

CONTENTS

PREFACE TO FIFTH EDITION	xii
PREFACE TO FOURTH EDITION	xiii
ACKNOWLEDGMENTS	xiv
1 INTRODUCTION TO SOIL CHEMISTRY	1
1.1 The soil chemistry discipline	1
1.2 Historical background	3
1.3 The soil environment	6
1.3.1 Soil chemical and biological interfaces	6
1.3.2 Soil solids	10
1.3.3 Soil interaction with the hydrosphere	11
1.3.4 Interaction of soil and the atmosphere	12
1.4 Chemical reactions in soils	15
1.4.1 Flow of chemical energy in soils	17
1.4.2 Soil chemical speciation	18
1.4.3 Chemical reaction types in soils	19
1.5 Soil biogeochemical cycling	22
1.6 Soil chemical influences on food production	22
1.7 Soils and environmental health	23
1.7.1 Soil chemistry and environmental toxicology	24
1.8 Units in soil chemistry	26
1.8.1 Converting units	26
1.9 Summary of important concepts in soil chemistry	26
Questions	29
Bibliography	29

2	PROPERTIES OF ELEMENTS AND MOLECULES	31
2.1	Introduction	31
2.2	Ionization and ionic charge	33
2.3	Ionic radius	33
2.4	Molecular bonds	36
2.5	Nature of water and hydration of ions	37
2.6	Ligands and metal bonds	40
2.7	Summary of important concepts of elemental and molecular properties	42
	Questions	42
	Bibliography	42
3	CHARACTERISTICS OF CHEMICALS IN SOILS	43
3.1	Introduction	43
3.2	Occurrence of elements in soils	43
3.3	Essential elements	47
3.3.1	Plant deficiency	49
3.4	Inorganic contaminants in the environment	49
3.4.1	Assessing contamination status of soils	51
3.5	Anthropogenic organic chemicals in the soil environment	53
3.5.1	Pesticides in the environment	54
3.5.2	Chemicals of emerging concern in the environment	54
3.5.3	Chemical factors affecting organic chemical reactions in soil	57
3.6	Properties of the elements in soils	58
3.6.1	Alkali and alkaline earth cations	59
3.6.2	Major soluble anions in soils	61
3.6.3	Poorly soluble anions	63
3.6.4	Poorly soluble metal cations	67
3.6.5	Common toxic elements in soils	69
3.6.6	Major biogeochemical elements: carbon, nitrogen, and sulfur	71
3.7	Summary of important concepts for chemicals in the soil environment	75
	Questions	75
	Bibliography	76
4	SOIL WATER CHEMISTRY	77
4.1	Introduction	77
4.2	Thermodynamic approach to aqueous soil chemistry	78
4.2.1	Example using thermodynamics to calculate gypsum solubility in soils	79
4.2.2	Types of equilibrium constants	82
4.3	Calculation of ion activity	83
4.3.1	Use of ionic strength to calculate activity coefficients	84
4.3.2	Example calculation of activity coefficient	86
4.4	Acids and bases	86
4.4.1	Bases	87
4.4.2	Weak acids	87
4.5	Gas dissolution	89
4.5.1	Predicting dissolution of ammonia in water	90
4.5.2	Predicting pH of water due to CO ₂ dissolution	91
4.6	Precipitation and dissolution reactions	91
4.6.1	Solubility of minerals	92
4.6.2	Iron and aluminum dissolution from oxides and hydroxides	93

4.6.3	Calcite and carbon dioxide in soils	95
4.6.4	Solubility of minerals in soils	97
4.6.5	Solubility of contaminant metals from minerals	100
4.7	Cation hydrolysis	102
4.8	Complexation	105
4.8.1	Predicting equilibrium for complexation reactions	106
4.8.2	Chelate reactions with metals	106
4.8.3	Trends in cation ligand affinity	109
4.8.4	Predicting complexation using the hard and soft acid-base (HASB) concept	110
4.9	Using software to predict soil solution equilibrium	110
4.10	Kinetics of chemical reaction in soil solution	111
4.11	Summary of important concepts for soil solution chemistry	116
	Questions	116
	Bibliography	117
5	REDOX REACTIONS IN SOILS	119
5.1	Introduction	119
5.2	Redox reactions in nature	121
5.2.1	Photosynthesis redox reactions	121
5.2.2	Electron donors in nature	122
5.2.3	Electron acceptors in nature	122
5.3	Basic approaches for characterizing soil redox processes	126
5.3.1	Using chemical species in soils to monitor redox status of soils	127
5.3.2	Predicting redox processes in soil using chemical reactions	128
5.3.3	Quantifying redox potential with a redox electrode	130
5.3.4	Relating Eh to p_e	132
5.4	The role of protons in redox reactions	133
5.5	Redox potential limits in natural systems	133
5.6	p_e -pH diagrams	135
5.7	Prediction of oxidation and reduction reactions in soils	137
5.7.1	Reduction reactions on the redox ladder	139
5.7.2	Oxidation reactions on the redox ladder	140
5.8	Redox measurement in soils	141
5.8.1	Other methods to assess redox status of soils	141
5.9	Soil redoximorphic features and iron reduction in wetlands	142
5.10	Nitrogen redox reactions in soils	144
5.10.1	Nitrogen assimilation	145
5.10.2	Ammonification	145
5.10.3	Nitrification	145
5.10.4	Denitrification	146
5.10.5	Biological nitrogen fixation	146
5.10.6	Anammox and dissimilatory nitrogen reduction to ammonium	147
5.10.7	Limitations to theoretical nitrogen redox reaction predictions	147
5.11	Summary of important concepts in soil redox reactions	147
	Questions	148
	Bibliography	148
6	MINERALOGY AND WEATHERING PROCESSES IN SOILS	150
6.1	Introduction	150
6.2	Common soil minerals	152

6.3	Crystal chemistry of minerals	153
6.3.1	Bonds in minerals	154
6.3.2	Rules for assembling minerals	154
6.3.3	Isomorphic substitution	159
6.3.4	Mineral formulas	160
6.4	Common primary mineral silicates in soils	161
6.4.1	Nesosilicates	162
6.4.2	Inosilicates	162
6.4.3	Phyllosilicates	162
6.4.4	Tectosilicates	163
6.4.5	Cations in primary silicates	163
6.5	Minerals and elements in rocks	164
6.5.1	Elemental composition of rocks	164
6.6	Stability of silicates to weathering	165
6.7	Chemistry of soil weathering and mineral formation	167
6.7.1	Initial breakdown of primary minerals	167
6.7.2	Formation of soil minerals	167
6.7.3	Weathering effects on element composition in soils	169
6.8	Formation of secondary minerals in soils	170
6.8.1	Prediction of secondary mineral formation	172
6.9	Soil carbonates	174
6.10	Evaporites	176
6.11	Soil phosphate minerals	177
6.12	Sulfur minerals	177
6.13	Time sequence of mineral formation in soils	178
6.14	Measurement of soil mineralogy	180
6.14.1	Principles of X-Ray Diffraction (XRD) for clay mineralogy	180
6.14.2	Example calculation of d-spacing from a diffractogram	183
6.14.3	Selective extraction of iron oxides and amorphous aluminosilicates from soils	184
6.15	Important concepts in soil mineralogy	184
	Questions	184
	Bibliography	185
7	CHEMISTRY OF SOIL CLAYS	186
7.1	Introduction	186
7.2	Structural characteristics of phyllosilicates	187
7.2.1	1:1 phyllosilicates	189
7.2.2	2:1 phyllosilicates	191
7.3	Relation of phyllosilicate structure to physical and chemical properties	193
7.3.1	Interlayer bond	193
7.3.2	Surface area	193
7.3.3	c-spacing	194
7.3.4	Cation adsorption and layer charge	194
7.3.5	Shrink and swell behavior and interlayer collapse	195
7.4	Detailed properties of phyllosilicates	199
7.4.1	Kaolins	199
7.4.2	Smectite	200
7.4.3	Vermiculite	200
7.4.4	Mica and Illite	201
7.4.5	Chlorite	204
7.5	Allophane and imogolite	204

7.6	Zeolite	205
7.7	Oxide minerals	205
7.7.1	Aluminum oxides	206
7.7.2	Iron oxides	207
7.7.3	Titanium oxides	208
7.7.4	Manganese oxides	210
7.8	Summary of soil clays	210
	Questions	211
	Bibliography	212
8	PRODUCTION AND CHEMISTRY OF SOIL ORGANIC MATTER	214
8.1	Introduction	214
8.1.1	Components in SOM	215
8.1.2	Studying SOM	216
8.2	Ecosystem carbon storage and fluxes	217
8.3	Soil organic matter formation factors	219
8.3.1	Residence time of SOM	219
8.3.2	Climate effects on SOM	220
8.3.3	SOM in wetlands	220
8.3.4	Soil mineral effects on SOM	221
8.4	Organic chemistry of SOM	221
8.5	Plant and microbial compounds input into soil	223
8.6	SOM decay processes	225
8.7	SOM composition and structure	229
8.8	NaOH extraction of SOM	231
8.9	Function of organic matter in soil	233
8.9.1	Organic nitrogen, sulfur, and phosphorus	235
8.9.2	SOM influences on chemical processes	236
8.9.3	SOM influences on physical properties	237
8.9.4	Organic chemical partitioning	237
8.10	Summary of SOM	237
	Questions	238
	Bibliography	238
9	SURFACE PROPERTIES OF SOIL COLLOIDS	240
9.1	Introduction	240
9.2	Permanent charge	240
9.3	pH-dependent charge	241
9.3.1	Balancing surface charge	243
9.3.2	Variable charge on phyllosilicates	243
9.3.3	pH-dependent charge on iron and aluminum oxides	245
9.4	Point of zero charge of variable charged surfaces	247
9.5	pH-dependent charge of SOM	250
9.6	Hydrophobic regions of soil organic matter	252
9.7	Summary of important concepts in soil surface charge	252
	Questions	253
	Bibliography	253
10	ADSORPTION PROCESSES IN SOILS	255
10.1	Introduction	255
10.1.1	Outer-sphere adsorption	256

10.1.2	Inner-sphere adsorption	257
10.1.3	Adsorption of non-charged chemicals to soil particles	258
10.1.4	Desorption	258
10.2	Physical model of charged soil particle surfaces	260
10.2.1	Force of ion attraction to charged surfaces	260
10.2.2	The diffuse double layer	261
10.2.3	Surface potential on variable charged surfaces	263
10.2.4	Stern modification of the Gouy-Chapman DDL theory	264
10.2.5	Interacting diffuse double layers from adjacent particles	264
10.3	Cation exchange on soils	266
10.3.1	Cation exchange selectivity	267
10.3.2	Cation exchange equations	270
10.3.3	Measuring CEC	273
10.4	Inner-sphere adsorbed cations	273
10.4.1	Inner-sphere adsorption of cations on minerals	276
10.4.2	Metal adsorption selectivity on minerals	277
10.4.3	Inner-sphere metal adsorption on soil organic matter	278
10.4.4	Inner-sphere metal adsorption in soils	278
10.5	Anion adsorption	281
10.5.1	Outer-sphere adsorbed anions	282
10.5.2	Inner-sphere adsorption of anions	283
10.6	Adsorption of anthropogenic organic chemicals in soils	286
10.6.1	Mechanisms of organic chemical retention	286
10.6.2	Adsorption of charged pesticides	287
10.6.3	Retention of nonionic organic chemicals	289
10.6.4	Predicting organic chemical retention in soil	290
10.6.5	Aging effects on organic chemical adsorption	291
10.7	Summary of important concepts for adsorption and desorption reactions in soils	292
	Questions	293
	Bibliography	294
11	MEASURING AND PREDICTING SORPTION PROCESSES IN SOILS	296
11.1	Introduction	296
11.2	Adsorption experiments	296
11.3	Predicting adsorption using empirical models	297
11.3.1	Linear adsorption isotherms	298
11.3.2	Nonlinear adsorption isotherms	298
11.4	Predicting adsorption using mechanistic models	300
11.5	Rates of adsorption	304
11.5.1	Modeling adsorption kinetics	305
11.6	Reactive transport	306
11.7	Surface precipitation	309
11.8	Analytical methods for determining adsorption mechanisms	310
11.9	Summary of important concepts for modeling surface reactions in soils	311
	Questions	312
	Bibliography	312
12	SOIL ACIDITY	314
12.1	Introduction	314
12.1.1	Measurement of soil acidity	314
12.2	History of soil acidity	317

12.3	The role of aluminum in soil pH	318
12.3.1	Creation of exchangeable aluminum	318
12.4	Base cations in soil solutions	319
12.4.1	Aqueous chemistry of base cations	319
12.4.2	Exchangeable base cations	320
12.4.3	Total exchangeable acidity	321
12.5	Soil acidification processes	321
12.5.1	Organic matter influences on pH	322
12.5.2	Acidity from the nitrogen cycle	323
12.5.3	Phosphate and sulfate fertilizer additions to soil acidity	325
12.5.4	Plant root influences on soil acidity	325
12.5.5	Protonation and deprotonation of mineral surfaces	325
12.5.6	Pollution sources of soil acidity	325
12.5.7	Redox reaction influence on soil acidity	326
12.6	Aluminum and manganese toxicity	326
12.7	Plant nutrients in acid soils	327
12.8	Managing acidic soils	327
12.8.1	Predicting lime requirement	327
12.8.2	Optimal management of soil pH	328
12.9	Summary of important concepts in soil acidity	329
	Questions	329
	Bibliography	330
13	SALT-AFFECTED SOILS	331
13.1	Introduction	331
13.2	Distribution and origin of salt-affected soils	331
13.2.1	Mineral weathering sources of salts	332
13.2.2	Salinity from fossil salts	332
13.2.3	Atmospheric salt sources	332
13.2.4	Topographic influence on soil salt concentrations	332
13.2.5	Human sources of soil salinity	333
13.3	Characterization of salinity in soil and water	334
13.3.1	Total dissolved solids	334
13.3.2	Electrical conductivity	334
13.3.3	Sodium hazard	336
13.3.4	Exchangeable sodium percentage	337
13.3.5	Bicarbonate hazard	339
13.3.6	Other problematic solutes in irrigation water	340
13.4	Describing salt-affected soils	340
13.4.1	Saline soils	340
13.4.2	Saline-sodic soils	340
13.4.3	Sodic soils	341
13.5	Effects of salts on soils and plants	341
13.6	Salt balance and leaching requirement	343
13.7	Reclamation	344
13.8	Summary of important concepts in soil salinity	345
	Questions	345
	Bibliography	346
	INDEX	347