

# Contents

*Preface ix*

- 1 Introduction 1**
- 2 Humic substances – a brief review 4**
  - 2.1 Natural organic matter and humic substances 4
  - 2.2 Isolation and classification of humic substances 6
  - 2.3 Formation and decomposition of humic substances 10
  - 2.4 Chemical and physical properties of humic substances 13
  - 2.5 Environmental concentrations of humic substances 24
  - 2.6 Humic substances – accident or design? 30
- 3 Environmental solution and surface chemistry 32**
  - 3.1 Solutions and solutes 32
  - 3.2 Natural particulate matter 34
  - 3.3 Physico-chemical interactions in environmental aqueous systems 37
  - 3.4 Equilibrium and kinetics 44
  - 3.5 Chemical speciation 45
  - 3.6 Calculation of equilibrium concentrations 46
- 4 Proton dissociation from weak acids 52**
  - 4.1 Acids and bases 52
  - 4.2 Buffering 55
  - 4.3 Kinetics 55
  - 4.4 Diprotic acids 57
  - 4.5 Extension to higher polyprotic acids 59
  - 4.6 Electrostatic interactions among sites 61
  - 4.7 Proton dissociation from well-defined polymers 73
  - 4.8 Proton dissociation from humic substances 76

<b>5</b>	<b>Metal–ligand interactions</b>	<b>77</b>
5.1	Coordination	77
5.2	Chemical equilibria involving metal ions, protons and simple weak acid ligands	86
5.3	Multisite ligands	98
5.4	Electrostatic interactions	99
5.5	Results with well-defined macromolecules	99
<b>6</b>	<b>Methods for measuring cation binding by humic substances</b>	<b>103</b>
6.1	The humic sample	103
6.2	Determination of proton binding by potentiometry	104
6.3	Analytical determination of acid group contents	108
6.4	Direct measurement of equilibrium metal binding – principles	110
6.5	Separation methods to quantify equilibrium metal binding	113
6.6	Competition methods	119
6.7	Electrochemical techniques	121
6.8	Spectroscopic methods	123
6.9	Measurement of the kinetics of metal–humic interactions	126
<b>7</b>	<b>Quantitative results with isolated humic substances</b>	<b>128</b>
7.1	Proton dissociation	128
7.2	Equilibrium binding of metal ions	136
7.3	Kinetics of metal ion binding	151
<b>8</b>	<b>Cation binding sites in humic substances</b>	<b>157</b>
8.1	Proton-dissociating groups	157
8.2	Binding sites for metals – information from binding studies	159
8.3	Information from spectroscopy	162
8.4	Viscometry	169
8.5	Summary	169
<b>9</b>	<b>Parameterised models of cation–humic interactions</b>	<b>171</b>
9.1	Overview and philosophy	171
9.2	Models that describe the binding of a single cation	173
9.3	Simpler models that include competition	183
9.4	The site heterogeneity/polyelectrolyte models of Marinsky and colleagues	192
9.5	Modelling electrostatic effects in humic substances	194
9.6	Humic Ion-Binding Models V and VI	201
9.7	The NICA and NICCA models	206
9.8	Summary	209

- 10 Applications of comprehensive parameterised models** 210
- 10.1 Interactions with protons 210
  - 10.2 Binding of single metal cations interpreted with Model V 216
  - 10.3 Binding of single metal cations interpreted with Model VI 220
  - 10.4 Application of the NICCA model 229
  - 10.5 Metal binding as a function of ionic strength 235
  - 10.6 Non-specific binding 240
  - 10.7 Competition between metals 240
  - 10.8 Proton–metal exchange 246
  - 10.9 Comparison of the NICCA–Donnan model and Model VI 249
  - 10.10 Applications of the models to field situations 251
- 11 Predictive modelling** 253
- 11.1 Electrostatic interactions 253
  - 11.2 Binding sites 254
  - 11.3 Prospects for predictive modelling 260
- 12 Cation–humic binding and other physico-chemical processes** 262
- 12.1 The conformation of humic matter 262
  - 12.2 Aggregation of humic substances 266
  - 12.3 Adsorption of humic substances by mineral surfaces 270
  - 12.4 Binding of organic cations by humic substances 278
  - 12.5 Colloid stability 278
  - 12.6 Dissolution of minerals 282
  - 12.7 Formation of mineral precipitates 285
  - 12.8 Other processes 287
  - 12.9 Concluding remarks 287
- 13 Cation binding by humic substances in natural waters** 288
- 13.1 Chemical speciation calculations 288
  - 13.2 Interactions with major ions and protons 290
  - 13.3 Interactions of humic substances with major cations 301
  - 13.4 Competition 308
  - 13.5 Interactions of heavy metals with humic substances in natural waters 315
  - 13.6 Modelling heavy metal speciation in natural waters 320
  - 13.7 Interactions with metallic radionuclides 331
  - 13.8 Binding by dissolved humic matter compared to adsorption by suspended particulates 331

<b>14</b>	<b>Cation binding by humic substances in soils and sediments</b>	<b>334</b>
14.1	Components of the soil system	335
14.2	Sorption of major cations by organic-rich acid soils	339
14.3	Sorption of major cations by mineral soils	347
14.4	Sorption of trace cations by soil solids	352
14.5	Dissolved organic matter (DOM) in soil solution	359
14.6	Colloids in soil and aquifer porewaters	371
14.7	Cation–humic interactions in sediments	371
<b>15</b>	<b>Research needs</b>	<b>380</b>
15.1	Research needs for isolated humic materials	380
15.2	Research needs in field studies	385
15.3	Cation–humic interactions in catchments	387
	<i>References</i>	<i>391</i>
	<i>Index</i>	<i>422</i>