CONTAMINANT HYDROGEOLOGY

Second Edition

Contaminated groundwater has life-threatening repercussions for human, plant, and animal life. The monetary costs of maintaining clean water can be great, but not as great as those incurred from health risks that prevail if we ignore groundwater contamination. In many countries, the government obligates public water suppliers to furnish water that meets specific drinking-water standards; if it does not meet the standards when withdrawn from the source, it must be treated.

Written for courses in mass transport and contaminant hydrogeology, this authoritative text is aimed at students who have completed basic courses in hydrogeology, chemistry, calculus, and physics. It balances theory with the practical application of technology for the study and effective remediation of contaminants in soils and groundwater. Additionally, in a field that has seen an increase in career opportunities, the text is a valuable resource for professionals working in either the private or public sector. Outstanding features include solved example problems and case studies.

Also available from Waveland Press . . .

Groundwater Hydraulics and Pollutant Transport Randall J. Charbeneau *ISBN 978-1-57766-479-6*

Physical Hydrology, Third Edition

S. Lawrence Dingman ISBN 978-1-4786-1118-9

Waveland Press, Inc.

www.waveland.com



Contents

Preface

Cha		0
Cna	prer	One

Introduction

1.1	Ground Water as a Resource 1
1.2	Types of Ground-Water Contaminants 2
1.3	Drinking-Water Standards 11
1.4	Risk and Drinking Water 13
1.5	Sources of Ground-Water Contamination 18
	1.5.1 Category 1: Sources Designed to Discharge Substances 19
	1.5.2 Category II: Sources Designed to Store, Treat and/or Dispose of Substances 21
	1.5.3 Category III: Sources Designed to Retain Substances During Transport 27
	1.5.4 Category IV: Sources Discharging Substances as a Consequence of Other Planned Activities 27
	1.5.5 Category V: Sources Providing a Conduit for Contaminated Water to Enter Aquifers 30
	1.5.6 Category VI: Naturally Occurring Sources Whose Discharge is Created and/or Exacerbated by Human Activity 30
1.6	Relative Ranking of Ground-Water-Contamination Sources 31
1.7	Ground-Water Contamination as a Long-Term Problem 33
1.8	Review of Mathematics and the Flow Equation 34
	1.8.1 Derivatives 34
	1.8.2 Darcy's Law 37
	1.8.3 Scalar, Vector, and Tensor Properties of Hydraulic Head and Hydraulic Conductivity 37
	1.8.4 Derivation of the Flow Equation in a Deforming Medium 39
	1.8.5 Mathematical Notation 42
	References 43
	Problems 44

Chapter Two

Mass Transport in Saturated Media

2.1	Introduction 45	
2.2	Transport by Concentration Gradients 45	
2.3	Transport by Advection 50	
2.4	Mechanical Dispersion 52	
2.5	Hydrodynamic Dispersion 53	
2.6	Derivation of the Advection-Dispersion Equation for Solute Transport	55
2.7	Diffusion versus Dispersion 57	
2.8	Analytical Solutions of the Advection-Dispersion Equation 58	

xi

1

iv	Contents	
	2.8.2 Boundary and Initial Conditions 59	
		60
	2.8.4 One-Dimensional Continuous Injection into a Flow Field (Second-Type Bour	ndary) 61
	2.8.5 Third-Type Boundary Condition 65	
	2.8.6 One-Dimensional Slug Injection into a Flow Field 65	
	2.8.7 Continuous Injection into a Uniform Two-Dimensional Flow Field 66	
~ ~	2.8.8 Slug Injection into a Uniform Two-Dimensional Flow Field 70	
2.9	Effects of Transverse Dispersion 74	
2.10	Tests to Determine Dispersivity 75	
	2.10.1 Laboratory Tests 75	
	2.10.2 Field Tests for Dispersivity 78	
	2.10.3 Single-Well Tracer Test 79	
2.11	Scale Effect of Dispersion 80	
2.12	Stochastic Models of Solute Transport 86	
	2.12.1 Introduction 86	
	2.12.2 Stochastic Descriptions of Heterogeneity 87	
	2.12.3 Stochastic Approach to Solute Transport 89	
2.13	Fractal Geometry Approach to Field-scale Dispersion 92	
	2.13.1 Introduction 92	
	2.13.2 Fractal Mathematics 94	
	2.13.3 Fractal Geometry and Dispersion 95	
	2.13.4 Fractal Scaling of Hydraulic Conductivity 97	
2.14	Regression Analysis of Relationship between Apparent Longitudinal	
	Dispersivity and Field Scale 99	
2.15	Deterministic Models of Solute Transport 100	
	Case study: Borden Landfill Plume	
2.16	Transport in Fractured Media 107	
2.17	Summary 112	
	Chapter Notation 114	
	References 115	
	Problems 118	

35

120

Chapter Three

Transformation, Retardation, and Attenuation of Solutes

3.1	Introduction 120
3.2	Classification of Chemical Reactions 121
3.3	Sorption Processes 121
3.4	Equilibrium Surface Reactions 122
	3.4.1 Linear Sorption Isotherm 122
	3.4.2 Freundlich Sorption Isotherm 125
	3.4.3 Langmuir Sorption Isotherm 127
	3.4.4 Effect of Equilibrium Retardation on Solute Transport 129
3.5	Nonequilibrium (Kinetic) Sorption Models 132
3.6	Sorption of Hydrophobic (Organic) Compounds 135
	3.6.1 Introduction 135

~						
С.	0	n	te	n	ts	
~	~	•••		•••		

	 3.6.2 Partitioning onto Soil or Aquifer Organic Carbon 135 3.6.3 Estimating Koc from Kow Data 137 3.6.4 Estimating Koc from Solubility Data 137 3.6.5 Estimating Koc from Molecular Structure 142 3.6.6 Multiple Solute Effects 145 Case Study: Dissolution of creosote in water
3.7	Homogeneous Reactions 147
	3.7.1 Introduction 147
	3.7.2 Chemical Equilibrium 147
	3.7.3 Chemical Kinetics 148
	3.7.4 Tenads in Chemical Reactions 149
3.8	Radioactive Decay 151
3.9	Biodegradation 152
3.10	Colloidal Transport 156
	Case Study: Large-scale Field Experiment on the Transport of Reactive and
	Nonreactive Solutes in a Scale Aquifer under Natural Ground-Water
	Gradients—Borden, Ontario
3.11	Summary 164
	Chapter Notation 165
	References 166
	Problems 168

Chapter Four

Flow and Mass Transport in the Vadose Zone

4.1	Introduction 170
4.2	Soil as a Porous Medium 170
4.3	Soil Colloids 171
4.4	The Electrostatic Double Layer 172
4.5	Salinity Effects on Hydraulic Conductivity of Soils 173
4.6	Flow of Water in the Unsaturated Zone 174
	4.6.1 Soil-Water Potential 174
	4.6.2 Soil-Water Characteristic Curves 176
	4.6.3 Hysteresis 181
	4.6.4 Construction of a Soil-Water-Retention Curve 183
	4.6.5 Measurement of Soil-Water Potential 183
	4.6.6 Unsaturated Hydraulic Conductivity 186
	4.6.7 Buckingham Flux Low 189
	4.6.8 Richards Equation 190
	4.6.9 Vapor Phase Transport 190
4.7	Mass Transport in the Unsaturated Zone 191
4.8	Equilibrium Models of Mass Transport 193
4.9	Nonequilibrium Models of Mass Transport 195
4.10	Anion Exclusion 197
4.11	Preferential Flowpaths in the Vadose Zone 200

	^
VI	Contents

4.12	Summary	204	
	Chapter No	tation	205
	References	206	
	Problems	207	

Chapter Five

Multiphase Flow

5.1	Introduction 208
5.2	Basic Concepts 209
	5.2.1 Saturation Ratio 209
	5.2.2 Interfacial Tension and Wettability 209
	5.2.3 Capillary Pressure 210
	5.2.4 Relative Permeability 212
	5.2.5 Darcy's Law For Two-Phase Flow 217
	5.2.6 Fluid Potential and Head 217
5.3	Migration of Light Nonaqueous Phase Liquids (LNAPLs) 221
5.4	Volitilization of NAPLs 225
5.5	Measurement of the Thickness of a Floating Product 231
5.6	Effect of the Rise and Fall of the Water Table on the Distribution of LNAPLs 239
	Case Study: Spill of Jet Fuel — Effect of Water Table Decline on Product Recovery
5.7	Migration of Dense Nonaqueous Phase Liquids (DNAPLs) 242
	5.7.1 Relative Mobility 242
	5.7.2 Vadose Zone Migration 245
	5.7.3 Vertical Movement in the Saturated Zone 245
	5.7.4 Horizontal Movement in the Saturated Zone 247
	Case Study: Movement of Tetrachloroethene From a Controlled Release below
	the Water Table
	5.7.5 DNAPL Flow in Fracture Systems 253
	5.7.6 Dissolution of DNAPL 256
5.8	Monitoring for LNAPLs and DNAPLs 257
5.9	Summary 260
	Chapter Notation 260
	References 261
	Problems 263

Chapter Six

Inorganic Chemicals in Ground Water

6.1	Introduction 264	
6.2	Units of Measurement and Concentration	264

6.3 Chemical Equilibrium and the Law of Mass Action 265

264

Contents

6.4 Oxidation-Reduction Reactions 268 6.5 Relationship between pH and Eh 271 6.5.1 pH 271 6.5.2 Relationship of Eh and pH 273 6.5.3 Eh-pH Diagrams 274 6.5.4 Calculating Eh-pH Stability Fields 276 6.6 Metal Complexes 285 6.6.1 Hydration of Cations 285 6.6.2 Complexation 286 6.6.3 Organic Complexing Agents 287 6.7 Chemistry of Nonmetallic Inorganic Contaminants 288 6.7.1 Fluoride 288 6.7.2 Chlorine and Bromine 290 6.7.3 Sulfur 290 6.7.4 Nitrogen 292 6.7.5 Arsenic 293 6.7.6 Selenium 293 6.7.7 Phosphorus 294 6.8 Chemistry of Metals 295 6.8.1 Beryllium 295 6.8.2 Strontium 295 6.8.3 Barium 295 6.8.4 Vanadium 295 6.8.5 Chromium 295 Case History: Hexavalent Chromium Contamination of Groundwater—Odessa, Texas 6.8.6 Cobalt 297 6.8.7 Nickel 297 6.8.8 Molybdenum 298 6.8.9 Copper 298 6.8.10 Silver 300 6.8.11 Zinc 300 6.8.12 Cadmium 300 6.8.13 Mercury 300 6.8.14 Lead 301 6.9 Radioactive Isotopes 302 6.9.1 Introduction 302 6.9.2 Adsorption of Cationic Radionuclides 303 6.9.3 Uranium 304 Case History: Uranium Contamination of Groundwater—Fernald, Ohio 6.9.4 Thorium 307 6.9.5 Radium 307 6.9.6 Radon 310 6.9.7 Tritium 311 6.10 **Geochemical Zonation** 311 6.11 Summary 314 Chapter Notation 315 References 315 Problems 317

Chapter Seven

Organic Compounds in Ground Water

7.1	Introduction 318	
7.2	Physical Properties of Organic Compounds 318	
7.3	Organic Structure and Nomenclature 320	
	7.3.1 Hydrocarbon Classes 320	
	7.3.2 Aromatic Hydrocarbons 324	
7.4	Petroleum and Coal Tar 325	
	7.4.1 Petroleum Distillates 325	
	7.4.2 Coal Tar 329	
	7.4.3 Ground-Water Contamination Associated with Petroleum Products and Coal Tar 3	29
7.5	Functional Groups 332	
	7.5.1 Organic Halides 332	
	7.5.2 Alcohols 332	
	7.5.3 Ethers 336	
	7.5.4 Aldehydes and Ketones 336	
	7.5.5 Carboxylic Acids 337	
	7.5.6 Esters 338	
	7.5.7 Phenols 338	
	7.5.8 Organic Compounds Containing Nitrogen 339	
	7.5.9 Organic Compounds Containing Sulfur and Phosphorus 341	
7.6	Degradation of Organic Compounds 342	
	7.6.1 Introduction 342	
	7.6.2 Degradation of Hydrocarbons 342	
	7.6.3 Degradation of Chlorinated Hydrocarbons 346	
	7.6.4 Degradation of Organic Pesticides 349	
7.7	Field Examples of Biological Degradation of Organic Molecules 352	
	7.7.1 Introduction 352	
	7.7.2 Chlorinated Ethanes and Ethenes 352	
7.0	7.7.3 Aromatic Compounds 354	
7.8	Analysis of Organic Compounds in Ground Water 355	
7.9	Fingerprinting Petroleum Distillates and Coal Tar 361	
7.10	Summary 369	
	References 369	
	Problems 371	

Chapter Eight

Ground-Water and Soil Monitoring

8.1	Introdu	ction 374	
8.2	Monito	ring-Well Design 374	
	8.2.1	General Information 3	74
	8.2.2	Monitoring-Well Casing	375
	8.2.3	Monitoring-Well Screens	381

374

Contents

	8.2.4 Naturally-Developed and Filter-Packed Wells 382				
	8.2.5 Annular Seal 383				
	8.2.6 Protective Casing 384				
	8.2.7 Screen Length and Setting 385				
	8.2.8 Summary of Monitoring-Well Design 388				
8.3	Installation of Monitoring Wells 389				
	8.3.1 Decontamination Procedures 389				
	8.3.2 Methods of Drilling 390				
	8.3.3 Drilling in Contaminated Soil 395				
8.4	Sample Collection 396				
8.5	Installation of Monitoring Wells 399				
8.6	Monitoring-Well Development 404				
8.7	Record Keeping During Monitoring-Well Construction 407				
8.8	Monitoring Well and Borehole Abandonment 409				
8.9	Multiple-level Devices for Ground-Water Monitoring 409				
8.10	Methods of Collecting a Ground-Water Sample Without Drilling a Well 412				
8.11	Well Sampling 415				
	8.11.1 Introduction 415				
	8.11.2 Well Purging 415				
	8.11.2 Well Purging 415 8.11.3 Well-Sampling Devices 416				
8.12	8.11.3 Well-Sampling Devices 416				
8.12 8.13	8.11.3 Well-Sampling Devices 416				
	 8.11.3 Well-Sampling Devices 416 Low Flow Purging of Monitoring Wells 420 Soil-Gas Monitoring 421 8.13.1 Introduction 421 				
	8.11.3 Well-Sampling Devices 416 Low Flow Purging of Monitoring Wells 420 Soil-Gas Monitoring 421				
	 8.11.3 Well-Sampling Devices 416 Low Flow Purging of Monitoring Wells 420 Soil-Gas Monitoring 421 8.13.1 Introduction 421 				
8.13	 8.11.3 Well-Sampling Devices 416 Low Flow Purging of Monitoring Wells 420 Soil-Gas Monitoring 421 8.13.1 Introduction 421 8.13.2 Methods of Soil-Gas Monitoring 422 				
8.13	8.11.3Well-Sampling Devices416Low Flow Purging of Monitoring Wells420Soil-Gas Monitoring4218.13.1Introduction4218.13.2Methods of Soil-Gas Monitoring422Soil-Water Sampling4238.14.1Introduction4238.14.2Suction Lysimeters423				
8.13 8.14	8.11.3Well-Sampling Devices416Low Flow Purging of Monitoring Wells420Soil-Gas Monitoring4218.13.1Introduction4218.13.2Methods of Soil-Gas Monitoring422Soil-Water Sampling4238.14.1Introduction4238.14.2Suction Lysimeters4238.14.3Installation of Suction Lysimeters424				
8.13	8.11.3Well-Sampling Devices416Low Flow Purging of Monitoring Wells420Soil-Gas Monitoring4218.13.1Introduction4218.13.2Methods of Soil-Gas Monitoring422Soil-Water Sampling4238.14.1Introduction4238.14.2Suction Lysimeters423				

Chapter Nine

Site Remediation

9.1	Introdu	ction 429	
9.2	Source	Control Measures 430	
	9.2.1	Solid Waste 430	
	9.2.2	Removal and Disposal 430	
	9.2.3	Containment 431	
	9.2.4	Hydrodynamic Isolation 436	
9.3	Pump-a	nd-Treat Systems 438	
	9.3.1	Overview 438	
	9.3.2	Capture Zones 441	
	9.3.3	Computation of Capture Zones 442	
	9.3.4	Optimizing Withdrawal-Injection Systems	451
	9.3.5	Permanent Plume Stabilization 452	

x	Contents	
9.4	Treatment of Extracted Ground Water 453 9.4.1 Overview 453	
	9.4.2 Treatment of Inorganic Contaminants 453	
	9.4.3 Treatment of Dissolved Organic Contaminants 454	
9.5	Recovery of Nonaqueous Phase Liquids 455	
9.6	Removal of Leaking Underground Storage Tanks 459	
9.7	Soil Vapor Extraction 462	
9.8	Air Sparging and Bioslurping 466	
9.9	Bioremediation 467	
	9.9.1 Introduction 467	
	9.9.2 Intrinsic Biodegradation of Hydrocarbons 468	
	9.9.3 Enhanced Bioremediation of Hydrocarbons 469	
	9.9.4 Bioremediation of chlorinated Organic Compounds 471	
9.10	Combination Methods 473	
	Case Study: Effectiveness of Pump and Treat Remediation in a Ground Water Bas Case Study: Recovery of DNAPL Pooled Below the Water Table	in e
	Case Study: Remediation of Soil and Ground Water at the Site of an Automotive	
	Manufacturer's Plant	
9.11	Summary 482	
	Chapter Notation 484	
	References 484	
A 1	- A Department of the second second	
Append		
Error Fun	nction Values	487
	ai Water Sampling	
Append	ix B	
Bessel Fu	unctions	488
	the second se	
Append	ix C	
W(t _D ,B)		401
vv (ID,D)	values	491
Annond	ix D	
Append		States Alle
Exponen	itial Integral	493
100 I		
Append	ix E	
Unit Abb	previations	494
Appendi	ix F	
and the second second	ODFLOW Instructions (from Schlumberger Water Services)	495
VISUUI M	er ter man ochons (nom schonberger vider services)	475
Index		497
INCEA	LCA ampieve sont house	47/