

GROUND WATER CONTAMINATION

TRANSPORT AND REMEDIATION

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To Cindy, Eric, and Courtney
To my parents for their guidance
To all of my students and colleagues
PBB

To CJ, Imo, Steve and Meaux
To my parents
HSR

To June, Wynne, Mark, Jon, and Phil
To Hanadi, for everything
CJN

C O N T E N T S

PREFACE **xiii**

**1 INTRODUCTION TO GROUND WATER
CONTAMINATION** **1**

- 1.1 The Hydrologic Cycle 1
- 1.2 Ground Water Hydrology 3
- 1.3 Ground Water Contamination and Transport 6
- 1.4 Evolution of Ground Water Information 11
- 1.5 Ground Water Remediation 12

2 GROUND WATER HYDROLOGY **15**

- 2.1 Introduction 15
- 2.2 Properties of Ground Water 16
- 2.3 Ground Water Movement 23
- 2.4 General Flow Equations 34
- 2.5 Dupuit Equations 37
- 2.6 Streamlines and Equipotential Lines 41
- 2.7 Unsaturated Flow and the Water Table 45

3 GROUND WATER FLOW AND WELL MECHANICS **49**

- 3.1 Steady-State Well Hydraulics 49
- 3.2 Steady One-Dimensional Flow 50
- 3.3 Steady Radial Flow to a Well—Confined 50
- 3.4 Steady Radial Flow to a Well—Unconfined 52
- 3.5 Well in a Uniform Flow Field 54
- 3.6 Multiple-Well System 55
- 3.7 Unsteady Well Hydraulics 58

4 SOURCES AND TYPES OF GROUNDWATER CONTAMINATION 75

4.1	Introduction	75
4.2	Underground Storage Tanks	83
4.3	Landfills	85
4.4	Surface Impoundments	87
4.5	Waste Disposal Injection Wells	88
4.6	Septic Systems	90
4.7	Agricultural Wastes	92
4.8	Land Application and Mining	93
4.9	Radioactive Contaminants	94
4.10	Military Sources of Contamination	97
4.11	Classification of Organic Compounds	98
4.12	Inorganic Compounds in Groundwater	107
4.13	A Typical Industrial Waste Site	108

5 HYDROGEOLOGIC SITE INVESTIGATIONS 113

by Robert S. Lee and John A. Connor

5.1	Introduction	113
5.2	Development of Conceptual Site Model	114
5.3	Strategy for Hydrogeologic Site Investigations	115
5.4	Development of a Detailed Site Investigation Workplan	122
5.5	Data Collection Methods	125
5.6	Geologic Data Acquisition	126
5.7	Hydrologic Data Acquisition	142
5.8	Acquisition of Soil and Groundwater Quality Data	148
5.9	Data Evaluation Procedures	152

6 CONTAMINANT TRANSPORT MECHANISMS 159

6.1	Introduction	159
6.2	Advection Process	161
6.3	Diffusion and Dispersion Processes	162
6.4	Mass Transport Equations	165
6.5	One-Dimensional Models	170

6.6	Governing Flow and Transport Equations	175
6.7	Analytical Methods	177
6.8	Multidimensional Methods	181
6.9	Tests for Dispersivity	185
6.10	Natural Gradient Field Tests for Dispersion	190

7 CONTAMINANT FATE PROCESSES 203

by Joseph B. Hughes

7.1	Introduction	203
7.2	Sorption and Desorption	204
7.3	Abiotic Fate Processes	215
7.4	Volatilization	218
7.5	Biodegradation	219
7.6	Evaluation of Fate Processes	231

8 MODELING BIODEGRADATION AND NATURAL ATTENUATION 237

8.1	Kinetics and Rates of Biodegradation	237
8.2	Modeling Biodegradation	244
8.3	Biodegradation Models	246
8.4	Analytical Natural Attenuation Models	258
8.5	Numerical Natural Attenuation Models	266
8.6	Field Site Applications	274

9 FLOW AND TRANSPORT IN THE UNSATURATED ZONE 289

by Manar El-Beshry

9.1	Capillary Action	289
9.2	Soil-Water Characteristic Curves	291
9.3	Unsaturated Hydraulic Conductivity	294
9.4	Governing Equation for Unsaturated Flow	295
9.5	Measurement of Soil Properties	297

9.6	Infiltration Models	298
9.7	Transport Processes in the Unsaturated Zone	303
9.8	Governing Equations for Vapor Transport	308
9.9	Vadose Zone Flow and Transport Models	315

10 NUMERICAL MODELING OF CONTAMINANT TRANSPORT 335

10.1	Introduction	335
10.2	Numerical Methods	345
10.3	Finite Difference Methods	353
10.4	Finite Element Methods	364
10.5	Method of Characteristics (MOC)	365
10.6	Numerical Flow Models	367
10.7	Contaminant Transport Models	371
10.8	Modeling With Graphical Pre-Processors	375
10.9	Applying Numerical Models to Field Sites	381

11 NONAQUEOUS PHASE LIQUIDS 391

11.1	Introduction	391
11.2	Types of NAPLs	397
11.3	NAPL Transport — General Processes	401
11.4	NAPL Transport — Computational Methods	414
11.5	Fate of NAPLs in the Subsurface	422
11.6	Characterizing NAPLs at Remediation Sites	429

12 NATURAL ATTENUATION AND RISK BASED CORRECTIVE ACTION 441

12.1	Introduction	441
12.2	General Principles Behind Natural Attenuation	448
12.3	Natural Attenuation Protocols and Guidance	451
12.4	Demonstrating Natural Attenuation	456
12.5	Risk-Based Corrective Action (RBCA)	471

13 GROUND WATER REMEDIATION ALTERNATIVES 479

13.1	Introduction to Remediation Methods	479
13.2	Remedial Alternatives	481
13.3	Containment Methods for Source Control	483
13.4	Hydraulic Controls and Pump and Treat Systems	488
13.5	Bioremediation	497
13.6	Soil Vapor Extraction Systems	501
13.7	Remediating NAPL Sites	507
13.8	Emerging Remediation Technologies	512
13.9	Case Studies of Remediation	521

14 LEGAL PROTECTION OF GROUND WATER 545

by James B. Blackburn

14.1	The Process of Ground Water Protection	546
14.2	The Safe Drinking Water Act of 1974	547
14.3	The Resource Conservation and Recovery Act of 1976	550
14.4	The Hazardous and Solid Waste Amendment of 1984 (HSWA)	558
14.5	CERCLA	562
14.6	Superfund Amendment and Reauthorization Act of 1986 (SARA)	573

HOMEWORK PROBLEMS 577

INDEX 597

P R E F A C E

The 1970s ushered in a new decade of environmental awareness in response to major air pollution and water quality problems throughout the country. One of the primary missions of the newly formed Environmental Protection Agency (EPA) was to define, maintain, and protect the quality of the nation's surface waters and subsurface aquifers. The field of environmental engineering was in its infancy, but hydrologists, civil and environmental engineers, hydrogeologists and other scientists were needed to provide the necessary expertise and engineering designs for water pollution control of surface waters.

By the late 1970s, the discovery of hazardous wastes at sites such as Love Canal in New York, the Denver Arsenal in Colorado, and a number of chlorinated organics sites in California and Arizona ushered in a new era in hazardous waste site problems. In the early 1980s, a large number of major disposal sites were discovered associated with industrial and military practices. These sites had been in place for decades. As a result, literally thousands of studies of active and abandoned waste sites and spills were conducted, as required by Resource Conservation and Recovery Act (RCRA) and the Superfund legislation administered by EPA, all designed to protect ground water quality (Chapter 14). During this time, hydrogeologists and consulting engineers were collecting samples, characterizing geology, analyzing data, and remediating hazardous waste sites with respect to ground water contamination. More than 1500 hazardous waste sites were eventually placed on the National Priorities List and thousands of other sites still remaining to be cleaned up.

By 1985, leaking underground fuel tanks became one of the most ubiquitous of all subsurface contamination issues. In addition, chlorinated hydrocarbon sites were recognized as some of the most difficult to remediate due to the presence of newly discovered non-aqueous phase liquids (NAPLs). But as these sites and others were being investigated and remediation systems were being designed and installed across the country, it became clear by 1989 that many of these systems were not working to cleanup aquifers to drinking water standards. By the early 1990s, EPA and the National Research Council found that the nation was wasting large sums of money on ineffective remediation systems, such as pump and treat (see Chapter 13).

Along with the maturing of environmental engineering and related ground water fields in the eighties, attention to hazardous waste problems has greatly expanded the scope and emphasis of traditional ground water investigations. Contaminant transport in the subsurface is of paramount importance and encompasses physical, chemical, and biological mechanisms which affect rates of migration, degradation, and ultimate remediation. In the nineties, many of these complex transport mechanisms were evaluated at actual field sites or in supporting laboratory studies.

After all of the efforts spent on analyzing and remediating soluble contaminant plumes, scientists and engineers in the nineties and beyond 2000 must be prepared to deal

INTRODUCTION TO GROUND WATER CONTAMINATION

1.1 THE HYDROLOGIC CYCLE

The definition of **hydrology** includes the study of storage and movement of water in streams and lakes on the surface of the earth, as well as in ground water aquifers in the subsurface. An **aquifer** represents a geological unit, which can store and supply significant quantities of water for a variety of uses. Many shallow and deep aquifers have been investigated and identified as having elevated levels of contaminants from releases that may have occurred decades ago. Modern hydrology encompasses both flow and water quality transport aspects of the water cycle.

Figure 1.1 shows the various components of the hydrologic cycle, including both natural processes and manmade or engineered processes and transport pathways. These concepts are covered in detail in modern texts on hydrology (Bedient and Huber, 1992; Gupta,

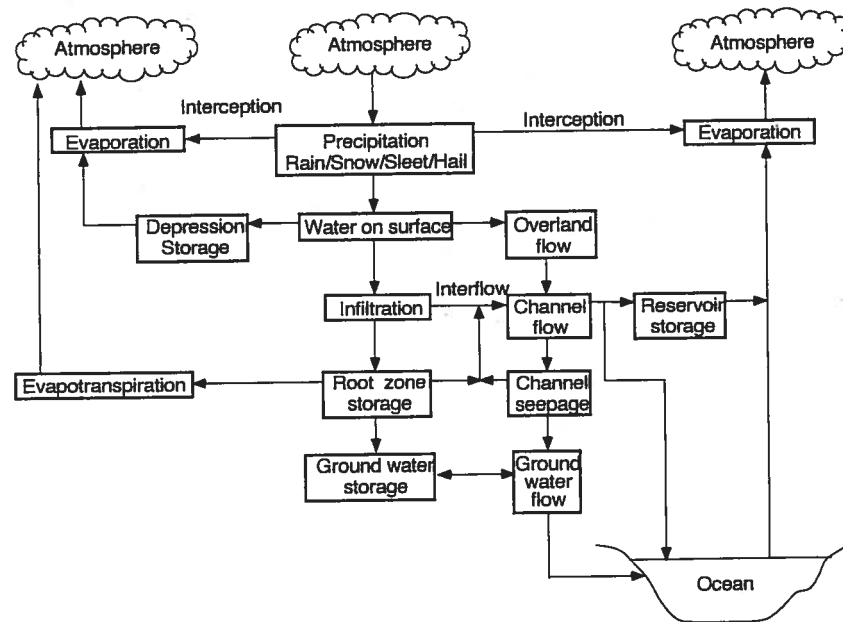


Figure 1.1 Components of the hydrologic cycle.

1989, Chow et al., 1988). Atmospheric water and solar energy provide the main inputs for the generation of precipitation, which falls over the land and oceans. Rainfall can infiltrate into the soil system, percolate to deeper ground water, evaporate from detention areas, transpire through vegetation back to the atmosphere, or runoff to the nearest stream or river. Infiltrating water is the main source of recharge to the root zone and ground water aquifers below. Rivers can also recharge aquifers or can act as discharge points for aquifer outflows. The ocean is the ultimate receptor of surface and ground water contributions from surrounding land areas, and provides the main source of water for evaporation back to the atmosphere.

Manmade changes to the cycle have been recorded since the beginning of civilization. They include changes in infiltration patterns and evaporation due to land development, changes in runoff and evaporation patterns due to reservoir storage, increases in streamflow due to channelization and piping, and changes in ground water levels due to pumping of aquifers. Since the 1930s, hydrologists traditionally have spent much time and effort designing alterations to the natural hydrologic cycle for man's use. Such alterations include providing surface or ground water supplies for industrial, agricultural, and municipal needs; providing water treatment for drinking water and the disposal of wastewater; meeting water supply needs through building of dams and reservoirs or drilling of water supply well fields; provid-

ing drainage and flood control via channelization and dams; and providing water quality and recreational benefits through development and maintenance of reservoirs and stream corridors.

Due to the complexity of the hydrologic cycle shown in Figure 1.1, not all of the transport pathways and storage elements can be measured easily, and some components can be determined only indirectly as unknowns in the overall hydrologic water balance equation. Infiltration and evaporation are often computed as losses from the system and are not usually measured directly. Precipitation rates and stream levels can be directly measured by rainfall and stream gages that have been located within a particular watershed being studied. Ground water levels and flow rates are measured from wells installed into aquifers with screens across the permeable zones. In complex geological settings, multiple layers are monitored for water and contaminant levels. Methods include use of flow meters within the well casing and electronic water level meters. Pumps and individual bailers are used to collect water samples for the analysis of water quality levels in wells.

Overall water balances for a watershed or ground water basin can be computed if the above hydrologic data is available. Computer methods have been developed beginning in the 1970s to assist the hydrologist in watershed analysis, ground water assessment, and hydrologic design. Surface water aspects of the hydrologic cycle are usually covered in modern hydrology texts such as Viessman et al. (1989), Chow et al. (1988), and Bedient and Huber (1992).

1.2 GROUND WATER HYDROLOGY

Ground water is an important source of water supply for municipalities, agriculture, and industry. Figure 1.2 indicates the percentage of various types of ground water use in the United States through 1995. Primary users are agriculture, municipalities, industry, and rural areas where alternate surface supplies are inadequate. Agricultural irrigation use is clearly the largest category. Figure 1.3 depicts ground water use relative to total water use for each state in the continental United States, indicating that western and midwestern areas are more dependent on ground water aquifers than are states in the east and northeast.

Ground water hydrology has traditionally included the characterization of aquifers, application of Darcy's law for ground water flow through porous media, infiltration into soils, and flow in shallow and deep aquifer systems. More advanced topics include the mechanics of well flow in radial coordinates for single or multiple well systems. Techniques for the analysis of aquifer characteristics using slug tests, pump tests, or tracer tests are a major part of ground water investigations. The prediction of flow rates and directions in confined (under pressure) and unconfined (water table) aquifers is the starting point for understanding ground water contamination issues. The **water table** in a shallow aquifer is defined as the level to which water will rise in a dug well under atmospheric conditions. The **piezometric surface** is the level to which water rises in a confined aquifer under pressure (see Chapter 2).

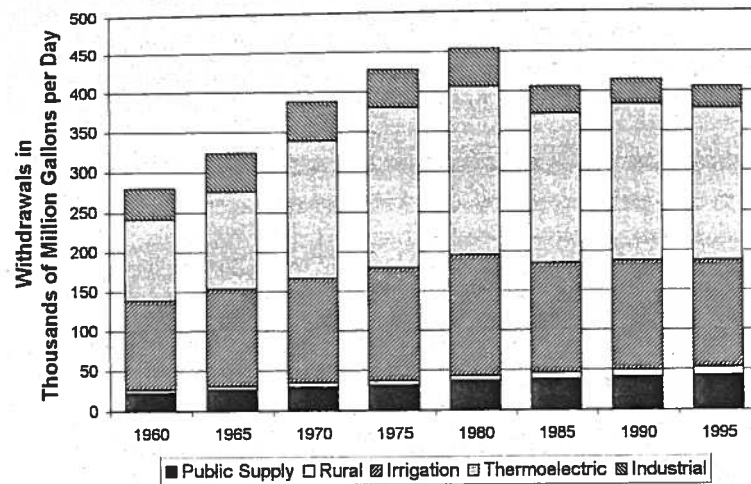


Figure 1.2 Trends in water withdrawals (fresh and saline) by water use category and total (fresh and saline) withdrawals, 1960-95. Source USGS, 1995.

Ground water hydrology is of great importance because of the use of aquifer systems for water supply and because of the threat of contamination from leaking hazardous waste sites, which occur at or below the ground surface. Recently, more attention has been given to the connection between the unsaturated zone and shallow aquifers just below the water table as it relates to migration of contaminants from the surface or from buried tanks, pipes, or waste ponds. Properties of the porous media and subsurface geology govern both the rate and direction of ground water flow in any aquifer system. The injection or accidental spill of hazardous wastes into an aquifer or the pumping of the aquifer for water supply may alter the natural hydrologic flow patterns. In order for the hydrologist, hydrogeologist, civil engineer, or environmental engineer to obtain a full understanding of the mechanisms that lead to ground water contamination from spills or continuous leaks, it is necessary to address first the properties of ground water flow and well mechanics, as covered in Chapters 2 and 3.

Geological aspects of ground water, sometimes referred to as hydrogeology, are of importance to understanding ground water flow and the fate and transport of contaminants in the subsurface. Regional geological aspects have been covered in detail in books by Freeze and Cherry (1979), Fetter (1994), and Domenico and Schwartz (1998) and will be addressed in this text only to a limited basis. One useful generalization is the concept of ground water regions, which are geographical areas of similar occurrence of ground water. Meinzer (1923), considered the father of modern hydrogeology in the United States, proposed a classification

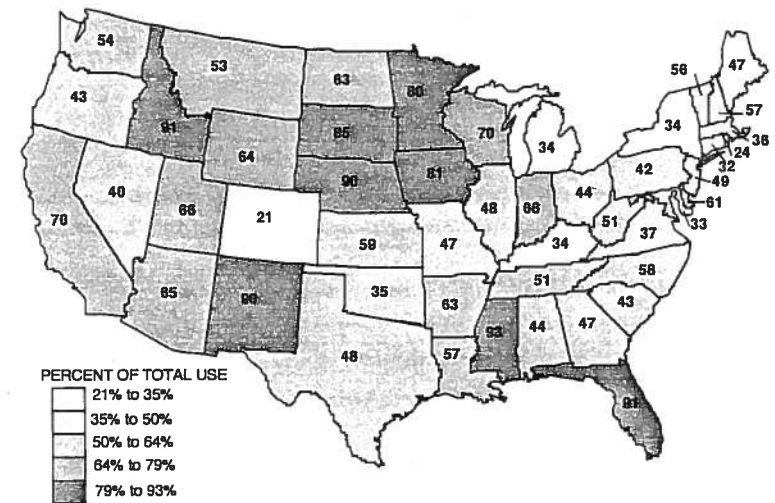


Figure 1.3 Ground water use as a percent of total water use, 1985. Source Solley, et al., 1988.

system based on 21 different ground water provinces. Thomas (1952) devised the system based on 10 ground water regions, and Heath (1984) revised Thomas' system to include 15 different regions. Heath based his system on five features of ground water systems:

1. The components of the system and their arrangement;
2. The nature of the water-bearing openings of the dominant aquifer or aquifers with respect to whether they are of primary or secondary origin;
3. The mineral composition of the rock matrix of the dominant aquifers with respect to whether it is soluble or insoluble;
4. The water storage and transmission characteristics of the dominant aquifer or aquifers; and
5. The nature and location of recharge and discharge areas.

The various regions for the United States are shown in Figure 1.4 and are based on the DRASTIC system (Aller et al, 1987).

Each of the above regional geologic categories is unique in its own right and important to understanding the underlying stratigraphy that may be impacting the transport of contaminants in the subsurface. Extensive studies exist on each of the regions from the United States Geological Survey or from State Geological Surveys, but some areas have been more inten-

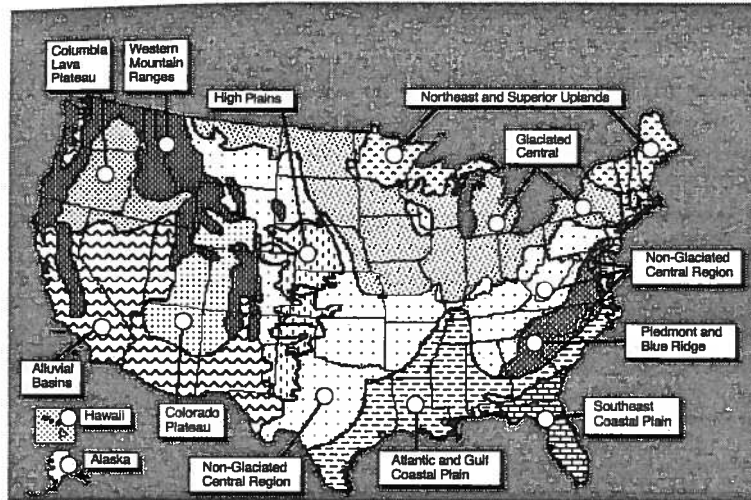


Figure 1.4 Ground water regions of the United States. Source Newell, et al., 1990.

sively evaluated than others. In many cases of practical interest, the first few shallow layers of sand or silty sand (5m to 50 m depth) may be the only zones of concern from a contamination and remediation standpoint. These relatively shallow zones may not have been evaluated by qualified hydrogeologists in a consistent manner, which has led to significant errors in the prediction of flow rates and contaminant impacts associated with some hazardous waste sites.

The revised text presents detailed methods and examples of hydrogeological site investigations in shallow and deep ground water in Chapter 5, as well as various remediation methods that can be used at hazardous waste sites in Chapters 12 and 13. It is important for students and professionals alike to understand the relationship between the regional geological setting and the local, shallow stratigraphy surrounding a waste site. Often, the overall regional setting has very little to do with shallow aquifers near the surface (within 20 m), which are often the main pathways for contaminant migration in the subsurface. However, an understanding of the regional setting is important to evaluate the extent to which the aquifer is used for water supply.

1.3 GROUND WATER CONTAMINATION AND TRANSPORT

The occurrence of ground water contamination and the quality of ground water have become major issues since the discovery of numerous hazardous waste sites in the late seventies.

Waste sites such as Love Canal in New York, the Denver Arsenal in Colorado, and Hughes Plant 44 in Arizona are three examples where hazardous wastes have created serious ground water contamination problems for decades to come. Over 1500 sites nationwide were on the National Priority List from EPA. Sources of ground water contamination are widespread as shown in Figure 1.5 and include thousands of accidental spills, landfills, surface waste ponds, underground storage tanks, above ground tanks, pipelines, injection wells, land application of wastes and pesticides, septic tanks, radioactive waste disposal sites, salt water intrusion, and acid mine drainage.

An engineering hydrologist today must be able to address mechanisms of ground water flow, contaminant transport, biodegradation and sorption, pure phase impacts in source areas and plumes, and remediation schemes. This text is designed to assist engineering and science students, hydrogeologists, and other professionals in dealing with these major processes in ground water, not always covered in earlier texts in a comprehensive way.

A review of ground water flow in the subsurface, including well mechanics, is required before one can make any progress toward explaining or predicting contamination processes. Chapter 2 provides a working knowledge of methods that have been developed to predict rates of flow according to Darcy's Law, and directions of movement in aquifer systems. Chapter 3

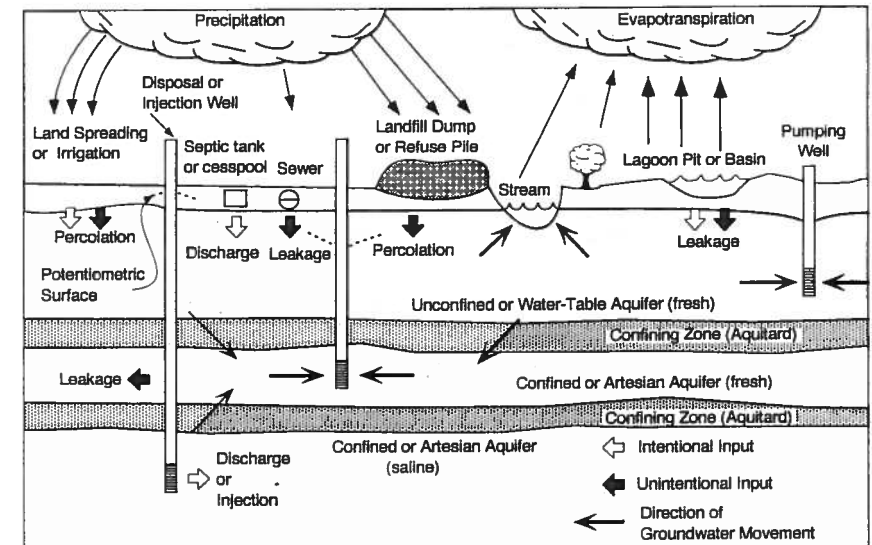


Figure 1.5 How waste disposal practices contaminate the ground water system.

follows with coverage of steady and unsteady well mechanics and a review of standard aquifer tests (pump tests, slug tests, tracer tests) for determining hydraulic conductivity (permeability) in the field. A number of homework problems and examples are also included on ground water flow and well mechanics.

Sources of ground water contamination are widespread and include thousands of accidental spills, landfills, surface waste ponds, underground storage tanks, pipelines, injection wells, land application of wastes and pesticides, septic tanks, radioactive waste disposal, salt water intrusion, and acid mine drainage. These various sources are described in more detail in Chapter 4, which has been greatly expanded for the second edition. The main contaminants of concern still include petroleum hydrocarbons such as benzene, toluene, and xylene; chlorinated organics such as perchloroethylene (PCE), trichloroethylene (TCE) and its associated daughter products; heavy metals such as lead, zinc, and chromium, and certain inorganic salts. A section on organic chemicals is also included.

Sampling and monitoring methods (direct and indirect) have advanced significantly over the past two decades with vast improvements in microelectronics and low level organic chemical analyses. Cone penetrometers, push technology, and specialized multi-level samplers are routinely used as part of site investigations. Data collection and monitoring methods, and the preparation of site work plans for hydrogeologic investigations are described in Chapter 5, which has been updated for the second edition.

Chapter 6 introduces discussion of contaminant transport processes, theory, and equations, including mechanisms of advection, dispersion, and adsorption. These are still considered some of the most important mechanisms in that they all contribute to the spatial and temporal changes in concentration often observed in plumes. These processes also are important for natural attenuation of plumes in aquifer systems. Many examples and analytical methods are presented in this chapter, and tracer results from the Borden Landfill and studies at Otis Air Force Base are highlighted. A number of homework problems are included to reinforce the concepts that are presented.

Chapter 7 is a new chapter on contaminant fate processes and covers topics such as adsorption, abiotic transformation, volatilization and biodegradation associated with organic contaminants. Chapter 8 on biodegradation modeling has been greatly expanded to include new examples and a discussion of new models that apply to fuel contaminants and chlorinated solvents. Both chapters address modern mechanisms of transport that relate directly to natural attenuation in aquifer systems.

Chapter 9 has been extensively rewritten for the new edition and presents a concise treatment of flow and transport in the unsaturated zone. This zone has received major attention with the discovery in the 1980s and early 1990s that soil vapor extraction (SVE) is a viable remediation method for many fuel spill sites. Both analytical and numerical modeling approaches for SVE systems are presented along with detailed examples. A major SVE case study is depicted in Chapter 13.

Chapter 10 describes modern approaches to numerical modeling of ground water flow and transport systems, including a detailed treatment of finite difference methods. A number of the standard models used in the industry are presented in detail with examples on their application at field sites. Modeling approaches have become even more important in recent

years as budgets have shrunk for the collection of data and the drilling of extensive monitoring well networks. New visualization tools have greatly improved our ability to set up and use models to assist in data collection and decision making.

Chapter 11 covers nonaqueous phase liquids (NAPLs) in the subsurface, an important topic which has received considerable attention in the past decade as it relates to the remediation of hazardous waste sites (EPA, 1992; National Research Council, 1994; Pankow and Cherry, 1996). NAPLs, which can provide a source of continuing contamination for decades, are often associated with fuel leaks and chlorinated organic contaminants. Special treatment of source areas contaminated with NAPLs cannot be overlooked, and in earlier years led to the selection of ineffective remediation methods at many sites. The presence of DNAPL at a site may represent the most difficult problem to cleanup due to vertical migration associated with dense, often chlorinated, solvents and organics. Figure 1.6 presents the current conceptual model for what happens to a typical LNAPL hydrocarbon spill in the subsurface. It is now widely recognized that understanding NAPLs transport and remediation may be the most important ground water problem of the nineties. Figure 1.7 indicates the transport mecha-

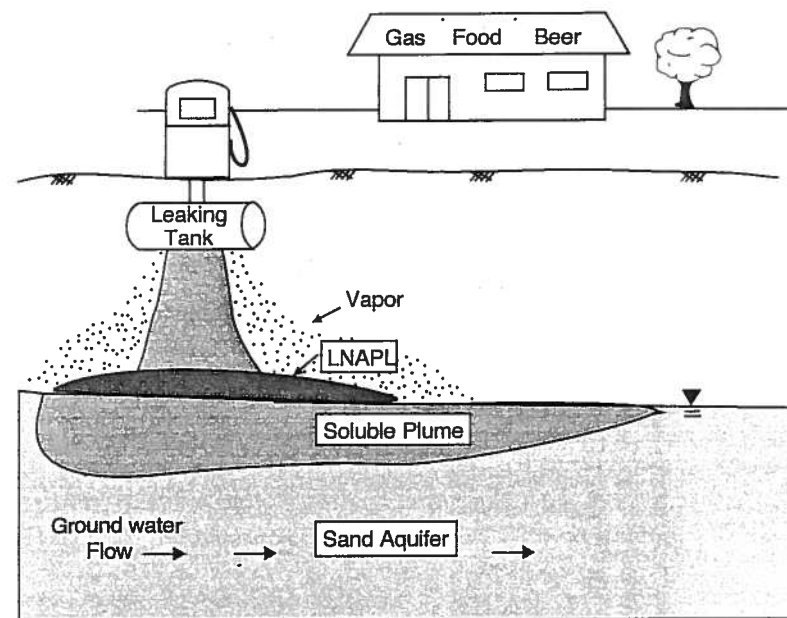


Figure 1.6 Typical hydrocarbon spill.

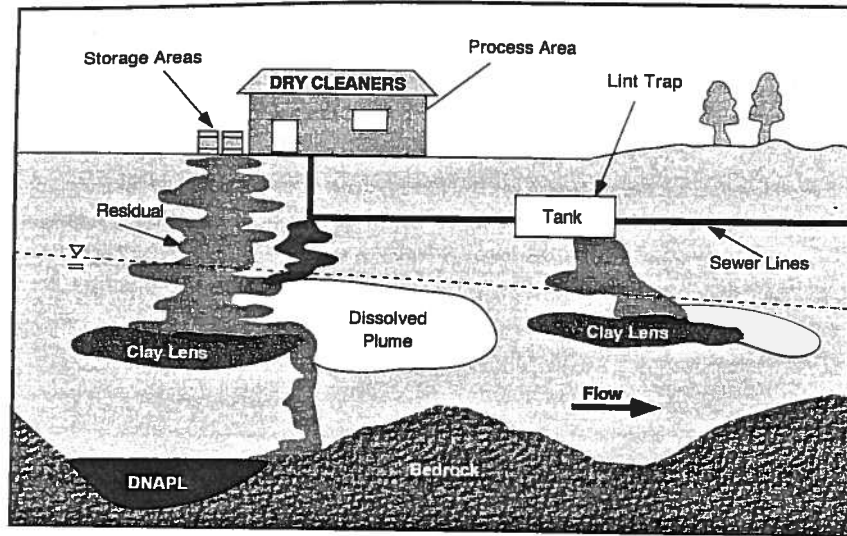


Figure 1.7 Transport mechanisms associated with DNAPLs at a chlorinated solvent site.

nisms associated with DNAPL at a typical dry cleaner site where chlorinated solvents have been used.

A relatively new approach for managing ground water plumes, natural attenuation, is reviewed in Chapter 12. With this approach, plume history, geochemical indicators, and ground water modeling are used to demonstrate that naturally occurring processes such as dispersion, sorption, dilution, and, most importantly, biodegradation, are effective at controlling plume migration. Methods for evaluating natural attenuation data are presented along with a summary of natural attenuation protocols and guidance documents. An overview of a related plume management approach, risk-based corrective action (RBCA) is also provided in Chapter 12. Under RBCA, a risk assessment is performed for the ground water pathway, and the data are used to develop cleanup standards that are protective of human health and the environment. Depending on the location of receptors and hydrogeologic and source conditions, the cleanup standards either will be higher than existing concentrations (indicating no active remediation is required) or will be more stringent than existing concentrations (indicating that either active remediation, containment, or institutional controls will be required).

Chapter 13 covers ground water remediation and design, which has experienced the greatest change since 1994, the publication of the first edition of the book. The chapter has been largely redone, with emphasis on those methods that have emerged as the clear winners in the list of possible active remediation techniques. New examples are included and older examples have been updated and improved with new data and ideas relating to cleanup and

natural attenuation. Barrier systems, funnel and gate, and treatment walls are described in detail in the revised edition. Emerging methods for soil flushing with surfactants and co-solvents are highlighted for DNAPL extraction tested at Hill Air Force Base.

Chapter 14 reviews the important legal measures relating to ground water contamination that have arisen due to legislation, which has guided the EPA's mission to protect ground water quality in the United States. Federal legislation such as the Safe Drinking Water Act (SDWA, 1974), the Resource Conservation Recovery Act (RCRA, 1976), the Clean Water Act (1977), the Toxic Substances Control Act (TSCA, 1976), and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, 1980) provide a complex and comprehensive group of laws to protect the quality of ground water. Together, these laws have created an entire industry devoted to the evaluation and remediation of ground water.

1.4 EVOLUTION OF GROUND WATER INFORMATION

A number of classic textbooks in the ground water field have been written over the past thirty years. The field of ground water hydrology has expanded greatly since the first American textbook by Tolman (1937). Todd's (1959) text, *Ground Water Hydrology*, stood as a classic in the field for many years and was updated with a new edition in 1980. DeWiest's text in 1965 and Davis and DeWiest in 1966 further advanced the subject with their books on geohydrology and hydrogeology. Bear's texts written in 1972 and 1979 were departures from earlier approaches and emphasized the hydraulics of ground water, providing a very theoretical development of flow and transport in both the saturated and unsaturated zone for engineers, hydrologists, and hydrogeologists. In 1979, Freeze and Cherry's *Ground Water* quickly replaced others as the standard in the ground water field for more than a decade. Their chapters on transport, chemical properties, and contamination are still of great use even today. The new book by Pankow and Cherry (1996) provides a modern and comprehensive coverage of DNAPLs and chlorinated solvents.

There has been an explosion of literature in the past two decades, and there are numerous new sources of information and data in the ground water hydrology area. The United States Geological Survey (USGS) has primary responsibility for the collection of ground water data and evaluation of these data in terms of impacts on water supply, water quality, water depletion, and potential contamination. Studies performed by engineering consultants for EPA and for industry during the remedial investigation or feasibility study of RCRA and Superfund sites also provide a useful description of applied methods in ground water. Other primary sources of information are state environmental and water resources agencies, the American Geophysical Union, and the National Ground Water Association. Journals such as *Water Resources Research*, *Ground Water*, *Journal of Hydrology*, the *ASCE Journal of Environmental Engineering*, and *Environmental Science and Technology* are major resources for exchange of information.

The current text is a departure from past efforts in that it is written from both a theoretical and an engineering viewpoint with hydrologic and transport theory applied to hazardous waste site characterization, transport modeling, and remediation. For the first time, chapters on numerical methods and discussions of model applications to actual field sites exist alongside discussions of advection, adsorption, dispersion, chemical reaction, and biodegradation. Chapters on monitoring, hydrogeologic site characterization, and remediation are included along with detailed case studies that illustrate the various techniques currently being applied.

1.5 GROUND WATER REMEDIATION

The discovery of hazardous wastes at Love Canal in Niagara, New York, and at numerous other sites across the United States brought to light a new era in hazardous waste issues and problems. During the hazardous waste decade of the 1980s, hydrologists, hydrogeologists, civil and environmental engineers, and other scientists were involved in characterizing, evaluating, and remediating hazardous waste sites with respect to ground water contamination. The field of ground water has seen a virtual explosion in the number of remedial investigation studies related to the thousands of abandoned and active hazardous waste disposal sites and leaking tanks across the United States. One of the main objectives of this text is to provide engineers and scientists with a modern treatment of remediation methods currently being practiced, but with an eye towards the future.

Emerging new technologies are rapidly coming into place as we learn more about some of the failures of the past. Earlier pump and treat systems, which did not consider the presence of NAPLs in source zones, have not cleaned aquifers to the required levels. Many of the original systems worked adequately for a period of time, but after they were turned off, many sites had contaminant levels return to even higher values than before remediation. There have been success stories as well, with the discovery that many fuel (BTEX) plumes are limited in their extent due to natural attenuation processes. It is now widely recognized that EPA has given up the objective of trying to remediate shallow aquifers to drinking water standards. The actual use of these aquifers is now being considered in the overall evaluation of remedial options.

Chapters 11, 12, and 13 in the revised text address some of the above issues in detail, but the reader is cautioned that ground water remediation is a rapidly changing and dynamic industry. For example, the use of treatment walls and funnel and gate systems and soil flushing technologies were barely in existence in 1993, and have emerged as useful new approaches today. Natural attenuation is more accepted than ever before for certain types of plumes. Preferred remedial methods have changed dramatically just in the past five years, and the general literature should be consulted for the latest results on emerging new methods.

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