dissolved oxygen, and presence of ferrous iron, may indicate conditions favorable for movement of elements such as manganese, mercury, chromium, and arsenic. Arsenic (V) under oxidizing conditions may be considered immobile, but under reducing conditions, arsenic (III) is often the predicted "stable" species of arsenic and is frequently more toxic and more mobile than As(V) due to higher volubility (Holm and Curtis, 1984).

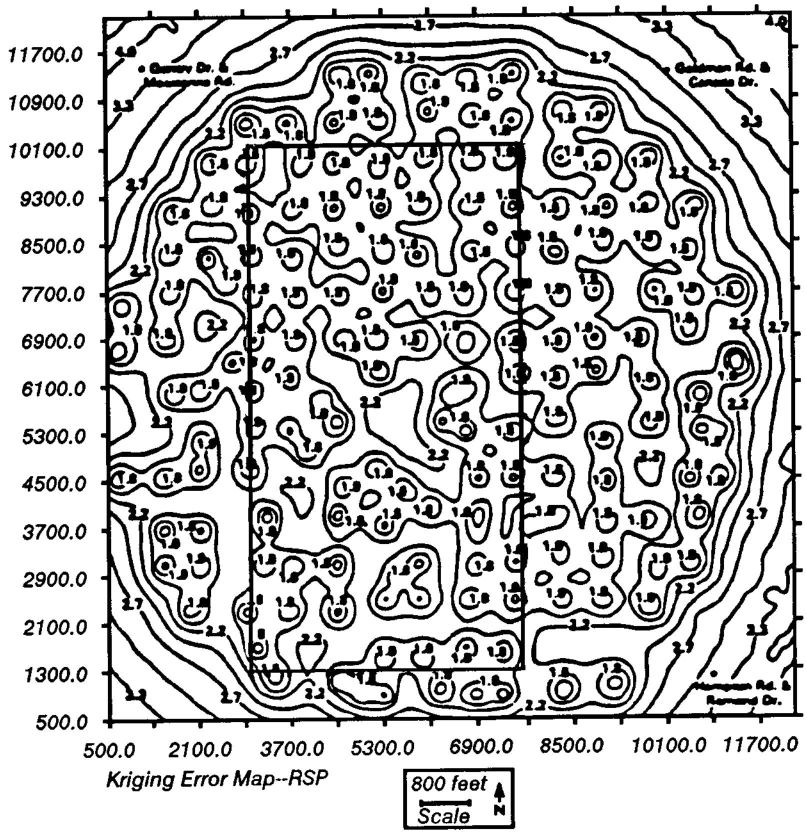


Figure 7-11. Kriging standard deviation map for lead concentrations around a smelter (from Flatman, 1986).

Table 7-6. Reported Values of Ranges of Correlation of Soil Physical and Chemical Properties

| Source | Parameter | Range or Scale (m) | Site |
|---|---|---|---|
| Burgess and Webster (1980) | Sodium | 61 | Approx. 50 ha, Plas Gogerddan (Gr. Britain), 440 samples, 0-15 cm depth |
| | Depth cover loam | 100 | Approx. 18 ha, Hole Farm (Gr. Britain), 450 observations |
| Campbell (1978) | Sand content | 30 | Ladysmith series, mesic Pachic Argiustolls (Kansas), 8 x 20 grid at 10-m spacing in B2 horizons |
| | Sand content | 40 | Pawnee series, mesic Aquic Argiudoll (Kansas) (as above) |
| | Soil pH | Random | Pawnee and Ladysmith |
| Clifton and Neuman (1982) | Log of transmissivity | 9600 | Avra Valley (Arizona), about 15 x 50 km, 148 wells |
| Folorunso and Rolston (1984) | Flux of $N_2$ and $N_2O$ at surface | <1 | Yolo loam, Typic Xerorthents (California) 100 x 100 m area |
| Gajem et al. (1981) | Sand content | >5 | Pima clay loam, Typic Torrifluvents (Arizona), 20-m transect, 20-cm spaces, 50-cm depth. |
| | Soil pH | 1.5 | Pima, as above, 4 transects |
| | | 21 | Pima, as above but 4 transects, 2-m spacing |
| | | 260 | Pima, as above, 1 transect, 20-m spacing, 100 points |
| Kachonoski et al. (1985) | Depth and mass of A-horizon | <2 | Mix of Typic Haploborolls and Typic Argiborolls (Saskatchewan) |
| McBratney and Webster (1981) | pH | 20 | |
| Russo and Bresler (1981a, 1981b) | Saturated conductivity | 34 | Surface, Harma Red Rhodoxeralf (Israel), 30 random sites in 0.8 ha |
| | Saturated water content | 14 | 90-cm depth, as above |
| | | 28 | 90-cm as above |
| | Sorptivity | 37 | Surface |
| | | 39 | 90-cm, as above |
| | Wetting front | 16-30 | Simulated for above site, 1 to 12.5 h |
| Sisson and Wierenga (1981) | Steady-state infiltration | 0.13 | Sandy clay loam, Typic Torrifluvents (New Mexico), 6.4 x 6.4 m plot, transect of 125 contiguous 5-cm rings |
| van Kuilenberg et al. (1982) | Moisture supply capacity | 600 | Cover sand, 30 mapping units, 9 soil types including Haplaquepts, Humaquepts, and Psammaquents (Netherlands), 2 by 2 km, 1191 borings |
| Vauclin et al. (1982) | Surface soil temperature | 8-21 | Yolo loam clay, Typic Xerorthents (California), 55 x 160 m area |
| Vauclin et al. (1983) | Sand content | 35 | Sandy clay loam (Tunisia), 7 x 4 grid at 10-m spacing, 20-40 cm depth |
| | pF 2.5 | 25 | Same |
| Vieira et al. (1981) | Steady-state infiltration | 50 | Yolo loam, Typic Xerorthents (California), 55 x 160 l area |
| Wollum and Cassel (1984) | Log of most probable number of Rhizobium japonicum | | Pocalla loamy sand, thermic Arenic Plinthic Paleudults (N. Carolina) |
| | | 1 | 0 °, 3-m spacing |
| | | >12 | 0 °, 20-cm spacing |
| | | Random | 90 °, 3-m spacing |
| | | >12 | 90 °, 20-cm spacing |
| Yost et al. (1982) | Soil pH | 14,000-32,000 | Various transects on Island of Hawaii at 1 to 2 km intervals, 10-15 cm depth |
| | Phosphorus sorbed at 0.02 mg P/L | 32,000 | As above |
| | Phosphorus sorbed at 0.2 mg P/L | 58,000 | As above |

Source: Adapted from Warrick et al. (1986)

**Table 7-7. Sources of Information on Techniques for Anailzing Soil and Water-Quality Data**

| Topic | References |
|---|---|
| Basic Statistical Approaches | |
| *General* | *Bandat and Pierson (1986), Bury (1975), Gilbert (1987), Jessen (1978), tin (1966), Ott (1984)* |
| *Nonparametrics* | *Hollander and Wolfe (1973), Lehmann (1975), Seigel (1956)* |
| *Time series* | *Chatfield (1984)* |
| *Exploratory data (Median-Polish)* | *Tukey (1977), Velleman and Hoaglin (1981), Alhajjar et al (1990)* |
| *Geostatistics (basic)* | *Clark (1979), Englund and Sparks (1988), Gilbert and Simpson (1965), Journaf (1984), Olea (1974, 1975), Yates and Yates (1990)* |
| *Geostatistics (adv.)* | *David (1977), Journal and Huijbregts (1978), Isaaks and Srivastava (1989), Matheron (1971)* |
| Soil Data Analysis | |
| *Population properties* | *Butler (1980), Sinclair (1986), Webster (1977)* |
| *Geostatistics* | *Sinclair (1986), Trangmar et al. (1985), Warrick et al. (1986). See also Table 7-6* |
| *Contaminated soils* | *Flatman (1964), Flatman and Yfantis (1984), and Flatman (1986)* |
| Soil Gas Data | See *Table 9-5* |
| Water Quality Data | |
| *General* | *Beck and van Stratten (1983), Gillham et al (1983), U.S. EPA (1989)* |
| *Contaminant detection* | *Chapman and El-Shaarawi (1989), Davis and McNichols (1988), Gibbons (1987a,b; 1990), McBean and Rovers (1990), McNichols and Davis (1988)* |
| *Geostatistics* | *Delhomme (1978, 1979), Hughes and Lettenmaier (1981), Samper and Neuman (1985), Sophocleous et al (1982)* |
| *Population properties* | *Harris et al. (1987), Montgomery et al. (1987)* |
| *Spatial data* | *Lawrence and Upchurch (1976), McBean et al.* (1988) |
| *Time series data* | *Close (1989), Harris et al. (1987), McBean et al. (1988), Montgomery et al (1987), Sgambat and Stedinger (1981), Yevjevich and Harmancioglu (1989)* |

**Table 7-8. Effects of Censoring Analyte Signals at and Below the Limit of Detection**

| *Sample* | *Heavily Censored* | *Negatively Censored* | *Uncensored* |
|---|---|---|---|
| *1* | *<3* | *2* | *2* |
| *2* | *<3* | *0* | *-2* |
| *3* | *<3* | *0* | *-1* |
| *4* | *4* | *4* | *4* |
| *5* | *3* | *3* | *3* |
| *6* | *<3* | *0* | *-3* |
| *7* | *<3* | *1* | *1* |
| *8* | *<3* | *0* | *-1* |
| *9* | *<3* | *0* | *0* |
| *10* | *<3* | *2* | *2* |
| *Mean* | *3.5* | *1.2* | *-0.5* |
| *95% Conf.* | *0.14-2.26* | *1.13* | *-2.13* |

*Source: ASTM (1987)*

## 7.5 References

ACS Committee on Environmental Improvement. 1980. Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry. Analytical Chemistry 52:2242-2249.

Alhajjar, B.J., G. Chesters, and J.M. Harkin. 1990. Indicators of Chemical Pollution from Septic Systems. Ground Water 28(4):559-568.

American Public Health Association. 1990. Standard Methods for the Examination of Water and Wastewater, 17th ed. APHA, Washington, DC.

American Society for Testing and Materials (ASTM). Annual Books of ASTM Standards. Water and Environmental Technology, Volumes 11.01 and 11.02 (Water). ASTM, Philadelphia, PA.

American Society for Testing and Materials (ASTM). 1987. Standard Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data. In: Annual Book of ASTM Standards, Vol. 11.01, D4210-83. ASTM, Philadelphia, PA.

American Society for Testing and Materials (ASTM), Subcommittee 019.02.1983. Annual Book ASTM Standards, Volume 11.01, Chapter D, pp. 4210-4283.

Barcelona, M.J. 1988. Overview of the Sampling Process. In: Principles of Environmental Sampling, L.H. Keith (ed.), ACS Professional Reference Book, American Chemical Society, Washington, DC, pp. 1-23.

Barcelona, M.J. and J.A. Helfrich. 1986. Effects of Well Construction Materials on Ground Water Samples. Environ. Sci. Technol. 20(11):1179-1184.

Barcelona, M.J., J.P. Gibb, and R.A. Miller. 1983. A Guide to the Selection of Materials for Monitoring Well Construction and Ground-Water Sampling. ISWS Contract Report 327. Illinois State Water Survey, Champaign, IL.

Barcelona, M.J., J.A. Helfrich, E.E. Garske, and J.P. Gibb. 1984. A Laboratory Evaluation of Ground-Water Sampling Mechanisms. Ground Water Monitoring Review 4(2):32-41.

Barcelona, M.J., J.P. Gibb, J.A. Helfrich, and E.E. Garske. 1985. Practical Guide for Ground-Water Sampling. EPA 600/2-85/104 (NTIS PB86-137304). Also published as ISWS Contract Report 374, Illinois State Water Survey, Champaign, IL.

Barcelona, M.J., J.A. Helfrich, and E.E. Garske. 1988. Verification of Sampling Methods and Selection of Materials for Ground-Water Contamination Studies. In: Ground-Water Contamination: Field Methods, A.G. Collins and A.I. Johnson (eds.), ASTM STP 963, American Society for Testing and Materials, Philadelphia, PA, pp. 221-231.

Barcelona, M.J., D.P. Lettenmaier, and M.R. Schock. 1989. Network Design Factors for Assessing Temporal Variability in Ground-Water Quality. Environmental Monitoring and Assessment 12:149-179.

Bardossy, A., I. Bogardi, and L. Duckstein. 1990. Fuzzy Regression in Hydrology. J. Hydrology 26(7):1497-1508.

Bamett, P.R. and E.C. Mallory, Jr. 1971. Determination of Minor Elements in Water by Emission Spectroscopy. U.S. Geological Survey TWI 5-A2.

Beck, B.F. and G. Van Strateen (eds.). 1983. Uncertainty and Forecasting of Water Quality. Springer-Verlag, New York.

Bendat, J.S. and A.G. Piersol. 1986. Random Data, Analysis and Measurement Procedures, 2nd ed. Wiley-Interscience, New York.

Burgess T.M. and R. Webster. 1980. Optimal Interpolation and Isarithmic Mapping of Soil Properties I. The Variogram and Punctual Kriging. J. Soil Sci. 31:315-331.

Bury, K.V. 1975. Statistical Models in Applied Science. John Wiley & Sons, New York.

Butler, B.E. 1980. Soil Classification for Soil Survey, Chapter 2. Oxford University Press, New York.

Campbell, J.A. and W.R. Mabey. 1985 A Systematic Approach for Evaluating the Quality of Ground Water Monitoring Data. Ground Water Monitoring Review 5(4):58-22.

Campbell, J.B. 1978. Spatial Variability of Sand Content and pH within Continuous Delineations of Two Mapping Units. Soil Sci. Soc. Am. J. 42:46044.

Chapman, D.T. and A.H. El-Shaarawi. 1989. Statistical Methods for the Assessment of Point Source Pollution. Environmental Monitoring and Assessment 13(2/3):1-467. [Special issue with 21 papers].

Chatfield, C. 1984. The Analysis of Time Series: Theory and Practice, 3rd ed. Chapman and Hall, London.

Clark, I. 1979. Practical Geostatistics. Applied Science Publishers, London.

Clifton, P.M. and S.P. Neuman. 1982. Effects of Kriging and Inverse Modeling on Conditional Simulation of the Avra Valley in Southern Arizona. Water Resources Research 18:1215-1234.

Close, M.E. 1989. Effect of Serial Correction on Ground Water Quality Sampling Frequency. Water Resources Bulletin 25(3):507-515.

David, M. 1977. Geostatistical Ore Reserve Estimation. Elsevier, New York.

Davis, C.B., and R.J. McNichols. 1988. Discussion of “Statistical Prediction Intervals for the Evaluations of Ground-Water Quality.” Ground Water 25(1):90-91.

Delhomme, J.P. 1978. Kriging in the Hydrosciences. Adv. Water Resources 1:251-266.

Delhomme, J.P. 1979. Spatial Variability and Uncertainty in Groundwater Flow Parameters: A Geostatistical Approach. Water Resources Research 15:269-280.

Einarson, J.H. and P.C. Pei. 1988. A Comparison of Laboratory Performances. Environ. Sci. Technol. 22:1121-1125.

Englund, E.J. and A.R. Sparks. 1988. Geo-EAS (Geostatistical Environmental Assessment Software) User’s Guide. EPA/600/4-88/033a (Guide: NTIS PB89-151252, Software: PB89-151245).

Evans, R.B. 1986. Ground-Water Monitoring Data Quality Objectives for Remedial Site Investigations. In: Quality Control in Remedial Site Investigation: Hazardous and Industrial Solid Waste Testing, Fifth Volume, C.L. Perket (ed.), ASTM STP 925, American Society for Testing and Materials, pp. 21-33.

Flatman, G.T. 1984. Using Geostatistics in Assessing Lead Contamination Near Smelters. In: Environmental Sampling for Hazardous Wastes, G.E. Schweitzer and J.A. Santolucito (eds.), ACS Symp. Ser. 267, American Chemical Society, Washington, DC, pp. 43-52.

Flatman, G.T. 1986. Design of Soil Sampling Programs: Statistical Considerations. In: Quality Control in Remedial Site Investigation: Hazardous and Industrial Solid Waste Testing, 5th volume, C.L. Perket (ed.), ASTM STP 925, American Society for Testing and Materials, Philadelphia, PA, pp. 43-56.

Flatman, G.T. and A.A. Yfantis. 1984. Geostatistical Strategy for Soil Sampling: The Survey and the Census. Environmental Monitoring and Assessment 4:335-350.

Folorunso, O.A. and D.E. Rolston. 1984. Spatial Variability of Field Measured Denitrification Gas Fluxes. Soil Sci. Soc. Am. J. 48:1214-1219.

Fresenius, W., K.E. Quentin, and W. Schneider (eds.). 1988. Water Analysis: A Practical Guide to Physico-Chemical and Microbiological Water Examination and Quality Assurance. Springer-Verlag, New York.

Gajem, Y. M., A. W. Warrick, and D.E. Myers. 1981. Spatial Dependence of Physical Properties of a Typic Tornfluvent Soil. Soil Sci. Soc. Am. J. 46:709-715.

Gibb, J.P, R.M. Schuller, and R.A. Griffin. 1981. Procedures for the Collection of Representative Water Quality Data from Monitoring Wells. ISWS/IGS Cooperative Ground Water Report 7. Illinois State Water Survey, Champaign, IL.

Gibbons, R.D. 1987a. Statistical Prediction Intervals for the Evaluation of Ground-Water Quality. Ground Water 25(4):455-465.

Gibbons, R.D. 1987b. Statistical Models for the Analysis of Volatile Organic Compounds in Waste Disposal Facilities. Ground Water 25:572-580.

Gibbons, R.D. 1990. A General Statistical Procedure for Ground-Water Detection Monitoring at Waste Disposal Facilities. Ground Water 28(2):235-243.

Gilbert, R.O. 1987. Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold, New York.

Gilbert, R.O. and J.C. Simpson. 1985. Kriging from Estimating Spatial Pattern of Contaminants: Potential and Problems. Environmental Monitoring and Assessment 5:113-135.

Gillham, R. W., M.J.L. Robin, J.F. Barker and J.A. Cherry. 1983. Groundwater Monitoring and Sample Bias. API Publication 4367. American Petroleum Institute, Washington, DC.

Gilliom, R.J. and D.R. Helsel. 1986. Estimation of Distributional Parameters for Censored Trace Level Water Quality Data: 1. Estimation Techniques. Water Resources Research 22:135-146.

Gilliom, R.J., R.M. Hirsch, and E.J. Gilroy. 1984. Effect of Censoring Trace-Level Water-Quality Data on Trend-Detection Capability. Environ. Sci. Technol. 18:530-536.

Goerlitz, D.F. and E. Brown. 1972. Methods for Analysis of Organic Substances in Water. U.S. Geological Survey TWI 5-A3. (updated by Wershaw et al., 1987).

Harris, J., J.C. Loftis, and R.H. Montgomery. 1987. Statistical Methods for Characterizing Ground-Water Quality. Ground Water 25(2): 185-193.

Helsel, D.R. and R.J. Gilliom. 1986. Estimation of Distributional Parameters for Censored Trace Level Water Quality Data: 2. Verification and Applications. Water Resources Research 22:146-155.

Hem, J.D. 1985. Study and Interpretation of the Chemical Characteristics of Natural Water. U.S. Geological Survey Water-Supply Paper 2254.

Ho, J.S-Y. 1983. Effect of Sampling Variables on Recovery of Volatile Organics in Water. J. Am. Water Works Ass. 12:583-586.

Hollander, M. and D.A. Wolfe. 1973. Nonparametric Statistical Methods. John Wiley & Sons, New York.

Holm, T.R. and C.D. Curtis. 1984. A Comparison of Oxidation-Reduction Potentials Calculated from the As(V)/As(III) and Fe(III)/Fe(II) Couples with Measured Platinum Electrode Potentials in Ground Water. J. Contaminant Hydrology 5:67-81.

Hughes, J.P. and D.P. Lettenmaier. 1981. Data Requirements for Kriging: Estimation and Network Design. Water Resources Research 17:1641-1650.

International Union of Pure and Applied Chemistry (IUPAC). 1978. Nomenclature, Symbols, Units and their Usage in Spectrochemical Analysis—II. Data Interpretation. Spectrochimica Acts B 33B:242-245.

Isaaks, E.H. and R.M. Srivastava. 1989. Applied Geostatistics. Oxford University Press, New York.

Jenne, E.A. (ed.). 1979. Chemical Modeling in Aqueous Systems: Speciation, Sorption, Volubility, and Kinetics. ACS Symp. Series 93. American Chemical Society, Washington, DC.

Jessen, R.J. 1978. Statistical Survey Techniques. John Wiley & Sons, New York.

Journal, A.G. 1984. New Ways of Assessing Spatial Distribution of Pollutants. In: Environmental Sampling for Hazardous Wastes, G.E. Schweitzer and J.A. Santolucito (eds.), ACS Symp. Ser. 267, American Chemical Society, Washington, DC, pp. 109-118.

Journal, A.G. and C.J. Huijbregts. 1978. Mining Geostatistics. Academic Press, New York.

Kachonoski, R.G., D.E. Rolston, and E. deJong. 1985. Spatial and Spectral Relationships of Soil Properties and Microtopography: I. Density and Thickness of A Horizon. Soil Sci. Soc. Am. J. 49:804-812.

Keith, S.J., M.T. Frank, G. McCarty, and G. Massman. 1983. Dealing with the Problem of Obtaining Accurate Ground-Water Quality Analytical Results. In: Proc. 3rd Nat. Symp. on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, Dublin, OH, pp. 272-283.

Kirchmer, C.J. 1983. Quality Control in Water Analyses. Environ. Sci. Technol. 17(4):174A-181A.

Kite, G. 1989. Some Statistical Observations. Water Resources Bulletin 25(3):483-490. [See also 1990 discussion by Kirby et al., and reply by Kite in Water Resources Bulletin 26(4)693-698].

Klute, A. (ed.). 1986. Methods of Soils Analysis, Part l-Physical and Mineralogical Methods, 2nd ed. ASA Monograph 9. American Society of Agronomy, Madison, WI.

Kopp, J.F. and G.D. McKee. 1983. Methods for Chemical Analysis of Water and Wastes. EPA 600/4-74-020 (NTIS PB84-128677). [supersedes report with the same title dated 1979].

Lawrence, F.W. and S.B. Upchurch. 1976. Identification of Geochemical Patterns in Groundwater by Numerical Analysis. In: Advances in Groundwater Hydrology, AWRA Proc. Ser. No. 21. American Water Resources Association, Bethesda, MD.

Lehmann, E.L. 1975. Nonparametrics: Statistical Methods Based on Ranks. Holden Day, San Francisco, CA, and McGraw-Hill, New York.

Lin, P.C.L. 1986. User-Friendly IBM PC Computer Programs for Solving Sampling and Statistical Problems. EPA/600/4-86/023 (NTIS PB86-203783).

Long, G.L. and J.D. Winefordner. 1983. Limit of Detection, a Closer Look at the IUPAC Definition. Analytical Chemistry 55(7):712A-724A.

Longbottom, J.E. and J.J. Lichtenberg. 1982. Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. EPA/600/4-82-057 (NTIS PB83-201798).

Mann, J.C. 1987. Misuses of Linear Regression in Earth Sciences. In: Use and Abuse of Statistical Methods in the Earth Sciences, W.B. Size (ed.), Oxford University Press, New York, pp.74-106.

Matheron, G. 1971. The Theory of Regionalized Variables and Its Applications. Cahiers du Centre de Morphologic Mathematique de Fontainebleau. No. 5.

McBean, E.A. and F.A. Rovers. 1984. Alternatives for Handling Detection Limit Data in Impact Assessments. Ground Water Monitoring Review 4(2):42-44.

McBean, E.A. and F.A. Rovers. 1990. Flexible Selection of Statistical Discrimination Tests for Field-Monitored Data. In: Ground Water and Vadose Zone Monitoring, ASTM STP 1053, D.M. Nielsen and A.I. Johnson (eds.), American Society for Testing and Materials, Philadelphia, PA, pp. 256-265.

McBean, E. A., M. Kompter, and F. Rovers. 1988. A Critical Examination of Approximations Implicit in Cochran's Procedure. Ground Water Monitoring Review 8(1):83-87.

McBratney, A.B. and R. Webster. 1981. Spatial Dependence and Classification of the Soil Along a Transect in Northeast Scotland. Guoderma 26:63-82.

McNichols, R.J. and C.B. Davis. 1988. Statistical Issues and Problems in Ground Water Detection Monitoring at Hazardous Waste Facilities. Ground Water Monitoring Review 8(4):135-150.

Melchior, D.C. and R.L. Bassett (eds.). 1990. Chemical Modeling of Aqueous Systems II. ACS Symp. Series 416. American Chemical Society, Washington, DC.

Montgomery, R.H., J.C. Loftis, and J. Harris. 1987. Statistical Characteristics of Ground Water Quality Variability. Ground Water 25(2): 176-184.

Mueller, W., D.L. Smith, and L.H. Keith. 1991. Compilation of EPA's Sampling and Analysis Methods. Lewis Publishers, Chelsea, MI, 465 pp. [On diskette EPA's Sampling and Analysis Methods Database, Vol. 1 (Industrial Chemicals), Vol. 2 (Pesticides, Herbicides, Dioxins and PCBS), and Vol. 3 (Elements and Water Quality Parameters)].

Noblett, J.G. and J.M. Burke. 1990. FGD Chemistry and Analytical Methods Handbook, 1: Process Chemistry—Sampling, Measurement, Laboratory, and Process Performance Guidelines, Revision 1. EPRI CS-3612. Electric Power Research Institute, Palo Alto, CA. [Originally published in 1984, see Radian Corporation (1988) for Volume 2].

Olea, R.A. 1974. Optimal Contour Mapping Using Universal Kriging. J. Geophysical Research 79(5):696-702.

Olea, R.A. 1975. Optimum Mapping Techniques Using Regionalized Variable Theory. KGS Series on Spatial Analysis No. 2. Kansas Geological Survey, Lawrence, KS.

Ott, L. 1984. An Introduction to Statistical Methods and Data Analysis, 2nd ed. Duxbury Press, Boston, MA, 775 pp.

Page, A.L., R.H. Miller, D.R. Keeney (eds.). 1982. Methods of Soils Analysis, Part 2-Chemical and Microbiological Properties, 2nd ed. ASA Monograph 9. American Society of Agronomy, Madison, WI.

Pennino, J.D. 1988. There's No Such Thing as a Representative Ground Water Sample. Ground Water Monitoring Review 8(3):4-9.

Porter, P.S. 1986. A Description of Measurement Error Near Limits of Detection. In: Monitoring to Detect Changes in Water Quality Series, D. Lerner (ed.), Int. Ass. of Hydrological Sciences Pub. No. 157.

Porter, P.S., R.C. Ward, and H.F. Bell. 1988. The Detection Limit. Environ. Sci. Technol. 22:856-861.

Provost L.P. and R.S. Elder. 1985. Choosing Cost-Effective QA/QC Programs for Chemical Analysis. EPA/600/4-85/056 (NTIS PB85-241461).

Radian Corporation. 1988. FGD Chemistry and Analytical Methods Handbook, Vol. 2: Chemical and Physical Test Methods, Revision 1. EPRI CS-3612. Electric Power Research Institute, Palo Alto, CA. [Originally published in 1984, see Noblett and Burke (1990) for Volume 1].

Rainwater, F.H. and L.L. Thatcher. 1960. Methods for Collections and Analysis of Water Samples. U.S. Geological Survey Water-Supply Paper 1454.

Rice, G., J. Brinkman, and D. Muller. 1988. Reliability of Chemical Analyses of Water Samples-The Experience of the UMTRA Project. Ground Water Monitoring Review 8(3):71-75.

Russo, D. and E. Bresler. 1981a. Effect of Field Variability in Soil Hydraulic Properties on Solutions and Unsaturated Water and Salt Flows. Soil Sci. Soc. Am. J. 45:675-681.

Russo, D. and E. Bresler. 198lb. Soil Hydraulic Properties as Stochastic Processes I. An Analysis of Field Spatial Variability. Soil Sci. Soc. Am J. 45:682-687.

Samper, F.J. and S.P. Neuman. 1985. Geostatistical Analysis of Hydrochemical Data from the Madrid Basin, Spain (Abstract). Eos (Trans. Am. Geophysical Union) 66(46):905.

Schuller, R.M., J.P. Gibb, and R.A. Griffin. 1981. Recommended Sampling Procedures for Monitoring Wells. Ground Water Monitoring Review 1(1):42-46.

Seigel, S. 1956. Nonparametric Statistics for the Behavioral Sciences, McGraw-Hill, New York.

Sgambat, J.P. and J.R. Stedinger. 1981. Confidence in Ground-Water Monitoring. Ground Water Monitoring Review l(Spring):62-69.

Sinclair, A.J. 1986. Statistical Interpretation of Soil Geochemical Data. In: Exploration Geochemistry, Design and Interpretation of Soil Surveys. Reviews in Economic Geology 3:97-115.

Skoog, D.A. 1985. Principles of Instrumental Analysis, 3rd ed. Saunders College Publishing, Philadelphia, PA.

Skougstad, M.W. et al. (eds.). 1979. Methods for Determination of Inorganic Substances in Water and Fluvial Sediments. U.S. Geological Survey TWI 5-Al.

Sisson, J.B. and P.J. Wierenga. 1981. Spatial Variability of Steady-State Infiltration Rates as a Stochastic Process. Soil Sci. Soc. Am. J. 45:699-704.

Smith, K.A. (ed.). 1991. Soil Analysis: Modem Instrumental Methods, 2nd ed. Marcell Dekker, New York.

Sophodeous, M. J.E. Paschetto, and R.A. Olea. 1982. Gmund-Water Network Design for Northwest Kansas, Using the Theory of Regionalized Variables. Ground Water 20:48-58.

Starks, T.H. and G.T. Flatman. 1991. RCRA Ground-Water Monitoring Decision Procedures Viewed as Quality Control Schemes. Environmental Monitoring and Assessment 16:19-37.

Summers, K.V., G.L. Rupp, G.F. Davis, and S.A. Gherini. 1985. Ground Water Data Analysis at Utility Waste Disposal Sites. EPRI EA-4165. Electric Power Research Institute, Palo Alto, CA.

Thompson, C.M., et al. 1989. Techniques to Develop Data for Hydrogeochemical Models. EPRI EN-6637. Electric Power Research Institute, Palo Alto, CA.

Trangmar, B.B., R.S. Yost and G. Uehara. 1985. Application of Geostatistics to Spatial Studies of Soil Properties. Advances in Agronomy 38:45-93.

Tukey, J.W. 1977. Exploratory Data Analysis. Addison-Wesley, New York, 506 pp.

U.S. Environmental Protection Agency (EPA). 1988. Field Screening Methods Catalog: User's Guide. EPA/540/2-88/005. FSMC System Coordinator, OERR, Analytical Operations Branch (WH-548-A), U.S. EPA, Washington, DC 20460.

U.S. Environmental Protection Agency (EPA). 1989. Guidance Document on Statistical Analysis of Ground-Water Monitoring Data at RCRA Facilities-Interim Final Guidance. Office of Solid Waste Management Division (NTIS PB89-151047).

van Kuilenburg, J., J.J. DeGruijter, B.A. Marsma, and J. Bourna. 1982. Accuracy of Spatial Interpretation Between Point Data on Soil Moisture Supply Capacity Compared with Estimations from Mapping Units. Geoderma 27:311-325.

Vauclin, M., S.R. Vieira, R. Bernard, and J.L. Hatfield. 1982. Spatial Variability of Surface Temperature Along to Transects on a Bare Soil. Water Resources Research 18:1677-1686.

Vauclin, M., S.R. Vieira, G. Vachaud, and D.R. Nielsen. 1983. The Use of Co-Kriging with Limited Field Soil Observations. Soil Sci. Soc. Am. J. 47:175-184.

Velleman, P.F. and D.C. Hoaglin. 1981. Applications, Basics, and Computing of Exploratory Data Analysis. Duxbury Press, Boston, MA, 354 pp.

Vieira, S.R., D.R. Nielsen, and J.W. Biggar. 1981. Spatial Variability of Field Measured Infiltration Rate. Soil Sci. Soc. Am. J. 45:1040-1048.

Warrick, A.W., D.E. Myers, and D.R. Nielsen. 1986. Geostatistical Methods Applied to Soil Science. In: Methods of Soil Analysis, Part I—Physical and Mineralogical Methods, 2nd ed., A. Klute (ed.), ASA Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 53-82.

Webster, R. 1977. Quantitative and Numerical Methods in Soil Classification and Survey. Oxford University Press, New York.

Wershaw, R.L., M.J. Fishman, R.R. Bragge, and L.E. Lowe (eds.). 1987. Methods for the Determination of Organic Substances in Water and Fluvial Sediments. U.S. Geological Survey TWI 5-A3. (Revision of Goerlitz and Brown, 1972).

Westerman, R.L. 1990. Soil Testing and Plant Analysis, 3rd ed. Soil Science Society of America, Madison, WI, 812 pp.

Willard, H. H., L.L. Merritt, Jr., J.A. Dean, and F.A. Settle, Jr. 1988. Instrumental Methods of Analysis, 7th ed. Wadsworth Publishing Co., Belmont, CA.

Wilson, B.G., B.J. Adams, and B.W. Karney. 1990. Bias in Log-Transformed Frequency Distributions. J. Hydrology 118:19-37.

Wollum II, A.G. and D.K. Cassel. 1984. Spatial Variability of *Rhizobium japonicum* in Two North Carolina Soils. Soil Sci. Soc. Am. J. 48:1082-1086.

Wood, W.W. 1976. Guidelines for Collection and Field Analysis of Ground-Water Samples for Selected Unstable Constituents. U.S. Geological Survey TWI 1-D2

Yates, S.R. and M.V. Yates. 1990. Geostatistics for Waste Management: A User's Manual for the GEOPACK (Version 1.0) Geostatistical Software System. EPA/600/8-90/004 (NTIS PB90-186420/AS).

Yevjevich, V. and N.B. Harmancioglu. 1989. Description of Periodic Variation in Parameters of Hydrologic Time Series. Water Resources Research 25(3):421-428.

Yost, R.S., G. Uehara, and R.L. Fox. 1982. Geostatistical Analysis of Soil Chemical Properties of Large Land Areas. I. Variograms. Soil Sci. Sco. Am. J. 46:1028-1032.

# Chapter 8

# Geochemical Variability of the Natural and Contaminated Subsurface Environment

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This chapter focuses on subsurface geochemical processes and environmental parameters that may significantly affect the accuracy of geochemical sampling to characterize the natural and contaminated subsurface. Subsequent chapters examine in more detail subsurface physiochemical and degradation processes that affect the fate and transport of contaminants. Table 8-1 indexes references on topics covered in this chapter.

## 8.1 Overview of Subsurface Geochemistry

A basic assumption in performing remediation is that one cannot remediate what is not observed. Consequently, complete geochemical characterization of the subsurface requires an understanding of what to observe and how to go about making the observations. Elements and compounds in the subsurface may exist in one or more of three phases (solid, liquid, or gas). Within a phase, a substance may exist as several forms or species (e.g., ions, neutral molecules, and complex molecules in water). The partitioning of natural constituents and contaminants between solid, liquid, and gas or their transformation to other chemical forms is dependent on both the thermodynamics and kinetics of different types of chemical processes. Thermodynamic prediction and reaction kinetics may be strongly influenced by subsurface environmental conditions. Information on indicators of ground-water conditions, such as pH, Eh, temperature, and pressure, therefore, is essential for interpreting geochemical data.

### *8.1.1 Geochemical Processes*

Major geochemical processes in the subsurface include (1) acid-base equilibria (also called ionization); (2) sorption-desorption; (3) precipitation-dissolution; (4) oxidation-reduction (redox reactions); and (5) hydrolysis (see Chapters 10, 12, and 13). Microorganisms frequently are the catalysts or promoters of reactions in the subsurface. Volatilization is another important process affecting contaminants that readily move into the gas phase. Interactions between these various processes are typically complex and must be understood in terms of both thermodynamic and kinetic controls.

Thermodynamically, a chemical system is in equilibrium when its free energy is minimized; thus, thermodynamic principles define the stability of substances within the system and whether a reaction will tend to occur. Thermodynamic calculations can predict whether a chemical reaction is likely to occur under specified conditions but give no indication of how fast the reaction will occur. Kinetics describe the rate of chemical reactions. Some reactions, such as the reaction that occurs when a strong acid is added to water, will occur almost instantaneously; other reactions, such as the hydrolysis of cyanides at low pH, may take tens of thousands of years.

In nonequilibrium systems, chemical processes act to alter the chemical composition and/or phase of the system, and the system may tend to approach equilibrium. Simple systems, such as dilute mixtures of sodium chloride and water, attain solution equilibrium quickly, whereas complex systems may only tend towards equilibrium. For example, geochemical modeling by Apps et al. (1988) suggests that Gulf Coast brines are not in equilibrium after tens of thousands of years with respect to magnesium and sulfate concentration. Lindberg and Runnells (1984) have suggested that ground water is rarely, if ever, in complete equilibrium with respect to redox reactions.

Equilibrium implies that as long as no significant changes in environmental factors or phases occur within the system, the chemical composition of the system will be predictable. An equilibrium state does not imply that chemical reactions cease, rather that the rates of forward and reverse reactions compensate one other.

### *8.1.2 Environmental Parameters*

The act of sampling the subsurface tends to alter its chemical equilibrium and results in reactions that may remove or release some of the chemical constituents being measured. The potential geochemical effects of drilling methods, materials used for well construction and sampling devices, and sampling methods all must be considered when developing a sampling protocol. The sensitivity of a chemical system to disturbance depends on a number of physical and chemical environmental parameters. Some of the most important of these parameters are discussed below, along with examples of how sampling may bias the results of laboratory analyses.

The major geochemical parameters that characterize the subsurface include (1) water content, (2) hydrogen ion concentration (pH), (3) redox potential (Eh), (4) microbial popu-

*Table 8-1. Sources of Information on Natural and Contaminant Variability of Geochemical Parameters In the Subsurface*

| Topic | References |
|---|---|
| **Soil Chemical Parameters** | |
| *General chemistry* | *Bohn et al. (1985), Bolt and Bruggenwert (1978), Dragun (1988), Fairbridge and Finkl (1979), Sparks (1986, 1989), Sposito (1984, 1989)* |
| *Background levels* | *Connor and Shacklette (1975), Ebens and Shacklette (1982), Shacklette et al. (1971a,b, 1973, 1974)* |
| *Redox chemistry* | *Brookins (1988), Ponnamperuma (1972), Ransom and Smeck (1986)* |
| *Contaminants* | *Loehr et al. (1986)* |
| *Soil gases* | *Barber et al. (1990), van Cleemput and El-Sebaay (1985)* |
| **Soil Physical Parameters** | |
| *Variability* | *Jury (1985). See also Table 7-6* |
| *Flow channels* | *Bouma et al (1983), Miller (1975), Simpson and Cunningham (1982), White (1985)* |
| **Vadose Zone** | |
| *General* | *Arnold et al. (1982), Evans and Nicholson (1987), Rijtema and Wassink (1969), Yaron et al. (1984), Zimmie and Riggs (1979)* |
| *Water movement* | *Barnes (1989), Diment and Watson (1985), Hill and Parlange (1972), Raats (1973)* |
| **Water Chemistry** | |
| *General* | *Drew (1989), Eriksson (1985), Faust and Aly (1981), Garrels and Christ (1965), Hem (1985), Lloyd and Heathcote (1985), Morel (1983), Pagendorf (1978), Stumm and Morgan (1981)* |
| *Background levels* | *Durum and Haffty (1961), Durum et al. (1971), Ebens and Shacklette (1982), Ledin et al. (1989), Leenheer et al. (1974), Thurman (1985), White et al. (1963)* |
| *Redox Chemistry* | *Baas-Backing et al. (1960), Back and Barnes (1965), Barcelona et al. (1989a), Champ et al. (1979), Edmunds (1973), Hem and Cropper (1959), Lindberg and Runnells (1984), Smith et al. (1991), Zehnder and Stumm (1988), ZoBell (1946). (See also, Tables 8-9 and 8- 10.)* |
| *Biochemical Changes* | *Bouwer and McCarty (1984), Ghiorse and Wilson (1988), Smith et al. (1991), Wood and Bassett (1973)* |
| *Corrosion/scaling* | *Barnes and Clarke (1969), Langelier (1936), Larson and Buswell (1942), Ryzner (1944), Singley et al. (1985), Stiff and Davis (1952).* |
| *Variability* | *Back and Hanshaw (1988), Montgomery et al. (1987), Schmidt (1977), Seaber (1965), van Beek and van Puffelen (1987). (See also Tables 7-9 and 7-10.)* |

lation, (5) salinity and dissolved constituents, (6) physical and chemical character of solids, (7) temperature, and (8) pressure. Eh, pH, and pressure are probably the most important parameters affecting sampling of near-surface aquifers; these factors strongly influence microbial population. Dissolved constituents and the physical and chemical character of subsurface solids are highly site specific and influenced primarily by geologic and soil-forming processes. Salinity, temperature, and solution composition gain increasing importance as the depth of sampling increases.

*pH and Alkalinity.* The pH and alkalinity are master variables that help to describe solution composition and potential for preeipitation reactions. For example, pump-and-treat operations using air stripping to remove volatile organic compounds (VOCs) can increase pH by 0.5 to 1 pH unit through removing carbon dioxide, with subsequent precipitation of calcium carbonate and iron oxides. Table 7-2 identifies changes in pH that may result from sampling methods and materials. Table 8-2 identifies the effects of pH on a number of subsurface geochemical processes,

Alkalinity indicates the buffer capacity or resistance to change in pH, A solution with high buffer capacity has a large resistance to change in pH, requiring the addition of a proportionally large amount of acid or base to change the solution pH condition in the water. Since carbonate buffering is common to most natural waters, the solution pH may be quite sensitive to volatilization of $CO_2$ during sampling operations.

*Redox Potential. The* oxidation-reduction potential, or Eh, is an expression of the intensity of redox conditions in a system. It is measured in volts or millivolts (mV) as the potential difference between a working electrode and the standard hydrogen electrode. Positive readings in natural water generally indicate oxidizing conditions, and negative readings indicate reducing conditions. Ponnamperuma (1972) suggests that Eh values of +200 mV or lower indicate reducing conditions in near-surface soils and sediments. Surface water bodies are generally around 400 to 600 mV because they are often in equilibrium with oxygen in the atmosphere. Principal oxidizing species in ground-water systems are oxygen and perhaps some hydrogen peroxide (the intermediate species in the reduction of oxygen to water). Other oxidizing species in ground water include nitrate and manganese (IV) and Fe(III). Under reducing conditions, Fe(III) species will tend to be reduced to Fe(II), sulfate is reduced to sulfide, and

*Table 8-2. **Effects of pH on Subsurface Geochemical Processes and Other Environmental Factors***

| *Process/Factor* | *pH Effect* |
|---|---|
| *Acid-base* | *Measures acid-base reactions. Strong acids (bases) will tend to change pH: weak acids (bases) will buffer solutions to minimize pH changes.* |
| *Adsorption-desorption* | *Strongly influences adsorption, because hydrogen ions play an active role in both chemical and physical bonding processes. Abbility of heavy metals is strongiy influenced by pH. Adsorption rates of organics are also PH dependant.* |
| *Precipitation-dissolution* | *Strongly influences precipitation-dissolution reactions. Mixing of solutions with different pH often results in precipitation reactions. Sea also reservoir matrix below.* |
| *Complexation* | *Strongly influences positions of equilibria involving complex ions and metal chelate formation.* |
| *Oxidation-reduction* | *Redox systems generally become more reducing with increasing pH (ZoBell, 1946).* |
| *biodegradation* | *in combination with Eh, strongly influences the types of bacteria that will be present. High-to medium-pH, low-Eh environments will generally restrict bacterial populations to sulfate reducers and heterotrophic anaerobes (Baas-Becking et al., 1960).* |
| *Eh* | *increasing pH generally lowers Eh.* |
| *Salinity* | *pH-induced dissolution increases salinity: pH-induced precipitation decreases salinity.* |
| *Reservoir matrix* | *Acidic solutions tend to dissolve carbonates and clays; highly alkaline solutions tend to dissolve silica and clays. Greater pH generally increases cation-exchange capacity of clays.* |
| *Temperature* | *pH-driven exothermic (heat-releasing) reactions will increase fluid temperature: pH-driven endothermic (heat-consuming) reactions will decrease fluid temperature.* |
| *Pressure* | *Will not infiuence pressure unless pH-induced reactions result in a significant change in the volume of reaction products.* |

*Source: Adapted from U.S. EPA (1989)*

carbon dioxide to methane. Oxidation/reduction processes are discussed further in Section 12.1.3.

Most redox reactions in the subsurface are microbially mediated. The measurement of the major by-products of these reactions may be a better indicator of the strength of the reducing environment than Eh measurements or calculated equilibrium potentials. A sequence of redox reactions under increasing reducing conditions may be (1) denitrification reactions which deplete nitrate and produce nitrogen gas, (2) sulfate reduction which depletes sulfate and produces hydrogen sulfide, and (3) methanogenic reactions which deplete carbon dioxide and produce methane. Microbially mediated redox processes are discussed further in Section 12.2.3.

Redox potential measurements or calculated potentials are only measures of intensity. Reduction capacity measures the resistance to change in the redox potential, and is analogous to buffer capacity for pH in water. Reduction capacity is measured by how much oxidizing or reducing constituent must be added to change redox conditions. Ground-water systems tend to have some natural reduction capacity due to the presence of organic carbon in aquifer solids. The introduction of organic contaminants, which serve as an energy source for microorganisms to ground water, increases the tendency to shift towards more reducing conditions. In contrast bias can easily be introduced into analytical results by the addition of oxygen during the sampling process. Increases in dissolved oxygen, resulting in decreased Fe(II) concentrations in samples (see Table 7-2), and precipitation of iron oxides are common biases introduced by the exposure of ground-water samples to the atmosphere.

The concept of biologically mediated redox zones is useful for evaluating the biodegradation of organic contaminants in ground water. Table 8-3 shows how the degradation of various organic micropollutants might occur with increasing distance from a point of injection.

When organic contaminants are present in relatively low concentrations, as with artificial recharge of treated sewage effluent, oxygen is present near the zone of injection and compounds susceptible to aerobic biodegradation will decompose. As the redox potential declines at a greater distance from the point of injection, denitrifying conditions develop, and compounds such as carbon tetrachloride, which are not susceptible to aerobic degradation, may be degraded. If redox potential declines further and conditions favorable for sulfate-reducing bacteria exist, cresols and chlorophenols may be degraded. Finally, where methanogenic bacteria predominate, halogenated aliphatics that may have passed through the denitrification zone may be degraded.

Implicit in this redox zone model is that compounds that pass through the zone in which they are susceptible to biodegradation will persist in ground water unless immobilized or altered by inorganic chemical processes. In heavily contaminated ground water, this sequence may be reversed, with the greatest reducing conditions closest to the point of contamination grading to mildly oxygenated conditions (in shallow aquifers, at least) at the outside edge of the contaminant plume.

*Salinity and Dissolved Constituents.* Total dissolved solids (TDS) content can be qualitatively estimated in the field by measuring specific conductance. The major dissolved constituents in ground water may be near equilibrium with conditions at their location, although subject to seasonal fluctuations (see Section 8.4). During well development, if purging or sampling-process ground water is mixed with water of differing salinity or chemical composition, the result may be precipitation-dissolution and redox reactions that significantly change the inorganic chemistry of a sample. Geochemical sampling of water wells that tap multiple aquifers is especially problematic because of these effects. The more saline the water, or the more different in chemical composition the two waters, the greater the bias that can be introduced to geochemical samples.

*Soil/Aquifer Matrix.* The mineralogy and particle size distribution of the unsaturated and saturated zones strongly influence geochemistry of subsurface waters. As particle size decreases, the surface area increases, providing more opportunities for chemical reactions between solids and water. A particularly important chemical parameter of solids is the cation exchange capacity (CEC). CEC is a function of mineralogy, particle size, and previous geochemical history. It may be a good measure of the potential attenuation of pollutants by ion exchange or sorption reactions. The CEC of clays is strongly dependent on crystalline structure, with the high shrink-swell smectite group (80 to 150 meq/100 g) having the highest CEC and the nonswelling clays such as kaolinite the lowest (3 to 15 meq/100 g). Characterization of clay mineralogy can provide considerable insight into subsurface geochemistry.

*Temperature and Pressure.* Temperature and pressure directly influence the rate of chemical reactions. As pressure increases, the amount of dissolved gases in solution tend to increase. Consequently, sampling methods that allow gases and VOCs to degas to the atmosphere at the land surface may tend to underestimate concentrations. The deeper the sampling, the greater the potential for errors resulting from pressure changes.

*Microbial Activity.* Virtually all ground waters contain diverse populations of microorganisms. The main limitation to microbial growth in the subsurface is low levels of nutrient and dissolved organic carbon. Microorganisms exist that are capable of adapting to transform many types of organic contaminants. Unfortunately, most organic contaminants are more readily degraded under aerobic conditions, and any contaminant loading that adds more than traces of contaminants will rapidly deplete the available natural oxygen supply. As shown in Table 8-3, halogenated aliphatic hydrocarbons and brominated methanes may be degraded under anaerobic conditions. Phenols, alkyl phenols, and chlorophenols also may be degraded under these conditions (Wilson and McNabb, 1983).

Tetra- and trichloroethylene are readily degraded under anaerobic conditions to intermediate daughter products, including 1,2-dichloroethenes and 1,1 -dichloroethene, until vinyl chloride is formed. Unfortumtely, vinyl chloride is resistant to anaerobic degradation, although it readily degrades under aerobic conditions. Other anaerobic degradation sequences that end in relatively resistant compounds include carbon tetrachloride to chloroform to methylene chloride and 1,1,1-trichloroethane to 1,1-dichloroethane to chloroethane (Wood et al., 1985).

Whether a specific contaminant will be degraded depends on geochemical conditions and on the presence of microorganisms that are capable of adaptation. Redox potential and water chemistry can provide considerable insight into subsurface microbial activity even when samples are not taken for microorganisms. Nitrogen, ammonia, hydrogen sulfide, and methane in ground water are all indicators of microbial activity. Carbon dioxide also may indicate microbial activity; however, its presence is more difficult to interpret because carbon dioxide also may come from inorganic sources such as calcium carbonate and dolomite. Section 13.2 discusses microbiological transformations in the subsurface in more detail.

### 8.1.3 The Vadose and Saturated Zones

The vadose and saturated zones have distinct geochemical differences that must be considered when sampling to evaluate contamination. The vadose zone is a dynamic environment with gases moving across the surface, the presence of abundant organic matter, and solutes moving in and out of the saturated zones. Gas transfers of interest include oxygen going in, carbon dioxide moving out, and gases like nitrous oxide or nitrogen being generated by bacteria. Organic matter accumulation, weathering of minerals in the soil profile to form clays, and the presence of air create a chemically reactive environment.

The vadose zone also is characterized by considerable heterogeneity in hydraulic conductivity. Macropores such as old root channels, animal burrows, and channels between soil structural units allow much more rapid movement of water and associated contaminants than the aggregated soil particles (see references in Table 8-l). These variations make representative sampling of soluble contaminants in the vadose zone extremely difficult.

*Table 8-3. Redox Zones for Biodegradation of Organic Micropollutants*

*Increasing Distance from Injection Point —>*

| Biological Conditions | | | |
|---|---|---|---|
| *Aerobic heterotrophic respiration* | *Denitrification* | *Sulfate respiration* | *Methanogenesis* |
| Organic Pollutants Transformed | | | |
| *Chlorinated benzenes<br>Ethylbenzene<br>Styrene<br>Naphthalene* | *Carbon tetrachloride<br>Bromodichloromethane<br>Dibromochloromethane<br>Bromoform* | *Phenol<br>Cresols<br>Chiorophenols* | *$C_1$ and $C_2$ Halogenatad aliphatics* |

*Source: Adapted from Bouwer and McCarty (1984)*

*Table 8-4. Dissolved Solids in Potabie Water -a Tentative Classification of Abundance*

**Major Constituents (1.0 to 1000 ppm)**

*Sodium*
*Calcium*
*Magnesium*
*Silica*
*Bicarbonate*
*Sulfate*
*Chloride*

**Secondary Constituents (0.01 to 10.0 ppm)**

*iron*
*Strontium*
*Potassium*
*Boron*
*Carbonate*
*Nitrate*
*Fluoride*

**Minor Constituents (0.0001 to 0.1 ppm)**

*Antimony**
*Aluminum*
*Arsenic*
*Barium*
*Bromide*
*Cadmium**
*Chromium**
*cobalt*
*Copper*
*Germanium**
*iodide*
*Lead*
*Lithium*
*Manganese*
*Molybdenum*
*Nickel*
*Phosphate*
*Rubidium**
*Selenium*
*Titanium**
*Uranium*
*Vanadium*
*Zinc*

**Trace Constituents (generally <0.001 ppm)**

*Beryllium*
*Bismuth*
*Cerium**
*Cesium*
*Gallium*
*Gold*
*Iridium*
*Lanthanum*
*Niobium**
*Platinum*
*Radium*
*Ruthenium**
*Scandium**
*Silver*
*Thallium**
*Thorium**
*Tin*
*Tungsten**
*Ytterbium*
*Yttrium**
*Zirconium**

** Element which occupies an uncertain position in the list.*

*Source: Adapted from Davis and DeWiest (1966)*

## 8.2 Background Levels and Behavior of Chemical Constituents

Interpretation of subsurface geochemical data requires some knowledge of background levels as a baseline for evaluating possible contamination and the chemical behavior of individual constituents. Tables 8-4 and 8-5 show two classification schemes for the abundance of dissolved species in ground water. The first for potable water, includes only dissolved solids and has four classes: major (1.0 to 1,000 ppm), secondary (0.1 to 10 ppm), minor (0.0001 to 0.1 ppm), and trace (generally less than 0.001 ppm). The second scheme is for highly mineralized water (>1,000 mg/L), and includes gases and organic acids. The classification of the organic acids is based on data from the petroleum-bearing Frio formation in Texas (Kreitler et al., 1988). Organic acids for nonpetroleum-bearing reeks would typically be in the minor category.

Table 8-1 lists some sources of information on background levels of trace constituents in soils and ground water. The U.S. Geological Survey is a good source of background information on elemental composition of soils (Connor and Shacklette, 1975; Ebens and Shacklette, 1982 and Shacklette et al. 197 la,b, 1973, 1974) and water (Durum and Haffty, 1961; Durum et al. 1971; Ebens and Shacklette, 1982; White et al., 1963). Thurman (1985), using data primarily from Leenheer et al. (1974), reported the following median concentrations of organic carbon in various types of aquifers: sand and gravel and limestone and sandstone - 0.7 mg/L; igneous - 0.5 mg/L; oil shales - 3.0 mg/L; organically rich recharge waters - 10.0 mg/L, and petroleum associated wastes - 100 mg/L.

Table 8-1 also lists a number of general references on soil and water chemistry and sources of information on more specific geochemical topics such as redox chemistry, soil gases, biochemical changes, and corrosion and sealing in ground water. Tables 8-6 and 8-7 describe sources of information on the chemical behavior of inorganic and organic natural constituents and contaminants in the subsurface, respectively.

*Table 8-5.* ***ClassIfication of Dissolved Species in Deep- Water Injection Zones***

| *Abundance* | *Cations* | *Anions* | *Gases* | *Organic Acids* |
|---|---|---|---|---|
| *Major* | *Sodium*<br>*Calcium*<br>*Magnesium* | *Chloride*<br>*Bicarbonate*<br>*Sulfate* | *Carbon Dioxide* | *Acetate*<br>*Propionate* |
| *Intermediate* | *Silica*<br>*Barium*<br>*Potassium*<br>*Strontium*<br>*Boron*<br>*Iron*[b] | *Nitrate*<br>*Nitrite*<br>*Orthophosphate*<br>*Bromide*<br>*Iodide* | *Nitrogen*<br>*Hydrogen Sulfide* [b]<br>*Methane* | *Butyrate* |
| *Minor* | *Aluminun*[b]<br>*Manganes*[b]<br>*Arsenic*<br>*Beryllium*<br>*Cadmium*<br>*Chromium*<br>cobalt<br>*Copper*<br>*Lead*<br>*Lithium*<br>*Molybdenum*<br>*Nickel*<br>*Selenium*<br>*Zinc* | *Fluoride* | | |

[a] *Abundance classification criteria (mg/L): Major: $10^3$-$10^5$ Intermediate: 10'-$10^3$; Minor: <10'.*

[b] *Of possible special significance in assessing reactivity with injected wastes.*

*Source: U.S. EPA (1989)*

## 8.3 Spatial Variability

Spatial variability of the subsurface is a result of scale effects and physical and chemical gradients, which generally exist both horizontally and vertically. Table 8-8 summarizes typical ranges of subsurface environmental parameters that may be found at a site. In general, contaminated sites have a greater range of geochemical variation for all parameters than do undisturbed sites. Spatial gradients for individual parameters are discussed below.

### *8.3.1 Scale*

Soil and ground-water geochemistry vary regionally primarily as a function of changes in climate and geology. An important factor affecting ground-water chemistry is distance from the recharge zone. In recharge zones, ground water tends to be less mineralized than in areas of discharge. Regional-scale changes in ground water are characterized by hydrochemical facies (Seaber 1965); dominant chemical constituents change with a shift in facies. Regional-scale patterns in ground-water chemistry (e.g., Back and Hanshaw, 1971, on carbonate equilibria) may not apply on the site scale. This is particularly true with respect to oxygen-sensitive species, because of disturbed land surface and substantial variability of local recharge in surficial aquifers at the site level, which influences oxygen concentration.

The maximum transport distance for contaminants depends on the source and the medium of transport. Soil contamination from atmospheric sources of heavy metals (lead, zinc, cadmium) from smelters can extend from hundreds of meters to kilometers. Contamination from underground storage tanks (hydrocarbons and nonaqueous phase liquids [NAPLs]) can have a radius of influence of about 50 to 2,000 m. NAPLs can migrate vertically 50 to 100 m.

### *8.3.2 Physical Gradients*

*Temperature Gradients.* Temperature gradients affect mixing, reaction paths and rate, and volubility. Vertical temperature gradients can vary greatly, being very steep in geothermal areas, but a good rule of thumb is that temperature increases 1°F for every 50 to 60 feet of depth. Ground water downgradient from a landfill may exhibit temperatures 8 to 12°F higher than water upgradient from a landfill.

*Pressure Gradients.* Vertical pressure gradients are on the order of an atmosphere every 30 ft. Sampling mechanisms used effectively at or near the land surface may not be valid when used at 2 to 5 atmospheres (pressure at depths in excess of 60 ft). Volatiles are in greater danger of being lost during sampling when brought to the surface where the pressure is lower.

*Table 8-6. Sources of Information on Chemical Behavior of Natural Inorganic Constituents and Contaminants in the Subsurface*

| *Reference* | *Description* |
|---|---|
| *Aubert and Pinta (1977)* | *Text on trace elements in soils. Includes chapters on Bo, Cr, Co, Cu, I, Pb, Mn, Mo, Ni, Se, Ti, V, and Zn, and a chapter on 10 other minor elements (Li, Rb, Cs, Ba, Sr, Bi, Ga, Ge, Ag, and Sn).* |
| *Bar-Yosef et al. (1989)* | *Collection of papers on behavior of inorganic contaminants in the vadose zone.* |
| *Callahan et al. (1979)* | *Data on environmental water-related fate of 129 organic and inorganic priority pollutants.* |
| *Copenhaver and Wilkinson (1979)* | *Bibliography with abstracts of articles from 1970 to 1974 on mobility of As, asbestos, Be, Cd, Cr, Cu, cyanide, Pb, Hg, Se, and Zn in soil.* |
| *Förstner and Wittmann (1979)* | *Comprehensive text on behavior of metal contaminants in the aquatic environment.* |
| *Fuller (1977)* | *Review containing over 200 references on the movement of metals in soil.* |
| *Jacobs (1989)* | *Edited volume with 11 chapters on selenium in agriculture and the environment.* |
| *Kabata-Pendias and Pendias (1984)* | *Text on trace elements in soils and plants.* |
| *Kramer and Duinker (1984)* | *Contains 42 papers on the complexation behavior of trace metals in natural waters.* |
| *Lisk (1972)* | *Review paper on occurrence and chemistry of trace elements in soils and toxicities for plants and animals.* |
| *McBride (1989)* | *Review paper on reactions controlling heavy metal solubility in soils.* |
| *Moore and Ramamoorthy (1984a)* | *Book on behavior of heavy metals (As, Cd, Cr, Cu, Hg, Ni, and Zn) in natural waters.* |
| *National Research Council Canada (1982)* | *Data summary sheets on 16 selected toxic elements. NRCC reports on individual elements include: chromium (1976), arsenic (1978a), lead (1978b), mercury (1979a), cadmium (1979b), and nickel (1981).* |
| *Nelson et al. (1983)* | *17 contributed chapters on chemical mobility and reactivity of the soil system with sections on principles of chemical mobility and reactivity, biological activity and chemical mobility, and environmental impacts of toxic chemical transport.* |
| *Purves (1977)* | *Text on trace element contamination of the environment focused primarily on soil.* |
| *Rai and Zachara (1984)* | *Provides data on chemical attenuation rates, coefficients, and constants for 21 elements related to leachate migration: Al, Sb, As, Ba, Be, B, Cd, Cr, Cu, F, Fe, Pb, Mn, Hg, Mo, Ni, Se, Na, S, V, and Zn.* |
| *Rai and Zachara (1988)* | *Report containing laboratory data and equilibrium constants for key reactions needed to predict the geochemical behavior of chromium in soil and ground water.* |
| *Singer (1973)* | *Contains 13 contributed chapters on trace metals and metal-organic interactions in natural waters.* |
| *Thornton (1983)* | *Contains 16 contributed chapters on principles of environmental geochemistry with emphasis on heavy metals.* |

*Velocity Gradients.* Velocity gradients are a function of pressure differences and hydraulic conductivity. Ground water may flow at a rate of 10 to 100 m a day in the vicinity of pumping wells. Increased velocity resulting from pumping may have pronounced geochemical effects on ground-water quality. Evidence of chemical zonation tends to be more pronounced when water movement is rapid in relation to the rate of chemical reactions (Baedecker and Back, 1979).

### *8.3.3 Chemical Gradients*

A factor of 10 gradient in chemical concentrations over vertical distances of less than 10 m is possible. Smith et al. (1991) observed a 27-fold increase in bacterial abundance in a 9-m interval where an aquifer contained nitrate and organic contaminants, Figure 8-1 shows changes in Eh, pH, oxygen, and hydrogen sulfide in an aquifer from its point of outcropping where recharge occurs to about 24 km downdip. Dissolved oxygen dropped to zero about 11 km from the outcrop. At the point that oxygen disappeared, Eh dropped significantly from 400 mV to about 100 mV and continued to decline slowly to around 0 mV at 24 km. Ground-water pH showed a general upward trend. Once reducing conditions prevailed in the aquifer, sulfate reduction, as evidenced by hydrogen sulfide, was observed in 4 of the 10 sampling points.

At the site level, redox potential can vary by a factor of 5 or 10 from the surface of a sand and gravel aquifer to a depth of 100 feet in the same aquifer. Figure 8-2 shows vertical changes in Eh, oxygen, and Fe(II). As in Figure 8-1, when oxygen drops to zero at around 30 m, Eh drops and the concentration of reduced Fe(II) increases dramatically. Tables 8-9 and 8-10 summarize examples of horizontal and vertical redox gradients at the site and regional scales, respectively. An uncontaminated aquifer may have a gradient in redox potential of 30 or 50 mV/m vertically. In contaminated situations, redox potential may show a gradient of 150 mV/m horizontally.

*Table 8-7. Sources of Information on Chemical Behavior of Natural Organic Constituents and Contaminants in the Subsurface*

| *Reference* | *Description* |
|---|---|
| *Bitton and Gerba (1984)* | *Contains 14 papers focusing on the subsurface behavior of microorganisms as pollutants.* |
| *Callahan et al. (1979)* | *Data on environmental water-related fate of 129 organic and inorganic priority pollutants.* |
| *Cheng (1990)* | *Collection of papers on the fate and transport of pesticides in soils.* |
| *Faust and Hunter (1971)* | *Contains 24 papers on the origin, occurrence, and behavior of organic compounds in aquatic environments.* |
| *Gerstl et al. (1989)* | *Collection of papers on the fate of toxic organic chemicals in soil and ground water.* |
| *Gherini et al. (1988, 1989)* | *Compilation of data relevant to predicting the release, transport, transformation and fate of more than 50 organic compounds.* |
| *Ghiorse and Wilson (1988)* | *Review of literature on biodegradation of organic contaminants in ground water.* |
| *Gibson (1984)* | *Contains 15 papers on microbial degradation of organic compounds.* |
| *Goring and Hamaker (1972)* | *Two volumes containing 13 chapters on the behavior of organic chemicals in the soil environment.* |
| *Huang and Schnitzer (1986)* | *Contains 15 contributed chapters on interactions of soil minerals with microbes and natural organic compounds.* |
| *Howard et al. (1991)* | *Handbook of data on environmental degradation rates for more than 300 organic compounds.* |
| *Kobayashi and Rittmann (1982)* | *Literature review summarizing about 90 examples of biodegradation of hazardous organic compounds.* |
| *Lyman et al. (1982)* | *Handbook on methods to estimate environmental behavior of organic compounds.* |
| *Mabey et al. (1982)* | *Aquatic fate process data for organic priority pollutants.* |
| *Maki et al. (1980)* | *Contains 19 contributions to a workshop on biotransformation and fate of chemicals in the aquatic environment.* |
| *Montgomery and Welkom (1989), Montgomery (1991)* | *Volume 1 contains chemical data on 137 organic compounds commonly found in ground water and the unsaturated zone. Volume 2 contains data on 267 additional compounds.* |
| *Moore and Ramamoorthy (1984b)* | *Book on behavior of organic chemicals (aliphatic hydrocarbons, mono- and polycyclic aromatic hydrocarbons, chlorinated pesticides, petroleum hydrocarbons, phenols, PCBs and PCDD) in natural waters.* |
| *Morril et al. (1982)* | *Text on sorption, degradation, and persistence of organic compounds in soils.* |
| *Overcash (1981)* | *Contains 43 papers on decomposition of chlorinated organics, agricultural chemical, phenols, aromatic and polynuclear aromatics, urea resins, and surfactants in soil.* |
| *Sabljib (1987)* | *Sorption coefficient data for 72 nonpolar and 159 polar and ionic organic compounds.* |
| *Sawhney and Brown (1989)* | *18 contributed chapters on reactions and movement of organic chemicals in soil.* |
| *Tabak et al. (1981)* | *Results of biodegradability studies for 114 organic priority pollutants.* |
| *Zehnder (1988)* | *Contains 14 papers on the biology of anaerobic microorganisms* |

Changes of a factor of four or five in pH, alkalinity, or redox potential can mean magnitude changes in many chemical constituents. For example, in oxidizing conditions there is virtually no dissolved iron in ground water. In anoxic ground water reduced ferrous iron ($Fe^{+2}$) can commonly approach 3 to 4 mg/L.

Samples from large-screen intervals in ground-water monitoring wells may give a misleading picture of subsurface geochemistry as a result of mixing chemically different ground waters. For example, Cowgill (1988) sampled a 10-m screen by taking discrete grab samples from the top, middle, and bottom of the screen interval and found that some metal constituents differed by as much as a factor of 10.

## 8.4 Temporal Variability

Variations by a factor of two to five in the concentration of the major ionic constituents (mg/L) in ground water can occur for no apparent reason over the course of a hydrologic year. Very little data are available for µ/L level natural constituents in ground water.

Shallow aquifers are particularly sensitive to changes in pH and Eh in response to recharge events. Recharge at one

*Table 8-8. Ranges of Geochemically Significant Physical, Biological, and Chemical Values of Natural and Disturbed Near-Surface Ground Water*

| Variable | Effects | Natural | Disturbed |
|---|---|---|---|
| | | Physical Variables | |
| ***Temperature*** | ***Mixing; reaction path and rates; solubility*** | ***3°-20°C (Δ10-15°C)*** | ***3°-35°C (Δ10-25°C)*** |
| ***Pressure*** | ***Gas solubility*** | ***1-10 bar*** | ***1-1000 bar*** |
| ***Velocity*** | ***Head differences/gradients*** | | |
| | ***From pumping*** | ***<1-10 m/day*** | ***<1-100 m/day*** |
| | ***Mixing from rapid infiltration*** | ***<1-1000 m/day*** | ***<1-1000 m/day*** |
| | | Biological Variables | |
| ***Biomass*** | ***Catalytic or transformation potential*** | ***$10^1$-$10^8$ cells/g*** | ***$10^4$-$10^8$ cells/g*** |
| ***Activity*** | ***Turnover rates*** | ***0.1 µg/L·hr*** | ***?*** |
| ***$V_{max}$ Glucose (Specific activity)*** | ***Metabolic status*** | ***0.03-0.06 x $10^{-9}$ µg glucose/hr·cell*** | |
| | | Chemical Variables | |
| ***pH*** | ***See Table 7-2*** | ***5.5 to 9.5*** | ***3 to 12*** |
| ***Conductance*** | ***Indicator of salinity*** | ***100 to 5000+*** | ***100 to 10000+*** |
| ***Eh (mV)*** | ***Redox status*** | ***+600 to -100*** | ***+600 to -250*** |
| ***Dissolved Oxygen (mg/L)*** | ***Redox status*** | ***<0.3 to 10*** | ***<0.3 to >10*** |
| ***Alkalinity (mg/L $CaCO_3$)*** | ***Buffer capacity*** | ***100 to 1000*** | ***<100 to >1000*** |

time of the year may result in a set of chemical reactions affecting chemical composition, whereas 6 months later an entirely different set of reactions may occur. Thus, "representative" concentrations of background constituents may vary seasonally.

Tables 8-11 and 8-12 summarize data on short-term (minutes to days) and long-term (seasons to decades) variations of ionic constituents and several contaminants, respectively. In general, both short-and long-term temporal variations are less than an order of magnitude, with nitrate sometimes showing a greater than order of magnitude variation (13X) and $Fe^{2+}$ showing up to two orders of magnitude variation (110X). Short-term variations generally result from individual ground-water recharge events or well pumping and purging. Seasonal variability generally results from variations in precipitation or irrigation, and multiyear trends typically result from human activities such as salt-water intrusion from pumping, irrigation, and fertilizer applications and nonagricultural contamination.

Table 8-13 shows subjective estimates of strength of seasonality or trend in 28 chemical constituents at three different sites. The Sand Ridge site, which is far removed from any sources of contamination, shows strong seasonal trends in temperature and weak seasonal trends in alkalinity, calcium, and magnesium concentrations. At the Beardstown site, monitoring wells are located up- and down-gradient from an anaerobic treatment lagoon for hog processing waste. The contaminated downgradient wells at the Beardstown site exhibited seasonality or trends for 16 constituents. The upgradient ground water showed seasonality or trends for 12 constituents, an intermediate value between the pristine and contaminated ground water. For further information on references that list methods for analyzing time-series water quality data for seasonality and trend, see Table 7-7.

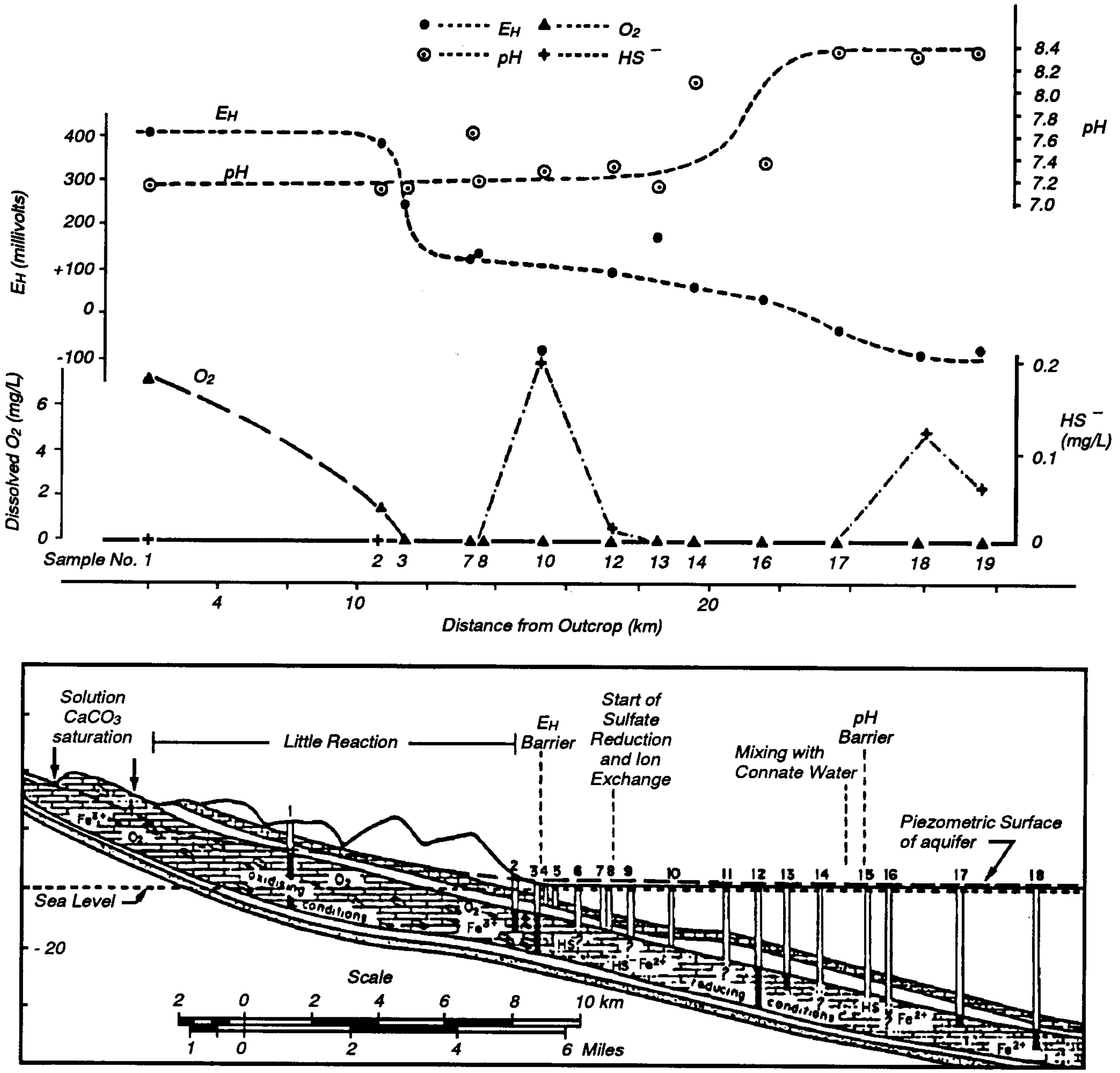


Figure 8-1. Horizontal gradients in uncontaminated oxidation-reduction conditions, Lincolnshire limestone (from Champ et al., 1979, after Edmunds, 1973).

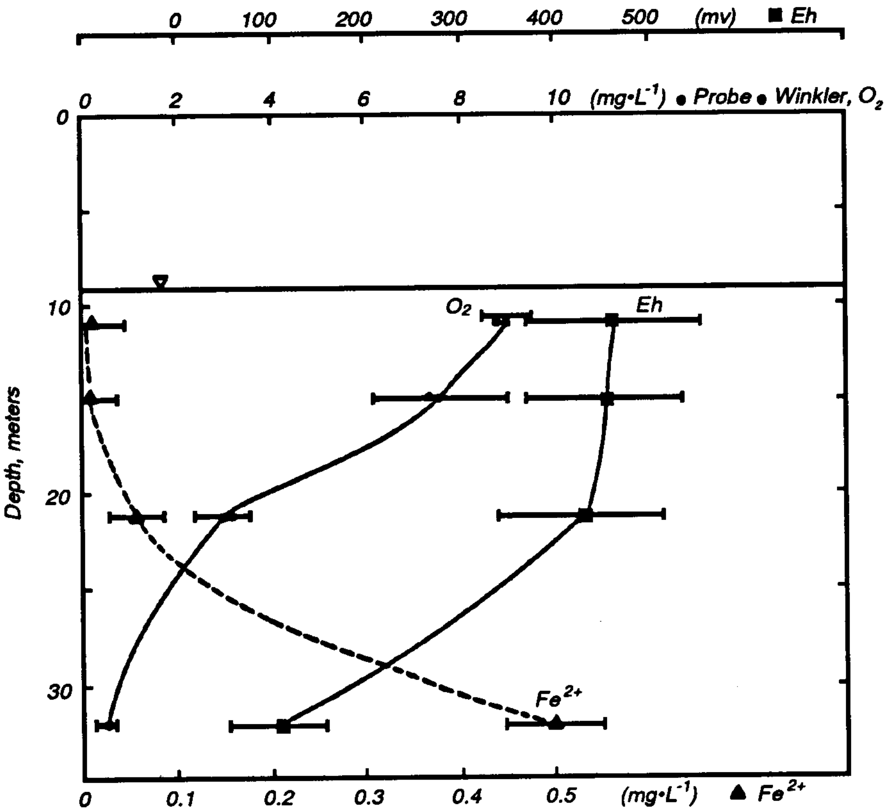


Figure 8-2. Vertical gradients in uncontaminated oxidation-reduction conditions, Sand Ridge State Forest, Illinois (from Barcelona et al., 1989a).

*Table 8-9. Spatial Gradients in Subsurface Oxidation-Reduction Conditions, Site Scale*

| *Type of Environment* | *Redox Gradient*<br>*▲$O_2$, mg $L^{-1}$ $M^{-1}$* | <br>*▲ Eh, mV/m* | *Contaminant?* | *Reference* |
|---|---|---|---|---|
| | | Horizontal (along general ground-water flow path) | | |
| *Unconfined sand* | | *+1* | *landfill leachate* | *Nicholson et al. (1983)* |
| *Unconfined sand* | *-0.04* | *-2* | *high organic carbon recharge* | *Jackson and Patterson (1982)* |
| *Unconfined sand/gravel* | *+0.1* | | *landfill leachate* | *Baedecker and Back (1979)* |
| *Unconfined sand/gravel* | | *-3* | *inorganic fertilizer plume* | *Barcelona and Naymik (1984)* |
| *Unconfined sand* | | *-1.5*[a] | *anaerobic treatment leachate* | *this study (Beardstown)* |
| *Confined sand/gravel* | *-0.01* | *-2.5* | *high organic carbon recharge water* | *Jackson and Patterson (1982)* |
| *Confined sand/gravel* | *+0.5* | | *artificial recharge* | *Van Beek and Van Puffelen (1987)* |
| | | Vertical (increasing depth) | | |
| *Unconfined sand* | | *-10 to -15* | *background* | *Jackson et al. (1985)* |
| *Unconfined sand* | *-0.34*[b] | *-2 to -40*[b] | *landfill leachate* | *Jackson et al. (1985)* |
| *Unconfined sand/gravel* | *-0.7* | *-30* | *high organic carbon recharge water* | *Jackson and Patterson (1982)* |
| *Unconfined sand/gravel* | *-0.2 to 0.77*[a] | *-2 to -30*[c] | *background* | *this study (Sand Ridge)* |
| *Unconfined sand* | | *-8 to -27*[a] | *anaerobic treatment leachate* | *this sutdy (Beardstown)* |

[a] *Eighteen month average between wells 8 and 10.*

[b] *Values available from two separate sampling periods.*

[c] *Thirty month average range between wells 1 and 3 and 3 and 4, respectively.*

*Source: Barcelona et al., 1989a*

*Tabie 8-10. Spatial Gradients in Subsurface Oxidation-Reduction Conditions, Large Scale*

| *Type of Gradient* | *Type of Environment* | *Redox Gradient*<br>*▲$O_2$, mg $L^{-1}$ $Km^{-1}$* | <br>*▲ Eh, mV/km* | *Reference* |
|---|---|---|---|---|
| *Horizontal (along general ground-water flow path)* | *confined sandy clay/gravel (Patuxent)* | | *-34* | *Back and Barnes (1965)* |
| | *confined sand/clay, lignite (Raritan-Magothy)* | | *-57* | *Back and Barnes (1965)* |
| | *confined carbonate chalk (Berkshire)* | *-0.30* | *-30* | *Edmunds et al. (1984)* |
| | *confined limestone (Lincolnshire)* | *-0.34* | *-180* | *Edmunds et al. (1984)* |
| | *confined sandstone/siltstone (Foxhills-Basal Hell Creek)* | *none* | *-0.4 to +5* | *Thorstenson et al. (1979)* |
| | *unconfined sand/gravel (Tucson Basin)* | *+1* | *+23* | *Rose and Long (1988)* |

*Source: Barcelona et al., 1989a*

*Table 8-11. Observations of Temporal Variations in Ground-Water Quality: Short-Term Variations*

| | | *Nature of variability* | | |
|---|---|---|---|---|
| | ***Constituents (Concentration variation)*** | ***Period*** | ***Probable Cause*** | ***Reference*** |
| *Agricultural Sources* | *Se (±2 mg • $L^{-1}$)* | *Monthly* | *Irrigation/return/indeterminate* | *Crist (1974)** |
| | *$NO_3$ - (1-3X)*<br>*$SO_4$ = (3-7X)* | *Minutes* | *Pumpage/head changes and leaching from unsaturated zone* | *Schmidt (1977)** |
| | *$NO^3$ (1-4X)* | *Minutes* | *Pumpage/vertical stratification* | *Eccles et al. (1977)** |
| | *$NO_3$ - (1-10X)*<br>*$SO_4$ = (1-1.5X)* | *Monthly* | *Irrigation/fertilizer applications/ leaching; locational differences apparent* | *Spalding and Exner (1980)* |
| | *$NO_3$ - (0.5-2x)*<br>*Atrazine (1-5X)* | *Hours to weeks* | *Surface runoff recharge* | *Libra et al. (1986)* |
| *Nonagricultural or mixed sources* | *$H_2S$ (1-5X)*<br>*$SO_4$ = (1-1.2X)*<br>*$NH_3$ (1-3X)* | *Minutes to hours* | *Pumping rate and well drilling* | *Colchin et al. (1978)** |
| | *$NO_3$ - (1-13X)*<br>*$SO_4$ = (1-2X)* | *Minutes to hours* | *Pumping rate and purging* | *Humenick et al. (1980)** |
| | *Fe (1-3X)*<br>*Mn (1-1.5X)* | *Minutes* | *Purging* | *Wilson and Rouse (1983)* |
| | *PCE, TCE, 1,2-t-DCE (1-10X)* | *Minutes* | *Purging rate and purging* | *Keely and Wolf (1983)** |
| | *TCE (2-10X)*<br>*$Fe^{2+}$ (1-110X)*<br>*S = (1-15X)* | *Monthly to weekly* | *Pumping rate and development of cone of depression* | *McReynolds (1986)** |
| | *Volatile halocarbons (1-8X)* | *Minutes* | *Purging* | *Barcelona and Helfrich (1986)* |

**Denotes variations observed in water supply production wells, PCE = perchloroethylene, TCE = trichloroethylene, 1,2-t-DCE = 1,2 trans-dichloroethylene*

*Source: Barcelona et al., 1989b*

*Table 8-12. Observations of Temporal Variations in Ground- Water Quality: Long-Term* Variations

| | | *Nature of variability* | | |
|---|---|---|---|---|
| | *Constituents (Concentration variation)* | *Period* | *Probable Cause* | *Reference* |
| *Agricultural sources* | *Cl - (+1.5X)*<br>$SO_4$ *= (2-4X)* | *Decades* | *Irrigation recharge* | *Evenson (1965)** |
| | $NO^3$ *- (3-6X)*<br>$SO_4$ *= (3-7X)* | *Seasonal* | *Irrigation/precipitation* | *Tenorio* et al. *(1969)** |
| | $NO^3$ *- (±48 mg • L*$^{-1}$ *yr* $-^1$*)* | *Seasonal* | *Leaching/recharge* | *Tryon (1976)* |
| | $NO_3$ *- (1-12X)*<br>$SO_4$ *= (1- 1.5X)* | *Seasonal* | *Irrigation/fertilizer applications* | *Spalding and Exner (1980)* |
| | $NO_3$ *- (1-5X)* | *Seasonal* | *Recharge/fertilizer applications* | *Rajagopal and Talcott (1983)* |
| | $NO_3$ *- (1-1.5X)*<br>*Pesticides (1-1.5X)* | *Years-seasonal* | *Infiltration/recharge* | *Libra* et al. *(1986)* |
| *Nonagricultural or mixed sources* | *Conductance (2-3X)*<br>$SO_4$ *= (1-3.5X)*<br>*Hardness (2-6X)* | *Seasonal* | $H_2O$ *level fluctuations freezing/thawing recharge* | *Feulner and Schupp (1963)* |
| | *Conductance (+2,000 µS • cm-)* | *Decades* | *Irrigation/upcoming of saline water* | *Handy* et al. *(1969)** |
| | $NO_3$ *-(±55 mg • L*$^{-1}$ *yr*$^{-1}$*)* | *Seasonal* | *Sewage/fertilizer recharge and applications* | *Perlmutter and Koch (1972)* |
| | *C1-(1-3X)* | *Seasonal* | *Oil field brine/recharge* | *Pettyjohn (1976, 1982)* |
| | *PCE ±1-20X)* | *Seasonal* | *Infiltrated surface water quality variations* | *Schwarzenbach* et al. *(1983)* |
| | *TCE (±1-3X)* | *Seasonal* | *Pumping rate and patterns in well field* | *McReynolds (1986)** |

** Denotes variations observed in water supply production wells, PCE = perchloroethylene, TCE = trichloroethylene*

*Source: Barcelona et al., 1989b*

*Table 8-13.* ***Subjective Estimate of Strength of Seasonality or Trend Ground- Water Constituents In Uncontaminated (Sand Ridge and Upgradient Beards town) and Contaminated (Downgradient Beardstown) Sites***

| | Sand Ridge (1-4) | Beardstown (upgradient) | Beardstown (downgradient) | Number of violations |
|---|---|---|---|---|
| pH | | | | 0 |
| Cond | ° | + | + | 2 |
| TempC | + | + | + | 6 |
| TempW | + | + | + | 4 |
| Eh | | | | 1 |
| Probe $O_2$ | | | | 0 |
| Wink $O_2$ | | | | 0 |
| Alk | ° | + | ° | 1 |
| $NH_3$ | | | | 3 |
| $NO_3N$ | | | | 1 |
| $NO_3NO_2N$ | | | | 0 |
| HS- | | | ° | 0 |
| $SO_4$ | | ° | ° | 0 |
| $SiO_2$ | | ° | | 0 |
| o-$PO_4$ | | | ° | 1 |
| T-$PO_4$ | | | ° | 1 |
| Cl- | | ° | + | 2 |
| $Fe^2$ | | | ° | 3 |
| Ca | ° | ° | + | 1 |
| Mg | ° | ° | | 2 |
| Na | | ° | ° | 3 |
| K | | ° | ° | 3 |
| $Fe_T$ | | | | 0 |
| $Mn_T$ | | ° | + | 0 |
| TOX | | | | 2 |
| VOC | | | | 6 |
| NVOC | | | ° | 4 |
| TOC | | | ° | 3 |

*+ Indicates strongly seasonal.*
*° Indicates apparent trend or possible seasonality.*

*TOC = VOC + NVOC; Total Organic Carbon = Volatile Organic Carbon + Nonvolatile Organic Carbon.*

*Source: Barcelona et al., 1989b*

## 8.5 References

Allen H., E.M. Perdue, and D. Brown (eds.). 1990. Metal Speciation in Groundwater. Lewis Publishers, Chelsea, MI.

Apps, J., L. Tsao, and O. Weres. 1988. The Chemistry of Waste Fluid Disposal in Deep Injection Wells. In: Second Berkeley Symposium on Topics in Petroleum Engineering, LBL-24337, Lawrence Berkeley Laboratory, Berkeley CA, pp. 79-82.

Arnold, E. M., G.W. Gee, and R.W. Nelson (eds.). 1982. Proceedings of the Symposium on Unsaturated Flow and Transport Modeling. NUREG/CP-0030. U.S. Nuclear Regulatory Commission, Washington, DC.

Aubert, H and M. Pints. 1978. Trace Elements in Soils. Elsevier, New York, 396 pp.

Baas-Becking, L.G.M., I.R. Kaplan, and D. Moore. 1960. Limits of the Natural Environment in Terms of pH and Oxidation-Reduction Potentials. J. Geology 68(3):243-284.

Back, W. and I. Barnes. 1965. Relation of Electrochemical Potentials and Iron Content to Ground Water Flow Patterns. U.S. Geological Survey Professional Paper 498-C.

Back, W. and B. Hanshaw. 1971. Rates of Physical and Chemical Processes in a Carbonate Aquifer. In: Non-Equilibrium Concepts in Natural Water Chemistry, ACS Adv. in Chemistry Series 106, American Chemical Society, Washington, DC, pp. 77-93.

Baedecker, MJ. and W. Back. 1979. Modem Marine Sediments as a Natural Analog to the Chemically Stressed Environment of a Landfill. J. Hydrology 43:393-414.

Barber, C., G.B. Davis, D. Briegel, and J.K. Ward. 1990. Factors Controlling the Concentration of Methane and Other Volatiles in Groundwater and Soil-Gas Around a Waste Site. J. Contaminant Hydrology 5:155-169.

Barcelona, M.J. and J.A. Helfrich. 1986. Effects of Well Construction Materials on Ground Water Samples. Environ. Sci. Technol. 20(1 1):1179-1184.

Barcelona, M.J. and T.G. Naymik. 1985. Dynamics of a Fertilizer Contaminant Plume in Ground Water. Environ. Sci. Technol. 18(4):257-261.

Barcelona M.J., T.R. Helm, M.R. Schock, and G.K. George. 1989a. Spatial and Temporal Gradients in Aquifer Oxidation-Reduction Conditions. Water Resources Research 25(5):991-1003.

Barcelona, M.J., D,P. Lettenmaier, and M.R. Schock. 1989b. Network Design Factors for Assessing Temporal Variability in Ground-Water Quality. Environmental Monitoring and Assessment 12:149-179.

Barnes, C.J. 1989. Solute and Water Movement in Unsaturated Soils. Water Resources Research 25(2):38-42.

Barnes, I. and F.E. Clarke. 1969. Chemical Properties of Ground Water and Their Corrosion and Encrustation Effects on Wells. U.S. Geological Survey Professional Paper 498-D.

Bar-Yosef, B., N.J. Barrow, and J. Goldschmid (eds.), 1989. Inorganic Chemicals in the Vadose Zone. Springer-Verlag, New York.

Bitton, G. and C.P. Gerba (eds.). 1984. Groundwater Pollution Microbiology. Wiley-Interscience, New York.

Bohn, H.L., B.L. McNeal, and G.A. O'Connor. 1985. Soil Chemistry, 2nd ed. Wiley-Interscience, New York.

Bolt, G.H. and M.G.M. Bruggenwert (eds.). 1978. Soil Chemistry. A. Basic Elements. Elsevier, New York, 282 pp.

Bouma, J., C. Belmans, L.W. Dekker, and W.J.M. Jeurissen. 1983. Assessing the Suitability of Soils with MacroPores for Subsurface Liquid Waste Disposal. J. Environ. Qual. 12(3):305-311.

Bouwer, E.J. and P.L. McCarty. 1984. Modeling of Trace Organics Biotransformation in the Subsurface. Ground Water 22:433-440.

Brookins, D.G. 1988. Eh-pH Diagrams for Geochemistry. Springer-Verlag, New York, 176 pp.

Callahan, M.A. et al. 1979. Water-Related Environmental Fate of 129 Priority Pollutants (2 Volumes). EPA/440/4-79-029a-b.

Champ, D.R., J. Gulens, and R.E. Jackson, 1979. Oxidation-Reduction Sequences in Ground Water Flow Systems. Can. J. Earth Sci. 16:12-23.

Cheng, H.H. (ed.). 1990. Pesticides in the Soil Environment: Processes, Impacts and Modeling, Soil Science Society of America, Madison, WI, 554 pp.

Colchin, M.P., LJ. Turk, and MJ. Humenick. 1978. Sampling of Ground Water Baseline and Monitoring Data for In Situ Processes. Water Resources Research Center Report EHE 78-01, University of Texas, Austin, TX.

Connor, J.J. and H.T. Shacklette. 1975. Background Geochemistry of Some Rocks, Soils, Plants, and Vegetables in the Conterminous United States. U.S. Geological Survey Professional Paper 574-F.

Copenhaver, E.D. and B.K. Wilkinson. 1979. Movement of Hazardous Substances in Soil: A Bibliography, Vol. I: Selected Metals, Municipal. EPA/600/9-79-024a (NTIS PB80-113103).

Cowgill, U. 1988. Sampling Waters: The Impact of Sample Variability on Planning and Confidence Levels. In Principles of Environmental Sampling, L.H. Keith (ed.), ACS Professional Reference Book, American Chemical Society, Washington, DC, Chapter 11.

Crist, M.A. 1974. Selenium in Waters in and Adjacent to Kendrick Project, Natrona County, WY. U.S. Geological Survey Water-Supply Paper 2023.

Davis, S.N. and RJ. DeWiest. 1966. Hydrogeology. John Wiley & Sons, New York.

Diment, G.A. and K.K. Watson. 1985. Stability Analysis of Water Movement in Unsaturated Porous Materials 3. Experimental Studies. Water Resources Research 21(7):979-984.

Dragun, J. 1988. The Soil Chemistry of Hazardous Materials. Hazardous Materials Control Research Institute, Silver Spring, MD, 447+ pp.

Drever, J.I. 1989. The Geochemistry of Natural Water, 2nd ed. Prentice-Hall, Englewood Cliffs, NJ.

Durum, W .H. and J. Haffty. 1961. Occurrence of Minor Elements in Water. U.S. Geological Survey Circular 445.

Durum, W.H., J.D. Hem, and S.G. Heidel. 1971. Reconnaissance of Selected Minor Elements in Surface Waters of the United States, October 1970. U.S. Geological Survey circular 643.

Ebens, R.J. and H.T. Shacklette. 1982. Geochemistry of Some Rocks, Mines Spoils, Stream Sediments, Soils, Plants and Waters in the Western Energy Region of the Conterminous United States. U.S. Geological Survey Professional Paper 1238.

Eccles, L. A., J.M. Klein, and W.F. Hardt. 1978. USGS Scientists Bring California Water Supply into Compliance with Federal Regulations. Water Well Journal 13(2):42-45.

Edmunds, W.M. 1973. Trace Element Variations Across an Oxidation-Reduction Barrier in a Limestone Aquifer. In Proc. Symp. on Hydrogeochemistry and Biogeochemistg (Tokyo, 1970), E. Ingerson (ed.), Clarke Company, Washington, DC, pp. 500-528.

Edmunds, W.M., D.L. Miles, and J.M. Cook. 1984. A Comparative Study of Sequential Redox Processes in Three British Aquifers. In: Hydrochemical Balances of Fresh-water Systems, Int. Ass. of Hydrological Sciences Pub. No. 150, pp. 55-70.

Eriksson, E. 1985. Principles and Applications of Hydrochemistry. Chapman and Hall, New York.

Evans, D.D. and T.J. Nicholson (eds.). 1988. Flow and Transport Through Unsaturated Fractured Rock. AGU Geophysical Monograph 42. American Geophysical Union, Washington, DC.

Evenson, R.E. 1965. Suitability of Irrigation Water and Changes in Ground-Water Quality in the Lompoc Subarea of the Santa Ynez River Basin, Santa Barbara, CA. U.S. Geological Survey Water-Supply Paper 1809-S.

Fairbridge, R.W. and C.W. Finkl, Jr. (eds.). 1979. The Encylcopedia of Soil Science, Part 1: Physics, Chemistry, Biology, Fertility, and Technology. Dowden, Hutchinson & Ross, Stroudsburg, PA, 646 pp.

Faust, S.D. and O.M. Aly. 1981. Chemistry of Natural Waters. Ann Arbor Science Publishers, Ann Arbor, MI.

Faust, S.D. and J.V. Hunter (eds.). 1971. Organic Compounds in Aquatic Environments. Marcel Dekker, New York.

Feulner, A.J. and R.G. Schupp. 1963. Seasoml Changes in the Chemical Quality of Shallow Ground Water in Northwestern Alaska. U.S. Geological Survey Professional Paper 475-B, pp. B189-B191.

Förstner, U. and G.T.W. Wittmann. 1979. Metal Pollution in the Aquatic Environment. Springer-Verlag, New York.

Fuller, W.H. 1978. Movement of Selected Metals, Asbestos and Cyanide in Soils: Applications to Waste Disposal Problems. EPA/600/2-77-020 (NTIS PB 266905).

Garrels, R.M. and C.L. Christ. 1965. Solutions, Minerals and Equilibria. Freeman, Cooper & Co., San Francisco, CA.

Gerstl, Z., Y. Chen, U. Mingelgrin, and B. Yaron (eds.). 1989. Toxic Organic Chemicals in Porous Media. Springer-Verlag, New York.

Gherini, S. A., K.V. Summers, R.K. Munson, and W.B. Mills. 1988. Chemical Data for Predicting the Fate of Organic Compounds in Water, Vol. 2: Database. EPRI EA-5818. Electric Power Research Institute, Palo Alto, CA.

Gherini, S.A., K.V. Summers, R.K. Munson, and W.B. Mills. 1989. Chemical Data for Predicting the Fate of Organic Compounds in Water, Vol. 1: Technical Basis. EPRI EA-5818. Electric Power Research Institute, Palo Alto, CA.

Ghiorse, W.C. and J.T. Wilson. 1988. Microbial Ecology of the Terrestrial Subsurface. Adv. Appl. Microbiol. 33:107-172.

Gibson, D.T. (ed.). 1984. Microbial Degradation of Organic Compounds. Marcel Dekker, New York.

Goring, C.A.I. and J.W. Hamaker. 1972. Organic Chemicals in the Soil Environment, 2 Volumes. Marcel Dekker, New York.

Handy, A.H., R.W. Mower, and G.W. Sandberg. 1969. Changes in the Chemical Quality of Ground Water in Three Areas in the Great Basin, UT. U.S. Geological Survey Professional Paper 650-D, pp. D228-D234.

Hem, J.D. 1985. Study and Interpretation of the Chemical Characteristics of Natural Water, 3rd ed. U.S. Geological Survey Water-Supply Paper 2254.

Hem, J.D. and W.H. Croper. 1959. Survey of Ferrous-Ferric Chemical Equilibria Redox Potentials. U.S. Geological Survey Water-Supply Paper 1959-A.

Hill, D.E. and J.-Y. Parlange. 1972. Wetting Front Instability in Layered Soils. Soil Sci. Sco. Am. Proc. 36(5):697-702.

Howard, P. H., W.F. Jarvis, W.M. Meylan, and E.M. Mikalenko. 1991. Handbook of Environmental Degradation Rates. Lewis Publishers, Chelsea, MI, 700+ pp.

Huang, P.M. and M. Schnitzer. 1986. Interactions of Soil Minerals with Natural Organics and Microbes. SSSA Sp. Pub. No. 17. Soil Science Society of America, Madison. WI, 606 pp.

Humenick, M.J., L.J. Turk, and M.P. Colchin. 1980. Methodology for Monitoring Ground Water at Uranium Solution Mines. Ground Water 18(3):262-273.

Jackson, R.E. and R.J. Patterson. 1982. Inteq)retation of pH and Eh Trends in a Fluvial-Sand Aquifer System. Water Resources Research 18(4):1255-1268.

Jackson, R.E., R.J. Patterson, B.W. Graham, J. Bahr, D. Belanger, J. Lockwood, and M. Priddle. 1985. Contaminant Hydrogeology of Toxic Organic Chemicals at a Disposal Site, Gloucester, Ontario. 1. Chemical Concepts and Site Assessment. National Hydrologic Research Institute Paper 23. Canadian Department of Environment, Inland Water Branch, Ottawa, Ontario.

Jacobs, L.W. (ed.). 1989. Selenium in Agriculture and the Environment. SSSA Sp. Pub. No. 23. Soil Science Society of America, Madison, WI, 233 pp.

Jury, W.A. 1985. Spatial Variability of Soil Physical Parameters in Solute Migration: A Critical Literature Review. EPRI EA-4228. Electric Power Research Institute, Palo Alto, CA.

Kabata-Pendias, A. and H. Pendias. 1984. Trace Elements in Soils and Plants. CRC Press, Boca Raton, FL, 336 pp.

Keely, J.F. and F. Wolf. 1983. Field Applications of Chemical Time-Series Sampling. Ground Water Monitoring Review 3(4):26-33.

Kobayashi, H. and B.E. Rittmann. 1982. Microbial Removal of Hazardous Organic Compounds. Environ. Sci. Technol. 16:170A-183A.

Kramer, C.J.M. and J.C. Duinker. 1984. Complexation of Trace Metals in Natural Waters. Martinus Nijhoff/Dr W. Junk Publishers, Boston.

Kreitler, C.W., M.S. Akhter, and A.C.A. Donnelly. 1988. Hydrogeologic-Hydrochemical Characterization of Texas Gulf Coast Formations Used for Deep-Well Injection of Chemical Wastes. Bureau of Economic Geology, University of Texas-Austin, TX.

Langelier, W .F. 1936. The Analytical Control of Anti-Corrosion Water Treatment. J. Am. Water Works Ass. 28:1500-1521.

Larson, T.E. and A.M. Buswell. 1942. Calcium Carbonate Saturation Index and Alkalinity Interpretations. J. Am Water Works Ass. 34:1667-1684.

Ledin, A., C. Pettersson, B. Allard, and M. Aastrup. 1989. Background Concentration Ranges of Heavy Metals in Swedish Groundwaters from Crystalline Rocks: A Review. Water, Air, and Soil Pollution 47:419-426. Includes: Cr. Cu, Zn, Cd, Pb.

Leenheer, J.A., R.L. Malcolm, P.W. McKinley, and L.A. Eccles. 1974. Occurrence of Dissolved Organic Carbon in Selected Groundwater Samples in the United States. J. Res. U.S. Geological Survey 2:361-369.

Libra, R.D., G.R. Hallberg, B.E. Hoyer, and L.G. Johnson. 1986. Agricultural Impacts on Ground Water Quality: The Big Spring Basin Study, Iowa. In: Proc. of Agricultural Impacts on Ground Water (Omaha, NB), National Water Well Association, Dublin, OH, pp. 252-273.

Lindberg, D.K. and D.D. Runnells. 1984. Ground Water Redox Reactions: An Analysis of Equilibrium State Applied to Eh Measurements and Geochemical Modeling. Science 225:925-928.

Lisk, D.J. 1972. Trace Metals in Soils, Plants and Animals. Advances in Agronomy 24:267-325.

Lloyd, J. W, and J.A. Heathcote. 1985. Natural Inorganic Hydrochemistry in Relation to Groundwater. Oxford University Press, New York.

Loehr, R.C., J.H. Martin, Jr., E.F. Neuhauser. 1986. Spatial Variation of Characteristics in the Zone of Incorporation at an Industrial Waste Land Treatment Site. In: Hazardous and Industrial Solid Waste Testing: Fourth Symposium, ASTM STP 886, J.K. Petros, Jr., W.J. Lacy, and R.A. Conway (eds.), American Society for Testing and Materials, Philadelphia, PA, pp. 285-298.

Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt (eds.). 1982. Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds. McGraw-Hill, New York.

Mabey, W.R., et al. 1982. Aquatic Fate Process Data for Organic priority Pollutants. EPA/440/4-81-O14 (NTIS PB87-169090).

Maki, A.W., K.L. Dickson, and J. Cairns, Jr. (eds.). 1980. Biotransformation and Fate of Chemicals in the Aquatic Environment. American Society for Microbiology, Washington, DC.

McBride, M.A. 1989. Reactions Controlling Heavy Metal Volubility in Soils. In Advances in Soil Science, B.A. Stewart (ed.), Spnnger-Verlag, New York, Vol. 10.

McReynolds, L. 1986. Monitoring Organic Contaminants in Los Angeles San Fernando Valley Ground Water Basin. In: Proc. of the 15th Biennial Conference on Ground Water, J.J. Devries (ed.), California Water Resources Center, San Diego, CA, pp. 53-60.

Miller, E.E. 1975. Physics of Swelling and Cracking Soils. J. Colloid and Interface Science 52(3):434-443.

Montgomery, J.H. 1991. Ground Water Chemical Desk Reference, Vol. 2. Lewis Publishers, Chelsea, ML

Montgomery, J.H. and L.M. Welkom. 1989. Ground Water Chemicals Desk Reference. Lewis Publishers, Chelsea, MI.

Montgomery, R.H., J.C. Loftis, and J. Harris. 1988. Statistical Characteristics of Ground Water Quality Variability. Ground Water 25(2):176-184.

Moore, J.W. and S. Ramamoorthy. 1984a. Heavy Metal in Natural Waters: Applied Monitoring and Impact Assessment. Springer-Verlag, New York.

Moore, J.W. and S. Ramamoorthy. 1984b. Organic Chemicals in Natural Waters: Applied Monitoring and Impact Assessment. Springer-Verlag, New York.

Morel, F.M.M. 1983. Principles of Aquatic Chemistry. Wiley Interscience, New York, 435+ pp.

Morril, L.G., B. Mahalum, and S.H. Mohiuddin. 1982. Organic Compounds in Soils: Sorption, Degradation and Persistence. Ann Arbor Science/The Butterworth Group, Wobum, MA, 326 pp.

National Research Council Canada, 1976. Effects of Chromium in the Canadian Environment, NRCC Report No. 15018. Ottawa, Ontario.

National Research Council Canada, 1978a. Effects of Arsenic in the Canadian Environment. NRCC Report No. 15391. Ottawa, Ontario.

National Research Council Canada, 1978b. Effects of Lead in the Environment - 1978: Quantitative Aspects. NRCC Report No. 16736. Ottawa, Ontario.

National Research Council Canada, 1979a. Effects of Mercury in the Canadian Environment. NRCC Report No. 16739. Ottawa, Ontario.

National Research Council Canada, 1979b. Effects of Cadmium in the Canadian Environment. NRCC Report No. 16743. Ottawa, Ontario.

National Research Council Canada, 1981. Effects of Nickel in the Canadian Environment. NRCC Report No. 18568 (Reprint). Ottawa, Ontario.

National Research Council Canada. 1982. Data Sheets on Selected Toxic Elements. NRCC Report No. 19252. Ottawa, Ontario. Includes: Sb, Ba, Be, Bi, B, Cs, Ga, Ge, In, Mo, Ag, Te, Tl, Sn (inorganic and organic), U, Zr.

Nelson, D.W., D.E. Elrick, and K.K. Tanji. 1983. Chemical Mobility and Reactivity in Soil Systems. SSSA Sp. Pub. No. 11. Soil Science Society of America, Madison, WI, 262 pp.

Nicholson, R. V., J.A. Cherry and E.J. Reardon. 1983. Migration of Contaminants in Ground Water at a Landfill, a Case Study: 6. Hydrogeochemistry. J. Hydrology 63:131-176.

Overcash, M.R. (ed.). 1981. Decomposition of Toxic and Nontoxic Organic Compounds in Soil. Ann Arbor Science/The Butterworth Group, Wobum, MA, 375 pp.

Pagendorf, G.K. 1978. Introduction to Natural Water Chemistry. Marcel Dekker, New York.

Perlmutter, N.M. and E. Koch. 1972. Preliminary Hydrogeologic Appraisal of Nitrate in Ground Water and Streams, Southern Nassau County, Long Island, NY. U.S. Geological Survey Professional Paper 800-B, pp. B225-B235.

Pettyjohn, W.A. 1976. Monitoring Cyclic Fluctuations on Ground-Water Quality. Ground Water 14(6):472480.

Pettyjohn, W.A. 1982. Cause and Effect of Cyclic Changes in Ground-Water Quality. Ground Water Monitoring Review 2(1):43-49.

Ponnamperuma, F.N. 1972. The Chemistry of Submerged Soils. Advances in Agronomy 24:29-98.

Purves, D. 1978. Trace-Element Contamination of the Environment. Elsevier, New York.

Raats, P.A.C. 1973. Unstable Wetting Fronts in Uniform and Nonuniform Soils. Soil Sci. Sco. Am. Proc. 37:681-685.

Rai, D. and J.M. Zachara. 1984. Chemical Attenuation Rates, Coefficients and Constants in Leachate Migration. Vol. 1: A Critical Review. Vol. 2: Annotated Bibliography, EPRI EA-3356. Electric Power Research Institute, Palo Alto, CA.

Rai, D. and J.M. Zachara. 1988. Chromium Reactions in Geologic Materials. EPRI EA-5741. Electric Power Research Institute, Palo Alto, CA.

Rajagopal, R. and R.L. Talcott. 1983. Patterns in Groundwater Quality Selected Observations in Iowa. Environmental Management 1(5):465-474.

Ransom, M.D. and N.E. Smeck. 1986. Water Table Characteristics and Water Chemistry of Seasonally Wet Soils of Southwestern Ohio. Soil Sci. Sco. Am. J. 50:1281-1290.

Rijtema, P.E., and H. Wassink (eds.). 1969. Water in the Unsaturated Zone, 2 Volumes. Studies and Reports in Hydrology No. 2, UNESCO, Paris.

Ryzner, J.W. 1944. A New Index for Determining Amount of Calcium Carbonate Scale Formed by Water. J. Am. Water Works Ass. 36:472-486.

Rose, S. and A. Long. 1988. Dissolved Oxygen Systematic in the Tucson Basin Aquifer. Water Resources Research 24(1):127-136.

Sablic, A. 1988. On the Prediction of Soil Sorption Coefficients of Organic Pollutants by Molecular Topology. Environ. Sci. Technol, 21(4):358-366.

Sawhney, B.L. and K. Brown (eds.). 1989. Reactions and Movement of Organic Chemicals in Soils. SSSA Special Publ. No. 22. American Society of Agronomy, Madison, WI.

Schmidt, K.D. 1978. Water Quality Variations for Pumping Wells. Ground Water 15(2):130-138.

Schwarzenbach, R.P., W. Giger, E. Hoehn, and J.K. Schneider. 1983. Behavior of Organic Compounds During Infiltration of River Water to Ground Water Field Studies. Environ. Sci. Technol. 17(8):472-479.

Seaber, P.R. 1965. Variations in ChemicaI Character of Water in the Englishtown Formation, New Jersey. U.S. Geological Survey Professional Paper 498-B.

Shacklette, H.T. et al. 1971a. Elemental Composition of Surficial Materials in the Conterminous United States. U.S. Geological Survey Professional Paper 574-D. Includes: Al, Ba, Be, Bo, Ca, Ce, Cr, Co, Cu, Ga, Fe, La, Pb, Mg, Mo, Ne, Ni, Nb, P, K, Sc, Na, Sr, Ti, V, Y, Yb, Zn, Zr.

Shacklette, H.T. et al. 1971b. Mercury in the Environment—Surficial Materials of the Conterminous United States. U.S. Geological Survey Circular 644.

Shacklette, H.T. et al. 1973. Lithium in Surficial Materials of the Conterminous United States and Partial Data on Cadmium. U.S. Geological Survey Circular 673.

Shacklette, H.T. et al. 1974. Selenium, Fluorine, and Arsenic in Surficial Materials of the Conterminous United States. U.S. Geological Survey Circular 692.

Simpson, T.W. and RL. Cunningham. 1982. The Occurrence of Flow Channels in Soils. J. Environ. Qual. 11(1):29-30.

Singer, P.C. 1973. Trace Metals and Metal Organic Interactions in Natural Waters. Ann Arbor Science, Ann Arbor, MI.

Singley, J.E., R.A. Pisigan, Jr., A. Ahmadi, P.O. Pisigian, and T-Y. Lee. 1985. Corrosion and Calcium Carbonate Saturation Index in Water Distribution Systems. EPA/600/2-85/079 (NTIS PB85-228112)

Smith, R.L., R.W. Harvey, and D.R. LeBlanc. 1991. Importance of Closely Spaced Vertical Sampling in Delineating Chemical and Microbiological Gradients in Groundwater Studies. J. Contaminant Hydrology 7:285-300.

Spalding, R.F. and M.E. Exner. 1980. Areal, Vertical and Temporal Differences in Ground Water Chemistry: I. Inorganic Constituents. J. Env. Quality 9(3):466-479.

Sparks, D.L. (ed.). 1986. Soil Physical Chemistry. CRC Press, Boca Raton, FL, 320 pp.

Sparks, D.L. 1989. The Kinetics of Soil Chemical Processes. Academic Press, New York.

Sposito, G. 1984. The Surface Chemistry of Soils. Oxford University Press, New York.

Sposito, G. 1989. The Chemistry of Soils. Oxford University Press, New York.

Stiff, H.A. and L.E. Davis. 1952. A Method for Predicting the Tendency of Oil Field Water to Deposit Calcium Carbonate. AIME Trans. Petroleum Div. 195:213-216

Stumm, W. and JJ. Morgan. 1981. Aquatic Chemistry, 2nd ed. Wiley Interscience, New York.

Tabak, H.H. et al. 1981. Biodegradability Studies with Organic Priority Pollutant Compounds. J. Water Pollution Control Federation 53(10):1503-1518.

Tenorio, P. A., R.H.F. Young, and H.C. Whitehead. 1969. Identification of Return Irrigation Water in the Subsurface. Water Resources Research Center Tech. Report 30, University of Hawaii, Honolulu, HI.

Thornton, I. (ed.). 1983. Applied Environmental Gochemistry. Academic Press, New York.

Thorstenson, D.C., D.W. Fisher, and M.G. Croft. 1979. The Geochemistry of the Fox Hills-Basal Hell Creek Aquifer in Southwestern North Dakota and Northwestern South Dakota. Water Resources Research 15(6):1479-1498.

Thurman, E.M. 1985. Humic Substances in Groundwater. In: Humic Substances in Soil, Sediment, and Waten Geochemistry, Isolation, and Characterization, Aiken, G.R., D.M. McKnight R.L. Wershaw, and P. MacCarthy (eds.), John Wiley & Sons, New York, pp. 87-103.

Tryon, C.P. 1976. Ground-Water Quality Variations in Phelps County, Missouri. Ground Water 14(4):214-223.

U.S. Environmental Protection Agency (EPA). 1989. Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste A Reference Guide. EPA/625/6-89-025a.

Van Beek, C.G.E.M. and J. Van Puffelen. 1988. Changes in the Chemical Composition of Drinking Water after Well Infiltration in an Unconsolidated Sandy Aquifer. Water Resources Research 23(1):69-76.

Van Cleemput, O. and A.S. El-Sebaay. 1985. Gaseous Hydrocarbons in Soil. Advances in Agronomy 38:159-181.

White, R.E. 1985. The Influence of MacroPores on the Transport of Dissolved and Suspended Matter Through Soil. In: Advances in Soil Science, B.A. Stewart (ed.), Springer-Verlag, New York, Vol. 3.

White, D.E., J.D. Hem, and G.A. Waring. 1963. Chemical Composition of Subsurface Waters. U.S. Geological Survey Professional Paper 440-F.

Wilson, J.T. and J.F. McNabb. 1983. Biological Transformation of Organic Pollutants in Groundwater. Eos (Trans. Am. Geophysical Union) 20:997-1002.

Wilson, L.C. and J.V. Rouse. 1983. Variations in Water Quality During Initial Pumping of Monitoring Wells. Ground Water Monitoring Review 3(1):103-109.

Wood, W.W. and R.L. Bassett. 1973. Chemical Quality of Recharge Water as a Function of Bacterial Activity Beneath a Recharge Basin. Eos (Trans. Am. Geophysical Union) 54:261.

Wood, P.R., R.F. Lang, and I.L. Payan. 1985. Anaerobic Transformation, Transport and Removal of Volatile Chlorinated Organics in Ground Water. In: Ground Water Quality, C.H. Ward, W. Giger, and P.L. McCarty, (eds.), Wiley Interscience, New York, pp. 493-511.

Yamn, B., G. Dagan, and J. Goldschmid (eds.). 1984. Pollutants in Porous Media: The Unsaturated Zone Between Soil Surface and Groundwater. Springer-Verlag, New York.

Zimmie, T.F. and C.O. Riggs (eds.) 1979. Permeability and Groundwater Contaminant Transport. ASTM STP 746. American Society for Testing and Materials, Philadelphia, PA.

Zehnder, A.J.B. (ed.). 1988. Biology of Anaerobic Microorganisms. Wiley-Interscience, New York.

Zehnder, AJ.B. and W. Stumm. 1988. Geochemistry and Biogeochemistry of Anaerobic Habitats. In: Biology of Anaerobic Microorganisms, A.J.B. Zehnder (ed.), Wiley-Interscience, New York, pp. 1-38.

ZoBell, C.E. 1946. Studies on Redox Potential of Marine Sediments. Bull. Am. Ass. Petroleum Geol. 30(4):477-513.

# Chapter 9
# Geochemical Sampling of Subsurface Solids and Ground Water

J. Russell Boulding and Michael J. Barcelona

## 9.1 General Considerations

### *9.1.1 Types of Monitoring*

A complete sampling program for subsurface site characterization includes several types of monitoring, each with its own goal. The goal of detection monitoring is generally to determine the presence of contaminated conditions. Unfortunately, drinking water wells have been among the most common detective monitoring systems historically. Assessment monitoring seeks to identify the extent and magnitude of contamination. If assessment monitoring results indicate a degree of contamination requiring remediation, evaluation monitoring is used to provide data necessary to design the remediation system. Performance monitoring is designed to evaluate the success of remediation efforts. Each stage of monitoring often requires the placement of additional monitoring wells and piezometers for water level measurements. Other types of monitoring include litigation monitoring in response to legal actions at contaminated sites and research monitoring aimed at specific scientific objectives.

### *9.1.2 Sampling Protocol*

The goal of a sampling program with an overall monitoring design is often to avoid underestimating a particular impact either in terms of concentration or spatial distribution. Characterization of geochemical variability also is necessary to identify potential chemical problems that may affect selection and design of systems for ground-water treatment.

The field sampling protocol is often the weakest link in soil and ground-water sampling programs. Most initial effort and fiscal resources should be spent on characterizing basic site geology and hydrology. An optimal program may call for the placement of three or four times as many piezometers than wells for water-quality sampling. Initial selection of locations for sampling must be based on a good preliminary characterization of the geology and hydrogeology of the site. This may require spending more of the available financial resources on hydrogeologic characterization than on chemical sampling and analyses. Additional sample locations should be added as understanding of the site evolves.

As discussed in Section 7.1.4, sample location and frequency are among the most critical aspects of sampling because sample collection and sample analysis sometimes can give entirely erroneous results even when approached and executed carefully. Good vertical and horizontal resolution of hydrogeologic conditions are essential before choosing sample locations. Uncertainty, hydrogeologic variability, and quality-assurance decision-making need to be addressed from the initial design stage. Later, an effective sampling strategy and written protocols should be prepared. These measures can improve confidence in subsequent chemical results. Documentation of all sampling procedures is essential, because data collected for a particular purpose may end up being used and interpreted for other objectives.

Sampling protocols should leave room for evolutionary development of the network design. For example, sampling experiments can be used to determine spatial correlation for solid samples. A large number of surface samples or split-spoon samples can be collected but it may only be necessary to analyze a certain percentage (20 to 50 percent) to achieve adequate spatial coverage. If the initial sample groups indicate sufficient sampling resolution, the other samples need not be analyzed. If necessary, additional samples can be analyzed until geostatistical analysis indicates an adequate sampling intensity has been achieved. Samples should not be thrown away if there is any possibility that somebody may use them in the future and if adequate preservative measures are feasible.

Many references thoroughly cover one or more aspects of developing a sampling program and protocol for subsurface solids and/or ground-water. Table 9-1 lists and summarizes 29 of these major reference sources. Rehm et al. (1985) probably contains the most comprehensive review of the literature on methods for hydrogeologic investigations up to 1985. The rest of this chapter focuses on developments since that time, although particularly relevant pre-1985 references are occasionally cited.

Table 9-2 lists sources of information on four aspects of general sample design: (1) general theory, (2) soil sampling, (3) vadose zone sampling, and (4) ground-water sampling. General aspects of selecting sample location, frequency, and size are discussed in the remainder of this section. Section 9.2 reviews sampling of subsurface solids and vadose zone water further, and Section 9.3 covers sampling of ground water.

*Table 9-1. Major Reference Sources on Subsurface Sampling Methods*

| *Reference* | *Description* |
|---|---|
| *Barcelona et al. (1983)* | *Guide to selection of materials for monitoring well construction and ground-water sampling.* |
| *Barcelona et al. (1985a)* | *Ground-water sampling guide covering QA/QC procedures, analyte selection, drilling methods, monitoring well design, well development, sampling, and recommended sampling protocols.* |
| *Berg (1982)* | *Handbook focusing on all aspects of water and wastewater sampling, sample preservation, and QA/QC procedures. One chapter covers sampling of ground water and another covers sampling/ preservation and storage considerations for trace organics.* |
| *Collins and Johnson (1988)* | *Contains 37 papers on field methods on the investigation of ground-water contamination.* |
| *Dunlap et al. (1977)* | *EPA report on sampling for organic chemicals and microorganisms in the subsurface.* |
| *Everett et al. (1976)* | *EPA report describing ground-water-related measuring techniques applicable to the land surface, topsoil, vadose zone and zone of saturation. Also presents cost data on various methods.* |
| *Fenn et al. (1977)* | *Procedures manual for ground-water monitoring at solid waste disposal facilities. Covers monitoring networks, monitoring and well technology, chemical parameters for indicators of leachate and sampling.* |
| *Ford et al. (1984)* | *Manual covering sampling methods for solids, gases, and liquids at hazardous waste sites.* |
| *GeoTrans (1989)* | *Manual developed for the electric utility industry detailing the design, implementation, and maintenance of a ground-water monitoring program.* |
| *Gibb et al. (1981)* | *Contains recommendations for procedures to collect representative ground-water quality samples based on tests of different procedures at six monitoring wells at waste disposal sites in Illinois.* |
| *Gillham et al. (1983)* | *Focuses on sources of sample bias resulting from hydrogeologic factors and chemical alterations; examines chemical characteristics of inorganic and organic parameters, sampling installations, sample collections and methods.* |
| *Holden (1984)* | *Primer focusing on ground-water sampling for volatile organic compounds.* |
| *Howsam (1990)* | *Proceedings of the international conference on water well monitoring, maintenance, and rehabilitation.* |
| *NCASI (1982)* | *Guide to ground-water sampling with chapters on preparation for sampling, sample collection, and sample pretreatment and field analysis.* |
| *Nielsen (1991)* | *Handbook covering all aspects of vadose zone and ground-water monitoring.* |
| *NJDEP (1988)* | *Manual on field sampling procedures prepared by New Jersey Department of Environmental Protection.* |
| *Niaki and Broscious (1986)* | *EPA report describing over 30 methods for detecting leaks in underground tanks.* |
| *Oudjik and Mujica (1989)* | *Handbook focusing on field methods for identification, location, and investigation of pollution sources affecting ground water.* |
| *Rehm et al. (1985)* | *Comprehensive review of methods for solids, unsaturated zone, and ground-water physical and chemical characterization. Bibliography contains over 600 references on these topics.* |
| *Scalf et al. (1981)* | *Manual covering drilling methods, collection of ground-water samples, field tests and preservation, with a short chapter on sampling subsurface solids.* |
| *Simmons (1991)* | *Edited volume covering sampling and analysis of hazardous wastes.* |
| *Sisk (1981)* | *Manual for ground-water/subsurface investigations at hazardous waste sites. Appendix on information sources is especially useful.* |
| *Summers and Gherini (1987)* | *Manual focusing on water sample QA/QC procedures, and procedures for collecting samples.* |
| *Tinlin (1976)* | *EPA report containing nine case studies illustrating procedures for monitoring various classes of ground-water pollution sources.* |
| *Todd et al. (1976)* | *EPA report describing a 15-step monitoring methodology for ground-water quality.* |
| *UNESCO (1983)* | *Proceedings of an international symposium on methods and instrumentation for the investigation of ground water; contains over 60 papers.* |
| *U.S. EPA (1985)* | *EPA guide for developing administrative orders to address RCRA ground-water monitoring violations at interim-status land disposal facilities.* |
| *U.S. EPA (1986a)* | *EPA's RCRA ground-water monitoring technical enforcement guidance document.* |
| *U.S. EPA (1986b)* | *EPA test methods for evaluating solid waste. Part IV in Volume II (Field Methods) defines acceptable and unacceptable designs and practices for ground-water monitoring.* |
| *U.S. Geological Survey (1977+)* | *USGS National Handbook of Recommended Methods for Water Data Acquisition. Individual chapters have come out at different dates. Pertinent chapters include: (2) Ground Water (1980); (4) Biological and Microbiological Quality of Water (1983); (5) Chemical Quality (1982); and (6) Soil Water (1982).* |
| *van Duijvenbooden and van Waegeningh (1987)* | *Proceedings of international conference containing a number of papers on soil and ground-water monitoring strategies and vulnerability mapping.* |
| *Wood (1976)* | *USGS guidelines for collection and field analysis of ground-water samples for selected unstable constituents.* |

*Table 9-2. Sources of Information on General Sample Design*

| Topic | References |
|---|---|
| **General theory** | |
| *Elementary* | *Gilbert (1987), Slonim (1957), Tanur (1978), Williams (1978)* |
| *Advanced* | *Cochran (1977), Deming (1950), Hansen et al. (1953), Hendricks (1956), Jessen (1978), Kish (1965), Pitard (1989), Sukhatme and Sukhatme (1970), Yates (1981)* |
| **Soil** | |
| *Sample Design* | *Barth et al. (1989), Di et al. (1989), Hoffman (1986), Loehr et al (1986), Peterson and Calvin (1986), Williams et al. (1989). See also Table 7-7* |
| *Compositing* | *Peterson and Calvin (1986), Williams et al. (1989)* |
| **Vadose Zone** | |
| *Monitoring Concepts* | *Everett et al. (1982), Everett et al. (1984), Kirschner and Bloomsburg (1988)* |
| *Network Design* | *Bumb et al. (1988), McKee and Bumb (1988)* |
| **Ground water** | |
| *Compositing* | *Rajagopal and Williams (1989)* |
| *General* | *Steele (1986)* |
| *Network Design* | *Hsueh and Rajagopal (1988), Hughes and Lettenmaier (1981), Loaiciga (1989), McNichols and Davis (1988), Nightingale and Bianchi (1979), Sophocleous et al. (1982)* |
| *Sample frequency* | *Close (1989), Hsueh and Rajagopal (1988), Loaiciga (1989), Sgambat and Stedinger (1981), Rajagopal (1986)* |

## 9.1.3 Sample Location

Table 9-3 summarizes major types of sampling designs and when they should be used for characterizing subsurface geochemistry. In general, haphazard water-quality or solid sampling is not an appropriate approach to designing sampling for subsurface geochemical characterization, even though professional judgment alone, is probably the most frequently used method for siting ground-water monitoring wells. Figure 9-1 illustrates some two-dimensional probability sampling designs for spatial characterization. The trends or patterns that commonly exist in subsurface contamination mean that simple random sampling will not give as accurate an estimate of population characteristics as stratified random and grid sampling designs.

Hydrogeologic characterization, initially using surface geophysical techniques followed by piezometers and preliminary well tests to estimate the distribution of hydrogeologic parameters, should come before the location and installation of monitor wells, Good vertical resolution is essential in sampling to characterize distribution of oxidized and reduced species, contaminants, and microbiota. Achieving this resolution requires more discrete well completions with short screens. In most cases, 5-ft to 1.5-m well screens should give adequate vertical resolution.

The spatial distribution of contamination is a major concern with sampling solids. The intensity and number of samples depends on the nonsampling variance, which is the variability of concentration that is unrelated to sampling procedures. Spatial structure determines the distance between samples that have essentially the same concentration, called the range of correlation, to avoid oversarnpling (see Section 7.3.2).

*Table 9-3. Summary of Sampling Designs and CondItions for Their Use*

| Type of Sampling Design | Conditions When the Sampling Design is Useful |
|---|---|
| Haphazard sampling | *A very homogeneous population over time and space is essential if unbiased estimates of population parameters are needed. This method of selection is not recommended due to difficulty in verifying this assumption.* |
| Judgment sampling | *The target population should be clearly defined, homogeneous, and completely assessable so that sample selection bias is not a problem. Or specific environmental samples are selected for their unique value and interest rather than for making inferences to a wider population.* |
| Probability sampling | |
| *Simple random* | *The simplest random sampling design. Other designs below will frequently give more accurate estimates of means in the population that contains trends or patterns of contamination.* |
| *Stratified random* | *Useful when a heterogeneous population can be broken down into parts that are internally homogeneous.* |
| *Multistage* | *Needed when measurements are made on subsamples or aliquots of the field sample.* |
| *Cluster* | *Useful when population units cluster together (schools of fish, clumps of plants, etc.) and every unit in randomly selected clusters can be measured. Soil and ground-water contamination rarely, if ever, exhibit this characteristic.* |
| *Systematic* | *Usually the method of choice when estimating trends or patterns of contamination over space. Also useful for estimating the mean when trends and patterns in concentrations are not present or they are known a priori or when strictly random methods are impractical.* |
| *Double* | *Useful when there is a strong linear relationship between the variable of interest and a less expensive or more easily measured variable.* |
| Search Sampling | *Useful when historical information, site knowledge, or prior samples indicate where the object of the search may be found.* |

*Source: Adapted from Gilbert (1987)*

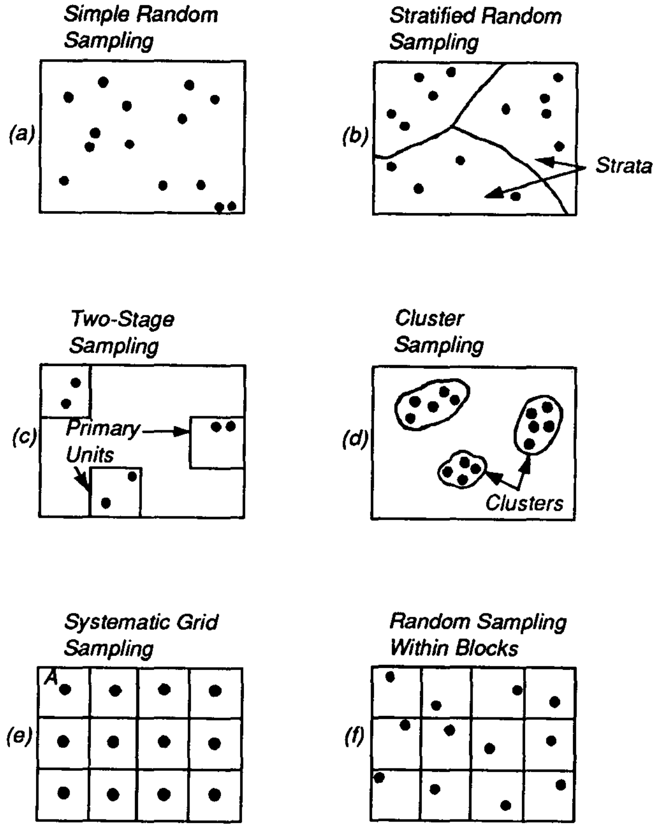


Figure 9-1. Some two-dimensional probability sampling designs for sampling over space (from Gilbert, 1987). See Table 9-3 for description of when these sampling designs are useful.

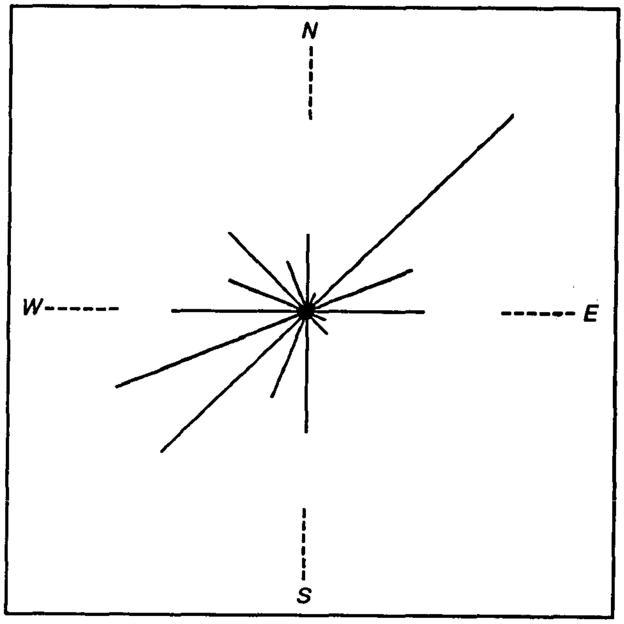


Figure 9-2. Palmerton wind rose, 1978-1979 data (from Starks et al., 1986).

There are two broad designs for soil sampling: (1) grids in which samples are taken from a matrix of squares or quadrants at a site, and (2) transects in which samples are taken at specified intervals along a line. Figure 7-10 in Chapter 7 shows contours of lead concentration in soil drawn from grid sampling. Grids presume an aerial or dispersed source of some kind, and transects presume a preferential source. For example, Starks et al. (1986) established sampling transects where the length was proportional to the frequency with which wind blew in a particular direction to characterize metal contamination from a smelter near Palmerton, Pennsylvania (see Figures 9-2 and 9-3). Flatman (1986) describes use of geostatistics for determining sampling intensity. Grids can be used to estimate short-range correlation. Transects along the path of ground-water or contaminant movement provide the best way to look at long-range correlation. The combination of the two strategies coupled with the initial analysis of selected solid samples at alternate grid or transect locations can be quite effective.

The combined strategy also can avoid the potential collection of redundant information. Using geostatistical analysis techniques of successive analytical subsets minimizes the number of samples actually analyzed. Transects could be both parallel and perpendicular to the axis of ground-water movement, along with some random samples from a grid, as shown in Figure 9-1 (f). Analysis of samples from four equally spaced locations on a transect or grid within the area of influence is a good starting point to estimate the distance of short-range correlation. For soils, at least 5 percent of sampling points should be duplicated to help determine the sampling variability, so it can be analyzed with geostatistical techniques. At least 5 percent of the samples should be split as well.

Preliminary efforts that can help guide the location of initial wells for ground-water sampling include (1) surface geophysical techniques for mapping extent of contaminant plumes; (2) soil gas sampling techniques; (3) Hydropunch® sampling; and (4) selective sampling of piezometers for simple constituents such as pH, conductance, and possibly iron or dissolved oxygen concentrations.

Soil gas monitoring (see Section 5.2.5) and Hydropunch® ground-water sampling (see Section 9.3.4) probably give the best pictures of short-range variability in three dimensions. Sampling from monitoring wells usually gives some sort of integrated value depending on the relative width or thickness of the hydrogeologic formation of interest and the length of the screen. Disadvantages of soil gas concentrations include (1) lack of the ability to directly calibrate, because all values are relative and difficult to reproduce, (2) decontamination, and (3) short circuiting of air from the surface, which can distort results.

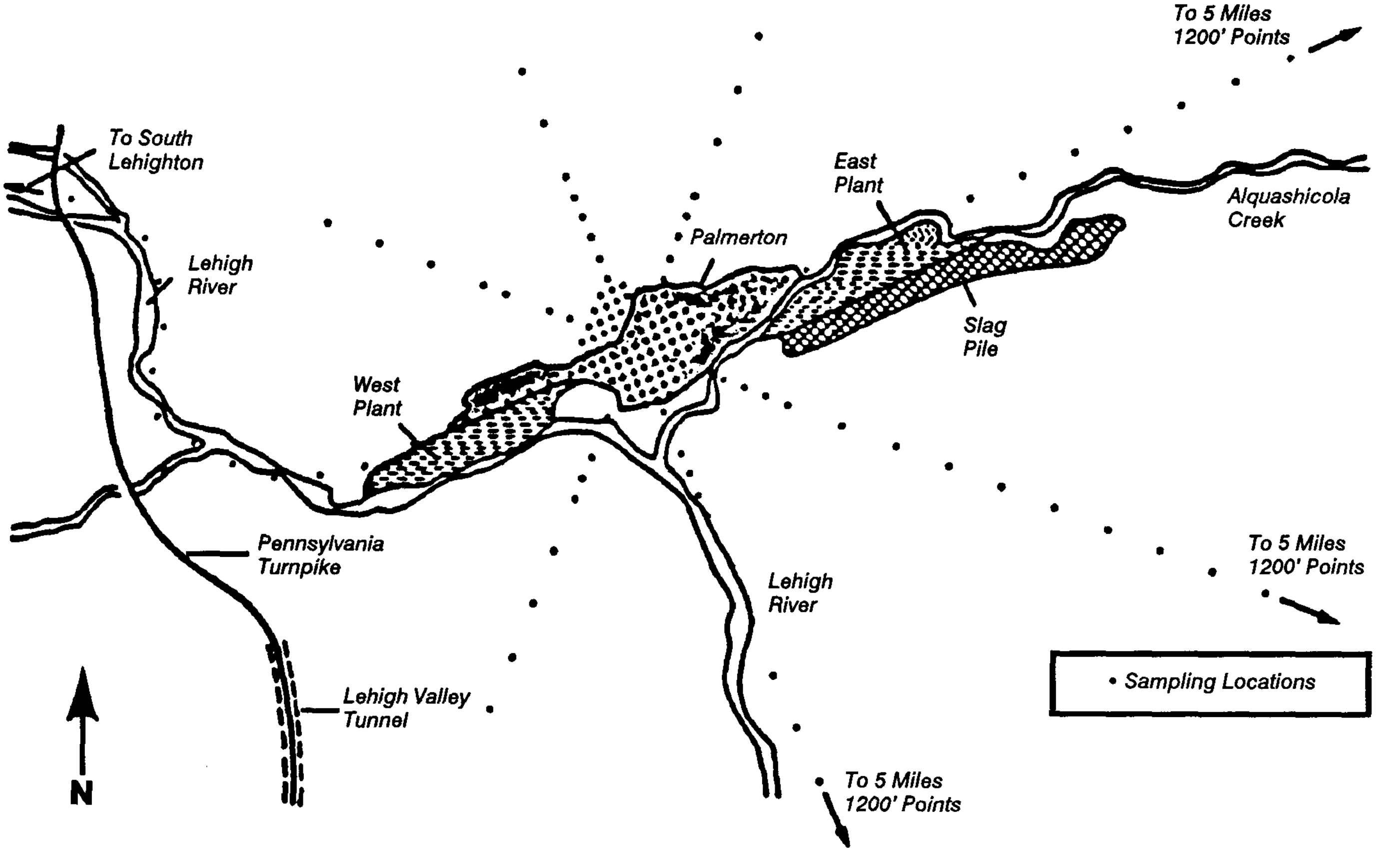


**Figure 9-3.** **Sample pattern for the initial Palmerton survey (1"= 4250') (from Starks et al., 1986).**

### *9.1.4 Sampling Frequency*

Table 9-4 shows estimated ranges of sampling frequency in months necessary to maintain information loss at less than 10 percent for selected types of chemical parameters. For many chemical constituents, quarterly sampling is adequate for characterizing short-term (i.e., monthly to 1 or 2 years) changes over time. For some reactive constituents such as iron and other redox-sensitive constituents, bimonthly sampling may be required.

With intermittent sources of contamination, it is especially important that the frequency of sampling not allow a contaminant to be missed. Barcelona et al. (1985a) describe a procedure for estimating sample frequency to detect contaminant plumes based on the type of plume (slug, intermittent, or continuous) and hydrogeologic parameters of gradient, hydraulic conductivity, effective porosity, and distance along the flow path. Figure 9-4 shows a nomograph that can be used when these parameters are known. When the contaminant plume is a slug source or intermittent, sampling frequency should probably be more frequent to ensure that the plume is not missed. One advantage to the slow movement of ground water is that if there are questions about a sample, resampling, a week later will yield roughly the same ground water.

Precise estimation of optimum sampling frequency is probably impractical for most investigations. For example, Bell and DeLong (1988) found that tetrachloroethylene at concentrations of 200 to 300 µg/L exhibited variations of a factor of one or two over the course of a year. Their work points out that data collection may be required for 4 years or more in order to estimate the optimal sampling frequency to determine seasonal variability. Therefore, it is important to select sampling frequency on the basis of an initial period of monitoring in the context of the duration of the program.

It should not be necessary to sample all monitoring wells every time samples are taken. Sampling selected wells can develop a preliminary picture, with additional follow-up sampling at additional wells rounding out the picture.

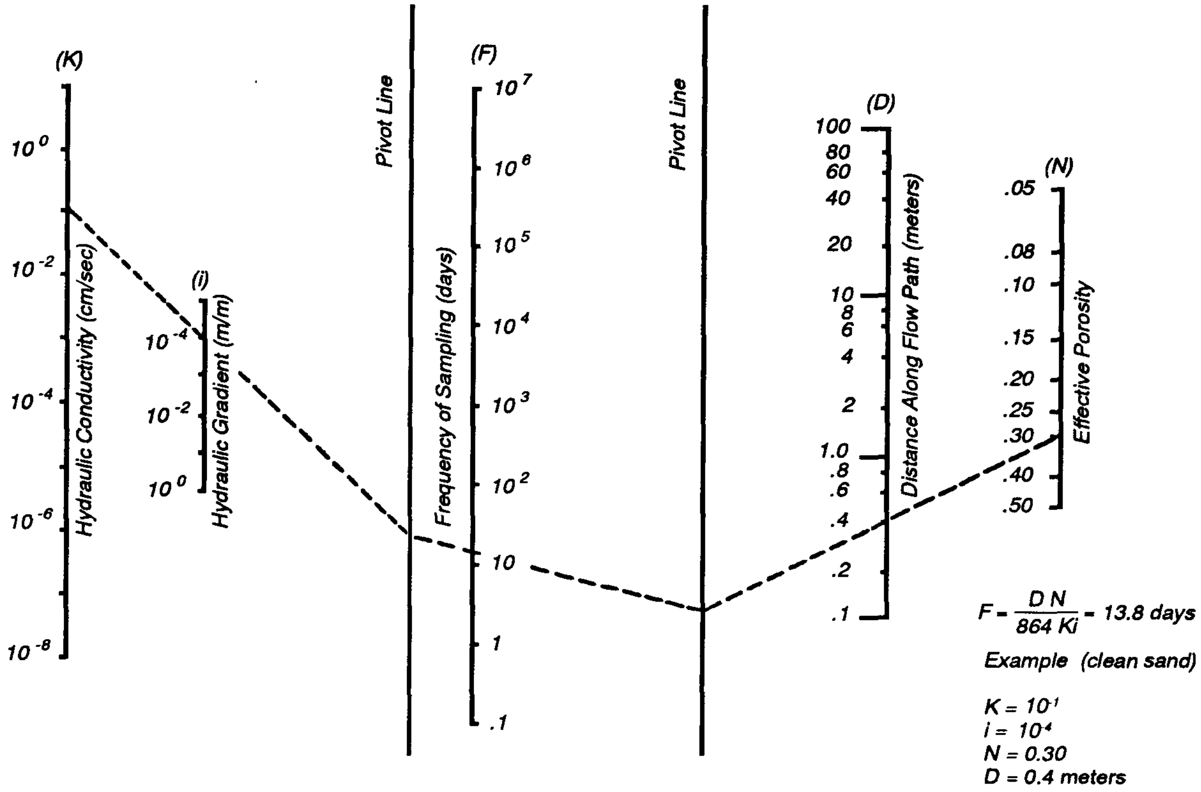
### 9.1.5 Sample Type and Size

Soil sampling must take into account fractures in earth materials and the fact that the subsurface is heterogeneous (as scales ranging from centimeters to meters). If the soil has obvious fractures and channels in the subsurface, sampling should sample both affected and apparently nonfractured areas for comparison. Soil sample quantities of less than 100 g tend to be unrepresentative even of the areas where the sample is taken. In the laboratory, the sample can be mixed, subsampled prior to analysis.

Compositing samples is often beneficial for soil investigations. However, where volatile constituents are involved, compositing is not practical because handling samples in the air for compositing will result in the loss of the contaminant. One way to get around this problem is to take two or three samples within each identifiable core segment and put them into a sealed glass vial immediately after sampling. In this case, a volume of methyl alcohol in the sealed vial can improve volatile recovery and expedite analysis. However, it is possible that the sampling variance from potential loss of

**Table 9-4.** ***Estimated Ranges of Sampling Frequency (in Months) to Maintain information Loss at <10% for Selected Types of Chemical Parameters***

| *Type of Parameter* | *Pristine background conditions* | *Contaminated* | |
|---|---|---|---|
| | | *Upgradient* | *Downgradient* |
| **Water quality** | | | |
| *Trace constituents (<1.0 mg/L)* | *2 to 7* | *1 to 2* | *2 to 10* |
| *Major constituents* | *2 to 7* | *2 to 38* | *2 to 10* |
| **Geochemical** | | | |
| *Trace constituents (<1.0 mg/L)* | *1 to 2* | *<2* | *1 to 5* |
| *Major constituents* | *1 to 2* | *7 to 14* | *1 to 5* |
| **Contaminant indicator** | | | |
| *TOC* | *2* | *3* | *3* |
| *TOX* | *6 to 7* | *24* | *7* |
| *Conductivity* | *6 to 7* | *24* | *7* |
| *pH* | *2* | *2* | *1* |



$$F = \frac{D\,N}{864\,Ki} = 13.8 \text{ days}$$

*Example (clean sand)*

$K = 10^{-1}$
$i = 10^{-4}$
$N = 0.30$
$D = 0.4$ meters

**Figure 9-4. Sampling frequency nomograph (from Barcelona et al., 1985).**

volatiles involved in handling the sample may far exceed the actual variability in the field.

Williams (1989) compares the results of one 500-g sample, twenty 25-g composite samples, and ten 50-g composite samples. He found that a single 25-g composite sample was the most accurate and precise technique for determining radium concentrations in contaminated surface soil. Initial soil samples of 100-g are about the best size for such composite analyses.

### *9.1.6 Vadose versus Saturated Zone*

Careful sampling of gases and solids in the vadose zone can provide information for better locating monitoring wells in the saturated zone. The mass of contaminant, or at least the most persistent contaminants, are often associated with the solids.

## 9.2 Sampling Subsurface Solids and Vadose Zone Water

### *9.2.1 Analyte Selection*

Halocarbons, chlorinated hydrocarbon solvents (e.g., tetra- and trichloroethylene), and fuel constituents (e.g., toluene, benzene, ethyl benzene, and xylenes) are amenable to preliminary delineation by soil gas methods. Soil gas samples for carbon dioxide, methane, oxygen, and nitrogen can provide additional insights into subsurface chemistry, particularly microbiological activity.

In addition to examining chemical constituents, analyzing solid samples for grain-size distribution and correlation with permeability can be helpful.

### *9.2.2 Sampling Devices and Techniques*

Table 9-5 lists sources of information on sampling soil and vadose zone solids, water, and gases.

Simple techniques for surface sampling of soils include the hand auger, brace and bit, and posthole diggers. The most commonly used core sampling devices are split spoons or Shelby tubes that provide a continuous or driven core during drilling operations. Sampling continuously or ahead of hollow-stem- drilling augers are good ways to obtain uncontaminated and minimally disturbed soil samples. Section 3.1 provides some additional discussion of these sampling methods for obtaining information on subsurface stratigraphy. Where the surface layer of soil is known to be heavily contaminated, as with sites involving smelters and uranium mills, the surface should be scraped away before sampling at lower levels so the sampler is not contaminated as it passes through the contaminated surface.

Figure 9-5 shows a soil core sampling apparatus described by Myers et al. (1989) that can obtain undisturbed cores for laboratory leaching experiments. A variety of samplers are available that advance in front of an auger. The better devices have a plunger or cylinder that maintains a partial vacuum to prevent the soil material from falling out of the core (Munch and Killey, 1985; and Zapico et al., 1987). This vacuum is particularly important for saturated sands that simply flow out of normal sampling tubes. Figure 9-6 shows a modified wireline piston design for sampling cohesionless sediments and Figure 9-7 shows how this device can be used to take samples through a hollow-stem auger. In careful use, the more sophisticated devices can achieve a 50 percent core recovery. Heaving sands create special problems. Filling the auger with water sometimes helps prevent clogging from heaving sands by maintaining hydrostatic pressure.

Suction lysimeters can be used to sample pore water in the vadose zone. Extremely variable transmissive properties of surface soils make accurate interpretation of soil pm water concentrations very difficult. Virtually all of the water movement and associated contaminant transport may occur in about 5 percent of the soil profile. The zone of sampling influence with a suction lysimeter is about 10 or 20 cm for a 24-hour period (Morrison and Lowery, 1990). In some instances, longer suction sampling periods may extend the influence to 50 cm.

Sampling for microbiological parameters requires both the collection of soil samples and the paring of any outside portion that may have been in contact with the sampling apparatus. This operation should be done before placing the samples in sterile glass vials.

***Table 9-5. Sources of Information on Sampling Soil and Vadose Zone Solids, Solutes, and Gases***

| *Topic* | *References* |
|---|---|
| *Cohesive* | *Barth and Starks (1985), Cameron et al. (1966), Ford et al. (1984), Rehm et al. (1985), Mason (1983), Myers et al. (1989)* |
| *Noncohesive* | *Munch and Killey (1985), Zapico et al. (1987), Armstrong et al. (1988)* |
| *Volatiles in Soil* | *Slater and McLaren (1983)* |
| Vadose zone solute sampling methods | |
| *Overviews* | *Everett et al. (1982, 1983, 1984), Rehm et al. (1985), U.S. EPA (1986c), Wilson (1980), Wilson (1983)* |
| *Physical Properties* | *Wilson (1982)* |
| *Moisture Potential* | *Wilson (1981)* |
| *Moisture Content* | *See overview references.* |
| *Solute Sampling* | *Brown (1987), Everett and McMillion (1985), Johnson and Cartwright (1980), Litaor (1988), Stevenson (1978)* |
| Soil gas sampling | |
| *Gas Properties* | *Mackay and Shiu (1981)* |
| *Overviews* | *Devitt et al. (1987), Kerfoot and Barrows (1986), Marrin (1987), Marrin and Kerfoot (1988)* |
| *Case Studies* | *See Table 9-6* |

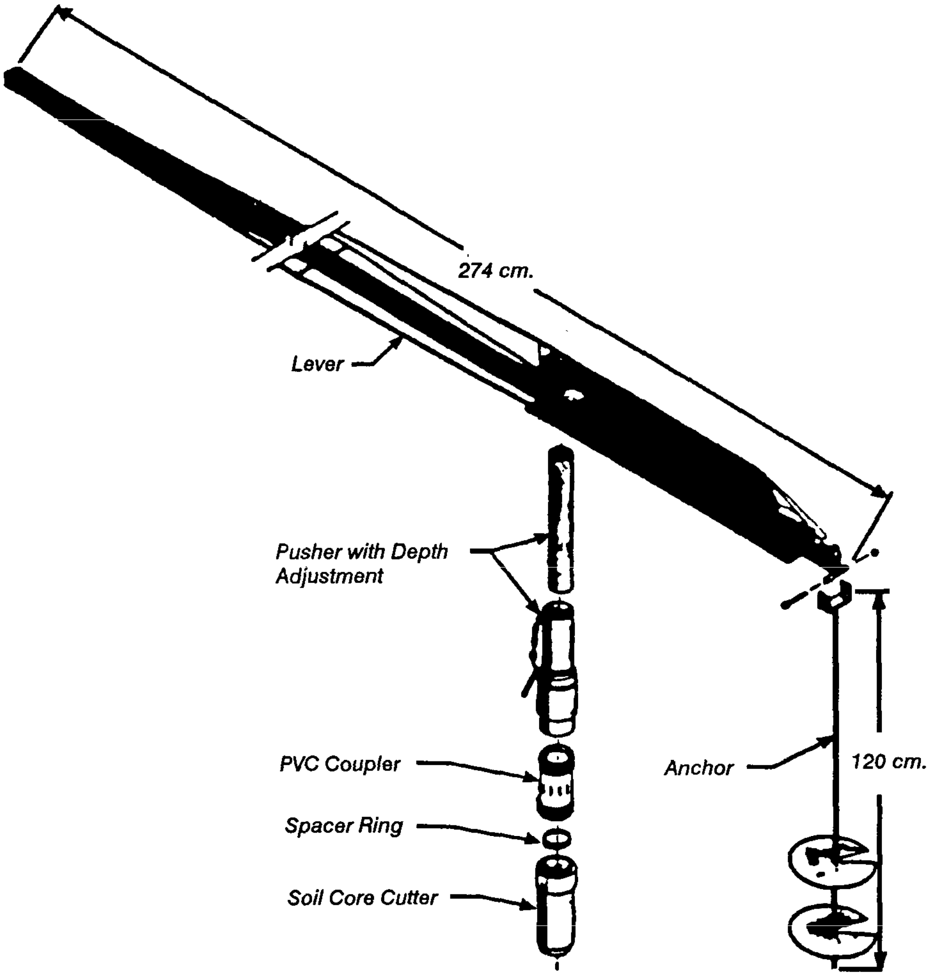


**Figure 9-5.** **Undisturbed soil core sampling apparatus (from Myers et al., 1989).**

Soil gas sampling generally involves driving a probe into the subsurface. Typically, the probes are driven by hand or with some kind of pneumatic or electric hammer. Soil gas is obtained by applying a vacuum that brings the soil gas into the vicinity of the tip of the probe. Samples are collected in fluorocarbon bags or syringes and analyzed on site or in a laboratory. Analysis techniques can be as simple and nonspecific as a hand-held gas survey meter, and as detailed and specific as an analytic laboratory's instrumentation allows. Mobile laboratories provide an intermediate level of analytical detail; they provide semiquantitative results with precision on the order of plus or minus 100 percent. At least 5 percent of air-filled porosity is required to pull a vacuum to obtain samples.

Table 9-6 summarizes information from 14 soil gas investigations. Soil gas samples for areal characterization are usually taken at a uniform depth with the specific depth typically from 1 to 6 ft below the surface, although Glaccum et al. (1983) sampled immediately above the water table, which was as much as 10 m deep. Vertical profiles may provide additional insight into contaminant behavior. Figure 9-8 shows six types of vertical concentration profiles that develop under different subsurface conditions. Special care should be taken to identify any underground utility lines to avoid accidental puncture with the probe. Buried sewers or product lines may be the source of soil gas contamination, and other utility lines may provide a directional component to contamination (Marrin and Thompson, 1987). See Section 5.2.5 for additional discussion of soil gas sampling methods.

## 9.3 Sampling Ground Water

Figure 9-9 shows a generalized flow diagram of ground-water sampling steps, and Table 9-7 lists additional sources of information on various aspects of ground-water sampling.

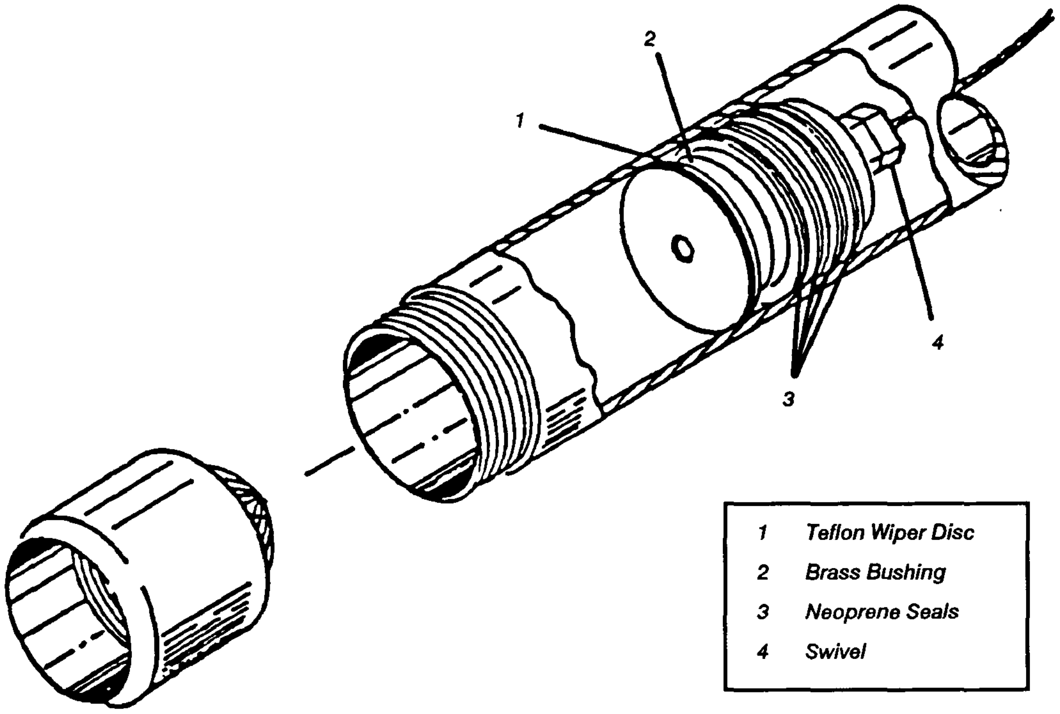


**Figure 9-8.** **Modified wireline piston design (from Armstrong et al., 1988).**

References that provide good general coverage of ground-water sampling include Barcelona et al. (1985), GeoTrans (1989), Gillham et al. (1983), Rehm et al. (1985), and Scalf et al. (1981).

### *9.3.1 Analyte Selection*

Tables 9-8 and 9-9 identify chemical constituents of interest for various types of ground-water monitoring activities. In hazardous waste site investigations, regulations will generally specify the contaminants to be tested for. Focusing on priority pollutants alone, however, may not provide a complete geochemical picture of contamination. The source of contamination may involve a large number of individual contaminants that are not classified as hazardous. Also, determination of redox-sensitive constituents (dissolved oxygen and dissolved iron), pH, and conductance, may provide valuable insight into subsurface contaminant geochemistry.

Highly mineralized ground water, commonly encountered in formations being evaluated for deep-well injection of wastes, may require more complete analyses for natural inorganic and organic constituents. Table 9-10 lists analytical results for ground-water samples from four deep-well injection sites and the Frio formation in Texas (which has received more deep-well injected wastes than any other formation in the United States). Not all of the studies analyzed the same constituents in all samples, but an examination of this table may give some guidance for analyte selection.

Iron, an inexpensive constituent to determine analytically, can be used as an indicator of redox conditions and potential mobility for heavy metals. Dissolved gases are excellent indicators of redox conditions and microbial activity. For example, Leenheer and Malcolm (1973) analyzed for $H_2$ $N_2$, $CH_4$, $CO_2$, and $H_2S$ in serial samples from a well through which a plume of deep-well injected wastes passed. They used changes in the relative percentages of the different gases as indicators of changing microbial activity. Malcolm and Leenheer (1973) suggest that separate analysis for dissolved organic carbon DOC) and suspended organic carbon (SOC) can yield more complete analytical results.

Calcium carbonate and iron/manganese concentrations are especially important parameters if remediation involves air stripping. Air-stripping towers are particularly susceptible to fouling by calcium carbonate and metal oxide precipitates.

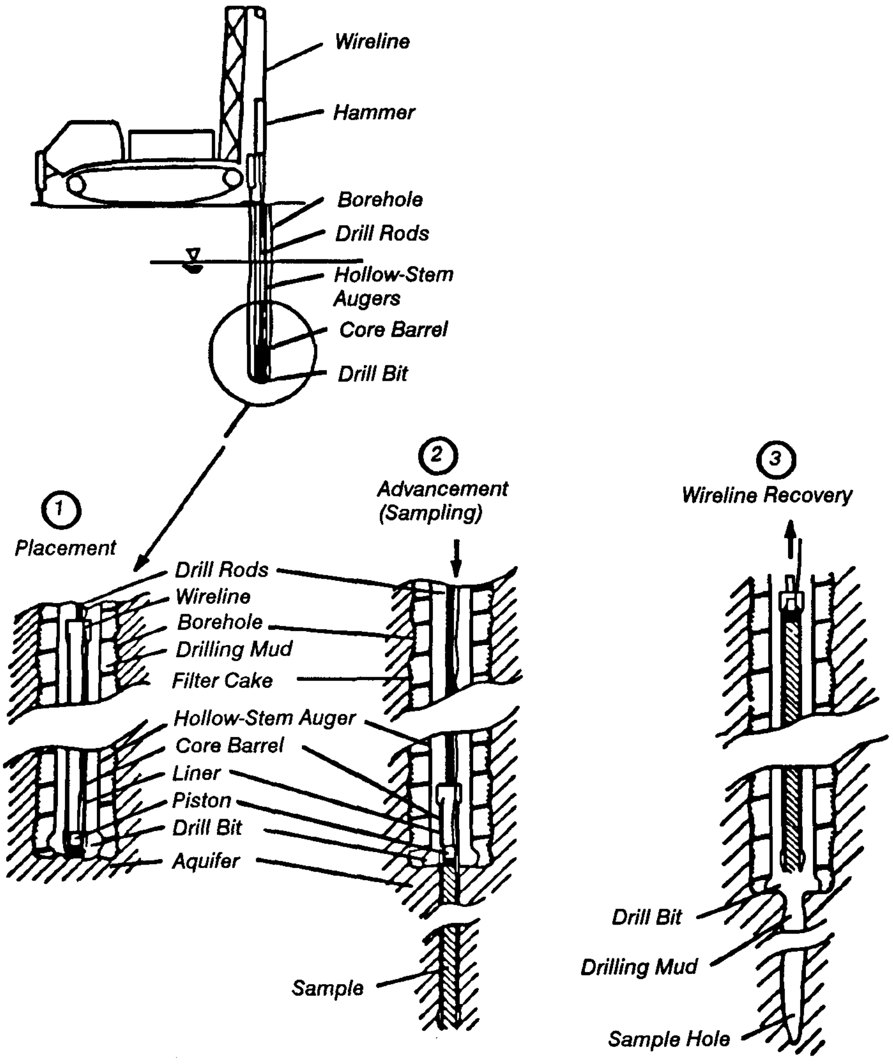


**Figure 9-7. Wireline piston core barrel sampling operation (from Zapico et al., 1987).**

When trichloroethylene (TCE) is involved as a contaminant, it is important also to analyze for biotransformation products (e.g., 1,2-dichloroethene, 1,1-dichloroethene, and vinyl chloride), The vinyl chloride monomer metabolic product is more toxic than TCE and resistant to degradation under anaerobic conditions.

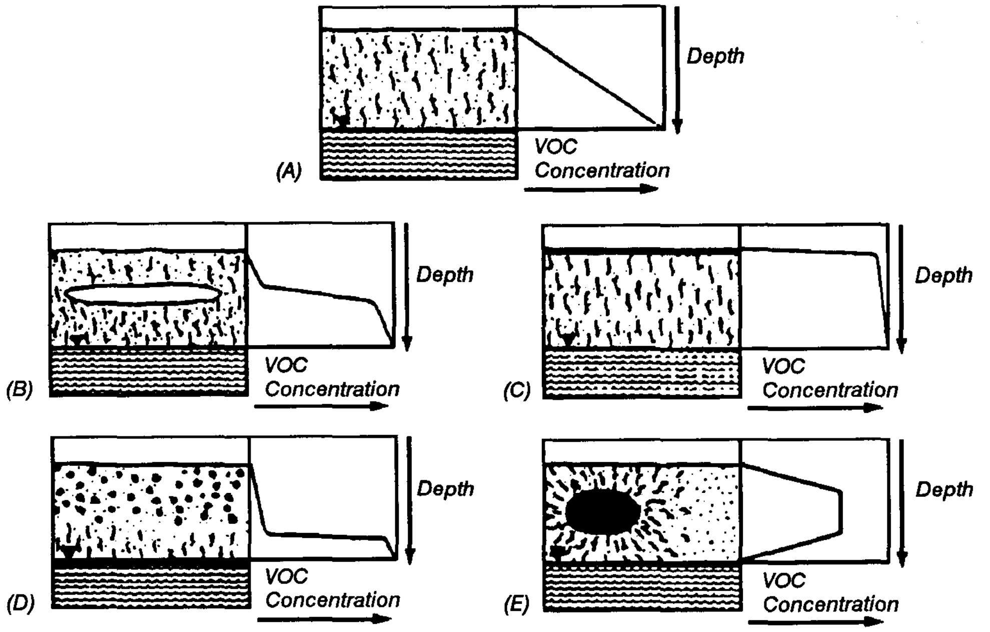
Battista and Connelly (1989) found that inorganic parameters such as chemical oxygen demand, specific conductance, chloride, alkalinity, and hardness were reasonably good indicators for predicting VOC contamination from landfills. When the inorganic parameters were detected above background levels in monitoring wells, VOCs were also usually present. Out of 49 ground-water samples at landfill sites in Wisconsin, VOCs and elevated inorganic parameters were detected at about the same frequency in 20 (41 percent), elevated inorganic parameters without VOCs were detected in 11 (22 percent), and VOCs without elevated inorganic parameters were detected in 3 wells (6 percent). The remaining 15 wells in the study showed neither VOCs nor elevated inorganic parameters.

### *9.3.2 Well Development*

Well development, which involves the removal of fines created during the drilling process, is essential before sampling begins. Pumping rates generally used for well development are 5 to 10 gpm. Bailing, swabbing, pumping, and air-lifting are common methods used for development. Table 4-2 compares the advantages and disadvantages of the most commonly used well development techniques. Air development may increase the possibility of environmental exposure to workers at the surface where volatiles are involved.

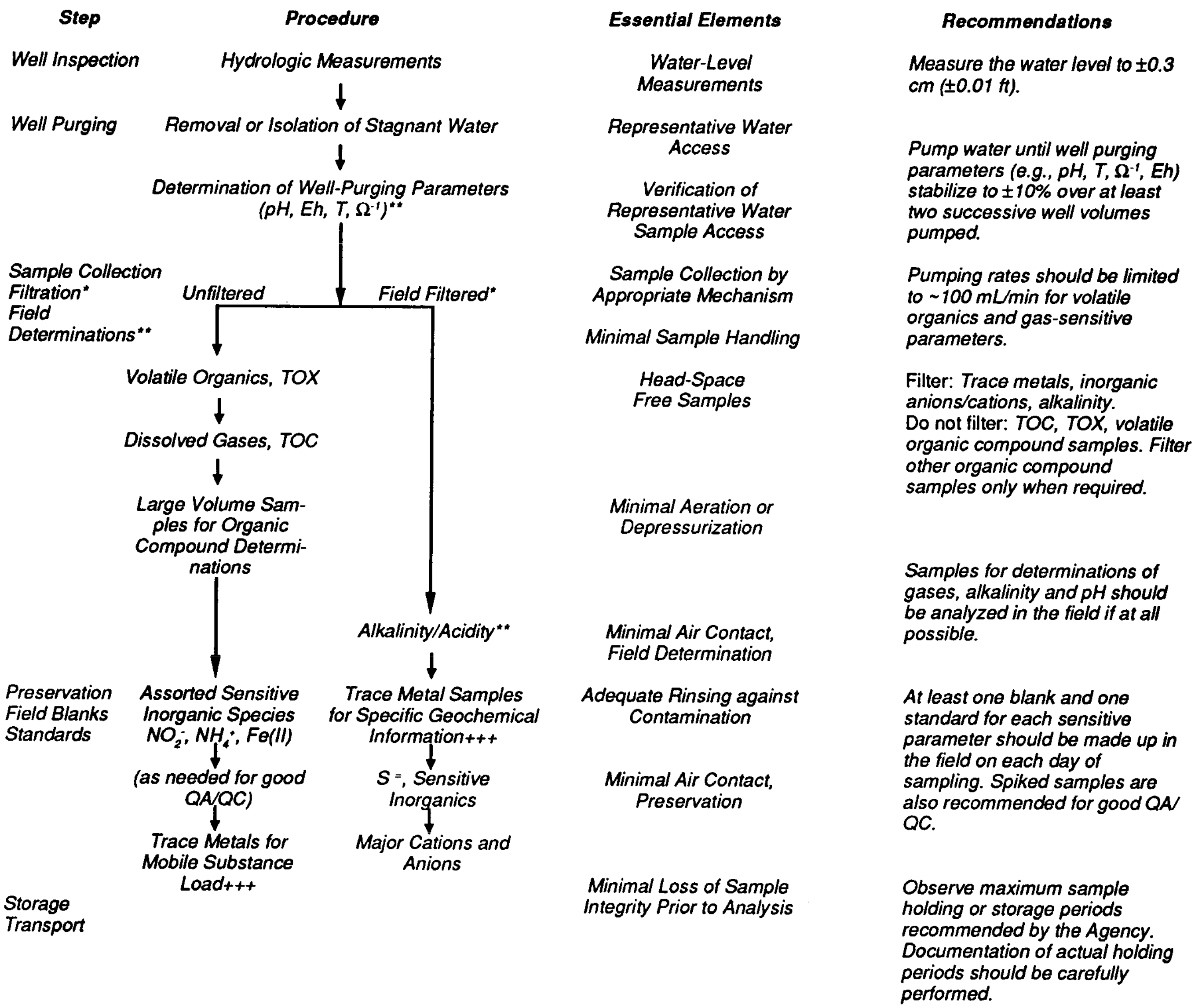
*Table 9-6. Soil Gas Sampling Case Studies*

| *Location* | *Contaminant/Soil Gas Sample Methods* | *Reference* |
|---|---|---|
| *Las Vegas, NV* | *Benzene, chlorobenzene. Dynamic samples above water table (up to 10 m deep).* | *Glaccum et al. (1983)* |
| *Tucson, AZ (Water table 120')* | *Trichloroethylene (TCE). Dynamic, areal (<2 m); vertical (6 m intervals).* | *Marrin and Thompson (1984, 1987)* |
| *Denver, CO* | *Tetrachloroethylene (PCE). 3-day static samples near surface.* | *Voorhees et al. (1984)* |
| *Northern CA (Water table 25')* | *1,1,2-Trifluorotrichloroethane (F-113). Dynamic, area (10'), vertical to 20'.* | *Marrin and Thompson (1984)* |
| *New England* | *TCE. Dynamic, areal at 18".* | *Spittler et al. (1985)* |
| *Sudbury, MA* | *Gasoline. Dynamic, areal at 18 and 30" (Site 1), 12 and 24" (Site 2).* | *Spittler et al. (1985)* |
| *Battle Creek, MI* | *1,2-Dichloroethene, PCE. Dynamic, areal at 4.5'.* | *Wittmann et al., (1985)* |
| *Not specified* | *Gasoline. Dynamic, areal (depth not specified).* | *Goodwin and Burger (1989)* |
| *Sandwich, MA (Water table 7 ')* | *Gasoline. Dynamic, multiple vertical profiles at 1 ft intervals to 8'.* | *Kerfoot and Soderberg (1988)* |
| *4 unspecified locations* | *Volatile hydrocarbons (3 sites); TCE (1 site). Dynamic, areal at 3'.* | *Newman et al. (1988)* |
| *Military facility* | *Diesel fuel. Dynamic, vertical profiles at 2-3' intervals to around 10'* | *Diem et al. (1988)* |
| *2 unspecified sites* | *Chlorinated solvents (TCE, TCA, vinyl chloride, F-113. Dynamic, areal at 4 to 6'.* | *Shangraw et al (1988)* |



*(A) Homogeneous Porous Material with Sufficient Air-filled Porosity*
*(B) Impermeable Subsurface Layer (e.g., Clay or Perched Water)*
*(C) Impermeable Surface Layer (e.g., Pavement)*
*(D) Zone of High Microbiological Activity (Circles and Wavy Lines Indicate Different Compounds)*
*(E) VOC Source in the Vadose Zone*

**Figure 9-8. Soil-gas ooncentrations under a variety of conditions (from Marrin and Kerfoot, 1988).**



* Denotes samples that should be filtered to determine dissolvad constituents. Filtration should be accomplished preferably with in-line filters and pump pressure or by $N_2$pressure methods. Samples for dissolved gases or volatile organics should not be filtered. in instances where well development procedures do not allow for turbidity free samples and may bias analytical results. split samples should be spiked with standards before filtration. Both spiked samples and regular samples should be analyzed to determine recoveries from both types of handling.

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

+++ See Puls and Barcelona (1989).

**Figure 9-9. Generalized flow diagram of ground-water sampling steps (adapted from Barcelona et al., 1985).**

*Table 9-7. Sources of Information on Various Aspects of Ground-Water sampling*

| Topic | References |
|---|---|
| Analyte identification | Barcelona (1983), Battista and Connelly (1989), Spruill (1988) |
| Well construction | Aller et al. (1989), Cohen and Rabold (1988), Hackett (1988), Palmer at al. (1987), Pennino (1988), Perry and Hart (1985), Sykes et al. (1986). See also Table 9-12 |
| Purging | Barcelona and Helrich (1986), Barber and Davis (1987), Gibs and Imbrigiotta (1990), Herzog et al. (1988), Oliveros et al. (1988), Palmer et al. (1987), Panko and 8arth (1988), Pennino (1988), Robbins (1989), Robin and Gillham (1987), Smith et al. (1988), Unwin and Maltby (1988). See also, Table 9-11 |
| Sample devices | |
| Chemical changes | Barcelona et al. (1985b), Barker and Dickhout (1988), Holm et al. (1988), Pannino (1988), Stolzenburg and Nichols (1985), Schalla et al. (1988), Rose and Long (1988) |
| Comparisons | Barcelona et al. (1984), 8arcelona et al. (1988), Pohlmann and Hess (1988), Nielsen and Yeates (1985) |
| Packer samplers | Anderson (1979) |
| Hydropunch | Cordry (1986), Edge and Cordry (1989) |
| Discrete point | McPherson and Pankow (1988) |
| Sampling procedures | |
| Decontamination | Meade and Ellis (1985), Mickam et al. (1989) |
| Metals | Puls and Barcelona (1989) |
| Volatiles | Barker and Dickhout (1988), Schalla et al. (1988), Unwin and Maltby (1988) |
| Oil-water mixtures | Borst (1987) |
| Field measurement | Garner (1988), Garske and Schock (1986), Holm et al. (1987) |

*Table 9-8. Chemical Constituents of Interest in Ground- Water Monitoring*

| Type of Analyte | Where Done | Information Applications | | | | |
|---|---|---|---|---|---|---|
| | L = Lab<br>F = Field<br>FF = Field Filtered | Water quality | Drinking water | Contamination | Possible source impacts | Geochemical evaluation of data |
| **Geochemical** | | | | | | |
| pH, Eh | F | X | X | X | X | X |
| Conductivity | F | X | X | X | X | X |
| Temperature | F | X | X | X | X | X |
| Dissolved oxygen | F | X | | | | X |
| Alkalinity | F(FF) | | | X | X | X |
| $Ca^{++}$, $Mg^{++}$ | L(FF) | | | | | X |
| $Na^+$, $K^+$ | L(FF) | X | X | | | |
| $Cl^-$, $SO_4^=$, $PO_4^=$ | F(FF) | X | X | X | X | X |
| Silicate | L(FF) | | | | | X |
| **Water quality** | | | | | | |
| Trace Metals (Fe, Mn, Cr Cd, Pb, Cu) | L(FF) | X | X | X | X | X |
| $NO_3^-$, $NH_4^+$ | L(FF) | X | X | X | X | X |
| $F^-$ | L | X | X | | X | |
| TOC | L | X | X | X | X | |
| TOX | L | X | X | X | X | |
| TDS | L(FF) | X | X | X | X | X |
| Organic compounds | L | X | X | X | X | |

*Source: Modified from Barcelona et al. (1989)*

*Table 9-9. Recommended Analytical Parameters for Detective Monitoring*

| | | *Analytes* | |
|---|---|---|---|
| *Type of Parameter* | *Where Measured F = Field, L = Lab* | *Required by regulation* | *Suggested for Completeness* |
| *Well-purging* | *F* | *pH, conductivity* | *Temperature*<br>*Redox potential* |
| *Contamination indicators* | *F* | *pH, conductivity* | |
| | *L* | *TOC (total organic carbon)* | |
| | *L* | *TOX (total organic halogen)* | |
| *Water quality* [a] | *L* | $Cl^-$, *Fe, Mn*, $Na^+$, $SO_4^=$ | *Alkalinity (F) or acidity (F)* |
| | *L* | *Phenols* | $Ca^{++}$, $Mg^{++}$, $K^+$,<br>$NO_3^-$, $PO_4^=$, $NH_4^+$, *silicate* |
| *Drinking water suitability* [b] | *L* | *As, Ba, Cd, Cr*, $F^-$, *Pb*, $NO_3^-$, *Se, Ag* | |
| | *L* | *Endrin, lindane, methoxychlor, toxaphene, 2,4-D, 2,4,5-TP (Silvex)* | |
| | *L* | *Radium, gross alpha/beta* | |
| | *L* | *Coliform bacteria* | |

[a] *All parameters required to be determined quarterly for the first year of network operations (RCRA Part 265.92).*

[b] *These parameters are excluded from the annual reporting requirements of RCRA after the first year.*

*Source: Barcelona et al. (1985a)*

## *9.3.3 Purging*

Purging involves removing stagnant water from a monitoring well before taking a sample for analysis. Once monitoring well locations have been selected, inadequate purging procedures probably account for more sampling error than any other step of the sampling process (see Table 7-2), There is no universally correct purge volume. Monitoring wells finished in materials of widely varying hydraulic conductivity may require different purge volumes since chemical constituents are likely to migrate towards a pumped well at different rates (Gibs and Imbriggiotta, 1990).

Recommended rules of thumb such as using 3 to 5 volumes (Fenn et al., 1977) should be treated only as a starting point. Consistent estimation of purge volume requires knowing (1) well yield, determined from a slug or pumping test and (2) the stagnant volumes of both the well casing and the sand pack. Pumping rates for purging (i.e., generally 1 to 5 gpm) should be below the rate used for development (generally 5 to 20 gpm) to avoid well damage, which could induce the migration of fines into the screened interval. The length of time required to remove the stagnant water at the planned pumping rate can readily be estimated from the well yield and stagnant volume calculations. In most cases, it is important to minimize the purge requirement to avoid dealing with large volumes of contaminated water.

Monitoring pH, conductance, and temperature during purge pumping can provide indications of background chemistry. After the stagnant water has been removed or isolated, these indicators should continue to be monitored until they reach a consistent end point (no upward or downward trend) before sampling. Even after stagnant water has been removed, some constituents may show increasing or decreasing trends. Table 9-11 summarizes the results of observations in seven studies where concentrations were measured as a function of well volumes pumped, Increasing or decreasing concentration trends usually will reach a constant level, although volatile constituents may show considerable variance (see below). The site- and constituent-specific nature of concentration trends with purging is evident from the fact that bicarbonate, nitrate, and specific conductance exhibited both increasing and decreasing trends in different studies.

In studies by Smith et al. (1988), measurements of trichloroethylene ranged from 0 to 250 mm as a function of purge volumes from 0 to 25 volumes inside the well casing and the volume inside the sand pack. After two to three well volumes, trichloroethylene concentrations reached 100 to 125 µg/L. Five to ten well volumes averaged 150 to 175 µg/L, so at least five well volumes was required to obtain samples near the average. Concentrations dropped quickly after purging stopped, and purging a day later yielded similar results. This effect is probably the result of volatile losses from the stagnant water.

## *9.3.4 Well Construction and Sampling Devices*

The Hydropunch® collects one-time ground-water samples in unconsolidated material (see Figure 9-10). It is driven into the soil and when the bottom of the probe is at least 5 ft below the water table, the outer cylinder can be pulled back exposing a perforated stainless steel sample entry barrel covered with either a nylon or polyethylene filter material (see Figure 9-11a). Hydrostatic pressure forces ground water that is relatively free of turbidity into the sample compartment (see Figure 9-11b). About 6 to 10 water samples of between 500 and 1,000 mL each often can be obtained in this manner if no major problems occur. Geologic materials that can be augured or sampled with a split spoon are suitable for sampling with the Hydropunch®.

All decisions preceding monitoring well construction and sample collection have to be quality-assured and documented. Among the references listed in Table 9-1, Barcelona et al. (1983) and Aller et al. (1989) focus primarily on monitoring well design and construction. Screen slot size selection should be justified, preferably by a quick sieve analysis in the field.

*Table 9-10. Chemical Constituents of Formation Waters Analyzed in Studies Related to Deep-Well Injection*

| Constituent | Wilmington NC | Pensacola FL | Belle Glade FL | Marshall IL | Frio TX |
|---|---|---|---|---|---|
| Depth (ft) | 900 | 1,430 | 1,200 | 2,395 | 7,000 |
| Temperature (C) | 22.7 | 35.2 | 26.0 | — | 107 |
| Specific gravity | 1.009 | — | 1.008 | — | — |
| pH | 7.4 | 7.4 | 8.1 | 9.1 | 8.2 |
| Eh | — | -0.032 | — | -154 | — |
| Conductance | 31,800 | 22,320 | — | 22,000 | — |
| TDS | 20,800 | 13,700 | — | 22,000 | 118,802 |
| Alkalinity | — | — | 136 | 380 | 2,448 |
| Pheno. alkalinity | | | | 66 | — |
| Hardness | 2,110 | 1,060 | — | — | — |
| COD | — | — | 36 | — | — |
| Silica | 9 | 18 | 19 | 8 | 30 |
| Calcium | 333 | 181 | 140 | 147 | 9,460 |
| Magnesium | 309 | 142 | 140 | 117 | 2,980 |
| Sodium | 6,750 | 4,920 | — | 8,370 | 43,300 |
| Potassium | 186 | 65 | — | 73 | 356 |
| Bicarbonate | 230 | 302 | — | — | 948 |
| Sulfate | 273 | 0 | 540 | 182 | 120 |
| Chloride | 12,100 | 8,150 | 1,680 | 12,700 | 71,400 |
| Fluoride | <1 | 3 | 1 | 20 | — |
| Bromide | — | 28 | — | — | 247 |
| Iodide | — | 2 | — | — | 33 |
| Nitrite/nitrate | <0.1 | 0 | — | 25 | — |
| Ammonium (N) | — | 8 | <1 | — | — |
| Organic N | — | 2 | <1 | — | — |
| Orthophosphate | <0.1 | 0 | <0.1 | <0.1 | — |
| Hydrogen sulfide | tr. | 1 | 4 | — | — |
| DOC | <1 | 2 | — | — | — |
| Organic carbon | — | — | 2 | — | — |
| Acetate | — | — | — | — | 1,270 |
| Propionate | — | — | — | — | 207 |
| Butyrate | — | — | — | — | 24 |
| Total Org. acids | — | — | — | — | 1,500 |
| Titrated org. alk. | — | — | — | — | 1,457 |
| Aluminum | <1 | — | — | <0.1 | — |
| Arsenic | <0.01 | <0.1 | — | <0.1 | — |
| Barium | <1 | — | — | 1 | 89 |
| Boron | — | 5 | — | — | 474 |
| Beryllium | — | — | — | <0.01 | — |
| Cadmium | <0.1 | — | — | <0.03 | — |
| Chromium | <0.1 | — | — | <1 | — |
| Cobalt | <0.01 | — | — | <0.03 | — |
| Copper | <0.1 | <0.1 | — | <0.03 | — |
| Iron (total) | 2 | — | — | <1 | 999 |
| Ferrous iron | — | 2 | — | — | — |
| Lead | <0.01 | <0.1 | — | <0.03 | — |
| Lithium | <1 | <1 | — | — | — |
| Manganese | <1 | <0.1 | — | <1 | — |
| Mercury | 0.01 | — | — | — | — |
| Molybdenum | <0.01 | — | — | <.1 | — |
| Nickel | <0.01 | — | — | <0.05 | — |
| Selenium | <0.01 | — | — | — | — |
| Strontium | 19 | 22 | — | — | 405 |
| Zinc | <0.1 | <0.1 | — | <0.03 | — |

Sources: *Wilmington, NC. (Leenheer et al., 1976); Pensacola, FL (Goolsby, 1972); Belle Glade, FL (Kaufman et al., 1973); Marshall, IL (Roy et al., 1989); Frio formation, TX (Kreitler et al., 1988)*

*Table 9-11.* ***Observed Trends in Measured Concentrations with Well Volumes Pumped***

| *Parameter* | *References Indicating Trend in Measured Concentration*<br>*Increasing* | *Constant* | *Decreasing* |
|---|---|---|---|
| *Arsenic* | *2* | | |
| *Alkalinity* | | *1* | *1* |
| *Ammonium* | | | *3* |
| *Bicarbonate* | *5* | *1,3,5* | *1,3,5* |
| *Boron* | | *2,3* | |
| *Cadmium* | | *2* | |
| *Calcium* | | *1,2,3,5* | |
| *Carbonate* | | | *3,5* |
| *Chloride* | | *1,3,5* | *7* |
| *Chromium* | | *5* | |
| *Copper* | | | *2,5* |
| *DOC* | *3* | | |
| *Hardness* | | *1* | *1* |
| *Iron* | | *2* | *2* |
| *Fluoride* | | *3,5* | |
| *Magnesium* | *2* | *1,2,3,5* | |
| *Manganese* | | *2* | *5* |
| *Nitrate* | *1,6,7* | *1* | *4,6* |
| *pH* | | *1,3* | *1,5* |
| *Potassium* | | *2,3,5* | |
| *Selenium* | *2* | | |
| *Sodium* | | *1,2,3,5* | |
| *Specific Conductance* | *7* | *1,3* | *1,3,4,6* |
| *Sulfate* | | *1,2,5* | *5* |
| *TDS* | | *1,3* | *1* |
| *Temperature* | *7* | | |
| *Zinc* | | | *2,5* |

*References:*
*1 Chapin (1981)*
*2 Gibb et al. (1981)*
*3 Slawson et al. (1982)*
*4 Schmidt (1982)*
*5 Marsh and Lloyd (1980)*
*6 Nightingale and Bianchi (1980)*
*7 Keith et al. (1982)*

*Source: Adapted from Rehm et al. (1985)*

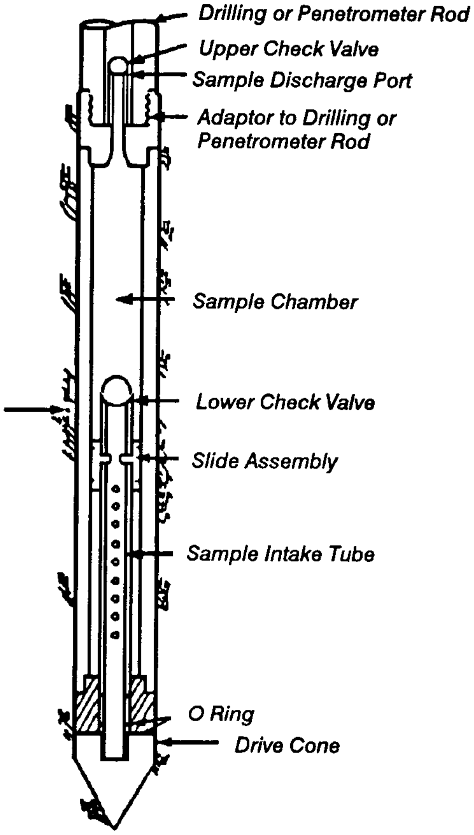


**Figure 9-10. HydroPunch® schematic (from Edge and Cordry, 1989).**

Common rigid well-casing materials that might be used include polyvinyl chloride, stainless steel, and polytetrafluoroethylene. Table 4-3 summarizes the advantages and disadvantages of these and other well casing and screen materials. Figure 9-12 shows a sample decision tree for the selection of rigid materials for casing.

Table 9-12 summarizes data on the leaching and sorption characteristics of well casing materials. Stainless steel may be the best overall metal easing and screening material, but it is still susceptible to microbiological corrosion. In most instances, casing and screen materials should last for at least 30 years without corrosion closing down the effective area of the screen. Teflon® and polyvinyl chloride have structural problems for emplacement in deeper holes. All common easing and tubing materials may be expected to sorb hydrophobic organics to some extent. The impact of sorptive losses or leaching contamination can be expected to be different with aged materials than with the virgin material.

Figure 9-13 summarizes recommended sampling methods for various parameters for detective monitoring programs and Figure 9-14 shows a decision tree for selection of sampling mechanisms. With sampling devices, pressure changes and the loss of volatiles are the main concern. Sampling within 30 feet of the surface involves little pressure change and most samplers may be expected to perform similarly for volatile and gas-sensitive species. Sampling at depths in excess of 60 ft (two or more atmospheres) can be expected to yield differences in sampling devices. Teflon®, polypropylene, and polyethylene are the best tubing materials for sampling. Polyvinyl chloride, Tygon®, and silicone rubber tubing should be avoided, particularly if VOCs are involved, due to documented major losses of these species. Dedicated sampling devices can greatly increase the cost efficiency of taking samples.

A *bladder pump* is a cylinder with an internal bladder that can be compressed and expanded under the influence of a gas. The squeezing and release of pressure can be controlled with a frequency that will give virtually pulseless flow. Bladder pumps operate on air or nitrogen and air compressors are available that are relatively easy to move around for supplying them. Bladder pumps provide precise flow rates at given operating pressures and frequencies of pressure/release. They have worked reliably with continuous submersion in the same well for extended periods. Any malfunction such as a leak in a bladder pump is immediately apparent because it will stop working. Repair in the field is also relatively easily accomplished. Bladder pumps are best adapted for purging small-diameter monitoring wells (less than 4 in.) and their depth range is limited to about 450 ft.

*Bailers* are commonly used sampling devices, but have a number of disadvantages compared to bladder pumps. The basic performance difficulties with bailers are that virtually all individuals bail differently, and in-line determination of pH, conductance, temperature, and dissolved oxygen are not possible. Also, sample transfer can be inconsistent, which creates variability that shouldn't be in the sample data set. Another major problem with bailers is the difficulty of determining where a sample is actually retrieved. In this case, bailers may malfunction without the operator knowing when the check valve actually sealed. Bailers or grab samplers can minimize volatilization losses, and are probably the best way to sample NAPLs at the water table surface. Newer bailer designs allow filtration in the field and transfer of volatile samples without contact with the atmosphere, but to not address the problem of inconsistency in bailing. Bailers should *not* be used for purging because all they do is homogenize the volume within the well bore.

*Electric submersibles* can be useful for purging large-diameter deep wells with high volume purging requirements, particularly when flow rates can be controlled. They may not be good for sampling unless the flow rate for sampling can be controlled or diverted from the main pumping stream. In general the accuracy is poor for gas-sensitive parameters, not only volatile organics, but also oxygen and carbon dioxide.

*Suction pumps, venturi mechanism pumps, and some grab-driven mechanisms* create turbulence that puts negative pressure on the sample for volatiles. Flow is generally difficult to control, particularly to obtain preferable low flows (i.e., 100 mL to 2 L/min) for sampling.

Sampling devices and sample handling should be executed so as to minimize temperature and pressure changes. Reproducible flow rates and freedom from operator-induced errors tend to yield the most precise results. Figure 9-15 contains a matrix rating the suitability of different chemical devices for different chemical constituents. Figure 9-16 rates suitability of 12 devices (described in Table 9-13) for use with 12 types of ground-water parameters. If VOCs are sampled

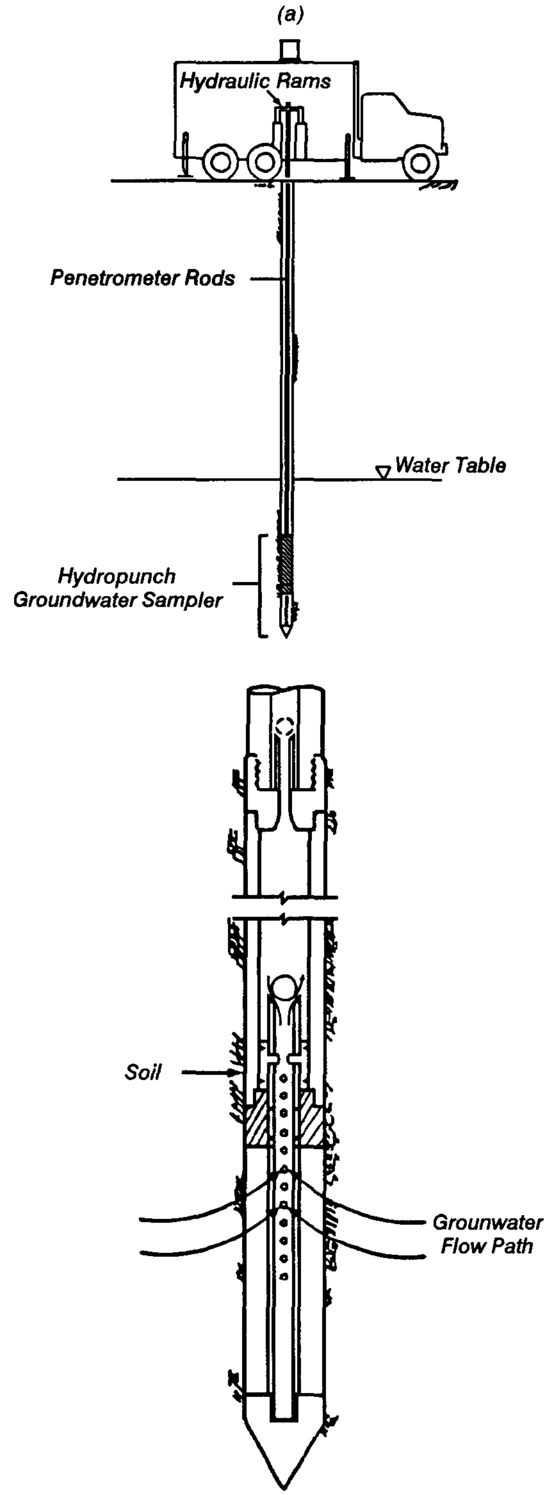


**Figure 9-11.** HydroPunch® sampling operation. (a) HydroPunch® is pushed Into target ares with a cone-penetrometer rig. (b) Once exposed, ground water flows through the intake tube and into the sample chamber (from Edge and Cordry, 1989).

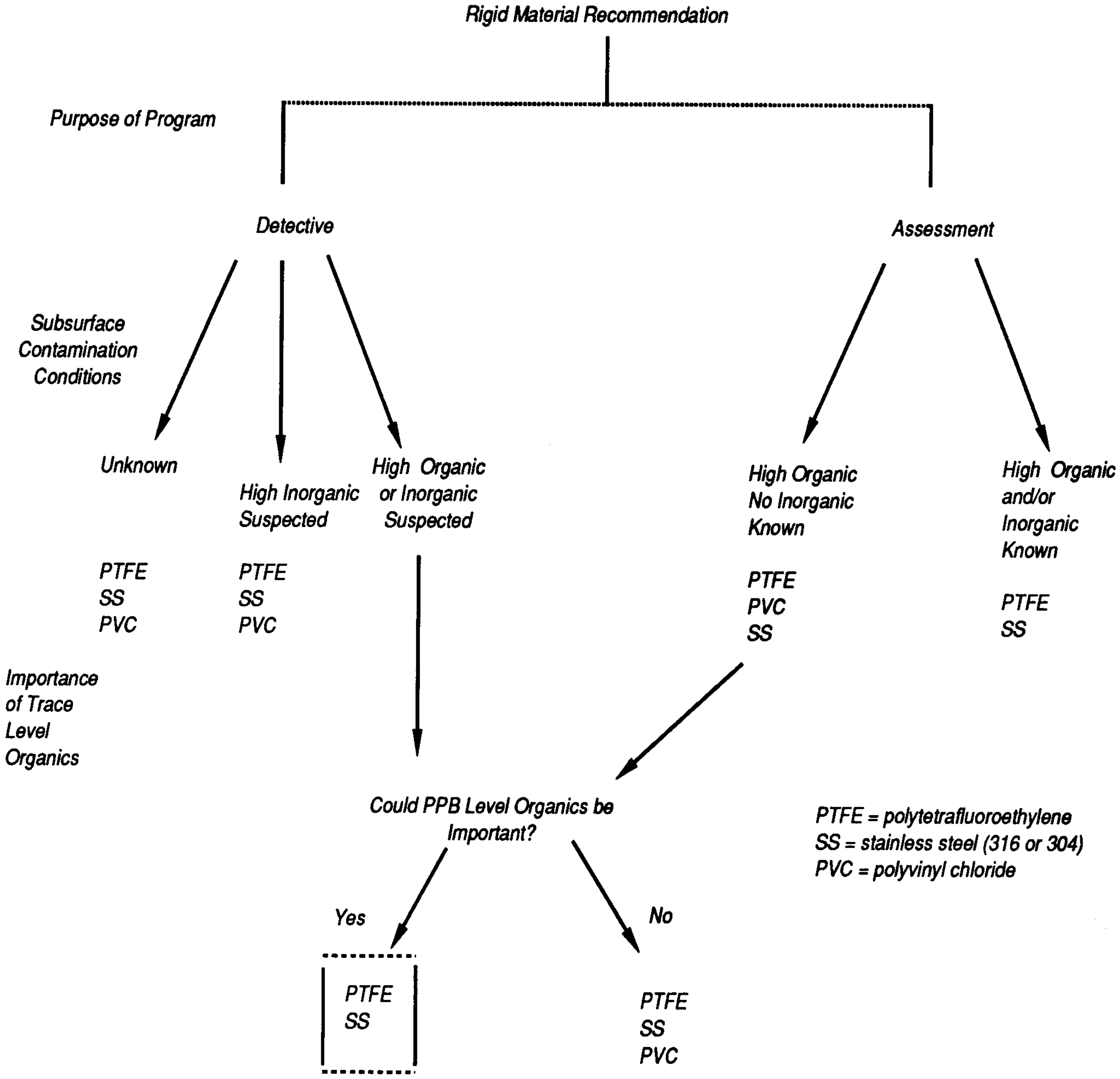


Figure 9-12. Decision tree for recommended well-casing/screen materials. Adapted by Barcelona and Gibb (1888) from Barcelona et al. (1985).

effectively, the results with most other constituents may be expected to be reproducible and accurate.

Studies of sampling errors associated with the sampling mechanisms alone have found that bladder pumps and bailers come out with sampling error consistently less than the analytical error. However, most comparisons of bladder pumps and bailers have been conducted at shallow lifts. At depths up to 200 or 300 m, bladder pumps are probably superior. Vacuum devices, peristaltic and suction pumps, on the other hand, yield a sampling error on about the same order as the level of sorptive losses or handling errors. Where sensitive constituents are involved, bladder pumps and bailers are the most frequently used devices. A bladder pump is probably the best overall sampling device and will probably provide 50 to 100 percent better recovery and far better precision for volatiles than a bailer.

Once samples are collected, procedures for the handling and preservation of samples should be carefully followed to minimize errors from this stage of the sampling process. Table 9-14 summarizes recommended sample handling and preservation procedures for a comprehensive detective monitoring program.

**Table 9-12. Effects of Well Casing Materiail on Trace Concentration in Well Water**

| Parameter | Leaches From | Adsorbed By |
|---|---|---|
| Arsenic | ABS* | |
| Cadmium | Steel, Galvanized [2] | |
| Chromium | Steel | |
| Copper | Steel | |
| Dissolved Organic Carbon | ABS, PVC** | |
| iron | Steel, Galvanized [1] | |
| Manganese | Steel, Galvanized[2] | |
| Total Organic Carbon | ABS, PVC | ABS |
| Zinc | Steel, Galvanized [1] | ABS |
| Lithium | | ABS |
| Mercury | | ABS |
| Molybdenum | | ABS |
| Selenium | | ABS |

Source: Adapted from Houghton and Berger (1984)

* Acrylonitrile-butadiene-styrene copolvmer

** Polyvinyl chloride

[1] Suggested by data from Gibb et al. (1981)

[2] Barcelona et al. (1983)

| Parameters (type) | Mechanism (material)* | Hydrogeologic Conditions (yield capability) | |
|---|---|---|---|
| | | >100 mL/min yield | <100 mL/min yield |
| | | Flowing samples | Discrete samples |
| Well-purging ($pH$, $Eh$, $T$, $\Omega^{-1}$) | Pump (T, S, P, O)<br>Flow rates: 0.1-1.0 L/min | Positive displacement bladder pump (air, $N_2$) | |
| | Grab (T, S, G, P, O) | | Dual check valve bailers "thief" samplers |
| Contamination Indicators ($pH$, $\Omega^{-1}$) | Pump<br>Flow rates: 0.1-1.0 L/min | Positive displacement bladder pump. (air, $N_2$) | bladder pump (air, $N_2$) |
| | Grab (T, S, G, P, O) | | Dual check valve bailers "thief" samplers |
| (TOC, TOX) | Pump (T, S preferred; O,P only where supporting data exist) | (Mechanism as above operated at flow rates not to exceed 100 mL/min) Vials or bottles filled gently from bottom up and allowed to overflow→Teflon capped w/o headspace | (Volatile fractions of TOC and TOX may be lost depending on conditions and operator skill) |
| | Grab (T, S, G preferred; O, P only where supporting data exist) | | 40-mL vials (500-mL Teflon-sealed glass bottles for TOX) filled from bottom up and allowed to overflow or gently poured down the side of the vial. Teflon capped w/o headspace |
| Water Quality<br>Dissolved Gases ($O_2$, $CH_4$, $CO_2$) | Pump (T, S, P, O) | (Mechanism as above operated at flow rates not to exceed 100 mL/min) Glass containers filled gently from bottom up and allowed to overflow→Teflon capped w/o headspace | (Not recommended) |
| Alky/Acdy | Grab (T, S, G, P, O) | | |
| (Fe, Mn, $PO_4^{=}$, $Cl^-$, $Na^+$, $SO_4^{=}$, $Ca^{++}$, $Mg^{++}$, $K^+$, $NO_3^-$, Silicate | Pump (T, S, P, O) | Positive displacement bladder pump, (air, $N_2$) | Fe values sensitive to most grab mechanisms |
| | Grab (T, S, G, P, O) | | Large volumes required may have to be sequentially collected |
| (Ammonium, Phenols) | Pump (T, S preferred; O, P only where supporting data exist) | (Mechanisms as above operated at flow rates not to exceed 1000 mL/min) Glass containers filled from bottom up | (Volatile species may be lost depending on conditions |
| | Grab (T, S, G preferred; O, P only where supporting data exist) | | Glass containers filled from bottom up |
| Drinking Water Suitability | Pump (T, S, P. O) | Positive displacement bladder pump, (air, $N_2$) | |
| (As, Ba, Cd, Cr, Pb, Hg, Se, Ag, $NO_3^-$, $F^-$) | Grab (T, S, G, P, O) | | Dual check valve bailers "thief" samplers |
| (Remaining Parameters) | Pump (T, S, P, O)<br>Grab (T, S, G, P, O)<br>(both with precautions if radiologic hazards exist) | Positive displacement bladder pump, (air $N_2$)<br>Flow rates should not exceed 1000 mL/min | (Volatile compounds may be lost depending on conditions) |

*Materials in order of preference include: Teflon® (T); stainless steel (S): PVC, polypropylene, polyethylene (P); borosilicate glass (G); other materials: silicone, polycarbonate, mild steal, etc. (0)

**Figure 9-13. Recommended sample collection methods for detective monitoring programs (from Barcelona et al., 1985).**

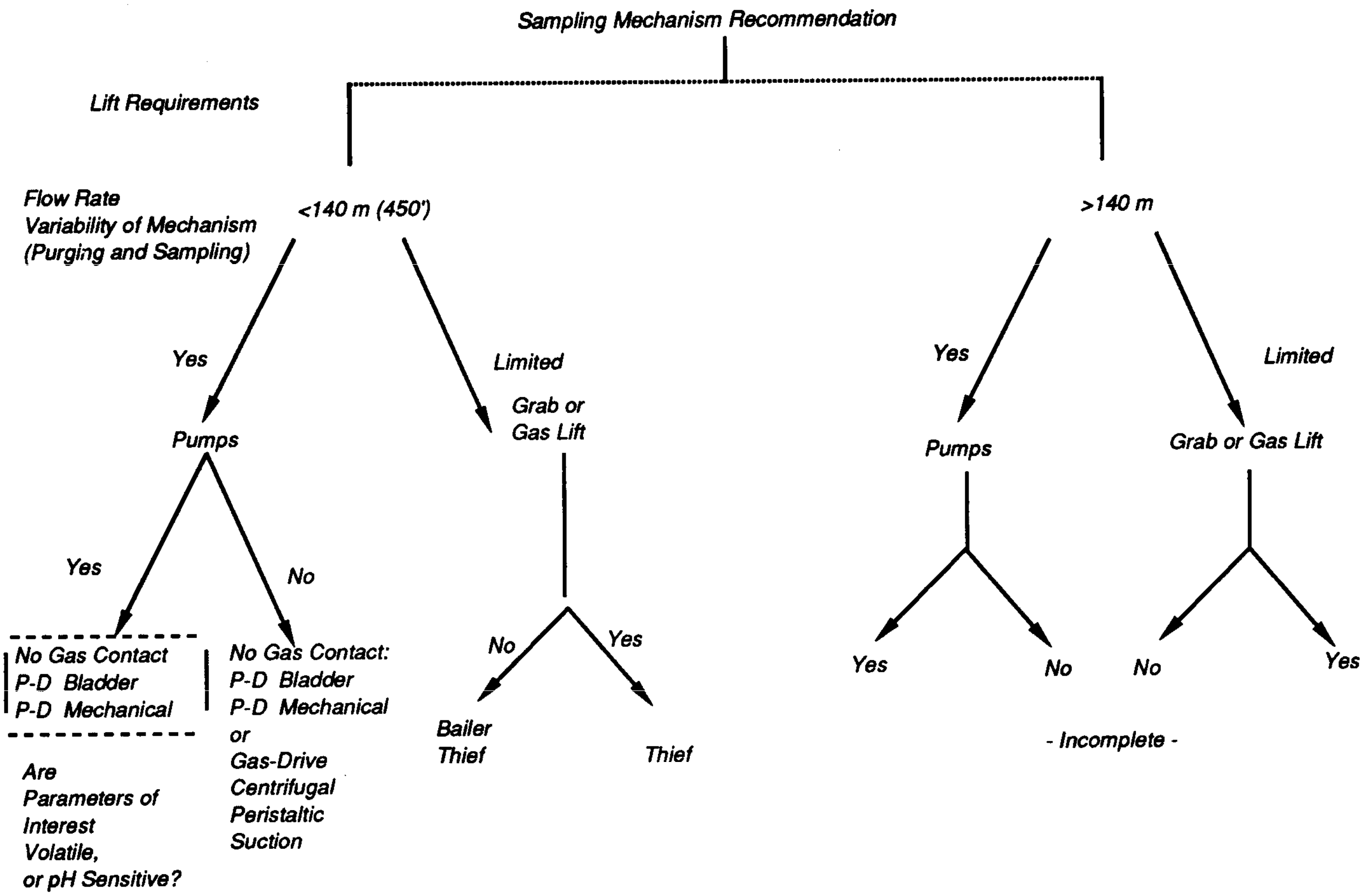


Figure 9-14. Decision tree for recommended purge and sampling mechanism. Adapted by Barcelona and Gibb (1988) from Barcelona et al. (1985).

| Type of Constituent | Example of Constituent | | Positive Displacement Bladder Pumps | Thief, in Situ or Check Valve Bailers | Mechanical Positive Displacement Pumps | Gas-drive Devices | Suction Mechanisms |
|---|---|---|---|---|---|---|---|
| | | | ← Increasing Reliability of Sampling Mechanisms | | | | |
| Volatile Organic Compounds<br>Organometallics | Chloroform<br>TOX<br>$CH_3Hg$ | ↑ Increasing Sample Sensitivity | Superior performance for most applications | May be adequate if well purging is assured | May be adequate if design and operation are controlled | Not recommended | Not recommended |
| Dissolved Gasses<br>Well-Purging Parameters | $O_2$, $CO_2$<br>pH, $\Omega^{-1}$<br>Eh | | Superior performance for most applications | May be adequate if well purging is assured | May be adequate if design and operation are controlled | Not recommended | Not recommended |
| Trace Inorganic Metal Species<br>Reduced Species | Fe, Cu<br>$NO_2^-$, $S^=$ | | Superior performance for most applications | May be adequate if well purging is assured | Adequate | May be adequate | May be adequate if materials are appropriate |
| Major Cations & Anions | $Na^+$, $K^+$, $Ca^{++}$ $Mg^{++}$<br>$Cl^-$, $SO_4^=$ | | Superior performance for most applications | Adequate<br>May be adequate if well purging is assured | Adequate | Adequate | Adequate |

Figure 9-15. Matrix of sensitive chemical constituents and various sampling mechanisms (from Barcelona et al., 1985).

|  |  |  |  |  |  | Ground Water Parameters |  |  |  |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Inorganic |  |  |  |  |  |  | Organic |  |  |  | Radioactive |  | Biol. |
|  |  | **Device** | **Approximate Maximum Sample Depth** | **Minumum Well Diameter** | **Sample † Delivery Rate or Volume** | EC | pH | Redox | Major Ions | Trace Metals | Nitrate, Fluoride | Dis-solved Gasses | Non-volatile | Volatile | TOC | TOX | Radium | Gross Alfa & Beta | Coli-form Bacteria |
| Portable Sampling Devices * | Grab | Open bailer | No Limit | 1/2 in | Variable | • |  |  | • | • | • |  | • |  |  |  | • |  | • |
|  |  | Point-source bailer | No Limit | 1/2 in | Variable | • | • | • | • | • | • |  | • | • | • | • | • |  | • |
|  |  | Syringe sampler | No Limit | 1 1/2 in | 0.01-0.2 gal | • | • | • | • | • | • |  | • |  |  |  | • | • | • |
|  | Positive Displacement (submersible) | Gear-drive | 200 ft | 2 in | 0-0.5 gpm |  |  |  |  |  |  |  |  | • |  |  |  |  |  |
|  |  | Bladder pump | 400 ft | 1 1/2 in | 0-2 gpm | • | • | • | • | • | • | • | • | • | • | • | • | • | • |
|  |  | Helical rotor | 160 ft | 2 in | 0-1.2 gpm | • | • | • | • | • | • | • | • | • | • | • | • | • |  |
|  |  | Piston pump (gas-drive) | 500 ft | 1 1/2 in | 0-0.5 gpm | • |  |  | • | • | • |  | • |  |  |  | • | • |  |
|  |  | Centrifugal | Variable | 3 in | Variable | • |  |  | • |  | • |  |  |  |  |  | • | • |  |
|  | Suc-tion lift | Peristaltic | 26 ft | 1/2 in | 0.01-0.3 gpm | • |  |  | • |  | • |  | • |  |  |  | • |  | • |
|  | Gas Contact | Gas-lift | Variable | 1 in | Variable |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | Gas-drive | 150 ft | 1 in | 0.2 gpm | • |  |  | • |  | • |  | • |  |  |  | • |  |  |
| In Situ Sampling Devices* |  | Pneumatic | No Limit | Not Applicable | 0.01-0.13 gal | • | • | • | • | • | • |  | • |  |  |  | • | • | • |

* Sampling devices on this chart are divided into two categones: (1) portable devices for sampling existing monitoring wells; and (2) in situ monitoring devices (often multilevel) that are permanently installed. Sampling device construction materials (including tubing, haul lines, etc.) should be evaluated for suitability in analyzing specific ground water parameters. It is assumed on this chart that existing monitoring wells are properly installed and constructed of materials suitable for detection of the parameters of interest. See references for additional information.

† Sample delvivery rates and volumes are average ranges based on typical field conditions. Actual delivery rates area function of diameter of monitoring installation, size and capacity of sampling device, hydrogeologic conditions, and depth to sampling point. For all devices, delivery rate should be carefully controlled to prevent aeration or degassing of the sample.

Ž Indicates device is generally suitable for application (assuming device is cleaned and operated properly and is constructed of suitable materials).

**Figure 9-16. Generalized ground-water sampling device matrix (from Pohlmann and Hess, 1988).**

**Table 9-13. Description of Ground-Water Sampling Devices and Construction Materials Commonly Used in Ground- Water Monitoring (see also Figure 8-16)**

| Sample Device | Description |
|---|---|
| Open bailer | Open top. Bottom sealed or fitted with foot valve. Available in wide range of rigid materials. |
| Point-source bailer | Check valve at both top and bottom. Valves are opened by cable operated from ground surface. Available in wide range of rigid materials. |
| Syringe sampler | Sample container is pressurized or evacuated and lowered into sampling installation. Opening the container and/or releasing the pressure allows sample to enter the device. Materials may include stainless steel 316, Teflon®, polyethylene, glass. |
| Gear-drive pump | Electric motor rotates a set of Teflon gears, which drives the sample up the discharge line. Constructed of stainless steel 304, Teflon, and Viton®. |
| Bladder pump | Flexible bladder within device has check valves at each end. Gas from ground surface is cycled between bladder and sampler wall, forcing sample to enter bladder and then be driven up the discharge line. Gas does not contact sample. Materials may include stainless steel 316, Teflon, Viton, polyvinyl chloride (PVC), silicone, Neoprene®, polycarbonate, Delrin®. |
| Helical-rotor pump | Water sample is forced up discharge line by electrically driven rotor-stator assembly. Materials may include stainless steel 304, ethylene propylene rubber (EPDM), Teflon, Viton, polypropylene. |
| Gas-driven pump | Piston is driven up and down by gas pressure controlled from the surface. Gas does not contact sample. Materials may include stainless steel 304, Teflon, Delrin, polypropylene, Viton, acrylic, polyethylene. |
| Centrifugal pump | Electrically driven rotating impeller accelerates water within the pump body, building up pressure and forcing the sample up discharge line. Commonly constructed of stainless steel, rubber, and brass. |
| Peristaltic pump | Self priming vacuum pump is operated at ground surface and is attached to tubing, which is lowered to the desired sampilng depth. Sample contacts vacuum. Materials may include Tygon®, silicone, Viton, Neoprene, rubber, Teflon. |
| Gas-lift devices | Gas emitted from gas line at desired depth forces sample to surface through sampling installation. Another method utilizes gas to reduce effective specific gravity of water, causing it to rise. Wide variety of materials available for tubing. |
| Gas-drive devices | Positive gas pressure applied to water within device's sample chamber forces sample to surface. Materials may include polyethylene, brass, nylon, aluminum oxide, PVC, polypropylene. |
| Pneumatic | in situ device generally utilizes the same operating principles as syringe samplers: a pressurized or evacuated sample container is lowered to the sampling port and opened, allowing the sample to enter. Materials may include PVC, stainless steel, polypropylene, Teflon. |

Source: Pohlmann and Hess (1988)

***Table 9-14. Recommended Sample Handling and Preservation Procedures for a Detective-Monitoring Program***

| Parameters (Type) | Volume Required (mL) 1 Sample[a] | Containers (Material) | Preservation Method | Maximum Holding Period |
|---|---|---|---|---|
| Well purging | | | | |
| pH (grab) | 50 | T,S,P,G | None; field det. | <1 hr [b] |
| $\Omega^{-1}$ (grab) | 100 | T,S,P,G | None; field det. | <1 hr [b] |
| T (grab) | 1,000 | T,S,P,G | None; field det. | None |
| Eh (grab) | 1,000 | T,S,P,G | None; field det. | None |
| Contamination indicators | | | | |
| pH, $\Omega^{-1}$ (grab) | As above | As above | As above | As above |
| TOC | 40 | G,T | Dark, 4 °C | 24 hr[d] |
| TOX | 500 | G,T | Dark, 4 °C | 5 days |
| Water quality | | | | |
| Dissolved gases ($O_2$, $CH_4$, $CO_2$) | 10 mL minimum | G,S | Dark, 4 °C | <24 hr |
| Alkalinity/acidity | 100 | T,G,P | 4 °C/None | <6 hr[b]<br><24 hr |
| | Filtered under pressure with appropriate media | | | |
| (Fe, Mn, $Na^+$, $K^+$, $Ca^{++}$, $Mg^{++}$) | All filtered 1,000 mL [f] | T,P | Field acidified to pH <2 with $HNO_3$ | 6 months[c] |
| ($PO_4^-$, $Cl^-$, Silicate) | @50 | (T,P,G glass only) | 4 °C | 24 hr/ 7 days [e];<br>7 days |
| $NO_3^-$ | 100 | T,P,G | 4 °C | 24 hr [d] |
| $SO_4^-$ | 50 | T,P,G | 4 °C | 7 days [e] |
| $OH_4^+$ | 400 | T,P,G | 4 °C/$H_2SO_4$ to pH <2 | 24 hr/ 7 days |
| Phenols | 500 | T,G | 4 °C/$H_2PO_4$ to pH <4 Drinking Water | 24 hr |
| Same as suitability As, Ba, Cd, Cr, Pb, Hg, Se, Ag | Same as above for water quality cations (Fe, Mn, etc.) [f] | Same as above | 6 months | |
| $F^-$ | Same as chloride above | Same as above | Same as above | 7 days |
| Remaining organic parameters | As for TOX/TOC, except where analytical method calls for acidification of sample | | | 24 hr |

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

[b] Temperature correction must be made for reliable reporting. Variations greater than ±10% may result from a longer holding period.

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

[d] 28-day holding time if samples are preserved (acidified).

[e] Longer holding times in EPA (1986b).

[f] Filtration is not recommended for samples intended to indicate the mobile substance lead. See Puls and Barcelona (1989) for more specific recommendations for filtration procedures involving samples for dissolved species.

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

Source: Adapted from Scalf et al. (1981) and U.S. EPA (1986b)

## 9.4 References

Aller, L., T.W. Bennett G. Hackett, Rebecca J. Petty, J.H. Lehr, H. Sedoris, D.M. Nielsen. 1989. Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells. EPA/600/4-89/034 (NTIS PB90-159807). Also published in NWWA/EPA series, National Water Well Association, Dublin, OH.

Andersen, L.J. 1983. Sampling Techniques of Groundwater from Water Wells. In: Proc. UNESCO Symp. Methods and Instrumentation for the Investigation of Groundwater Systems, Committee for Hydrological Research, CHO-TNO, The Hague, The Netherlands, pp. 521-527.

Armstrong, J.M., W. Korreck, L.E. Leach, R.M. Powell, S.V. Vandegrift, and J.T. Wilson. 1988. Bioremediation of a Fuel Spill: Evaluation of Techniques for Preliminary Site Characterization. In: Proc. 5th NWWA/API Conf. Petroleum Hydrocarbons and Organic Chemicals in Ground Water-Prevention, Detection and Restoration, National Water Well Association, Dublin, OH, pp. 931-948.

Barber, C. and G.B. Davis. 1987. Representative Sampling of Ground Water from Short-Screened Boreholes. Ground Water 25(5):581-587.

Barcelona, M.J. 1983. Chemical Problems in Ground-Water Monitoring Programs. In: Proc. 3rd Nat. Symp. on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, Dublin, OH, pp. 263-271.

Barcelona, M.J. and J.P. Gibb. 1988. Development of Effective Ground-Water Sampling Protocols. In: Ground-Water Contamination: Field Methods, A.G. Collins and A.L Johnson (eds.), ASTM STP 963, American Society for Testing and Materials, Philadelphia, PA, pp. 17-26.

Barcelona, M.J. and J.A. Helfrich. 1986. Well Construction and Purging Effects on Ground-Water Samples. Environ. Sci. Technol. 20:1179-1184.

Barcelona, M.J., J.P. Gibb, and R.A. Miller. 1983. A Guide to the Selection of Materials for Monitoring Well Construction and Ground-Water Sampling. ISWS Contract Report 327. Illinois State Water Survey, Champaign, IL.

Barcelona, M.J., J.A. Helfrich, E.E. Garske, and J.P. Gibb. 1984. A Laboratory Evaluation of Ground Water Sampling Mechanisms. Ground Water Monitoring Review 4(2):32-41.

Barcelona, M.J., J.P. Gibb, J.A. Helfrich, and E.E. Garske, 1985a. Practical Guide for Ground-Water Sampling. EPA/600/2-85/104 (NTIS PB86-137304). Also published as ISWS Contract Report 374, Illinois State Water Survey, Champaign, IL.

Barcelona, MJ., J.A. Helfrich, and E.E. Garske. 1985b. Sampling Tubing Effects on Groundwater Samples. Anal. Chem. 57:460-464.

Barcelona, MJ., J.A. Helfrich, and E.E. Garske. 1988. Verification of Sampling Methods and Selection of Materials for Ground-Water Contamination Studies. In Ground-Water Contamination: Field Methods, A.G. Collins and A.I. Johnson (eds.), ASTM STP 963, American Society for Testing and Materials, Philadelphia, PA, pp. 221-231.

Barcelona, M.J., D.P. Lettenmaier, and M.R. Schock. 1989. Network Design Factors for Assessing Temporal Variability in Ground-Water Quality. Environmental Monitoring and Assessment 12:149-179.

Barker, J.F. and R. Dickhout. 1988. An Evaluation of Some Systems for Sampling Gas-Charged Ground Water for Volatile Organic Analysis. Ground Water Monitoring Review 8(4):112-119.

Barth, D.S. and T.H. Starks. 1985. Sediment Sampling Quality Assurance User's Guide. EPA/600/4-85&8 (NTIS PB85-233542).

Barth, D.S., B.J. Mason, and T.H. Starks. 1989. Soil Sampling Quality Assurance User's Guide, 2nd ed. EPA/600/8-89/046 (NTIS PB89-189864), 225 pp.

Battista, J.R. and J.P. Connelly. 1989. VOC Contamination at Selected Wisconsin Landfills-Sampling Results and Policy Implications. WDNR PUBL-W-094 89. Wisconsin Department of Natural Resources, Madison, WI.

Bell, H.F. and H.P. DeLong. 1988. Data Characteristics Ground Water Monitoring's Catch 22. ACS Abstracts 28(2):20-24.

Berg, E.L. 982. Handbook for Sampling and Sample Preservation of Water and Wastewater. EPA/600/4-82-029 (NTIS PB83-124503).

Borst, M. 1987. Sampling Oil-Water Mixtures at OHMSEIT. EPA/600/2-87/073 (NTIS PB88-102892).

Brown, K.W. 1987. Efficiency of Soil Core and Soil-Pore Water Sampling Systems. EPA/OO/2-86/083 (NTIS PB87-106100).

Bumb, A.C., C.R. McKee, R.B. Evans, and L.A. Eccles. 1988. Design of Lysimeter Leak Detector Networks for Surface Impoundments and Landfills. Ground Water Monitoring Review 8(2):102-114.

Cameron, R.E., et al. 1966. Sampling and Handling of Desert Soils. Technical Report No. 32-908. Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 37 pp.

Chapin, R.I. 1981. Short-Term Variations, Sampling Techniques and Accuracy of Analysis of the Concentrations of Nitrate in Produced Municipal Ground Waters—North Texas. M.A. Thesis, University of Texas, Austin.

Close, M.E. 1989. Effect of Serial Correction on Ground Water Quality Sampling Frequency. Water Resources Bulletin 25(3):507-515.

Cochran, W.G. 1977. Sampling Techniques, 3rd ed. John Wiley & Sons, New York.

Cohen, R.M. and R.R. Rabid. 1988. Simulation of Sampling and Hydraulic Tests to Assess a Hybrid Monitoring Well Design. Ground Water Monitoring Review 8(1):51-59.

Collins, A.G. and A.I. Johnson (eds.). 1988. Ground-Water Contamination: Field Methods. ASTM STP 963. American Society for Testing and Materials, Philadelphia, PA.

Cordry, K. 1986. Ground Water Sampling Without Wells. In: Proc. 6th Nat. Symp. on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, Dublin, OH, pp. 266-271.

Deming, W.E. 1950. Some Theory of Sampling. John Wiley & Sons, New York. (available as a Dover reprint, 1966).

Devitt, D. A., R.B. Evans, W.A. Jury, T.H. Starks, and B. Eklund. 1987. Soil Gas Sensing for Detection and Mapping of Volatile Organics. EPA/600/8-87/036 (NTIS PB87-228516).

Di, H.J., B.B. Trangmar, and R.A. Kemp. 1989. Use of Geostatistics in Designing Sampling Strategies for Soil Survey. Soil Sci. Soc. Am. J.53:1163-1167.

Diem, D.A., B.E. Ross and H.B. Kerfoot. 1988. Field Evaluation of a Soil-Gas Analysis Method for Detection of Subsurface Diesel Fuel Contamination. In: Proc. 2nd Nat. Outdoor Action Conf. on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, National Water Well Association, Dublin, OH, pp. 1015-1031.

Dunlap, W.J., J.F. McNabb, M.R. Scalf, and R.L. Cosby. 1977. Sampling for Organic Chemicals and Microorganisms in the Subsurface. EPA/600/2-77/176 (NTIS PB272 679).

Edge, R.W. and K. Cordry. 1989. The Hydropunch: An In Situ Sampling Tool for Collecting Ground Water from Unconsolidated Sediments Ground Water Monitoring Review 9(3):177-183.

Everett, L.G., K.D. Schmidt, R.M. Tinlin, and D.K. Todd. 1976. Monitoring Groundwater Quality: Methods and costs. EPA/600/4-76/023 (NTIS PB257133).

Everett, L.G. and L.G. McMillion. 1985. Operational Ranges for Suction Lysimeters. Ground Water Monitoring Review 5(3):5 1-60.

Everett, L.G., L.G. Wilson, and L.G. McMillion. 1982. Vadose Zone Monitoring Concepts for Hazardous Waste Sites. Ground Water 20(3):312-324,

Everett, L.G., L.G. Wilson, and E.W. Hoylman. 1983. Vadose Zone Monitoring for Hazardous Waste Sites. EPA/600/X-83/064 (NTIS PB84-212752). Also published in 1984 by Noyes Data Corporation, Park Ridge, NJ.

Everett, N. G., E.W. Hoylman, L.G. Wilson, and L.G. McMillion. 1984. Constraints and Categories of Vadose Zone Monitoring Devices. Ground Water Monitoring Review 4(1):26-31.

Fenn, D., E. Cocozza, J. Isbister, O. Braids, B. Yare, and P. Roux. 1977. Procedures Manual for Ground Water Monitoring at Solid Waste Disposal Facilities.EPA/530/SW611 (NTIS PB84-174820).

Flatman, G.T. 1986. Design of Soil Sampling Programs: Statistical Considerations. In: Quality Control in Remedial Site Investigation: Hazardous and Industrial Solid Waste Testing, 5th volume, C.L. Perket (ed.), ASTM STP 925, American Society for Testing and Materials, Philadelphia, PA, pp. 43-56.

Ford, P.J., P.J. Turina, and D.E. Seely. 1984. Characterization of Hazardous Waste Sites—A Methods Manual: Vol. II. Available Sampling Methods, 2nd ed. EPA/600/4-84-076 (NTIS PB85-521596).

Garner, S. 1988. Making the Most of Field-Measurable Ground Water Quality Parameters. Ground Water Monitoring Review 8(3):60-66.

Garske, E.E. and M.R. Schock. 1986. An Inexpensive Flow-Through Ceil and Measurement System for Monitoring Selected Chemical Parameters in Ground Water. Ground Water Monitoring Review 6(3):78-84.

GeoTrans, 1989. Groundwater Monitoring Manual for the Electric Utility Industry. Edison Electric Institute, Washington, DC.

Gibb, J.P, R.M. Schuller, and R.A. Griffh. 1981. Procedures for the Collection of Representative Water Quality Data from Monitoring Wells. ISWS/lGS Cooperative Ground Water Report 7. Illinois State Water Survey, Champaign, IL.

Gibs, J. and T.E. Imbrigiotta. 1990. Well-Purging Criteria for Sampling Purgeable Organic Compounds. Ground Water 28(1):68-78.

Gilbert, R.O. 1987. Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold, New York.

Gillham, R.W., M.J.L. Robin, J.F. Barker and J.A. Cherry. 1983. Groundwater Monitoring and Sample Bias. API Publication 4367. American Petroleum Institute, Washington, DC.

Glaccum, R., M. Noel, R. Evans, and L. McMillion. 1983. Correlation of Geophysical and Organic Vapor Analyzer Data Over a Conductive Plume Containing Volatile Organics. In Proc. 3rd Nat. Symp. on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, Dublin, OH, pp. 421-427.

Goodwin, C.D. and R.M. Burger. 1989. Inexpensive but Effective Soil Gas Screening—A Case Study. In: Proc. 3rd Nat. Outdoor Action Conf. on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, National Water Well Association, Dublin, OH, pp. 263-271.

Goolsby, D. A. 1972. Geochemical Effects and Movement of Injected Industrial Waste in a Limestone Aquifer. In: Symposium on Underground Waste Management and Environmental Implications (Houston, TX), T.D. Cook (ed.), Am. Ass. Petr. Geol. Mere. 18, pp. 355-368.

Hackett G. 1988. Drilling and Constructing Monitoring Wells with Hollow-Stem Augers: Part 2. Monitoring Well Installation. Ground Water Monitoring Review 8(1)60-68.

Hansen, M.H. W.N. Hurwitz, and W.G. Madow. 1953. Sample Survey Methods and Theory, Vols. I and H. John Wiley & Sons, New York.

Hendricks, W.A. 1956. The Mathematical Theory of Sampling. Scarecrow Press, New Brunswick, NJ.

Henzog, B.L., S.-F. Chou, J.R. Valkenberg, and R.A. Griffin. 1988. Changes in Volatile Organic Chemical Concentrations After Purging Slowly Recovering Wells. Ground Water Monitoring Review 8(4):93-99.

Hoffman, S.J. 1986. Soil Sampling. In: Exploration Geochemistry, Design and Interpretation of Soil Surveys. Reviews in Economic Geology 3:39-71.

Holden, P.W. 1984. Primer on Well Water Sampling for Volatile Organic Compounds. Water Resources Research Center, University of Arizona, Tucson, AZ.

Holm, T.R., G.K. George, and M.J. Barcelona. 1987. Fluorometric Determination of Hydrogen Peroxide in Groundwater. Anal. Chem. 59:582-586.

Holm, T.R., G.K. George and M.J. Barcelona. 1988. Oxygen Transfer through Flexible Tubing and Its Effects on Ground Water Sampling Results. Ground Water Monitoring Review 8(3):83-89.

Houghton, R.L. and M.E. Berger. 1984. Effects of Well-Casing Composition and Sampling Method on Apparent Quality of Ground Water. In: Proc. 4th Nat. Symp. on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, Dublin, OH, pp. 203-213.

Howsam, P. (ed.). 1990. Proceedings of International Groundwater Engineering Conference on Water Wells: Monitoring, Maintenance, and Rehabilitation. Chapman and Hall, London, 422 pp.

Hsueh, Y-W. and R. Rajagopal. 1988. Modeling Ground Water Quality Sampling Decisions. Ground Water Monitoring Review 8(4):121-133.

Hughes, J.P. and D.P. Lettenmaier. 1981. Data Requirements for Kriging: Estimation and Network Design. Water Resources Research 17:1641-1650.

Jessen, R.J. 1978. Statistical Survey Techniques. John Wiley & Sons, New York.

Johnson, T.M. and K. Cartwright. 1980. Monitoring of Leachate Migration in the Unsaturated Zone in the Vicinity of Sanitary Landfills. ISGS Circular 514. Illinois State Geological Survey, Champaign, IL.

Kaufman, M. I., D.A. Goolsby, and G.L. Faulkner. 1973. Injection of Acidic Industrial Waste into a Saline Carbonate Aquifer Geochemical Aspects. In: Symposium on Underground Waste Management and Artificial Recharge, J. Braunstein (ed.), Int. Ass. of Hydrological Sciences Pub. No. 110, pp. 526-551.

Keith, S.J., L.G. Wilson, H.R. Fitch, and D.M. Esposito. 1982. Sources of Spatial-Temporal Variability in Ground-Water Quality Data and Methods of Control: Case Study of the Cortaro Monitoring Program, Arizona. In: Proc. 2nd Nat. Symp. on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, Dublin, OH, pp. 217-227.

Kerfoot, H.B. and J. Soderberg. 1988. Three-Dimensional Characterization of a Vadose Zone Plume in Irregularly Interbedded Silt and Sand Deposits. In: Proc. 2nd Nat. Outdoor Action Conf. on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, National Water Well Association, Dublin, OH, pp. 1071-1087.

Kerfoot, H.B. and L.J. Barrows. 1987. Soil Gas Measurement for Detection of Subsurface Organic Contamination. EPA/600/2-87/027 (NTIS PB87-174884).

Kirschner, Jr., F.E. and G.L. Bloomsburg. 1988. Vadose Zone Monitoring: An Early Warning System. Ground Water Monitoring Review 8(2):49-50.

Kish, L. 1965. Survey Sampling. John Wiley & Sons, New York.

Kreitler, C.W., M.S. Akhter, and A.C.A. Donnelly. 1988, Hydrologic-Hydrochemical Characterization of Texas Gulf Coast Formations Used for Deep-Well Injection of Chemical Wastes. University of Texas at Austin, Bureau of Economic Geology.

Leenheer, J.A. and R.L. Malcolm. 1973. Case History of Subsurface Waste Injection of an Industrial Organic Waste. In: Symposium on Underground Waste Management and Artificial Recharge, J. Braunsteirt (ed.), Int, Ass. of Hydrological Sciences Pub. No 110, pp. 565-579.

Leenheer, J. A., R.L. Malcolm, and W.R. White. 1976, Physical, Chemical and Biological Aspects of Subsurface Organic Waste Injection near Wilmington, North Carolina. U.S, Geological Survey Professional Paper 987.

Litaor, M.I. 1988. Review of Soil Solution Samplers. Water Resources Research 24(5):727-733.

Loaiciga, H.A. 1989. An Optimization Approach for Groundwater Quality Monitoring Network Design. Water Resources Research 25(8):1771-1782.

Loehr, R.C., J.H. Martin, Jr., E.F. Neuhauser. 1986. Spatial Variation of Characteristics in the Zone of Incorporation at an Industrial Waste Land Treatment Site. In: Hazardous and Industrial Solid Waste Testing: Fourth Sympsium, ASTM STP 886, J.K. Petros, Jr., W.J. Lacy, and R.A. Conway (eds.), American Society for Testing and Materials, Philadelphia, PA, pp. 285-297.

Mackay, D. and W.Y. Shiu. 1981. A Critical Review of Henry's Law Constants for Chemicals of Environmental Interest. J. Phy. Chem. Ref. Data 10(4):1 175-1199.

MacPhemon. Jr., J.R. and J.F. Pankow. 1988. A Discrete Point Sampler for Ground Water Monitoring Wells. Ground Water Monitoring Review 8(3):160-164.

Malcolm, R.L. and J.A. Leenheer. 1973. The Usefulness of Organic Carbon Parameters in Water Quality Investigations. In: Proc. of the Inst. of Env. Sciences 1973 Annual Meeting (Anaheim, CA), pp. 336-340. Available from J.A. Leenheer, USGS MS 408, Box 25046, Federal Center, Denver CO, 80225.

Marrin, D.L. 1987. Soil Gas Sampling Strategies: Deep vs. Shallow Aquifers. In: Proc. 1st Nat. Outdoor Action Conf. on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, National Water Well Association, Dublin, OH, pp. 437-454.

Marrin, D.L. and W.B. Kerfoot. 1988. Soil Gas Surveying Techniques. Environ. Sci. Technol. 22(7)-740-745.

Marrin, D.L. and G.M. Thompson. 1984. Remote Detection of Volatile Organic Contaminants in Ground Water Via Shallow Soil Gas Sampling. In: Proc. 1st NWWA/API Conf. Petroleum Hydrocarbons and Organic Chemicals in Ground Water-Prevention, Detection and Restoration, National Water Well Association, Dublin, OH, pp. 172-187.

Marrin, D.L. and G.M. Thompson. 1987. Gaseous Behavior of TCE Overlying a Contaminated Aquifer. Ground Water 25(1):21-27.

Marsh, J.M. and J.W. Lloyd. 1980. Details of Hydrochemical Variations in Flowing Wells. Ground Water 18(4):366-373.

Mason, B.J. 1983. Preparation of Soil Sampling Protocol: Techniques and Strategies. EPA/600/4-83-020 (NTIS PB83-206979).

McKee, C.R. and A.C. Bumb. 1988. A Three-Dimensional Analytical Model to Aid in Selecting Monitoring Locations in the Vadose Zone. Ground Water Monitoring Review 8(2):125-136.

McNichols, R.J. and C.B. Davis. 1988. Statistical Issues and Problems in Ground Water Detection Monitoring at Hazardous Waste Facilities. Ground Water Monitoring Review 8(4):135-150.

Meade, J.P. and W.D. Ellis. 1985. Decontamination Techniques for Mobile Response Equipment Used at Waste Sites (State-of-the-Art Survey). EPA/600/2-85/105 (NTIS PB85-247021).

Mickam, J.T., R. Bellandi, and E.C. Tifft, Jr. 1989. Equipment Decontamination Procedures for Ground Water and Vadose Zone Monitoring Programs: Status and Prospects. Ground Water Monitoring Review 9(2):100-121.

Morrison, R.D. and B. Lowery. 1990. Sampling Radius of a Porous Cup Sampler Experimental Results. Ground Water 28(2):262-267.

Munch, J.H. and R.W.D. Killey. 1985. Equipment and Methodology for Sampling and Testing Cohesionless Sediments. Ground Water Monitoring Review 5(1):38-42.

Myers, R.G., C.W. Swallow, and D.E. Kissel. 1989. A Method to Secure, Leach and Incubate Undisturbed Soil Cores. Soil Sci. Soc. Am. J. 53:467-471.

National Council of the Paper Industry for Air and Stream Improvement (NCASI). 1982. A Guide to Groundwater Sampling. Technical Bulletin 362, NCASI, New York, NY.

New Jersey Department of Environmental Protection (NJDEP). 1988. Field Sampling Procedures Manual. Hazardous Waste Program, NJDEP, Trenton, NJ.

Newman, W., J.M. Armstrong, and M. Ettenhofer. 1988. An Improved Soil Gas Survey Method Using Adsorbent Tubes for Sample Collection. In: Proc. 2nd Nat. Outdoor Action Conf. on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, National Water Well Association, Dublin, OH, pp. 1033-1049.

Niaki, S. and J.A. Broscious. 1986. Underground Tank Leak Detection Methods: A State-of-the-Art Review. EPA/600/2-86/001 (NTIS PB86-137155).

Nielsen, D.M. (ed.). 1991. Practical Handbook of Ground Water Monitoring. Lewis Publishers, Chelsea, MI (published in cooperation with National Water Well Association, Dublin, OH), 717 pp.

Nielsen, D.M. and G.L. Yeates. 1985. A Comparison of Sampling Mechanisms Available for Small-Diameter Ground Water Monitoring Wells. Ground Water Monitoring Review 5(2):83-99.

Nightingale, H.I. and W.C. Bianchi. 1979. Influence of Well Water Quality Variability on Sampling Decisions and Monitoring. Water Resources Bulletin 15(5):1394-1407.

Nightingale, H.I. and W.C. Bianchi. 1980. Well Water Quality Changes Correlated with Well Pumping Time and Aquifer Parameters-Fresno, California. Ground Water 18:275-280.

Olivems, J.P., D.A. Vroblesky, and M.M. Lorah. 1988. Increasing Purging Efficiency Through the Use of Inflatable Packers. In: Proc. 2nd Nat. Outdoor Action Conf. on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, National Water Well Association, Dublin, OH, pp. 457-469.

Oudjik, G. and K. Mujica. 1989. Handbook for Identification, Location and Investigation of Pollution Sources Affect: ing Ground Water. National Water Well Association, Dublin, OH.

Palmer, C.D., J.F. Keely, and W. Fish. 1987. Potential for Solute Retardation on Monitoring Well Sand Packs and Its Effect on Purging Requirements for Ground Water Sampling. Ground Water Monitoring Review 7(2):40-47.

Panko, A.W. and P. Barth. 1988. Chemical Stability Prior to Ground-Water Sampling: A Review of Current Well Purging Methods. In: Ground-Water Contamination: Field Methods, A.G. Collins and A.I. Johnson (eds.), ASTM STP 963, American Society for Testing and Materials, Philadelphia, PA, pp. 232-239

Pennino, J.D. 1988. There's No Such Things as a Representative Ground Water Sample. Ground Water Monitoring Review 8(3):4-9.

Perry, C.A. and R.J. Hart. 1985. Installation of Observation Wells on Hazardous Waste Sites in Kansas Using a Hollow-Stem Auger. Ground Water Monitoring Review 5(4):70-73.

Peterson, R.G. and L.D. Calvin. 1986. Sampling. In: Methods of Soil Analysis, Part I—Physical and Mineralogical Methods, 2nd ed., A. Klute (ed.), ASA Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 33-51.

Pitard, F.F. 1989. Pierre Gy's Sampling Theory and Sampling practice, Vol. I Heterogeneity and Sampling, Vol. II Sampling Correctness and Sampling. CRC Press, Boca Raton, FL.

Pohhnann, K.F. and J.W. Hess. 1988. Generalized Ground Water Sampling Device Matrix. Ground Water Monitoring Review 8(4):82-84.

Puls, R.W, and M.J. Barcelona. 1989. Ground Water Sampling for Metals Analyses. Superfund Ground Water Issue Paper. EPA/548/4-89/001.

Rajagopal, R. 1986. The Effect of Sampling Frequency on Ground Water Quality Characterization. Ground Water Monitoring Review 6(4)65-73.

Rajagopal, R. and L.R. Williams. 1989. Economics of Sample Compositing as a Screening Tool in Ground Water Quality Monitoring. Ground Water Monitoring Review 9(1):186-192.

Rehm, B.W., T.R. Stolzenburg, D.G. Nichols. 1985. Field Measurement Methods for Hydrogeologic Investigations: A Critical Review of the Literature. EPRI AA-4301. Electric Power Research Institute, Palo Alto, CA.

Robbins, G.A. 1989. Influence of Using Purged and Partially Penetrating Monitoring Wells on Contaminant Detection. Mapping, and Modeling. Ground Water 27(2):155 -162.'

Robin, M.J.L. and R.W. Gillham. 1987. Field Evaluation of Well Purging Procedures. Ground Water Monitoring Review 7 4):85-93.

Rose, S.R. and A. Long. 1988. Monitoring Dissolved Oxygen in Ground Water Some Basic Considerations. Ground Water Monitoring Review 8(1):93-97.

Roy W.R., S.C. Mravik, I.G. Krapac, D.R. Dickerson, and R.A. Griggin. 1989. Geochemical Interactions of Hazardous Wastes with Geological Formations in Deep-Well Systems. ISGS Environmental Geology Notes 130. Illinois State Geological Survey, Champaign, IL.

Scalf M.R., J.F. McNabb, W.J. Dunlap, R.L. Cosby, and J. Fryberger. 1981. Manual of Ground-Water Quality Sampling Procedures. EPA/600/2-81/160, (NTIS PB82-103045). Also published in NWWA/EPA Series, National Water Well Association, Dublin OH.

Schalla, R., D.A. Myers, M.A. Simmons, J.M. Thomas, and A.P. Toste. 1988. The Sensitivity of Four Monitoring Well Sampling Systems to Low Concentrations of Three Volatile Organics. Ground Water Monitoring Review 8(3):90-96.

Schmidt, K.D. 1982. How Representative are Water Samples Collected from Wells? In: Proc. 2nd Nat. Symp. on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, Dublin, OH, pp. 117-128.

Sgambat, J.P. and R. Stedinger. 1981. Confidence in Ground-Water Monitoring. Ground Water Monitoring Review l(Spring):62-69.

Shangraw, T.C., D.P. Michaud, T.M. Murphy. 1988. Verification of the Utility of a Photovac Gas Chromatography for Conduct of Soil Gas Surveys. In: Proc. 2nd Nat. Outdoor Action Conf. on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, National Water Well Association, Dublin, OH, pp. 1089-1108.

Simmons, M.S. 1991. Hazardous Waste Measurements. Lewis Publishers, Chelsea, MI, 315 pp.

Sisk, S.W. 1981. NEIC Manual for Groundwater/Subsurface Investigations at Hazardous Waste Sites. EPA/330/9-81-002 (NTIS PB82-103755).

Slater, J.P. and F.R. McLaren. 1983. Sampling and Analysis of Soil for Volatile Organic Compounds. In: Proc. NWWA/EPA Conf. on Characterization and Monitoring of the Vadose (Unsaturated) Zone (Las Vegas, NV), National Water Well Association, Dublin, OH, pp. 623-658.

Slawson, Jr., G.C., K.E. Kelly, and L.G. Everett. 1982. Evaluation of Ground Water Pumping and Bailing Methods—Application in the Oil Shale Industry. Ground Water Monitoring Review 2(3):27-32.

Slonim, M.J. 1957. Sampling in a Nutshell. J. Am. Statistical Ass. 52:143-161.

Smith, J. S., D.P. Steele, M.J. Malley, and M.A. Bryant. 1988. Groundwater Sampling. In: Principles of Environmental Sampling, L.H. Keith (ed.), ACS Professional Reference Book, American Chemical Society, Washington, DC, pp. 255-260.

Sophocleous, M., J.E. Paschetto, and R.A. Olea. 1982. Ground-Water Network Design for Northwest Kansas, Using the Theory of Regionalized Variables. Ground Water 20:48-58.

Spittler, T.M., W.S Clifford, and L.G. Fitch. 1985. A New Method for Detection of Organic Vapors in the Vadose Zone. In: Proc. 2nd Conf. on Characterization and Monitoring in the Vadose (Unsaturated) Zone, National Water Well Association, Dublin, OH, pp. 236-246.

Spruill, T.B. 1988. Use of Total Organic Carbon as an Indicator of Contamination from an Oil Refinery, South-Central Kansas. Ground Water Monitoring Review 8(3)76-82.

Starks, T.H, K.W. Brown, and N.J. Fisher. 1986. Preliminary Monitoring Design for Metal Pollution in Palmerton, Pennsylvania. In: Quality Control in Remedial Site Investigation: Hazardous and Industrial Solid Waste Testing, 5th Volume, C.L. Perket (ed.), ASTM STP 925, American Society for Testing and Materials, Philadelphia, PA, pp. 57-66.

Steel, T.D. 1986. Converting Water Quality Information Goals into Statistical Design Criteria. In: Monitoring to Detect Changes in Water Quality Series, D. Lemer (ed.), Int. Ass. of Hydrological Sciences Pub. No. 157, pp. 71-79,

Stevenson, C.D. 1978. Simple Apparatus for Monitoring Land Disposal Systems by Sampling Percolating Soil Waters. Environ. Sci. Technol. 12:329-331.

Stolzenburg, T.R. and D.G. Nichols. 1985. Preliminary Results on Chemical Changes in Groundwater Samples Due to Sampling Devices. EPRI EA-4118. Electric Power Research Institute, Palo Alto, CA,

Sukhatme, P.V. and B.V. Sukhatme. 1970. Sampling Theory of Surveys with Applications, 2nd ed. Iowa State University Press, Ames, IA.

Summers, K.V. and S.A. Gherini. 1987. Sampling Guidelines for Groundwater Quality. EPRI EA-4952. Electric Power Research Institute, Palo Alto, CA.

Sykes, A.L., R.A. McAllister, and J.B. Homolya. 1986. Sorption of Organics by Monitoring Well Construction Materials. Ground Water Monitoring Review 6(4):44-47.

Tanur, J.M., (ed.). 1978. Statistics: A Guide to the Unknown. Holden-Day, San Francisco.

Tinlin, R.M. 1976. Monitoring Groundwater Quality: Illustrative Examples. EPA/600/4-76-036 (NTIS PB257 936).

Todd, D.K., R.M. Tinlin, K.D. Schmidt, and L.G. Everett. 1976. Monitoring Ground-Water Quality: Monitoring Methodology. EPA/600/4-76-026 (NTIS PB256-068).

UNESCO. 1983. proceedings of the Symposium-Methods and Instrumentation for the Investigation of Groundwater Systems. Committee for Hydrological Research, CHO-TNO, The Hague, The Netherlands.

Unwin, J. and V. Maltby. 1988. Investigations of Techniques for Purging Ground-Water Monitoring Wells and Sampling Ground Water for Volatile Organic Compounds. In: Ground-Water Contamination: Field Methods, A.G. Collins and A.I. Johnson (eds.), ASTM STP 963, American Society for Testing and Materials, Philadelphia, PA, pp. 240-252.

U.S. Environmental Protection Agency (EPA). 1985. RCRA Ground-Water Monitoring Compliance Order Guidance. EPA Office of Solid Waste and Emergency Response (NTIS PB87-19371O).

U.S. Environmental Protection Agency (EPA). 1986a. RCRA Ground Water Monitoring Technical Enforcement Guidance Document. EPA OSWER-9950.1. Also published in NWWA/EPA Series, National Water Well Association, Dublin, OH.

US. Environmental Protection Agency (EPA). 1986b. Test Methods for Evaluating Solid Waste, 3rd ed., Vol. II Field Manual Physical/Chemical Methods. EPA/530/SW-846 (NTIS PB88-239223) First update, 3rd ed. EPA/530/SW-86.3-l (NTIS PB89-148076).

U.S. Environmental Protection Agency (EPA). 1986c. Permit Guidance Manual on Unsaturated Zone Monitoring for Hazardous Waste Land Treatment Units. EPA/530/SW-86-040.

U.S Geological Survey. 1977+. National Handbook of Recommended Methods for Water Data Acquisition. USGS Office of Water Data Coordination, Reston, VA.

van Duijvenbooden, W. and H.G. van Waegeningh (eds.). 1987. Vulnerability of Soil and Groundwater to Pollutants. Committee for Hydrological Research, CHO-TNO, The Hague, The Netherlands.

Voorhees, K.J., J.C. Hickey, and R.W. Klusman. 1984. Analysis of Groundwater Contamination by a New Surface Static Trapping/Mass Spectrometry Technique. Anal. Chem. 56:2602-2604.

Williams, L.R., R.W. Leggett, M.L. Espegren, and C.A. Little. 1989. Optimization of Sampling for the Determination of Mean Radium-226 Concentration in Surface Soil. Environmental Monitoring and Assessment 12:83-96.

Williams, W.H. 1978. A Sampler on Sampling. John Wiley& Sons, New York.

Wilson, L.G. 1980. Monitoring in the Vadose Zone: A Review of Technical Elements. EPA/600/7-80-134 (NTIS PB81-125817).

Wilson, L.G. 1981. Monitoring in the Vadose Zone: Part I. Ground Water Monitoring Review 1(3):32-41.

Wilson, L,G. 1982. Monitoring in the Vadose Zonti Part II. Ground Water Monitoring Review 2(1):3 1-42.

Wilson, L.G. 1983. Monitoring in the Vadose Zone Part III. Ground Water Monitoring Review 3(2):155-166.

Wittmann, S. G., K.J. Quinn, and R.D. Lee. 1985. Use of Soil Gas Sampling Techniques for Assessment of Ground Water Contamination. In: Proc. NWWA/API Conf. Petroleum Hydrocarbons and Organic Chemicals in Ground Water—Prevention, Detection and Restoration, 1985, National Water Well Association, Dublin, OH, pp. 291-309.

Wood, W .W. 1976. Guidelines for Collection and Field Analysis of Groundwater Samples for Selected Unstable Constituents. U.S. Geological Survey TWI 1-D2.

Yates, F. 1980. Sampling Methods for Censuses and Surveys, 4th ed. MacMillan, New York.

Zapico, M.M., W. Vales, and J.A. Cherry. 1987. A Wireline Piston Core Barrel for Sampling Cohesionless Sand and Gravel Below the Water Table. Ground Water Monitoring Review 7(3); 74-82.

# PART II: PHYSICAL AND CHEMICAL PROCESSES IN THE SUBSURFACE

## Chapter 10

## Physiochemical Processes: Organic Contaminants

Carl D. Palmer and Richard L. Johnson

### 10.1 Overview of Physiochemical Processes

The characterization of hazardous waste sites to design remediation strategies requires a broad range of background information. As discussed in Chapter 9, good sampling methods and strategies are required to determine the contamination level and the extent to which contaminants have moved within the subsurface. Understanding of the physical processes discussed in Chapters 4 and 5 allows determination of the rate and direction in which contaminated ground water is flowing. This information also can be used to determine whether the contaminants will be captured and removed by extraction wells. However, this information by itself is not sufficient for optimal choice of remediation schemes. Critical questions such as how much water must pass through a section of an aquifer to remove the contaminants or how much time is required for contaminants to diffuse out of low-permeability zones also must be answered. The answers to these questions depends on the physiochemical processes occurring within the subsurface.

The next three chapters address the physiochemical processes that recur within the subsurface, the parameters required for their characterization, and the implications of these processes for remediation design. In this chapter, the discussion is limited to processes occurring below the water table that affect the concentration, transport, and hence removal of organic contaminants. Chapter 11 addresses the transport of volatile organic compounds through the unsaturated zone, and Chapter 12 discusses inorganic contaminants.

The design of optimal remediation schemes often requires some “prediction” of the distribution of contaminants within the subsurface over time. These predictions then can be used to evaluate different remediation scenarios. The basis for making such predictions is generally the application of the concepts of mass balance. A common method for applying mass balance concepts to dissolved chemical constituents in ground-water systems is the advection-dispersion equation, which is written in its one-dimensioml form as:

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \pm RXN \qquad [10\text{-}1]$$

where v is the ground-water velocity (L/T), D is the dispersion coefficient ($L^2/T$), C is the concentration of the dissolved constituent ($M/L^3$), t is time, and RXN represents a general chemical reaction term. The frost term in eq. 10-1 describes the net advective flux of the contaminant in and out of a volume of the aquifer (Figure 10-1). The second term describes the net dispersive flux of the contaminant. The first term on the right-hand side of the equation describes the change in concentration of the contaminant in the water contained within the volume of aquifer. The second term on the right-hand side represents the amount of contaminant that may be added or lost to the ground water by some chemical or biological reaction. If there is no reaction term, then the equation describes the transport of a conservative, nonreacting tracer such as chloride or bromide. More detailed information about the development and derivation of eq. 10-1 is found in Palmer and Johnson (1989), Gillham and Cherry (1982), Freeze and Cherry (1979), or Bear (1979, 1969).

Some understanding of this mass balance equation is useful even to the individual who is not directly responsible for making mathematical representations of the distribution of contaminants within the subsurface. The equation is an example of the current understanding of the processes controlling the fate and transport of contaminants in the subsurface. The equation lists the parameters that should be quantified either by performing appropriate field or laboratory measurements or by using the best known values. The results of the application of this modeling are unlikely to ever exactly “predict” how the contaminants behave at a particular field site but they can provide a general set of expectations that are useful in the design of a remedial system. These results also can be used to compare aquifer remediation performance.

According to eq. 10-1, two parameters that must be determined are the ground-water velocity, v, and the dispersion coefficient, D. These parameters are described in Chapters 4 and 5 as well as in other sources (e.g., Palmer and Johnson, 1989 a,b). Chemical processes that can affect the fate and transport of organic contaminants below the water table include (1) abiotic degradation, (2) biotic degradation, (3) dissolution nonaqueous phase liquids (NAPLs), (4) sorption reactions, and (5) ionization. Both abiotic and biotic

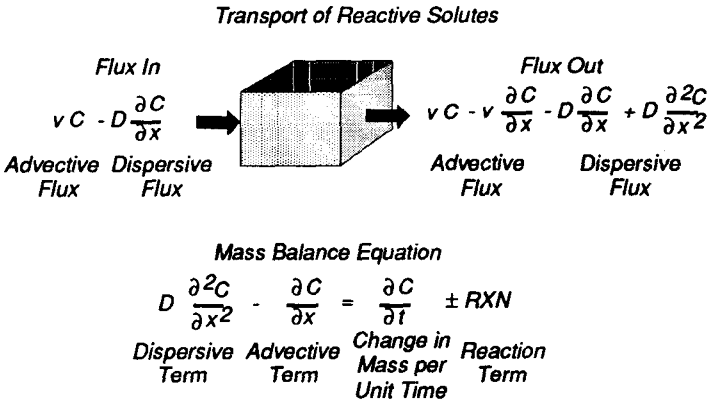


**Figure 10-1.** Mass balance equation for the transport of reactive solutes through porous media.

degradation are discussed in Chapter 13. The discussion in this chapter is limited to the three latter processes.

## 10.2 Dissolution of Nonaqueous Phase Liquids

Many of the organic chemicals of environmental concern enter the subsurface in the nonaqueous phase. How these solvents move through the soil depends on the grain size of the aquifer material, the degree of water saturation in the pore space, and the density and viscosity of the solvent relative to water (Palmer and Johnson, 1989c; Schwille, 1988). For example, if there is a spill of nonaqueous phase liquid that has a density greater than water (DNAPL), as it flows through the unsaturated zone, because the water is in the wetting phase, it will pass through the center of the pores. If there is residual water within the unsaturated zone then the combination of higher density and lower viscosity of the DNAPL relative to water results in unstable flow or significant fingering of the DNAPL as it moves through the porous media. If the spill is large enough so that the DNAPL can penetrate the capillary fringe and move below the water table, this fingering continues to occur. The transport of the DNAPLs is also very sensitive to small changes in permeability. Therefore, the DNAPL tends to spread laterally as it encounters lenses of finer grained material in the subsurface. This combination of viscous fingering and lateral flow results in a series of fingers and pools of DNAPL. The DNAPL in the fingers tends to drain to some residual saturation while the pools contain DNAPL above the residual saturation.

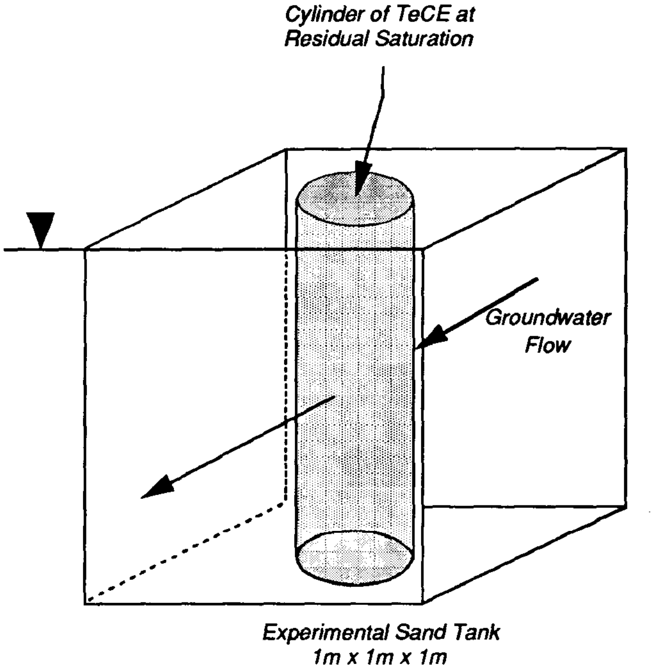
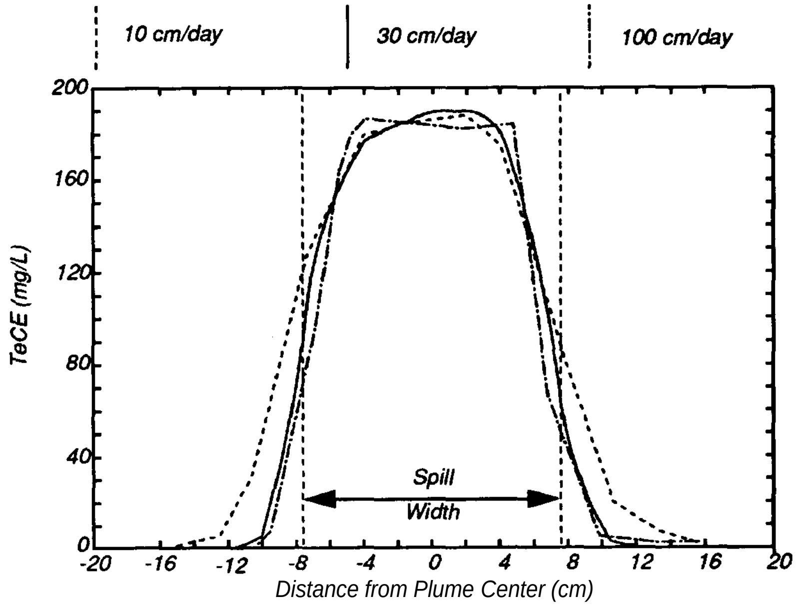


**Figure 10-2.** Cylindrical source of tetrachloroethylene (TeCE) used in the experiments by Anderson (1988).

As ground water flows through the fingers, the DNAPL is dissolved by the passing ground water. Laboratory experiments (Anderson, 1988; Anderson et al., 1987) using a 15-cm-diameter cylindrical finger of tetrachloroethylene (TeCE) (Figure 10-2) demonstrate that the ground water passing through the fingers can quickly reach saturation with the TeCE. This was found to be true for ground-water velocities ranging from 10 to 100 cm/day (Figure 10-3). However, these results do not imply that where a DNAPL spill has occurred the sampled ground water is saturated with the solvent. Indeed, sampling results usually indicate that most waters are highly undersaturated with respect to the DNAPLs. Although the water that passes through the fingers or very close to the pools of DNAPL within the subsurface is saturated with the DNAPL, mass transfer of the dissolved DNAPL to the areas further from these fingers and pools is predominantly by molecular diffusion. As a result, many areas within the aquifer that lie between the pools and fingers contain little or no dissolved solvent. While the distance between such fingers and pools is generally unknown, it is probably at least as great as the mean distance between the small-scale beds within the aquifer. For the Borden aquifer in Ontario, Sudicky (1986) found this distance to be about 10 cm in the vertical direction. A typical monitoring well would have an intake length of at least 2 m. Thus, the water saturated with the solvent is mixed



**10-3. Concentration of TeCE across the flow field at the end tank in the sand box experiments conducted byAnderson (1988).**

with the uncontaminated ground water resulting in measured concentrations that are substantially below saturation.

Estimating the time required to remove the nonaqueous phase liquid from the subsurface is difficult. Estimates require knowledge of the amount that was spilled and the distribution of the solvent within the aquifer. While the former piece of information is often difficult to obtain, the latter is virtually impossible. If the solvent is assumed to be uniformly distributed (a residual saturation, $S_r$) within the aquifer, and the ground water flowing through the aquifer instantaneously equilibrates with the solvent, then the time required to remove the solvent by dissolution, $t_r$, is

$$t_r = S_r \theta L/(C_{eq} q) \qquad [10\text{-}2]$$

where q is the porosity of the aquifer, L is the length of the aquifer containing the solvent through which the ground water flows, $C_{cq}$ is the equilibrium concentration of the contaminant in the ground water, and q is the ground-water flux. Estimates of removal times based on eq. 10-2, however, underestimate the actual removal time because the equation does not account for the role of soil heterogeneity, the differential times the ground water takes to flow along different flowlines, or the limitations in mass transfer of pools of NAPL that are above residual saturation. If a pump-and-treat remediation scheme is already in place, remediation time can be roughly estimated by dividing the total mass of solvent in the aquifer by the mass being removed per unit time by extraction wells.

## 10.3 Sorption Phenomena

### *10.3.1 Adsorption Isotherms*

Once an organic compound has been dissolved into the ground water, it will be transported away from the source area by ground-water flow. The contaminants do not travel at the same velocity as the ground water but can be slowed by their interaction with the soil matrix. This interaction with the soil is often described graphically as an adsorption isotherm. An adsorption isotherm is simply a plot of the concentration of the contaminant on the soil versus the concentration of the contaminant in solution. Isotherms are so named because they are conducted at constant temperature. Different types of adsorption isotherms are defined according to their general shape and mathematical representation. For a Langmuir isotherm, the concentrations on the soil increase with increasing ground-water concentrations until a maximum concentration on the soil is reached (Figure 10-4). The isotherm can be represented by the equation

[10-3]

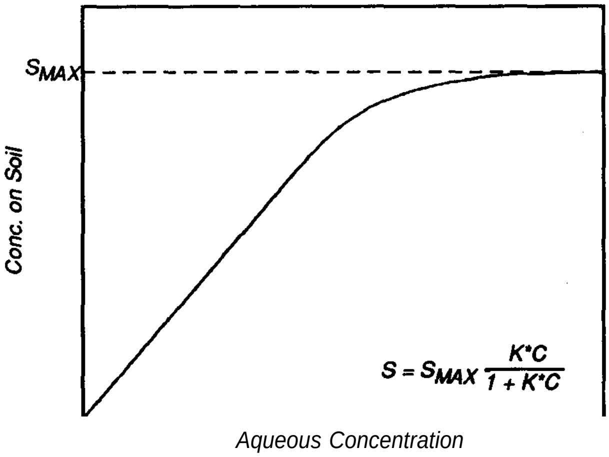


**Figure 10-4. Lndmuir adsorption isotherm.**

where S (M/M) is the concentration on the soil, $S_{max}$ (M/M) is the maximum concentration on the soil, K($L^3$/M) is the Langmuir adsorption constant, and C (M/$L^3$) is the concentration in the ground water. A Freundlich (or Küster) isotherm is given by the equation:

$$S = KC^a \qquad [104]$$

where K is the Freundlich adsorption constant and *a is* a positive parameter. The shape of a Freundlich isotherm depends on the value of a. If a is greater than 1.0, the isotherm becomes steeper with increasing concentrations in the ground water. If *a* is less than 1.0, the isotherm becomes steeper at lower concentrations (Figure 10-5).

A linear isotherm is a special case of the Freundlich isotherm where the parameter a is equal to unity. Linear isotherms are of particular interest because (1) many nonpolar, hydrophobic organic compounds tend to follow linear isotherms (Figure 10-6) over a wide range of conditions and (2) the application of a linear isotherm simplifies the mathematical model used to simulate the rate of contaminant movement in the subsurface and reduces the number of parameters that need to be obtained during characterization.

Another way of representing the partitioning between the soil and the ground water is by a "partition coefficient," $K_p$. The partition coefficient is the ratio of the change in concentration of the contaminant on the soil to the change in concentration of the contaminant in the ground water or more simply, the slope of the isotherm. When the isotherm for a particular soil is linear, the partition coefficient is constant.

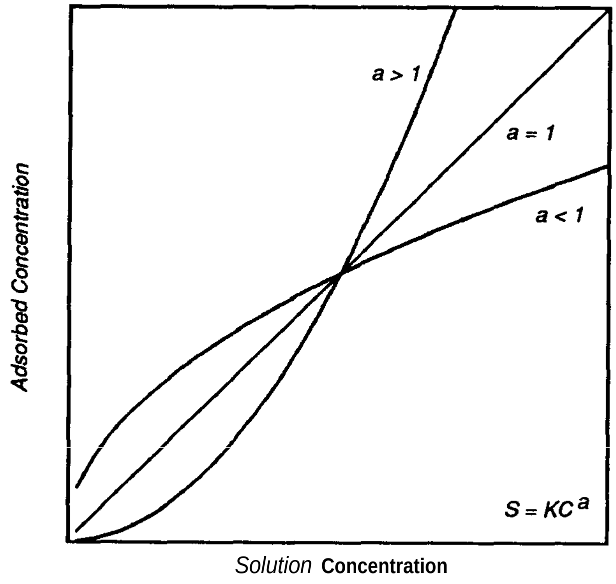


**Figure 10-5. Freundlich adsorption isotherm.**

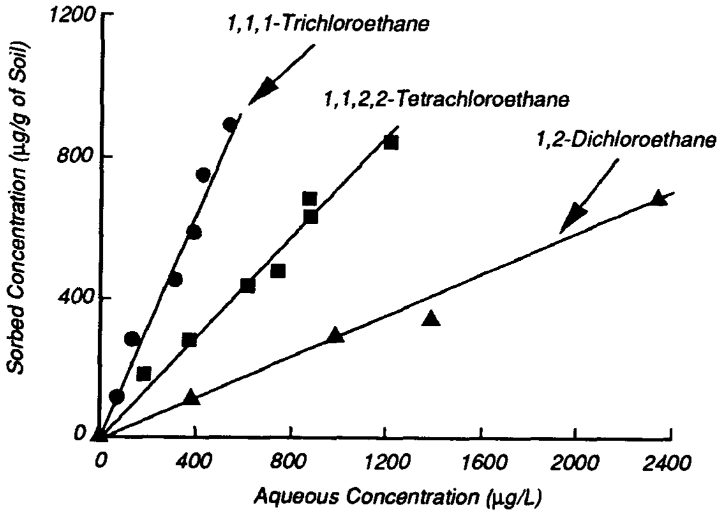


**Figure 10-6. Linear sorption isotherms obtained for several priority pollutants (after Chlou et al., 1979).**

The partition coefficient of an organic chemical is not constant for every soil. In general, $K_p$ increases as the fraction of organic carbon, $f_{oc}$, increases in the soil (Karickhoff, 1981). In other words, the sorption of nonpolar, hydrophobic organic compounds in soils is primarily an equilibrium partitioning process into soil organic matter. $K_p$ can be represented by

$$K_p = f_{oc} K_{oc} \qquad [10\text{-}5]$$

where $K_{oc}$ is the slope of the experimentally determined $K_p$ versus $f_{oc}$ curves like those in Figure 10-7. Alternatively, $K_{oc}$: can be considered to be the partition coefficient for the organic compound into an hypothetical pure organic carbon phase.

If sorption is the primary reaction occurring in the subsurface, the right-hand side of eq. 10-1 represents the change in the total mass of contaminant within a volume of the aquifer. The total change in mass in the volume of the aquifer is equal to the change in mass in the ground water plus the change in mass on the solid phase. The reaction term in eq. 10-1 is then written as $(\rho_b/\theta)\ \partial S/\partial t$ where $\rho_b$ and $\theta$ are the dry bulk density and volumetric water content of the soil, respectively. Substituting

$$\frac{\partial S}{\partial t} = \frac{\partial S}{\partial C}\frac{\partial C}{\partial t} \qquad [10\text{-}6]$$

into this reaction term and recognizing that $\partial S/\partial C$ is equal to $K_p$ for a linear adsorption isotherm, eq. 10-1 can now be written as

$$\frac{D}{R}\frac{\partial^2 C}{\partial x^2} - \frac{v}{R}\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \qquad [10\text{-}7]$$

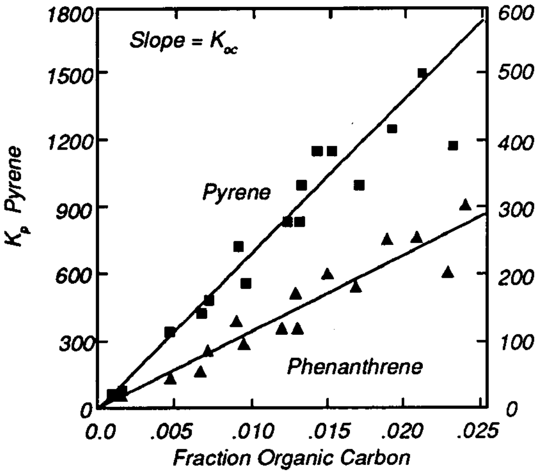


**Figure 10-7. Partition coefficients for pyrene and phenanthrene versus the fraction of organic carbon in the soil (after Karickhoff, 1981).**

where the constant

$$R = 1 + K_p\rho/\theta \qquad [10\text{-}8]$$

is known as the "retardation factor." The general form of the equation only changes by the constant R. All of the mathematical solutions that are used to solve the transport of nonreacting tracers can be used to solve for the transport of nonpolar hydrophobic organic compounds if the ground-water velocity and dispersion coefficient are divided by R.

The retardation factor can be interpreted in slightly different but equally valid ways. It is the ratio of the ground-water velocity, v, to the solute velocity, $v_s$, (i.e., $R = v/v_s$). It is also the ratio of the time for the solute to travel from a source to an observation point divided by the time for the ground water to travel that same path. The retardation factor also can be thought to represent the number of pore volumes that must be flushed through a soil to remove the contaminant. All of these definitions assume that the only process occurring is linear sorption.

Application of the new expression (eq. 10-7) requires knowledge of the additional parameter R. This parameter can be obtained by several methods including (1) calculation from eq. 10-8, where $K_p$ is obtained from correlation techniques; (2) calculation from eq. 10-8, with $K_p$, obtained from batch sorption tests; (3) measurement from column tests and (4) estimation from field data. The other parameters in eq. 10-8 (porosity and dry bulk density) are physical parameters that can be obtained using common techniques (see Chapter 4 and Palmer and Johnson, 1989c).

### *10.3.2 Determining Retardation Factors Using $f_{oc}$ and $K_{oc}$*

The relationship between the $K_{oc}$ value and other known properties of organic contaminants has been examined by numerous researchers (Kenaga and Goring, 1980; Karickhoff, 1981, Schwartzbach and Westall, 1981; Chiou et al., 1982 and 1983), For example, some research has revealed linear relationships between the log of the volubility of the contaminant and the log ($K_{oc}$) (Figure 10-8). Similarly, Karickhoff suggested that the partitioning of organic contaminants into soil organic matter must be analogous to the partitioning of those contaminants into other organic compounds such as octanol. He found a linear relationship (Figure 10-9) between log ($K_{oc}$) and log ($K_{OW}$), where $K_{OW}$ is the octanol-water partition coefficient. Several regression equations relating the properties of organic compounds to the $K_{oc}$ have been derived (Table 10-1). Thus, by knowing the name of the compound of interest, these properties can be found in tables of chemical properties (Mabey et al., 1982) and the regression equations used to approximate $K_{oc}$. The goal, however, is to determine the partition coefficient and ultimately the retardation factor. To do this, eq. 10-5 must be applied and a measurement of the fraction of organic carbon must be obtained.

The many methods of measuring the amount of organic carbon in the soil can be broadly classified as either wet combustion or dry combustion techniques. Wet combustion techniques involve the addition of a strong oxidizing agent

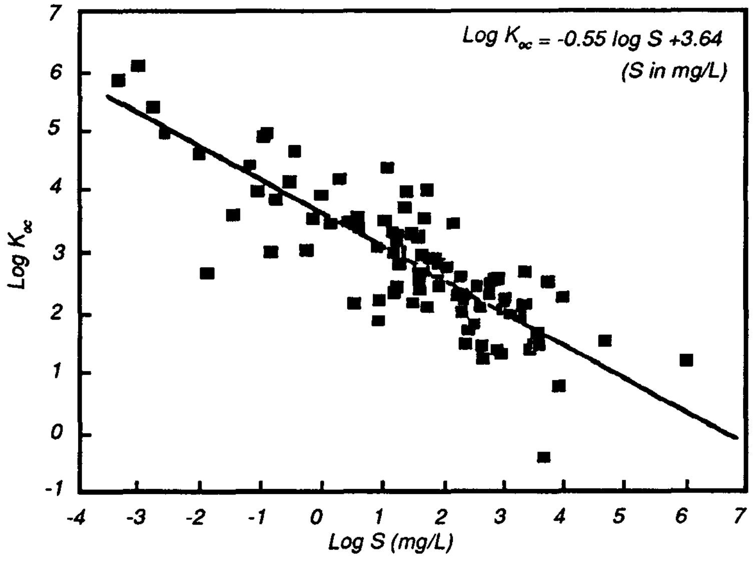


**Figure 10-8. Log $K_{oc}$ versus logarithm of the volubility of the compound in water (after Kenaga and Goring, 1980).**

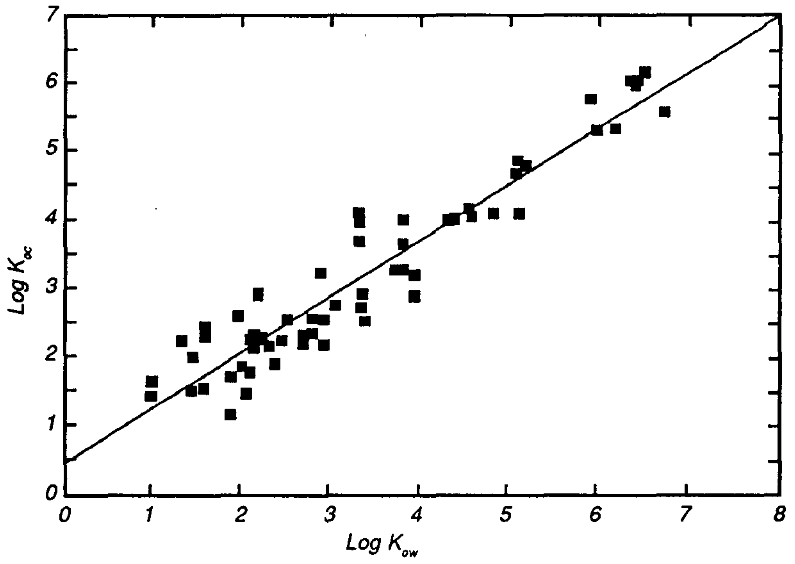


**Figure 10-9. Log $K_{oc}$ versus the octanol-water partition coefficient. Data from Karickhoff (1981).**

such as bichromate to the soil. There are several such wet combustion techniques including the Walkley-Black method and the modified Mebius procedure; these procedures are discussed in detail by Nelson and Sommers (1982). In spite of some limitations, these methods can provide a relatively rapid and inexpensive method for obtaining estimates of $f_{oc}$.

Dry combustion methods generally involve heating the soil sample in the presence of oxygen. The oxygen reacts with the soil carbon to form carbon dioxide that can be detected by a variety of techniques.

To estimate the linear retardation factor, the $K_{oc}$ obtained from one (or more) of the regression equations given in Table 10-1 is multiplied by the fraction of organic carbon to yield the partition coefficient (eq. 10-1). The retardation factor is obtained from the $K_p$, $\rho_b$, and $\theta$ by eq. 10-8.

There are several limitations to the use of the correlation techniques described above. The linear relationship between $f_{oc}$ and $K_p$ is not always easy to determine. In particular, the relationship is most likely to fail when (1) the $f_{oc}$ is very low (<0,001), (2) when there are large amounts of swelling clays present, and (3) the organic compound is polar (e.g., compounds that contain amine or carboxylic acid groups) (Pankow,

*Table 10-1. Some Reported Correlation Equations*

| Equation | Data Base[a] | Reference |
|---|---|---|
| $\log K_{oc} = 0.544 \log K_{ow} + 1.377$ | aromatic hydrocarbons (8)<br>carboxylic acids and esters (5)<br>P containing insecticides (5)<br>ureas and uacils (7)<br>symmetrical triazines (6)<br>miscellaneous (14) | Kenaga and Goring (1978) |
| $\log K_{oc} = 1.00 \log K_{ow} - 0.21$ | polycyclic aromatics (8)<br>chlorinated hydrocarbons (2) | Karickhoff et al. (1979) |
| $\log K_{oc} = -0.55 \log S_w + 3.64$ [b] | aromatic hydrocarbons (8)<br>carboxylic acids and esters (5)<br>P containing insecticides (5)<br>ureas and uacils (7)<br>symmetrical triazines (6)<br>miscellaneous (14) | Kenaga and Goring (1978) |
| $\log K_{oc} = -0.56 \log S_w + 0.93$ [b,c] | polychlorinated biphenyls (3)<br>pesticides (4)<br>halogenated ethanes & propanes (6)<br>tetrachloroethene<br>1,2-dichlorobenzene | Chiou et al. (1979) |
| $\log K_{oc} = -0.54 \log x_s + 0.44$ [d] | polycyclic aromatics<br>chlorinated hydrocarbons | Karickhoff (1979) |

[a] Number in parentheses refer to the number of compounds in data base.
[b] $S_w$ is the solubility of the compound in water in ppm.
[c] Derived from the original equation assuming $K_a = 1.7\ K_{om}$
[d] $X_s$ is the mole fraction solubulity at 25°C.

After Pankow, 1984

1984). There are also several reasons why the relationship between log ($K_{oc}$ and log ($K_{oW}$) may not always be linear (Pankow, 1984). If mechanisms other than simple partitioning into soil organic carbon are contributing to the adsorption of the organic contaminant, then the $K_{oc}$ value, computed as the ratio $K_p/f_{oc}$, will be in error. Also, If the molecule is large it may not fit into the soil organic matter to the same extent as it would in octanol (steric limitations). Finally, if the adsorption is strong, a contaminant may take a substantial period of time to equilibrate with the soil organic carbon.

### 10.3.3 *Determining Retardation Factors Using Batch Tests*

Retardation factors also can be measured with batch tests. These tests are, in principle, easy to perform, and the method is outlined in Figure 10-10. A known volume of solution, $V_w$, containing an initial concentration, $C_0$, of a contaminant is placed into a container. A known mass of soil, $M_s$, is then added and the mixture is shaken and allowed to equilibrate. The soil then is separated from the solution by centrifuging, and an aliquot of the supernatant is sampled. The concentration of the contaminant in this aliquot, C, is measured and the concentration on the soil, S, is calculated by

$$S = V_w(C_0 - C)/M_s \qquad [10\text{-}9]$$

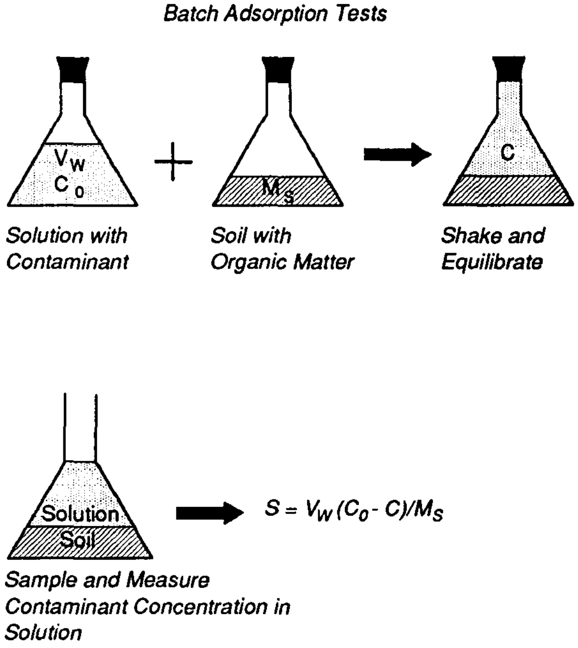


**Figure 10-10. Batch adsorption tests.**

This test can be run several times with different initial concentrations or different masses of soil. The result is a series of contaminant concentrations with corresponding aqueous phase concentrations that yield an isotherm when they are plotted. If the isotherm is linear, the slope, or partition coefficient, can be easily determined. The retardation factor then cart be calculated from $K_p$, $p_b$, and O using eq. 10-8.

Prior to conducting such batch adsorption tests, the soil is prepared by drying and then sieving through a 2-mm sieve. The sieving is to ensure that aggregated soil particles are relatively small, thus reducing the time for the contaminant to diffuse into the particles and equilibrate with the soil. Another important preparatory step is to estimate the $K_p$ using, for example, the correlation methods described in Section 10.3.2. This is important in choosing the proper amount of soil to use in the tests. If $K_p$ is large and too much soil is added to the reaction vessel, then most of the contaminant is partitioned to the soil and the concentration in solution cannot be accurately determined. Similarly, if $K_p$ is small and too little soil is added to the reaction vessel, then the measured contaminant concentration falls within the analytical error of the initial concentration and an accurate estimate of the contaminant concentration of the soil cannot be obtained. Both of these cases lead to poor measures of the partition coefficient.

There are some problems that complicate the use of batch tests for determining $K_p$. For example, batch tests assume that equilibrium is established between the soil and the solution, but some contaminants may take a very long period of time to equilibrate. Experiments on the resorption of hexachlorobenzene from soils (Karickhoff and Morris, 1985) indicated that even after 35 days equilibrium was not obtained (Figure 10-11).

Another problem involves nonsettling particles. The separation of the soil and the water is assumed to be complete before sampling of the supernatural however, very fine, coloidal-size particles may remain in suspension. The contaminants attached, to these particles are stripped during the analysis of the water, which causes overestimation of the aqueous phase concentration. This results in underestimation of the partition coefficient (e.g., Gschwend and Wu, 1984). The magnitude of the effect depends on the concentration of nonsettling particles (NSPS) and the true partition coefficient onto those particles (Figure 10- 12). If the partition coefficient is small, then most of the mass of the contaminant is in solution and the error caused by the NSPS is negligible. If the partition coefficient is large, then a significant mass of the contaminant is really partitioned onto the soil particles causing significant errors in the aqueous phase concentration and hence $C_p$

A third problem arises from the loss of contaminant by volatilization during equilibration, sampling, and analysis. This problem can be minimized by eliminating head-space and using properly sealed reaction vessels.

Uncontaminated background soils are recommended for batch adsorption tests. If the soils contain any NAPLs, the contaminant being investigated will partition into the NAPL, yielding a potentially large and incorrect partition coefficient. Once $K_p$ is determined in the batch test, the retardation factor, R, can be estimated by using eq. 10-8.

### 10.3.4 Determining Retardation Factors from Column Tests

A third method for estimating linear repartition factors is with column tests. In these tests, a column of soil is prepared,

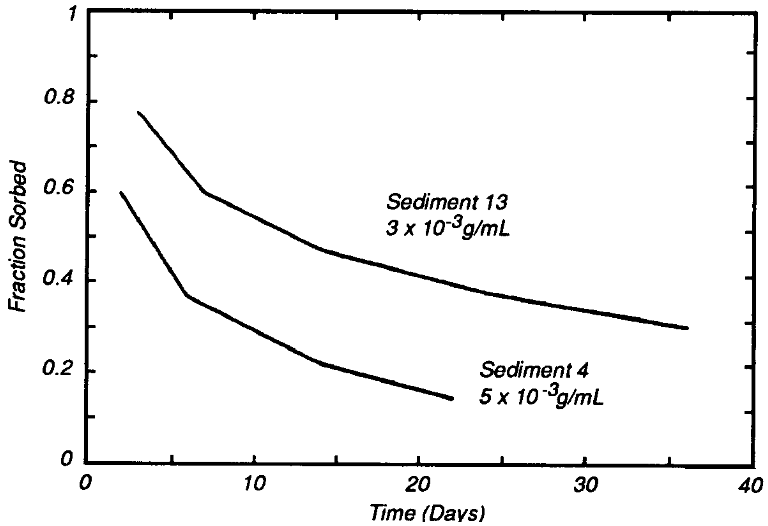


**Figure 10-11. The fraction of hexachlorobenzene sorbed to two soils versus time during desorption teats (after Karickhoff and Morris, 1985).**

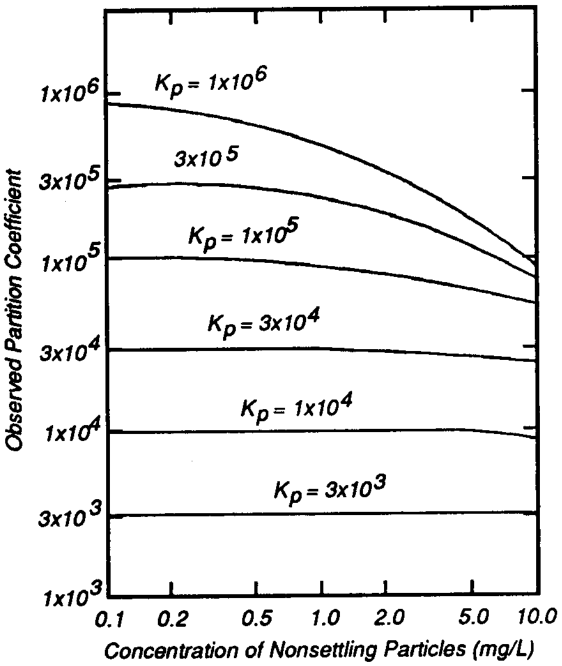


**Figure 10-12.** **The effects of nonsettling particles on the observed partition coefficient (after Pankow, 1984).**

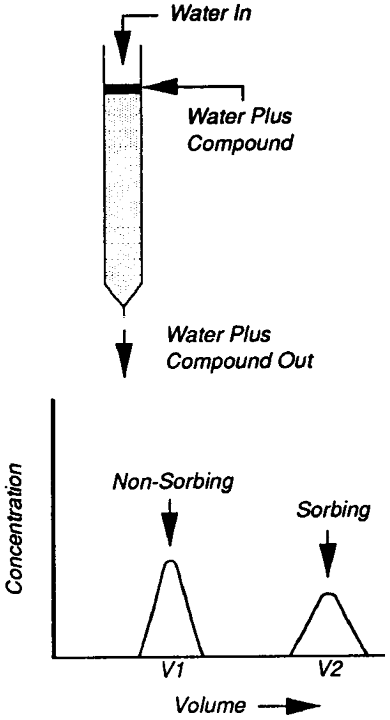


**Figure 10-13.** **Column tests for determination of retardation**

and a solution containing a nonadsorbing tracer and the contaminant of interest is run through the column (Figure 10-13). The concentrations of the tracer and contaminant can be measured in the water that has passed through the column. The retardation factor is then the ratio of the time (or volume) for the center of mass of the contaminant to break through the column to the time (or volume) for the center of mass of the nonreactive tracer to break through the column. This technique provides a direct measure of R; however, it is only well suited for those contaminants that have a relatively small (< 10) retardation factor. Contaminants with retardation factors much greater than 10 require too much time to measure to be practical. Other disadvantages of using column tests include the slow flow rates in fine-grained material, the destruction of soil structure by soil repacking, and the difficulty in distinguishing kinetic behavior from the heterogeneous packing within the column.

### *10.3.5 Determining Retardation Factors from Field Data*

Site-specific field information obtained during the Remedial Investigation/Feasibility Study (RI/FS) can, in some cases, be used to estimate contaminant retardation. While in principle retardation factors can be back-calculated from breakthrough curves obtained at monitoring wells or through the spatial distribution of the contaminants in the subsurface, in practice, only the latter is likely to be obtained. The retardation factors can be estimated by dividing the velocity of ground water by the velocity of the contaminant. The groundwater velocity can be estimated from Darcy's Law and the porosity, or alternatively by the distance some nonadsorbing solute travels after the release. The solute velocity can be estimated by dividing the mean distance the contaminant has traveled by the time since its release into the subsurface. One of the potential disadvantages of this method is that other processes that are not included in the data analysis are occurring within the aquifer. Ignoring these processes can result in poor estimates of the retardation factor.

### *10.3.6 Comparison of Methods for Estimation of Retardation*

Each of the methods for estimating the retardation factor has advantages and disadvantages. One of the key questions, however, is how do these different methods for estimating retardation compare. The best technique for comparison is to look to large-scale field tracer experiments where very accurate field values have been obtained. This has been done for the Stanford-Waterloo tracer experiment that was conducted in the sandy aquifer on Canadian Forces Base Borden in Ontario, Canada. Details of the experiment and analysis of the results can be found in Mackay et al. (1986); Roberts et al. (1986); Curtis et al. (1986); Freyburg (1986); and Sudicky (1986).

A summary of the retardation factors obtained for five different compounds using a correlation method, batch tests, and temporal and spatial data from the field experiment is given in Table 10-2. The batch tests agree closely with the field data. The correlation technique tends to consistently underestimate the retardation factors. The underestimation of the retardation factors may be the result of poor estimates of the fraction of organic carbon (e.g., Powell et al., 1989) or errors in the assumptions in eq. 10-5, or they may be the result

*Table 10.2 Comparison of Methods for Retardation Factors*

| Solute | Office Estimated | Lab Batch | Field Values Temporal | Field Values Spatial |
|---|---|---|---|---|
| CTET | 1.3 | 1.9 | 2.7 | 2.1 |
| BROMO | 1.2 | 2.0 | 1.7 | 2.2 |
| TeTE | 1.3 | 3.6 | 3.3 | 4.3 |
| DCB | 2.3 | 6.9 | 2.7 | 6.2 |
| HCB | 2.3 | 5.4 | 4.0 | 6.5 |

*After Curtis et al. (1986)*

of the inherent error in the regression equations. Recall that the regression equations are based on the logarithms of the values; therefore, the best estimates of the $K_{oc}$ and hence the retardation factor may be a factor of 2 or 3 from the "true" value. Nonetheless, the correlation techniques do provide the correct order of magnitude estimate of the retardation factor at very little expense. Such values would be appropriate for the preliminary design of the remedial strategies. If more accurate estimates are required, then the more expensive batch or column tests should be used. Enough samples should be tested, however, to estimate the uncertainty of the retardation factor for each of the important geologic units.

### 10.3.7 Applicability and Limitations of Linear Partitioning and Retardation

Most of the emphasis in this section has been on the linear partitioning and retardation model for the adsorption of neutral, hydrophobic organic compounds in the environment. While this model is adequate for many situations, it is important to recognize the limitations in the assumptions so that it is not applied to situations where it is imppropriate.

Retardation only describes the process of the partitioning of the contaminant between the ground water and soil organic matter. If the nonaqueous solvent phase is dissolving or the organic compounds are degrading, then these additional processes also must be taken into account. However, for describing the partitioning process, the linear retardation model is reasonable for many compounds if the concentration of the contaminant is less than $10^{-5}$ molar or less than half the volubility, whichever is lower (Karickhoff et al., 1979; Karickhoff, 1984). At high or low concentrations the linear isotherm may deviate. Some data on the adsorption of TCE to glacial till suggest that the partition coefficient is not constant but may vary by as much as 50-fold over range in groundwater concentrations from 10 to 10,000 parts per billion (ppb) (Figure 10-14). This variation occurs even though the partition coefficient is approximately constant over the range from 100 to several thousand ppb.

The linear retardation model assumes that equilibrium is achieved quickly. In some circumstances, the rate of adsorption and resorption can bean important factor. As mentioned in Section 10.3.3, Karickhoff and Morris (1985) found that during the resorption of hexachlorobenzene, equilibrium was not achieved even after 35 days of reaction time (Figure 10-11).

## 10.4 Ionization and Cosolvation

Another important reaction that can affect sorption and hence the rate of removal of organic contaminants from the subsurface is ionization. Acidic compounds such as phenols, catechols, quinoline, and organic acids can lose or gain protons ($H^+$) depending upon the pH. The resultant ions are much more soluble and less hydrophobic than the uncharged forms. Therefore, the ionized forms have much lower $K_{oc}$ values than the uncharged forms, The pH at which this reduction in $K_{oc}$ becomes substantial can be predicted based on the acidity of the compound. This acidity is often represented as the $pK_a$ of the compound, which is the pH at which 50 percent of the molecules are ionized.

Table 10-3 lists $pK_a$'s for a number of environmentally significant ionizing compounds. For example, trichlorophenol ionizes to a phenolate (Figure 10-15). The trichlorophenol has a relatively large $K_{oc}$ value (2330) and readily partitions into the soil organic matter. The ionized form is not as hydrophobic and its $K_{OC}$ value is substantially smaller than the $K_{oc}$ of the trichlorophenol. As the pH increases, the fraction of the phenol that is ionized increases and the $K_{oc}$ decreases (Figure 10-16). Therefore, the $K_{oc}$ value based on the total concentration of the phenolic compound is dependent on the degree of ionization of the compound. While the phenolate compound may be retarded mainly by anion adsorption to oxide surfaces in low carbon soils, there is evidence that the phenolate also partitions into the soil organic carbon Schellenberg et al., 1984).

Studies with other compounds also have indicated the relative importance of ionization of organic compounds. Studies of quinoline in low carbon soils suggest that the main mechanism for sorption is primarily by ion adsorption (Zachara et al., 1986; Ainsworth et al., 1987).

It often is assumed that water at hazardous waste sites has about the same chemical properties as pure water and that the solubilities of hydrophobic organic contaminants are relatively constant within a very narrow range. However, many of the chemical properties of mixtures of solvents, such as water and methanol, can change as the fraction of the cosolvent in the mixture changes. The thermodynamic basis for some of these cosolvation effects is described by Rao et al. (1985) and Woodburn et al. (1986). Of particular interest is that the volubility of many organic compounds can be increased by orders of magnitude within mixtures of water and other miscible solvents (Nkedi-Kizza et al., 1985; Fu and Luthy, 1986a and 1986b; Zachara et al., 1988). For example, the partition coefficient of anthracene decreases more than an order of magnitude as the fraction of methanol (the cosolvent) is increased from O to 50 percent (Figure 10-17).

Such cosolvation effects may be either advantageous or disadvantageous depending on the specific problem. If these miscible liquid cosolvents have been codisposed with priority pollutants on site and the main concern is compliance monitoring, then the lower partition coefficient results in higher transport rates to the compliance boundary. If the focus, however, is on remediation, then the cosolvation effect may allow a technology such as pump-and-treat to be considered a

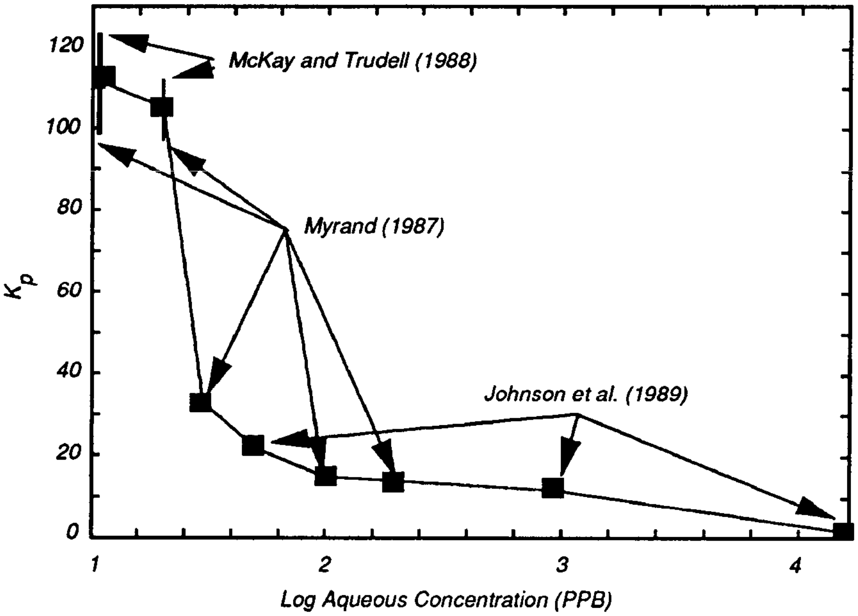


**Figure 10-14. Partition coefficients for TCE on glacial till.**

*Table 10-3. Acid Dissociation Constants for Several Priority Pollutants*

| *Compound* | *$pK_a$* |
|---|---|
| *phenol* | *9.89* |
| *2-chlorophenol* | *8.85* |
| *2,4-dichlorophenol* | *7.85* |
| *2,4,6-trichlorophenol* | *5.99* |
| *pentachlorophenol* | *4.74* |
| *2-nitrophenol* | *8.28* |
| *4-nitrophenol* | *7.15* |
| *2,4-nitrophenol* | *3.96* |
| *2,4-dimethylphenol* | *10.6* |
| *4,6-dinitrocresol* | *4.35* |
| *benzidine* | *4.66, 3.57* |

*Source: Mabey et al., 1982.*

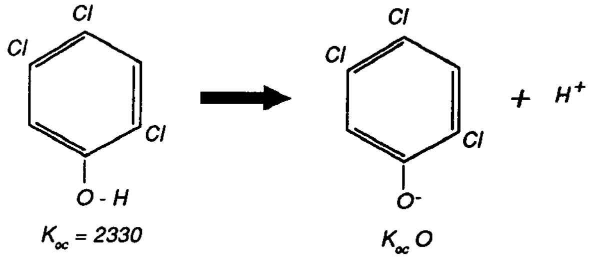


**Figure 10-15. Ionization of trichlorophenol to trichlorphenolate.**

viable option. Alternatively, the addition of cosolvents to the subsurface for the express purpose of enhancing the removal of these organic contaminants in a timely and cost-effective manner may be a possibility; however, such technology has yet to be demonstrated in the field.

## 10.5 Expressions for Other Chemical Processes

The emphasis in the discussion above centered mostly on the dissolution of the NAPL phases and equilibrium adsorption with linear partitioning. These processes are emphasized because under many conditions they are the more important processes controlling the rate of transport and removal of organic contaminants from the subsurface. However, other chemical processes may be taking place within the subsurface and equilibrium may not always be a reasonable assumption. These other equilibrium and nonequilibrium processes also can be represented in the general expression given by eq. 10-1. A few of the expressions for different chemical processes are given in Table 10-4. If one of these other expressions is required to describe the reactions that are occurring within the subsurface, then other parameters must be measured or estimated. For example, if adsorption/desorption for a particular compound is rate-controlled rather than equilibrium-controlled, then the rates of adsorption and resorption should be determined. These rates can be inferred from batch or column tests similar to those described above, but they require measurements over time and a more sophisticated level of interpretation and analysis. Such models should be called upon if required for understanding the processes at a particular site.

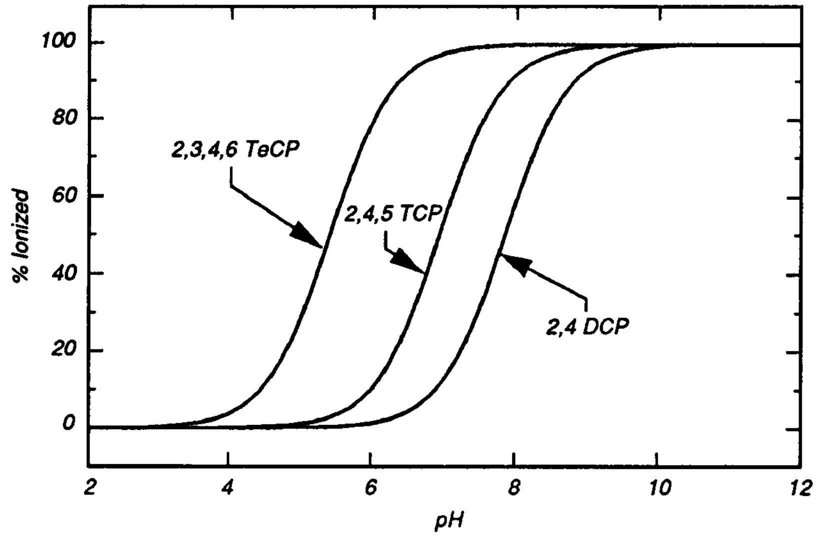


Figure 10-16. Percent of ionization of three different chlorophenolic compounds versus pH. Based on data from Schellenberg et al. (1984).

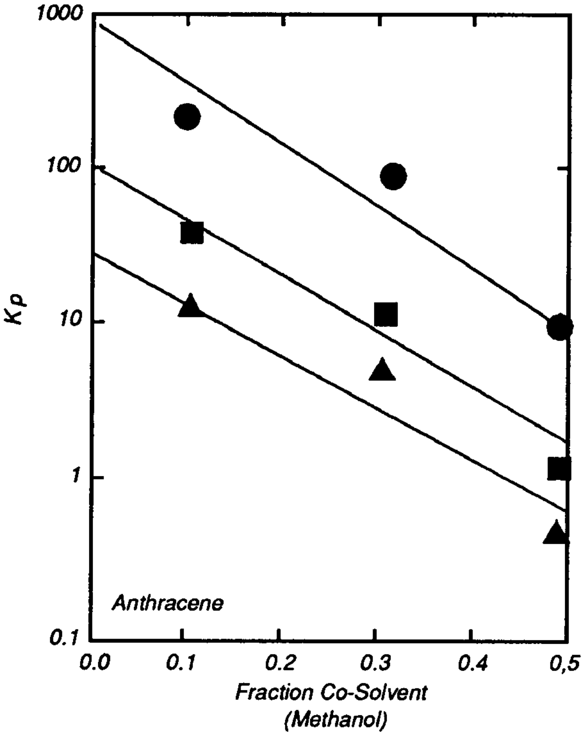


Figure IO-17. Partition coefficient of anthracene on three different soils versus fraction of methanol present as a cosolvent (adapted from Nkedi-Kizza et al., 1985).

*Table 10-4. Reaction Terms for Various Chemical Processes*

| Process | Reaction Term in Mass Balance Equation |
|---|---|
| Zero Order Production | $K$ |
| First Order Decay | $-KC$ |
| nth Order Decay | $-KC^{n}$ |
| Langmuir Adsorption | $(\rho_b/\theta_s)S_{max}K/(1+KC)^2$ |
| Freundlich Isotherm | $(\rho_b/\theta_s)\ aKC^{a-1}$ |
| First Order Kinetics | $(k_r/\theta_s)S - (k_f/\theta_s)C$ |
| Langmuir Kinetics | $(k_r/\theta_s)S - (k_f/\theta_s)C(S-S_{max})$ |
| Nonlinear Kinectics | $(k_r/\theta_s)S - (k_f/\theta_s)C^{n}$ |

## 10.6 References

Ainsworth, C.C., J.M. Zachara, and R.L. Schmidt. 1987. Quinoline Sorption on Na-Montmorillonite: Contributions of the Protonated and Neutral Species. Clays and Clay Minerals 35:121-128.

Anderson, M.A. 1988. Dissolution of Tetrachloroethylene into Ground Water. PhD Dissertation, Oregon Graduate Center, Beaverton, OR.

Anderson, M.A., J.F. Pankow, and R.L. Johnson. 1987. The Dissolution of Residual Dense Non-Aqueous Phase Liquid (DNAPL) from a Saturated Porous Medium. In: Proc. NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water-Prevention, Detection and Restoration, National Water Well Association, Dublin, OH, pp. 409-428.

Bear, J. 1969. Hydrodynamic Dispersion. In: Flow Through Porous Media, R.J.M. De Wiest (ed.), Academic Press, New York, pp. 109-199.

Bear, J. 1979. Hydraulics of Groundwater. McGraw-Hill, New York.

Chiou, C.T., D.W. Schmedding and M. Manes. 1982. Partitioning of Organic Compounds on Octanol-Water Systems. Environ. Sci. Technol. 16:4-10.

Chiou C.T., L.J. Peters and V.H. Freed. 1979. A Physical Concept of Soil-Water Equilibria for Nonionic Organic Compounds. Science 206:831-832.

Chiou, C.T., P.E. Porter and D.W. Schmedding. 1983. Partition Equilibria of Nonionic Organic Compounds Between Soil Organic Matter and Water. Environ. Sci. Technol. 17:227-231.

Curtis, G.P, P.V. Roberts, M. Reinhard, 1986. A Natural Gradient Experiment on Solute Transport in a Sand Aquifer, 4, Sorption of Organic Solutes and Its Influence on Mobility. Water Resources Research, 22(13):2059-2067.

Freeze, R.A. and J.A. Cherry. 1979. Groundwater. Prentice-Hall, Englewood Cliffs, NJ.

Freyberg, D.L. 1986. A Natural Gradient Experiment on Solute Transport in a Sand Aquifer. 2. Spatial Moments and the Advection and Dispersion of Nonreactive Tracers. Water Resources Research 22(13):2031-2046.

Fu, J.K. and R.G. Luthy. 1986a. Aromatic Compound Solubility in Solvent/Water Mixtures. J. Environ. Eng. 112:328-345.

Fu, J.K. and R.G. Luthy. 1986b. Effect of Organic Solvent on Sorption of Aromatic Solutes onto Soils. J. Environ. Eng. 112346-366.

Gillham R.W. and J.A. Cherry. 1982. Contaminant Migration in Saturated Unconsolidated Geologic Deposits. In: Recent Trends in Hydrogeology, T.N. Narasimhan, (ed.), Geological Society of America Special Paper 189, pp. 31-62.

Gschwend, P.M. and S-C. Wu, 1984. On the Constancy of Sediment-Water Partition Coefficients of Hydrophobic Organic Pollutants. Environ. Sci. Technol. 19:90-96.

Johnson, R.L., S.M. Brillante, L.M. Isabelle, J.E. Houck, and J.F. Pankow. 1985. Migration of Chlorophenolic Compounds at the Chemical Waste Disposal Site at Alkali Lake, OR-2. Contaminant Distributions, Transport, and Retardation. Ground Water 23(5):652-666.

Johnson, R. L., J.A. Cherry, and J.F. Pankow, 1989. Diffusive Contaminant Transport in Natural Clay: A Field Example and Implications for Clay-Lined Waste Disposal Sites. Environ. Sci. Technol. 23:340-349.

Karickhoff, S.W. and K.R. Morris. 1985. Sorption Dynamics of Hydrophobic Pollutants in Sediment Suspensions. Environ. Toxicol. Chem. 4:469-479.

Karickhoff, S.W., D.S. Brown and T.A. Scott. 1979. Sorption of Hydrophobic Pollutants on Natural Sediments. Water Research 13:241-248.

Karickhoff, S.W. 1984. Organic Pollutant Sorption in Aquatic Systems. J. Hydraulic Engineering ASCE 110:707-735.

Karickhoff, S.W. 1981. Semi-Empirical Estimation of Sorption of Hydrophobic Pollutants on Natural Sediments and Soils. Chemosphere 10:833-846.

Kenaga, E.E. and C.A.I. Goring, 1980. Relationship between Water Volubility, Soil-Sorption, Octanol-Water Partitioning, and Bioconcentration of Chemicals in Biota. In: Aquatic Toxicology (Proc. 3rd Annual Symp. on Aquatic Toxicology), ASTM STP 707, American Society for Testing and Materials, Philadelphia, PA, pp. 78-115.

Mabey, W.R., et al. 1982. Aquatic Fate Process Data for Organic Priority Pollutants. EPA/440/4-81-014 (NTIS PB87-169090), Chapter 4,

Mackay, D. and B. Powers. 1987. Sorption of Hydrophobic Chemicals From Water A Hypothesis for the Mechanism of the Particle Concentration Effect. Chemosphere 16:745-757.

Mackay, D. M., D.L. Freyberg, P.V. Roberts, and J.A. Cherry. 1986. A Natural Gradient Experiment on Solute Transport in a Sand Aquifer, 1. Approach and Overview of Plume Movement. Water Resources Research 22(13):2017-2030.

McKay, L.D. and M.R. Trudel. 1987. Sorption of Trichloroethylene in Clayey Soils at the Tricil Waste Disposal Site near Sarnia. Ontario. Unpublished report. University of Waterloo Institute for Ground Water Research.

Myrand, D., 1987. Diffusion of Volatile Organic Compounds in Natural Clay Deposits. M. SC. Thesis, Department of Earth Sciences, University of Waterloo, Waterloo, Ontario.

Nelson, D.W. and L.E. Sommers. 1982. Total Carbon, Organic Carbon, and Organic Matter. In: Methods of Soil Analysis, Part 2, Chemical and Biological Properties, A.L. Page, R.H. Miller, and D.R. Keeney (eds.), ASA Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 539-580.

Nkedi-Kizza, P., P.S.C. Rao, and A.G. Hornsby. 1985. Influence of Organic Cosolvents on Sorption of Hydrophobic Organic Chemicals by Soils. Environ. Sci. Technol. 19:975-979.

Palmer, C.D. and R.L. Johnson. 1989a. Physical Processes Controlling the Transport of Contaminants in the Aqueous Phase. In: Transport and Fate of Contaminants in the Subsurface, EPA/625/4-89/O19, pp. 5-22.

Palmer, C.D and R.L. Johnson. 1989b. Physical Processes Controlling the Transport of Non-Aqueous Phase Liquids in the Subsurface. In: Transport and Fate of Contaminants in the Subsurface, EPA/625/4-89/019, pp. 23-27.

Palmer, C.D. and R.L. Johnson. 1989c. Determination of Physical Transport Parameters. In: Transport and Fate of Contaminants in the Subsurface, EPA/625/4-89/019, pp. 29-40.

Pankow, J. 1984. Groundwater Contamination by Organic Compounds: Principles of Contaminant Migration and Determimtion. Short Course Notes, Oregon Graduate Institute, Beaverton, Oregon.

Powell, R.M., B.E. Bledsoe, G.P. Curtis, and R.L. Johnson, 1989. Interlaboratory Methods Comparison for the Total Organic Carbon Analysis of Aquifer Materials. Environ. Sci. Technol. 23(10):1246-1249.

Rae, P.S.C., A.G. Hornsby, D.P. Kilcrease, and P. Nkedi-Kizza. 1985. Sorption and Transport of Toxic Organic Substances in Aqueous and Mixed Solvent Systems. J. Environ. Quality 14:376-383.

Roberts, P. V., M.N. Goltz, and D.M. Mackay. 1986. A Natural Gradient Experiment on Solute Transport in a Sand Aquifer 3. Retardation Estimates and Mass Balances for Organic Solutes. Water Resources Research 22(13):2047-2058.

Schellenberg, K.C., C. Leuenberger, and R.P. Schwarzenbach. 1984. Sorption of Chlorinated Phenols by Natural Sediments and Aquifer Materials. Environ. Sci. Technol. 18:1360-1367.

Schwarzenbach, R., and J. Westall. 1981. Transport of Nonpolar Organic Compounds from Surface Water to Ground Water Laboratory Sorption Studies. Environ. Sci. Technol. 15:1360-1367.

Schwille, F. 1988. Dense Chlorinated Solvents in Porous and Fractured Media: Model Experiments. Lewis Publishers, Chelsea, MI.

Sudicky, E.A. 1986. A Natural Gradient Experiment in a Sand Aquifer Spatial Variability of Hydraulic Conductivity and Its Role in the Dispersion Process. Water Resource Research 22(13):2069-2082.

Witkowski, P.J., P.R. Jaffe, and R.A. Ferrara. 1988. Sorption and Resorption Dynamics of Aroclor 1242 to Natural Sediment. J. Contaminant Hydrology 2:249-269.

Woodbum, K.B., 1986. Solvaphobic Approach for Predicting Sorption of Hydrophobic Organic Chemicals on Synthetic Sorbents and Soils. J. Contaminant Hydrology 1:227-241.

Wu, S.-C. and P.M. Gschwend. 1986. Sorption Kinetics of Hydrophobic Organic Compounds to Natural Sediments and Soils. Environ. Sci. Technol. 20:717-725.

Zachara, J.M., C.C. Ainsworth, L.J. Felice, and C.T. Resch. 1986. Quinoline Sorption to Subsurface Materials: Role of pH and Retention of the Organic Cation. Environ. Sci. Technol. 20:620-627.

Zachara, J.M., C.C. Ainsworth, C.E. Cowan, and B.L. Thomas. 1987. Sorption of Binary Mixtures of Aromatic Nitrogen Heterocyclic Compounds on Subsurface Materials. Environ. Sci. Technol. 21:397-402.

Zachara, J.M., C.C. Ainsworth, R.L. Schmidt, and C.T. Resch. 1988. Influence of Cosolvents on Quinoline Sorption by Subsurface Materials and Clays. J. Contaminant Hydrology 2:343-364.

# Chapter 11
# Physiochemical Processes: Volatilization and Gas-Phase Transport

Carl D. Palmer and Richard L. Johnson

Many nonaqueous phase liquids (NAPLs) are volatile organic compounds of environmental concern (e.g., chlorinated solvents, gasoline). They frequently enter ground-water systems after they have been spilled on the surface and pass through the unsaturated zone (Figure 1l-l). As these NAPLs flow through the unsaturated zone, a portion of the liquid remains behind in fingers at residual saturation, in pools of material on small heterogeneities, or above the capillary fringe (e.g., Palmer and Johnson, 1989a Feenstra and Cherry, 1987; Schwille, 1967 and 1988). The NAPL that remains in the unsaturated zone is an important source of contamination because it is dissolved by (1) the passing recharge water, and (2) the passing ground water as the water table rises. Such sources of contamination can last for many years and contaminate large volumes of ground water. However, in addition to these pathways, contaminants also can be transported through the unsaturated zone in the gas phase. This transport pathway may spread the contaminants over a much broader area of the aquifer. Another complicating factor is the mass transfer of the contaminants across the atmosphere-soil boundary. Of greater interest is the implication that these sources of ground-water contamination can be quickly remediated by actively pumping the soil gas and removing the volatile organic contaminants from the unsaturated zone to the surface where they may be treated. As with the transport of dissolved contaminants, the design of optimal remediation schemes requires

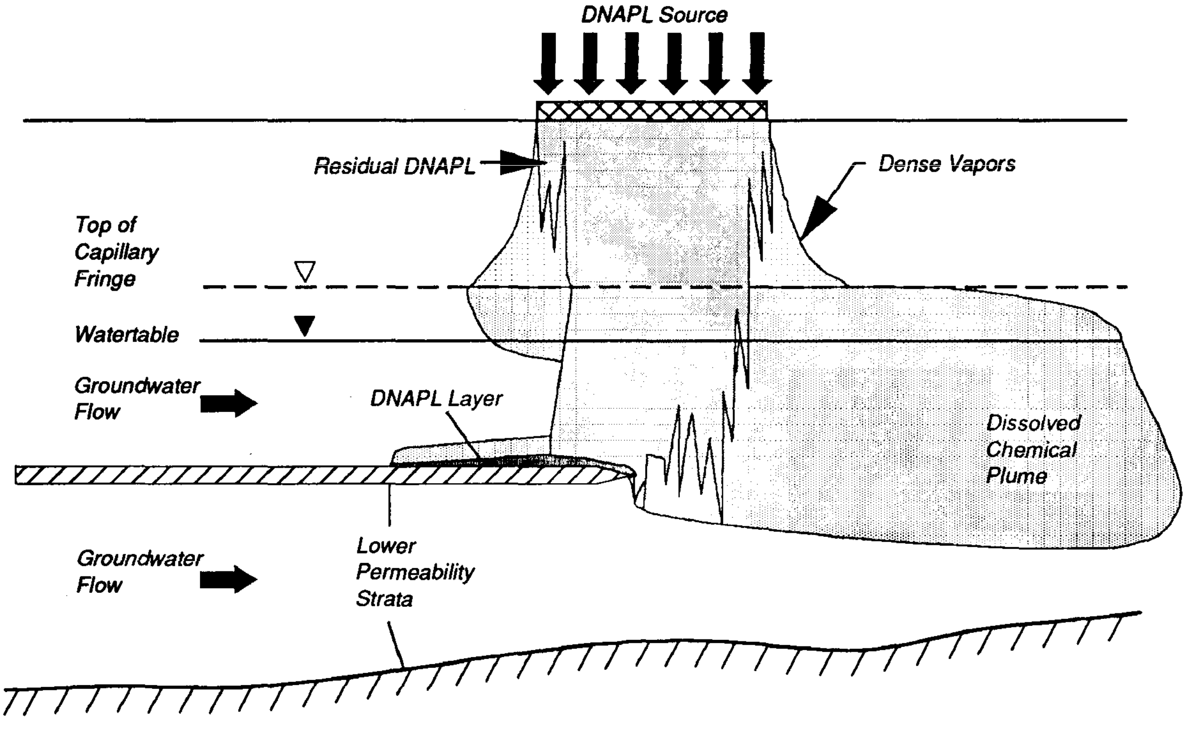


**Figure 11-1. Transport of a DNAPL into the subsurface illustrating the distribution of the DNAPL, the dense vapors, and the dissolved chemical plume (after Feenstra and Cherry, 1988).**

knowledge of the physiochemical processes that control transport pathways. Mercer and Cohen (1990) provide a recent review of the literature on properties, models, characterization, and remediation of NAPLs.

## 11.1 Volatilization

Near a NAPL spill, a four-phase system exists. The phases include (1) the aquifer matrix, (2) the residual soil water, (3) the NAPL, and (4) the air-filled pore space (Figure 11-2). A volatile NAPL partitions from the NAPL phase into the gas phase where it then can be transported to other portions of the unsaturated zone. The vapor pressure of a particular contaminant, $P_k$, in the gas phase can be calculated from Raoult's Law:

$$P_k = X_k P_k^0 \qquad [11\text{-}1]$$

where $X_k$ is the mole fraction of component k in the NAPL and $P_k^0$ is the vapor pressure above the pure component. For example, if the NAPL is gasoline, the partial pressure on benzene, one of the many components of gasoline, is the mole fraction of benzene in the gasoline times the ideal vapor pressure above pure benzene. The concentration of the gas in the soil atmosphere then can be calculated from the ideal gas law:

$$(n/V)_k = P_k/(RT) \qquad [11\text{-}2]$$

where n is the number of mole of component k, V is the volume of gas, T is the kelvin temperature, and R is the gas constant (0.082057 liter-atm $\text{mole}^{-1}$ $\text{ddg}^{-1}$).

## 11.2 Gas-Phase Transport

The movement of the contaminants in the gas phase of the unsaturated zone can be described by performing a mass balance on a volume of aquifer (Figure 11-3) in a manner similar to the approach taken in Chapter 10 (see Section 10.1).

### *11.2.1 Diffusion*

Under nonpumping conditions, Fickian diffusion is the prime process for gas-phase transport. The mass balance or transport equation can then be written in its one-dimensional form as:

$$\tau_a \theta_a D \frac{\partial^2 G}{\partial x^2} = \frac{\partial(\theta_a G)}{\partial t} \qquad [11\text{-}3]$$

where G is the concentration of the contaminant in the gas phasa, $0_1$, is the air-filled porosity, D is the free air diffusion coefficient and $\tau_a$ is the air-phase tortuosity factor. The $\tau_a$

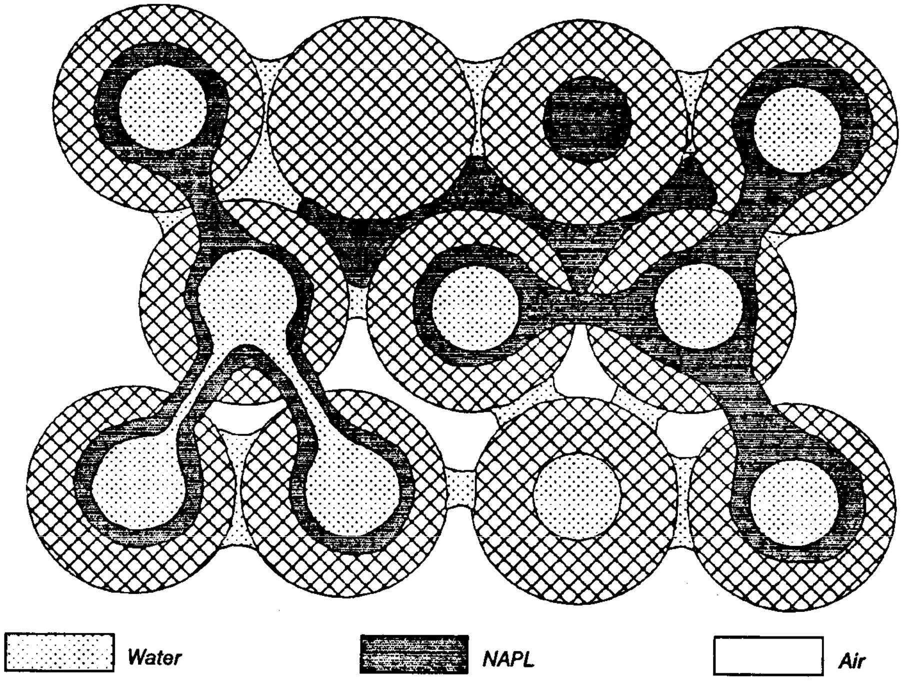


**Figure 11-2. Four-phase system consisting of soil matrix, water, NAPL and air (after Schwille, 1988).**

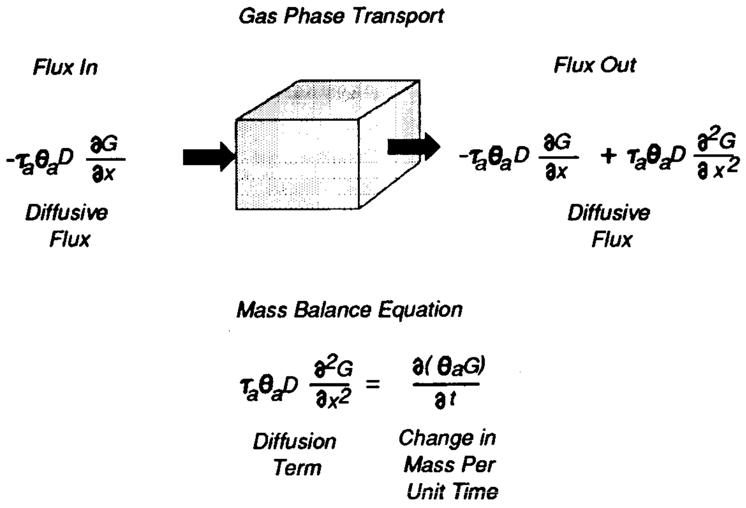


**Figure II-3. Mass balance equation for the transport of contaminants in the gas phase.**

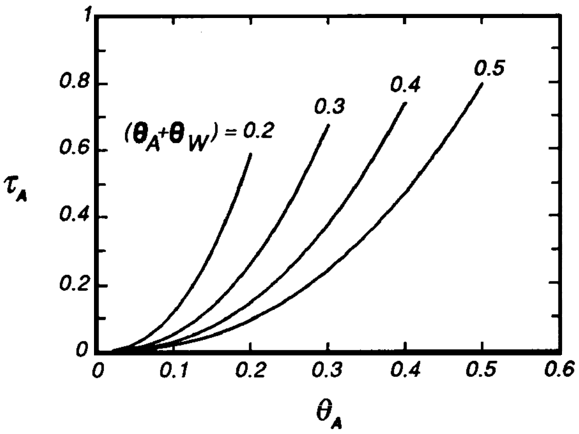


**Figure 11-4. The air tortuosity factor based on the Millington-Quirk equation (Millington, 1959) as a function of air porosity for four different total porosities.**

term accounts for the diffusion taking place in a porous medium rather than in an open air space such as a room. The individual molecules must travel around the sand grains and water films that are present in the porous medium. The term on the right-hand side of eq. 11-3 represents the net diffusive flux per unit time of the contaminant in and out of the volume of soil. The term on the left-hand side of eq. 11-3 represents the change in mass of gas within the volume per unit time. Again, this equation is a useful example, listing the minimum parameters that must be obtained if vapor transport is to be described.

The air-filled porosity is a physical parameter that can be obtained by finding the difference of the porosity and the volumetric water content by using the methods referred to in Chapter 5 and in Palmer and Johnson (1989b). The air tortuosity factor can be obtained from empirical equations that are provided from detailed studies of gas-phase transport. For example, one such equation is the Millington-Quirk (Millington, 1959) equation:

$$\tau_a = \theta_a^{2.333} / \theta_t^2 \qquad [11\text{-}4]$$

where 6 is the total porosity,, which is equal to the sum of the **air-filled porosity and the volumetric water content** $(\theta_a+\theta_w)$**.** So the air-phase tortuosity can be calculated from physical parameters that are already obtained. The actual value of the air-phase tortuosity factor varies from O when the entire pore space is occupied by water (saturated conditions) to about 0.8 when the porosity is high and the medium is dry (Figure 11-4).

The third important parameter, the free air diffusion coefficient, sometimes can be found for the specific compound of interest in reference tables. If the diffusion coefficient for the specific compound ($D_1$) cannot be found, it can be estimated from the diffusion coefficient ($D_2$) and molecular weight ($M_2$) of another compound and the molecular weight of the compound of interest ($M_1$) by:

$$D_1/D_2 = (M_2/M_1)^{0.5} \qquad [11\text{-}5]$$

### *11.2.2 Gas-Phase Retardation*

The example given in eq. 11-3 describes the diffusive transport of a gas-phase contaminant moving through the air-filled pores of the unsaturated zone, but it does not account for any chemical interactions with either the soil water or the soil matrix. The expression should be modified by adding a general reaction term, RXN, to account for these processes. At equilibrium, partitioning of the contaminant between the gas phase and the water phase is defined by the dimensionless Henry's constant, $K_H$:

$$G = K_H C \qquad [11\text{-}6]$$

where G is the gas concentration and C is the water-phase concentration. For most neutral, nonpolar hydrophobic organic compounds, the partitioning between the water phase and the soil organic carbon can be described by a linear isotherm ($S = K_p C$) that can be written in terms of the gas-phase concentrations as:

$$S = K_p G/K_H \qquad [11\text{-}7]$$

where S is the concentration of contaminant on the soil and $K_p$ is the linear partition coefficient from the water phase to the soil organic carbon. Including the reaction term, RXN,

$$RXN = \theta_w \frac{\partial C}{\partial t} + \rho_b \frac{\partial S}{\partial t} \qquad [11\text{-}8a]$$

or

$$RXN = \theta_w \frac{\partial C}{\partial G}\frac{\partial G}{\partial t} + \rho_b \frac{\partial S}{\partial C}\frac{\partial C}{\partial G}\frac{\partial G}{\partial t} \qquad [11\text{-}8b]$$

and recognizing that

$$\frac{\partial C}{\partial G} = \frac{1}{K_H} \qquad [11\text{-}9a]$$

$$\frac{\partial S}{\partial C} = K_p \qquad [11\text{-}9b]$$

the addition of these two sinks (sources) of contaminant within the volume of aquifer (Figure 11-2) results in a mass balance equation (paradigm):

$$\frac{\tau_a \theta_a D}{R_a} \frac{\partial^2 G}{\partial x^2} = \frac{\partial(\theta_a G)}{\partial t} \qquad [11\text{-}10]$$

where $R_1$ is a gas-phase retardation factor that is defined by

$$R_a = 1 + \theta_w/(\theta_a K_H) + \rho_b K_p/(\theta_a K_H) \qquad [11\text{-}11]$$

where $r_b$ is the dry bulk density of the soil. This retardation factor is a constant if the water content of the soil does not change and is analogous to the retardation factor, R, for the movement of organic contaminants in the saturated zone. The second term in eq. 11-11 represents the partitioning of the contaminant from the gas phase to the water phase. The third term represents the partitioning from the gas phase, through the water phase, to the solid phase. In this modified example, the retardation factor, $R_a$, must be determined. Methods for determining the physical parameters $\theta_a$, $\theta_w$, and $\rho_b$ already have been identified. Methods for obtaining the partition coefficient, $K_p$, are discussed in Chapter 10. The remaining parameter, $K_H$, can be obtained from tables of chemical properties (Mabey et al., 1982).

A more physical interpretation to this air-phase retardation factor, $R_a$ can be given. As the contaminated gas diffuses through the air-filled pores, the rate of diffusion of the contaminant in the air phase is less than that of the air itself because of the loss of mass from the air phase. This mass is lost from the residual water contained within the pore space and/or the soil organic carbon that is part of the soil matrix. The retardation factor, therefore, can be defined as the ratio of the rate of diffusion of the air to the rate of diffusion of the contaminant front in the soil atmosphere. $R_a$. is also the minimum number of pore volumes that must pass through a three-phase contaminated soil system (soil, water, and air) to remove the contaminants. It is a minimum because the approach ignores the effects of mass transfer limitations between phases. The effects result from heterogeneity and kinetics and unequal travel times along flow lines from the edge of the contaminated area to the vapor extraction well.

Another, more direct, method for obtaining $\tau_a D/R_a$ (an effective diffusion coefficient) is through column tests such as those used by Johnson et al. (1987). These column tests (Figure 11-5) use a dead-end column with a mixture of nitrogen and the organic contaminants maintained at one end. The only process that can carry the contaminant into the column is molecular diffusion. If a sampling line is fitted to the interior of the column, then samples can be obtained over time and the concentration breakthrough curve obtained. This curve can be fitted to a one-dimensional analytical solution to the diffusion equation to obtain a fitted, effective diffusion equation.

### *11.2.3 Processes Affecting Gas-Phase Transport*

Some insight into the migration of contaminants in the vapor phase can be attained by considering the different processes included in eq. 11-9. If there is no partitioning of the contaminant between the gas phase and the soil ($K_p$ is zero), and if the Henry's constant, $K_H$, is large (i.e., there is no

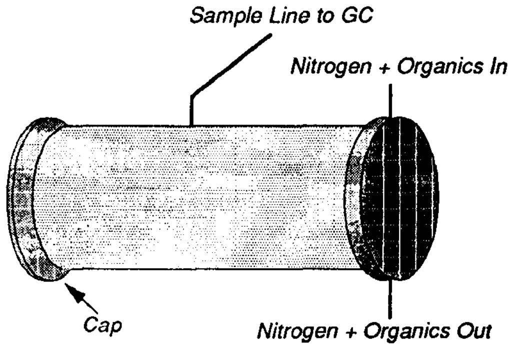


**Figure 11-5. Column for measuring effective vapor phase diffusion coefficients.**

significant mass loss to the water phase), then the retardation factor is close to unity and the contaminants move through the porous medium with the air. As the value of $K_H$ becomes smaller, the retardation factor at a given porosity and water content becomes larger because of the partitioning into the water phase (Figure 11-6). For example, the amount of retardation for benzene increases with increasing water content (Figure 11-7) because it partitions into the water phase (i.e., $K_H$ is small). In contrast, the retardation factor for pentane is insensitive to changes in volumeric water content because it does not significantly partition into the water phase (Figure 11-7).

These effects are also seen in column tests (Johnson et al. 1987). The breakthrough curves for methane, trichloroethene (TCE), and chlorobenzene were obtained in a sand-filled column under both dry and wet conditions (Figure 11-8). Methane, with the largest Henry's constant and smallest $K_{oc}$ values of the three compounds is observed to be the frost to break through. TCE and chlorobenzene break through later because of the larger $K_{oc}$ and smaller $K_H$ values. The difference between the damp sand and the dry sand reflects the differences in the Henry's constants for the compounds. In another test, two columns were prepared, one containing virtually no soil organic carbon (SOC) and another containing approximately 1 percent SOC. The breakthrough curves for methane, octane, and benzene in these two columns (Figures 11-9 and 11-10) demonstrate the role of SOC in the retardation of the compounds. The differences in the breakthrough curves for the three compounds in the column containing no SOC (Figure 11-9) can be attributed to the differences in the Henry's constants. The column containing 1 percent SOC requires more pore volumes to achieve breakthrough of the octane and benzene, and the differences between the compounds are much greater (Figure 11-10). This increased retardation is the result of the greater partitioning of the contaminant from the gas phase to the SOC with the larger $K_{oc}$ values for these compounds.

Temperature can have a significant influence on the rate of migration of gas-phase volatile organic contaminants. The diffusion coefficients increase with increasing temperature. The effect of this temperature dependence can be calculated from:

$$D_1/D_2 = (T_1/T_2)^m \quad [11\text{-}12]$$

where T is the kelvin temperature. The exponent, m, should theoretically be 1.5; however, experimental data yield values between 1.75 and 2.0 (Hamaker, 1972). The temperature also affects the vapor pressure of the compounds (Figure 11-11) and, therefore, the concentration in the gas phase (eq. 11-2). The Henry's constant also shows a temperature dependence by increasing with increasing temperature (Figure 11-12). From the definition of the gas-phase retardation factor (eq. 11-11), the increased Henry's constant is reflected as a decrease in $R_a$ (Figure 11-13). Thus, fewer pore volumes of air need to be moved through a contaminated soil to remove the contaminant at 35°C than at 10°C.

The concentration of volatile organic contaminants in the gas phase of the unsaturated zone is influenced by the pres-

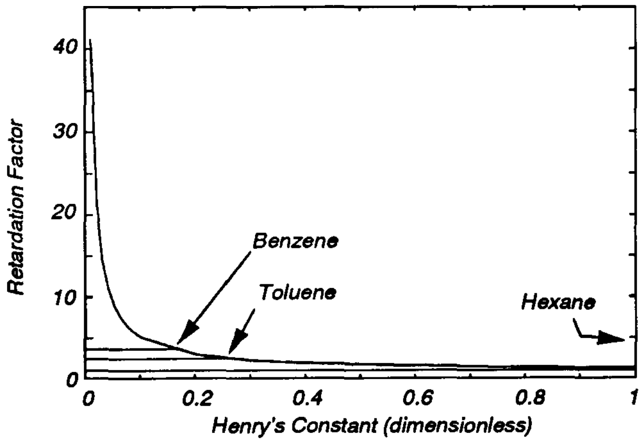


Figure 11-6. Retardation factor as a function of dimensionless Henry's constant when there is no adsorption (after Johnson et al., 1987).

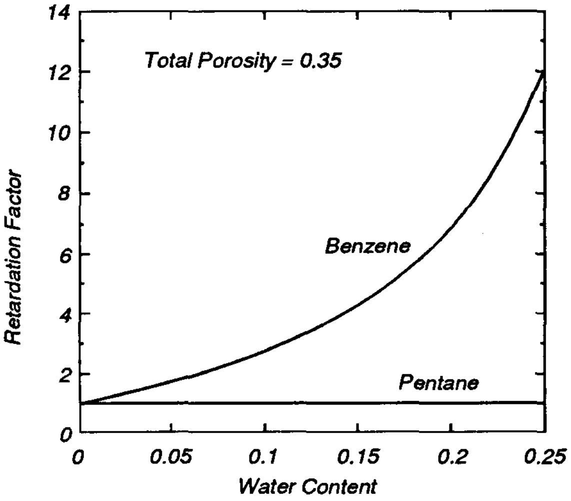


Figure 11-7. Retardation factor versus water content for benzene and pentane (after Johnson et al., 1987).

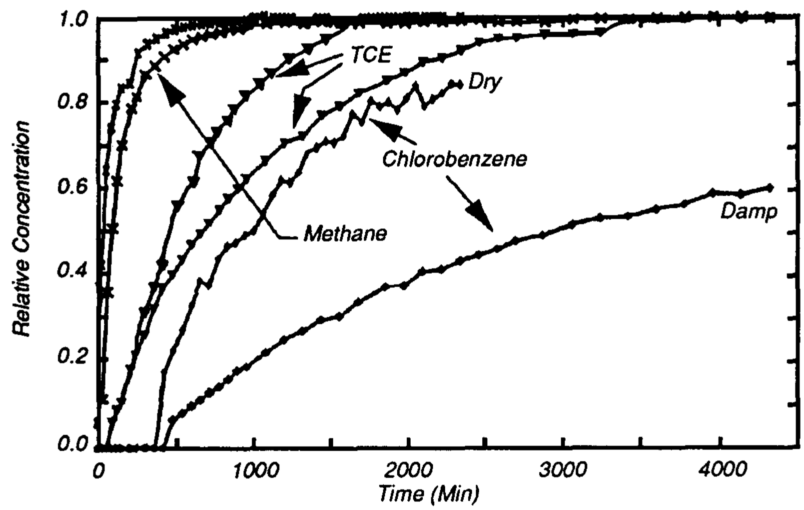


**Figure 11-8.** Relatlve gas phaae concentration versus time in a column experiment (after Johnson et al., 1987).

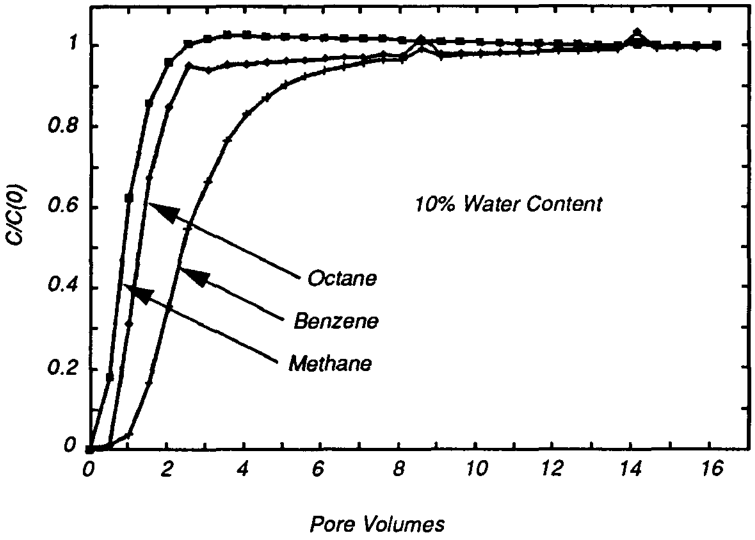


**Figure 11-9.** Relative gas phase concentration versus the number of pore volumes of air moved through an unsaturated column with no soil organic carbon (after Johnson et al., 1987).

ence of boundaries that can impede the rate of migration. Spills of solvents and hydrocarbons often occur in industrial and urban areas where parking lots, roads, and foundations can act as low permeability boundaries that limit the mass transfer of the contaminated gases from the unsaturated zone to the atmosphere. In the absence of such barriers, concentrations of the contaminants in the soil-gas phase should remain low very near the surface. When these barriers are present, the concentrations in the soil-gas phase can be much greater. The effect of these impermeable caps is illustrated in the numerical simulations by Baehr (1987). The mass of total hydrocarbon that is in the soil-gas phase is about 2.5 times greater when there is a cap present than when there is no cap (Figure 11-14).

Measuring permanent gases such as $O_2$ and $CO_2$ in addition to the priority pollutants can provide insight into processes that are occurring in the subsurface. Measurements of the distribution of total hydrocarbons in the unsaturated zone near an oil spill in Bemidji, Minnesota, (Hult and Grabbe, 1985) show that the concentrations are greatest near the source and decrease with greater distance from the pooled material (Figure 11-15a). $O_2$ is near atmospheric values far from the source and nearly depleted near the spill area (Figure 11-15b). $CO_2$ distributions are opposite to those of oxygen, with the highest concentrations being near the source (Figure 11-15c). While the diffusion and retardation processes discussed above have an important role in the distribution of the total hydrocarbons, the depletion of $O_2$ and the generation of

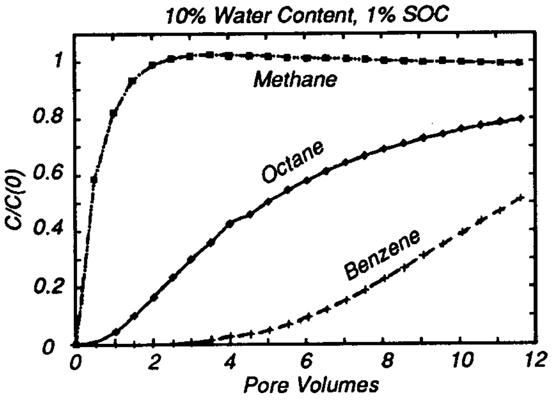


Figure 11-10. Relative gas phase concentration versus the number of pore volumes of air moved through an unsaturated column with 1% soil organic carbon (SOC) (after Johnson et al., 1987).

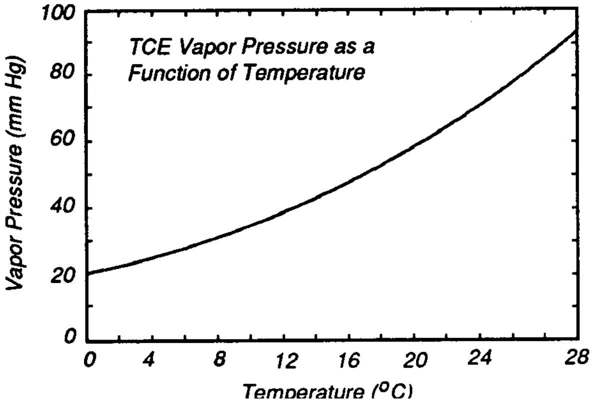


Figure 11-11. The vapor pressure of TCE as a function of temperature.

CO$_2$ near the source area suggest that biodegradation of the hydrocarbons is also Occurring (see Chapter 13).

There are other factors that affect the migration of organic vapors. Cultural factors such as underground utility conduits, trenches, sewers, and pipes can act as preferential pathways along which these gases may travel. The type of backfill used around underground storage tanks affects the water content and retardation of the gas-phase contaminants. Other environmental factors such as variations in atmospheric pressure, fluctuations in the elevation of the water table, and the amount of infiltration in the contaminated area also have a significant influence on transport of contaminants in soil gas at certain sites.

## 11.3 Vapor Extraction

Vapor phase extraction is an important method for removing residual volatile organic solvents from the subsurface.

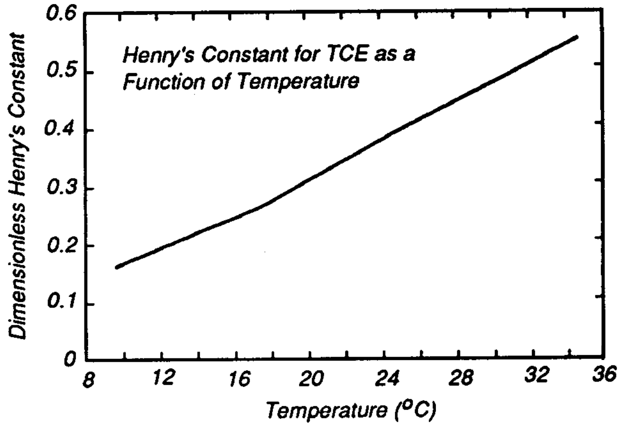


Figure 11-12. Dimensionless Henry's constant for TCE versus temperature.

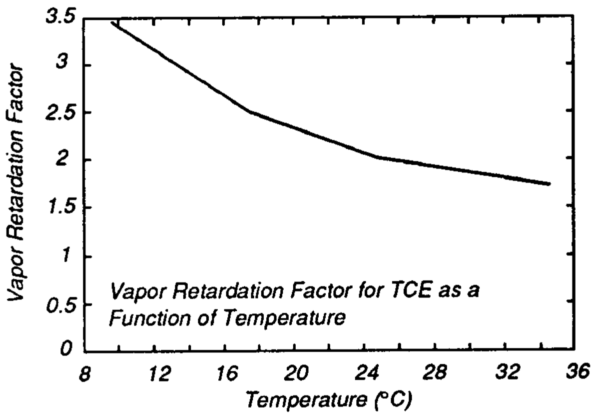


Figure 11-13. Vapor retardation factor for TCE versus temperature.

In principle, the technique works by removing the volume of contaminated air from the subsurface. As more air moves into the contaminated area, the contaminants partition from the NAPL to the air phase. The extraction is continued until sufficient pore volumes of air have passed through the contaminated zone to remove the entire mass of the NAPL from the subsurface.

Many of the same problems that are encountered in ground-water pump-and-treat systems also are expected in vapor extraction systems. As the contaminated air is extracted from the unsaturated zone, the highly contaminated soil gas that was initially present is removed. The concentrations may then begin to decrease and remain at some concentration that is substantially lower than the initial concentration but significantly higher than the target level (Figure 11-16). This "tailing" is the result of several processes. One factor is the rate of resorption of the organic contaminants from the soil organic matter (Figure 11-17). Although little is known about these rates, some data on hexachlorobenzene (Karickhoff and Morris, 1985) show that the rate is initially rapid and decreases with

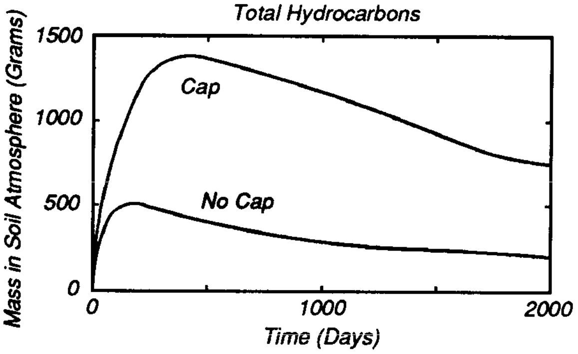


Figure 11-14. Comparison of total hydrocarbons present in a soil with a cap versus without a cap (after Baehr, 1987).

time, and the equilibration may take more than 30 days (e.g., Figure 10-11, Chapter 10); this time scale is significant compared to the rate of movement of the air. Another consideration is the form of the isotherm itself. If the isotherm is nonlinear (Langmuir- or Freundlich-type isotherm with the exponent less than unity), there can be tailing in the concentration versus time curves.

If the NAPL in the porous media is locally surrounded by water, then the concentrations in the air that is being advected through the adjacent pores may be limited by the rate of diffusion through the water (Figure 11-18). In the air, velocity is low relative to the rate of diffusion (this is the case when there is no extraction), and the concentrations are limited by the vapor pressure of the compound. If the air velocities are large relative to the rate of diffusion, then the concentration of the contaminant is limited by diffusion through the water. An analogous situation may arise when thick pools of NAPL are being removed by vapor extraction. The more volatile components from the upper surfaces of the NAPL are removed first. If the air velocity is large relative to the rate of diffusion of those volatile components through the NAPL, then the concentrations in the gas phase are limited by this rate of diffusion through the NAPL.

Another important aspect of NAPLs that are composed of more than one component is that as the more volatile components are removed, their concentration in the NAPL (as a mole fraction) decreases. This decrease in the mole fraction decreases the vapor pressure (eq. 11-2) and hence the gas-phase concentration.

Soil heterogeneity plays a major role in controlling the concentration of contaminants in gases extracted from the unsaturated zone. As NAPLs infiltrate into the subsurface they spread into pools on top of lenses of finer grained material within the aquifer. The NAPL also may be drawn into the fine-grained zones by capillary action: As air is advected through the contaminated soil (Figure 11-19a), those parcels that pass through the fingers or very close to the pools are close to saturation with respect to the NAPLs. The concentration of the volatiles in the parcels of air between the fingers and pools is controlled by the rate of vapor diffusion from the

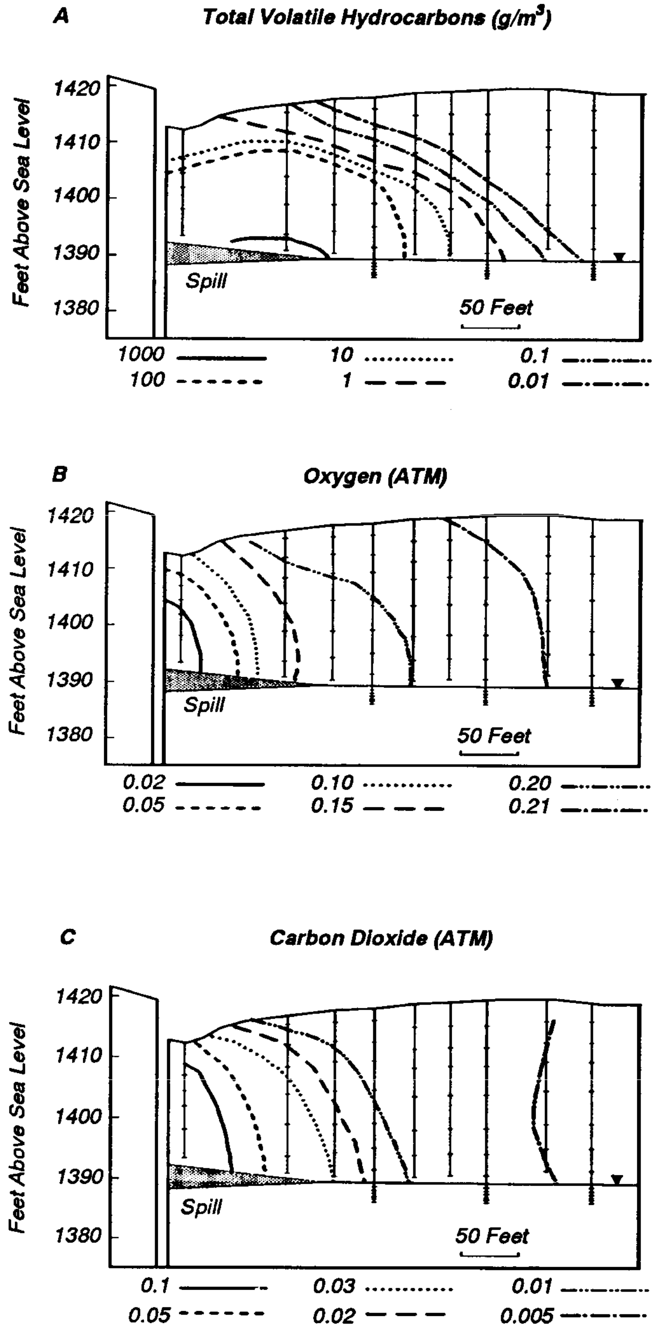
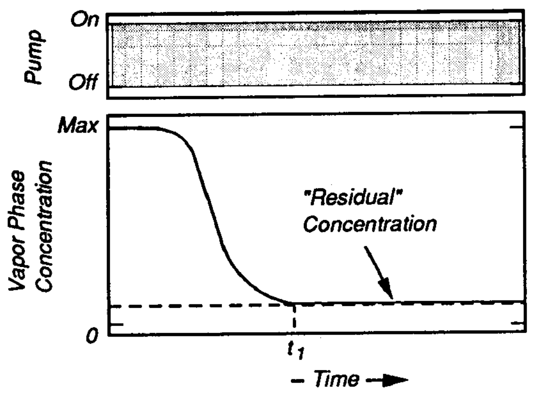


Figure 11-15. Distribution of gases near an oil spill in Bemidji, MN (after Hult and Grabbe, 1985).



Tailing in the vapor concentration versus time curve for a vapor extraction well.

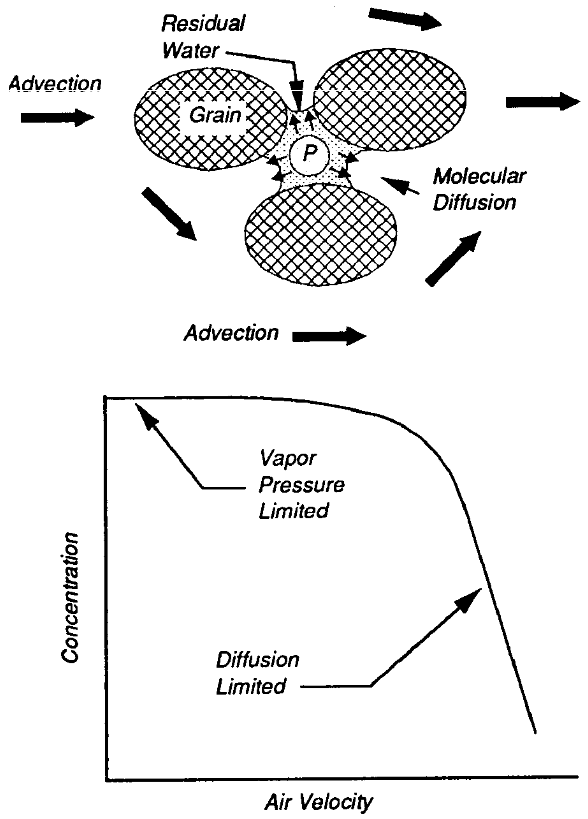


Figure 11-18. The gas phase concentration controlled by either the vapor pressure or the rate of diffusion of the volatile organic through the water phase. P denotes the residual product.

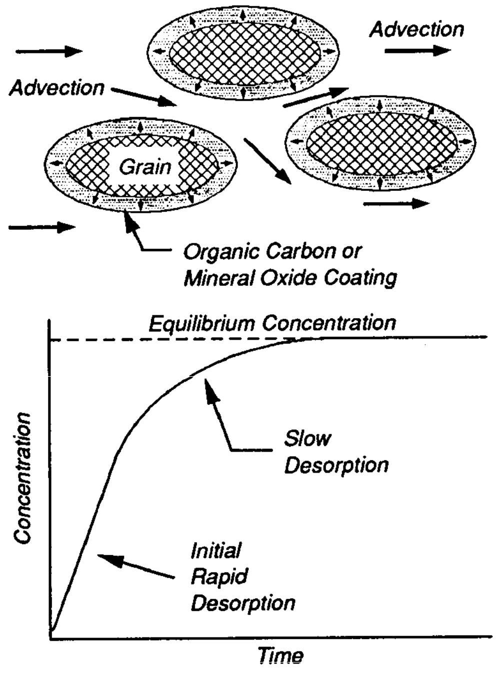


Figure 11-17. The concentration in the gas phase controlled by the rate of desorption.

pools and fingers. During vapor extraction, the fingers are likely to be removed before the pools (Figure 1l-19b), because there is generally less mass of NAPL in the fingers than in the pools. Also, a greater surface area of the NAPL exposed in the fingers facilitates the mass transfer to the advected air. As the residual fingers are removed, the concentrations in the extracted air should decrease as the less contaminated air between the pools is mixed with the more contaminated air from just above the pools. Removal from the pools may require a substantial period of time (years) to complete. The NAPL that moved into the finer grained zones is effectively removed from the advective air flow. Under these conditions, the removal of NAPL is limited by the relatively slow diffu-

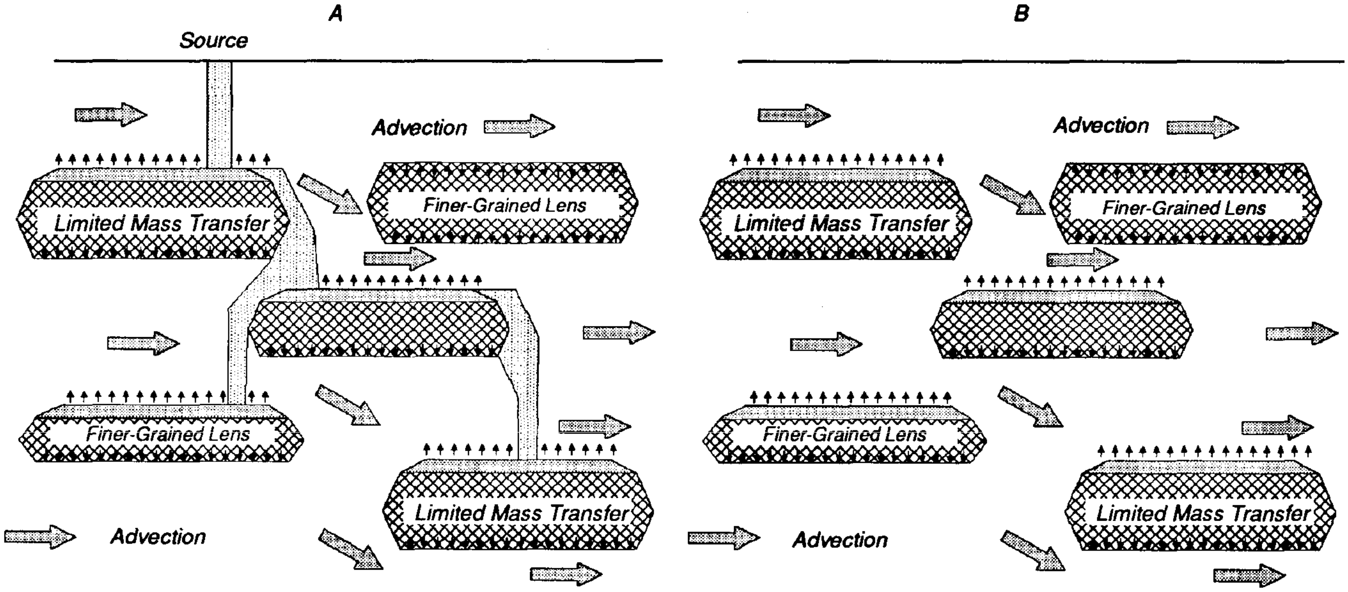


**Figure 11-19. The transport of air through a heterogeneous media with fingers and pools of NAPL present (A) and at a later time when only pools are present (B).**

sion of the NAPL out of the finer grained zone. If a substantial mass of NAPL is trapped in this way, remediation could require many years to complete.

## 11.4 References

Baehr, A.L. 1987. Selective Transport of Hydrocarbons in the Unsaturated Zone Due to Aqueous and Vapor Phase Partitioning. Water Resources Research 23(10):1926-1938.

Feenstra, S. and J.A. Cherry. 1987. Dense Organic Solvents in Ground Water An Introduction. In: Dense Chlorinated Solvents in Ground Water, Progress Report 0863985, Institute for Ground Water Research, University of Waterloo, Waterloo, Ontario.

Hamaker, J.W. 1972. Diffusion and Volatilization. In: Organic Chemicals in the Soil Environment Vol. 1., C.A.I. Goring and J.W. Hamaker (eds.), Marcel Dekker, New York, Chapter 5.

Huh, M.F. and R.R. Grabbe. 1985. Distribution of Gases and Hydrocarbon Vapors in the Unsaturated Zone. In: Proceedings, U.S. Geological Survey Second Toxic Waste Technical Meeting, Cape Cod, MA, October 1985, U.S. Geological Survey Open File Report 86-0481, pp. C21-C25.

Johnson, R.A., C.D. Palmer, and J.F. Keely. 1987. Mass Transfer of Organics Between Soil, Water, and Vapor Phases: Implications for Monitoring, Biodegradation and Remediation. In Proc. NWWA/API Symp. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water-prevention, Detection and Restoration, National Water Well Association, Dublin, OH, pp. 493-507.

Karickhoff, S.W. and K.R. Morris. 1985. Sorption Dynamics of Hydrophobic Pollutants in Sediment Suspensions. Environ. Toxicol. Chem. 4:469-479.

Mabey, W.R., et al. 1982. Aquatic Fate Process Data for Organic Priority Pollutants. EPA 440/4-81/014 (NTIS PB87-169090), Chapter 4.

Mereer, J.W. and R.M. Cohen. 1990. A Review of Immiscible Fluids in the Subsurface Properties, Models, Characterization and Remediation. J. Contaminant Hydrology 6:107-163.

Millington, R.J. 1959. Gas Diffusion in Porous Media. Science 130100-102.

Palmer, C.D. and R.L. Johnson. 1989a. Physical Processes Controlling the Transport of Non-Aqueous Phase Liquids in the Subsurface. In: Transport and Fate of Contaminants in the Subsurface, EPA/625/4-89/019, pp. 23-27.

Palmer, C.D. and R.L. Johnson. 1989b. Determination of Physical Transport Parameters. In: Transport and Fate of Contaminants in the Subsurface, EPA/625/4-89/O19, pp. 29-40.

Schwille, F. 1967. Petroleum Contamination of the Subsoil - A Hydrological Problem. In: The Joint Problems of the Oil and Water Industries, Peter Hepple (ed.), Elsevier, New York, pp. 23-53.

Schwille, F. 1988. Dense Chlorinated Solvents in Porous and Fractured Media. Lewis Publishers, Chelsea, ML

# Chapter 12
# Physiochemical Processes: Inorganic Contaminants

Carl D. Palmer and William Fish

Inorganic compounds are a common and widespread class of contaminants at many hazardous waste sites. The relative importance of these inorganic contaminants is illustrated in the Records of Decision (RODS) signed by EPA between 1982 and 1986 (Booz-Allen and Hamilton, Inc., 1987). Of the 108 RODS, 56 percent involved Superfund sites where inorganic compounds were designated as a potential threat or problem (Palmer et al., 1988). While organics/volatile organic compounds (VOCs) are the most frequently reported contaminants, heavy metals and inorganic are the second and third most frequently reported categories of hazardous substances (Figure 12-1). Inorganic waste problems can be particularly severe because they often occur at sites that cover many square miles. Remediation of such sites is often difficult simply because of the size of the affected area.

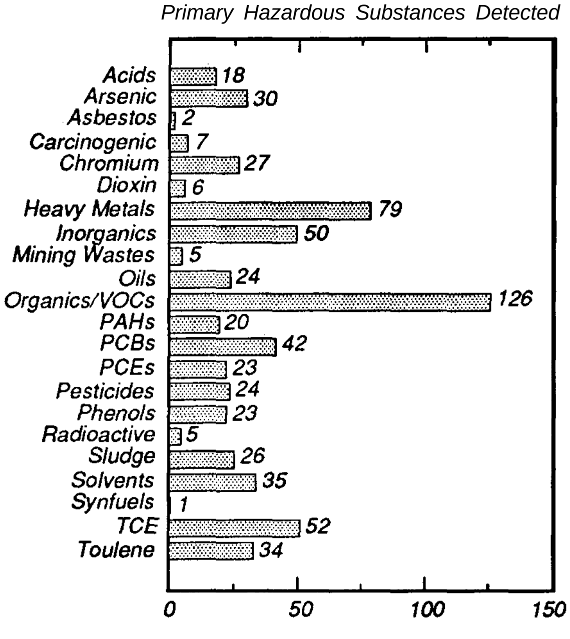


**Figure 12-1.** Primary hazardous substances detected at hazardous waste sites. Based on data from Booz-Allen and Hamilton, Inc. (1987), from Palmer et al. (1988).

The most common inorganic constituents of concern are the 13 priority pollutant metals (Table 12-1). However, other inorganic substances such as nitrate, phosphate, cyanide, and radionuclides may be found at levels far exceeding drinking water standards. Iron, manganese, aluminum, calcium, silica, and carbonates are not priority pollutants but also can contribute to the overall cost of a remediation scheme by increasing maintenance and disposal costs. For example, air strippers at several sites have been temporarily disabled by iron precipitation problems.

The behavior and toxicity of inorganic compounds are affected by chemical and physical processes. Understanding these processes may lead to more cost-effective restoration of contaminated sites and can reveal how inorganic substances may affect the cleanup of sites, even at sites where organic contaminants are the main concern.

*Table 12-1. The 13 Priority Metals*

- *Silver*
- *Arsenic*
- *Barium*
- *Cadmium*
- *Chromium*
- *Nickel*
- *Mercury*
- *Lead*
- *Selenium*
- *Thallium*
- *Antimony*
- *Copper*
- *Zinc*

## 12.1 Chemical Processes

Several chemical processes affect the concentration, specific form, rate of transport, and ease of removal of inorganic substances from the subsurface. These processes include (1) chemical speciation, (2) oxidation/reduction, (3) dissolution and precipitation of solid phases, (4) ion exchange and adsorption onto the soil matrix, and (5) transport of particles in the subsurface. One of the difficulties in working with inorganic contaminants is that all of these processes can be operating simultaneously. Therefore, it is sometimes difficult to determine which is the most important at a particular site. The relative importance of these processes not only varies from site to site but may vary from one area to another within a given site. The relative importance of these processes also may change during the cleanup operation as subsurface chemical conditions are altered. Each of these processes is discussed below.

### *12.1.1 Speciation*

When a water sample is sent to the laboratory for metals analysis, the results are usually returned as total concentrations. In reality, the metals interact with anions (or ligands) that exist in the ground water to form different chemical species or "aqueous complexes." For example, cadmium may exist in solution as $Cd^{2+}$, $CdCl^{+}$, $CdCl_2^0$, $CdOH^{+}$, or as other complexes. In addition to $Cl^-$ and $OH^-$, petal ions can combine with $SO_4^{2-}$, $CO_3^{2-}$, $F^-$, $S^{2-}$, $NH_4^+$, $PO_4^{3-}$, $CN^-$, or polyphosphates. Complex formation of transition metals is more extensive than for other metals. The relative tendency of metals to form complexes is in the order

$$\text{Fe(III)} > \text{Hg} > \text{Cu} > \text{Pb} > \text{Ni} >$$
$$\text{Zn} > \text{Cd} > \text{Fe(II)} > \text{Mn} > \text{Ca} > \text{Mg}$$

(Hanzlik, 1976). The concentration of aqueous complexes depends upon the concentration of the metal ion of interest, the ligand with which it forms the complex (Figure 12-2), and the concentration of the other metal ions that may compete for the ligand. Because chemical reactions usually are governed by the amount of free ion rather than by the total metal, knowledge of the concentration of complexes is important to properly identify the role of processes such as adsorption, mineral dissolution, and precipitation.

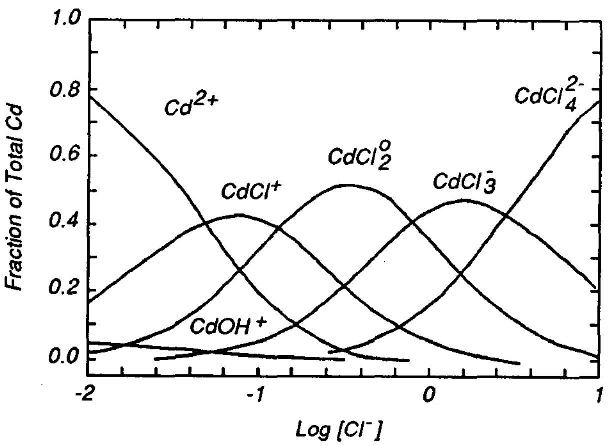


**Figure 12-2. Fraction of total Cd in various chemical complexes versus the $Cl^-$ concentration (after Moore and Ramamoorthy, 1984).**

The formation of inorganic aqueous complexes is often a rapid process that can be described by equilibrium expressions. For example, the formation of the mercuric chloride complex, $HgCl^+$, can be written as the chemical reaction:

$$Hg^{2+} + Cl^- + HgCl^+$$

which can then be written in terms of an equilibrium constant as:

$$K_a = \{Hg^{2+}\}\ \{C1^-\}/\{HgCl^+\} \qquad [12\text{-}1]$$

where the braces represent the thermodynamic concentration or "activity" of the chemical species. The activity of the species is simply the product of the concentration of that chemical species and an "activity coefficient," y. For example, the activity of $Hg^{2+}$ can be written as:

$$\{Hg^{2+}\} = \gamma_{Hg}{}^{2+}[Hg^{2+}] \qquad [12\text{-}2]$$

where $K_a$, is an equilibrium (or stability) constant for the above reaction and the brackets indicate the concentration of the chemical species. The activity coefficient accounts for the change in chemical reactivity due to electrostatic interactions among ions in solution. Several methods are used to calculate activity coefficients. See Stumm and Morgan (1981), Morel (1983), or Sposito (1986) for more detailed discussions of these methods.

Calculation of the concentrations of each chemical species in solution requires the total concentration of each metal and each ligand in solution as well as the equilibrium constant for the formation of each complex. Total concentrations are obtained from chemical analysis of the water sample. Equilibrium constants (or more fundamental thermodynamic data) for inorganic complex formation have been studied by many researchers and are tabulated in a variety of references (e.g., Ball et al., 1980; Felmy et al., 1984; Smith and Marten, 1976). An extensive list of thermodynamic data sources is given by Nordstrom and Munoz (1985).

While in principle it is easy to calculate the concentration of these aqueous complexes, it does not take too many combinations of metals and ligands to result in a series of equations that are unmanageable to solve by hand. Fortunately, computational algorithms can quickly perform these calculations, so time can be better invested in interpreting the results of the calculations.

### *12.1.2 Dissolution/Precipitation*

Ground water passing through an aquifer may be in direct contact with a wide variety of mineral phases. Dissolution or weathering of those mineral phases contributes greatly to the natural chemical composition of the ground water. Generally, dissolution refers to a reaction where all of the chemical species that comprise the mineral come into solution. Some common minerals that undergo dissolution in shallow aquifer systems include gypsum ($CaS0_4 \cdot H_2O$), calcite ($CaCO_3$) and quartz ($Si0_2$). Weathering is a partial dissolution process in which certain ions come into solution while others remain as part of secondary mineral phases. During the initial stages of weathering of aluminosilicates, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, and some $H_4SiO$ go into solution while the remaining ions become clays such as kaolinite and montmorillonite, If the concentrations of certain ions are sufficiently high, they may be removed from solution by the formation of a solid phase (i.e., by precipitation). These precipitated minerals may dissolve later if physiochemical conditions within that portion of the aquifer change.

These types of reactions can have a great effect on the concentrations of priority pollutants within the aquifer. For example, the weathering of fly-ash piles can yield selenium, arsenate, lithium, and heavy metals (Honeyman et al., 1982; Murarka and Macintosh, 1987). $BaCrO_4$ may precipitate in an aquifer contaminated with $Cr0_4$ and later it may dissolve during remediation, thus prolonging the time required to restore the aquifer. Pb can be removed from solution by precipitation as $PbCO_3$. In addition, dissolution of naturally occurring minerals can neutralize acid or alkaline waters and thus enhance the adsorption or precipitation of priority metals. The precipitation of calcite or hydrous ferric oxides may reduce the permeability of the aquifer, clog well screens, and increase the cost of treatment and disposal. Therefore, it is advantageous to be aware of the potential for these types of reactions and to include their effects in the cost and design of remediation.

Equilibrium between the ground water and a solid phase can be expressed in terms of an equilibrium constant (or volubility product). For example, the dissolution or precipitation of $BaCrO_4$, which involves two priority metals, is written as:

$$BaCrO_4(s) \leftrightarrow Ba^{2+} + CrO_4^{2-}$$

and at equilibrium this can be expressed as:

$$K_{sp} = \{Ba^{2+}\}\{CrO_4^{2-}\} \qquad [12\text{-}3]$$

where $K_{sp}$ is the volubility product. As with the aqueous complexes, the terms in the braces refer to the activity of the particular species and not the total concentration of the elements. The equilibrium constants for many solid phases can be found in the same references given for the aqueous complexes. The ability of a ground water to dissolve or precipitate a solid phase is sometimes expressed as a saturation index (SI), which is defined as:

$$SI = \log (IAP/K_{sp}) \qquad [12\text{-}4]$$

where the IAP or "ion activity product" is the same expression of ion activities used for the volubility product but at the concentrations found in the ground water rather than at equilibrium. For example, the ion activity product for barium chromate is $\{Ba^{2+}) \{Cro^{2-}_4\}$. If the ground water is in equilibrium with the solid phase, then the IAP is equal to the $Ks_p$ and the saturation index is equal to zero. If the saturation index is less than zero, the water is undersaturated with that solid phase and the ground water has the potential to dissolve that phase if it is present. If the saturation index is greater than zero, then the water is supersaturated with respect to the solid phase and has the potential to precipitate that phase provided that the reaction is fast enough to occur with the time scales of interest. Calculation of the saturation indices for mineral phases requires knowledge of the concentration of the aqueous complexes. Therefore, the computational tools used to calculate the concentration of aqueous complexes also can be used to calculate saturation indices.

Saturation indices at waste sites can be useful for identifying potential sources and sinks for metal ions. If calculated saturation indices for $PbCO_3$ are close to zero, then Pb is likely being removed from solution and may not move very far from the source. If the saturation indices for $BaCrO_4$ are close to zero, there may be a large reserve of solid phase in the aquifer that could prolong a pump-and-treat remediation scheme for the removal of the $CrO_4$. If the waters of interest are undersaturated or supersaturated with respect to solid phases of interest, the amount of the solid phase that must be dissolved or precipitated per liter of water to reach equilib rium can be calculated. Such theoretical calculations may be particularly useful in evaluating the potential for mineral precipitation as a result of mixing contaminated and uncontaminated waters in extraction wells. Note that saturation indices alone do not prove the presence or absence of a mineral phase. However, saturation indices are relatively easy to obtain and are valuable for identifying possible mineral phases.

### *12.1.3 Oxidation/Reduction*

The number of electrons associated with an element dictates its oxidation state. Elements can exist in several oxidation states. For example, iron commonly exists in the +2 or +3 state, arsenic as +3 or +5, and chromium as +3 or +6. Oxidation-reduction (redox) reactions involve a transfer of electrons and, therefore, a change in the oxidation state of elements. Redox reactions are important to studies of subsurface contamination because the chemical properties for the elements can change substantially with changes in the oxidation state. For example, in slightly acidic to alkaline environments, Fe(III) is fairly insoluble and precipitates as a solid phase (hydrous ferric oxide) that has a large adsorption capacity for metal ions. In contrast, Fe(II) is fairly soluble and its oxides have a much lower adsorption capacity. As the Fe(III) solid phase is reduced, not only is the Fe(II) brought into solution but so are any contaminants that may have been adsorbed onto it (Evans et al., 1983; Sholkovitz, 1985). Another environmentally important redox-active element is chromium. Hexavalent chromium, Cr(VI), exists in ground water as the relatively mobile and toxic anions $HCrO^-_4$ and $CrO^{2-}_4$. The reduced form of chromium, Cr(III), is a cation that under slightly acidic to alkaline conditions is fairly insoluble, readily adsorbed, and much less toxic than Cr(VI). Selenium also undergoes important redox transformations. Selenate (Se(VI)) is more mobile and less toxic than selenite (Se(IV)).

Because redox reactions involve the transfer of electrons, the change in oxidation state of one element necessitates a change in the oxidation state of another. For example, as Cr(Vl) is reduced to Cr(III), it must gain three electrons from another element. One possible electron donor is ferrous iron (Fe(II)):

$$HCrO_4 + 3Fe^{2+} + 7H^{+} \leftrightarrow 3Fe^{3+} + Cr^{3+} + 4H_2O$$

Redox reactions cannot occur unless there is both a suitable electron donor and a suitable electron acceptor.

The expected form of an element at equilibrium depends on the pH and the redox state of the water. The redox state is measured by an electrical potential (in volts (v) or millivolts (mV)) at a standard electrode. This potential is called the EH of the ground water. Alternatively, the redox conditions are sometimes reported in terms of the "pe," which is the negative logarithm of the activity of the electron. This is a direct analogy to pH, which is the negative logarithm of the activity of H+. The $E_H$ and pe of a watar measure the same property, but due to differences in definition they are not numerically equivalent. Redox conditions within natural aquifers vary from highly oxidizing conditions (high EH, - +800-900 mV) to very reducing conditions (low $E_H$,~ -200 mV). Variation within contaminated aquifers is at least as great as this range, but often is marked by abrupt transitions over much smaller scales than is typical of uncontaminated aquifers (see Sections 8.3.3 and 8.4).

The conditions of pH and $E_H$ for which a particular redox species is theoretically stable are represented graphically on an $E_H$-pH diagram. These diagrams are also known as pe-pH and Pourbaix diagrams. For example, the $E_H$-pH diagram for Fe (Figure 12-3) illustrates the predominance of the iron hydroxide solid at slightly acidic to alkaline conditions and high $E_H$ conditions, whereas aqueous $Fe^{z+}$ predominates at low $E_H$ and slightly alkaline to acid conditions. Methods for the construction of such diagrams can be found in Garrels and Christ (1965), Drever (1989), and Stumm and Morgan (1981). A collection of $E_H$-pH diagrams for many metals was prepared by Brookins (1988).

In theory, knowledge of the $E_H$, pH, and total elemental concentrations in a ground water allows the quantitative prediction of the concentration of each redox-active species in solution. However, many redox reactions are microbially catalyzed, nonreversible, and, therefore, not found in a state of mutual equilibrium. Redox species that are not at equilibrium with each other often have been observed to occur together (Lindberg and Runnels, 1984). Except for a very few situations, it is impossible to predict general redox behavior in aquifers using equilibrium concepts. Nonetheless, there are observable and consistent trends in redox conditions in natural aquifers that suggest that at least qualitative estimates of behavior are possible. Because of the importance of redox reactions it is important to know at least the *possible* changes in the redox state. Some idea of the transformations that may be taking place within the aquifer can be obtained in certain cases (e.g., for Cr, Se, As) by directly measuring the concentrations of different oxidation states of the contaminants. More must be learned about the rates of redox reactions if these reactions are to be put into proper perspective with regard to the transport and removal of inorganic contaminants from the subsurface. A review by Fish (1990) summarizes these concepts, problems, and some possible solutions.

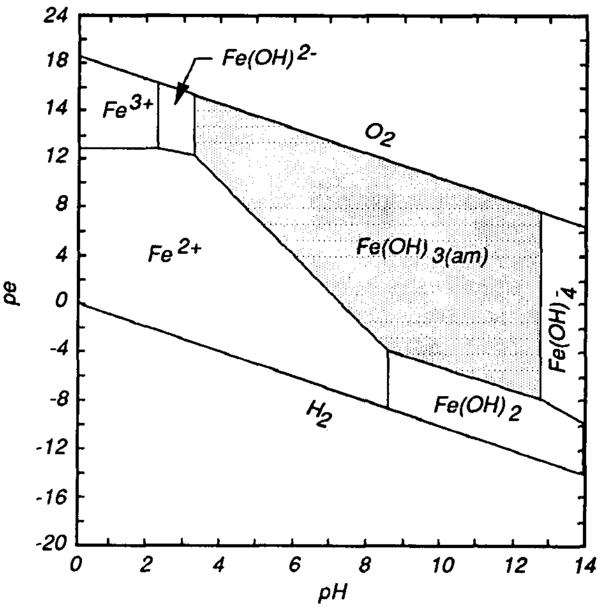


**Figure 12-3. pe-pH diagram for the Fe-$H_2O$ system.**

## *12.1.4 Adsorption/Ion Exchange*

Ion exchange and adsorption can exert a great influence on the concentrations of ions in solution. Clay minerals are important ion-exchangers in subsurface systems. During ion exchange, ions in certain layers of the three-dimensional structure of clays are replaced by ions in solution, while a constant total charge within the clay layer is maintained. For example, Ca-Na exchange can be written as:

$$2NaX + Ca^{2+} \leftrightarrow CaX + 2Na^{+}$$

and using the Vanselow (1932) convention can be expressed in terms of a "selectivity coefficient", $K_s$, as:

$$K_s = \frac{X_{CaX}\{Na^{+}\}^2}{X^2_{NaX}\{Ca^{2+}\}} \qquad [12\text{-}5]$$

where NaX and CaX represent the Na and Ca on the clay and $X_{NaX}$ and $X_{CaX}$ are the mole fractions of exchangeable sites occupied by Na and Ca, respectively. The selectivity coefficients are empirical and vary with the concentration of the cations in the ground water (Reichenberg, 1966) so that location-specific values must be used.

Knowledge about ion exchange is important to understand the binding of alkali metals and the alkaline earths and some anions to clays and condensed humic matter (Sposito, 1984; Helfferich, 1962). However, ion exchange does not adequately describe the interaction of many transition metals with mineral surfaces. These interactions are better described by adsorption processes. Ionic adsorption involves the coordination bonding of metal cations and anions to surfaces of minerals exposed in the pore space of the aquifer. In ion exchange, the total electrostatic charge of the solid phase is constant, whereas for adsorption, the charge of the surface varies with solution pH and the amount of ions adsorbed. At this time, no generally accepted model for the adsorption of inorganic ions exists, so several approaches are discussed below.

As with organic solutes, adsorption isotherms for inorganic compounds can be constructed and Langmuir- and Freundlich-type isotherms can be utilized. In general, anions tend to follow Langmuir isotherms while cations tend to follow Freundlich isotherms (Dzombak, 1986). For the organic contaminants considered in Chapter 10, linear isotherms were found for many compounds allowing a constant retardation factor to be applied in transport calculations. There is no model of comparable simplicity that can properly describe the transport of inorganic substances in the subsurface. One of the key reasons why an analogous model does not work for inorganic constituents is the strong dependence of the amount of adsorption on the pH of the ground water. This is illustrated in a "pH-edge" which is a plot of the fraction of the total mass of a metal adsorbed versus the pH of the solution (Figure 12-4).

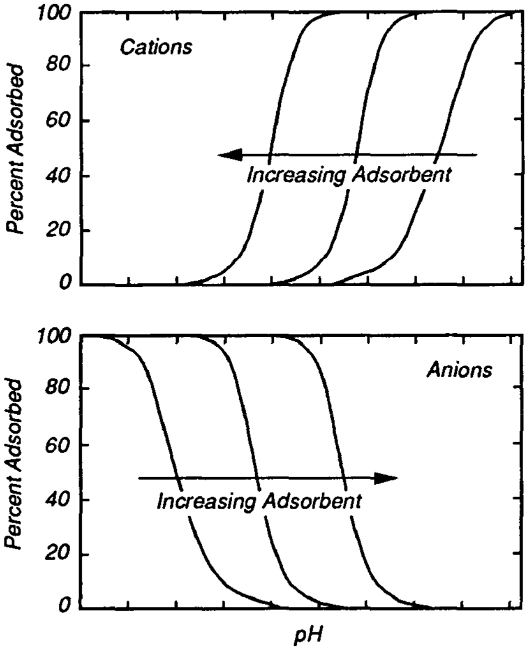


**Figure 12-4.** pH adsorption edges for cations and anions (after Dzombak, 1986). The arrows illustrate the shift in the edge with increased adsorbent concentration.

For cations, very little of the metal is adsorbed onto the aquifer material at low PH. As the pH increases, the fraction adsorbed onto the soil increases until virtually all of the metal is adsorbed or all metal-binding sites are occupied. The exact position of the pH-edge on the diagram depends on the specific ion considered, the concentration of the metal, the amount of adsorbent, and the concentration of other ions in solution, These additional ions may compete for adsorption sites or form complexes with the metal ion and shift the edge (Figure 12-5) (Benjamin and Leckie, 1981). The pH-edges for anions are approximately mirror images of those for cations, with maximum adsorption Occurring at low pH and decreasing with increasing pH. Any useful model of ionic adsorption of metal ions should account for the pH dependence of adsorption. The so-called "surface complexation models" for ion adsorption meet this criterion (e.g., Stumm et al., 1976 Schindler, 1981; Schindler and Stumm, 1987; Dzombak and Morel, 1990). These models have a foundation in chemical theory and if used for a well-defined system, may be applied over a somewhat wider range of conditions than the specific experiments used to determine the particular model parameters. Surface complexation models are based on the concept that ions form complexes with solid-phase atoms at the oxide/solution interface. These complexes are analogous to complexes formed in solution between metals and ligands. There is, however, an added difficulty due to the formation of a surface charge at the oxide-water interface.

An oxide can be viewed as an array of metal ions and oxygen atoms (Figure 12-6a). When the oxide is immersed in an aqueous solution, water molecules arrange themselves around the surface metal ions (Figure 12-6b). Some of these adsorbed water molecules then dissociate, and the resulting hydrogen ions bind to the adjacent surface oxygen atoms (Figure 12-6c). Adsorption of anions and cations to the oxide surface can be described as an exchange of the metal ions for the $H^+$ and the ligands for the OH groups on the surface of the

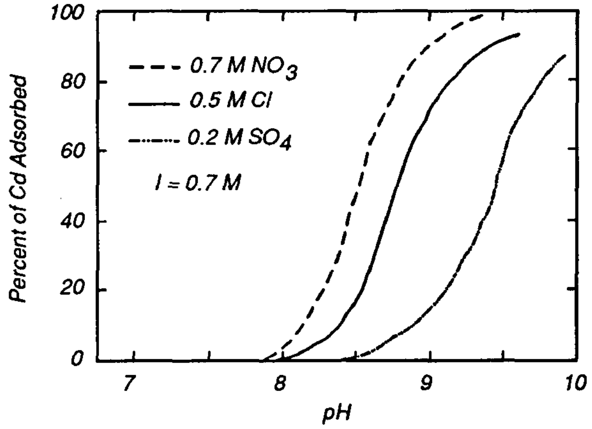


**Figure 12-5.** The effect of anions on the adsorption of Cd on $SiO_2$ (after Benjamin and Leckie, 1981).

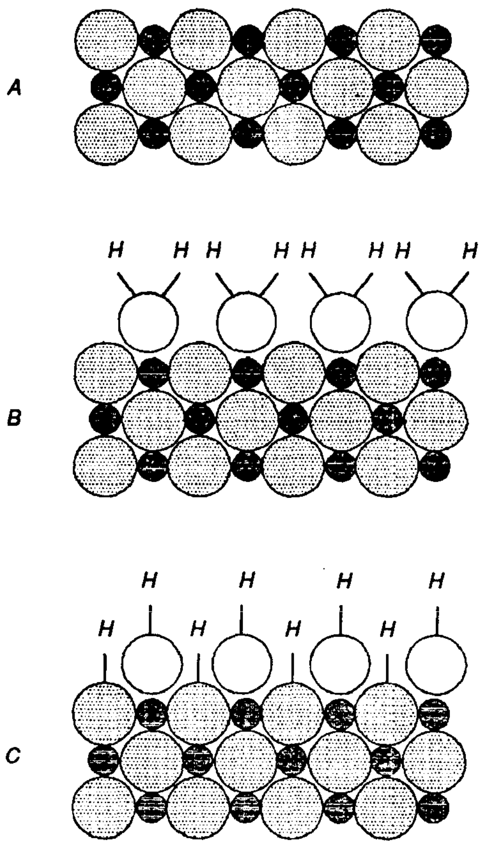


Figure 12-6. Formation of a hydroxylated oxide surface in water (after Schindler, 1981).

oxide (Figures 12-7 and 12-8). Such adsorption reactions can be written in a manner similar to the solution complex reactions discussed above:

$$\equiv OH + M^{2+} \leftrightarrow \equiv OM^{+} + H^{+} \qquad ; K_1$$

$$\equiv OH + L^{-} \leftrightarrow \equiv L + OH^{-} \qquad ; K_2$$

where the symbol = denotes the oxide surface, $M^{2+}$ is a divalent cation, and $L^{-}$ is a monovalent anion. Equilibrium constant expressions for these reactions are

These equations are analogous to the equilibrium expressions **for the aqueous complexes, except for the $\gamma_{-}$, terms which** describe the effect of the electrostatic charge near the surface of the oxide.

Several surface complexation models have been developed. The most important feature that distinguishes one surface complexation model from another is the treatment of the electrostatic term. Computation of the electrostatic effects on adsorption requires postulation of a particular arrangement of electrical charges near the surface. These charge distributions are developed by hypothesizing one or more layers of charges near the surface. The three types of surface complexation models often used are two-layer models, Stem-layer models, and triple-layer models. More detailed discussions of these models are given by Dzombak (1986) and Dzombak and Morel (1990). These models represent increasing complexity in the geometric view of the oxide-water interface and require an increasing number of fitted parameters in addition to the equilibrium constants. Despite apparent differences in their sophistication, all three of these surface complexation models equally describe acid-base titration data for oxide surfaces (Westall and Hohl, 1980; Dzombak, 1986). In addition, Dzombak (1986) found that the simpler two-layer model was quite capable of modeling anion adsorption and cation adsorption if the cation concentrations were not extremely high. Therefore, the choice of model is best based on which is the most parsimonious; the obvious choice in many cases is the two-layer model.

One of the major disadvantages to using this type of adsorption model is a lack of knowledge about the equilibrium constants. The problem in using constants reported in the literature is that they are specific to the adsorption model used to fit the experimental data. Therefore, reported constants are quite dissimilar from those appropriate for a different adsorption model. To overcome this limitation, Dzombak (1986) and Dzombak and Morel (1990) reinterpreted the raw data from adsorption experiments for different ions on hydrous ferric oxides (HFO) using the basic two-layer model. This effort provides a set of consistent constants based on a common adsorption model and makes more widespread use of such models feasible. If the main adsorbent in the aquifer is HFO, the derived constants provided by Dzombak and Morel (1990) should be adequate. However, natural porous media may contain many oxides and other surfaces to which metal ions

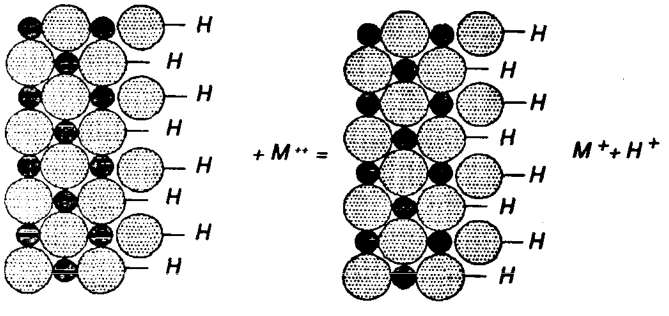


Figure 12-7. Adsorption of a divalent cation on a hydroxylatad oxide surface (from Palmer et al., 1988).

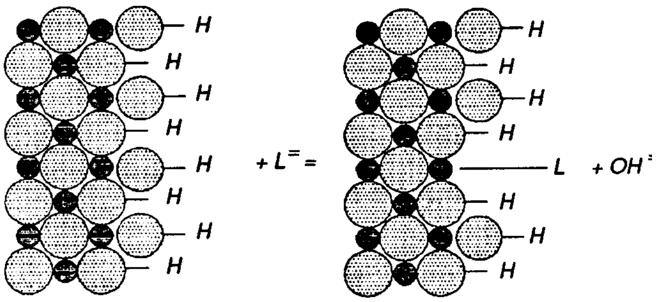


**Figure 12-8. Adsorption of a monovalent anion on a hydroxylatad oxide surface (from Palmer et al., 1988).**

can bind (Figure 12-9), and a consistent set of equilibrium adsorption constants has yet to be derived for other types of surfaces. It also is unclear whether mixtures of surfaces are linearly additive.

## 12.2 Particle Transport

A potentially important mechanism for the migration of inorganic substances is particle transport. These particles may be inorganic, organic, or biological and may include bacteria, viruses, natural organic matter, inorganic precipitates, asbestos, and clay. Inorganic ions may migrate as integral constituents of the particles or they maybe adsorbed onto the surfaces of the particles. The distance these particles move depends upon the size of the particles relative to the size of the pores through which they must pass as well as the chemical conditions in the subsurface.

Particles can be removed from solution by three major mechanisms: (1) surface filtration, (2) straining, or (3) physical-chemical processes (McDowell-Boyer et al., 1986). If the particles are larger than the largest pores within the aquifer, they cannot penetrate the aquifer and they are filtered out at the interface between the medium and the source of the particles (surface filtration). If the particles are smaller than the largest pores but larger than the smallest pores, the particles can travel some distance into the aquifer before they encounter a pore through which they cannot pass; they will then be strained from solution (straining). If the particles are smaller than the smallest pores in the medium, then they can travel great distances. However, the particles still can be removed from solution by adhering to the sand grains because of collision. Collision with the sand grains occurs as a result of sedimentation, interception, and Brownian motion. Particles in the subsurface also can aggregate if chemical conditions such as pH or ionic strength change significantly (physical-chemical processes). The particle aggregates then can be removed from the water by straining.

Particle transport is not likely to be an important factor in every environment. Therefore, it is useful to target those situations where particle transport is most likely to be important Such situations include environments where there are high concentrations of organic carbon, dissolved solids, or suspended solids. Movement of particles may be induced in areas where the flow rates are very high, either because of natural flow conditions or more commonly because of high pumping rates. Any time there is an abrupt transition in pH or redox conditions within the aquifer subsurface, there is an opportunity for the precipitation of colloidal-size particles that can travel through the aquifer. When a water appears to be supersaturated with common mineral phases that are normally expected to be at equilibrium, then particle transport should be suspected. A simple example of the latter would be high iron concentrations in the presence of oxygen under mildly acidic to alkaline conditions. The iron is likely to precipitate as a fine colloid and to be included in the total iron analysis of the water (Fish, in press). If the particle transport is believed to be important, there are several techniques for particle detection. These techniques include filtration, microscopy, electrophoresis, and light scattering. A review of light-scattering techniques is provided by Rees (1987).

Particle transport has been documented for at least two different ground-water contamination sites. It has been observed in a contaminant plume emanating from rapid infiltration beds used to recharge treated sewage to a sand and gravel aquifer at Otis Air Force Base on Cape Cod, Massachusetts (Gschwend and Reynolds, 1987). Particles near the source were relatively small (< 6nm) but down-gradient from the infiltration beds, apparently mobile particles about 100 nm in diameter were observed (Figure 12-10). Chemical analysis of the particles indicated that they were composed of Fe(II) and $PO_4$ and may be the mineral vivianite $(\mathrm{Fe},(\mathrm{PO}_4)_2)$. As the treated sewage, which was high in organic carbon, was recharged to the aquifer, reducing conditions were created within the plume. Reductive dissolution of the naturally existing HFO or other iron-containing minerals resulted in elevated levels of $Fe^{2+}$ in solution. Phosphate entered the aquifer in wastewater percolating through the infiltration basins. The phosphorus originated from detergents used prior to the mid-1970s. As phosphate entered the aquifer with the recharge water and mingled with Fe(II), the water eventually reached saturation and began to precipitate the Fe-phosphate solid phase (Figure 12-11). However, the precipitate remained in solution as fine particles that migrated through the sand and gravel aquifer.

Another documented example of particle transport involves the migration of radionuclides at the Nevada Test Site (Buddemeir and Hunt, 1988). Large volumes of water were passed through a series of ultrafilters to measure the concentration of radionuclides in different size fractions of particles. The results (Figure 12-12) indicate that some nuclides such as $^{125}$Sb are almost entirely in solution (<3 nm), while nuclides such as $^{54}$Mn are transported on relatively large particles. Yet other nuclides, such as $^{105}$Ru, are not associated with any particular particle size but are evenly distributed over the different particle sizes.

The definition of what is a molecule in solution and what is a colloidal particle is arbitrary. For many years the 450-nm pore size was used as the standard break between what is in solution and what is a particle. However, this pore size corresponds to molecular weights in the range of several hundred thousand atomic-weight units. Materials of this size are now thought to be more properly defined as colloidal

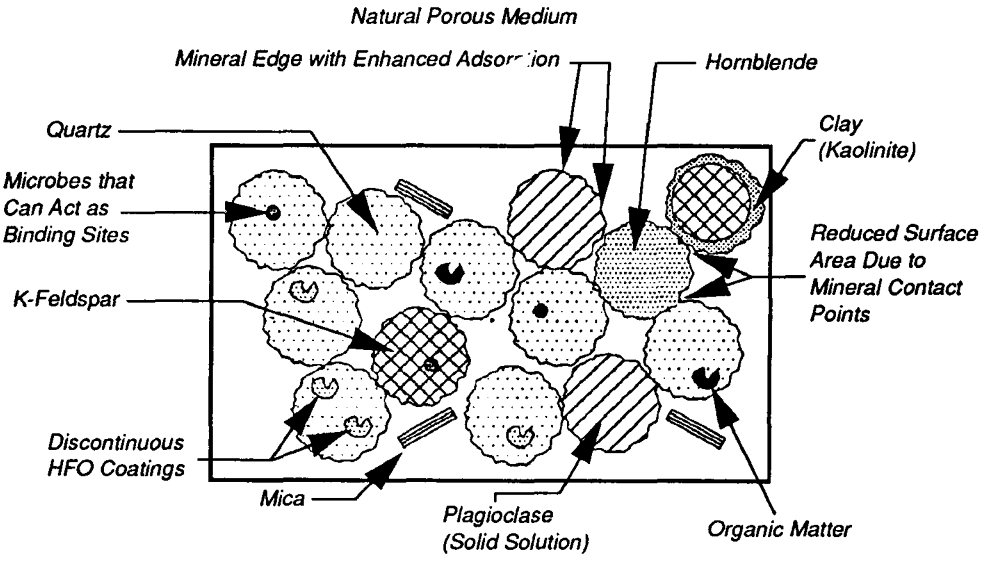


**Figure 12-9. Natural porous media containing many different types of adsorption surfaces (from Palmer et al., 1988).**

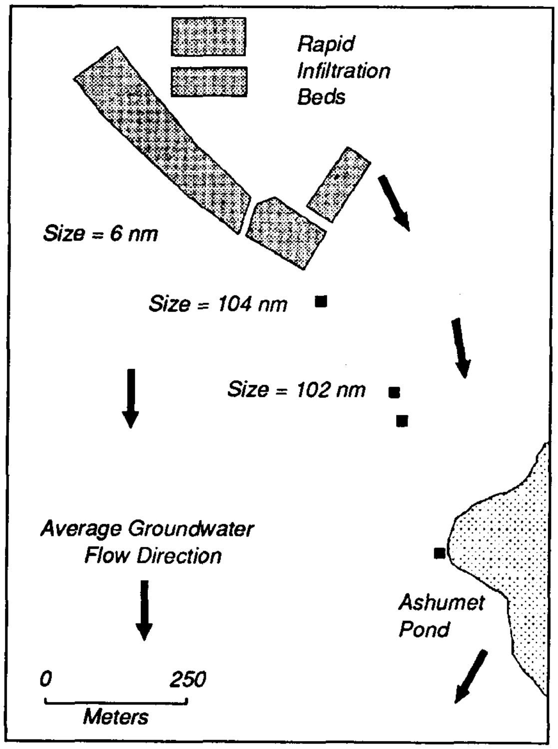


**Figure 12-10. Particle sizes measured in the subsurface at the Otis Air Force Base, Cape Cod, MA (modified from Gschwend and Reynolds, 1987).**

particles. Consequenty, smaller pore-diameter filters are increasingly used to distinguish "particles" from "solutes." However, there is no objective standard of what constitutes the proper dividing size.

Particle transport is particularly important for sites where the contaminant is highly toxic and the general expectation is that the contaminant is not mobile because of its high affinity for adsorption. However, if the material to which it is adsorbed is fairly mobile, then the sorbate may move rapidly beyond the site.

For remediation efforts, particle transport can be a benefit or a liability. If particle transport is significant, it may be possible to remove a significantly greater mass of contaminant per unit time (hence per unit cost) than if the contaminant were adsorbed onto immobile particles. However, particles can plug injection wells or aggregate in the subsurface and reduce the permeability of the formation near the extraction wells. These effects may increase the overall cost of aquifer restoration if filter presses and longer pumping schedules are required to overcome these problems.

## 12.3 Organic-Inorganic Interactions

Mixtures of many types of wastes are found in landfills, dumps, and ground-water contamination sites. Consequently, it is not unusual to find both inorganic and organic contaminants together. For example, an analysis of leachate from a municipal landfill in Brookhaven Town, Long Island, New York, revealed 660 µg/L Cr (VI), 127 µg/L lead, 151 µg/L

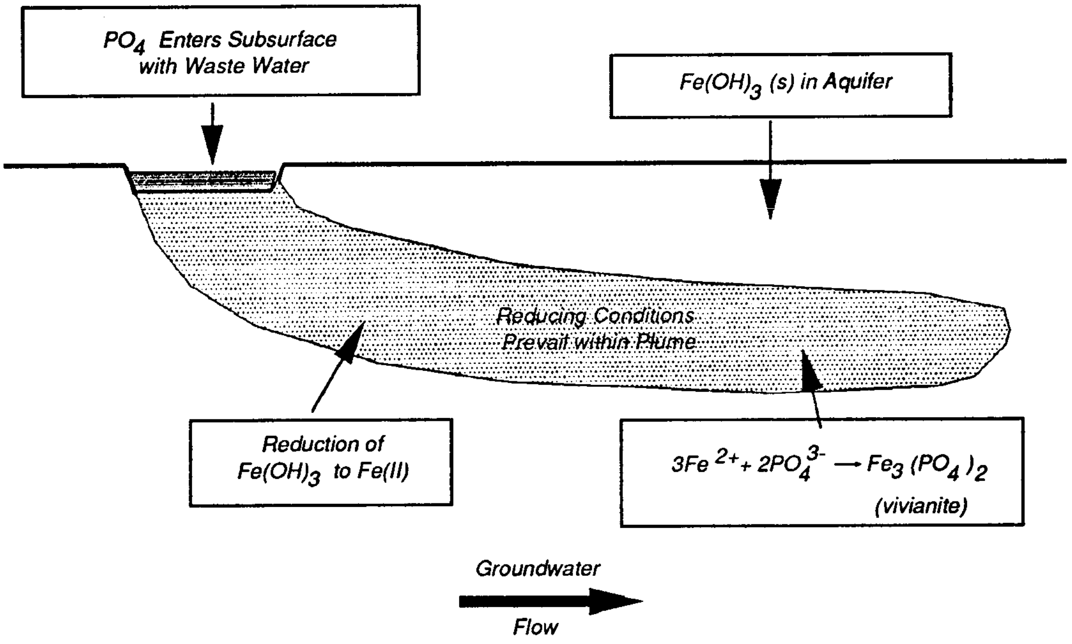


**Figure 12-11. Formation of particles at the Otis Air Force Base site, Cape Cod, MA.**

xylenes, 40 µg/L methylene chloride, 27 µg/L naphthalene, and 25 µg/L benzene (Black and Heil, 1982). At Woburn, Massachusetts, Cr (VI) levels of over 2,000 µg/L were measured in ground-water samples that contained high levels of p-chloro-m-cresol, phenol, p-nitrophenol, N-nitroso-diphenylamine, phthalate esters, and 35 other organic compounds (Cook and DiNitto, 1982). The behavior of inorganic constituents in such waste mixtures can be dramatically different from their behavior when the inorganic contaminants are found by themselves.

The interactions among organic and inorganic compounds can be classified as either direct or indirect. Direct interactions include processes such as complexation (chelation) of metal ions with organic solutes, oxidation-reduction reactions between organic and inorganic constituents, and the competition between organic and inorganic solutes for adsorption sites. Indirect interactions refer to the changes in pH and redox conditions as a consequence of degradation of organic contaminants in the subsurface. Most of the research on direct interactions between organic and inorganic materials has focused on finding or characterizing synthetic pathways for the commercial production of chemicals, for example, the oxidation of alcohols with Cr(VI) to produce aldehydes or carboxylic acids. Often this research has been conducted under extreme conditions of concentrations and pH that are of little environmental significance. The few studies that are of environmental interest indicate that organic-inorganic reactions are important in several situations. Stone (1986) found that phenols can be oxidized in the presence of $MnO_z$. Voudrias and Reinhard (1986) reviewed several investigations of the oxidation of organic compounds by metal-substituted clays. Laha and Luthy (1990) studied the oxidation of aniline and other aromatic amines by $MnO_z$. Fish and Elovitz (1990) observed the reduction of hexavalent chrome by cresols. They found that the rate of reduction was strongly dependent on the pH and the particular isomer involved in the reaction. While the implications of these results for remediation have yet to be seriously considered, the results may have implications on the design of systems where waters may potentially mix in extraction wells and treatment trains.

Even at sites contaminated only by organic compounds, inorganic constituents cannot be ignored. While elevated concentrations of inorganic ions may result directly from waste leachate, they also may result from mobilization of naturally occurring ions in response to the changing pH and redox conditions induced by organic contamimnts. Such changing conditions are typical consequences of biodegradation (Figure 12-13). Biodegradation consumes oxygen, thereby decreasing the $E_H$(pe) within the contaminant plume. $CO_z$, a by-product of biodegradation, forms carbonic acid and decreases the pH within the plume. Organic acid by-products also may decrease the pH. These processes can result in the resorption of metal ions and the dissolution of hydrous ferric oxide (an important adsorbent).

An example of such conditions is found at a creosote plume in Pensacola, Florida (Cozzarelli et al.( 1987). Elevated concentrations of Fe, $CO_z$, and $CH_4$ and depleted concentrations of dissolved oxygen and $NO^-_3$ are associated with the biodegrading creosote plume. Barium, molybdenum, manganese, nickel, and strontium are as much as two orders of magnitude greater than background levels.

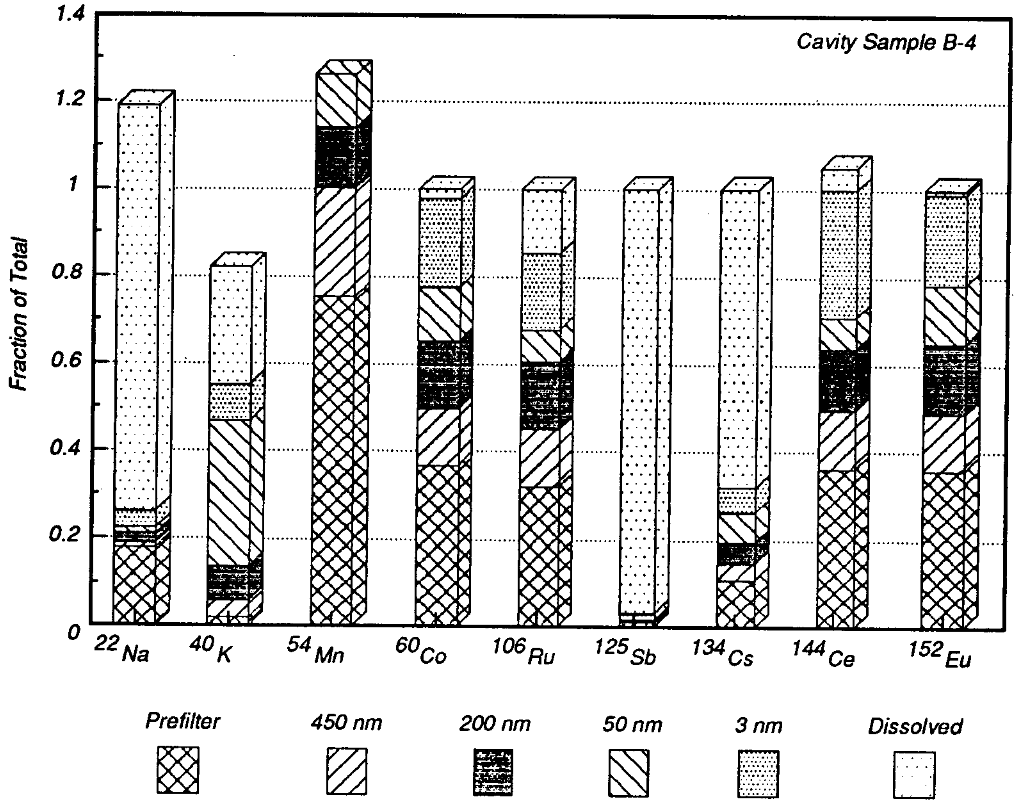


**Figure 12-12. Fraction of isotopes in different sized fraction in ground water near the Nevada Test Site (data from Buddemeir and Hunt, 1988).**

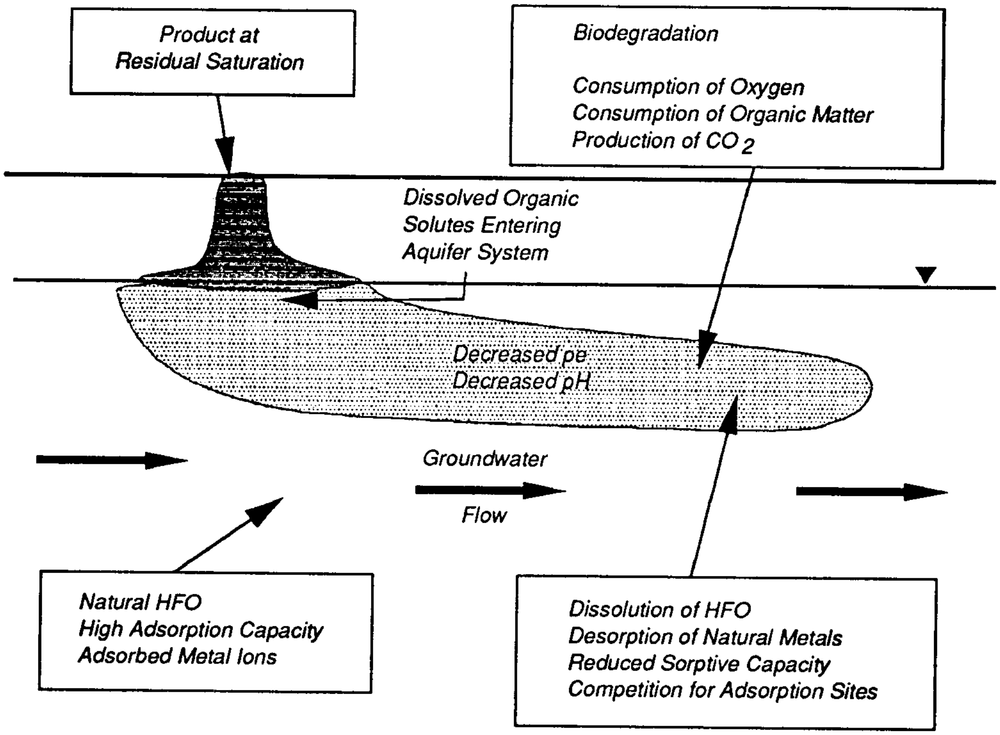


**Figure 12-13. Indirect effects of biodegradation of organic contaminants on inorganic constituents.**

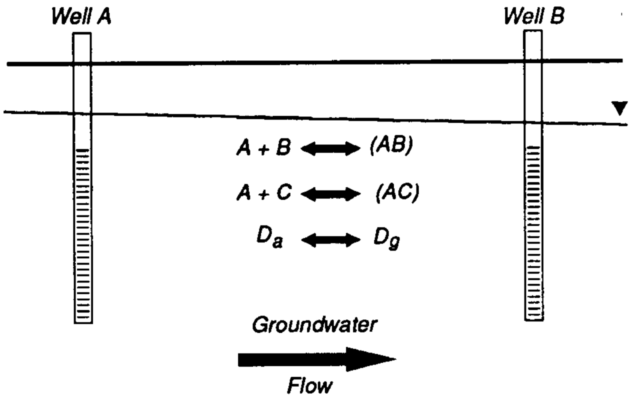


**Figure 12-14. Application of mass balance computational models.**

These chemical alterations are found over a much wider area both horizontally and vertically than the organic contaminants themselves. Similar conditions also have been described at a crude oil spill in Bemidji, Minnesota, (Siegel, 1987) where elevated concentrations of iron, aluminum, and silica are reported. While many of these elements are not toxic they can nevertheless pose costly problems of scaling and clogging during pump-and-treat remediation.

## 12.4 Computational Tools

The sections above discussed the importance of complexation to understanding the controlling processes of site remediation with inorganic contaminants. Determining the concentration of each of the complexes is a computationally complex task that is left to computational algorithms. In addition, other types of computationally intensive chemical calculations would be useful, and there are a variety of computational tools to assist in such calculations. In general, these tools can assist in the calculation of (1) mass balance, (2) chemical speciation, (3) mass transfer, and (4) multicomponent transport. While some of these algorithms are readily available at little or no cost, others are still classified as research tools and are not likely to be available for general use for several years.

### *12.4.1 Mass Balance*

Mass balance calculations can be applied to a system such as that illustrated in Figure 12-14. If the chemical composition of the water is known at locations A and B along the flow path, then the change in concentration of each of the elements along the flow path is known. If the reactions that take place between the two wells are known, then the amount of each reaction can be calculated. Reactions such as (1) mineral dissolution/precipitation, (2) gas exchange, (3) ion exchange, (4) simple isotope balances, (5) oxidation-reduction, and (6) the mixing of waters can be included in such calculations. The code BALANCE (Parkhurst et al., 1982) is a readily available FORTRAN code that can run on personal computers. So far this code has been used to study the geochemical evolution of natural waters (e.g., Plummer and Back, 1980), yet it has not been applied to the transport of contaminants or the performance of remediation activities. A mass balance model such as BALANCE should not be used by itself but should be used in conjunction with chemical speciation and mass transfer tools as well as practical knowledge of chemical systems.

### *12.4.2 Chemical Speciation*

Chemical speciation algorithms are used to calculate the concentration and activities of each of the chemical species that are in solution. The data requirements for the proper use of such models include accurate field pH, temperature, and alkalinity. In addition, a *complete* inorganic chemical analysis is required. A complete chemical analysis requires the concentration of all of the major anions and cations and the priority metals and anions under investigation. Some knowledge of the redox conditions within the aquifer is useful, particularly the total concentration of each of the redox states of the metals of concern. Most chemical speciation models also calculate and print out the mineral saturation indices.

There are several chemical speciation models available. WATEQ4F and SOLMNEQ88 are versions of models that were originally published in the mid- 1970s by the United States Geological Survey (e.g., Kharaka et al., 1988; Ballet al., 1979; Kharaka and Barnes, 1973; Plummer et al., 1976 Truesdell and Jones, 1974). Chemical speciation also is performed by mass transfer models (see below); it maybe more practical to have a single program for all such calculations.

### *12.4.3 Mass Transfer*

Mass transfer models allow calculation of how much of a given mineral phase must react for the water to reach equilibrium with that phase and achieve the pH and $E_H$ of the equilibrated solution. The basic data requirements for the use of this type of model are similar to those for chemical speciation models. There are several available mass transfer models, including PHREEQE (Parkhurst et al., 1980), EQ3/6 (Wolery, 1979, 1983), and MINTEQ (Felmy et al., 1984). MINTEQ has an extensive data base that includes many of the priority metals that are of interest at waste sites. MINTEQ is also the only model that includes choices for adsorption processes, including (1) ion exchange, (2) Langmuir isotherms, (3) Freundlich isotherms, (4) double-layer model, (5) Stem-layer model, and (6) triple-layer model.

### *12.4.4 Multicomponent Transport*

The ultimate tool for assisting in the design of aquifer remediation strategies is a computational algorithm that accounts for the physical process of advection as well as all of the chemical processes discussed above. While progress has been made in this area (Jennings et al., 1982; Yeh and Tripathi, 1989), these models are not generally available. Although these models are still considered to be research tools, there is much work being done to complete models that soon will be available for general use.

## 12.5 References

Ball, J.W., E.A. Jenne, and D.K Nordstrom. 1979. WATEQ2 — A Computerized Chemical Model for Trace and Major Element Speciation and Mineral Equilibria of Natural Waters. In: Chemical Modeling in Aqueous Systems: Speciation, Sorption, Volubility, and Kinetics, E.A. Jenne (ed.), ACS Symp. Series 93, American Chemical Society, Washington, DC, pp. 815-836.

Ball, J. W., D.K. Nordstrom, and E.A. Jenne. 1980. Additional and Revised Thermochemical Data and Computer Code for WATEQ2: A Computerized Chemical Model for Trace and Major Element Speciation and Mineral Equilibria of Natural Waters. U.S. Geological Survey Water Resources Investigations No. 78-116.

Benjamin, M.M. and J.O. Leckie. 1981. Multiple-Site Adsorption of Cd, CU. Zn, and Pb on Amorphous Iron Oxyhydroxides. J. Coll. Interface Sci. 79(2):209-221.

Black, J.A. and J.H. Heil. 1982. Municipal Solid Waste Leachate and Scavengerwaste: Problems and Prospects in Brookhaven Town. In: Proceedings of the Northeast Conference on the Impact of Waste Storage and Disposal on Ground-Water Resources, R.P. Voitski and G. Levine (eds.), U.S. Geological Survey and Cornell University, 2.1:1-12.

Booz-Allen and Hamilton, Inc. 1987. ROD (Record of Decision) Annual Report FY 1986. U.S. Environmental Protection Agency (NTIS PB87-199550), 182 pp.

Brookins, D.G. 1988. Eh-pH Diagrams for Geochemistry. Springer-Verlag, New York, 176 pp.

Buddemeir, R.W. and J.R. Hunt. 1988. Transport of Colloidal Contaminants in Groundwater Radionuclide Migration at the Nevada Test Site. Applied Geochemistry 3:535-548.

Cook, D.K. and R.G. DiNitto. 1982. Evaluation of Groundwater Quality in East and North Wobum, Massachusetts. In: Proceedings of the Northeast Conference on the Impact of Waste Storage and Disposal on Ground-Water Resources, R.P. Voitski and G. Levine (eds.), U.S. Geological Survey and Cornell University, 4.2:1-20.

Cozzarelli, I.M., M.J. Baedecker, and J.A. Hopple. 1987. Effects of Creosote Products on the Aqueous Geochemistry of Unstable Constituents in a Surficial Aquifer. In: U.S. Geological Survey Program on Toxic Waste-Ground-Water Contamination: Proceeding of the Third Technical Meeting, Pensacola, Florida, March 23-27, 1987, B.J. Franks (ed.), U.S. Geological Survey Open-File Report 87-109, pp. A15-A16.

Drever, J.I. 1989. The Geochemistry of Natural Waters, 2nd ed. Prentice-Hall, Englewood Cliffs, NJ. [First edition 1982].

Dzombak, D.M. 1986. Towards a Uniform Model for Sorption of Inorganic Ions Hydrous Oxides. PhD Dissertation, Department of Civil Engineering, Massachusetts Institute of Technology.

Dzombak, D.A. and F.M.M. Morel. 1986. Sorption of Cadmium on Hydrous Ferric Oxide at High Sorbate/Sorbent Ratios: Equilibrium, Kinetics, and Modelling. J. Colloid Interface Sci. 112 2):588-598.

Dzombak, D.A. and F.M.M. Morel. 1990. Surface Complexation Modelling, Hydrous Ferric Oxide. John Wiley & Sons, New York, 393 pp.

Dzombak, D.A., W. Fish, and F.M.M. Morel. 1986. Metal-Humate Interaction. 1. Discrete Ligand and Continuous Distribution Models. Environ. Sci. Technol. 20:669-675.

Evans, D. W., J.J. Alberts, and R.A. Clark. 1983. Reversible Ion-Exchange of Cesium-137 Leading to Mobilization from Reservoir Sediments. Geochimica et Cosmochimica Acta 47(ll):1041 -1049.

Felmy, A.R., D.C. Girvin, E.A. Jenne. 1984. MINTEQ A Computer Program for Calculating Aqueous Gemchemical Equilibria. EPA/600/3-84-032 (NTIS PB84-157148).

Fish, W. 1990. Subsurface Redox Chemistry: A comparison of Equilibrium and Reaction-Based Approaches. In: Metal Speciation in Groundwater, H. Allen E.M. Perdue, and D. Brown (eds.), Lewis Publishers, Chelsea, MI.

Fish, W. (in press). Subsurface Transport of Gasoline-Derived Lead. Ground Water.

Fish, W. and M.S. Elovitz. 1990. Redox and Solvation Interactions between Hexavalent Chromium and Hydroxylated Organic Compounds. U.S. EPA Contract Report 90-R-8 14136-01-0.

Garrels, R.M. and C.L. Christ. 1965. Solutions, Minerals, and Equilibria. Harper and Row, New York, 450 pp.

Gschwend, P.M. and M.D. Reynolds. 1987. Monodisperse Ferrous Phosphate Colloids in an Anoxic Groundwater Plume. J. Contaminant Hydrology 1:309-327.

Hanzlik, R.P. 1976. Inorganic Aspects of Biological and Organic Chemistry. Academic Press, New York.

Helfferich, F. 1962. Ion Exchange. McGraw-Hill, New York.

Honeyman, B. D., K.F. Hayes, and J.O. Leckie. 1982. Aqueous Chemistry of As, B, Cr, Se, and V with Particulm Reference to Fly-ash Transport Water. EPRI-91O-1. Electric Power Research Institute, Palo Alto, California.

Jennings, A. A., D.J. Kirkner, and T.L. Theis. 1982. Multicomponent Equilibrium Chemistry in Ground Water Quality Models. Water Resources Reach 18: 1089 -l096.

Kharaka, Y.K. and I. Barnes. 1973. SOLMINEQ: Solution-Mineral Equilibrium Computations. U.S. Geological Survey, Menlo Park, CA (NTIS PB215-899).

Kharaka, Y.K., W.D. Gunter, P.K. Aggarwal, E.H. Perkins, and J.D. DeBraal. 1988. SOLMINEQ.88: A Computer Program for Geochemical Modeling of Water-Rock Interactions. U.S. Geological Survey Water-Resources Investigations Report 88-4227, 420 pp.

Laha, S. and R.G. Luthy. 1990. Oxidation of Aniline and Other Primary Aromatic Amines by Manganese Dioxide. Environ. Sci. Technol. 24:363-373.

Lindberg, R.D., and D.D. Runnels. 1984. Ground Water Redox Reactions: An Analysis of Equilibrium State Applied to Eh Measurements and Geochemical Modeling. Science 225:925-927.

McDowell-Boyer, J.R. Hunt, and N. Sitar. 1986. Particle Transport Through Porous Media. Water Resources Research 22:1901-1921.

Moore, J.W. and S. Ramamoorthy. 1984. Heavy Metals in Natural Waters. Springer-Verlag, New York, 268 pp.

Morel, F.M.M. 1983. Principles of Aquatic Chemistry. Wiley Interscience, New York.

Murarka, I.P. and D.A. McIntosh. 1987. Solid-Waste Environmental Studies (SWES): Description, Status, and Available Results. EPRI EA-5322-SR. Electric Power Research Institute, Palo Alto, CA.

Nordstrom, D.K. and J.L. Munoz. 1985. Geochemical Thermodynamics. Benjamin/Cummings Publishing, Menlo Park, CA, 477 pp.

Palmer, C. D., W. Fish, and J.F. Keely. 1988. Inorganic Contaminants: Recognizing the Problem. In: Proc. Second Nat. Outdcmr Action Conf. on Aquifer Restoration, Ground Water Monitoring, and Geophysical Methods, National Water Well Association, Dublin, OH, pp. 555-579.

Parkhurst, D.L., D.C. Thorstenson, and L.N. Plummer. 1980. PHREEQ — A Computer Program for Geochemical Calculations. U.S. Geological Survey Water-Resources Investigations Report 76-13, 81 pp.

Parkhurst, D.L., L.N. Plummer, and D.C. Thorstenson. 1982. BALANCE-A Computer Program for Calculating Mass Transfer for Geochemical Reactions in Ground Water. U.S. Geological Survey Water-Resources Investigations Report 82-14 (NTIS PB82-255902), 29 pp.

Plummer, D.L. and W. Back. 1980. The Mass Balance Approach: Application to Interpreting the Chemical Evolution of Hydrologic Systems. Am. J. Science 280:130-142.

Plummer, L.N., B.F. Jones, and A.H. Truesdell. 1976. WATEQF — A FORTRAN IV Version of WATEQ, a Computer program for Calculating Chemical Equilibrium of Natural Waters. U.S. Geological Survey Water-Resources Investigations Report 75-61, 73pp.

Rees, T.F. 1987. A Review of Light-Scattering Techniques for the Study of Colloids in Natural Waters. J. Contaminant Hydrology 1:431-439.

Reichenbcrg, D. 1966. Ion Exchange Selectivity. In: Ion Exchange and Solvent Extraction, Vol. 1, J.A Marinsky (ed.), Marcel Dekker, New York, pp. 227-276.

Schindler, P.W. 1981. Surface Complexes at Oxide-Water Interfaces. In: Adsorption of Inorganic at Solid-Liquid Interfaces, M.A. Anderson and A.J. Rubin (eds.), Ann Arbor Science, Ann Arbor, MI, pp. 1-49.

Schindler, P.W. and W. Stumm. 1987. The Surface Chemistry of Oxides, Hydroxides, and Oxide Minerals. In: Aquatic Surface Chemistry, W. Stumm (ed.), John Wiley & Sons, New York, pp. 83-110.

Sholkovitz, E.R. 1985. Redox-related Geochemistry in Lakes: Alkali Metals, Alkaline Earth Metals, and Cesium-137, In: Chemical Processes in Lakes, W. Stumm (ed.), Wiley-Interscience, New York.

Siegel, D.I. 1987. Geochemical Facies and Mineral Dissolution, Bemidji, Minnesota, Research Site. In: U.S. Geological Survey Program on Toxic Waste-Ground-Water Contamination: Proceeding of the Third Technical Meeting, Pensacola, Florida, March 23-27, 1987, B.J. Franks (ed.), U.S. Geological Survey Open-File Report 87-109, pp. C13-C15.

Smith, R.L. and A.E. Marten. 1976. Critical Stability Constants. Plenum, New York.

Sposito, G. 1984. The Surface Chemistry of Soils. Oxford University Press, New York.

Sposito, G. 1986. Sorption of Trace Metals by Humic Materials in Soils and Natural Waters. CRC Critical Reviews in Environmental Control 16:193-229.

Stone, A.T. 1986. Adsorption of Organic Reductants and Subsequent Electron Transfer on Metal Oxide Surfaces. In: Geochemical Processes at Mineral Surfaces, J.A. Davis and K.F. Hayes (eds.s), ACS Symp. Series 323, American Chemical Society, Washington, DC, pp. 446-461.

Stumm, W. and J.J. Morgan. 1981. Aquatic Chemistry, 2nd ed. Wiley Interscience, New York.

Stumm, W., H. Hohl, F. Dalang. 1976. Interaction of Metal Ions with Hydrous Oxide Surfaces. Croat. Chem. Acts. 48(4):491-504.

Truesdell, A.H. and B.F. Jones. 1974. WATEQ, A Computer Program for Calculating Chemical Equilibria of Natural Waters. J. Research U.S. Geological Survey 2:233-248.

Vanselow, A.P. 1932. Equilibria of the Base Exchange Reactions of Bentonites, Permutites, Soil Colloids and Zeolites. Soil Science 33:95-113.

Voudrias, E.A. and M. Reinhard. 1986. Abiotic Organic Reactions at Mineral Surfaces. In: Geochemical Processes at Mineral Surfaces, J.A. Davis and K.F. Hayes (eds.), ACS Symp. Series 323, American Chemical Society, Washington, DC, pp. 462-486.

Westall, J.C. and H. Hohl. 1980. A Comparison of Electrostatic Models for the Oxide/Solution Interface. Advances Coll. Interface Sci. 12(2):265-294.

Wolery, T.J. 1979. Calculation of Chemical Equilibrium Between Aqueous Solutions and Minerals: The EQ3/6 Software Package. Report UCRL 52658. Lawrence Livermore National Laboratory, Livermore, CA.

Wolery, P.J. 1983. EQ3NR, a Computer Program for Geochemical Aqueous Speciation-Volubility Calculations. Report UCRL 53414. Lawrence Livermore National Laboratory, Livermore CA.

Yeh, G.T. and V.S. Tripathi. 1989. A Critical Evaluation of Recent Developments in Hydrogeochemical Transport Models of Reactive Multichemical Components. Water Resources Research 25:93-108.

# Chapter 13

# Characterization of Subsurface Degradation Processes

J. Michael Henson

When chemical constituents enter the subsurface environment, they are subjected to physical, chemical, and biological processes that ultimately determine their fate and transport characteristics. Knowledge of the degradation processes that determine the fate of organic compounds in the subsurface can be used to guide remediation efforts at sites that have been affected. The physical processes that control the transport of constituents in the subsurface are discussed in previous chapters, This chapter describes biological and nonbiological processes that may control the fate of organic chemicals once they have entered the subsurface. An understanding of these principles will aid in the efficient and cost-effective remediation of releases of organic constituents. Objectives of this chapter are to:

- Present information about abiotic degradation processes.
- Present information about biological degradation processes.
- Provide a basis for site evaluation to determine the potential for biological remediation.
- Build the foundation for the discussion of bioremediation of soils (Section 15.2.2) and ground water (Section 16.3).

This chapter discusses two classes of transformations that may occur in the subsurface-abiotic and biologic transformation. Abiotic reactions are those reactions that do not involve metabolically active organisms, a product of a living cell, or a product of a previously living organism. Some examples of products of cells are extracellular enzymes, hemoprotein, iron porphyrins, cytochromes, flavins, and reduced pyridine nucleotides.

## 13.1 Abiotic Transformation Reactions

Hydrolysis, substitution, elimination, and oxidation-reduction are the abiotic reactions that will be discussed in this chapter. These reactions produce a variety of end-products whose presence may play a role in decisions made to select compounds for the remedial investigation phase. The results of an abiotic reaction may enhance the biological degradability of a compound and provide possible treatment of the parent compound. Dragun (1988) provides an excellent presentation of abiotic reactions.

### *13.1.1 Hydrolysis*

Hydrolysis reactions are those reactions where an organic chemical reacts with either water or a hydroxide ion to produce an alcohol. The following equations represent these reactions:

$$\text{R-X} + \text{H}_2\text{O} \longrightarrow \text{R-OH} + \text{H}^+ + \text{X}$$

$$\text{R-X} + \text{OH} \longrightarrow \text{R-OH} + \text{X}$$

In these reactions, either $H_2O$ or OH act as a nucleophile and attack the electrophile, RX, to displace the leaving group, X. This type of reaction is referred to as a nucleophilic displacement reaction and in this example results in the formation of a daughter product that is an alcohol. For a more detailed discussion of this nucleophilic displacement reaction mechanism, see Dragun (1988). The rate of hydrolysis reactions is typically first order with respect to the concentration of the compound. The rate of a first-order reaction increases as the concentration of the organic compound increases. The first-order rate constant k can be calculated as:

$$k = (2.303/t)\ \log[C_0/(C_o - C_t)]$$

where t is time, $C_0$ is initial concentration, and $C_t$ is concentration at t.

The time required for half of the concentration of the compound to degrade is known as the half-life, $t_{½}$, and is calculated as:

$$t_{½} = 0.693/k$$

Some examples of hydrolysis half-lives for some organic compounds are presented in Table 13-1. A more extensive listing of hydrolysis half-lives can be found in Dragun (1988).

The rates of hydrolysis vary from compound to compound and can be on the order of hours to years. The rates of hydrolysis also indicate the susceptibility of the compounds to hydrolysis. Some examples of organic chemicals that are subject to hydrolysis are alkyl halides, carbamates, chlorinated amides, esters, and epoxides. Examples of chemicals

*Table 13-1. Selected Hydrolysis Half-Lives for a Variety of Organic Compounds*

| *Organic Compound* | *Hydrolysis Half-Life (pH = 7)* |
|---|---|
| *Atrazine* | *2.5 hours* |
| *Chloroethane* | *38 days* |
| *Chloromethane* | *339 days* |
| *Diazinon* | *9.5 days (pH = 6)* |
| *Dichloromethane* | *704 years* |
| *Epoxyethane* | *12 days* |
| *Ethyl acetate* | *136 days (pH = 6)* |
| *Iodoethane* | *49 days* |
| *Malathion* | *8.1 days (pH = 6)* |
| *Methyl parathion* | *10.9 days (pH = 6)* |
| *Parathion* | *17 days (pH = 6)* |
| *Tetrachloromethane* | *7000 years* |
| *Trichloromethane* | *3500 years* |
| *Trimethylphosphate* | *1.2 years* |

that are more resistant to hydrolysis are aldehydes, alkanes, alkenes, and compounds with carboxy - or nitro-substituents.

Once an organic compound enters the subsurface, environmental factors can decrease or increase the hydrolysis half-life that might be projected from the results of a laboratory evaluation. One effect that soil can have on the hydrolysis half-life is on localized pH differences. The pH at the surface of the soil particles can be very different from the overall soil pH. These localized effects may alter the half-life by enhancing or inhibiting the hydrolysis reaction. Another effect of soil on half-life results from metal ions that are present as normal components of the soil. These metals can serve as catalysts for organic reactions. A third environmental factor is adsorption of the organic compound to the soil particles, which can affect the rate of hydrolysis reactions. By adsorbing to the soil particle, the compound is in effect removed from the water. Other factors such as soil water content and the type of soil matrix also can affect the rate of hydrolysis.

### *13.1.2 Substitution*

Hydrolysis reactions are classified as a type of substitution reaction but they are presented first because of the predominance of water, which causes the reactions to occur. Other chemicals in the subsurface can cause substitution reactions to occur. An example of a substitution reaction involves hydrogen sulfide acting as the nucleophilic agent to attack organic compounds, which result in the production of sulfur-containing compounds.

### *13.1.3 Elimination*

Elimination reactions cause the loss of two adjacent groups from within the molecule resulting in the formation of a double bond. The reaction occurs as:

$$R\text{-}CHX_1\text{-}CH_2X_2 \longrightarrow R\text{-}CH{=}CH_2 + X_1 + X_2$$

One example of an elimination reaction is the formation of 1,1 -dichloroethene (1,1-DCE) from 1,1,1-trichloroethane (1,1,1-TCA). An additional formation product of an abiotic reaction was the detection of acetic acid formed as a result of substitution. The ratio of acetic acid to 1, 1-DCE was about 3:1 (Cline et al., 1988). Elimination also can result in the formation of bromoethene from 1,2-dibromoethane and bromopropene from l,2-dibromopropane (Dragun, 1988).

### *13.1.4 Oxidation-Reduction*

Oxidation is the net removal of electrons from an organic compound, while reduction is the net gain of electrons by an organic compound. These reactions are coupled by the transfer of electrons from one compound to another. The oxidation-reduction couples in soil systems are complex and multiple. In many instances, if a biological response to an organic compound occurs, the biological system will tend to become predominant. Inorganic redox reactions are discussed further in Section 12.1.3.

Abiotic reactions may occur in the subsurface by a variety of mechanisms and at varying rates. The use of abiotic reactions as a remediation technology has not received a lot of attention, but may provide an alternative treatment in some instances. Abiotic reactions may occur in conjunction with biological reactions and make some compounds more susceptible to biodegradation. Abiotic reactions may not always provide extensive treatment of the organic compound but the treatment that does occur may produce a compound of less environmental concern.

## 13.2 Microbiological Transformations in the Subsurface

Microbiological transformations are the second class of processes that have an impact on the fate of organic compounds once they enter the subsurface. This class of processes can result in either partial or complete degradation of the organic compounds to detoxify or remove them from the subsurface. The knowledge of biological responses to various organic compounds can be utilized during the site investigation process to collect data that will aid in evaluating potential remediation alternatives. These remediation alternatives can include biological remediation.

When addressing biological transformations, biodegradation is typically used to mean complete degradation. However, biodegradation specifically refers to the biological transformation of an organic compound without regard to the extent of transformation. Mineralization specifically refers to the conversion of an organic compound to carbon dioxide (or methane in anaerobic environments), water, and a halogen atom, if the parent compound was halogenated.

Knowledge of biological responses to organic compounds that may occur under different microbial growth conditions provides an understanding of the metabolic potential by which microorganisms may transform these compounds. For example, if partial degradation of an organic compound occurs, the daughter products formed may or may not be of environmental concern. The observation of microbial intermediates of metabolism indicates that a biological response to the parent compounds has occurred and that the potential for site remediation through biological processes exists.

The use of microorganisms for remediation of sites affected with organic compounds is gaining increasing interest. This process of bioremediation requires an integrated approach involving the disciplines of microbiology, hydrogeology, and engineering. The relationship of these three disciplines is analogous to a "three-legged stool," in that if one of the legs is weak, the stool cannot support much weight. These three disciplines also must be augmented with an awareness of the principles of the physical-chemical interactions that are the subject of previous chapters, and an understanding of the regulatory requirements in which the application of bioremediation will take place. This section will provide a basic understanding of the principles of microbial ecology as related to the subsurface. This understanding can aid in the evaluating of sites affected with organic compounds and provide a basis for the following chapters where examples of bioremediation will be presented.

### *13.2.1 Microbial Ecology of the Subsurface*

Although it is now known that significant numbers of microorganisms are distributed throughout the subsurface (Back, 1989; Ghiorse and Wilson, 1988), it was once suggested that numbers of microorganisms in soil decreased with depth (Waksman, 1916). More recent investigations, however, routinely detect microorganisms in aquifers. These investigations include aquifers not known to have been affected with organic compounds and aquifers that have received inputs of organic compounds.

The development of techniques to investigate water table aquifers was instrumental to the elucidation of the microbial ecology of the subsurface. McNabb and Mallard (1984) described sampling techniques designed to prevent the microbial contamination of samples retrieved from the terrestrial subsurface. These techniques rely on the collection of cores from the depth to be investigated. After collection, the outermost layer can be removed in the field with alcohol-sterilized devices designed to strip away the soils that were in contact with drilling equipment. These techniques produce a subcore of the original core in an aseptic manner. Subcores can be obtained in the laboratory by a variety of mechanisms, as long as aseptic techniques are used. For field or laboratory conditions, the subcore can be collected under anaerobic (Beeman and Suflita, 1987) as well as aerobic conditions.

The collection of subsurface samples using aseptic techniques to prevent intrusion of microorganisms not representative of the subsurface has yielded considerable information about the microbial ecology of the subsurface. For example, Wilson et al. (1983) and Balkwill and Ghiorse (1985) reported the presence of between 1 and 10 million microorganisms per gram of sediment using the Acridine Orange Direct Count (AODC) staining technique to count the microorganisms. The same authors, using a plate count assay to count viable microorganisms, detected between 200,000 and 2.5 million microorganisms per gram of sediment in two aquifers that were not known to have received input of organic compounds. Similar ranges of counts for microorganisms for shallow aquifers not receiving organic chemicals arc shown in Table 13-2.

Beeman and Suflita (1987) reported a range of 11 to 17x $10^6$ cells (g dry wgt) measured by AODC in a sand aquifer receiving landfill leachate in Norman, Oklahoma. Similar ranges of microbial counts by AODC were observed by Erlich et al. (1983) and Webster et al. (1985) for two different aquifers that were affected with creosote compounds.

The results of these investigations indicate that the terrestrial subsurface whether pristine or not is populated by microorganisms. These numbers of microorganisms are relatively high and were detected in a variety of geologic environments and depths. Analysis of subsurface samples indicates that the microorganisms are predominantly attached to the subsurface soil particles (Harvey et al., 1984). Evidence also is accumulating that even deeper geologic environments are inhabited by microorganisms (Updegraff, 1982).

Biochemical diversity of microorganisms present in the subsurface is evidenced by the variety of organic compounds reported to be metabolized. Petroleum hydrocarbons, including fuels, creosote constituents, and products of coal gasification, are reported to be substrates for subsurface microorganisms under a variety of growth conditions. Table 13-3 presents examples of organic compounds metabolized by subsurface microorganisms.

***Table 13-2. Microbial Cell Counts for Selected Aquifers That Were Not Receiving Known Inputs of Organic Compounds***

| *Study Site* | *Aquifer Type* | *Sample Depth (m)* | *Total Count x $10^6$ Cells g Dry Wgt* | *References* |
|---|---|---|---|---|
| *Lula, OK* | *Sand and Gravel* | *5* | *3.8 to 9.3* | *Balkwill and Ghiorse, 1985;*<br>*Wilson, et al. 1983* |
| *Pickett, OK* | *Sand* | *5.5* | *5.2* | *Balkwill and Ghiorse, 1985*<br>*Ghiorse and Balkwill, 1985* |
| *Fort Polk, LA* | *Loamy Clay* | *5* | *9.8* | *Ghiorse and Balkwill, 1983* |
| *Dayton, OH* | *Gravel* | *10-12* | *0.036 to 0.06* | *Ventullo and Larson, 1985* |
| *Alberta, Can.* | *Marmot Basin* | *1.5* | *0.05 to 2.5* | *Ladd et al., 1982* |

### 13.2.2 Relationship of Environmental Factors to Biodegradation

Microorganisms require a suitable set of environmental factors in order to grow. These factors include the chemical and physical parameters of pH, available water or osmotic pressure, temperature, and absence of toxic conditions.

The pH of the environment is an easily measured parameter and indicates the potential for microbial activity. Many microoganisms grow best in the pH range of 6 to 8. Microbial life at extremes of pH does occur and, therefore, a pH outside of the 6 to 8 range does not exclude microbial growth. Growth of microorganisms can raise or lower the pH by producing end-products that affect pH or by removing the parent compounds, thus, affecting the pH. The measurement of pH in ground water could indicate the potential for microorganisms to grow in the aquifer.

Temperature generally affects microbial growth in that an increase in temperature results in an increase in microbiological growth. Microorganisms have lower, upper, and optimum temperature limits for growth. Many microorganisms in the soil have an optimum temperature for growth between 10° and 30°C. Temperatures of ground waters within the United States are within this range (Dragun, 1988).

Microorganisms require water for active growth. The availability of water depends on the number of molecules present in the solution. An increase in the number of molecules, relative to the number of molecules within the microbial cells, results in the movement of water from the cell into the surrounding environment as a result of osmosis. The opposite effect occurs when the number of molecules outside the microbial cell is less than the number inside the microbial cell. The soil moisture content is sometimes critical to the growth of microorganisms. If the moisture content is near saturation, transfer of oxygen may become a growth-limiting factor. If the soil is dry, growth of the microorganisms will be very limited.

### 13.2.3 Microbial Metabolism

The ability of communities of microorganisms to metabolize many types of organic compounds including synthetic organic compounds is well documented (Alexander, 1981; Gibson, 1984). A number of these organic compounds are utilized by microorganisms as a source of carbon and energy. The degradation of the compounds may not occur at the initial time of release to the environment. A period of time may elapse before an increase in the rate of degradation is observed. This period of time is referred to as an adaptation or acclimation period. The adaptation period may vary with the compound and the environmental conditions into which the compound is released. For example, under anaerobic conditions, adaptation periods may be as long as several months. Once the adaptation occurs, however, the rate of degradation becomes a function of the processes controlling the availability of nutrients to the microorganisms and not of an intrinsic metabolic property of the microorganisms. In addition, once the microbial community adapts to a particular organic compound or compounds, the compound or compounds can continue to be added without re-adaptation. The microbial community, thus, becomes enriched in members that can metabolize the organic compounds.

An additional opportunity for microbial degradation is through a process of nongrowth metabolism. In this process, the microorganisms do not use the organic compound as a source of carbon and energy, which results in growth. Instead, the microorganisms cometabolize a substance that cannot be utilized for growth in the presence of a compound that can be utilized for growth. The cometabolized compound is often transformed into an intermediate that can undergo transformation by other microorganisms. A specific example, to be discussed in more detail later, is the degradation of trichloroethene and dichloroethene by microorganisms that are growing on methane and fortuitously react with the halogenated compounds.

The ability of microorganisms to degrade organic compounds depends on the presence of a terminal electron acceptor (TEA), as well as other nutrients. The TEA receives electrons from a series of oxidation-reduction reactions within the cell that generate energy allowing the microorganism to grow. Some microorganisms can use several TEAs whereas other microorganisms can use only one. If more than one TEA is present when an organic compound enters the environment, the one that results in the highest energy transfer will be used first. Next, the TEA with the second highest energy transfer will bc used, and so on until either the organic compound is removed or the TEAs have been consumed.

*Table 13-3. Representative Examples of the Diversity of Organic Compounds Metabolized by Subsurface Microorganisms*

| *Organic Compound Metabolized* | *Growth Conditions* | *References* |
|---|---|---|
| *Petroleum Hydrocarbons* | *Aerobic* | *Ehrlich, et al., 1985; Jamison, et al., 1975; Lee, et al., 1988; Lee and Ward, 1985; Raymond, et al., 1976; Wilson and Ward, 1987; Wilson, et al., 1985b* |
| *Hydrocarbons* | *Anaerobic* | *Grbic-Galic and Vogel, 1987; Vogel and Grbic-Galic, 1986; Wilson and Rees, 1985* |
| *Creosote/Coal Gas Compounds* | *Aerobic* | *Humenick, et al., 1982; McGinnis, et al., 1988; Wilson, et al., 1985a* |
| *Creosote Compounds* | *Anaerobic* | *Erlich, et al., 1983; Smolenski and Suflita, 1987* |

| | | | | |
|---|---|---|---|---|
| *Dayton, OH* | *Gravel* | *10-12* | *0.036 to 0.06* | *Ventullo and Larson, 1985* |
| *Alberta, Can.* | *Marmot Basin* | *1.5* | *0.05 to 2.5* | *Ladd et al., 1982* |

Table 13-4 presents the relative energy charge associated with the consumption of various TEAs. The succession of metabolic events will proceed from the reactions with TEAs that can transfer the most energy, which are denoted by the most negative values in Table 13-4. The succession also is related to the toxicity of TEAs for groups of bacteria. For example, methanogenic bacteria are inhibited by oxygen; therefore, the development of active methanogenesis usually does not occur until oxygen is removed from the environment and reducing conditions are established.

Aerobic respiration is the process of consuming organic compounds with oxygen serving as the TEA. The end-product of the respiration of oxygen is water. The degradation of hydrocarbons also requires oxygen as a cosubstrate where the oxygen is inserted into the hydrocarbon molecule.

Once the metabolic demand for oxygen exceeds the rate of supply, the anoxic conditions that are established allow other TEAs to be utilized. The next TEA that, if present, would be used is nitrate. The respiration of nitrate is referred to as denitrification and results in the production of nitrogen gas (Knowles, 1982). The transfer of energy is similar to that of the respiration of oxygen. Many of the organisms that use nitrate as an electron acceptor also use oxygen so that acclimation of a new population of microorganisms may not be required.

Once the nitrate has been consumed and the oxidation-reduction state becomes reducing, the respiration of sulfate can begin as a process known as sulfate reduction (Postgate, 1979). Sulfate reduction results in the production of hydrogen sulfide, which can be corrosive to equipment and potentially toxic to humans. Sulfate reduction does not yield as much energy, only about one-fourth, as does the respiration of nitrate or oxygen.

If nitrate is present in a reducing environment, its respiration does not result in the production of nitrogen gas; instead, ammonia is produced (Caskey and Tiedje, 1980). The respiration of nitrate under reducing conditions does not transfer as much energy as the respiration of oxygen.

As the conditions become more reducing and alternative TEAs are consumed, the respiration of carbonate will result in the production of methane. The microorganisms that carry out this reaction are known as methanogenic bacteria. The energy transferred during methane production is about one-fourth that of the respiration of oxygen or nitrate.

***Table 13-4.*** ***Comparison of Free Energy Values for Metabolism of Glucose in the Presence of Various Electron Acceptors***

| Equation | kcal/Electron Equivalent |
|---|---|
| Glucose + Nitrite - - -> $CO_2 + H_2O + N_2$ | -32.3 |
| Glucose + Oxygen - - -> $CO_2 + H_2O$ | -28.7 |
| Glucose + Nitrate - - -> $CO_2 + H_2O$ + Nitrite | -19.4 |
| Glucose + Sulfate- - -> $CO_2 + H_2O$ + Sulfide | -4.9 |
| Glucose + $CO_2$- - -> $CO_2 + H_2O$ + Methane | -4.3 |
| Glucose + Glucose- - -> $CO_2$ + Ethanol | -2.4 |

*Based on data from McCarty, 1975*

The ability of microorganisms to carry out a variety of respirations provides the opportunity to collect data during the site investigation phase that indicate whether a microbiological response to organic compounds has occurred. If accurate measurements of dissolved oxygen (DO) in ground water indicate that oxygen is present outside a plume of organic compounds and DO is not detected within the plume, then a biological response may have occurred to consume the oxygen. If methane or another of the respiratory end-products is detected within the plume, the results suggest that a biological response has occurred and that reducing conditions may exist.

In addition, the range of metabolic capabilities of microorganisms extends beyond the respiration of oxygen. Nitrate is more water soluble than oxygen and may be less costly to use in the treatment of some affected aquifers. Reducing conditions allow some biological transformations to occur that do not occur under oxidizing conditions. One example of this type of biological transformation is reductive dechlorination. This microbiological process removes chlorines from chlorinated compounds (discussed in Section 13.3.2).

### *13.2.4 Biological Reaction Kinetics*

The rate at which microorganisms can remove organic compounds from the subsurface can be expressed mathematically to approximate the time required for remediation. The first-order rate constant is based on the observation that as the concentration of the organic compound increases, the rate of degradation increases. The first-order rate constant k is calculated as:

$$k = (2.303/t) \log[C_0/(C_0 - C_t)]$$

where t is time, $C_0$ is initial concentration, and $C_t$ is concentration at t. The time required for half of the concentration of the compound to degrade is known as the half-life, $t_{1/2}$, and is calculated as follows:

$$t_{1/2} = 0.693/k$$

However, metabolism in microorganisms occurs via enzymes that become saturated; the substrates are degraded when the concentration of the substrate continues to increase. Once the enzymes become saturated, the rate of degradation cannot increase and the degradation rate curve becomes hyperbolic.

The use of the first-order rate kinetics provides a general expression of the rate of biodegradation for many compounds. Dragun (1988) provides a compilation of first-order degradation rates that should not be used without comparing the environments from which these samples were taken. A direct extrapolation of results obtained from one environment to another environment is typically not useful.

## 13.3 Bioremediation of Organic Compounds in the Subsurface

### 13.3.1 General Considerations

The basic premises of microbial ecology are related to bioremediation in that many organic compounds can be used by microorganisms as a source of carbon and energy. Many of the compounds that are considered hazardous can be degraded in the subsurface if the concentrations are not toxic to the microorganisms and the appropriate environmental parameters can be established. Bioremediation is based on the understanding of the carbon cycle and extrapolation of compound mineralization in other environments to the subsurface. Environmental factors, such as pH, oxidation-reduction potential, and temperature, may play a role in determining the potential for bioremediation. However, the rate at which nutrients, especially a TEA, can be delivered to the microorganisms may determine whether bioremediation is feasible. There are several reviews that provide detailed discussions of bioremediation (Lee et al., 1988; Thomas and Ward, 1989; Wilson et al., 1986; and Wilson and Ward, 1987).

Certain information is required before design of the bioremediation system can begin. An assessment of the site to evaluate history, geology, and hydrology can provide information valuable for bioremediation design. The delivery of nutrients to subsurface microorganisms for in situ remediation is dependent on the site hydrology. Sites with low permeability, such as those with clays, may not allow the delivery of nutrients in an efficient manner.

A thorough laboratory assessment of the microbiology also provides information to indicate whether bioremediation is an appropriate treatment technology. Some components of this assessment are:

- Evaluate the presence of requisite microorganisms.
- Assess potential toxicity to the microorganisms.
- Evaluate nutrient requirements to enhance degradation activity.
- Evaluate the compatibility of the site geochemistry with the nutrient solution proposed for addition.

Requisite microorganisms are the ones that are capable of degrading the organic compounds present at the site. For many sites, these microorganisms are naturally occurring and just need some nutrients to stimulate their growth. The presence of these microorganisms at the site is evaluated in samples representative of the environment to be remediatcd. If the remediation is an in situ aquifer remediation, then the samples should be collected from the aquifer. The microorganisms are predominantly attached to the soils; therefore, samples of the soils below the water table should be collected. Several methods exist for collecting the samples. Principles for collection are discussed in McNabb and Mallard (1984).

Microorganisms present in the samples should be enumerated in a manner to indicate the presence of viable microorganisms. Staining techniques exist, such as the AODC, but this technique is limited because it does not indicate the viability of the microorganisms. The results of viable counts suggest the environment that was sampled was not so toxic as to completely inhibit the presence of microorganisms. Techniques such as standard plate counts can be used to detect the number of general microorganisms present. Plate counts using a microbial medium containing the compound of interest also can be used to enumerate the bacteria present in the sample capable of growth on that compound. The numbers can be compared before and after treatment to assess whether the treatment resulted in an increase in the number of microbes capable of growth on the compound of interest. An increase in the observed number of bacteria would suggest an effective process.

The nutrients required to enhance microbial growth are assessed primarily on the nitrogen and phosphorous requirements of the microorganisms. However, the microorganisms may require other nutrients such as potassium, magnesium, manganese, and iron. The site's geochemistry may provide many of these necessary nutrients. The nutrient solution selected should be compatible with the geochemistry of the site to prevent possible precipitation of minerals, which might decrease the permeability of the aquifer. In addition, an evaluation of the compatibility of the TEA chosen with the site's geochemistry should indicate whether undesired reactions can occur.

The laboratory assessment for the removal of the parent compound can measure the disappearance of the compound, the rate of removal, and the production of daughter products. The rate of rcmoved usually reflects the laboratory conditions, however, and cannot be extrapolated directly to the rate of removal that would be expected in the field. Disappearance of the parent compound may, by itself, not always indicate that mineralization has occurred.

### 13.3.2 Compounds Appropriate to Consider for Bioremediation

During the initial evaluations for bioremediation of a site, existing information should be considered. Information about the volubility of the compound to be degraded indicates the potential availability of the compound to the microorganisms. Previous evaluations of the biodegradation of the compound often can be found in the scientific literature. These studies can provide information about the inherent degradability of the compound as well as the potential products of degradation. Information about the environmental factors that upon stimulation were critical to degradation also may be available. Dragun (1988), for example, contains a list of organic compounds and provides information about the conditions used in the evaluations to develop the rates of biodegradation presented.

In general, hydrocarbons are good candidates for bioremediation. The review paper by Atlas (1981) and the books edited by Gibson (1984) and Atlas (1984) provide an overview of the microbiological degradation of petroleum hydrocarbons. Many components of fuel hydrocarbons, such as benzene, toluene, and xylenes are degraded by a variety of microorganisms. Creosote, which is a by-product of the production of coke from coal, is composed of a number of high molecular weight hydrocarbons referred to as polycyclic aromatic hydrocarbons (PAHs). This complex mixture of hydrocarbons has components that are biodegradable with the degradation rate decreasing as the molecular weight of the hydrocarbons increases. Generally, the PAHs with three rings or less degrade at a greater rate than do the more complex PAHS.

A variety of organic compounds can biodegrade in the subsurface if the environmental conditions are appropriate. For example, alcohols, glycols, ketones, phenols, chlorinated phenols, and other organic compounds have the potential to biodegrade. Some factors that may enhance biodegradation are the water volubility and molecular weight of the compounds. Increasing volubility enhances the potential for biodegradation assuming the concentration does not reach levels toxic to the microorganisms. Increasing molecular weight or branching of organic compounds may tend to slow the rate of degradation.

Halogenated compounds generally tend to persist in aerobic environments, but continued research is providing evidence that biological alternatives to these compounds may exist. Under anaerobic conditions, several chlorinated compounds have been shown to undergo transformation. For example, tetrachloroethene (PCE) has been shown to be dechlorinated under environmental conditions that support the growth of anaerobic bacteria. This process is known as reductive dechlorination and is given as follows:

$$\text{PCE} \longrightarrow \text{TCE} + \text{Cl} \longrightarrow \text{DCE} + \text{Cl} \longrightarrow \text{CE} + \text{Cl} \longrightarrow \text{CO}_2 + \text{Cl}$$

The compounds produced are trichloroethene (TCE), the isomers of dichloroethene (DCE), and chloroethene (CE). The removal of the chlorine atoms enhances the potential for aerobic microorganisms to degrade the daughter products. DCE has a greater potential for aerobic degradation than does PCE.

A method to enhance the aerobic degradation of DCE is to create an environment for the growth of methane-utilizing bacteria. The addition of methane to soils and aquifers typically results in the growth of these bacteria within several days to a few weeks. These bacteria have been shown to degrade a variety of halogenated compounds including TCE, *cis-DCE, trans-DCE,* chloroform, dichloromethane, and 1,2-dichloroethane (Henson et al., 1989). It seems plausible that the series of reaction processes that enhances anaerobic reductive dechlorination of highly chlorinated compounds and yields the less chlorinated compounds that can undergo aerobic degradation may be a good mechanism to remove compounds from the subsurface environment. The value for this treatment process is further enhanced when the increased sorptive capacity of the higher chlorinated compounds is considered. Utilizing the microorganisms in an in situ treatment process can significantly expedite remediation.

Bioremediation of other halogenated compounds such as polychlorinated biphenyls (PCBs) also can be considered. The reductive dechlorination of PCBS was detected in the environment (Brown et al., 1987) and confirmed in the laboratory (Quensen et al., 1988). The anaerobic reductive dechlorination process removes chlorines from the PCBS, thus reducing potential toxicity and enhancing the aerobic degradability of the compounds. Anaerobic biological treatment followed by aerobic biological treatment is a technology that could remove these chlorinated compounds from the environment in a cost-effective and environmentally acceptable manner.

Bioremediation in the subsurface can remove a variety of organic compounds. The evaluation of the bioremediation process should include observation of the removal of the organic compound(s) in a manner so as to provide a mass balance. In the laboratory, mass balances can be approximated with the use of proper abiotic controls. The use of abiotic controls in the laboratory evaluation cannot be overemphasized. In the field, a mass balance can be approximated with the collection of samples prior to remediation to evaluate the amount of organic compound present. Samples collected subsequent to the initiation of bioremediation can be evaluated relative to the initial concentrations. If the bioremediation effort is succeeding, a reduction in the concentration of the organic compound should be observed. In areas not undergoing bioremediation, the concentration of the organic compound should remain relatively unchanged. If TEAs are added, removal of these compounds also suggests biological activity. The presence of metabolic intermediates also indicates that biological processes are occurring. Other observations, such as adaptation or acclimation or an increase in microbial activity of the compound being degraded, are positive indicators of the enhancement of naturally occurring bacteria to achieve bioremediation.

## 13.4 References

Alexander, M. 1981. Biodegradation of Chemicals of Environmental Concern. Science 211:132-138.

Atlas, R.M. 1981. Microbial Degradation of Petroleum Hydrocarbons: an Environmental Perspective. Appl. Environ. Microbiol. Vol. 45, pp. 180-209.

Atlas, R.M. 1984. Petroleum Microbiology. Macmillan, New York.

Back, W. 1989. Early Concepts of the Role of Microorganisms in Hydrogeology. Ground Water 27:618-622.

Balkwill, D.L. and W.C. Ghiorse. 1985. Characterization of Subsurface Bacteria Associated with Two Shallow Aquifers in Oklahoma. Appl. Environ. Microbiol. 50:560-588.

Beeman, R.E. and J.M. Suflita. 1987. Microbial Ecology of a Shallow Unconfined Ground-water Aquifer Polluted by Municipal Landfill Leachatc. Microb. Ecol. 14:39-54.

Brown, J.F., R.E. Wagner, H. Feng, DL. Bedard, M.J. Brennen, J.C. Carnahan, and R.J. May. 1987. Environmental Dechlorination of PCBS. Environ. Toxicol. Chem. 6579-593, Caskey, W.H. and J.M. Tiedje. 1980. The Reduction of Nitrate to Ammonium by a *Clostridium* sp. Isolated from Soil. J. Gen. Microbiol. 119:217-223.

Cline, P.V., J.J. Delfino, and T. Potter. 1988. Degradation and Advection of 1,1,1-Tricholorethane in the Saturated Zone Containing Residual Solvent. In: Superfund '88, Hazardous Materials Control Research Institute, Silver Spring, MD.

Dragun, J. 1988. The Soil Chemistry of Hazardous Materials. Hazardous Materials Control Research Institute, Silver Spring, MD.

Ehrlich, G.G., E.M. Godsy, D.F. Goerlitz, and M.F. Hult. 1983. Microbial Ecology of a Creosote-Contaminated Aquifer at St, Louis Park, Minnesota. Dev. Ind. Microbiol. 24:235-245.

Ehrlich, G.G., R.A. Schroeder, and P. Martin. 1985. Microbial Populations in a Jet-Fuel Contaminated Shallow Aquifer at Tustin, California. U.S. Geological Survey Open-File Report 85-335.

Genthner, B.R.S., W.A. Price, and H.P. Pritchard. 1989. Anaerobic Degradation of Chloroaromatic Compounds in Aquifer Sediments under a Variety of Enrichment Conditions. Appl. Environ. Microbiol. 55:1466-1471.

Ghiorse, W.C. and D.L. Balkwill. 1983. Enumeration and Morphological Characterization of Bacteria Indigenous to Subsurface Environments. Dev. Ind. Microbiol. 24:213-224.

Ghiorse, W.C. and D.L. Balkwill. 1985. Microbiological Characterization of Subsurface Environments. In: Ground-Water Quality, C.H. Ward, W. Giger, and P.L. McCarty (eds.), John Wiley & Sons, New York, pp. 536-556.

Ghiorse, W.C. and J.T. Wilson. 1988. Microbial Ecology of the Terrestrial Subsurface. Adv. Appl. Microbiol. 33:107-172.

Gibson, D. T. (ed.). 1984. Microbial Degradation of Organic Compounds. Marcel Dekker, New York.

Grbic-Galic, D. and T.E. Vogel. 1987. Transformation of Toluene and Benzene by Mixed Methanogenic Cultures. Appl. Environ. Microbiol, 53:254-260.

Harvey, R.W., R.L. Smith, and L. George. 1984. Effect of Organic Contaminants upon Microbial Distribution and Heterotrophic Uptake in a Cape Cod, Massachusetts Aquifer. Appl. Environ. Microbiol, 48:1197-1202.

Henson, J.M., M.V. Yates, and J.W. Cochran. 1989. Metabolism of Chlorinated Methanes, Ethanes, and Ethylenes by a Mixed Bacterial Culture Growing on Methane. J. Indust. Microbiol. 4:29-35.

Humenick, M.J.H., L.N. Bitton, and C.F. Maddox. 1982. Natural Restoration of Ground Water in UCG. In Situ 6:107-125

Jamison, V.W., R.L. Raymond, and J.O. Hudson. 1975. Biodegradation of High-Octane Gasoline in Groundwater. Dev. Ind. Microbiol. 16:305-312.

Knowles, R. 1982. Denitrification. Microbiol. Rev. 46:43-70.

Ladd, T.I., et al. 1982. Heterotrophic Activity and Biodegradation of Labile and Refractory Compounds by Ground Water and Stream Microbial Populations. Appl. Environ. Microbiol. 44:321-329.

Lee, M.D. and C.H. Ward. 1985. Biological Methods for the Restoration of Contaminated Aquifers. Environ. Toxicol. Chem. 4:721-726.

Lee, M.D., J.M. Thomas, R.C. Borden, P.B. Bedient, J.T. Wilson, and C.H. Ward. 1988. Biorestoration of Aquifers Contaminated with Organic Compounds. CRC Crit. Rev. Environ. Control 18:29-89.

McCarty, P.L. 1975. Energetics of Organic Matter Degradation. In: Water Pollution Microbiology, Vol. 1, R. Mitchell (ed.), Wiley-Interscience, New York, pp. 91-110.

McGinnis, G. D., H. Borazjani, L.K. McFarland, D.F. Pope, and D.A. Strobcl. 1988. Characterization and Laboratory Soil Treatability Studies for Creosote and Pentachlorophenol Sludges and Contaminated Soil. EPA/600/2-88-055 (NTIS PB89-10992O).

McNabb, J.F. and G.E. Mallard. 1984. Microbiological Sampling in the Assessment of Groundwater Pollution. In Groundwater Pollution Microbiology, G. Bitton and C. P. Gerba (eds.), John Wiley & Sons, New York, pp. 235-260.

Postgate, J.R. 1979. The Sulphate-Reducing Bacteria. Cambridge University Press, Cambridge.

Quensen, J.F., J.M. Tiedje, and S.A. Boyd. 1988. Reductive Dechlorination of Polychlorinated Biphenyls by Anaerobic Microorganisms from Sediments. Science 242:752-754.

Raymond, R. L., V.W. Jamison, and J.O. Hudson. 1976. Beneficial Stimulation of Bacterial Activity in Ground Water Containing Petroleum Products. AICE Symposium Series 73:390-404.

Roberts, P. V., L. Semprini, G.D. Hopkins, D. Grbic-Galic, P.L. McCarty, and M. Reinhard. 1989. In-Situ Restoration of Chlorinated Aliphatics by Methanotrophic Bacteria. EPA/600/2-89-033 (NTIS PB89-219992).

Smolenski, W.J. and J.M. Suflita. 1987. Biodegradation of Cresol Isomers in Anoxic Aquifers. Appl. Environ. Microbiol. 53:710-716.

Suflita, J.M., S.A. Gibson, and R.E. Beeman. 1988. Anaerobic Biotransformation of Pollutant Chemicals in Aquifers. J. Ind. Microbiol. 3:179-194.

Thomas, J.M. and C.H. Ward. 1989. In Situ Biorestoration of Organic Contaminants in the Subsurface. Environ. Sci. Technol. 23:760-766.

Updegraff, D.M. 1982. Plugging and Penetration of Petroleum Reservoir Rock by Microorganisms. In: Proc. 1982 Int. Conf. on Microbial Enhancement of Oil Recovery.

Ventullo, R.M. and R.J. Larson, 1985. Metabolic Diversity and Activity of Heterotrophic Bacteria in Ground Water, In Environ. Toxicol. Chem. 4:759-771.

Vogel, T.E. and D. Grbic-Galic. 1986. Incorporation of Oxygen into Toluene and Benzene During Anaerobic Fermentative Transformation. Appl. Environ. Microbiol. 52:200-202.

Waksman, S.A. 1916. Bacterial Numbers in Soil, at Different Depths, and in Different Seasons of the Year. Soil Science 1:363-380.

Webster, J.J., G.J. Hampton, J.T. Wilson, W.C. Ghiorse, and F.R. Leach. 1985. Determination of Microbial Numbers in Subsurface Environments. Ground Water 23:17-25.

Wilson, B.H. and J.F. Rees. 1985. Biotransformation of Gasoline Hydrocarbons in Methanogenic Aquifer Material. In: Proc. NWWA/API Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water-Prevention, Detection and Restoration, National Water Well Association, Dublin, OH, pp. 128-139.

Wilson, J.T. and C.H. Ward. 1987. Opportunities for Bioreclamation of Aquifers Contaminated with Petroleum Hydrocarbons. Dev. Indust. Microbiol. 27:109-116.

Wilson, J.T., J.F. McNabb, D.L. Balkwill, and W.C. Ghiorse. 1983. Enumeration and Characterization of Bacteria Indigenous to a Shallow Water-Table Aquifer. Ground Water 21:134-142.

Wilson, J.T. J.F. McNabb, J.W. Cochran, T.H. Wang, M.B. Tom son, and P.B Bedient. 1985a. Influence of Microbial Adaptation on the Fate of Organic Pollutants in Ground Water. Environ. Toxicol. Chem. 4:721-726.

Wilson, J.T., M.J. Noonan, and J.F. McNabb. 1985b. Biodegradation of Contaminants in the Subsurface. In: Ground-Water Quality, C.H. Ward, W. Giger, and P.L. McCarty, (eds.), John Wiley & Sons, New York, pp. 483-498.

Wilson, J.T., L.E. Leach, M. Henson, and J.N. Jones. 1986. In Situ Biorestoration as a Ground Water Remediation Technique. Ground Water Monitoring Review 6(4):56-64.

# PART III: SOIL AND GROUND-WATER REMEDIATION

## Chapter 14

## Soil and Ground-Water Remediation: Basic Approaches

Ronald C. Sims and Judith L. Sims

Subsurface remediation includes identifying, quantifying, and controlling contaminant source(s); considering cleanup levels required for each medium (air, soil, and ground water) to protect human health and the environment; and selecting treatment technologies based on information obtained concerning source(s) and cleanup levels. The challenge is to effectively relate site characterization activities to selecting the most appropriate remediation technologies for contaminated soils and ground water at hazardous waste sites. Effectively relating these activities with technology selection improves the efficiency, purpose, and results of both site characterization and remediation technique selection. This chapter addresses specific subsurface physical, chemical, and biological processes that have been discussed in previous chapters within the context of(1) site characterization requirements, (2) evaluation and selection of remediation techniques and treatment trains utilizing several techniques, and (3) design of monitoring programs.

There is currently a lack of methods and approaches for evaluating and selecting remedial technologies for site-specific scenarios in the area of subsurface remediation, including soil and ground-water remediation. This chapter presents a rational approach for addressing soil and ground-water remedial technologies, including evaluating and selecting new technologies as they become available to the user community. Specific soil and aquifer remediation techniques, including applications and limitations, also are discussed.

### 14.1 Conceptual Approach to Soil and Ground-Water Remediation

A conceptual framework for soil remediation technique evaluation, selection, and monitoring, based on current information and activities employed at hazardous waste sites is proposed. The conceptual framework is the chemical mass balance, the cornerstone of science and engineering research and industry. The concept of a chemical mass balance is familiar to professionals trained in the physical or life sciences or in engineering. It provides a rational and fundamental basis for asking specific questions and obtaining specific information that is necessary for determining fate and behavior, for evaluating and selecting treatment options, and for monitoring treatment effectiveness at both laboratory-scale and field-scale. A mass balance approach also meets the goal of obtaining quantitative accuracy about the amount of contaminants initially present at an uncontrolled site. While a mass balance, or materials balance, is routinely conducted on aboveground treatment processes (Bailey and Ollis, 1986; Benefield et al., 1982; Corbitt, 1989; Metcalf and Eddy, Inc., 1979), and for ground-water processes (Willis and Yeh, 1987; Wilson et al., 1989), a mass balance approach has generally not been applied to the soil environment or to the subsurface/surface system to link characterization activities and treatment technology selection. The information needed to *con*struct a mass balance for contamination at a site simultaneously addresses site characterization and remediation evaluation and selection.

The conceptual approach for the soil and ground-water subsurface environment at a contaminated site is illustrated in Figure 14-1. The contaminated subsurface is a system generally consisting of two phases (solid and fluid) and five compartments (gas, an inorganic mineral solid compartment an organic matter solid compartment, water, and oil [NAPL]) (Sims et al., 1989). Generally NAPLs are subdivided into two classes: those that are lighter than water (LNAPLs), and those with a density greater than water (DNAPLs). LNAPLs include hydrocarbon fuels, such as gasoline, heating oil, kerosene, jet fuel, and aviation gas. DNAPLs include chlorinated hydrocarbons, such as 1,1,1 -trichloroethane, carbon tetrachloride, chlorophenols, chlorobenzenes, tetrachloroethylene, and polychlorinated biphenyls (PCBs).

Specific subsurface processes concerning water movement, sampling, sorption and reaction, and degradation are discussed in the previous chapters. The processes and terminology described in the previous chapters will be used in this chapter for the discussion of the components of a mass balance and the mass balance approach to evaluation and selection of soil remediation techniques.

Interphase transfer potential for waste constituents among oil (waste or NAPL), water, air, and solid (organic and inorganic) phases of a subsurface system is affected by the relative affinity of waste constituents for each phase shown in Figure 14-1, and may be quantified through calculation of distribution coefficients (Loehr, 1989; Sims et al., 1988; U.S. EPA,

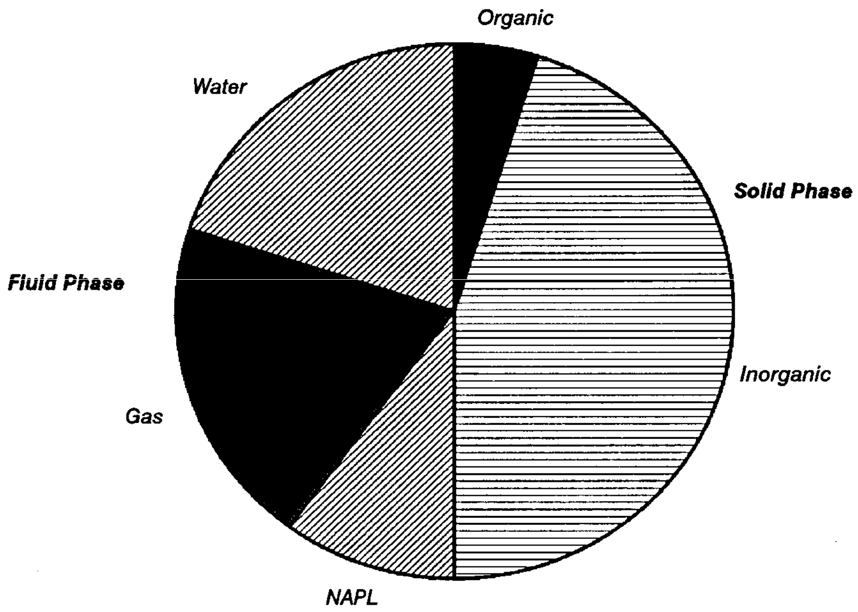


**Figure 14-1. Mass balance conceptual framework for the soil end ground-water subsurface environment at a contaminated site.**

1986). Distribution coefficients are calculated as the ratio of the concentration of a chemical in the soil (or aquifer materials), oil, or gas phases to the concentration of a chemical in the water phase. A waste chemical, depending on its tendency to be associated with each phase, will distribute itself among the phases, and can be quantified in terms of distribution coefficients. Distribution coefficients are available for a variety of chemicals and can be expressed as ratios of the concentrations of a chemical between two phases in the subsurface

$K_d$ = Concentration in solid phase/Concentration in aqueous phase

$K_o$ = Concentration in oil phase/Concentration in aqueous phase

$K_h$ = Concentration in air phase/Concentration in aqueous

When distribution coefficients are not available, they can be estimated using structure-activity relationships (SARs) or can be determined in laboratory tests (Sims et al., 1988). For additional detail concerning these processes, see Chapters 10 and 11.

Distribution coefficients have been used most successfully with organic chemicals. However, since metals distribute among the phases of the subsurface systems described previously, distribution coefficients also may be used, along with multiphase metal speciation information (Sims et al., 1984), to evaluate metal distribution in a contaminated subsurface system. For additional detail concerning these processes see Chapter 12.

Knowledge of migration and distribution of chemicals and chemical intermediates among the phases and compartments of a contaminated subsurface system (illustrated in Figure 14-2) provides fundamental information about the fate and behavior of contaminants, which can be used for selecting and evaluating subsurface remedial techniques. Retardation of the downward transport (leaching potential) and upward transport (volatilization potential) is referred to as immobilization of waste constituents, and has been related to the subsurface organic matter content, especially for hydrophobic chemicals (Nkedi-Kizza et al., 1983), soil moisture (Mahmood, 1989), and presence and concentration of organic solvents (Mahmood and Sims, 1986; Rao et al., 1985).

In summary, subsurface processes described above, combined with information about the movement of fluids as discussed in Chapters 4, 5, and 6 (gases, aqueous phase, and pure product flow) in the unsaturated and saturated zones, provide the inputs into the chemical mass balance that can be used for (1) characterizing a site; (2) assessing the problem of mobility; (3) evaluating treatment techniques; and (4) identi-

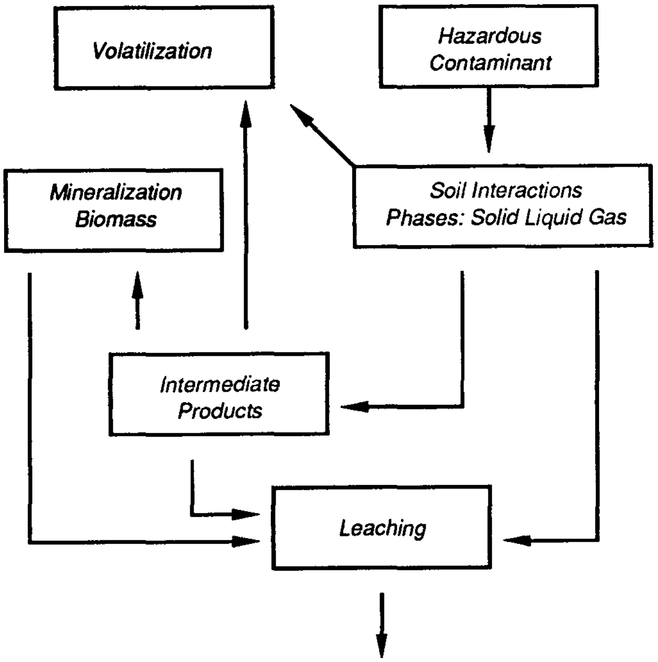


**Figure 14-2. Interphase transfer potential of chemicals in the subsurface (from Sims et al., 1990).**

fying chemicals in specific phases for monitoring treatment effectiveness.

## 14.2 Methodology

Using the chemical mass balance approach, the authors of this Handbook developed a methodology for integrating data collection activities at CERCLA sites to address simultaneous site characterization and remediation technique selection, The proposed methodology consists of four elements: (1) characterization, (2) assessment of the problem, (3) treatment (train) selection, and (4) monitoring treatment performance (Figure 14-3). The first element involves characterization in the context of waste/subsurface/site interactions to address the question, "Where is the contamination and in what form(s) does it exist?" The second element, assessment of the problem, utilizes subsurface fate and behavior information to address the question "Where is the contamination going under the influence of natural processes?" The problem can be define in the context of mobility versus degradation for chemicals at a site. Using mathematical models or other tools, the chemicals can be ranked in order of their relative tendencies to leach, to volatilize, to move in a NAPL phase and to remain in-place under site-specific conditions. Containment and/or treatment options then can be selected that are chemical-specific and that address specific escape and attenuation pathways (third

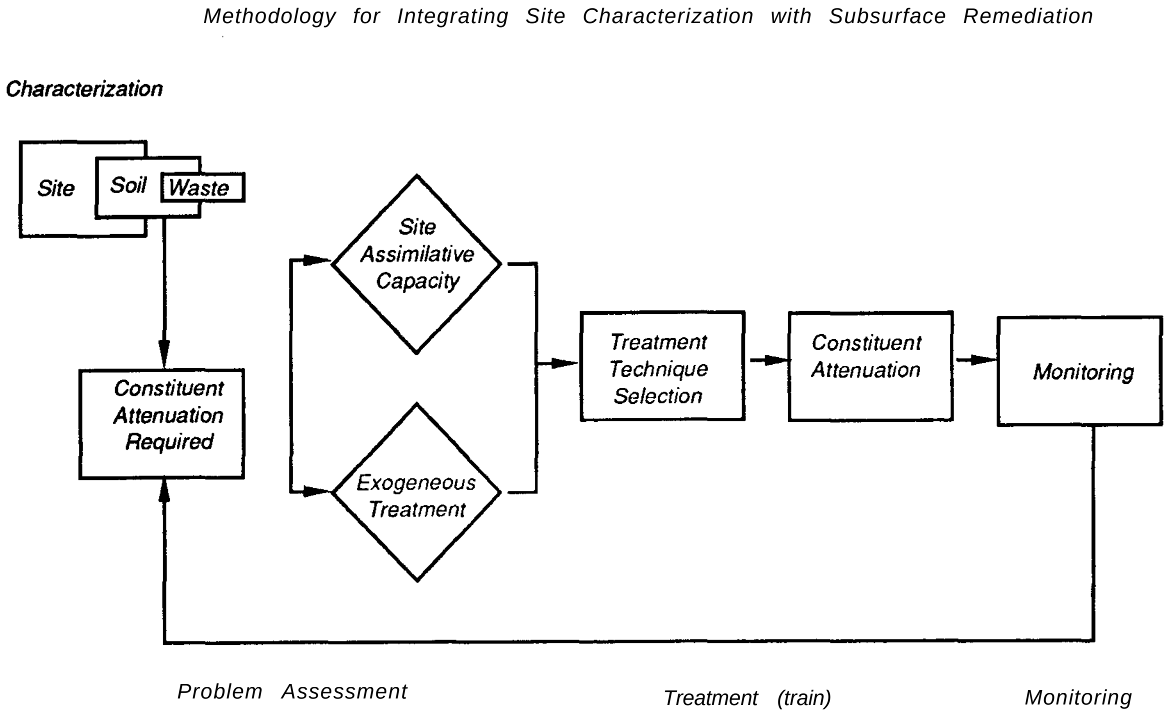


**Figure 14-3. Methodology using mass balance approach for integrating data collection activities at a contaminated site.**

element). Therefore, treatment trains can be selected to address specific waste phases at specific times during remediation (volatile, leachate, solid phase, and pure product), with the selection based upon results of a mass balance evaluation through time to identify the fate of each waste phase. Finally monitoring programs can be designed for specific chemicals in specific phases in the subsurface at specific times (fourth element).

The approach for using the methodology described above consists of applying a mass balance for each element of the methodology. This approach assists in the collection of specific information that is transferable among all four elements of the methodology, and also addresses the technical issues of soil remediation within the context of regulatory goals.

### 14.2.1 Site Characterization

Identifying waste sources by subsurface phases, i.e., identification and amount (if possible) of waste constituents associated with solid and fluid phases (Figure 14-1), allows assessment of the magnitude (mass) and physical form(s) of waste that must be treated. This assessment comprises the first step in the mass balance characterization of waste sources at a site.

Wastewater historically has been characterized and subsequently treated in terms of its interaction and potential impact of the assimilative capacity of surface water receiver systems, generally rivers or lakes (e.g., requiring measurement of characteristics such as oxygen-demanding substances, nutrients, and levels of substances toxic to aquatic organisms). However, a waste characterization program at a hazardous waste site addresses the vadose zone and ground water, in addition to surface water, as the receiver systems (e.g., requiring measurement of characteristics that reflect individual chemical mobility and destruction in the subsurface environment and those that affect human health as well as characteristics that affect environmental toxicity). Also, it describes the behavioral interaction of waste chemicals in each surface and subsurface phase. Thus, hazardous waste is more appropriately characterized in terms of the interaction and potential impact on the subsurface assimilative capacity.

Specific site characteristics important for describing and assessing the environmental behavior and fate of organic constituents in the soil and subsurface are listed in Table 14-1. For each chemical, or chemical class, required information includes (1) characteristics related to potential leaching (e.g., water solubility, octanol/water partition coefficient, solid sorption coefficient); (2) characteristics related to potential volatilization (e.g., vapor pressure, relative volatilization index); (3) characteristics related to potential degradation (e.g., half-life, degradation rate, degradability index); and (4) characteristics related to chemical reactivity (e.g., hydrolysis half-life, soil redox potential) (Sims et al., 1984). The information presented in Table 14-1 also is used to assess problem(s) concerning migration potential at a site and to evaluate and select containment- and treatment-management options.

If the distribution of waste chemicals among phases that comprise the soil and subsurface at a site are determined, then potential pathways of transport, or escape, from a site can be indicated. Therefore, exposure pathways for human health and the environment may be evaluated, i.e., risk assessment can be made. Through a determination of subsurface flow conditions as part of site characterization activities (aqueous, gas, and pure product flow in the vadose zone and aqueous plume and pure product movement in the saturated zone), the mass of material moving through a site and potential movement off site can be assessed:

concentration (mass/vol) X rate of flow (vol/time)
= mass flow at site (mass/time)

This information is combined with additional information, discussed in the next section, that is needed to assess the problem(s) with respect to treatment technique selection.

The U.S. Environmental Protection Agency (EPA's) Robert S. Kerr Environmental Research Laboratory, as part of its Superfund Technology Support Center Program activities, provides assistance to EPA regional offices and state regulatory agencies about appropriate site characterization activities at Superfund sites and other uncontrolled hazardous waste sites to support selection of effective remediation tcchnol~gies. Table 14-2 presents examples of recommended site evaluation and characterization actions as related to the use of soil and the subsurface as the receiver system at uncontrolled hazardous waste sites (Scalf and Draper, 1989).

### 14.2.2 Assessment of Problem

Assessment of the contamination involves organizing the information obtained from site characterization activities to evaluate the transport and degradation behavior of each chemical of concern at a site under consideration. Specifically, the rate of transport can be compared with the rate of degradation to determine if transport is significant relative to degradation. This approach to problem(s) assessment will allow chemicals to be prioritized individually according to (1) magnitude and rate of transport (escape) from a site, (2) persistence, and (3) pathway(s) of migration from a site. Treatment technique evaluation and selection then can be based upon specific combinations of chemical and physical phase-migration pathway.

Interfacing subsurface-based behavioral characteristics of specific contaminants (Table 14-1) with specific site and subsurface properties allows an assessment of the problem(s) related to contamination of other media (due to mobility), including the ground water under the contaminated area, the atmosphere over the site or at the site boundaries, surface waters, and/or persistence of chemicals at a site. Pathways of movement and potential mechanisms of removal of contaminants at a specific site are illustrated in Figure 14-2. This element of the methodology functions to identify chemicals that will (1) migrate upward (volatilization), (2) migrate downward (leaching), (3) migrate laterally (aqueous plume and pure product), (4) degrade, and (5) remain at the site as persistent chemicals. By ranking the chemicals in the order in which lhey migrate or persist, chemicals can be prioritized with regard to urgency for treatment and for monitoring.

*Table 14-1. Subsurface-Based Waste Characterization*

- *Chemical Class*
    - *Acid*
    - *Base*
    - *Polar neutral*
    - *Nonpolar neutral*
    - *Inorganic*
- *Chemical Properties*
    - *Molecular weight*
    - *Melting point*
    - *Specific gravity*
    - *Structure*
    - *Water solubility*
- *Chemical Reactivity*
    - *Oxidation*
    - *Reduction*
    - *Hydrolysis*
    - *Precipitation*
    - *Polymerization*
- *Soil Sorption Parameters*
    - *Freundlich sorption constants (K, N)*
    - *Sorption based on organic carbon content* ($K_{oc}$)
    - *Octanol water partition coefficient* ($K_{ow}$)
- *Soil Degradation Parameters*
    - *Half-life* ($t_{1/2}$)
    - *Rate constant (first order)*
    - *Relative biodegradability*
- *Soil Volatilization Parameters*
    - *Air: water partition coefficient* ($K_w$)
    - *Vapor pressure*
    - *Henry's Law constant*
    - *Sorption based on organic carbon content* ($K_{oc}$)
    - *Water solubility*
- *Soil Contamination Parameters*
    - *Concentration in soil*
    - *Depth of contamination*
    - *Date of contamination*

*Source: Sims et al., 1984*

Waste characteristics identified in Table 14-1, including potential sorption, degradation, and volatilization at a site, can be determined in laboratory mass balance tests, using waste/soil mixtures from a site. These characteristics can be used to evaluate the fate of the waste at the site, and to generate specific data that can be used to develop treatment approaches. Figure 14-4 illustrates a laboratory flask apparatus that can be used to develop a chemical mass balance by measuring interphase transfer potential of chemicals as well as degradation potential at a site (Park et al., 1990).

The contaminated material is placed in a flask, which is then closed and incubated under controlled conditions for a period of time. During the incubation period, air is drown through the flask and then through a sorbent material. Volatilized materials are collected by the sorbent and are measured to estimate volatilization loss of the constituents of interest. At the end of the incubation period, a portion of the contaminated soil is treated with an extracting solution to determine the extent of loss of the constituents in the soil matrix. This loss can be attributed to degradation and possible immobilization in the soil materials. It is necessary to select an appropriate extracting solution and procedure to maximize constituent recovery from a soil-waste mixture (Coover et al., 1987). Another portion of the soil is leached with water to determine leaching potential of the remaining constituents. Abiotic and biological processes involved in removal of the parent compound are evaluated by comparing microbially active soil/waste mixtures with mixtures that have been treated with a microbial poison, e.g., mercuric chloride or propylene oxide. Samples generated from the different phases of the system in microcosm mass balance studies identified above can be analyzed for intermediate degradation products and used in bioassay studies to provide information concerning transformation and detoxification processes.

The use of a procedure incorporating features illustrated by the use of this microcosm (Figure 14-4) is crucial to obtain a materials balance of waste constituents in the subsurface system, Examples of such protocols may be found in EPA guidance documents and research reports (Loehr, 1989; Sims et al., 1988; EPA, 1986; and Park et al., 1990). Contaminated materials also can be spiked with radiolabeled chemicals; tracking the fate of the chemicals as they move through the multiple phases of the soil system also provides a materials mass balance.

The mass balance approach identified above usually represents optimum conditions with respect to mixing, contact of solid materials with waste constituents, and homogeneous conditions throughout the laboratory microcosm; therefore, it does not incorporate site nonhomogeneity in the evaluation. This aspect must be defined during site characterization activities and evaluated with regard to potential effect on fate and behavior regarding migration and persistence at the site (problem assessment).

In addition to the laboratory tests described, bench-scale reactors, pilot-scale reactors and/or field-scale plots may be used to generate mass balance information for problem assessment. The set of experimental conditions (e.g., temperature, moisture, waste concentration) under which the studies were conducted and experimental results should be presented.

Information from the performance of site characterization and experimental mass balance studies may be integrated with the use of comprehensive mathematical modeling to aid in problem assessment. In general, models are used to analyze the behavior of an environmental system under both current (or past) and anticipated (or future) conditions (Donagian and Rao, 1986). A mathematical model provides a tool for (1) integrating degradation and partitioning processes with site-, soil-, and waste-specific characterization; (2) simulating the behavior of waste constituents in a contaminated soil; and (3) predicting the pathways of migration through the contaminated area, and therefore pathways of exposure to humans and to the environment. DiGiulio and Suffet (1988) and Weaver et al. (1989) have presented guidance on the selection of appropriate subsurface zone models for site-specific applications, focusing on recognition of limitations of process descriptions of models and difficulties in obtaining input parameters required by these process descriptions.

The Regulatory and Investigative Treatment Zone Model (RITZ), developed at the EPA's Robert S. Kerr Environmental Research Laboratory by Short (1986) is an example of a vadose zone model that has been used to describe the potential fate and behavior of organic constituents in a contaminated soil system (U.S. EPA, 1988a). The RITZ Model is based on

**Table 14-2. Examples of Suggested Site Characterization Activities Based on Soils and Subsurface Materials as Waste-Receiver Systems**

| Site | USEPA Region | Contaminants | Recommended Site Evaluation and Characterization Actions |
|---|---|---|---|
| *Stamina Mills Superfund Site North Smithfield, RI* | *I* | *TCE* | *Determination of soil-water partition coefficients; investigation of soil physical and hydraulic properties; Simulation of contaminant transport* |
| *W.R. Grace & Co. Superfund Site Acton, MA* | *I* | *Acetone, benzene, toluene* | *Selection of soil physical properties for fugacity modeling* |
| *Somersworth Landfill Somersworth, NH* | *I* | *Arsenic and organic compounds* | *Selection of leaching test suitable for high organic matter content soils to provide data for estimation of migration potential* |
| *Nascolite Superfund Site Millsville and Vineland, NJ* | *II* | *Methyl methacrylate (MMA)* | *Evaluation of residual soil concentrations during groundwater fluctuations; Development of appropriate extraction technologies based on chemical properties of MMA* |
| *Drake Chemical Superfund Site Lock Haven, PA* | *III* | *Various wastes* | *Development of laboratory procedures: Determination of site-specific partition coefficients; Development of ContPro Model (revised version of RITZ Model)* |
| *Tyson's Dump* | *III* | *1,2,3-trichloro-propane, xylene, toluene, and ethyl-benzene* | *Determination of causes for plugging of SVE extraction wells with tarry materials* |
| *Anderson Development Co. Spill Cleanup Adrian, MI* | *V* | *4,4-methylene-bis-2-chloroaniline (MBOCA)* | *Recommendation of use of site-specific biotreatability study to determine feasibility of use of soil bioremediation* |
| *Montrose Chemical Site Los Angeles, CA* | *IX* | *DDT* | *Recommendation to design of laboratory soil biotreatment feasibility studies* |
| *Time Oil Site Tacoma, WA* | *X* | *PCE, PCA, & TCE* | *Development of soil-water and soil-air partitioning relationships for implementation of SVE* |
| *Frontier Hard Chrome Vancouver, WA* | *X* | *Chromium, lead, nickel, & cyanide* | *Development of estimates of leachate concentrations of contaminants at equilibrium between soil and water* |

*Source: Scalf and Draper, 1989*

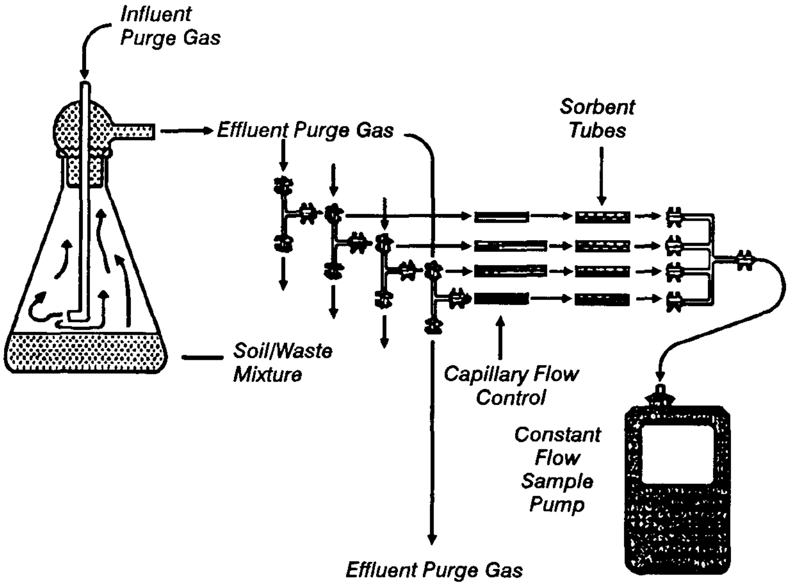


**Figure 14-4. Laboratory flask apparatus used for mass balance measurements (from Park et al., 1990).**

an approach developed by Jury et al. (1983). An expanded version of RITZ, the Vadose Zone Interactive Processes (VIP) model, incorporates predictive capabilities for the dynamic behavior of organic constituents in unsaturated soil systems under conditions of variable precipitation, temperature, and waste concentrations (McLean et al., 1988; Stevens et al. 1988, 1989; Symons et al., 1988; U.S. EPA, 1986). Both the RITZ and VIP models simulate vadose zone processes, including volatilization, degradation, sorption/desorption, advection, and dispersion (Grenney et al., 1987).

For example, the VIP model was used to evaluate the relative tendencies for a group of pesticides to volatilize and to leach under specific waste-soil conditions (McLean et al., 1988). Information input into the model included half-life (measured in laboratory tests), distribution coefficients ($K_d$,$K_h$,$K_o$) (calculated), soil texture and moisture (measured), and site-specific climatic data (rainfall and temperature). Results are presented in Table 14-3. The ranking of pesticides provided by the model indicated that the tendency of the pesticides to volatilize was not similar to their tendency to leach (McLean et al. 1988). This information can be used to assess which chemicals are likely to volatilize first, which chemicals are likely to leach first, and which chemicals are persistent under site-specific conditions. In addition to assisting in the problem assessment step of the methodology, mathematical models also can be used to design studies for evaluation and selection of treatment options for these chemicals, as well as to design monitoring strategies (i.e., which chemicals to monitor in which media).

With regard to ground-water models that can be used as part of the problem assessment, the International Ground Water Modeling Center (IGWMC), through EPA, published information about the kinds and availability of models, their specific characteristics, and the information, data, and technical expertise needed for their operation (U.S. EPA, 1988 b). Ground-water models also have been addressed within the context of scientific and regulatory applications, with selected case studies, by the National Research Council (NAS, 1990).

*Table 14-3.* ***Ratios of Concentration of Pesticides Between Water/Soil and Air/Soil at 15 cm After 81 Days (Ranked in Order from Greatest Potential for Leaching and Volatilization to Least Potential)***

| *Pesticide* | *Leaching potential (concentration in soil water/concentration in soil)* | *Pesticide* | *Volatilization potential (concentration in soil air/concentration in soil)* |
|---|---|---|---|
| *Disulfoton* | *330* | *Toxaphene* | *7.4* |
| *Phorate* | *23* | *Disulfoton* | $3.6 \times 10^{-2}$ |
| *Methylparathion* | *4.8* | *Phorate* | $5.2 \times 10^{-3}$ |
| *Toxaphene* | *0.5* | *Heptachlor* | $5.5 \times 10^{-3}$ |
| *Endosulfan* | *0.12* | *Endosulfan* | $4.0 \times 10^{-4}$ |
| *Parathion* | *0.06* | *Aldrin* | $2.0 \times 10^{-5}$ |
| *Heptachlor* | *0.06* | *Methylparathion* | $1.2 \times 10^{-5}$ |
| *Aldrin* | *0.0009* | *Parathion* | $1.6 \times 10^{-6}$ |

*McLean et al., 1988*

A numerical model, BIOPLUME, was developed to simulate oxygen-limited biodegradation in ground-water environments. BIOPLUME simulates advection, dispersion, and retardation processes as well as the reaction between oxygen and the contaminants under steady, uniform flow (Rifai et al., 1989). BIOPLUME was applied to an aviation gasoline spill site at Traverse City, Michigan. Model predictions for the rates of mass loss closely matched calculated rates from field data.

### *14.2.3 Treatment Approaches*

Information obtained from an integrated assessment (modeling) of the problem (migration and persistence), based upon a thorough characterization of waste/soil/site interactions, can be used to select treatment approaches for further evaluation with respect to technical and cost-effectiveness factors. Results of characterization and assessment efforts can aid in the identification of constituents that will require treatment in the following phases: (1) air (volatile) phase, (2) leachate phase, and (3) solid (soil) phase. This approach allows evaluation and comparison of different treatment systems identified previously (in situ and prepared bed). Specifically, if treatment is required, the information is used to (1) determine containment requirements to prevent contamination of offsite receiver systems; (2) develop techniques to maximize mass transfer of chemicals affecting a process (e.g., affecting microbial activity through addition of mineral nutrients, oxygen, additional energy sources, pH control products, or removal of toxic products in order to enhance bioremediation); and (3) design a cost-effective and efficient monitoring program to evaluate effectiveness of treatment.

*Containment Requirements.* If the major pathway of transport is volatilization, containment and treatment to control volatilization is required. An inflatable plastic dome erected over a contaminated site is a containment method that has been used to control escape of volatile constituents at hazardous waste silts (St. John and Sikes, 1988). Volatiles are drawn from the dome through a conduit and treated in an aboveground treatment system. If leaching has been identified as an important factor, control of soil water movement should be implemented. For example, if contaminated materials are expected to leach downward from the site, run-on and run-off controls can be implemented, or the contaminated materials can be temporarily removed from the site and a plastic or clay liner can be placed under the site (Lynch and Genes, 1989; Ross et al., 1988). When downward as well as upward migration are significant, both volatilization and leaching containment systems can be installed. Some hydrophobic chemicals do not tend to volatilize or to leach but are persistent within the soil solid phase; therefore, containment efforts may not be required. With regard to the saturated zone, containment is generally accomplished by physical barriers (e.g., slurry walls, sheet pilings, grout curtains) or hydraulic barriers (e.g., pump ing systems, french drains).

*Maximizing Chemical Mass Transfer.* An area of significant research concerns delivery and recovery technologies for maximizing mass transfer of chemicals that affect the rate and/or extent of treatment. Murdoch et al. (1988) discussed delivery and recovery technologies, many of which are derived from the petroleum and mining industries. While a liquid phase is usually employed for delivery of chemicals, some technologies utilize vapor and solid phases for delivery. Principal recovery technologies involve hydraulic, thermal, and chemical systems. Delivery and recovery techniques are important in influencing the success of technologies, including bioremediation, vapor extraction, and solidification/stabilization. Specific delivery and recovery systems for in situ treatment systems identified by EPA include hydraulic fracturing, radial well drilling, ultrasonic methods, kerfing, jet-induced slurry methods, carbon dioxide injection, hot brine injection, and cyclic pumping (U.S. EPA, 1990).

### 14.2.4 Monitoring Program

A mass balance approach to monitoring, the fourth element in the methodology (Figure 14-3), can be performed at laboratory, pilot, and field scales. Monitoring efforts can be focused on the appropriate environmental phase to evaluate treatment effectiveness for specific chemicals. If a comprehensive and thorough evaluation of a specific contaminated system has been conducted, not all chemicals may need to be monitored in each phase. Specific chemicals wall be associated with specific phases; therefore, a monitoring plan can be designed that is chemical/phase specific. This approach also focuses analytical efforts so that methods of development are chemical- and phase-specific.

The level of contamination associated with a particular treatment technology requires monitoring. In addition, the treatment system components, including delivery and recovery systems, maintenance, and structures such as infiltration galleries must be monitored.

## 14.3 Selection of Treatment Methods

### 14.3.1 Utility of Mathematical Models

A critical and cost-effective use of modeling in treatment (train) selection and evaluation is for analysis of proposed or alternative future conditions i.e., the model is used as a management or decision-making tool to help answer “what if" questions (Donagian and Rao, 1986). Models also may be used to approximate and estimate the rates and extent of treatment that may be expected at the field-scale under varying conditions. Attempting to answer such questions through data collection programs would be expensive and practically impossible in many situations. For example, information can be generated to evaluate the effects of using different appreaches for enhancing microbial activity and for accelerating biodegradation and detoxification of the contaminated area by altering environmental conditions that affect microbial activity. Therefore, modeling may be used to assist in the design of treatability studies for considering and evaluating the application of different treatment technologies, and therefore to assist in focusing available resources (time and money). Section 14.2.2 (Assessment of Problem) provides more information on the existence, applications, and limitations of mathematical models for vadose zone and ground-water analysis and management.

### 14.3.2 Treatability Studies

Treatability studies can be used for evaluating and comparing rate and extent of remediation among several technologies and also to provide specific information about the potential application of treatment technologies at field scale. Treatability studies can be conducted in laboratory microcosms or bench-scale reactors, pilot-sale facilities, or in the field. Laboratory treatability studies are generally screening studies used to (1) establish the validity of a technology, (2) generate data that can be used as indicators of potential to meet performance goals, and (3) identify parameters for investigation during bench- or pilot-scale testing. Laboratory treatability studies are generally not appropriate for generating design or cost data (U.S. EPA, 1989). Pilot-scale testing is conducted to generate information on quantitative performance, cost, and design information. Three proposed categories of treatability testing and associated descriptions are included in Table 14-4 (U.S. EPA, 1989 b).

Treatability study results are commonly used to provide information on rates and extent of treatment of hazardous organic constituents when mass transfer rates of potential limiting substances are not limiting the treatment. Treatability studies also usually represent optimum conditions with respect to mixing, contact of soil solid materials with waste constituents and with microorganisms, and homogeneous conditions throughout the microcosm. Therefore, treatability studies provide information concerning potential levels of treatment. Rates and extent of remediation in a prepared bed

*Table 14-4. General Comparison of Laboratory Screening, Bench-Scale Testing, and Pilot-Scale Testing*

| Tier | Type of data generated | Critical parameters | No. of replicates | Study size | Usual process type | Waste stream volume | lime required | Cost, $ |
|---|---|---|---|---|---|---|---|---|
| Laboratory screening | Qualitative | several | Single/ duplicate | Jar tests or beaker studies | Batch | Small | Hours/ day | 10,000-50,000 |
| Bench-scale testing | Quantitative | Few | Duplicate/ triplicate | Bench-top (some larger) | Batch or continuous | Medium | Days/ week | 50,000-250,000 |
| Pilot-scale testing | Quantitative | Few | Triplicate or more | Pilot-plant (onsite or offsite) | Batch or continuous | Large | Weeks/ month | 250,000<br>1,000,000 |

Source: U.S. EPA, 1989

or in situ system are generally limited by accessibility and rate of mass transfer of chemical substances to the contaminated soil and removal of inhibitory microbial degradation products (Symons and Sims, 1988).

Information from mass balance treatability studies, including laboratory screening-, bench- and pilot-scale studies, is combined with information about site and waste characteristics to determine applications and limitations of each technology. Information obtained from treatability studies should be focused on identifying ultimate limitations to the use of a remediation technology at a specific site. Limitations are usually related to (1) time required for cleanup, (2) level of cleanup attainable, and (3) cost of cleanup (Sims et al., 1989).

### *14.3.3 Treatment Trains*

The use of treatment trains also is important to consider in an engineering approach for using treatment techniques for subsurface site remediation. For example, vacuum extraction is known to be applicable to unsaturated sites characterized by permeable materials containing volatile chemicals. Vacuum extraction also can be used for the degradation of more semivolatile chemicals. This degradation is accomplished by providing a source of oxygen (air) to the subsurface environment microorganisms where anoxic conditions exist due to relative slow replenishment of oxygen through atmospheric diffusion. This is an example of the use of one technology for the treatment of both volatile and semivolatile chemicals in the subsurface.

Another example of the use of a treatment train for creosote-contaminated soil and ground water involves (1) product removal using a pumping system, (2) flushing with water and surfactants using pump-and-treat technology, and (3) in situ biodegradation of the residual contamination (Kuhn and Piontek, 1989). Each technology is employed in the order of ease of removal of creosote from the subsurface. The treatment train selected was based on a site characterization to identify where the creosote was located and the mass of creosote (including pure product) associated with subsurface phases, i.e., the vadose zone and aquifer materials. The problem assessment identified the following areas of concern: (1) potential offsite migration of pure product; (2) slow leaching of low levels of creosote contaminants sorbed to soil, subsurface, and aquifer materials; and (3) presence of high molecular weight polycyclic aromatic compounds that are toxic to human health, are nonvolatile, and have very low water solubilities. Each technology was evaluated in laboratory-scale treatability tests for treatment effectiveness and for case of application to contaminated materials obtained from the site. Engineering design and implementation was based on results of site characterization, mass balance determinations at the site, and treatability studies,

Information from treatability studies is used to prepare an approach to the engineering design and implementation of a remediation system at a specific site that combines the treatment techniques evaluated to construct an appropriate treatment train. The formulation of a treatment train for a site generally is based upon information from simulations (e.g., mathematical modeling) generated from mass balance studies, treatability studies, and site/soil characterization data.

## 14.4 Measurement and Interpretation of Treatment Effectiveness

Typically, subsurface samples are taken from a treatability reactor (in situ or prepared bed) from laboratory-, bench-, or pilot-scale studies, or from a field site. Waste constituents are extracted from the samples with a solvent or are thermally desorbed. Compound concentration is usually measured in the solvent extract or the thermal resorption stream using chemical instrumentation (e.g., gas or liquid chromatography with appropriate detectors). This information is termed the “apparent loss” of the compound and refers to the observation that the compound only has disappeared from the solvent or extraction phase, but does not necessarily represent a chemical mass balance (Park et al., 1990). The change in concentration of the compound in the solvent with time often is used to calculate rate and extent of decrease in concentration of the compound in soil. This information is commonly used to interpret treatment effectiveness for different technologies as well as to determine engineering strategies and management approaches, including (1) time required to attain cleanup target concentrations; and (2) effects of environmental factors or experimental variables (chemical, physical, or biological) on treatment effectiveness.

However, additional information is needed to accurately measure and interpret treatment effectiveness. In order to understand treatment mechanisms and to base the selection of treatment technologies on a rational approach, identification and measurement of distribution among the physical phases that comprise a subsurface system is necessary. In addition, the mechanisms by which a compound may be chemically altered in a subsurface system must be identified and differentiated (Dupont and Reineman, 1986; Goring et al., 1975; Guenzi, 1974; Park et al., 1988, 1990; Sims et al., 1988; Stevens et al. 1989; Unterman et al., 1988).

Information obtained about the rate of apparent loss of chemicals from a subsurface extract can be enhanced with information about the (1) interphase transfer potential between solid and gas phases of the subsurface, and (2) knowledge of mechanisms of interactions of compounds with subsurface phases. This information then provides the basis for a more rational approach to subsurface remediation. Evaluation of remediation technology effectiveness also can be based upon specific media (solid, air) and upon specific mechanisms, such as recovery of the air phase or enhancement of abiotic destruction or biological degradation, to improve treatment. Evaluation of interphase transfer also allows characterization of routes by which chemicals may migrate from the subsurface to the multimedia environment that then may lead to human exposure. Thus, measuring treatment effectiveness based upon interphase transfer potential (a mass balance approach) is also valuable for determining risk reduction and implementing risk management strategies (Park et al., 1990). The laboratory flask apparatus used for mass balance determinations (Figure 14-4) also can be used to measure and compare potential effectiveness for different treatment scenarios.

## 14.5 References

Bailey, J.E. and D.F. Ollis. 1986. Biochemical Engineering Fundamentals, 2nd ed. McGraw-Hill, New York, NY.

Benefield, L. D., J.F. Judkins, and D.L. Weand. 1982. Process Chemistry for Water and Wastewater Treatment. Prentice-Hall, Englewood Cliffs, NJ.

Coover, M.P., R.C. Sims, and W.J. Doucette. 1987. Extraction of Polycyclic Aromatic Hydrocarbons from Spiked Soil. Journal of the Association of Official Analytical Chemists 70:1018-1020.

Corbitt, R.A. 1989. Standard Handbook of Environmental Engineering. McGraw-Hill, New York, NY.

DiGiulio, D.C. and I.H. Suffet. 1988. Effects of Physical, Chemical, and Biological Variability in Modeling Organic Contaminant Migration through Soil. In: Superfund ’88, Hazardous Materials Control Research Institute, Silver Spring, MD, pp. 132-137.

Donigian, A. S., Jr. and P.S.C. Rao. 1986. Overview of Terrestrial Processes and Modeling. In: Guidelines for Field Testing Soil Fate and Transport Models, S.C. Hern and S.M. Melancon, (eds.), EPA/600/4-86/020 (NTIS PB86-209400), pp. 1-32.

Dupont, R.R. and J.A. Reineman. 1986. Evaluation of Volatilization of Hazardous Constituents at Hazardous Waste Land Treatment Sites. EPA/600/2-86/071 (NTIS PB86-233939).

Goring, C.A.I., D.A. Laskowski, J,W. Hamaker, and R.W. Miekle. 1975. Principles of Pesticide Degradation in Soil. In: Environmental Dynamics of Pesticides, R. Haque and W. H. Freek, (eds.), Plenum Press, New York, NY.

Grenney, W.J., C.L. Caupp, R.C. Sims, and T.E. Short. 1987. A Mathematical Model for the Fate of Hazardous Substances in Soil: Model Description and Experimental Results. Hazardous Wastes & Hazardous Materials 4:223-239.

Guenzi, W.D. (ed). 1974. Pesticides in Soil and Water. Soil Science Society of America, Madison, WI.

Jury, W.A., W.F. Spencer, and W.J. Farmer. 1983. Behavior Assessment Model for Trace Organics in Soil: Model Description. Journal of Environmental Quality 12:558-564.

Kuhn, R.C. and K.R. Piontek. 1989. A Site-Specific In Situ Treatment Process Development Program for a Wood Preserving Site. Paper presented at EPA Technical Program on Oily Waste Fate, Transport, Site Characterization, and Remediation Seminar, Denver, CO, May 17-18 (Organized by John Matthews, EPA Robert S. Kerr Laboratory, Ada, OK).

Loehr, R. 1989. Treatability Potential for EPA Listed Hazardous Chemicals in Soil. EPA/600/2-89/011 (NTIS PB89-166581/AS).

Lynch, J. and B.R. Genes. 1989. Land Treatment of Hydrocarbon Contaminated Soils. In: Petroleum Contaminated Soils, Vol. 1: Remediation Techniques, Environmental Fate, and Risk Assessment, P.T. Kostecki and E.J. Calabrese (eds.), Lewis Publishers, Chelsea, MI, pp. 163-174,

Mahmood, R.J. 1989. Evaluation of Enhanced Mobility of PAHs in Soil Systems. Ph.D. Dissertation, Department of Civil and Environmental Engineering, Utah State University, Logan, UT.

Mahmood, R.J. and R.C. Sims. 1986. Mobility of Organics in Land Treatment Systems. Journal of Environmental Engineering (ASCE) 112:236-245.

McLem, J.E., R.C. Sims, W.J. Doucette, C.L. Caupp, and W.J. Grcnney. 1988. Evaluation of Mobility of Pesticides in Soil using U.S. EPA Methodology. Journal of Environmental Engineering (ASCE) 114:689-703.

Metcalf and Eddy, Inc. 1979. Wastewater Engineering: Treatment, Disposal, and Reuse. McGraw-Hill, New York, NY.

Murdoch, L., B. Patterson, G. Losonsky, and W. Harrar. 1988. Innovative Technologies of Delivery or Recovery: A Review of Current Research and a Strategy for Maximizing Future Investigations. EPA/600/2-89/066 (NTIS PB90 156225/AS).

National Academy of Sciences (NAS). 1990. Ground Water Models: Scientific and Regulatory Applications. National Academy Press, Washington, DC.

Nkedi-Kizza, P., P.S.C. Rao, and J.W. Johnson. 1983. Adsorption of Diuron and 2,4,5-Ton Soil Particle Separates. Journal of Environmental Quality 12:195-197,

Park, K. S., R.C. Sims, W.J. Doucette, and J.E. Matthews. 1988. Biological Transformation and Detoxification of 7,12-Dimethylbenz(a) anthracene in Soil Systems. Journal Water Pollution Control Federation 60:1822-1825.

Park, K. S., R.C. Sims, R.R. Dupont, W.J. Doucette, and J.E. Matthews. 1990. Fate of PAH Compounds in Two Soil Types: Influence of Volatilization, Abiotic Loss and Biological Activity. Environ. Toxicol. Chem. 9:187-195.

Rao, P. S. C., A.G, Hornsby, D.P. Kilcrease, and P. Nkedi-Kizza. 1985. Sorption and Transport of Hydrophobic Organic Chemicals in Aqueous and Mixed Solvent Systems: Model Development and Preliminary Evaluation. Journal of Environmental Quality 14:376-383.

Rifai, H. S., P.B Bedient, R.C. Bordon, and J.F. Haasbeek. 1989. BIOPLUME II-Computer Model of Two-Dimensional Contaminant Transport Under the Influence of

Oxygen Limited Biodegradation in Ground Water (User's Manual Version 1.0; Preprocessor Source Code Version 1.0; Source Code Version 1.0). EPA/600/8-88/093 (NTIS PB89-151 120/AS).

Ross, D., T.P. Marziarz, and A.L. Bourquin. 1988. Bioremediation of Hazardous Waste Sites in the USA: Case Histories. In: Superfund '88, Hazardous Materials Control Research Institute, Silver Spring, MD, pp. 395-397.

Scalf, M.R. and D.C. Draper. 1989. RSKERL-Ada Superfund Technology Support Center The First Two Years. U.S. Environmental Protection Agency (Robert S. Kerr Environmental Research Laboratory, Ada, OK).

Short, T.E. 1986. Modeling Processes in the Unsaturated Zone. In: Land Treatment A Hazardous Waste Management Alternative, R.C. Loehr and J. F. Malina (eds.), Water Resources Symposium No. 13, University of Texas Press, Austin, TX, pp. 211-240.

Sims, R.C., D.L. Sorensen, J.L. Sims, J.E. McLean, R. Mahmood, and R.R. Dupont. 1984. Review of In-Place Treatment Technologies for Contaminated Surface Soils-Volume 2: Background Information for In-Situ Treatment. EPA-540/2-84-O03b (NTIS PB85-124899).

Sims, R.C., W.J. Doucette, J.E. McLean, W.J. Grenney, and R.R. DuPont. 1988. Treatment Potential for 56 EPA Listed Hazardous Chemicals in Soil. EPA/600/6-88/001 (NTIS PB88-174446).

Sims, J.L., R.C. Sims, and J.E. Matthews. 1989. Bioremediation of Contaminated Soils. EPA/600/9-89/073 (NTIS PB90-164047).

Sims J.L.. R.C. Sims, and J.E. Matthews. 1990. Approach to Bioremediation of Contaminated Soils. Hazardous Waste and Hazardous Materials 7(2): 117-149.

St. John. W.D. and D.J. Sikes. 1988. Complex Industrial Waste Sites. In: Environmental Biotechnology - Reducing Risks from Environmental Chemicals through Biotechnology, G.S. Omenn (ed.), Plenum Press, New York, NY, pp. 237-252.

Stevens, D.K., W.J. Grenney, and Z. Yan. 1988. User's Manual: Vadose Zone Interactive Processes Model. Utah State University, Logan, UT.

Stevens, D.K., W.J. Grenney, Z. Yan, and R.C. Sims. 1989. Sensitive Parameter Evaluation for a Vadose Zone Fate and Transport Model. EPA/600/2-89/039 (NTIS PB89-213987/AS).

Symons, B.D. and R.C. Sims. 1988. Assessing Detoxification of a Complex Hazardous Waste Using the Microtox™ Bioassay. Archives of Environmental Contamination and Toxicology 17:497-505.

Symons, B. D., R.C. Sims, and W.J. Grenney. 1988. Fate and Transport of Organics in Soil: Model Predictions and Experimental Results. Journal Water Pollution Control Federation 60:1684-1693.

Unterman, R., D.L. Bedard, M.J. Brennan, L.H. Bopp, F.J. Mondcllo, R.E. Brooks, D.P. Bobley, J.B. McDerrnotq C.C. Schwartz, and D.K. Dietrich. 1988. Biological Approaches for Polychlorinated Biphenyl Degradation. In Environmental Biotechnology - Reducing Risks from Environmental Chemicals through Biotechnology, G.S. Omenn (ed.), Plenum Press, New York, NY, pp. 253-269.

U.S. Environmental Protection Agency (EPA). 1984. Review of In-Place Treatment Techniques for Contaminated Surface Soils. EPA-540/2-84-O03a (NTIS PB85-124881).

U.S. Environmental Protection Agency (EPA). 1986. Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations. EPA-530/SW-86-032 (NTIS PB86-229184).

U.S. Environmental Protection Agency (EPA). 1988a. Interactive Simulation of the Fate of Hazardous Chemicals during Land Treatment of Oily Wastes: RITZ User's Guide. EPA/600/8-88-OOl (NTIS PB88-195540).

U.S. Environmental Protection Agency (EPA). 1988b. Groundwater Modeling: An Overview and Status Report. EPA/600/2-89/028 (NTIS PB89-229497). Also available from International Ground Water Modeling Center, Butler University, Indianapolis, IN.

U.S. Environmental Protection Agency (EPA). 1989. Guide for Conducting Treatability Studies under CERCLA. EPA/540/2-89/058.

U.S. Environmental Protection Agency (EPA). 1990. Handbook on In Situ Treatment of Hazardous Waste-Contaminated Soils. EPA/540/2-90-W2 (NTIS PB90-155607).

Weaver, J., C.G. Enfield, S. Yates, D. Kreamer, and D. White. 1989. Predicting Subsurface Contaminant Transport and Transformation: Considerations for Model Selection and Field Validation. EPA/600/2-89/045 (NTIS PB90-155615).

Willis, R. and W. W-G. Yeh. 1987. Groundwater Systems Planning and Management. Prentice Hall, Englewood Cliffs, NJ.

Wilson, J.T., L.E. Leach, J. Michalowski, S. Vandegrift and R. Callaway. 1989. In Situ Bioremediation of Spills from Underground Storage Tanks: New Approaches for Site Characterization, Project Design, and Evaluation of Performance. EPA/600/2-89/042 (NTIS PB89-219976/AS),

# Chapter 15
# Remediation Techniques for Contaminated Soils

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Currently, many remedial techniques are being used and evaluated for cleanup of contaminated soils. Tables 15-1 and 15-2 list participants in the U.S. Environmental Protection Agency (EPA) SITE program that are testing and evaluating remedial technologies applicable to contaminated soils (U.S. EPA, 1989f). Table 15-3 summarizes technologies applicable to contaminated soils that are currently being demonstrated and evaluated in the NATO/CCMS Pilot Study, *Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater* (U.S. EPA, 1989d).

Selected physical, chemical, biological, thermal, and fixation/ encapsulation soil remediation techniques were categorized as in situ and prepared bed and are summarized in Table 15-4 (Rich and Cherry, 1987; U.S. EPA, 1987, 1988c, 1989b). Each soil remediation technique also was evaluated with respect to function (separation, detoxification, etc.); potential for formation of residuals/transformation products; applications; and limitations. This chapter presents a subset of these techniques, evaluated at pilot or field scale, that were selected for additional description.

## 15.1 In Situ versus Prepared Bed Soil Remediation

The vadose zone is the region extending from the ground surface to the upper surface of the principal water-bearing formation. It is divided into three characteristic areas or belts. The uppermost belt consists of soil and other materials that lie near to the surface and discharge perceptible quantities of water into the atmosphere. The water is discharged by the action of plants or by soil evaporation and convection. The lowest belt, the capillary fringe, is located immediately above the water table and contains water drawn up from the zone of saturation by capillary action. The intermediate belt lies between the belt of soil water and the capillary fringe (Lehr, 1988). In this chapter, soil remediation techniques address the vadose zone and situations where the saturated zone is engineered to become unsaturated, e.g., when ground water is pumped to create an unsaturated zone.

The two soil treatment processes discussed in this chapter are in situ treatment and prepared bed treatment. In situ treatment consists of treating contaminated soil in place, i.e., the contaminated soil is not moved from the ground. Milestone publications that should be consulted for scientific and engineering information specifically addressing in situ treatment include Sims et al. (1984); U.S. EPA (1984); U.S. EPA (1990); Sims et al. (1989); and Dupont et al. (1988).

In a prepared bed system, the contaminated soil may be either (1) physically moved from its original site to a newly prepared area, which has been designed to enhance treatment and/or to prevent transport of contaminants from the site; or (2) removed from the site to a storage area while the original location is prepared for use, then returned to the bed, where treatment is accomplished. Preparation of the bed may include placement of a clay or plastic liner to retard transport of contaminants from the site or addition of uncontaminated soil to provide additional treatment medium. Treatment may be enhanced with biological and/or physical/chemical methods, as with in situ systems (Sims and Sims, 1986; Sims et al., 1989). Prepared bed treatment approaches are based on modifications of principles developed in the areas of land application of solid and liquid wastes and in land treatment of hazardous wastes (Sims et al., 1989, U.S. EPA, 1983, U.S. EPA, 1986).

## 15.2 In Situ Techniques

In situ treatment techniques addressed include (1) soil vacuum extraction, (2) bioremediation, (3) immobilization, and (4) mobilization.

### *15.2.1 Soil Vacuum Extraction (SVE)*

Referred to as soil vacuum extraction (SVE), forced air venting, or in situ air stripping, this technique involves extraction of air and contaminants from unsaturated soil. In contrast to a static equilibrium soil system where evaporation of a chemical is equal to the condensation of the chemical (Figure 15-1), with SVE, clean air is injected or passively flows into the unsaturated zone. Volatile chemicals then partition from soil water into soil air, with relative partitioning based on the air/water partition coefficient ($K_h$) or Henry's Law constant (Figure 15-2) and the vapor-laden air is removed using vacuum extraction wells.

Typically, components of SVE consist of vacuum extraction wells (Figure 15-3), air inlet wells, and vapor monitoring wells distributed across a contaminated site, and a blower(s) to control air flow. Extraction wells may be placed vertically or horizontally, although vertical alignment is typical for deeper contamination zones and for residues in radial flow

*Table 15-1.* ***SITE Demonstration Program Participants with Technoiogies Appiicabie to Remediation of Contaminated Soils***

| | | **Applicabie Waste**[a] | |
|---|---|---|---|
| *Deveioper* | *Technology* | *Inorganic* | *Organic* |
| *American Combustion Technologies, Inc.<br>Norcross, GA* | *Pyreton oxygen burner* | *NA* | *Non-specific* |
| *American Toxic Disposal Inc.<br>Waukegan, IL* | *Vapor extraction system* | *Volatile* | *Volatile and semivolatile organics includng PCBs, PAHs, PCPs, some pesticides* |
| *AWD Technologies, Inc.<br>Burbank, CA* | *integrated vapor extraction and steam vacuum stripping* | *NA* | *Volatile organic compounds* |
| *Biotrol, Inc.<br>Chaska, MN* | *Soil washing system* | *Metals* | *High molecular weight organics* |
| *CF Systems Corporation<br>Waltham, MA* | *Solvent extraction* | *NA* | *PCBs, volatile, and semivolatile organic compounds, petroleum byproducts* |
| *Chemfix Technologies, Inc.<br>Metairie, LA* | *Solidification/stabilization* | *Heavy metals* | *High molecular weight organics* |
| *Chemical Waste Management, Inc.<br>Oakbrook, IL* | *X*TRAX" low temperature thermal resorption* | *NA* | *Volatile and semivoiatile organics, PCBs* |
| *Dehydro-Tech Corporation<br>East Hanover, NJ* | *Carver-Greenfield process for extraction of oily waste* | *NA* | *PCBs, dioxin, oil-soluble organics* |
| *Ecova Corporation<br>Redmond, WA* | *in situ biological treatment* | *NA* | *Chlorinated solvents, non-chlorinatad organic compounds* |
| *EPOC Water, Inc.<br>Fresno, CA* | *Leaching and micro filtration* | *Specific for heavy metals* | *NA* |
| *Exxon Chemicals, Inc./<br>RioLinda Chemical Co.<br>Long Beach, CA* | *Chemical oxidation/cyanide destruction* | *Cyanide* | *NA* |
| *GeoSafe Corporation<br>Kirkland, WA* | *in situ vitrification* | *Non-specific* | *Non-specific* |
| *HAZCON, Inc.<br>Brookshire, TX* | *Solidification/stabilization* | *Heavy metals* | *Not an inhibitor* |
| *Horsehead Resources Development Co., Inc.<br>Monaca, PA* | *Flame (slagging) reactor* | *Heavy metals* | *NA* |
| *international Waste Technologies/<br>Gee-Con, Inc.<br>Wichita, KS* | *in situ solidification/ stabilization* | *Non-specific* | *PCBs, other non-specific organic compounds* |
| *MoTec, Inc.<br>Austin, Tx* | *Liquid/solid contact digestion* | *NA* | *Halogenated and non-halogenated organic compounds, pesticides* |
| *Ogden Environmental Services<br>San Diego, CA* | *Circulating fluidized bed combustor* | *NA* | *Halogenatad and non-halogenated organic compounds* |
| *Ozonics Recycling Corp.<br>Boca Raton, FL* | *Soil washing, catalytic/ozone oxidation* | *Cyanide* | *Semivolatiles, pesticides, PCBs PCP, dioxin* |
| *Resources Conservation Co.<br>Bellevue, WA* | *Solvent extraction (BEST)* | *NA* | *Specific for high molecular weight organics* |
| *Retech, Inc.<br>Ukiah, CA* | *Plasma reactor* | *Metals* | *Non-specific* |
| *S.M.W. Seiko, Inc.<br>Redwood City, CA* | *in situ solidificationl stabilization* | *Metals* | *Semivolatile organic compounds* |
| *Shirco Infrared Systems, Inc.* | *infrared thermal destruction* | *NA* | *Non-specific* |
| *Silicate Technology Corp.<br>Scottsdale, AZ* | *Solidification/stabilization with silicate compounds* | *Metals, cyanide, ammonia* | *High molecular weight organics* |
| *Soliditech, Inc.<br>Houston, TX* | *Solidification/stabilization* | *Metals* | *Non-specific* |
| *Solvent Services, Inc.<br>San Jose, CA* | *Steam injection and vacuum extraction (SIVE)* | *NA* | *Volatile and semivolatile organic compounds* |
| *Terra Vac, Inc.<br>San Juan, PR* | *in situ vacuum extraction* | *NA* | *Volatile and semivolatile organic compounds* |
| *Toxic Treatments (USA) Inc.<br>San Francisco, CA* | *in situ steam/air stripping* | *NA* | *Volatile organic compounds and hydrocarbons* |
| *Wastach, Inc.<br>Oak Ridge, TN* | *Solidification/stabilization* | *Non-specific radioactive* | *Non-specific* |

[a] *NA = non applicable*

*Source: U.S. EPA, 1989f*

*Table 15-2. SITE Emerging Technology Program Participants with Technologies Applicable to Remediation of Contaminated* Soils

| *Developer* | *Technology* | *Applicable Waste*<br>*Inorganic* | <br>*Organic* |
|---|---|---|---|
| *Babcock & Wilcox Co.*<br>*Alliance, OH* | *Cyclone combustor* | *Non-specific* | *Non-specific* |
| *Battelle Memorial Institute,*<br>*Columbus Division*<br>*Columbus, OH* | *In situ electroacoustic decontamination* | *Specific for heavy metals* | *NA* |
| *Enviro-Sciences, Inc.*<br>*Randolph, NJ* | *Low energy solvent extraction* | *NA* | *PCBs, other non-specific organic compounds* |
| *Harmon Environmental Services, Inc.*<br>*(formerly Envirite Field Services, Inc.)*<br>*Auburn, AL* | *Soil washing* | *NA* | *Heavy organic compounds* |
| *IT Corporation*<br>*Knoxville, TN* | *Batch steam distillation/ metal extraction* | *Non-specific* | *Non-specific* |
| *Western Research Institute*<br>*Laramie, WY* | *Contained recovery of oily wastes (CROW)* | *NA* | *Coal tar derivatives, petroleum byproducts* |

*NA = non applicable*

*Source: U.S. EPA, 1989f*

patterns (Hutzler, 1990). Schematics of a gas extraction well and a gas monitoring well are presented in Figures 15-4 and 15-5, respectively.

Important system variables that may affect the performance of SVE include properties of the chemical, such as vapor pressure and volatilization, and properties of the site, such as soil moisture content, soil texture, and distribution of contaminants. Vapor pressure is important when a chemical occurs in a pure phase in the subsurface. Vapor pressures above 14 mm Hg at 20°C are desirable for application of SVE. Vapor pressure values for selected subsurface contaminants are given in Table 15-5. When chemicals are distributed in the water phase in the soil, the Henry's Law constant is important, and a dimensionless Henry's constant above 0.01 (mg/L/mg/L) desirable for use of SVE. Table 15-6 gives Henry's Law constants for a set of selected organic chemicals where the application of SVE would be appropriate.

Since movement of volatile organic chemicals (VOCs) is generally 10,000 times faster in a gas phase than in a water phase, VOC removal is expected to be enhanced by decreasing soil moisture. However, when soil is very dry, which may occur when dry air is drawn through soil, VOCs may adsorb directly onto mineral surfaces, where the magnitude of sorption is increased and consequently volatilization is decreased (Figure 15-6). Henry's Law constant is not appropriate under these conditions, since partitioning is between air and soil phases only. When moisture is added to soil, the effect is reversible. The moisture content at which a decrease in vapor density becomes apparent is often termed the critical moisture content and generally is equivalent to approximately a monolayer of water molecules coating the soil particles (Spencer et al., 1969, 1973). The effect of soil water content on dieldrin vapor pressure is illustrated in Figure 15-7. Johnson and Sterrett (1988) noted that dichloropropane concentrations were correlated with ambient air moisture during the use of SVE at a site in Benson, Arizona.

If contaminated soil contains immiscible fluids in the form of oils, (e.g., petroleum hydrocarbons), the four-compartment system discussed previously is operative (water, air, oil, and soil as discussed in Chapter 14). In this system, chemical volatility will be affected by the chemical vapor pressure and mole fraction within the immiscible oil fluid, and governed by Raoult's Law:

$$P_a = X_a P_a^{\circ} \qquad [15\text{-}1]$$

where $P_a$= vapor pressure of solvent over solution (mm Hg), $X_a$= mole fraction of solvent in solution, and $P_a^{\circ}$ = vapor pressure of pure solvent (mm Hg).

For contamination by hydrocarbons with multiple components, volatilization will proceed such that lower molecular weight chemicals will volatilize before higher molecular weight compounds. Through this process of weathering of the waste/soil mixture, SVE extraction efficiency is observed to decrease to less than 10 percent when the fraction of gasoline remaining is approximately 40 percent (Figures 15-8 and 15-9) (Johnson, 1989). Therefore, measuring general parameters such as total hydrocarbons is not sufficient to indicate the removal efficiency of individual constituents.

Soil texture has been evaluated as it influences air permeability (DiGiulio et al., 1990). In less permeable media, such as glacial till and clayey soils, secondary permeability or porosity (fractures) will dominate air flow. There will be rapid removal of VOCs in fractures and slow removal in the soil matrix. In more permeable media, such as sands, sandy loams, and loamy sands, SVE is appropriate (see Figures 15-10 and 15-11). Pneumatic pump tests in the field are recommended for site-specific evaluation of SVE application.

Due to release of VOCs from the soil matrix, when extraction wells are temporarily turned off, concentrations of VOC increase in soil air (referred to as "VOC rebound effect"), with an equilibrium concentration that is determined by Henry's Law constant. When blowers are turned on, an increase in the concentration of extracted vapor from the soil will be observed. Diffusive release from subsurface stratigra-

**Table 15-3.** ***NATO/CCMS Projects for the Remediation of Contaminated Soils***

| **Treatment**<br>Organization/site | *Treatable Contaminants*<br>Aliphatic Hydrocarbons | <br>Aromatic Hydrocarbons | <br>Halogenated Hydrocarbons | <br>Heavy Metals | <br>Petroleum Fuels, Oil | Specfic Contaminants Treated | Treatment Location | Status of Technology |
|---|---|---|---|---|---|---|---|---|
| **Biological** | | | | | | | | |
| Enhanced aerobic restoration<br>U.S. Air Force, Battelle<br>Eglin Air Force Base, FL<br>United States | ✓ | ✓ | | | ✓ | Jet fuel | In-situ | Experimental |
| Microbial treatment<br>Former gas works<br>Fredensborg, Denmark | | ✓ | | ✓ | | Polycyclic aromatic hydrocarbons, phenols, cyanides | On-site, in-situ | Demonstration |
| Chemical/Physical | | | | | | | | |
| K-PEG process<br>U.S. Environmental Protection Agency<br>Wide Beach, NY United States | ✓ | ✓ | ✓ | ✓ | ✓ | PCBs, dioxin | On-site, mobile | Demonstrated |
| High pressure soil washing<br>Scrap metal & copper refinery<br>Berlin, Federal Republic of Germany | | ✓ | ✓ | ✓ | ✓ | Lead, PAHCs | On-site mobile | Commercial |
| High pressure soil washing and oxidation<br>Goldbeck Haus, Hamburg<br>Federal Republic of Germany | | ✓ | | | | Phenol, kresol | In-situ | Demonstration |
| Soil vapor extraction<br>U.S. Environmental Protection Agency<br>Verona Well Field<br>Battle Creek, Ml, United States | | ✓ | ✓ | ✓ | ✓ | Halogenated and aromatic hydrocarbons | In-situ | Demonstrated |
| Stabilization/Solidification | | | | | | | | |
| In-situ vitrification<br>Parsons Chemical Site<br>Michigan, United States | ✓ | ✓ | ✓ | ✓ | | Mercury | In-situ | Experimental |
| Electrokinetic | | | | | | | | |
| Electro-reclamation<br>Loppersum<br>The Netherlands | | | | ✓ | | Arsenic | In-situ | Commercial |
| Thermal | | | | | | | | |
| Thermal resorption and destruction (radiation heating)<br>Dekonta GmbH, Hamburg<br>Federal Republic of Germany | | ✓ | ✓ | | | Chlorobenzenes, Chlorophenols, Hexachlorocyclohexane, dioxins, furans | On-site | Experimental |

Source: U.S. EPA, 1989d

**Table 15-4. Selected Remediation Techniques Possibly Suitable for Cleanup of Contaminated Soils**

| Remediation Techniques<br>Type of Treatment Technology | Treatment Category | Function | Possible Residuals/ Transformation Products | Possible Applications | Possible Limitations |
|---|---|---|---|---|---|
| **Phyaical/Chemical Treatment** | | | | | |
| Low Temperature Thermal Stripping (including radio frequency heating) | In-tank<br>In situ | Separation | Off-gas; spent carbon or ash from afterburner; processed soil; hazardous emissions from in situ applications | Compounds of low water volubility and high volatility | Limited to organics with Henry's Law constant greater than 3.0 x 10 $^{-3}$ atm-m $^{-3}$/ mole and boiling points less than 800°; more effective for soils with low contents of organic matter and moisture |
| Soil Washing | In-tank | Separation; volume reduction | Extracted materials; water/flushing agent mix | Organics and inorganic; most suitable for soils contaminated with only a few specific chemicals | Unfavorable contaminant separation coefficients; less effective with complex mixtures of waste types and variation in waste imposition; unfavorable soil characteristics include: high humic content, soil/solvent reactions, high silt and clay content, and clay soils containing semivolatiles; unfavorable washing fluid characteristics include: difficult recovery of solvent or surfactant, poor treatability of washing fluid, reduction of soil permeability, and high toxicity of washing fluid |
| Soil Flushing | In situ | Separation; volume reduction | Extracted materials; water/washing agent mix | Organics and inorganic; most suitable for soils contaminated with only a few specific chemicals | Unfavorable contaminant separation coefficients: less effective with complex mixtures of waste types and variation in waste composition; unfavorable soil characteristics include: variable soil conditions, high organic matter content, soil/solvent reactions, high silt and clay content, and clay soils containing semivolatiles; unfavorable flushing fluid characteristics include: difficult recovery of solvent or surfactant, poor treatability of washing fluid, reduction of soil permeability, and high toxicity of washing fluid; requires containment of leachate and ground water to prevent off-site groundwater contamination |
| Soil Vacuum Extraction (SVE) | In situ<br>Prepared bed | Separation | Volatile organics and volatile toxic metals | Volatile organics and toxic metals; may be enhanced by the use of steam | Soil heterogeneity (e.g., permeability, texture); not applicable to saturated materials or miscible compounds |
| Glycolate Dechlorination | In-tank<br>In situ | Detoxification | Water/reagent mix; reaction products | Dehalogenation of aromatic halide compounds | Heat and excess reagent required for soils with greater than 20%. moisture and contaminant concentrations greater than 5%, and that contain competing reactive metals (e.g., aluminum) |

(continued)

*Table 15-4.* ***(Continued)***

*Remediation Techniques*

| *Type of Treatment Technology* | *Treatment Category* | *Function* | *Possible Residuals/ Transformation Products* | *Possible Applications* | *Possible Limitations* |
|---|---|---|---|---|---|
| *Neutralization* | *In situ*<br>*Prepared bed*<br>*In-tank* | *Detoxification; immobilization* | *Precipitated salts* | *Waste acids and alkalies to reduce reactivity and corrosiveness* | *Compatibility of waste and treatment chemical to prevent formation of more toxic or hazardous compounds* |
| *Oxidation* | *In situ*<br>*Prepared bed*<br>*In-tank* | *Detoxification* | *Oxidized reaction products* | *Cyanides and oxidizable organics* | *Possible explosive reactions; production of more toxic or hazardous products; non-selective* |
| *Photolysis* | *Prepared bed* | *Detoxification* | *Reaction products* | *Dioxins: nitrated wastes* | *Inability of light to penetrate soil* |
| *Precipitation* | *In situ*<br>*Prepared bed*<br>*In-tank* | *Separation; volume reduction; immobilization* | *Precipitated metals* | *Metals; certain anions* | *Unfavorable effects on soil permeability; long-term stability unknown* |
| *Reduction* | *In situ*<br>*Prepared bed*<br>*In-tank* | *Detoxification* | *Reduced reaction products* | *Chromium, silver, and mercury* | *Possible explosive reactions; production of more toxic or hazardous products; non-selective* |
| *Carbon Adsorption* | *In situ*<br>*Prepared bed* | *Separation; immobilization* | *Processed soil* | *Organic wastes wastes with high molecular weight and boiling point and low volubility and polarity* | *Long-term stability unknown* |
| *Ion Exchange* | *In situ*<br>*Prepared bed* | *Separation; immobilization* | *Processed soil* | *Metal contaminants* | *Selectivity/competition limitations; pH requirements* |
| *Thermal Treatment* | | | | | |
| *Fluidized Bed* | *In-tank* | *Volume reduction; detoxification* | *Off-gases (possibly acidic and with incomplete combustion products); treated materials with residual metals; fly ash: scrubber water* | *Halogenated and non-halogenated organics; inorganic cyanides* | *High maintenance requirements; waste size and homogeneity requirements; applicable to wastes with low sodium and metal contents* |
| *Infrared* | *In-tank* | *Volume reduction: detoxification* | *Off-gases (possibly* acidic *and with incomplete combustion products); treated materials with residual metals; fly ash; scrubber water* | *Halogenated and non-halogenated organics; inorganic cyanides* | *Limited particle sizes, so may require size reduction equipment* |
| *pyrolysis* | *In-tank* | *Volume reduction; detoxification* | *Nonvolatile char and ash (metals, salts, and particulates)* | *Wastes not conducive to conventional incineration; wastes with volatile metals or recoverable residues* | Small capacity |

***(continued)***

**Table 15-4. (Continued)**

Remediation Techniques

| Type of Treatment Technology | Treatment Category | Function | Possible Residuals/ Transformation Products | Possible Applications | Possible Limitations |
|---|---|---|---|---|---|
| Rotary Kiln | In-tank | Volume reduction; detoxification | Off-gases (possibly acidic and with incomplete combustion products); treated materials with residual metals; fly ash; scrubber water | Halogenatad and non-halogenated organics; inorganic cyanides | High particulate emissions; limited particle sizes, so may require size reduction equipment |
| Biological Treatment | | | | | |
| Aerobic bioremediation | In-tank; prepared bed; In situ | Detoxification | Hazardous volatile emissions; incomplete and possibly hazardous degradation products; leachates in soil systems | Biodegradable organic wastes | Ability to control environmental factors conducive to biodegradation; formation of more toxic or hazardous transformation products; prepared bed: areal limitations due to cost of bed preparation |
| Anaerobic bioremediation | In-tank; prepared bed In situ | Detoxification | Hazardous volatile emissions; carbon dioxide, methane and other gases; incomplete and possibly hazardous degradation products; leachates in soil systems | Certain halogenated organics | May require long treatment periods; incomplete treatment, possibly requiring aerobic conditions to complete degradation process |
| Biological Seeding | In-tank; prepared bed; in situ | Detoxification | Hazardous volatile emissions; incomplete and possibly hazardous degradation products; leachates in soil systems | Many biodegradable organic wastes | Survival and activity of organisms in introduced environment (affected by environmental factors and competition with native species) |
| Comporting | In-tank; prepared bed | Detoxification | Hazardous volatile emissions; incomplete and possibly hazardous degradation products; leachates and runoff water | Biodegradable organic wastes | Maintenance of optimum environmental conditions for biological activity; requires large amounts of compost materials mixed with only about 10% wastes |
| Enzyme addition | In-tank; prepared bed; In situ | Detoxification | Hazardous volatile emissions; incomplete and possibly hazardous degradation products; leachates in soil systems | Certain biodegradable organic wastes | Activity and stability of introduced enzymes in natural systems |
| Fixation/Encapsulation | | | | | |
| Cement solidification | In-tank<br>In situ | Storage; immobilization | Leachates; hazardous volatile emissions; solidified waste materials | Metal cations, latex and solid plastic wastes | Incompatible with large amounts of dissolved sulfate salts or metallic anions such as arsenates or borates; setting time increased by presence of organic matter, lignite, silt, or clay: requires complete and uniform mixing of soils and reagents; long term stability unknown; may reduce soil permeability and increase run-off |

*(continued)*

**Table 15-4. (Continued)**

Remediation Techniques

| Type of Treatment Technology | Treatment Category | Function | Possible Residuals/ Transformation Products | Possible Applications | Possible Limitations |
|---|---|---|---|---|---|
| **Fixation/Encapsulation** | | | | | |
| Classification/ vitification | In-tank<br>In situ | Storage; immobilization | Leachates; hazardous volatile emissions; glassifie or vitrified waste materials; aqueous scrub solution | Inorganic and some organics in liquids and contaminated soils | Long-term stability unknown; high energy requirements, especially with high soil water contents and low permeability; electrical shorting caused by buried metal drums; possible underground fire from combustible materials; volatile metals near surface may volatilize; site may require run-off controls |
| Lime Solidification (Silicate) | In-tank<br>In situ | Storage; immobilization | Leachates, hazardous volatile emissions; solidified waste materials | Metals, waste oils, and solvents | Long-term stability unknown; incompatible with borates, sulfates, carbohydrates; requires complete and uniform mixing of soils and reagents; may reduce soil permeability and increase run-off |
| Thermoplastic Microencapsulation | In-tank<br>In situ | Volume reduction; storage; immobilization | Leachates, hazardous volatile emissions; encapsulated waste materials | Complex, difficult to treat hazardous wastes | Wastes not treatable: wastes with high water content; strongly oxidizing contaminants: anhydrous inorganic salts, tetraborates, iron and aluminum salts, and organics with low molecular weights and high vapor pressures; long-term stability unknown; requires complete and uniform mixing of soils and reagents; may reduce soil permeability and increase run-off |

Sources: Rich and Cherry, 1987; U.S. EPA, 1987, 1988b, 1989b

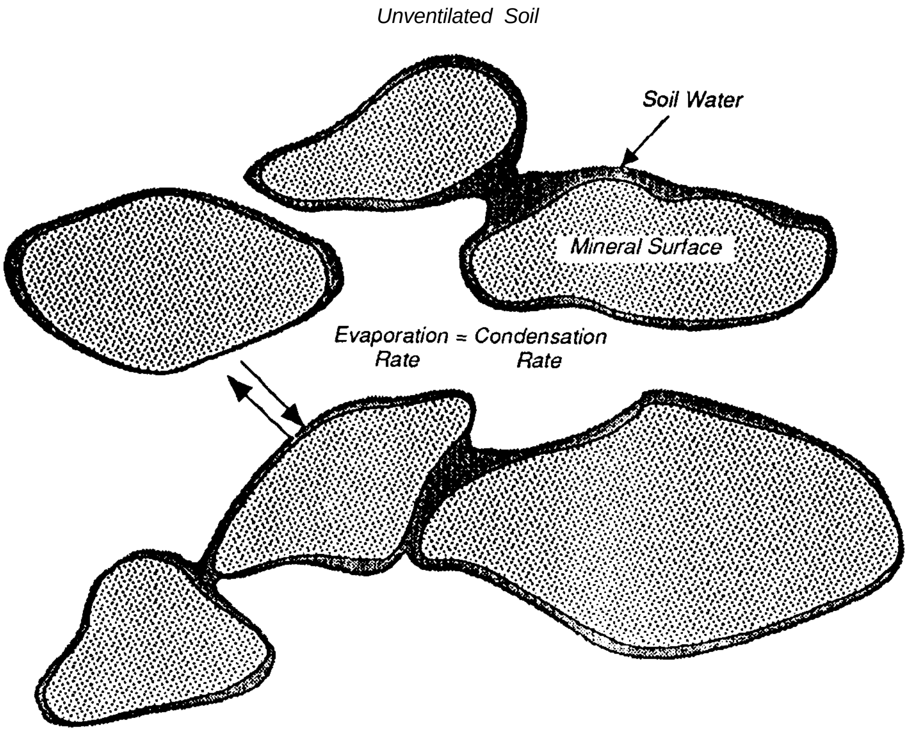


Figure 15-1. Static soil system in equilibrium (modified from Valsaraj and Thibodeaux, 1988).

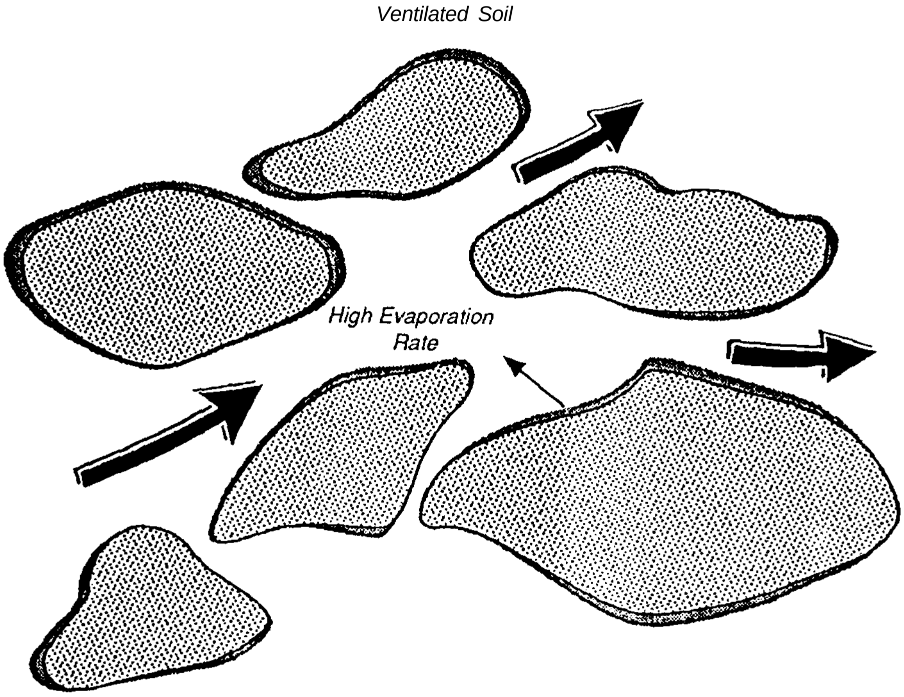


Figure 15-2. Enhancement of volatilization through application of soil vacuum extraction (modified from Valsaraj and Thibodeaux, 1988).

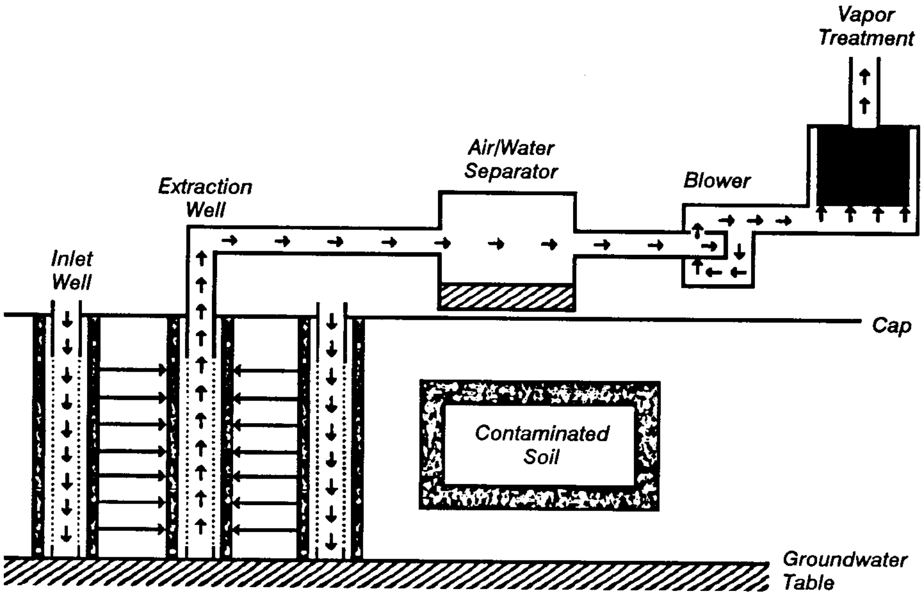


Figure 15-3. Typical components of a soil vacuum extraction system (from Hutzler et al., 1990).

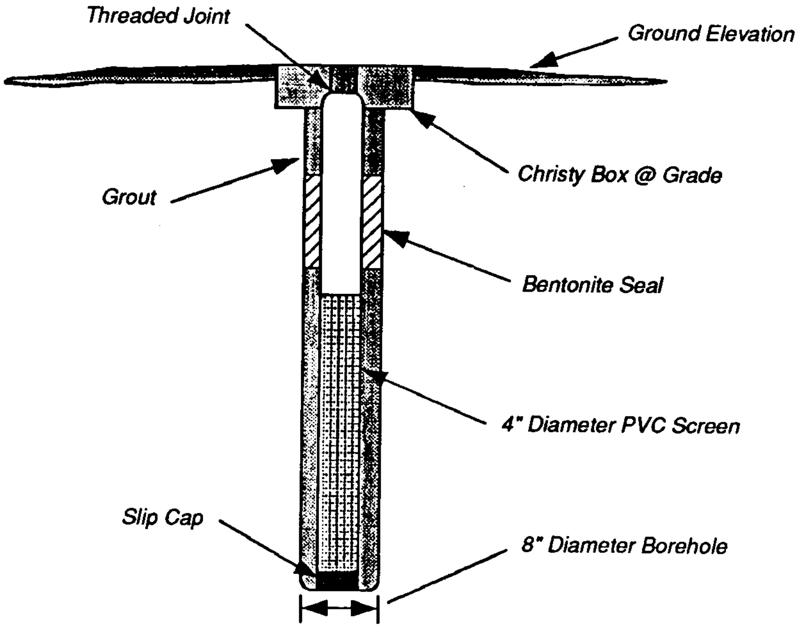


Figure 15-4. Schematic of a gas extraction weii used in a soil vacuum extraction system (from DiGiulio, 1989).

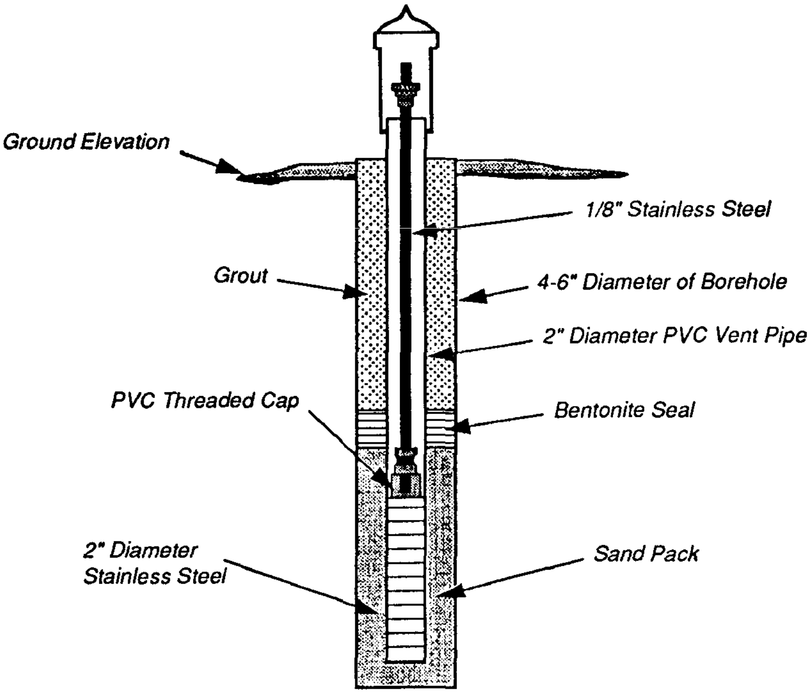


**Figure 15-5. Schematic of a gas monitoring well used in a soil vacuum extraction system (from DiGiulio, 1989).**

*Table 15-5. Comparative Vapor Pressures and Henry's Constants*

| *Compound* | *Vapor Pressure (mm Hg)* | *Henry's Constant (Dimensionless)* |
|---|---|---|
| *Methylene chloride* | *362* | *0.13* |
| *Acetone* | *200* | *miscible* |
| *Methyl ethyl ketone (MEK)* | *100* | *0.001* |
| *1,2-Dichloroethane (EDC)* | *61* | *0.037* |
| *Bis (chloromethyl) ether* | *30.0* | *0.008* |
| *Phenol* | *0.53* | *0.00002* |
| *Mercury ($Hg^o$)* | *0.0012* | *0.48* |
| *PCB-1260* | *4.05 x 10e-5* | *0.30* |

*Table 15-6. Oxygen Supply*

| *Water* | *lb carrier/lb $O_2$* |
|---|---|
| *Air Saturated* | *100,000* |
| *Pure $O_2$ Saturated* | *25,000* |
| *500 mg/l $H_2O_2$* | *10,000* |
| *Air* | *4* |

phy of less permeability will cause the slow continual release of chemicals into the soil-gas phase (Figure 15-12).

Design considerations that affect SVE include extraction well spacing and extraction well depth. As permeability decreases, well spacing decreases; typical well spacings of 10 m to 30 m are common (Figure 15-13). Also, air circulation generally is not significant below the screened interval for extraction wells. Where contamination is deep and permeability is high throughout the soil profile, the slotted (screened) interval should be extended to the maximum depth possible to maximize treatment, rather than slotted fully vertically (Figure 15-14).

A promising application of SVE is for enhancement of biodegradation of volatile and semivolatile chemicals in soils. SVE provides air to the vadose zone, and thus carries oxygen that can be used as the terminal electron acceptor (TEA) by soil microorganisms to biodegrade chemicals (Figure 15-15). Air has a much greater potential than water for delivering oxygen to soil on a weight-to-weight and volume-to-volume basis (Table 15-6). Oxygen provided by air is more easily delivered since the fluid is less viscous than water higher oxygen concentrations in air also provide a large driving force for diffusion of oxygen into less permeable areas within a soil formation (Miller, 1990).

Hinchee (1989) and Hinchee and Downey (1990) successfully applied SVE to enhance biodegradation of petroleum hydrocarbons in JP-4 jet fuel at Hill Air Force Base, Ogden, Utah, by increasing subsurface oxygen concentrations. Soil moisture was found to be a sensitive variable affecting biodegradation, with increased soil moisture (from 20 percent to 75 percent field capacity) related to increased biodegradation (Figure 15-16). Monitoring carbon dioxide and oxygen concentrations, as well as estimating the mass of VOC biodegraded, is recommended for evaluating potential enhancement of biodegradation using SVE.

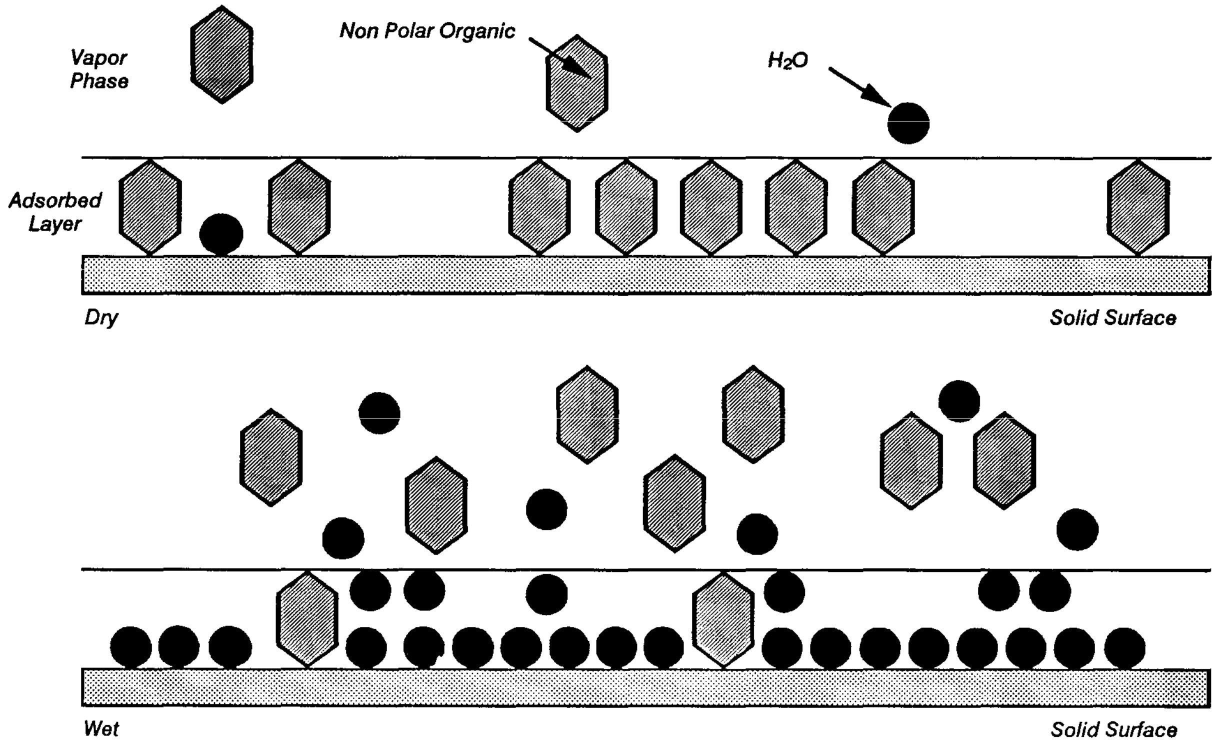


Figure 15-6. Volatile organic carbon adsorption to soil surface in the presence of two soil moisture regimes (from Reible, 1989).

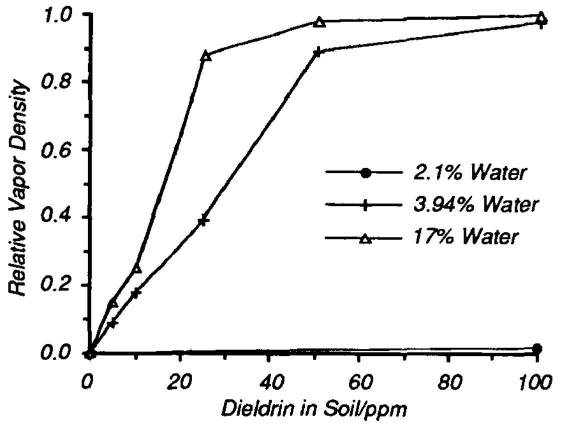


Figure 15-7. Effect of soil water content on dieldrin vapor pressure (modified from Spencer and Claith, 1989).

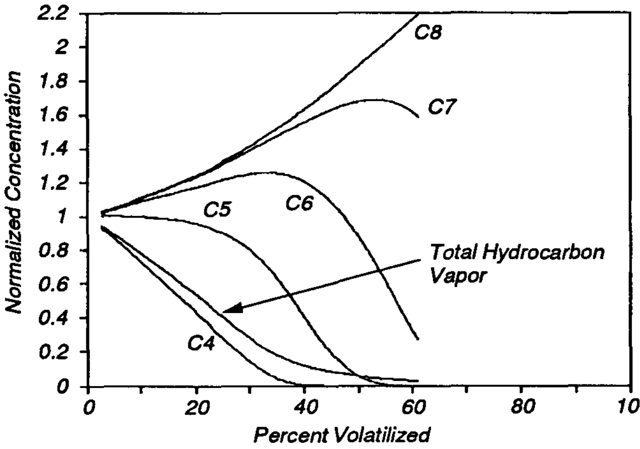


Figure 15-8. Volatilization of different hydrocarbon components in gasoline (from Johnson, 1989).

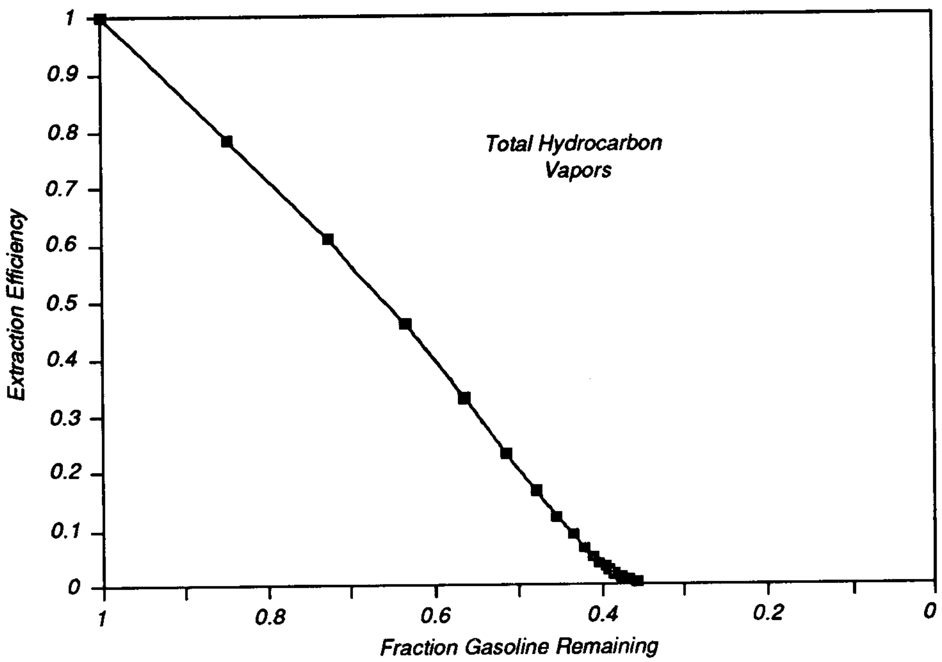


Figure 16-9. Soii vacuum extraction efficiency based on total hydrocarbon vapors (from Johnson, 1989).

*Vacuum Extraction Application Related to Soil Texture*

| | |
|---|---|
| *Stop and* Evaluate *Carefully* | *Clay, Silty Clay, Silty Clay Loam* |
| *Some Difficulty* | *Sandy Clay, Clay Loam* |
| *Good* | *Sandy Clay Loam, Silt Loam* |
| *Very Good* | *Sand, Loamy Sand, Sandy Loam, Loam* |

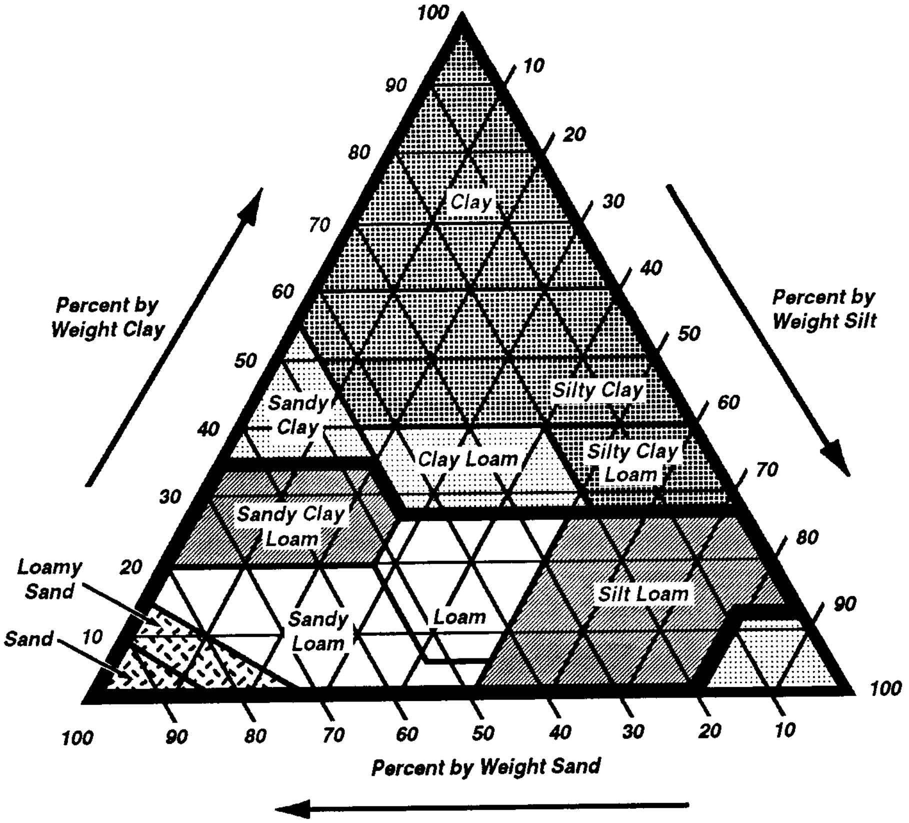


Figure 15-10. Soil texture trilinear diagram (modified from DiGiulio, 1989).

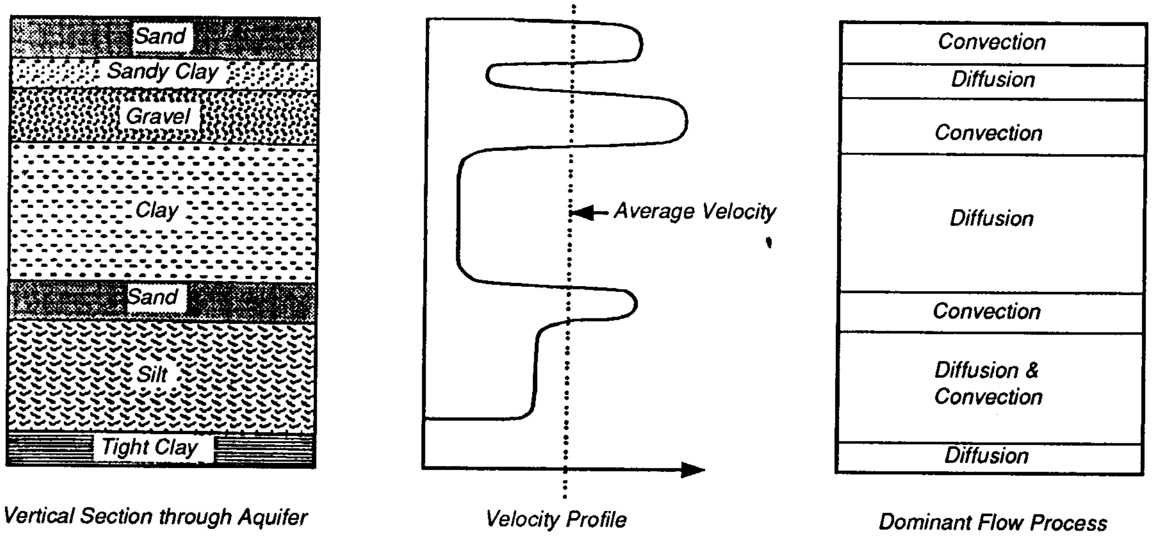


Figure 15-11. Effect of geologic stratification on velocity and resuitant dominant flow process (from Keely et ai., in press).

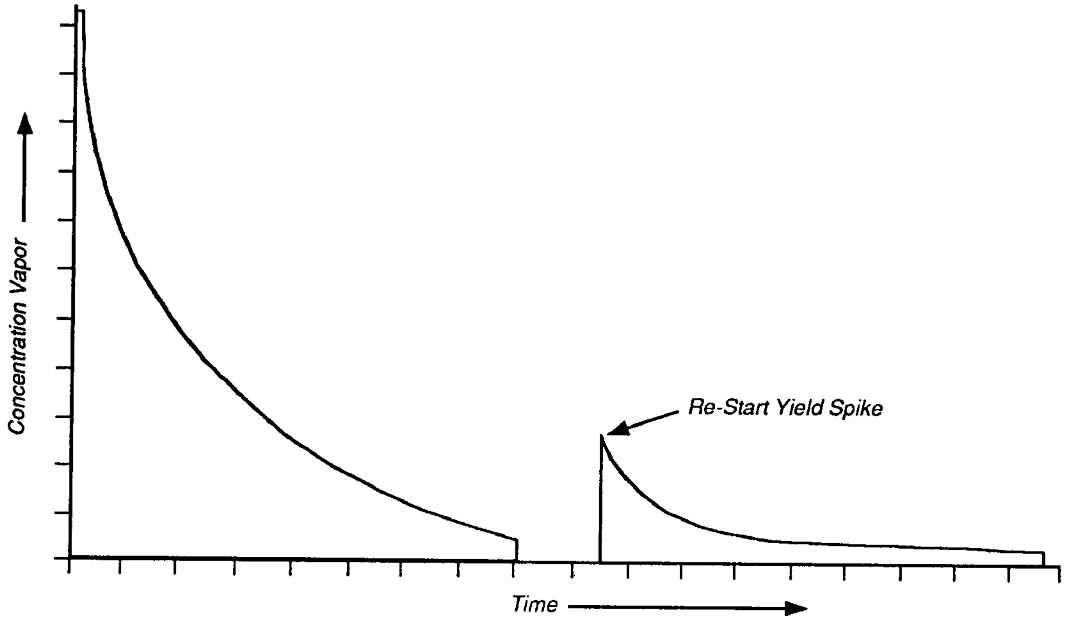


Figure 15-12. Chemicai concentration in the vapor phase versus time for a soil vacuum extraction system where the system is temporarily discontinued, then restarted (from DiGiulio et al., 1990).

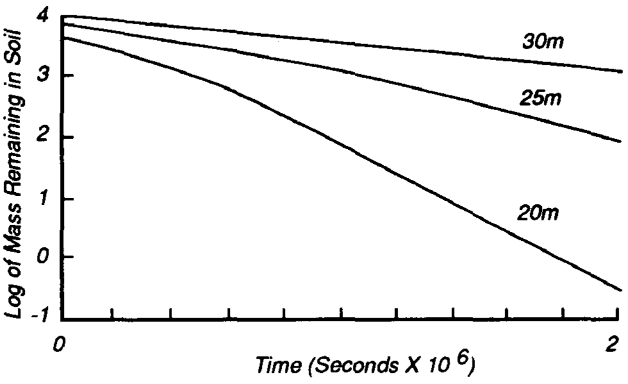


**Figure 15-13.** **Effect of well spacing on total solute mass remaining in soil with vacuum extraction time (from Wilson et al., 1989).**

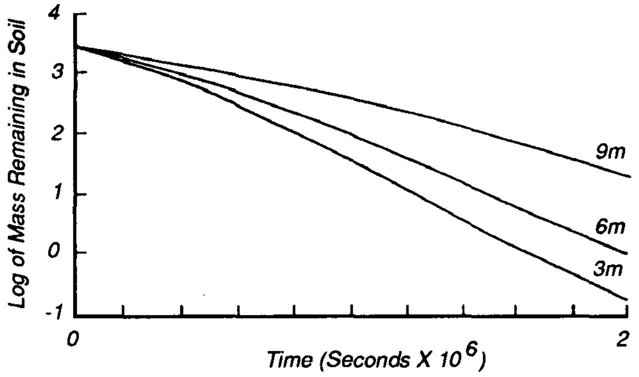


**Figure 15-14.** **Effect of well depth on total solute mass remaining in soil with vacuum extraction time (from Wilson et al., 1989).**

In situ vacuum extraction has been demonstrated in Massachusetts as part of the Superfund SITE program (U.S. EPA, 1989c, and 1989f), in Michigan and Puerto Rico (U.S. EPA, 1988a), and at several other locations in the United States (U.S. EPA, 1990).

### *15.2.2 Bioremediation*

Biotic reactions in the subsurface, including definitions and mechanisms, are addressed in Chapter 13. Wilson (1983) identified biological processes, including microbial degradation, as important mechanisms for attenuating contaminants during transport through the vadose zone to the ground water. In situ soil remedial measures using biological processes can reduce or eliminate continuing or potential ground-water contamination, thus reducing the need for extensive ground-water monitoring and treatment requirements (Wilson, 1981, 1982, 1983).

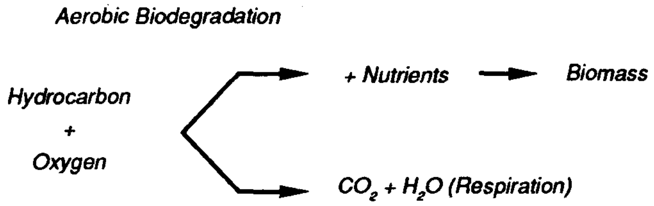


**Figure 15-15.** **Aerobic biodegradation using hydrocarbon as the electron donor and oxygen as the electron acceptor (from Hinchee, 1989).**

In situ biological remediation of soils contaminated with organic chemicals is also an alternative treatment technology for achieving a permanent cleanup remedy at hazardous waste sites, as encouraged by the EPA for implementation of the Superfund Amendments and Reauthorization Act (SARA) of 1986. Information for design of in situ bioremediation is based on land treatment systems designed for hazardous wastes (Overcash and Pal, 1979; U.S. EPA, 1983, 1986). These land treatment designs provide a significant information base for designing in situ soil remediation systems.

In situ bioremediation involves the use of naturally occurring microorganisms (in contrast to genetically engineered microorganisms) to degrade and/or detoxify hazardous constituents in the soil at a contaminated site to protect public health and the environment. Bioremediation techniques for contaminated soils have been addressed at several scientific meetings and conferences (AWMA/U.S. EPA, 1989, 1990; HMCRI, 1989; Omenn, 1988; Lewandowski et al., 1989; U.S. EPA, 1989a). The use of bioremediation techniques in conjunction with chemical and physical treatment processes, i.e., the use of a “treatment train,” is an effective means for comprehensive site-specific remediation (Ross et al., 1988).

Components of soil bioremediation systems generally include (1) delivery systems, such as injection nozzles, plows, and irrigation systems, deliver water, nutrients; oxygen; organic matter, specialized microorganisms, and/or other amendments, as required; and (2) run-on and run-off controls for moisture control and waste containment (U.S. EPA, 1984, 1990).

Four approaches are generally used for in situ biological treatment: (1) enhancement of biochemical mechanisms for detoxifying or degrading chemicals, (2) augmentation with exogenous acclimated or specialized microorganisms originating from uncontaminated or contaminated environments, (3) application of cell-free enzymes, and (4) vegetative uptake (U.S. EPA, 1990). Enhancement of biochemical mechanisms may involve (1) control of soil factors such as contaminant concentrations that do not severely inhibit microbial activity, soil moisture, pH, nutrients, and temperature in order to optimize microbial activity; (2) addition of organic amendments to stimulate cooxidation or cometabolism; (3) control of soil oxygen by moisture control to accomplish aerobic or anaerobic biodegradation; and (4) addition of colloidal gas aphrons (microscopic bubbles of gas) to increase the concentration of terminal electron acceptors (oxygen) in the soil and

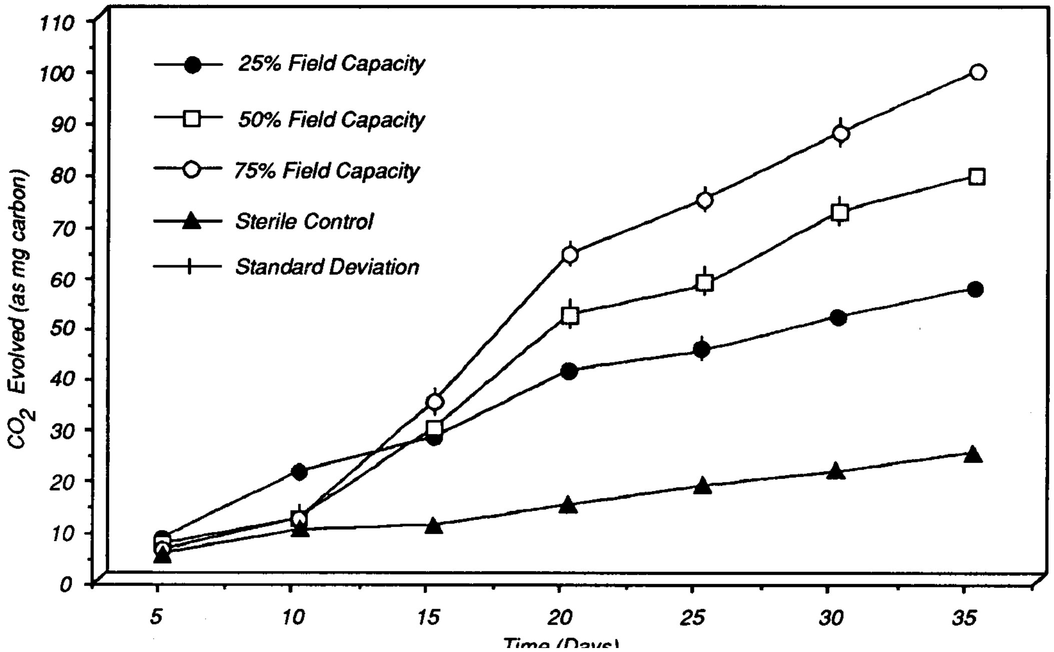


Figure 15-16. Enhancement of bioremediation of gasoline components using vacuum extraction of soil amended with nutrients and moisture (from Hinchse, 1989).

thereby enhance aerobic biodegradation (Keck et al., 1989; Sims et al., 1989; U.S. EPA 1989a, 1990).

The soil contaminant concentration effect on rate and extent of detoxification of contaminated soil is illustrated in Figure 15-17. Detoxification of the soil/waste mixture was measured using the Microtox™ bioassay. The Microtox™ assay is an aqueous general toxicity assay that measures the reduction in light output produced by a suspension of marine luminescent bacteria in response to an environmental sample (Bulich, 1979). Bioluminescence of the test organism depends on a complex chain of biochemical reactions. Chemical inhibition of any of the biochemical reactions causes a reduction in bacterial luminescence. Therefore, the Microtox™ test considers the physiological effect of a toxicant, not just mortality. Matthews and Bulich (1984) described a method of using the Microtox™ assay to predict the land treatability of hazardous organic wastes. Matthews and Hastings (1987) developed a method using the Microtox™ assay to determine an appropriate range of waste application loading for soil-based waste treatment systems. Symons and Sims (1988) utilized the assay to assess the detoxification of a complex petroleum waste in a soil environment. The assay also was included as a recommended bioassay in the EPA's *Permit Guidance Manual on Hazardous Waste Lund Treatment Demonstrations (1986).* Comparison of results presented in Figure 15-18 for a clay loam soil with results for the sandy loam soil shown in Figure 15-17 indicates that detoxification rate and extent for a waste is a function of soil type. Implications for management of heavily contaminated soils, therefore, may include the incorporation of additional treatment medium (uncontaminated soil) into contaminated soil. This incorpora-

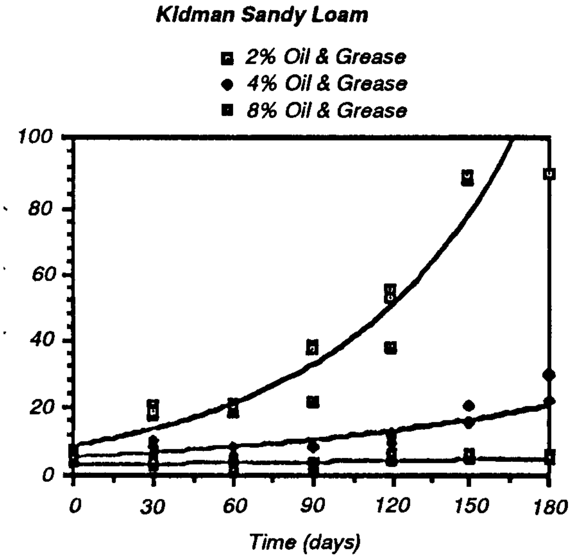


Figure 15-17. Detoxification of sandy loam soil measured by Microtox™ assay (from Symonsand Sims, 1988.

tion will decrease the concentration of contaminant to levels that are less inhibitory to soil microbial processes, thereby rendering treatment more rapidly and completely.

Acclimation of a soil to the presence of a waste is shown for a fossil fuel-contaminated soil in Table 15-7. The acclimated soil was exposed to the fossil fuel waste for one year before a repeat application of the waste. Results presented in Table 15-7 indicate that a higher percentage of waste was treated in the acclimated soil. Treatment also occurred more rapidly compared to treatment in unacclimated soil. Management of contaminated soil, therefore, may include the addition of lightly contaminated, preexposed, soil to more heavily contaminated and/or newly contaminated soil to increase the rate and extent of treatment..

The effect of soil moisture on treatment of contaminated soil is illustrated in Table 15-8 and Figure 15-19. The chemical degradation rates given in Table 15-8 indicate more rapid degradation at a soil moisture content of 60 to 80 percent of field capacity than at a soil moisture content of 20 to 40 percent. Microtox™ assay results for evaluation of the changes in toxicity of four wastes (Figure 15-19), two petroleum and two wood preserving, incubated in relatively dry sandy loam soil (20 to 40 percent field capacity) over a period of 360 days indicated little change in toxicity for three wastes and an increase in toxicity for one waste. Comparison of results obtained for lower soil moisture (Figure 15-19) with those for higher soil moisture (Figure 15-17) for petroleum wastes in sandy loam soil indicate the importance of soil moisture in influencing microbial activity in waste/soil mixtures.

The effect of temperature on apparent loss of polycyclic aromatic hydrocarbon (PAHs) compounds in a sandy loam soil is summarized in Table 15-9 (Coover and Sims, 1987). Temperature has an important effect on the fate and behavior of PAHs and, therefore, has implications for seasonal effects on the rate of biological remediation of soil contaminated with these chemicals. Microbial ecologists have identified ranges of critical environmental conditions that affect aerobic activity of soil microorganisms (Table 15-10). Many of these conditions are controllable and can be modified to enhance activity (Huddleston et al., 1986; Paul and Clark, 1989; Rochkind et al., 1986; Sims et al., 1984).

The application of cooxidation processes for the biodegradation of high molecular weight PAHs present in oil (NAPL) phases in soil has been investigated by Keck et al. (1989). In certain cases, PAH degradation may be limited by the rate of primary substrate (oil) degradation, which is limited by the rate of supply of terminal electron acceptors (oxygen) to the subsurface. In the study by Keck et al., aerobic conditions were not sufficient to stimulate biodegradation of high molecular weight PAHs present as a synthetic mixture in soil; however, when PAHs were present in an oily matrix in the soil, and the soil was supplied with oxygen, PAHs were observed to exhibit faster degradation kinetics (Figure 15-20). Results indicated that oxygen may limit the rate and extent of biodegradation in soil environments, in addition to saturated environments. Supplying oxygen to the contaminated vadose zone may allow biodegradation of oily components of soil wastes, which may result in simultaneous cooxidation of resistant PAHs present in the oily waste.

There is also increasing evidence that some halogenated compounds may be degraded under methanogenic conditions through a process of reductive dehalogenation (Suflita et al., 1982, 1983, 1984). Kobayashi and Rittmann (1982) determined that the redox potential of the environment must be below 0.35 V for significant reductive dechlorination to occur. Reductive reactions may be catalyzed by both abiotic and biochemical means in anaerobic environments.

Oxygen may be consumed faster than it can be replaced by diffusion from the atmosphere, and the soil may become anaerobic. Clay content of soil and the presence of organic matter also may affect oxygen content in soil. Clayey soils tend to retain a higher moisture content, which restricts oxygen diffusion, while organic matter may increase microbial activity and deplete available oxygen. Loss of oxygen as a metabolic electron acceptor induces a change in the activity and composition of the soil microbial population. Obligate anaerobic organisms and facultative anaerobic organisms, which use oxygen when it is present or switch to alternative electron acceptors such as nitrate or sulfate in the absence of oxygen, become the dominant populations. Additional information concerning in situ anaerobic bioremediation can be found in the document, *Handbook on In Situ Treatment of hazardous Waste-Contaminated Soils* (U.S. EPA, 1990).

The use of plants for stimulating microbial activity in soil results in increased biodegradation of target organic chemicals in contrast to the possibility of vegetative accumulation of chemicals for harvesting and removal from a site. This method is currently being investigated by Walton and Anderson (1990) and Aprill and Sims (1990). In soils with low levels of contamination, plant roots may stimulate the biodegradation of toxic chemicals by providing exudates that serve as carbon and energy substrates for soil microorganisms. The effects of prairie grasses on soil PAH concentrations are summarized in Table 15-11. For soil with initial concentrations of PAHs of approximately 10 to 50 mg/kg, the presence of vegetation in the soil (prairie grasses) resulted in a statistically significant reduction in PAHs, compared with nonvegetated soil.

The environmental factors presented in Table 15-10, as well as waste and soil/site characteristics identified in Chapter 14, interact to affect microbial activity at a specific contaminated site. Computer modeling techniques are useful design and evaluation tools to describe these interactions and their effects on bioremediation treatment techniques for organic constituents in a specific situation.

Measurement of physical abiotic loss mechanisms (discussed in Chapter 13) and partitioning of organic substances into air and soil phases (discussed in Chapters 10 and 11) should be used in degradation studies to ensure that generated information is related to disappearance mechanisms of the constituents in the soil system (Abbott and Sims, 1989; Armstrong and Konrad, 1974). This type of information is needed to more accurately evaluate and select treatment techniques. For example, for organophosphorus pesticides, sorp-

*Table 15-7 Acclimation of Soil to Complex Foesil Fuel Waste*

| PNA Constituent | Unacclimated Soil: Initial Soil Concentration (mg/kg-dry wt) | Unacclimated Soil: Reduction in 40 days (%) | Acclimated Soil: Soil Concentration after First Reapplication of Waste (after 168 days incubation at initial level) (mglkg-dry wt) | Acclimated Soil: Reduction in 22 days (%) |
|---|---|---|---|---|
| Naphthalene | 38 | 90 | 38 | 100 |
| Phenanthrene | 30 | 70 | 30 | 83 |
| Anthracene | 38 | 58 | 38 | 99 |
| Fluoranthene | 154 | 51 | 159 | 82 |
| Pyrene | 177 | 47 | 160 | 86 |
| Benz(a)anthracene | 30 | 42 | 40 | 70 |
| Chrysene | 27 | 25 | 33 | 61 |
| Benz(a)pyrene | 10 | 40 | 12 | 50 |

Source: Sims, 1986

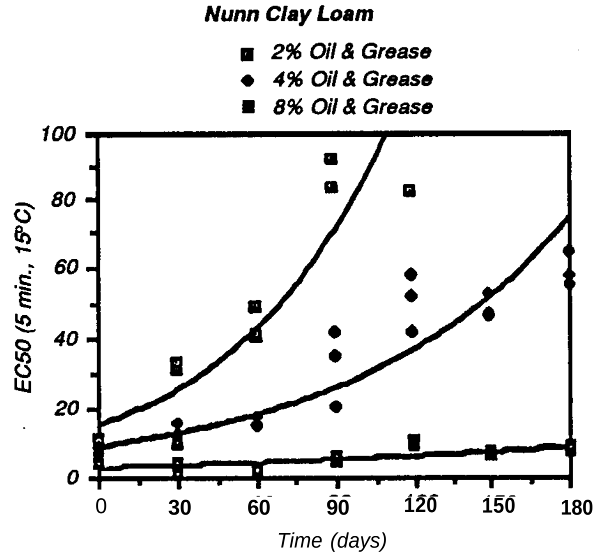


**Figure 15-18.** Detoxification of clay loam soil measured by Microtox™ assay (from Symons and Sims, 1988).

*Tabie 15-8. Effect of Soil Moisture on PNA Degradation (Reauits Presented as Half-Life in Days)*

| Moisture | Anthracene | Phenanthrene | Fluoranthene |
|---|---|---|---|
| 20-40% field capacity | 43 | 61 | 559 |
| 60-80% field capacity | 37 | 54 | 231 |

Source: Sims, 1986

tion-catalyzed hydrolysis of ester linkages is known to be an important influence on soil degradation. An understanding of abiotic reactions as influenced by sorption and pH of the system may allow the design of a more effective remediation strategy. If abiotic controls are not used, the disappearance of chemicals may be attributed solely to biological activity, though biological activity may not play the major role in the degradation of the chemical. Therefore, knowledge of the reaction mechanism is directly related to efficiency and effectiveness in remediation strategy design and remediation technique selection.

### 15.2.3 Immobilization

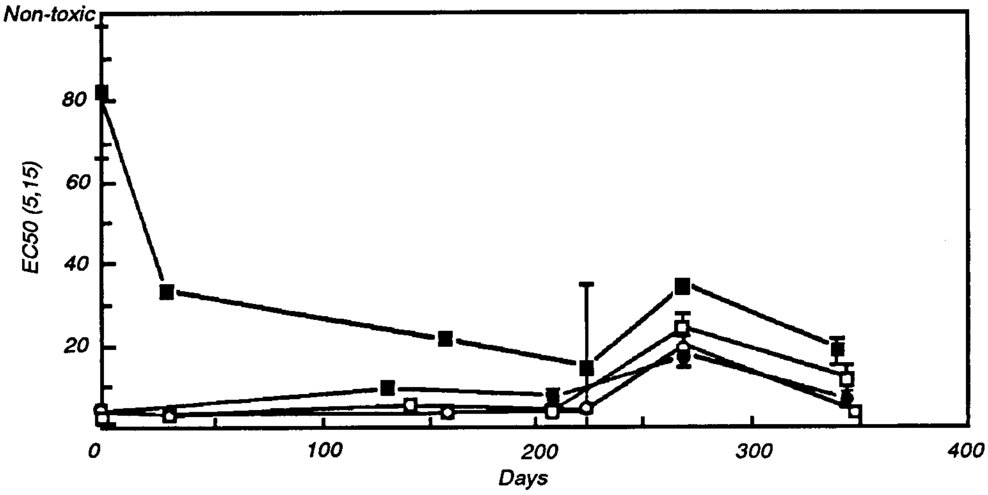
One way to predict and control the rate of transport of a constituent through a subsurface system is to describe its mobility (or relative immobility) by predicting its retardation (Borden and Bedient, 1987; Mahmood and Sims, 1986). Retardation describes the relative velocity of the constituent compared to the rate of movement of water through the subsurface (see Section 10.3 for more information). Retardation in unsaturated soil can be represented as:

$$R = 1 + (rK_d/q) \qquad [15\text{-}2]$$

where p = soil bulk density; $K_d$ = soil/water partition coefficient, which describes the partitioning between the soil solid phase and soil water; and θ = volumetric moisture content. For a saturated system, θ is replaced by the porosity of the system. For additional detail about this process, see Section 10.3.

This information can be used to evaluate treatment techniques for a contaminated soil system (e.g., techniques to modify the soil/water partition coefficient, such as control of soil moisture, changes in bulk density, or addition of amendments to the soil). Constituents can be "captured" or contained within the system by using these techniques, thus allowing time for degradation at the site or for engineering implementation and performance of other remediation treatment techniques, such as soil washing (Sims et al., 1989).

Linear retardation of chemicals in the vapor phase is discussed in Chapter 11. Variables in the equations given in



*Toxicity of water soluble fraction measured with the Microtox™ assay with incubation time for PCP-creosote mixed sludge (–□–), creosote sludge (–○–), API separator sludge (–■–), and slop c emulsion solids (–●–) mixed with a Kidman sandy loam soil. EC50 (5, 15°) denotes the effective concentration (vol/vol) of water soluble extract that reduces light emission of the Microtox™ organism by 50% five minutes after exposure to the test solution at 15°C. Values presented prior to 250 days o incubation are the average and standard deviation of duplicate samples. Values presented after 250 days were determined from single samples with a 95% confidence interval.*

**Figure 15-19. Microtox™ assay results for various materials (from Aprill et al., 1990).**

that chapter can be used by professionals involved in treatment technique selection to determine site conditions (pb, Kp, Ow, $\theta_A$) that may influence the effectiveness of specific treatment technologies. For additional detail about these processes, see Section 11.2.2.

Constituents in in situ and prepared bed treatment systems are generally immobilized through sorption, ion exchange, and/or precipitation reactions. These techniques reduce the rate of contaminant release from the soil environment so that concentrations along exposure pathways are held within acceptable limits. The effects of moisture and distribution coefficient, $K_d$, on immobilization are illustrated in Figure 15-21. Results indicate that for chemicals with $K_d$, values less than 10, management of soil moisture is important with regard to immobilizing chemicals; for chemicals with $K_d$ values greater than 10, management of soil moisture is less important. Appreaches for controlling soil moisture include run-on and run-off controls, temporary capping or covering, and irrigation scheduling.

The cation exchange capacity (CEC) of soil also can be evaluated with regard to organic as well as metal immobilization. Positively charged organic chemicals and metals will generally readily attach to soil materials with negatively charged functional groups and negatively charged clay particles. Addition of clays, synthetic resins, and zeolites will increase the CEC of soils and increase immobilization of chemicals sensitive to CEC characteristics of a soil (Sims et al., 1984; U.S. EPA, 1984). For inorganic chemicals that are negatively charged in soil systems and can exist in several oxidation states (e.g., chromium, selenium, and arsenic), immobilization, as well as the toxic form of the chemical, may potentially be controlled by managing the redox and pH of the soil system. Management of redox and pH may be short-term or long-term, depending upon the goals of site management (e.g., temporary immobilization while delivery and recovery systems are designed and implemented, followed by soil flushing with aqueous or surfactant solutions for removal and recovery of the contaminants) (Sims et al., 1984; U.S. EPA, 1984).

Solidification and stabilization are additional immobilization techniques that are applicable to in situ and prepared bed systems. These techniques are designed to accomplish one or more of the following: (1) production of a solid from a liquid or semisolid waste, (2) reduction of contaminant volubility, and/or (3) a decrease in the exposed surface area across which transfer may occur. Solidification may involve encapsulation of fine waste particles (microencapsulation) or large blocks of waste (macroencapsulation).

Stabilization refers to the process of reducing the hazardous potential of waste materials by converting contaminants into their least soluble, mobile, or toxic form (U.S. EPA, 1990). A milestone publication providing additional detail on this technique is the *Handbook for Stabilization Solidification of Hazardous Wastes* (Cullinane et al., 1986).

Systems for delivering reagents to the contaminated area include (1) injection systems; (2) soil surface applicators; and/or (3) delivery and application of electrical energy for melting

**Table 15-9. Percentages of PAH Remaining at the End of the 240-Day Study Period and Estimated Apparent Loss Half-Lives**

| | Percent of PAH Remaining | | | Estimated Half Life (day)[a] | | | Half lives reported in the literature (day) |
|---|---|---|---|---|---|---|---|
| Compound | 10°C | 20°C | 30°C | 10°C | 20°C | 30°C | |
| Acenaphthene | 5 | 0 | 0 | <60 | <10 | <10 | 96[b], 45[b], 0.3-4[c] |
| Fluorene | 8 | 3 | 2 | 60 (+11/-10) | 47 (+6/-5) | 32 (+5/-3) | 64[b], 39[b], 2-39[c] |
| Phenanthrene | 36 | 19 | 2 | 200 (+40/-40) | <60 | <60 | 69[b], 23[b], 26[c], 9.7[d], 14[d] |
| Anthracene | 83 | 51 | 58 | 460 (+310/-140) | 260 (+160/-70) | 200 (+90/-30) | 28[b], 17[b], 108-175[c], 17[d], 45[d] |
| Fluoranthene | 94 | 71 | 15 | f | 440 (+560/-160) | 140 (+40/-20) | 104[b], 29[b], 44-182[c], 39[d], 34[d] |
| Pyrene | 93 | 89 | 43 | f | 1900 (+6200/-800) | 210 (+160/-60) | 73[b], 27[b], 3-35[c], 58[d], 48[d] |
| Benz[a]anthracene | 82 | 71 | 50 | 680 (+300/-160) | 430 (+110/-70 | 240 (+40/-40) | 52[b], 123[b], 102-252[c], 240[d], 130[d] |
| Chrysene | 85 | 88 | 86 | 980 (+520/-270) | 1000 (+900/-250) | 730 (+370/-180) | 70[b], 42[b], 5.5-10.5[c], 328[d], 224[d] |
| Benzo[b]fluoranthene | 77 | 75 | 62 | 580 (+520/-180) | 610 (+590/-200) | 360 (+150/-80) | 73-130[e], 85[b], 65[b] |
| Benzo[k]fluoranthene | 93 | 95 | 89 | 910 (+690/-270) | 1400 (+3300/-560) | 910 (+4400/-410) | 143[b], 74[b] |
| Benzo[a]pyrene | 73 | 54 | 53 | 530 (+1700/-230) | 290 (+570/-120) | 220 (+160/-60) | 91[b], 69[b], 30-420[c], 347[d], 218[d] |
| Dibenz[a,h]anthracene | 88 | 87 | 83 | 820 (+1100/-300) | 750 (+850/-260) | 940 (+12000/-450) | 74[b], 42[b], 100-190[e] |
| Benzo[g,h,i]perylene | 81 | 76 | 75 | 650 (+650/-230) | 600 (+570/-190) | 590 (+1800/-250) | 179[b], 70[a,b] |
| Indeno[1,2,3-c,d]pyrene | 80 | 77 | 70 | 600 (+310/-150) | 730 (+1100/-270) | 630 (+2500/-280) | 57[b], 42[b], 200-600[e] |

[a] $t_{1/2}$ (95 percent confidence interval)
[b] T = 20°C Sims (1986)
[c] T = 15-25°C Sims and Overcash (1983)
[d] T = 20°C PACE (1985)
[e] T = 20°C Sims (1982)
[f] Least squares slope (for calculations of $t_{1/2}$) = zero with 95% confidence

Coover and Sims, 1987

**Table 15-10 Critical Environmental Factors for Microbial Activity**

| Environmental Factor | Optimum Levels |
|---|---|
| Available soil water | 25 - 85% of water holding capacity; - 0.01 MPa |
| Oxygen | Aerobic metabolism: Greater than 0.2 mg/l dissolved oxygen, minimum air-filled pore space of 10% by volume;<br>Anaerobic metabolism: $O_2$ concentrations less than 1% by volume |
| Redox potential | Aerobes and facultative anaerobes: greater than 50 millivolts;<br>Anaerobes: less than 50 millivolts pH 5.5 - 8.5 |
| Nutrients | Sufficient nitrogen, phosphorus, and other nutrients so not limiting to microbial growth (Suggested C:N:P ratio of 120:10:1) |
| Temperature | 15 - 45 °C (Mesophiles) |

Sources: Huddleston et al., 1986; Paul and Clark, 1989; Rochkind et al., 1986; Sims et al., 1984 soils and rocks that contain hazardous materials. Equipment required for preparing, mixing, and applying reagents depends upon the reagent process, and depth of contamination (U.S. EPA, 1990).

Important parameters identified by Truett et al. (1983) for solidification and stabilization of hazardous wastes include (1) reagent viscosity; (2) permeability of soils; (3) porosity of waste materials and soil; (4) distribution of waste in surrounding material (rocks, soils, etc.); and (5) rate of reaction. The most significant challenge in applying solidification/stabilization treatment in situ is achieving uniform mixing of added chemical agent(s) with the contaminated soils (U.S. EPA, 1990).

Design factors involve delivery and mixing systems to obtain complete and uniform distribution of added reagent throughout the contaminated soil (U.S. EPA, 1990).

In situ solidification/stabilization was applied and evaluated under the Superfund SITE program for treatment of polychlorinatcd biphenyl (PCB) contaminated soils (U.S. EPA, 1989e). Eight additional application sites have been summarized in U.S. EPA (1990).

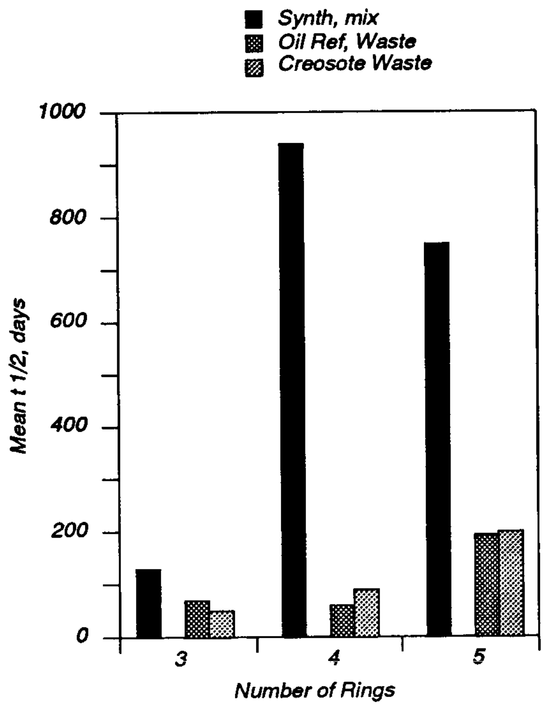


**Figure 15-20. Persistence in soil of PAH compounds as a function of number of fused benzene rings (from Keck et sl., 1989).**

*Table 15-11. Apparent Disappearance of PAH Compounds in Vegetated and Unvegetated Soii Using the Tissumizer™ Extraction Method*

| | Concentration at a Given Time/Initial Concentration (C/Co) (Average ± Std. Dev.) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Benz(a)anthracene | | Chrysene | | Benzo(a)pyrene | | Dibenz(a,h)anthracene | |
| Days of Incubation | Unvegetated | Vegetated | Unvegetated | Vegetated | Unvegetated | Vegetated | Unvegetated | Vegetated |
| 31 | 0.298[a]<br>±0.053 | 0.470[a]<br>±0.115 | 0.608[b]<br>±0.065 | 0.810[b]<br>±0.166 | 0.578[a]<br>±0.057 | 0.895[a]<br>±0.124 | 1.221[a]<br>±0.131 | 1.519[a]<br>±0.122 |
| 59 | 0.150<br>±0.030 | 0.144<br>±0.020 | 0.362<br>±0.063 | 0.325<br>±0.035 | 0.403<br>±0.127 | 0.381<br>±0.086 | 1.134<br>±0.240 | 1.011<br>±0.178 |
| 94 | 0.089<br>±0.027 | 0.061<br>±0.015 | 0.211[b]<br>±0.059 | 0.141[b]<br>±0.027 | 0.258<br>±0.103 | 0.165<br>±0.033 | 0.994[b]<br>±0.275 | 0.663[b]<br>±0.099 |
| 114[c] | 0.063 | 0.064 | 0.124 | 0.133 | 0.092 | 0.184 | 0.685 | 0.746 |
| 151 | 0.050[a]<br>±0.009 | 0.027[a]<br>±0.011 | 0.143[a]<br>±0.020 | 0.081[a]<br>±0.031 | 0.209[a]<br>±0.030 | 0.122[a]<br>±0.045 | 0.949<br>±0.255 | 0.629<br>±0.278 |
| 184 | 0.067[a]<br>±0.024 | 0.033[a]<br>±0.010 | 0.144[b]<br>±0.047 | 0.081[b]<br>±0.027 | 0.188[a]<br>±0.048 | 0.105[a]<br>±0.036 | 1.011[a]<br>±0.090 | 0.631[a]<br>±0.221 |
| 219 | 0.060[a]<br>±0.017 | 0.027[a]<br>±0.014 | 0.119[b]<br>±0.045 | 0.064[b]<br>±0.019 | 0.162[b]<br>±0.054 | 0.107[b]<br>±0.012 | 0.771[b]<br>±0.203 | 0.547[b]<br>±0.048 |

*[a] corresponding values are significantly different with 95% confidence using unpaired t-test comparison.*
*[b] corresponding values are significantly different with 90% confidence using unpaired t-test comparison.*
*[c] statistics not calculated, only one data point collected.*

*Aprill and Sims, 1990*

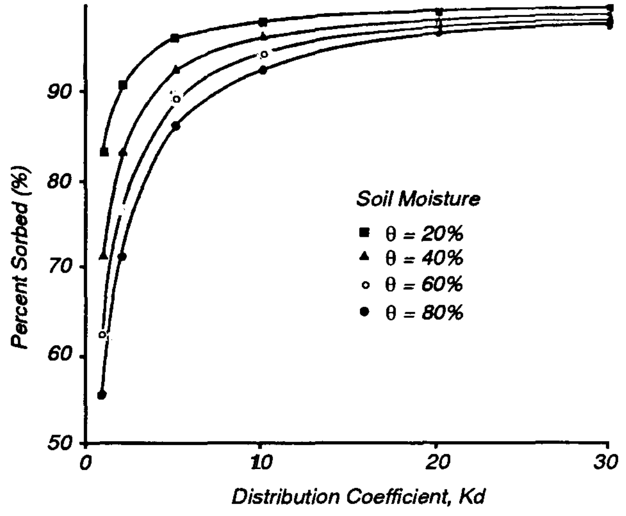


**Figure 15-21. Sorption of chemicals to soil as functions of soil moisture content and partition coefficient Kd (Sims et al., 1986).**

### *15.2.4 Contaminant Mobilization*

Mobilization of organic ant/or inorganic contaminants from soil may be accomplished using soil flushing and recovery and treatment of the elutriate (U.S. EPA, 1984, 1990). Flushing solutions generally include water, acidic and basic solutions, surfactants, and solvents. The solutions partition a contaminant into the liquid phase through the volume of added liquid or by decreasing the distribution coefficient between the soil and the flushing phase (Sims et al., 1984; Raghavan et al., 1990). A schematic of a soil flushing system is shown in Figure 15-22 (U.S EPA, 1984). Components consist of (1) the flushing solution, and (2) delivery and recovery systems, which may include injection and recovery wells, equipment for surface applications, and holding tanks for storing elutriate for reapplication (U.S. EPA, 1984, 1990).

Variables affecting application of the technique include (1) concentration and volume of contamination; (2) distribution coefficients of waste constituents; (3) interactions of flushing solutions with soil; and (4) suitability of site for installation of wells, drains, etc., for delivery and recovery. Design factors include sizing the delivery and recovery systems to ensure complete recovery of elutriate. Problems with respect to flushing of bulk fluids, or NAPLs, from soil systems are due to the following characteristics of bulk fluids: (1) low water volubility, (2) high interracial tension, and (3) poor relative permeability. Relative permeability is defined as:

$$M = [K_d/U_d] / [K_o/U_o] \qquad [15\text{-}3]$$

where M = mobility ratio; $K_d$ = fluid permeability (water); $K_o$ = oil permeability; $U_d$ = viscosity of fluid (water); and $U_o$ = viscosity of oil. Strategies for flushing of bulk liquids from soil generally involve control of one or more of the variables affecting the mobility ratio through adding chemicals to decrease mobility of water or increase mobility of oil (e.g., adding surfactants or steam to decrease $U_o$ or adding polymers to increase Ud).

Use of soil flushing in a treatment train with bioremediation has been evaluated by Dworkin et al. (1988) and by Kuhn and Piontek (1989) for wood preserving contaminated sites. Flushing using surfactant/polymer combinations was used to remove high concentrations of PAH compounds; residual low concentrations were treated using biological processes.

The effect of adding a solvent on the partitioning of PAHs between soil and solution (solvent) phases of a soil system is illustrated in Figure 15-23. When methanol was used as the solvent in a soil system to flush PAHs from a soil, the resultant concentration of the PAHs in the solution phase was several orders of magnitude higher than the concentration of the PAHs in water.

## 15.3 Prepared Bed Reactors

In a prepared bed system, the contaminated soil may be either (1) physically moved from its original site to a newly prepared area, which has been designed to enhance remediation and/or to prevent transport of contaminants from the site; or (2) removed from the site to a storage area while the original location is prepared for use, then returned to the bed, where the treatment is accomplished. Preparation of the bed may include placement of a clay or plastic liner to retard transport of contaminants from the site or addition of uncontaminated soil to provide additional treatment medium.

Possible prepared bed reactor technologies are identified in Table 15-4 and are evaluated for function as well as application and limitations. Treatment of contaminants with a prepared bed may be based on the techniques previously identified and described for in situ treatment.

An example of the use of a prepared bed reactor for soil remediation was described by Lynch and Genes (1989). Prepared bed treatment of creosote-contamimted soils from a shallow, unlined surface impoundment was demonstrated at a disposal facility for a wood-preserving operation in Minnesota. The contaminated soils contained creosote constituents consisting primarily of PAHs at concentrations ranging from 1,000 to 10,000 ppm. Prior to implementation of the full-scale treatment operation, bench-scale and pilot-scale studies simulating proposed full-scale conditions were conducted to define operation and design parameters. Over a 4-month period, 62 to 80 percent removal of total PAHs was achieved in all test plots and laboratory reactors. Two-ring PAH compounds were reduced by 80 to 90 percent, 3-ring PAHs by 82 to 93 percent, and 4+-ring PAHs by 21 to 60 percent.

The full-scale system involved preparation of a treatment area within the confines of the existing impoundment. A lined waste pile for temporary storage of the sludge and contami-

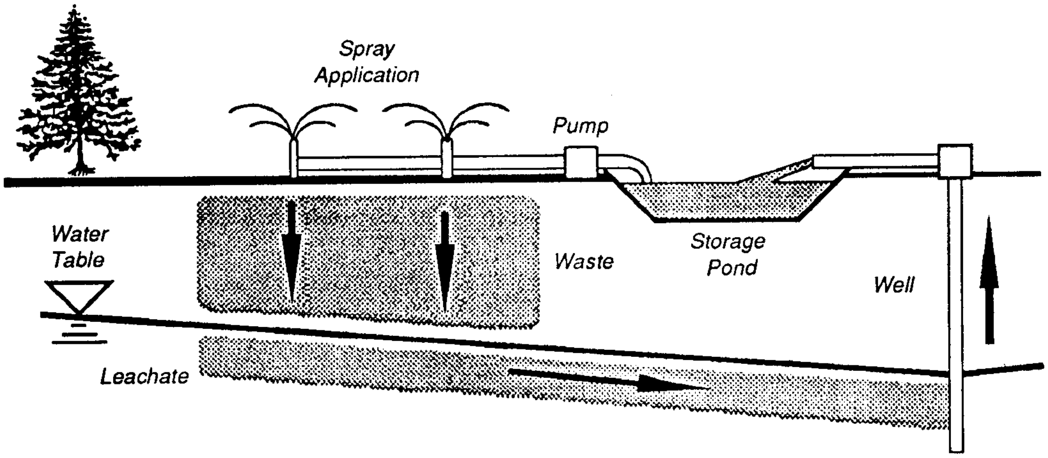


**Figure 15-22. Schematic of soil flushing and recycle system (U.S. EPA, 1990).**

nated soil from the impoundment was constructed. All standing water from the impoundment was removed, and the sludges were excavated and segregated for subsequent free oil recovery. Three to five feet of "visibly" contaminated soil was excavated and stored in the lined waste pile. The bottom of the impoundment was stabilized as a base for the treatment area. The treatment area was constructed by installation of a polyethylene liner, a leachate collection system, 4 feet of clean backfill, and addition of manure to achieve a carbon: nitrogen ratio of 50:1. A sump for collection of storm water and leachate and a center pivot irrigation system also were installed. The lined treatment area was required because natural soils at the site were highly permeable. A cap also was needed for residual contaminants left in place below the liner. Contaminated soil was periodically applied to the treatment facility and rototilled into the treatment soil. Soil moisture was maintained near field capacity with the irrigation system. During the first year of operation, greater than 95 percent reductions in concentration were obtained for 2- and 3-ring PAHs. Greater than 70 percent of 4- and 5-ring PAH compounds were degraded during the first year. Comparison of half-lives of PNAs in the full-scale facility were in the low end of the range of half-lives reported for the test plot units. Only two PNA compounds were detected in drain tile water samples, at concentrations near analytical detection limits.

Prepared bed treatment of a Texas oilfield site with storage pit backfill soils contaminated with styrene, still bottom tars, and chlorinated hydrocarbon solvents was demonstrated on a pilot scale (St. John and Sikes, 1988). The remediation efforts included biological, chemical, and physical treatment strategies. The pilot-scale, solid-phase biological treatment facility consisted of a plastic film greenhouse enclosure, a lined soil treatment bed with an underdrain, an overhead spray system for distributing water, nutrients, and inocula, an organic vapor control system consisting of activated carbon absorbers, and a fermentation vessel for preparing microbial inoculum or treating contaminated leachate from the backfill soils. Soils were excavated from the contaminated area and transferred to the treatment facility. Average concentrations of volatite organic compounds (VOCs) were reduced by more than 99 percent during the 94-day period of operation of the facility; most of the removal was attributed to air stripping. Biodegradation of semivolatile compounds reduced average concentrations by 89 percent during the treatment period.

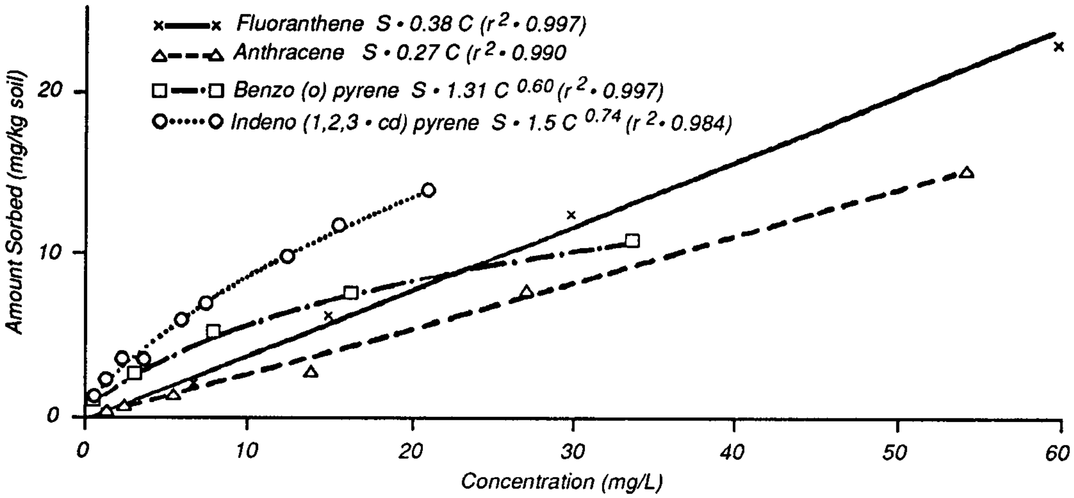


**Figure 15-23. PAH adsorption isotherms with methanol and clay loam soil (from Mahmood and Sims, 1985).**

## 15.4 References

Abbott, C. and R.C. Sims. 1989. Use of Bioassays to Monitor Polycyclic Aromatic Hydrocarbon Contamination in Soil. In: Superfund '89, Hazardous Materials Control Research Institute, Silver Spring, MD, pp. 23-26.

Aprill, W. and R.C. Sims. 1990. Evaluation of the Use of Prairie Grasses for Stimulating Polycyclic Aromatic Hydrocarbon Treatment in Soil. Chemosphere 20:253-265.

Aprill, W., R.C, Sims, J.L. Sims, and J.E. Matthews. 1990. Assessing Detoxification and Degradation of Wood Preserving and Petroleum Wastes in Contaminated Soil. Waste Manag. and Res. 8:45-65.

Armstrong, D.E. and J.G. Konrad. 1974. Nonbiological Degradation of Pesticides. In: Pesticides in Soil and Water, W. D. Guenzi (ed.), Soil Science Society of America, Madison, WI, Chapter 7.

AWMA/EPA. 1989. Proceedings of the International Symposium on Hazardous Waste Treatment: Biosystems for Pollution Control (Cincinnati, OH). Air and Waste Management Association, Pittsburgh.

AWMA/EPA. 1990. Proceedings of the International Symposium on Hazardous Waste Treatment: Treatment of Contaminated Soils (Cincinnati, OH). Air and Waste Management Association, Pittsburgh.

Borden, R.C., P.B. Bedient, M.D. Lee, C.H. Ward, and J.T. Wilson. 1986. Transport of Dissolved Hydrocarbons Influenced by Reaeration and Oxygen Limited Biodegradation. II. Field Application. Water Resources Research 22:1983-1990.

Bulich, A.A. 1979. Use of Luminescent Bacteria for Determining Toxicity in Aquatic Environments. In: Aquatic Toxicology, L.L. Markings and R.A. Kimerle, (eds.), American Society for Testing and Materials, Philadelphia, PA, pp. 98-106.

Coovcr, M.P. and R.C. Sims. 1987. The Effect of Temperature on Polycyclic Aromatic Hydrocarbon Persistence in an Unacclimated Soil. Hazardous Waste and Hazardous Materials 4:69-82.

Cullinane, Jr., M.J., L.W. Jones, and P.G. Malone. 1986. Handbook for Stabilization/ Solidification of Hazardous Wastes. EPA/540/2-86/OOl (NTIS PB87-116745/REB).

DiGiulio, D.C. 1989. U.S. EPA Robert S. Kerr Environmental Research Laboratory, Ada, OK, personal communication.

DiGiulio, D.C., J.S. Cho, R.R. DuPont, and M.W. Kemblowski. 1990. Conducting Field Tests for Evaluation of Soil Vacuum Extraction Application. In: Proc. 4th Nat. Outdoor Action Conf. on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, National Water Well Association, Dublin, OH, pp. 587-601.

Dupont, R. R., R.C. Sims, J.L. Sims, and D.L. Sorensen. 1988. In Situ Biological Treatment of Hazardous Waste-Contaminated Soils. In: *Biotreatment Systems*, D. L. Wise (ed.), CRC Press, Boca Raton, FL, Chapter 2.

Dworkin, D., D.J. Messinger, and R.M. Shapot. 1988. In Situ Flushing and Bioreclamation Technologies at a Creosote-Based Wood Treatment Plant. In: Proc. 5th National Conference on Hazardous Wastes and Hazardous Materials, Hazardous Materials Control Research Institute, Silver Spring, MD, pp. 67-78.

Hinchee, R. 1989. Enhanced Biodegradation Through Soil Venting. Presented at Workshop on Soil Vacuum Extraction held at US. EPA Robert S. Kerr Environmental Research Laboratory, Ada, OK, April 27-28 (Dominic DiGiulio, Technical Coordinator).

Hinchee R., and D. Downey. 1990. In Situ Enhanced Biodegradation of Petroleum Distillates in the Vadose Zone. In: Proceedings of the International Symposium on Hazardous Waste Treatment: Treatment of Contaminated Soils (Cincinnati, OH). Air and Waste Management Association, Pittsburgh, PA.

Hazardous Materials Control Research Institute (HMCRI). 1989. Symposium on Use of Genetically Altered or Adapted Organisms in the Treatment of Hazardous Wastes. HMCRI, Silver Spring, MD.

Huddleston, R.L., C.A. Bleckman, and J.R. Wolfe. 1986. Land Treatment Biological Degradation Processes. In: Land Treatment A Hazardous Waste Management Alternative, R.C. Loehr and J.F. Malina (eds.), Water Resources Symposium No. 13, University of Texas Press, Austin, TX, pp. 41-61.

Hutzler, N.J., B.E. Murphy, and J.S. Gierkc. 1990. State of Technology Review: Soil Vapor Extraction Systems. EPA/600/2-89/024 (NTIS PB89-195 184).

Johnson, R.L. 1989. Soil Vacuum Extraction: Laboratory and Physical Model Studies. Presented at Workshop on Soil Vacuum Extraction held at U.S. EPA Robert S. Kerr Environmental Research Laboratory, Ada, OK, April 27-28 (Dominic DiGiulio, Technical Coordinator),

Johnson, J.J. and R.J. Sterrett. 1988. Analysis of In Situ Air Stripping Data. In: Proc. 5th National Conference on Hazardous Waste and Hazardous Materials, Hazardous Materials Control Research Institute, Silver Spring MD, pp. 451-455.

Keck, J., R.C. Sims, M. Coorer, K. Park, and B. Symons. 1989. Evidence of CoOxidation of Polynuclear Aromatic Hydrocarbons in Soil. Water Research 23(12):1467-9476.

Keely, J.W., D.C. Bouchard, M.R. Scalf, and C.G. Enfield. Practical Limits to Pump and Treat Technology for Aquifer Remediation. Ground Water Monitoring Review. In press.

Kobayashi, H. and B.E, Rittmann. 1982. Microbial Removal of Hazardous Organic Compounds. Environ. Sci. Tcchnol. 16:170A-183A.

Kuhn, R.C. and K.R. Piontek. 1989. A Site-Specific In Situ Treatment Process Development Program for a Wood Preserving Site. Presented at Seminar on Oily Waste Fate, Transport, Site Characterization, and Remediation, Denver, CO, May 17-18 (John Matthews, Technical Coordinator, Robert S. Kerr Environmental Research Laboratory, Ada, OK).

Lehr, J. 1988. The Misunderstood World of Unsaturated Flow. Ground Water Monitoring Review 8(2):4-6.

Lewandowski, G., P. Armenante, and B. Baltzis (eds.). 1989. Biotechnology Applications in Hazardous Waste Treatment. Engineering Foundation, New York, NY.

Lynch, J, and B.R. Genes. 1989, Land Treatment of Hydrocarbon Contaminated Soils. In: Petroleum Contaminated Soils, Vol. I: Remediation Techniques, Environmental Fate, and Risk Assessment, P.T. Kostecki and E.J. Calabrese (eds.), Lewis Publishers, Chelsea, MI, pp. 163-174.

Mahmood, R.J. and R.C. Sims. 1985. Enhanced Motility of Polynuclear Aromatic Compounds in Soil Systems. In: Proc. 1985 Environmental Engineering Specialty Annual Conference (Boston, MA), American Society of Civil Engineers, pp. 128-135.

Mahmood, R.J. and R.C. Sims. 1986. Mobility of Organics in Land Treatment Systems. Journal of Environmental Engineering (ASCE) 112:236-245.

Matthews, J.E. and A.A. Bulich. 1984. A Toxicity Reduction Test System to Assist Predicting Land Treatability of Hazardous Wastes. In: Hazardous and Industrial Solid Waste Testing: Fourth Symposium, J.K. Petros, Jr., W.J. Lacy, and R.A. Conway (eds.), ASTM STP-886, American Society of Testing and Materials, Philadelphia, PA, pp. 176-191.

Matthews, J.E. and L. Hastings. 1987. Evaluation of Toxicity Test Procedure for Screening Treatability Potential of Waste i. Soil. Toxicity Assessment: International Quarterly 2:265-21.

Miller, R. 1990. A Field Scale Investigation of Enhanced Petroleum Hydrocarbon Biodegradation in the Vadose Zone Combining Soil Venting as an Oxygen Source with Moisture and Nutrient Addition. Ph.D. Dissertation, Department of Civil and Environmental Engineering, Utah State University, Logan, UT.

Omenn, G.S. (ed.). 1988. Environmental Biotechnology—Reducing Risks from Environmental Chemicals through Biotechnology. Plenum Press, New York, NY, 505 pp.

Ovcrcash, M.R. and D. Pal. 1979. Design of Land Treatment Systems for Industrial Wastes—Theory and Practice. Ann Arbor Science, Ann Arbor, MI.

PACE. 1985. The Persistence of Polynuclear Aromatic Hydrocarbons in Soil. PACE Report No. 85-2. Petroleum Association for Conservation of the Canadian Environment, Ottawa, Ontario, Canada.

Paul, E.A. and F.E. Clark. 1989. Soil Microbiology and Biochemistry. Academic Press, San Diego, CA.

Raghavan, R., E. Coles, and D. Dietz. 1990. Cleaning Excavated Soil Using Extraction Agents: A State-of-the-Art Review. EPA/600/2-89/034 (NTIS PB89-212757/AS).

Reible, D.D. 1989. Introduction to Physicochemical Processes Influencing Enhanced Volatilization. Presented at Workshop on Soil Vacuum Extraction held at U.S. EPA Robert S. Kerr Environmental Research Laboratory, Ada, OK, April 27-28 (Dominic DiGiulio, Technical Coordinator).

Rich, G. and K. Cherry. 1987. Hazardous Waste Treatment Technologies. Pudvan Publishing, Northbrook, IL, Chapter 7.

Rochkind, M.L., J.W. Blackbum, and G. Sayler. 1986. Microbial Decomposition of Chlorinated Aromatic Compounds. EPA/600/2-86/090 (NTIS PB87-116943/REB).

Ross, D., T.P. Marziarz, and A.L. Bourquin. 1988. Bioremediation of Hazardous Waste Sites in the USA: Case Histories. In: Superfund ’88, Hazardous Materials Control Research Institute, Silver Spring, MD, pp. 395-397.

Sims, R.C. 1982. Land Treatment of Polynuclear Aromatic Compounds. Ph.D Dissertation, Departmcnt of Biological and Agricultural Engineering, North Carolina State University, Raleigh, NC.

Sims, R.C. 1986. Loading Rates and Frequencies for Land Treatment Systems. In: Land Treatment—A Hazardous Waste Management Alternative, R.C. Loehr, and J.F. Malina (eds.), Water Resources Symposium No. 13, University of Texas Press, Austin, TX, pp. 151-170.

Sims, R.C., and M.R. Overcash. 1983. Fate of Polynuclcar Aromatic Compounds (PNAs) in Soil-Plant Systems. Residue Reviews 86:1-68.

Sims, R.C. and J.L. Sims. 1986. Cleanup of Contaminated Soil. In: Utilization, Treatment, and Disposal of Waste on Land, K.W. Brown, B.L. Carlile, R.H. Miller, E.M. Turledge, and E.C.A. Runge (eds.), Soil Science Society of America, Madison, WI, pp. 257-277.

Sims, R.C., D.L. Sorensen, J.L. Sims, J.E. McLean, R. Mahmood, and R.R. DuPont. 1984. Review of In-Place Treatment Technologies for Contaminated Surface Soils-Volume 2: Background Information for In-Situ Treatment. EPA/540/2-84-O03b (NTIS PB85-124899).

Sims, R.C., D. Sorensen, J.L. Sims, J. McLean, R.J Mahmood, R. Dupont, and J. Jurinak. 1986. Contaminated Surface Soils In-Place Treatment Techniques. Pollution Technology Review No. 132. Noyes Publications, Park Ridge, NJ, 536 pp.

Sims, J. L., R.C. Sims, and J.E. Matthews. 1989. Bioremediation of Contaminated Soils. EPA/600/9-89/073 (NTIS PB90-164047).

Spencer, W.F. and M.M. Cliath. 1969. Vapor Density of Dieldrin. Environ. Sci. Technol. 3:670-674.

Spencer, W.F., M.M. Cliath, and W.J. Farmer. 1969. Vapor Density of Soil-Applied Dieldrin as Related to Soil-Water Content, Temperature and Dieldrin Concentration. Soil Sci. Soc. Am. Proc. 33:509-511.

Spencer, W .F., W.J. Farmer, and M.M. Cliath. 1973. Pesticide Volatilization. Residue Reviews 49:1-47.

St. John, W. D., and D.J. Sikes. 1988. Complex Industrial Waste Sites. In: Environmental Biotechnology-Reducing Risks from Environmental Chemicals through Biotechnology, G.S. Omenn (ed.), Plenum Press, New York, NY, pp. 237-252.

Suflita, J. M., A. Horowitz, D.R. Shelton, and J.M. Tiedje. 1982. Dehalogenatiom a Novel Pathway for the Anaerobic Biodegradation of Haloaromatic Compounds. Science 218:ll15-1117.

Suflita, J.M., J.A. Robinson, and J.M. Tiedje. 1983. Kinetics of Microbial Dchalogenation of Haloaromatic Substrates in Methanogenic Environments. Appl. Environ. Microbiol. 45:1466-1473.

Suflita, J. M., J. Stout, and J.M. Tiedje. 1984. Dechlorination of (2,4,5-Trichlorophenoxy) Acetic Acid by Anaerobic Microorganisms. Journal of Agricultural and Food Chemistry 32:218-221.

Symons, B.D. and R.C. Sims. 1988. Detoxification of a Complex Hazardous Waste Using the Microtox™ Bioassay. Archives of Environmental Contamination and Toxicology 17:497-505.

Truett, J. B., R.L. Holbergcr, and K.W. Barrett, 1983. Feasibility of In Situ Solidification/Stabilization of Landfilled Hazardous Wastes. EPA/600/2-83/088 (NTIS PB83-261099).

U.S. Environmental Protection Agency (EPA). 1983. Hazardous Waste Land Treatment & EPA SW-874.

U.S. Environmental Protection Agency (EPA). 1984. Review of In-Place Treatment Techniques for Contaminated Surface Soils. EPA/540/2-84-O03a (NTIS PB85-124881).

U.S. Environmental Protection Agency (EPA). 1986. Permit Guidance Manual on Hazardous Waste Land Treatment Demonstrations. EPA/530/SW-86-032 (NTIS PB86-229 184).

U.S. Environmental Protection Agency (EPA). 1987. A Compendium of Technologies Used in the Treatment of Hazardous Wastes. EPA/625/8-87/O14 (Available from Center for Environmental Research Information, Cincinnati, OH).

U.S. Environmental Protection Agency (EPA). 1988a. Cleanup of Releases from Petroleum USTS: Selected Technologies. EPA/530/UST-88/OOl (NTIS PB88-241856).

U.S Environmental Protection Agency (EPA). 1988b. Technology Screening Guide for Treatment of CERCLA Soils and Sludges. EPA/540/2-88/O04 (NTIS PB89-132674/REB).

U.S. Environmental Protection Agency (EPA). 1989a. Bioremediation of Hazardous Waste Sites Workshop: Speaker Slide Copy and Supporting Information. EPA CERI-89-11 (NTIS PB89-169205/REB).

U.S. Environmental Protection Agency (EPA). 1989b. Corrective Action: Technologies and Applications. EPA/625/4-89/020 (Available from Center for Environmental Research Information, Cincinnati, OH).

U.S. Environmental protection Agency (EPA). 1989c. Demonstration Bulletin: In Situ Vacuum Extmct.ion, Terra Vac, Inc. EPA/540/M5-89/O03 (NTIS PB90-126665/GAR).

U.S Environmental Protection Agency (EPA). 1989d. Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater. In: Procccdings and Appendices, Third International Conference, NATO Committee on Challenges of Modern Society (CCMS) (Montreal, Canada), pp. v-vii.

U.S. Environmental Protection Agency (EPA). 1989e. Technology Evaluation Report: SITE Program Demonstration Test, International Waste Technologies, In Situ Stabilization/Solidification, Hialeah, Florida, Volume 1. EPA/540/5-89/004a (NTIS PB89-194161/AS).

U.S. Environmental Protection Agency (EPA). 1989f. The Superfund Innovative Technology Evaluation Program: Technology Profiles. EPA/540/5-89/O13 (NTIS PB90-249756/A07).

U.S. Environmental Prelection Agency (EPA). 1990. Handbook on In Situ Treatment of Hazardous Waste-Contaminated Soils. EPA/540/2-90-O02 (NTIS PB90-155607).

Valsaraj, K.T. and L.J. Thibodcaux. 1988. Equilibrium Adsorption of Chemical Vapors on Surface Soils, Landfills, and Landfarms-A Review. J. Hazardous Materials 19:79-99.

Wahon, B.T., and T.A. Anderson. 1990. Microbial Degradation of Trichlorocthylene in the Rhizosphere: Potential Application to Biological Remediation of Waste Sites. Appl. Environ. Microbiol. 56:1012-1016.

Wilson, L.G. 1981. Monitoring in the Vadose Zone: Part I, Storage Changes. Ground Water Monitoring Review 1(3):32-41.

Wilson, L.G. 1982. Monitoring in the Vadose Zone: Part II. Ground Water Monitoring Review 2(2):31-42.

Wilson, L.G. 1983. Monitoring in the Vadose Zone: Part III. Ground Water Monitoring Review 3(l): 155-166.

Wilson, D.J., R.O., Mutch, Jr., and A.N. Clarke. 1989. Modeling of Soil Vapor Stripping. Presented at Workshop on Soil Vacuum Extraction held at U.S. EPA Robert S. Kerr Environmental Research Laboratory, Ada, OK, April 27-28 (Dominic DiGiulio, Technical Coordinator).

# Chapter 16
# Aquifer Restoration

Ronald C. Sims and Judith L. Sims

Currently, several remedial techniques are being used to restore contaminated ground water and aquifer material. Participants in the U.S. Environmental Protection Agency's (EPA) SITE program that are testing technologies applicable to contaminated ground water are listed in Tables 16-1 and 16-2 (U.S. EPA, 1989a). Table 16-3 summarizes technologies applicable to contaminated ground water currently being evaluated and demonstrated in the NATO/CCMS Pilot Study on demonstration of remedial action technologies for contaminated land and ground water (U.S. EPA, 1989b).

The pattern of contamination from a release of contaminants into the subsurface environment, such as would occur from an underground leaking storage tank containing nonaqueous phase liquids (NAPLs), is complex (Figure 16-1) (Palmer and Johnson, 1989; Wilson et al., 1989). As contaminants move through the unsaturated zone, a portion is left behind, trapped by capillary forces. If the release contains volatile contaminants, a plume of vapors forms in the soil atmosphere in the vadose zone. If the release contains NAPLs less dense than water (LNAPLs), they may flow by gravity down to the water table and spread laterally. Ground water moving through subsurface sediments contacts the release and the more water-soluble components are dissolved into the water phase. Therefore, three distinct regions of contaminants are formed in the release: a plume of fumes in the soil atmosphere, a ground-water plume, and the region that contains the oily phase material that serves as the source area for both plumes. This latter region may include both recoverable free product (i.e., continuous phase material), and sorbed or capillary-held material (i.e., residual saturation material). If the release contains DNAPLs, these contaminants can penetrate to the bottom of an aquifer, forming pools in depressions.

This chapter discusses three techniques concerning aquifer restoration: (1) product removal, (2) pump-and-treat, and (3) biorestoration.

## 16.1 Product Removal

Product removal generally consists of product characterization, product location, and product recovery. Product characterization refers to identifying the type of product (e.g., petroleum, wood-preserving, or solvent) and associated individual chemicals (e.g., BXT, PAHs, TCE). Product locations include characterizing the product mobility at the site (e.g., LNAPL following the water table, DNAPL following the bedrock). Knowledge of whether the product is an LNAPL or a DNAPL may help locate the product in the subsurface.

Physical recovery techniques to remove free product include (1) a single pump system producing a mixture of hydrocarbon and water that must be separated, but requiring minimal equipment and drilling; (2) a two-pump, two-well system utilizing one pump to produce a water table gradient and a second well to recover floating product; or (3) a single well with two pumps in which a lower pump produces a gradient and an upper pump collects free product (Lee and Ward 1986). Vacuum extraction of volatilizing contaminants also may be used to recover floating free product from a perched water table.

Pumping systems commonly used for recovery of LNAPLs are shown in Figures 16-2 and 16-3. An aboveground oil/water separator generally is used to recover product for future use. Subsurface drains also have been used for recovery of DNAPLs (Figure 16-4a). When only the oil recovery drainline (ORD) is used (Figure 16-4b), water truncates the flow of product (DNAPL) due to the poor relative permeability of the product as described previously in the discussion of soil flushing. The water table depression drainline (WTDD) is an efficient method (see Figure 16-4c) to drag an oily product across the subsurface by viscous forces and thereby create a hydraulic head of oil above the ORD; however, oil also enters the WTDD, thereby creating the need for aboveground separation of product and water. When both ORD and WTDD are used (Figure 16-4d), subsurface separation of oil and water is achieved, thereby minimizing aboveground separation requirements. This system (Figure 16-4d) is also efficient since the permeability of oil is greatest in the oily contaminated subsurface, and the underground separation maintains water flowing in the water compartment and oil flowing in the oily compartment.

Caution should be exercised during product recovery of LNAPL when an extraction well is used to control local gradients and collect free product in a cone of depression. Due to capillary forces in the subsurface aquifer material, trapped residual will constitute a continuous source of contamination to ground water that will persist after product removal from the water table is completed.

*Table 16-1. SITE Demonstration Program Participants with Technologies Applicable* to Remediation of Contaminated *Ground Water*

| | | *Applicable Waste* | |
|---|---|---|---|
| *Developer* | *Technology* | *Inorganic* | *Organic* |
| *AWD Technologies, Inc.*<br>*Burbank, CA*<br>*(004)* | *Integrated Vapor Extraction and Steam Vacuum Stripping* | *NA* | *Volatile Organic Compounds* |
| *Biotrol, Inc.*<br>*Chaska, NM*<br>(003) | *Bioiogical Aqueous Treatment Systems* | *Can be applied to Nitrates* | *Chlorinated and Nonchlorinated Hydrocarbons* |
| *DETOX, inc.*<br>*Dayton, OH*<br>(003) | *Submerged Aerobic Fixed-Film Reactor* | *Metals inhibit process* | *Readily Biodegradable Organic Compounds* |
| *E.I. Du Pont de Nemours and Co./Oberiln Filter Co.*<br>*Newark, DE*<br>*(003)* | *Membrane Microfiltration* | *Heavy Metals, Cyanide, Uranium* | *Non-specific* |
| *Ecova Corporation*<br>*Redmond,* WA<br>(003) | *In Situ Biological Treatment* | *NA* | *Chlorinated Solvents, Nonchlorinated Organic Compounds* |
| *Exxon Chemicals, Inc./*<br>*Rio Linda Chemical Co.*<br>*Long Beach, CA*<br>*(004)* | *Chemical Oxidation/Organics Destruction* | *NA* | *Non-specific* |
| *Freeze Technologies Corp.*<br>*Raleigh, NC*<br>*(003)* | *Freezing Separation* | *Non-specific* | *Non-specific* |
| *Ozonics Recycling Corp.*<br>*Boca Raton, FL*<br>*(004)* | *Soil Washing, Catalytic/ Ozone Oxidation* | *Cyanide* | *Semivolatiles, Pesticides, PCBs, PCP, Dioxin* |
| *Silicate Technology Corp.*<br>*Scottsdale, AZ*<br>*(003)* | *Solidification/Stabilization with Silicate Compounds* | *Metals, Cyanide, Ammonia* | *High Molecular Weight Organics* |
| *Ultrox International, Inc.*<br>*Santa Ana, CA*<br>(003) | *Ultraviolet Radiation and Ozone Treatmen!* | *NA* | *Halogenated Hydrocarbons, Volatile Organic Compounds, Pesticides, PCBs* |
| *Zimpro/Passavant, Inc., Rothschild, WI*<br>*(002)* | *PACT®/Wet Air Oxidation* | *NA* | *Volatile and Semivolatile Organic Compounds* |

*NA = non applicable*

*U.S. EPA, 1989a*

## 16.2 Pump-and-Treat Remediation

Both hydrogeologic information and contaminant information are required for pump-and-treat remediation. Hydrogeologic information about ground-water flow includes geological and hydraulic factors (described in Chapters 3 and 4) as well as ground-water use/withdrawal factors.

When pump-and-treat remediation is selected, a decision needs to be made about the use of wells or drains (U.S. EPA, 1990). If the hydraulic conductivity is sufficiently high to allow flow to wells, then wells are recommended. For low-permeability material, drains may be required. Wells can be categorized as extraction, injection, or a combination. Injection wells reduce cleanup time required by flushing chemicals to the extraction wells. Design and management decisions concerning extraction wells include whether to use continuous pumping, pulsed pumping, or pumping combined with containment. While continuous pumping maintains an inward hydraulic gradient, pulsed pumping allows maximum concentrations to be pumped and requires only minimum volumes of pumping. Containment (physical or hydraulic) limits the amount of uncontaminated water that requires treatment. Injected water can contain nutrients or electron acceptors where bioremediation is used, or can contain enhanced oil recovery materials (EOR) for NAPL contaminants, or can be reinfected treated water without nutrient or EORs (U.S. EPA, 1990).

This chapter discusses pump-and-treat systems in two categories: (1) pumping systems, and (2) treatment systems. Pumping systems may be used for plume containment and

Table 16-2. SITE Emerging Technology Program Participants with Technologies Applicable to Remediation of Contaminated Ground Water

| Developer | Technology | Applicable Waste | |
|---|---|---|---|
| | | inorganic | Organic |
| Atomic Energy of Canada,<br>Ltd. Chalk River, Ontario<br>(EO1) | Chemical Treatment Ultrafiltration | Specific for Heavy Metals | NA |
| Bio-Recovery Systems, Inc.<br>Las Cruces, NM<br>(EO1) | Biological Sorption | Specific for Heavy Metals | NA |
| Electro-Pure Systems, Inc.<br>Amherst, NY<br>(E02) | A/C Electrocoagulation Phase Separated and Removal | Heavy Metals | Petroleum Byproducts, Coal-Tar Derivatives |
| Energy and Environmental<br>Engineering, Inc.<br>East Cambridge, MA<br>(EO1) | Laser Stimulated Photochemical Oxidation | NA | Non-specific |
| University of Washington,<br>Dept. of Civil Engineering<br>Seattle, WA<br>(E02) | Adsorptive Filtration | Metals | NA |
| Wastewater Tech. Centre<br>Burlington, Ontario<br>(E02) | Cross-Flow Pervaporation System | NA | Volatile Organic Compounds |

NA = non applicable
Source: U.S. EPA, 1989a

Table 16-3. NATO/CCMS Projects for Remediation of Contaminated Ground Water

| Matrix<br>Treatment<br>Organization/Site | Treatable Contaminant | | | | | Specific Contaminants Treated | Treatment Location | Status of Technology |
|---|---|---|---|---|---|---|---|---|
| | Aliphatic Hydrocarbons | Aromatic Hydrocarbons | Halogenated Hydrocarbons | Heavy Metals | Petroleum Fuels, Oils | | | |
| **Groundwater** | | | | | | | | |
| Biological<br>Enhanced Aerobic Restoration<br>U.S. Air Force, Battelle<br>Eglin Air Force Base, FL,<br>United States | ✓ | ✓ | | | ✓ | Jet fuel | In-situ | Experimental |
| Chemical/Physical<br>Pump and Treat Groundwater<br>Environment Canada<br>Ville Mercier, Quebec | ✓ | ✓ | ✓ | | | Dichloroethane, benzene, various mono- and poly-cyclic aromatics | On-site | Demonstrated |
| UV/Oxidation<br>Ultrox<br>San Jose, CA<br>United States | ✓ | ✓ | ✓ | | | TCE<br>1,1-DCA<br>1,1,1-TCA<br>Other VOCs | On-site | Demonstration |

Source: U.S. EPA, 1989b

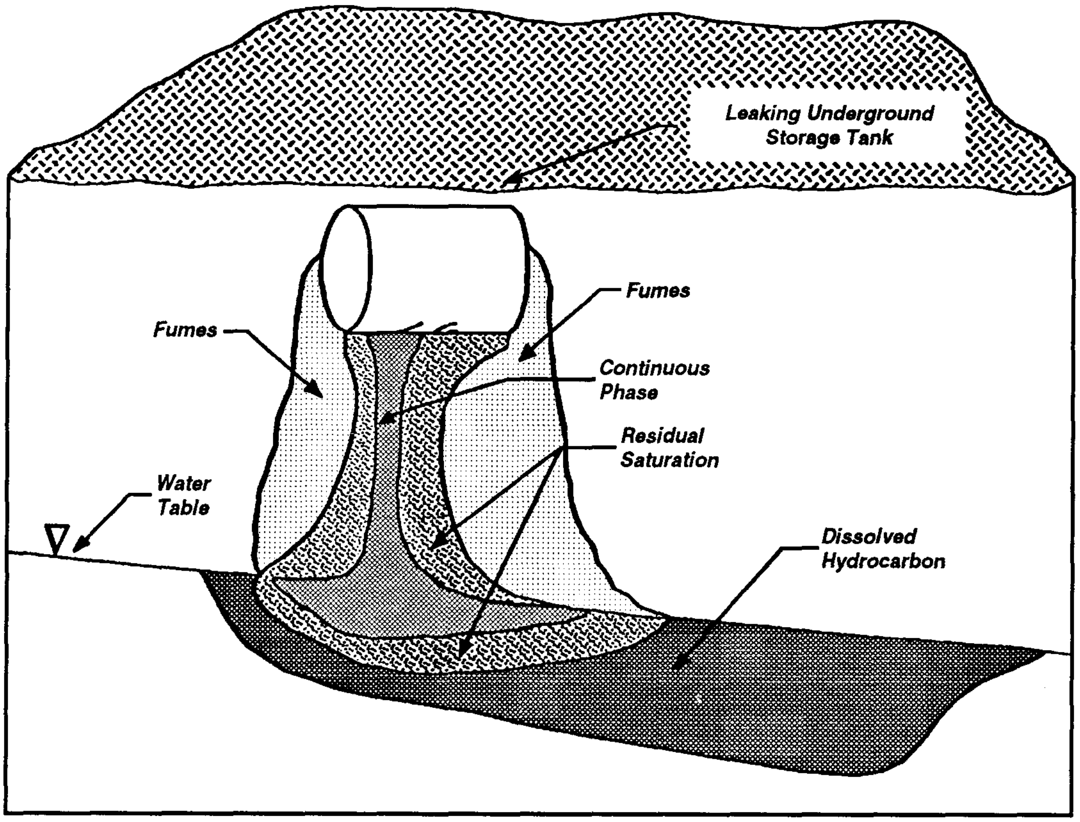


**Figure 16-1. Regions of contamination in a typical release from an underground storage tank (from Wilson et al., 1989).**

plume recovery for aboveground treatment (Figures 16-5 and 16-6). Ground-water pumping systems utilize the principle that ground water flows in response to a hydraulic gradient, i.e., a drop in hydraulic pressure created by the combined effects of elevation, fluid density, and gravity.

The migration of a plume away from its source area, which is related to hydraulic containment, often can be prevented by capturing the plume with a purge well. The well must pump hard enough to overcome regional flow in the aquifer. Hydrodynamic control of a contaminated groundwater plume is accomplished by manipulating the hydraulic gradient. Passive hydrodynamic controls, or interceptor systems, function by gravity. Active hydrodynamic controls rely on injection and production wells to control the hydraulic gradient (Canter and Knox, 1985).

Physical containment techniques include installing barriers to ground-water flow (e.g., slurry walls (see Figure 16-7), grout curtains, sheet pilings, block displacement, and clay liners) or diverting divert uncontaminated surface water away from waste sites or contaminated water away from clean areas (Ehrenfield and Bass, 1984). These containment systems also may provide for temporary containment while ground water is removed and treated and aquifer material is decontaminated.

Contaminated ground water that is withdrawn from an aquifer can be treated by various methods, depending on the type(s) of contamination. Treatment methods may include one or more of the following: (1) physical processes, such as adsorption onto activated carbon or resins, ion exchange, reverse osmosis, filtration, or transfer to the gaseous phase by air stripping; (2) chemical processes, such as neutralization, coagulation, precipitation, oxidation, or reduction reactions, which involve inactivating or immobilizing contaminants with chemical agents; or (3) biological processes, using conventional wastewater treatment methods such as suspended growth (e.g., activated sludge, lagoons, waste stabilization ponds, and fluidized bed reactors) and freed film (e.g., trickling filters and rotating biological contractors) processes (Thomas et al., 1987).

With pumping systems that are used to bring contaminated ground water to the surface for treatment contaminants are transported by advection (velocity) and dispersion. Water velocity for pumping systems can be calculated using Darcy's Law; however, spatial variability in hydraulic conductivity results in a corresponding distribution of flow velocities; therefore, contaminant removal and transport rates are distributed. Chemical contaminants in ground water also may not move at the same rate as the water due to subsurface processes, including sorption or retardation, ion-exchange, and

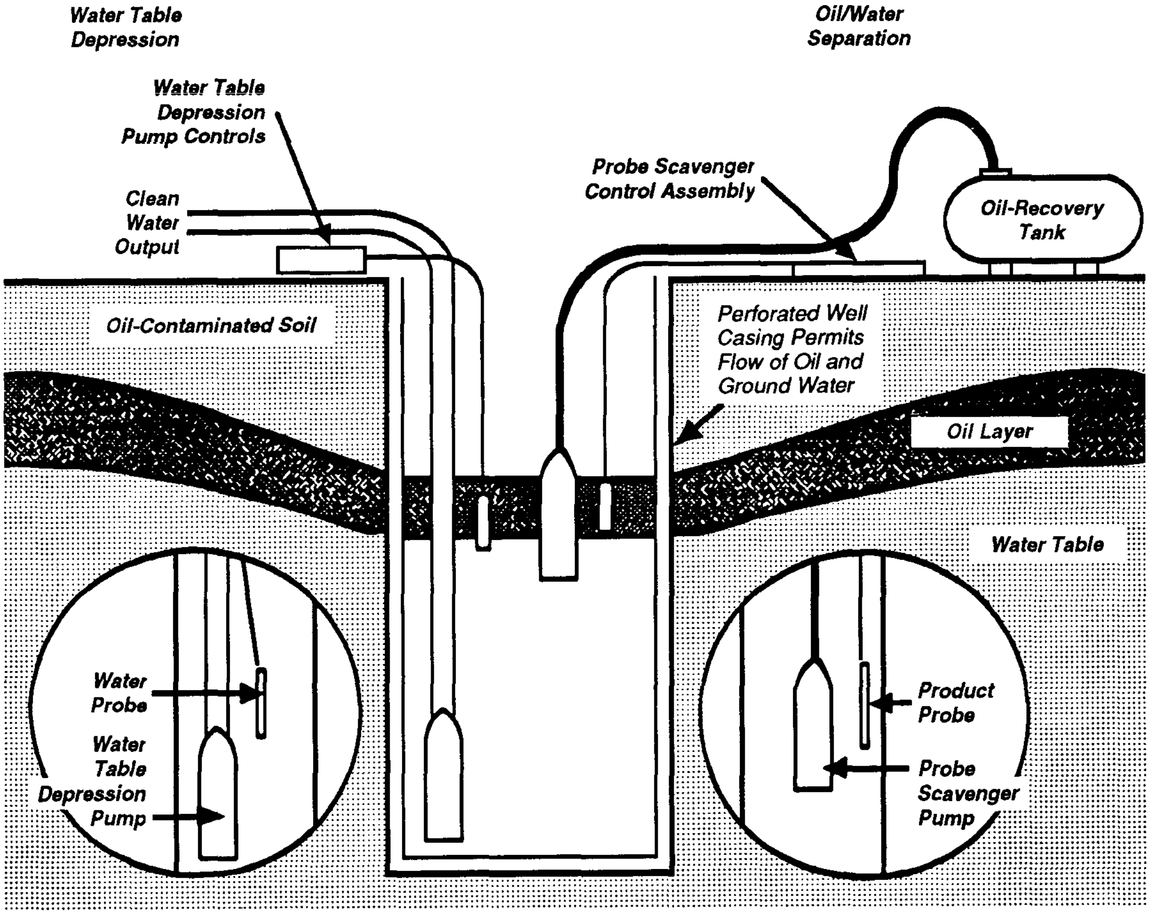


**Figure 162. Product recovery using two pumps in one well—a probe scavenger pump and a water table depression pump (from Nyer, 1985).**

chemical precipitation (described under soil immobilization techniques), and bioremediation (described under soil bioremediation).

Monitoring water and soil cores within the plume while pumping is occurring allows a determination of area of remediation and remediation rate. These results allow rational management of the remediation wellfield. Keely (1989) explains that, using this approach, the flow rates of extraction wells that pump from relatively clean zones would be decreased, while flow rates from extraction wells that pump from highly contaminated zones should be increased. Also, Keely (1989) points out that the exclusive use of monitoring points downgradient from a plume does not assist in an understanding of plume dynamics during remediation, except to indicate "out-of-control" conditions when contaminants are detected.

During the continuous operation of an extraction wellfield, the level of contamination in water flowing through the subsurface usually is decreased in a relatively short period of time, after which a low-level residual concentration is present in the extracted water (Figure 16-8). After the residual concentration in water is attained, a pump-and-treat system is usually characterized by treatment of large volumes of slightly contaminated water over a long period of time. In addition, if remediation is terminated before removal of residual contamination at a site, the concentration of contaminant(s) in the aquifer water may increase due to slow release of contaminant residuals relative to pumpage-induced water movement (Figure 16-9) (Keely, 1989). Transport processes that cause this contaminant behavior in the subsurface include (1) diffusion of contaminants in low-permeability sediments; (2) hydrodynamic isolation, or dead spots, within the wellfield (3) desorption of contaminants from sediment surfaces; and (4) liquid-liquid partitioning of immiscible contaminants (Keely, 1989).

One promising innovation in the use of pump-and-treat remediation is pulsed pumping. Pulsed pumping of hydraulic systems is the cycling of extraction or injection wells on and off in active and resting phases (Figure 16-10) (Keely, 1989).

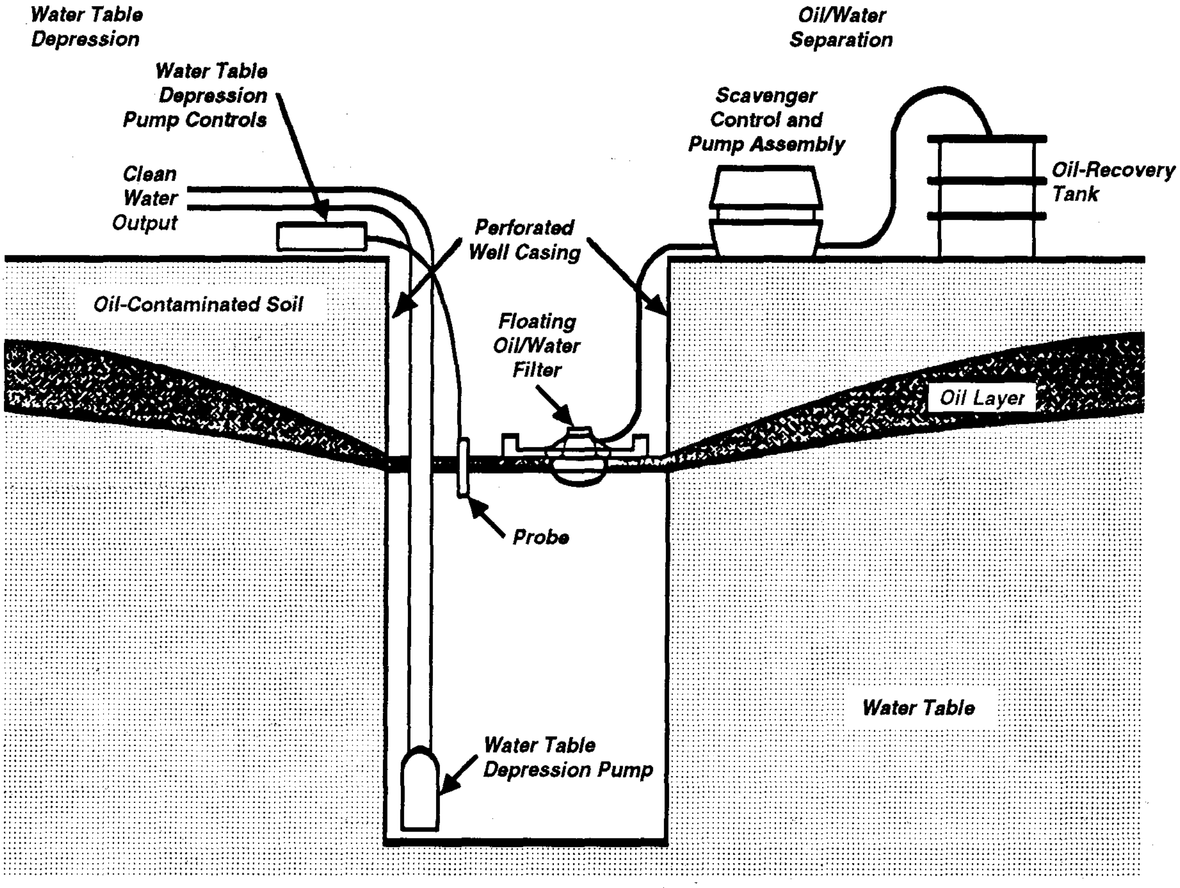


Figure 16-3. Product recovery using a watertable depression pump and a floating oil/water filter (from Nyer, 1985).

The resting phase allows chemical contaminants to move from low-permeability sediments, dead spots, sediment surfaces, and immiscible fluids in the subsurface into the water phase. The pumping phase removes the minimum volume of water at the maximum contaminant concentration. By periodically cycling selected wells, stagnation zones may be brought into active flow paths and remediated.

When pulsed pumping systems are used, peripheral gradient control must be ensured to prevent offsite migration of contamination. If migration is slow, water would be rapidly recovered by the high flow velocities back toward extraction well(s) during the pumping phase. If migration is rapid, then additional containment controls are necessary to prevent offsite migration during the resting phase of pulsed pumping.

## 16.3 Biorestoration

In addition to the overviews presented by Thomas and Ward (1989) and Lee et al. (1988), there are several milestone publications on biological restoration of contaminated ground waters. These publications include those that address (1) hydrogen peroxide as a supplemental source of oxygen (Huling et al., 1990); (2) new approaches for site characterization, project design, and performance evaluation (Wilson et al., 1989); (3) methanotrophic destruction of chlorinated aliphatic chemicals (Roberts et al., 1989); and (4) modeling aspects (Rifai et al., 1988 and 1989).

Biological in situ treatment of subsurface contaminants in aquifers is usually accomplished by stimulating indigenous subsurface microorganisms to degrade organic waste constituents (Thomas and Ward, 1989). The activity of microorganisms is stimulated by injection of inorganic nutrients and, if required, an appropriate electron acceptor, into aquifer materials. Most biological in situ treatment techniques currently used are variations of techniques developed by researchers at Suntech to remediate gasoline-contaminated aquifers. The Suntech process received a patent titled *Reclamation of Hydrocarbon Contaminated Ground Waters*

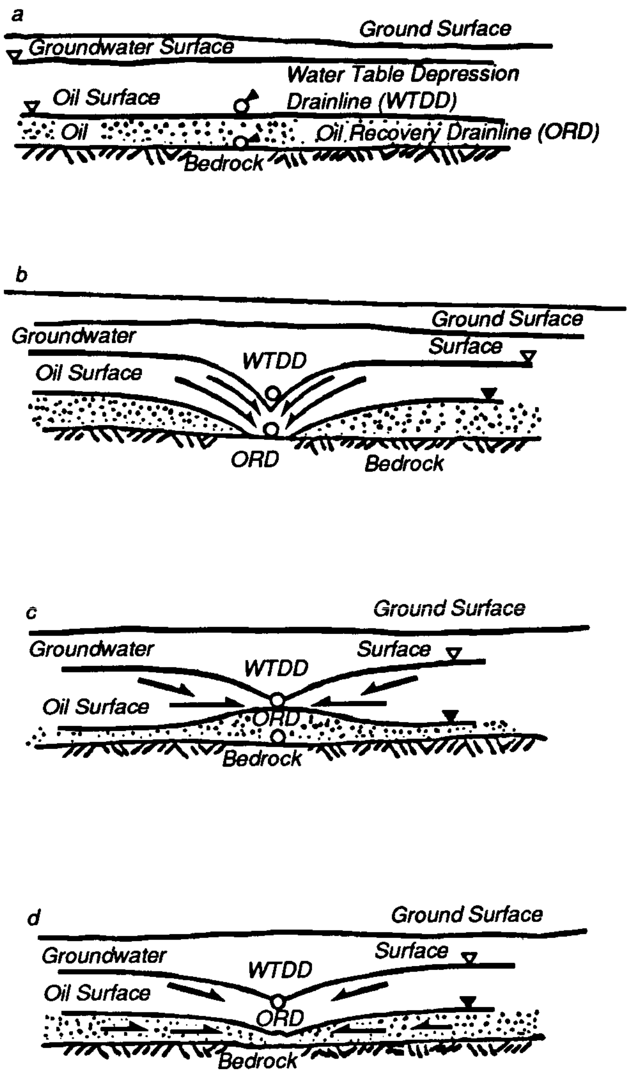


**Figure 16-4.** Recovery of dense nonaqueous phase liquid (DNAPL) from subsurface bedrock using drains to accomplish underground separation of DNAPL (oil) and water (from Sale and Piontek, 1989).

(Raymond, 1974). The process, as described by Lee et al. (1988), involves circulating oxygen and nutrients through a contaminated aquifer using injection and production wells. Well placement depends on the area of contamination and the porosity of the formation, but they are usually no more than 100 ft apart. The nutrient amendment consists of nitrogen, phosphorus, and other inorganic salts, as required, at concentrations ranging from 0.005 to 0.02 percent by weight. Oxygen for use as an electron acceptor in microbial metabolism is supplied by sparging air into the ground water. If the growth rate of microorganisms is 0.02 g/L per day, the process is estimated to require approximately 6 months to achieve 90 percent degradation of the hydrocarbons present. Cleanup is expected to be most efficient for ground waters contaminated with less than 40 ppm of gasoline. After termination of the process, the numbers of microbial cells are expected to return to background levels.

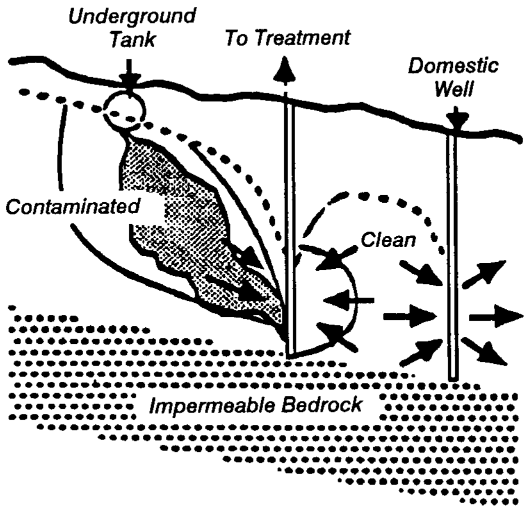


**Figure 16-5.** Cross-sectional view of pump-and-treat system (from U.S. EPA, 1985).

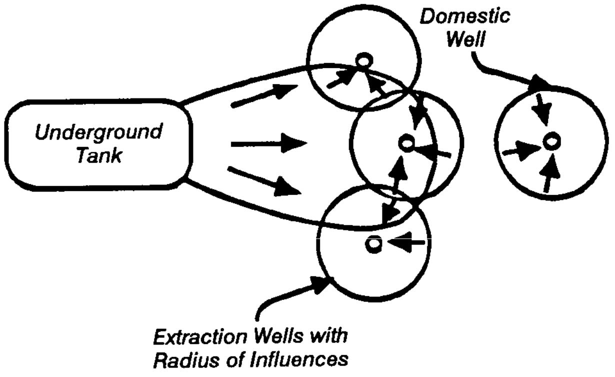


**Figure 16-8.** Plan view of pump-and-treat system (from U.S. EPA, 1985).

Another technique, which has not yet been fully demonstrated, is the addition of microorganisms with specific metabolic capabilities to a contaminated aquifer (Lee et al. 1988). Populations that are specialized in degrading specific compounds are selected by enrichment culturing, which involves exposure of microorganisms to increasing concentrations of a contaminant or mixture of contaminants. The type of organism (or group of organisms) that is selected, or acclimates, to the contaminant, depends on the source of the inoculum, the conditions used for the enrichment, and the substrate. Examples of changes that may occur during an acclimation period include (1) an increase in population of contaminant degraders; (2) a mutation that codes for new metabolic capabilities; and/or (3) induction or derepression of enzymes re-

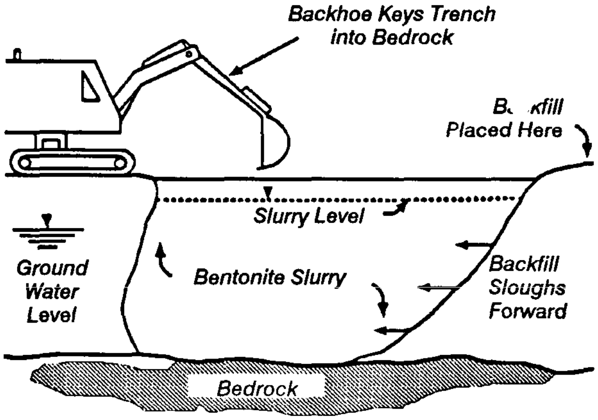


**Figure 16-7.** Schematic of the preparation of a slurry wall for physical containment of contaminated ground water or for diversions of clean water around a contaminated subsurface (from U.S. EPA, 1985).

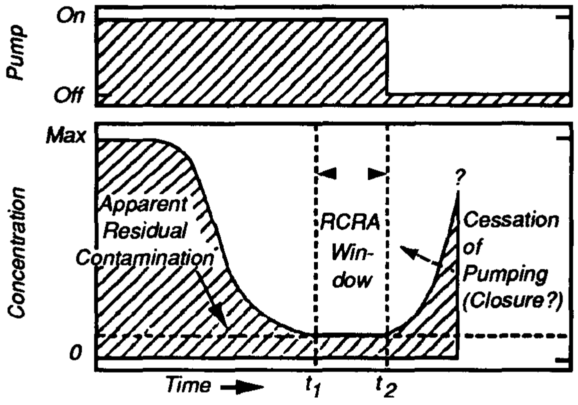


**Figure 18-9.** Following temporary termination of pumping, aquifer water concentration increases, or rebounds, due to the presence of contaminant residuals (from Keely, 1989).

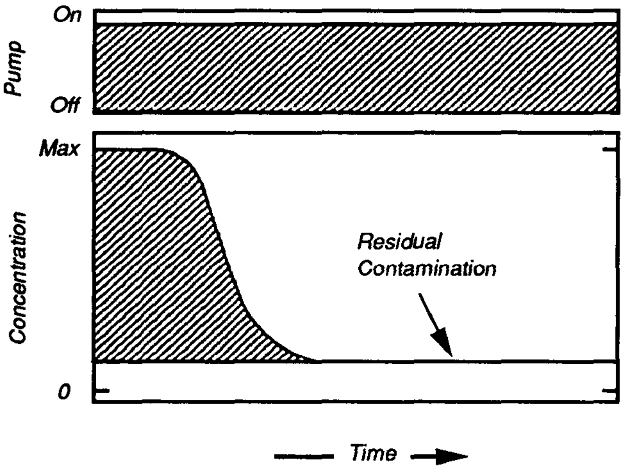


**Figure 16-8.** Decrease in aquifer water concentration caused by pump-and-treat system where contaminant concentration in pumped water reaches an irreducible level that is frequently above the regulated limit (from Keely, 1989).

sponsible for degradation of specific contaminants (Aelion et al., 1987).

However, inoculation of a specialized microbial population into the environment may not produce the desired degree of degradation for a number of reasons (Goldstein et al., 1985; Lee et al., 1988; Suflita 1989). Possible causes that may limit the success of inoculants include both abiotic and biotic factors. Environmental factors, such as pH, temperature, salinity, and osmotic or hydrostatic pressure may act alone or collectively to inhibit the survival of the microorganisms. The concentration of the specific organic constituent of concern may be too low to support growth and activity. The environment may contain substances or other organisms that are toxic or inhibitory to the growth and activity of the inoculated organism(s). The inoculated organism(s) may utilize some other organic compound than the one it was selected to metabolize. In addition, adequate mixing and transport to ensure contact of the organism with the specific organic constituent of concern may be difficult to achieve in ground water. Successful inoculation of organisms into simpler, more controllable environments (e.g., bioreactors such as wastewater treatment plants) to accomplish degradation has been demonstrated. However, effectiveness of inoculation into uncontrolled and poorly accessible environments (e.g., the subsurface) is much more difficult to achieve, demonstrate, and assess (Thomas and Ward, 1989).

In a contaminated aquifer, some regions will clean up faster than others, and the most contaminated flow path will be the last to be cleaned. If this flow path can be identified, then its properties can be used to determine how much effort and time are required to remediate the entire area. The time required to clean the most contaminated flow path can be determined using a modification of the relationship given by U.S. EPA (1989c), correcting for units:

Time required to clean most contaminated flow path=

$$\frac{\textbf{Mass of contaminant along flow path (Mass}_c\textbf{)}}{(\text{Mass}_c/\text{Mass}_{\text{oxygen}}) \times (\text{Mass}_{\text{oxygen}}/\text{Volume}_{\text{water}}) \times (\text{Volume}_{\text{water}}/\text{Time})}$$

where

$\text{Mass}_c/\text{Mass}_{\text{oxygen}}$ represents the stoichiometric amount of oxygen required to biodegrade (mineralize) contaminant (hydrocarbon) present;

$\text{Mass}_{\text{oxygen}}/\text{Volume}_{\text{water}}$ represents the concentration of oxygen in the ground water; and

$\text{Volume}_{\text{water}}/\text{Time}$ represents the seepage velocity along the contaminant flow path.

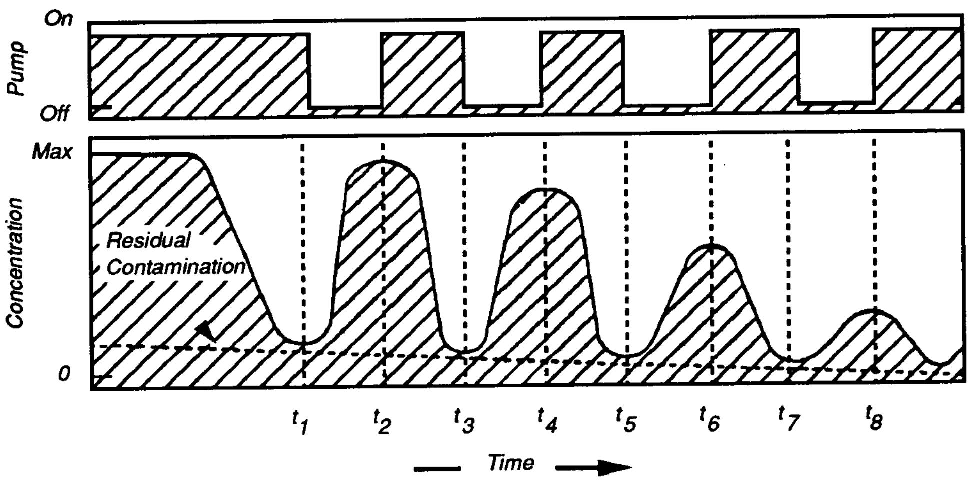


**Figure 16-10.** Pulsed pumping removal of residual contaminant minimizes volume of water required for pumping and maximlzes contaminant concentration in pumped water (from Keely, 1989).

Generally, if the supply of mineral nutrients is adequate, the rate of bioremediation is directly related to the rate of supply of electron acceptor. As a result, the rate of remediation is directly proportional to the concentration of electron acceptor in the injected water and the flow velocity of water through the contaminated area.

When in situ bioremediation of a contaminant groundwater plume involves using methods to enhance the process discussed above, such as the addition of nutrients, additional oxygen sources, or other electron acceptors, hydraulic controls might be required to minimize (i.e., contain) migration of the plume during the in situ treatment process (Thomas et al. 1987; U.S. EPA 1989c). In general, hydraulic control systems are less costly and time consuming to install than physical containment structures such as slurry walls. Well systems also are more flexible, because pumping rates and well locations can be altered as the system is operated over a period of time. Wells should be installed under the direction of a hydrogeologist to ensure proper placement and operation.

With respect to biorestoration of aquifers, pumping-injection systems can be used to (1) create stagnation (no flow) zones at precise locations in a flow field, (2) create gradient barriers to pollution migration, (3) control the trajectory of a contaminant plume, and (4) intercept the trajectory of a contaminant plume (Schafer, 1984). The choice of a hydraulic control method depends on geological characteristics, variability of aquifer hydraulic conductivities, background velocities, and sustainable pumping rates (Lee et al., 1988). Typical patterns of wells that are used to provide hydraulic controls include (1) a pair of injection-production wells, (2) a line of downgradient pumping wells, (3) a pattern of injection-production wells around the boundary of a plume, and (4) the "double-cell" hydraulic containment system. The "double-cell" system utilizes an inner cell and an outer recirculation cell, with four cells along a line bisecting the plume in the direction of flow (Wilson, 1984).

Well systems also serve as injection points to add materials used to enhance microbial activity into the aquifer and for control of circulation through the contaminated portion. The system usually includes injection and production wells and equipment for the addition and mixing of the nutrients (Lee et al., 1988). Figure 16-11 illustrates a typical system in which microbial nutrients are mixed with ground water and circulated through the contaminated portion of the aquifer through a series of injection and recovery wells (Raymond et al., 1978; Thomas and Ward, 1989). Wells should be screened to accommodate seasonal fluctuations in the level of the water table and air can be supplied through a system of diffusers. Some operational designs are closed loop in which the water

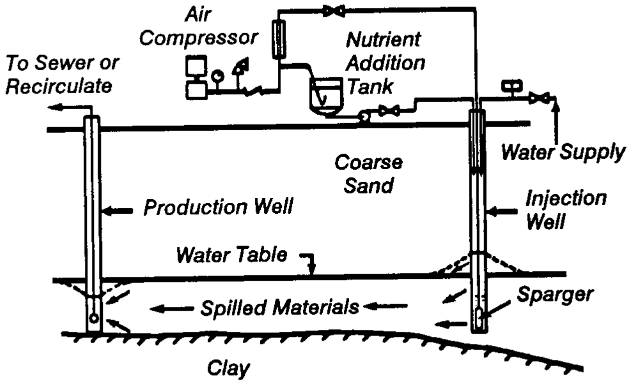


**Figure 16-11.** Typical schematic for aerobic subsurface bloremediation (from Thomas and Ward, 1989).

is recycled, thus, unused nutrients can be reinfected, disposal of potentially hazardous ground water is avoided, and the need for make-up water is reduced.

Materials also can be introduced into the aquifer through the use of infiltration galleries (Figure 16-12) (Brenoel and Brown, 1985; Thomas and Ward, 1989). Infiltration galleries allow movement of the injection solution through the unsaturated zone and the saturated zone, resulting in potential treatment of source materials that may be trapped in the pore spaces of the unsaturated zone.

Amendments to the aquifer are added to the contaminated aquifer in alternating pulses. Inorganic nutrients are usually added first through the injection system, followed by the oxygen source. Simultaneous addition of the two may result in excessive microbial growth close to the point of injection and consequent plugging of the aquifer. High concentrations of hydrogen peroxide (greater than 10 percent) can be used to remove biofouling and restore the efficiency of the system.

Inorganic nutrients may be added in batch or continuously, which is a more labor-intensive process. Continuous addition of oxygen is recommended because low dissolved oxygen levels are likely to be the rate-limiting factor in hydrocarbon degradation. Heterogeneities in the aquifer, such as impermeable lenses and varying hydraulic conductivities, can hinder the distribution of nutrients and oxygen.

Both the operation and effectiveness of the system should be monitored (Lee et al., 1988). Important operational factors include (1) delivery of inorganic nutrients, (2) delivery of the electron acceptor, (3) position of the delivery site in the aquifer in relation to the contaminated portion of the plume, and (4) effectiveness of containment and control of the contaminated plume.

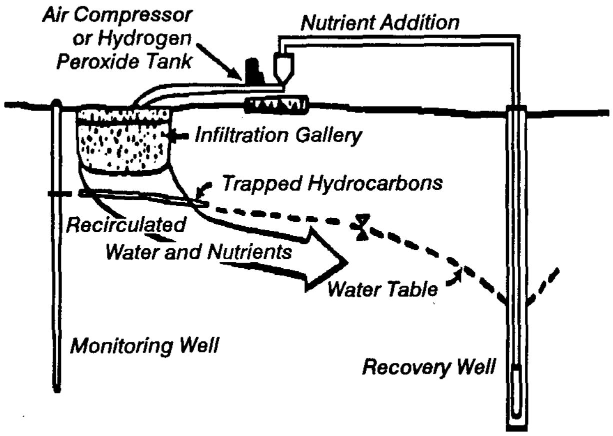


**Figure 16-12.** **Use of infiltration gallery for recirculation of water and nutrients in in situ bioremediation (from Thomas and Ward, 1989).**

Measurements of dissolved oxygen and nutrient levels in ground-water samples are recommended to assess whether or not bioremediation is successful. Increases in microbial numbers and/or activities in samples of aquifer materials also may be quantified relative to (1) plume areas prior to treatment (2) areas within the plume that did not receive treatment; and/or (3) control areas outside the plume. Carbon dioxide levels in ground-water samples also may be useful indicators of microbial activity (Suflita, 1989).

Measurement of contaminant levels should indicate that concentrations of contaminants are decreasing in areas that are receiving treatment and remaining relatively unchanged in areas that are not. If degradation pathways of specific contaminants are known, presence and concentrations of metabolic products may be measured to determine whether or not bioremediation is occurring. Both aquifer materials and ground-water samples should be collected and analyzed to develop a thorough evaluation of treatment effectiveness. The use of appropriate control samples, e.g., assays of untreated areas or areas outside the plume, is highly recommended to confirm the effectiveness of the bioremediation (Suflita, 1989).

The frequency of sampling should be related to the time expected for significant changes to occur along the most contaminated flow path (U.S. EPA, 1989). Important considerations include (1) time required for water to move from injection wells to monitoring wells, (2) seasonal variations in water table elevation or hydraulic gradient, (3) changes in the concentration of dissolved oxygen or alternative electron acceptor, and (4) costs of monitoring.

### *16.3.1 Example of the Use of Bioremediation: A Case Study*

Lee et al. (1988) described numerous applications of the bioremediation process used to restore contaminated aquifers. Most applications have been in the cleanup of hydrocarbon spills. The U.S. EPA Robert S. Kerr Environmental Research Laboratory is presently conducting a field-scale demonstration of the use of enhanced bioremediation at the site of an aviation fuel spill in Traverse City, Michigan. The overall objective of the test is to provide a quantitative demonstration of the method in order to develop a basis for process design (Thomas and Ward, 1989).

In 1969a spill of at least 25,000 gal of aviation gasoline from an underground storage tank at the U.S. Coast Guard Air Station at Traverse City contaminated a shallow sandy watertable aquifer (Figure 16-13) (Wilson et al., 1989). The aviation gasoline was composed primarily of branched-chain alkanes; approximately 10 percent of the spill was composed of alkylbenzenes. Underneath the spill site a long, narrow plume of contaminated ground water is located 15 to 17 ft below the ground surface (corresponding closely to the seasonal high and low water table at the site); it is moving in the direction of Lake Michigan. A large contaminated plume had moved off site, contaminating more than 40 private drinking-

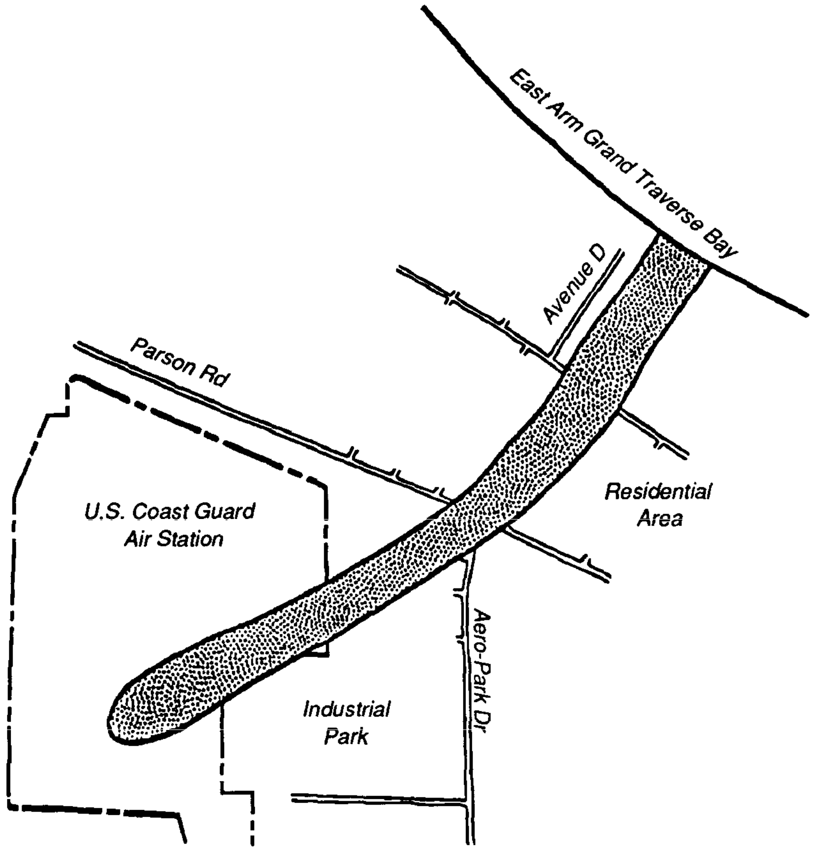


**Figure 16-13. Former plume of contamination resulting from a spill of aviation gasoline on the U.S. Coast Guard Air Station at Traverse City, Michigan. Beginning in 1985, the plume was intercepted by a series of wells at the Coast Guard property boundary (from Wilson et al., 1989).**

water wells. Beginning in 1985, the plume was interrupted by a series of wells at the U.S. Coast Guard property boundary.

In 1988, the U.S. Coast Guard and the Robert S. Kerr Environmental Research Laboratory initiated a pilot-scale in situ bioremediation study in the area of the original spill. The presence of alkylbenzenes is the object of regulatory concern. Bioremediation of the site will be considered completed when the concentration of alkylbenzenes is brought below 5 µg/L, as specified in a consent decree between the Michigan Department of Natural Resources and the U.S. Coast Guard. BIOPLUME II, developed at Rice University to predict contaminant transport affected by oxygen-limited biodegradation (Borden and Bedient, 1986; Borden et al., 1986; Rifai et al., 1989b), is the model that was used to design the well system and to estimate the time required for bioremediation.

Site characterization efforts included acquisition of cores from the source area to determine vertical and horizontal extent of contamination, concentration of total hydrocarbons in the contaminated interval, and concentrations of individual alkylbenzenes (benzene, toluene, and xylene [BTX]) (Wilson et al., 1989). This information was used to identify the most contaminated flow path through the spill. A series of miniature monitoring wells (designated BD-7, BD-31, BD-50, BD-62, BD-83, and BD-108) were installed along and below the most contaminated flow path (Figure16-14). The wells were constructed of 3/8-in. stainless steel with a stainless steel screen that was 6 in. long.

A set of injection wells was installed to perfuse the contaminated area with mineral nutrients and oxygen or hydrogen peroxide. The nutrient solution contained 380 mg/L ammonium chloride, 190 mg/L di-sodium phosphate, and 190 mg/L potassium phosphate. The temperature was 11 to 12°C, and pH was near neutrality. The seepage velocity (i.e., specific discharge) of the injected water in the aquifer averaged 10 ft per day. A tracer test using chloride was conducted for each monitoring well to determine the actual seepage velocity along the flow path to that particular well. Typical data obtained from tracer testing are given in Figure 16-15.

Injection began the first week of March 1988. The system was first acclimated with pure oxygen and then switched to perfusion with hydrogen peroxide. The concentration of hydrogen peroxide was increased slowly to allow time for microbial acclimation to concentrations of hydrogen peroxide, which are generally toxic to most heterotrophic bacteria.

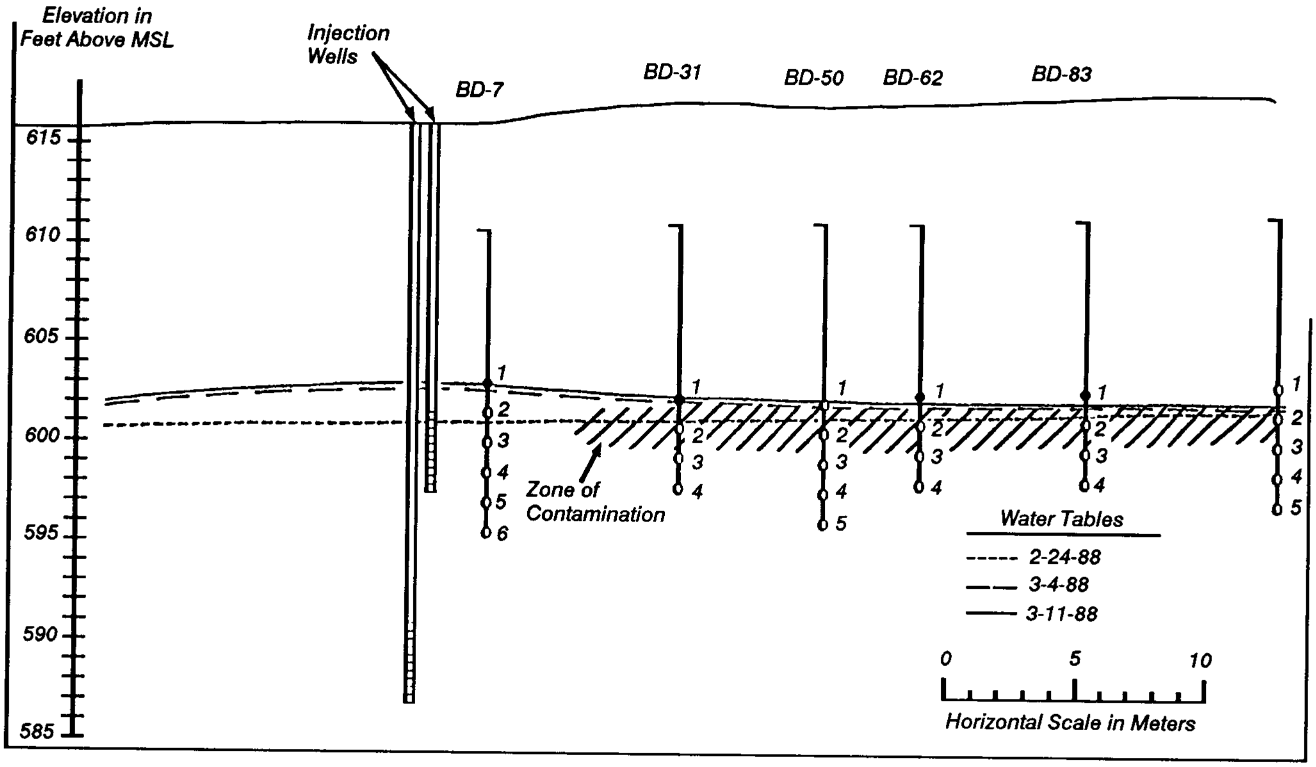


Figure 16-14. Cross section of a demonstration project for bioremediation of the aviation gasoline spill at Traverse City, Michigan (from Wilson et al., 1989).

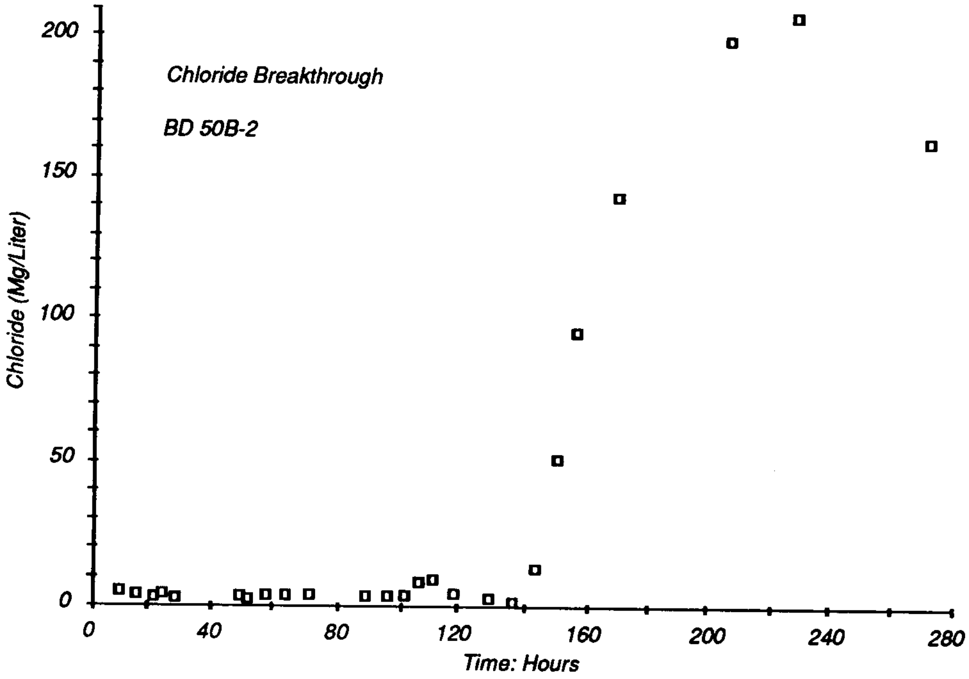


Figure 16-15. Tracer test in the flow line between the injection wells and a miniature monitoring well (BD 50B-2) 50 feet away (from Wilson et al., 1989).

The schedule of application of oxygen or hydrogen peroxide is shown in Figure 16-16.

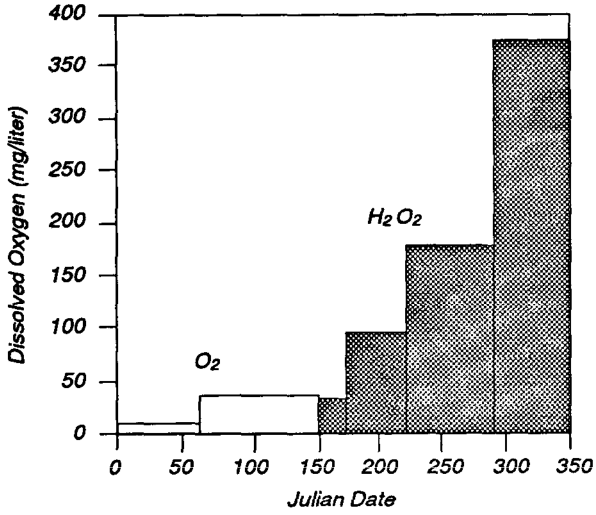


**Figure 16-16. Schedule of application of oxygen or hydrogen peroxide in the first year of the demonstration project (1988) (from Wilson et al., 1989).**

The concentration of fuel hydrocarbons in the most-contaminated flow path averaged 7,500 mg/kg of aquifer material. Based on the concentration of hydrocarbons, the length of the contaminated portion of the flow path, and an assumed stoichiometry for microbial respiration, the total oxygen (Table 16-4) required to remediate the flow paths to the monitoring wells at 31 and 50 ft was estimated.

The interval between the injection wells and the monitoring wells was considered remediated when detectable oxygen broke through and alkylbenzenes disappeared. The interval to the monitoring well at 31 ft was remediated after 220 days (Julian Date 281) (Figure 16-17). The interval to the monitoring well at 50 ft was remediated after 270 days (Julian Date 331) (Figure 16-18).

The seepage velocity of the ground water (as determined by the chloride tracer tests) was multiplied by the concentration of oxygen or hydrogen peroxide in the injection wells to determine the instantaneous flux of oxygen or hydrogen peroxide along the flow path. The cumulative flux at the time of remediation was considered the actual oxygen demand for remediation (Table 16-5).

The aquifer was purged of alkylbenzenes very quickly. The aviation gasoline was composed primarily of branched-chain alkanes, while only about 10 percent of the original spill was composed of alkylbenzenes. The quantity of oxygen and hydrogen peroxide required to remove alkylbenzenes from the wells agreed closely with the projected demand of the alkylbenzenes alone.

***Table 16-4. Stoiohiometry of Aerobic Bioremediation of the Aviation Fuel Spill***

| *Oxygen required* | *Monitoring Wells*<br>*BD 31-2* | <br>*BD 50B-2* |
|---|---|---|
| | *mg $O_2$/liter pore water* | |
| *Estimated based on:* | | |
| *Total Fuel Hydrocarbons* | *62,212* | *90,000* |
| *BTX only (8/87)* | *8,710* | *12,000* |
| *BTX only (3/88)* | *2,364* | *3,420* |
| *Actually required* | *2,989* | *2,952* |

Source: *Wilson et al., 1989*

The flow paths to the monitoring wells at 31 and 50 ft from the injection wells were remediated when only a small fraction of the total oxygen demand of the spill had been supplied. Some of the alkylbenzenes may have been washed from the source area by the flow of water, because of their relatively high water solubility. The significance of transport in the aqueous phase was evaluated by comparing the retardation factor of each alkylbenzene in the most contaminated interval to the number of pore volumes that had been delivered to a particular point. The results of this evaluation indicated that benzene easily could have been removed by water transport and a fraction of the toluene may have been removed by this process. The removal of xylenes, ethylbenzene, however, or trimethylbenzene would not be expected.

An additional portion of the alkylbenzenes may have been removed by anaerobic processes before the front of oxygen passed through. Water from anaerobic regions of the demonstration area contained significant concentrations of volatile fatty acids and was visibly turbid with microorganisms.

The spill was cored in August 1987 to provide information to design the pilot-scale field study and cored again in March 1988, just prior to the initiation of the study, to define the initial conditions (Table 16-5). In general, the concentration of alkylbenzenes declined from 1987 to 1988. Some of the alkylbenzenes may have been removed from the source area after the sampling in 1987 and before the initiation of the remediation action in 1988. This removal was probably due to anaerobic biological processes.

After 8 months of perfusion of the aquifer with mineral nutrients and oxygen sources, results of analyses of core samples taken at 31 ft from the injection wells showed that the aliphatic hydrocarbons remained near their initial concentrations, while the concentrations of the alkylbenzenes had decreased to below analytical detection limits. Since only a minor fraction of their oxygen demand had been supplied when the alkylbenzenes had disappeared from the aquifer, it

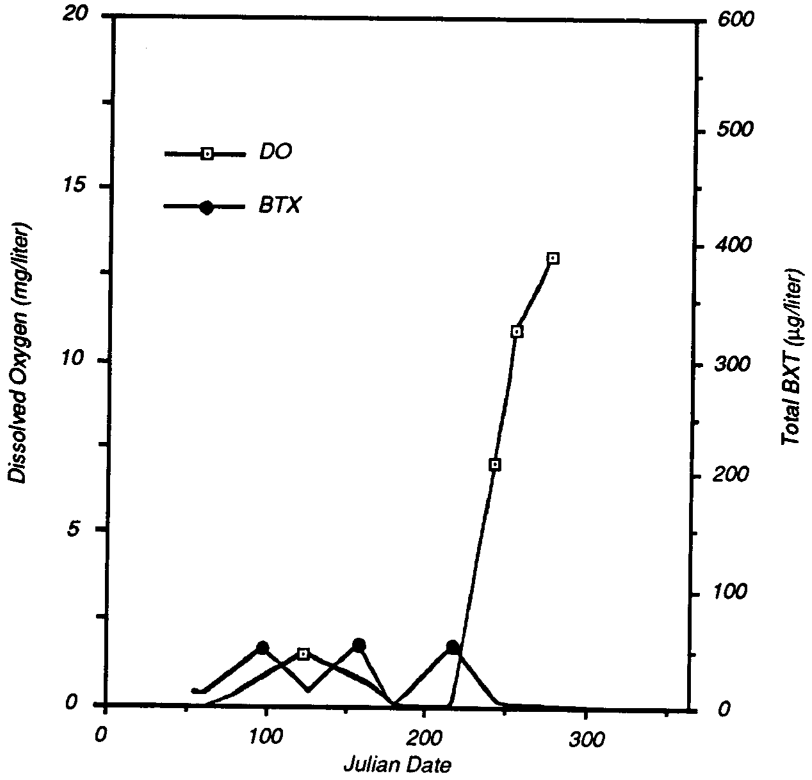


Figure 16-17. Breakthrough of oxygen and depletion of alkylbenzenes (BTX) in a miniature monitoring wail (BD 31-2) 31 feet from the injection wells (from Wilson et al., 1989).

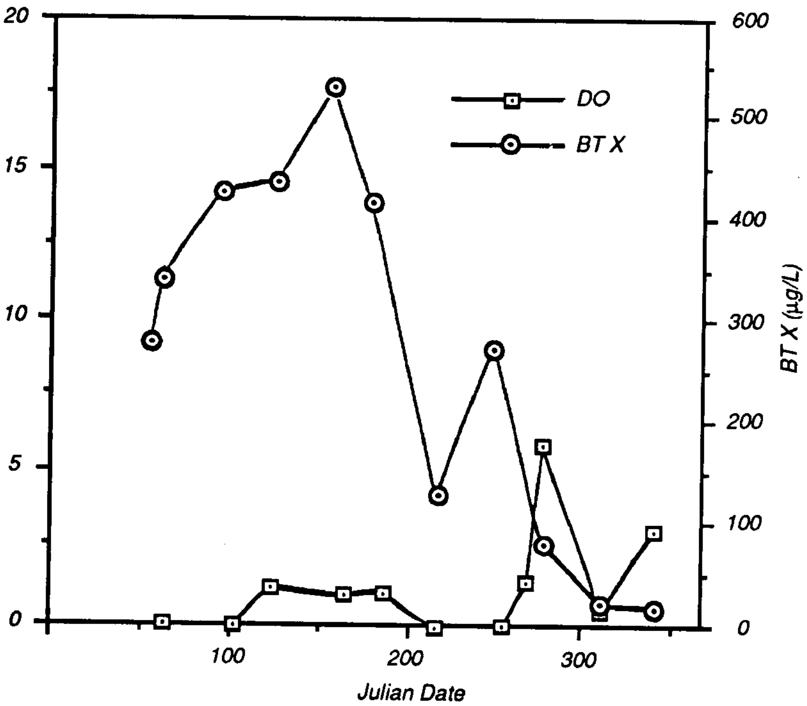


Figure 16-18. Breakthrough of oxygen and depletion of alkylbenzenes (BTX) in a miniature monitoring well (BD 50B-2) 50 feet from the injection wells (from Wilson et al., 1989).

*Table 16-5.* ***Changes in Concentrations of Alkylbenzenes and Total Fuel Hydrocarbon in Core Material During Bioremediation of an Aquifer Contaminated with Aviation Gasoline***

| Date | Oil and Grease | Fuel Hydrocarbon | Benzene | Toluene | Ethylbenzene | Xylenes |
|---|---|---|---|---|---|---|
| Core Number | | -------------------- mg/kg wet sample -------------------- | | | | |
| *Background conditions in an unweathered part of the spill area., June 1988.* | | | | | | |
| 50R6 | | 12,150 | 1.0 | 107 | 57 | 218 |
| 50R7 | | 5,220 | 1.0 | 170 | 24 | 100 |
| *Preliminary sampling used to design the bioremediation project near monitoring well BD-31-2, August 1987.* | | | | | | |
| 50A3 | 4,310 | 5,590 | 0.6 | 235 | 33 | 121 |
| 50I14 | 4,130 | 6,500 | 0.3 | 444 | 12 | 48 |
| 50D18 | 1,130 | 2,500* | 0.7 | 112 | 11 | 39 |
| *Sampled after four months of perfusion with mineral nutrients and oxygen, June 1988.* | | | | | | |
| 50T3 | | 3,330* | 1.4 | 1 | 7.3 | 23 |
| 50W3 | | 4,800* | 1.5 | 1 | 13 | 41 |
| *Sampled after eight months of perfusion with mineral nutrients and oxygen, October 1988.* | | | | | | |
| 50AE4 | | 8,400 | <0.3 | <0.3 | <0.3 | <0.3 |
| 50AE5 | | 2,370* | <0.3 | <0.3 | <0.3 | <0.3 |

**These cores included some uncontaminated material.*

*Wilson et al., 1989*

appears that the nonaromatic fraction of the spill remained in the aquifer.

When the region at 31 ft from the injection wells was cored in March 1989, almost all of the petroleum hydrocarbons had been removed, including the branched-chain alkanes. The study is continuing at the site, and additional information may be obtained from the U.S. EPA Robert S. Kerr Environmental Research Laboratory.

## *16.3.2 Advantages and Limitations in the Use of In Situ Bioremediation*

In situ bioremediation has been used most often, and with reasonably good success, to treat gasoline spills. It has been combined with other treatment processes to reduce organic contaminants in aquifers. In most cases, contaminated ground water is withdrawn, heated by a physical, chemical, or biological aboveground treatment technique, and then recharged to the aquifer after aeration and addition of nutrients. The role of bioremediation in such combination treatment schemes often is difficult to assess.

There are a number of advantages and disadvantages in the use of in situ bioremediation (Lee et al., 1988). Unlike other aquifer remediation technologies, it often can be used to treat contaminants that are sorbed to aquifer materials or trapped in pore spaces. In addition to treatment of the saturated zone, organic contaminants held in the unsaturated and capillary zones can be treated when an infiltration gallery is used. Complete aerobic biodegradation (mineralization) of organic compounds usually produces carbon dioxide, water, and an increase in cell mass.

The time required to treat subsurface contamination using in situ bioremediation often can be faster than withdrawal and treatment processes. A gasoline spill was remediated in 18 months using in situ bioremediation; pump-and-treat techniques were estimated to require 100 years to reduce the concentrations of gasoline to potable water levels (Raymond et al., 1976). Also, in situ bioremediation often costs less than other remedial options. The areal zone of treatment using bioremediation can be larger than with other remedial technologies because the treatment moves with the plume and can reach areas that would otherwise be inaccessible.

There are also disadvantages to in situ bioremediation programs (Lee et al., 1988). Many organic compounds in the subsurface are resistant to degradation. In situ bioremediation usually requires an acclimated population of microorganisms; however, an acclimated population may not have developed for recent spills or for recalcitrant compounds. Heavy metals and toxic concentrations of organic compounds may inhibit activity of indigenous microorganisms. Injection wells may become clogged from profuse microbial growth resulting from the addition of nutrients and oxygen. Nutrients added to the aquifer must be contained within the treatment zone because their transport to surface waters could result in eutrophication. Additionally, using nitrate as an electron acceptor may result in unacceptable levels of unused nitrate being transported through the ground water to potable ground-water or surface water supplies.

Metabolites resulting from partial degradation of organic contaminants also may impart objectionable tastes and odors. For example, incomplete degradation of gasoline under low dissolved oxygen conditions has been shown to result in phenol production, and phenol degradation required more aerobic conditions (Raymond et al., 1978). Increased micro bial biomass can exert an oxygen demand that can form anaerobic conditions in the aquifer, which may result in the production of hydrogen sulfide or other objectionable byproducts.

In situ bioremediation is difficult to implement in low-permeabllity aquifers that do not permit the transport of adequate supplies of nutrients or oxygen to active microbial populations. In addition, bioremediation projects require continuous monitoring and maintenance for successful treatment.

Costs associated with in situ bioremediation include (1) site characterization, (2) remedial design, (3) system design, (4) system installation, (5) materials and operating expenses, and (6) monitoring (U.S. EPA, 1989c).

## 16.4 References

Aelion, C.M., C.M. Swindoll, and F.K. Pfaender. 1987. Adaptation to and Biodegradation of Xenobiotic Compounds by Microbial Communities from a Pristine Aquifer. Appl. Environ. Microbiol. 53:2212-2217.

Borden, R.C. and P.B. Bedient. 1986. Transport of Dissolved Hydrocarbons Influenced by Reaeration and Oxygen Limited Biodegradation. I. Theoretical Development. Water Resources Research 22:1973-1982.

Borden, RC., P.B. Bedient, M.D. Lee, C.H. Ward. and J.T. Wilson. 1986. Transport of Dissolved Hydrocarbons Influenced by Reaeration and Oxygen Limited Biodegradation. II. Field Application. Water Resources Research 22:1983-1990.

Brenoel, M. and R.A. Brown. 1985. Remediation of a Leaking Underground Storage Tank with Enhanced Bioreclamation. In: Proc. Fifth Nat. Symp. on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, Dublin, OH, pp. 527.

Canter, L.W. and R.C. Knox. 1985. Ground Water Pollution Control. Lewis Publishers, Chelsea, MI.

Ehrenfield, J. and J. Bass. 1984. Evaluation of Remedial Action Unit Operations of Hazardous Waste Disposal Sites. Pollution Technology Review No. 110, Noyes Publications, Park Ridge, NJ.

Goldstein, R.M., L.M. Mallory, and M. Alexander. 1985. Reasons for Possible Failure of Inoculation to Enhance Biodegradation. Appl. Environ. Microbiol. 50:977-983.

Huling, S.G., B.E. Bledsoe, and M.V. White. 1990. Enhanced Bioremediation Utilizing Hydrogen Peroxide as a Supplemental Source of Oxygen: A Laboratory and Field Study. EPA/600/2-90/006 (NTIS PB90-183435/AS)

Keely, J.F. 1989. Performance Evaluations of Pump-and-Treat Remediations. Superfund Groundwater Issue Paper No. 5. EPA/540/4-89/005.

Lee, M.D. and C.H. Ward. 1986. Ground Water Restoration. Report submitted to JACA Corporation, Fort Washington, PA.

Lee, M.D., J.M. Thomas, R.C. Borden, P.B. Bedient, J.T. Wilson, and C.H. Ward. 1988. Biorestoration of Aquifers Contaminated with Organic Compounds. CRC Critical Reviews In Environmental Control 18:29-89.

Nyer, E.K. 1985. Groundwater Treatment Technology. Van Nostrand Reinhold, New York, NY.

Palmer, C.D. and R.L. Johnson. 1989. Physical processes Controlling the Transport of Non-Aqueous Phase Liquids in the Subsurface. In: Transport and Fate of Contaminants in the Subsurface. EPA/625/4-89/019, Chapter 3.

Raymond, R.L. 1974. Reclamation of Hydrocarbon Contaminated Ground Water. U.S. Patent 3,846,290, Nov. 5.

Raymond, R.L., V.W. Jamison, and J.O. Hudson. 1976. Beneficial Stimulation of Bacterial Activity in Groundwaters Containing Petroleum Products. AIChE Symposium Series 73:390.

Raymond, R.L., V.W. Jamison, J.O. Hudson, R.E. Mitchell, and V.E. Farmer. 1978. Field Application of Subsurface Biodegradation of Gasoline in a Sand Formation. API Publication 4430, American Petroleum Institute, Washington, DC.

Rifai, H. S., P.B. Bedient, J.T. Wilson, K.M. Miller, and J.M. Armstrong. 1988. Biodegradation Modeling at Aviation Fuel Spill Site. J. Environ. Engineering 114(5)1007-1029.

Rifai, H.S., P.B Bedient, R.C. Borden, and J.F. Haasbeek. 1989. BIOPLUME II-Computer Model of Two-Dimensional Contaminant Transport Under the Influence of Oxygen Limited Biodegradation in Ground Water (User's Manual Version 1.0; Preprocessor Source Code Version 1.0; Source Code Version 1.0). EPA/600/8-88/093 (NTIS PB89-151120/AS).

Roberts, P. V., L. Semprini, G.D. Hopkins, D. Grbic-Galic, P.L. McCarty, and M. Reinhard. 1989. In-Situ Aquifer Restoration of Chlorinated Aliphatics by Methanotrophic Bacteria. EPA/60012-89/033 (NTIS PB89-219992).

Sale, T, and K. Piontek. 1989. In Situ Removal of Waste Wood-Treating Oils from Subsurface Materials. Presented at Forum on Remediation of Wood Preserving Sites, Technical Assistance to U.S. EPA Region IX (Edwin Barth, U.S. EPA, Cincinnati, OH, and John Matthews, U.S. EPA, Ada, OK, Technical Coordinators).

Schafer, J.M. 1984. Determining Optimum Pumping Rates for Creation of Hydraulic Barriers to Ground Water Pollutant Migration. In: Proc. Fourth Nat. Symp. on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, Dublin, OH, pp. 50-62.

Suflita, J.M. 1989. Microbiological Principles Influencing the Restoration of Aquifers. In: Transport and Fate of Contaminants in the Subsurface, EPA/625/4-89/O 19, Chapter 8.

Thomas, J.M. and C.H. Ward. 1989. In Situ Biorestoration of Organic Contaminants in the Subsurface. Environ. Sci. Technol. 23:760-766.

Thomas, J.M., M.D. Lee, P.B. Bedient, R.C. Borden, L.W. Canter, and C.H. Ward. 1987. Leaking Underground Storage Tank Remediation with Emphasis on In Situ Biorestoration. EPA/600/2-87/108 (NTIS PB87-168084/REB).

U.S. Environmental Protection Agency (EPA). 1985. Remedial Action at Waste Disposal Sites. EPA/625/6-85/O06 (NTIS PB87-201O34).

U.S. Environmental Protection Agency (EPA). 1989a. The Superfund Innovative Technology Evaluation Program: Technology Profiles. EPA/540/5-89/013.

U.S. Environmental Protection Agency (EPA). 1989b. Demonstration of Remedial Action Technologies for Contaminated Land and Groundwater. In: proceedings and Appendices, Third International Conference, NATO Committee on Challenges of Modem Society (CCMS) (Montreal, Canada).

U.S. Environmental Protection Agency (EPA). 1989c. Bioremediation of Hazardous Waste Sites Workshop: Speaker Slide Copy and Supporting Information. EPA/CERI-89-11 (NTIS PB89-169205/REB).

US. Environmental Protection Agency (EPA). 1990. Basics of Pump-and-Treat Ground-Water Remediation Technology. EPA/600113-90/003.

Wilson, J.L. 1984. Double-Cell Hydraulic Containment of Pollutant Plumes. In: Proc. Fourth Nat. Symp. on Aquifer Restoration and Ground Water Monitoring, National Water Well Association, Dublin, OH, pp. 65-70.

Wilson, J.T., L.E. Leach, J. Michalowski, S. Vandegrift, and R. Callaway. 1989. In Situ Bioremediation of Spills from Underground Storage Tanks: New Approaches for Site Characterization, Project Design, and Evaluation of Performance. EPA/600/2-89/042 (NTIS PB89-219976/AS).

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