

Contents

Part I Geochemistry Revisited: Selected Aspects

1	Characterization of the Subsurface Environment	3
1.1	Subsurface Solid Phase	4
1.1.1	Silica Minerals	4
1.1.2	Clay Minerals	6
1.1.3	Minerals Other than Silica and Clay	13
1.1.4	Organic Matter	13
1.1.5	Electrically Charged Surfaces	17
1.2	Subsurface Liquid Phase	18
1.2.1	Near Solid Phase Water	19
1.2.2	Subsurface Aqueous Solutions	21
1.3	Subsurface Gaseous Phase	22
1.4	Aquifers	23
1.4.1	Aquifer Structure	23
1.4.2	Groundwater Composition	25
	References	26
2	Selected Geochemical Processes	29
2.1	Thermodynamics and Equilibrium	29
2.1.1	Enthalpy, Entropy, and the Laws of Thermodynamics	29
2.1.2	Equilibrium	31
2.1.3	Solubility, Chemical Potential, and Ion Activities	32
2.1.4	Kinetic Considerations and Reaction Rate Laws	34
2.2	Weathering	39
2.2.1	Dissolution and Precipitation	39
2.2.2	Redox Processes	42
2.3	Adsorption	45
2.3.1	Adsorption of Charged Ionic Compounds	46
2.3.2	Adsorption of Nonionic Compounds	48
2.3.3	Kinetic Considerations	49
	References	50

Part II Properties of Potential Contaminants: Environmental and Health Hazards

3 Inorganic and Organometallic Compounds	53
3.1 Nitrogen	53
3.2 Phosphorus	56
3.3 Salts	57
3.3.1 Agricultural Impacts	58
3.3.2 Impacts on Water Usage	59
3.3.3 Impacts on Infrastructure	60
3.3.4 Impacts on Biodiversity and the Environment	60
3.4 Radionuclides	61
3.5 Heavy Metals and Metalloids	63
3.5.1 Arsenic	63
3.5.2 Cadmium	65
3.5.3 Chromium	66
3.5.4 Lead	67
3.5.5 Nickel	68
3.6 Nanomaterials	70
References	72
4 Organic Compounds	79
4.1 Pesticides	79
4.1.1 Organochlorine Insecticides	81
4.1.2 Organophosphates	83
4.1.3 N-methyl Carbamate	83
4.1.4 Triazines	84
4.1.5 Paraquat and Diquat	84
4.2 Synthetic Halogenated Organic Substances	86
4.2.1 Chlorinated Hydrocarbons	86
4.2.2 Brominated Flame Retardants	89
4.3 Petroleum Hydrocarbons and Fuel Additives	91
4.4 Pharmaceuticals and Personal Care Products	94
4.4.1 Analgesics and Anti-inflammatory Drugs	96
4.4.2 Hormones	96
4.4.3 Antibacterial Drugs	97
4.4.4 Antiepileptic Drugs	98
4.4.5 Beta-Blockers	98
References	98

Part III Contaminant Partitioning in the Subsurface

5 Sorption, Retention, and Release of Contaminants	107
5.1 Surface Properties of Adsorbents.	107
5.2 Quantifying Adsorption	109
5.2.1 Adsorption–Desorption Coefficients	109
5.2.2 Adsorption Isotherms.	109
5.3 Kinetics of Adsorption	116
5.4 Adsorption of Ionic Contaminants	118
5.5 Adsorption of Nonionic Contaminants	123
5.6 Other Factors Affecting Adsorption	126
5.7 Nonadsorptive Retention of Contaminants	129
5.7.1 Contaminant Precipitation	129
5.7.2 Liquid Trapping	131
5.7.3 Particle Deposition and Trapping	132
5.8 Reversible and Irreversible Retention.	135
5.8.1 Genuine Hysteresis	135
5.8.2 Apparent Hysteresis	137
5.8.3 Bound Residues	138
References	141
6 Contaminant Partitioning in the Aqueous Phase	147
6.1 Solubility Equilibrium	148
6.2 Aqueous Solubility of Organic Contaminants	150
6.3 Ligand Effects.	151
6.4 Cosolvents and Surfactant Effects	153
6.5 Salting-Out Effect	156
6.6 Apparent Solubility	159
References	161
7 Partitioning of Volatile Compounds	163
7.1 Gas–Liquid Relationships	164
7.2 Volatilization from Subsurface Aqueous Solutions.	165
7.3 Vapor Pressure–Volatilization Relationship.	166
7.4 Volatilization of Multicomponent Contaminants	169
References	170
8 Selected Research Findings: Contaminant Partitioning	171
8.1 Partitioning Among Phases	171
8.2 Contaminant Volatilization	173
8.2.1 Inorganic Contaminants	175
8.2.2 Organic Contaminants	177
8.2.3 Mixtures of Organic Contaminants	180

8.3	Solubility and Dissolution	184
8.3.1	Acidity and Alkalinity Effects	185
8.3.2	Redox Processes	187
8.3.3	Dissolution from Mixtures of Organic Contaminants	189
8.3.4	Apparent Solubility	189
8.4	Contaminant Retention in the Subsurface	198
8.4.1	Contaminant Adsorption	198
8.4.2	Nonadsorptive Retention	220
8.5	Contaminant Release	223
8.6	Bound Residues	230
8.7	Contaminants in Urban Geosystems	233
	References	238

Part IV Contaminant Transport from Land Surface to Groundwater

9	Water Flow in the Subsurface Environment	247
9.1	Water Flow in Soils and the Vadose Zone	247
9.2	Flow Through the Capillary Fringe	250
	References	252
10	Transport of Passive Contaminants	255
10.1	Advection, Dispersion, and Molecular Diffusion	256
10.2	Preferential Transport	259
10.3	Non-Fickian Transport	261
	References	265
11	Transport of Reactive Contaminants	267
11.1	Contaminant Sorption	267
11.2	Colloids and Sorption on Colloids	269
11.3	Dissolving and Precipitating Contaminants	270
11.4	Transport of Immiscible Liquids	273
11.5	Transport of Contaminants by Runoff	279
11.5.1	Overland Runoff	279
11.5.2	Urban Runoff	281
	References	281
12	Selected Research Findings: Contaminant Transport	285
12.1	Heavy Metals and Metalloids	285
12.1.1	Heavy Metals	286
12.1.2	Metalloids	296
12.2	Engineered Nanoparticles (ENPs)	302
12.2.1	Fate of ENPs in Aqueous Solutions	302

12.2.2	Transport of ENPs in Sand and Glass Bead Columns . . .	304
12.2.3	Modeling ENP Transport in Porous Media.	312
12.2.4	Fate of ENPs in Soil Column Experiments.	312
12.2.5	ENP Transport in the Field	316
12.3	Pesticides	320
12.4	Colloid-Mediated Transport of Organic Contaminants	333
12.4.1	Surface Runoff	334
12.4.2	Transport in the Subsurface	335
12.5	Transport of Nonaqueous-Phase Liquids.	337
12.5.1	Infiltration into the Subsurface	338
12.5.2	Transport of Soluble NAPL Fractions in Aquifers.	341
	References	343

Part V Transformations and Reactions of Contaminants in the Subsurface

13	Abiotic Contaminant Transformations in Subsurface Water	349
13.1	Abiotic Contaminant Transformations in Natural Subsurface Water	349
13.1.1	Factors Affecting Contaminant Transformations	349
13.1.2	Reactions in Natural Waters.	351
13.2	Selected Contaminant Transformations in Sediments and Groundwater.	362
13.2.1	pH and Hydrolysis Reactions	362
13.2.2	Redox State and Reactions.	363
	References	369
14	Abiotic Transformation at the Solid-Liquid Interface	373
14.1	Catalysis.	373
14.2	Surface-Induced Transformation of Organic Contaminants	374
14.3	Surface-Induced Interactions of Inorganic Contaminants	379
	References	379
15	Biologically Mediated Transformations.	381
15.1	Subsurface Microbial Populations	381
15.2	Processes Governing Contaminant Attenuation	381
15.3	Biotransformation of Organic Contaminants	383
15.4	Biotransformation of Inorganic Contaminants	389
	References	394
16	Selected Research Findings: Transformations and Reactions	397
16.1	Abiotic Alteration of Contaminants	397
16.1.1	Transformation in Subsurface Water	397

16.1.2	Surface-Induced Transformation on Clays	412
16.1.3	Photochemical Reactions	416
16.1.4	Ligand Effects	422
16.1.5	Multiple-Component Contaminant Transformation	425
16.2	Biomediated Transformation of Contaminants	437
16.2.1	Petroleum Products	437
16.2.2	Pesticides	442
	References	452

Part VI Contaminant Induced Irreversible Changes in the Soil-Subsurface Regime

17	Contaminant-Induced Irreversible Changes in Groundwater Chemistry	457
17.1	Groundwater Salinization	458
17.1.1	Salinization Under Downward Flow Conditions	458
17.1.2	Salinization Under Lateral Flow Conditions	461
17.2	Groundwater Acidification	465
17.3	Groundwater Contamination by Inorganic Trace Elements	469
17.3.1	Radionuclides	470
17.3.2	Heavy Metals	471
17.3.3	Metalloids	476
17.4	Groundwater Contamination by Trace Organic Compounds	480
	References	497
18	Contaminant Impacts on the Soil-Subsurface Solid Phase	501
18.1	Impact of Contaminants Originating from Agriculture	501
18.1.1	Fertilizers	502
18.1.2	Micronutrients	505
18.1.3	Soil-Subsurface Amendments	507
18.1.4	Pesticides	517
18.2	Impact of Sodic Water	528
18.2.1	Swelling	528
18.2.2	Dispersion and Flocculation	531
18.2.3	Water Transmission Properties	533
18.3	Impact of Municipal and Industrial Contaminants	537
18.3.1	Acid Rain Input	538
18.3.2	Impact of Effluents	542
18.3.3	Impact of Sludge and Compost	546
18.3.4	Petroleum Products	557
	References	562
	Index	571