

# *Sediment Flux Modeling*

**Dominic M. Di Toro**

Wiley-Interscience

***A JOHN WILEY & SONS, INC. PUBLICATION***

New York / Chichester / Weinheim / Brisbane / Singapore / Toronto

FOR MARILYN

# Contents

<i>Preface</i>	<i>xv</i>
<i>Acknowledgments</i>	<i>xxi</i>
 <i>Part I Preliminaries</i>	
<i>1 Properties of Sediments</i>	<i>3</i>
1.1 <i>Physical Characteristics</i>	<i>3</i>
1.2 <i>Chemical Preliminaries</i>	<i>9</i>
1.3 <i>Chemical Characteristics</i>	<i>14</i>
1.4 <i>Biological Characteristics</i>	<i>20</i>
1.5 <i>Conclusion</i>	<i>24</i>
<i>2 Model Formulation</i>	<i>27</i>
2.1 <i>Framework</i>	<i>27</i>
2.2 <i>Mass Balance Equations</i>	<i>29</i>
2.3 <i>Sedimentation and Burial</i>	<i>33</i>
2.4 <i>Mixing Processes and Mass Transfer Coefficients</i>	<i>37</i>
2.5 <i>Two-Layer Mass Balance</i>	<i>42</i>
	 <i>vii</i>

viii CONTENTS

2.6	<i>Particulate Organic Nitrogen and Ammonia</i>	43
2.7	<i>Continuous Models</i>	48
	<i>Appendix 2A: Solution of Mass Balance Equations</i>	53
2A.1	<i>First-Order Equation</i>	53
2A.2	<i>Second-Order Equation</i>	54
	<i>Appendix 2B: MACSYMA Solutions</i>	55
<i>Part II Nutrients</i>		
3	<i>Ammonia</i>	63
3.1	<i>Introduction</i>	63
3.2	<i>Model Components</i>	63
3.3	<i>Mass Balance Equations</i>	65
3.4	<i>Data Analysis</i>	75
3.5	<i>Observations of Chesapeake Bay Nitrification</i>	81
3.6	<i>Nonsteady State Features</i>	82
3.7	<i>Conclusions</i>	84
	<i>Appendix 3A: Solution of Ammonia Mass Balance Equations</i>	84
	<i>Appendix 3B: Ammonia and Dissolved Oxygen Surface Mass Transfer Coefficients</i>	85
	<i>Appendix 3C: Regression Analysis</i>	90
4	<i>Nitrate</i>	93
4.1	<i>Introduction</i>	93
4.2	<i>Model Formulation and Solution</i>	93
4.3	<i>Nitrate Source from the Overlying Water</i>	98
4.4	<i>Nitrate Source from Nitrification</i>	102
4.5	<i>Model Applications</i>	102
4.6	<i>Flux Normalization and Parameter Estimation</i>	106
4.7	<i>Application to Chesapeake Bay</i>	110
4.8	<i>Estimate of the Denitrification Reaction Velocities</i>	111
4.9	<i>Observations of Chesapeake Bay Denitrification</i>	113
4.10	<i>Extent of Denitrification and the Nitrogen Balance</i>	115
4.11	<i>Conclusions</i>	116
	<i>Appendix 4A: MACSYMA</i>	117

5	<i>Steady State Model</i>	119
5.1	<i>Introduction</i>	119
5.2	<i>Modeling Framework</i>	121
5.3	<i>Mass Balance Equations</i>	121
5.4	<i>Solution For Anaerobic Layer Source</i>	123
5.5	<i>Solution For Aerobic Layer Source</i>	127
	<i>Appendix 5A: MACSYMA</i>	129
6	<i>Phosphorus</i>	131
6.1	<i>Introduction</i>	131
6.2	<i>Model Components</i>	132
6.3	<i>Solutions</i>	133
6.4	<i>Simplified Phosphate Flux Model</i>	138
6.5	<i>Steady State Numerical Model</i>	140
6.6	<i>Conclusions</i>	143
	<i>Appendix 6A: Positive and Negative Logarithmic Scale for Plotting</i>	143
7	<i>Silica</i>	149
7.1	<i>Introduction</i>	149
7.2	<i>Model Components</i>	149
7.3	<i>Solutions</i>	151
7.4	<i>Final Model</i>	154
7.5	<i>Conclusions</i>	158
 <i>Part III Oxygen</i>		
8	<i>Oxygen Equivalents</i>	161
8.1	<i>Introduction</i>	161
8.2	<i>Proposed Modeling Frameworks</i>	162
8.3	<i>Oxygen Equivalents</i>	167
8.4	<i>Sediment Oxygen Demand</i>	172
8.5	<i>Oxygen Equivalents and SOD</i>	175
8.6	<i>Conclusion</i>	182
9	<i>Sulfide</i>	183
9.1	<i>Introduction</i>	183

x CONTENTS

9.2	<i>Sulfide Production</i>	183
9.3	<i>Sulfide Oxidation</i>	185
9.4	<i>Solutions</i>	186
9.5	<i>Sediment Oxygen Demand</i>	189
9.6	<i>Data Analysis</i>	191
9.7	<i>Commentary</i>	194
10	<i>Methane</i>	195
10.1	<i>Introduction</i>	195
10.2	<i>Stoichiometry and Oxygen Equivalents</i>	195
10.3	<i>Dissolved Methane Mass Balance</i>	197
10.4	<i>Dissolved Oxygen Mass Balance</i>	201
10.5	<i>SOD Equation</i>	204
10.6	<i>Data Analysis</i>	210
10.7	<i>Relationship to Sulfide Oxidation</i>	216
	<i>Appendix 10A: Positive and Negative Logarithmic Scale for Plotting</i>	217
	<i>Appendix 10B: Solution of Dissolved Oxygen Mass Balance Equations</i>	219
11	<i>Sulfide and Methane</i>	221
11.1	<i>Introduction</i>	221
11.2	<i>Sulfate Consumption</i>	222
11.3	<i>Layers and Mass Transfer Resistances</i>	224
11.4	<i>Multilayer versus Two-layer Models</i>	226
11.5	<i>Depth of Sulfate Reduction</i>	227
11.6	<i>Sulfate and Methane Mass Balance Equations</i>	231
11.7	<i>Numerical Examples</i>	235
11.8	<i>Upper Potomac Estuary</i>	237
11.9	<i>Anacostia River</i>	242
11.10	<i>Conclusions</i>	242
	<i>Appendix 11A: MACSYMA Solution for the Three-Layer Equations</i>	243
	<i>Appendix 11B: MACSYMA Solution of the Sulfate Mass Balance Equations</i>	243
	<i>Appendix 11C: MACSYMA Solution of the Sulfide-Sulfate Mass Balance Equations</i>	243

*Part IV Time Variable Model Implementation*

<i>12 Diagenesis</i>	<i>251</i>
<i>12.1 Introduction</i>	<i>251</i>
<i>12.2 Mass Balance Equations</i>	<i>252</i>
<i>12.3 Diagenesis Stoichiometry</i>	<i>254</i>
<i>12.4 Diagenesis Kinetics</i>	<i>259</i>
<i>12.5 Depositional Flux</i>	<i>267</i>
<i>12.6 Sediment Composition</i>	<i>269</i>
<i>12.7 Sediment Algal Carbon</i>	<i>270</i>
<i>12.8 Conclusions</i>	<i>273</i>
<i>13 Mass Transport and Numerical Methods</i>	<i>275</i>
<i>13.1 Introduction</i>	<i>275</i>
<i>13.2 Transport Parameters</i>	<i>275</i>
<i>13.3 Sediment Solids</i>	<i>282</i>
<i>13.4 Effect of Varying Layer Thickness</i>	<i>284</i>
<i>13.5 Numerical Considerations</i>	<i>288</i>
<i>Appendix 13A: Fourier Series and the Boundary Conditions</i>	<i>293</i>

*Part V Model Calibration and Applications*

<i>14 Chesapeake Bay</i>	<i>299</i>
<i>14.1 Introduction</i>	<i>299</i>
<i>14.2 Ammonia</i>	<i>301</i>
<i>14.3 Nitrate</i>	<i>308</i>
<i>14.4 Sulfide</i>	<i>311</i>
<i>14.5 Oxygen</i>	<i>313</i>
<i>14.6 Phosphate</i>	<i>318</i>
<i>14.7 Silica</i>	<i>324</i>
<i>14.8 Station Composite Plots</i>	<i>328</i>
<i>14.9 Conclusions</i>	<i>332</i>
<i>15 MERL, Long Island Sound, and Lake Champlain</i>	<i>335</i>

**xii** CONTENTS

15.1	<i>Introduction</i>	335
15.2	<i>MERL</i>	335
15.3	<i>Long Island Sound</i>	349
15.4	<i>Lake Champlain</i>	355
15.5	<i>Summary of Parameter Values Used in All Applications</i>	361
16	<i>Steady State and Time Variable Behavior</i>	367
16.1	<i>Introduction</i>	367
16.2	<i>Steady State Model</i>	367
16.3	<i>Model Sensitivity</i>	371
16.4	<i>Time to Steady State</i>	379
16.5	<i>Conclusions</i>	387
	<i>Appendix 16A: Model Equations</i>	389
 <i>Part VI Metals</i>		
17	<i>Calcium and Alkalinity</i>	395
17.1	<i>Introduction</i>	395
17.2	<i>Calcium Carbonate</i>	395
17.3	<i>Chemistry and Simplifications</i>	396
17.4	<i>Closed System</i>	398
17.5	<i>Sediment Model Equations and Solutions</i>	401
17.6	<i>Application to Long Island Sound</i>	406
17.7	<i>Conclusion</i>	408
18	<i>Manganese I: Sediment Flux</i>	409
18.1	<i>Introduction</i>	409
18.2	<i>Steady State Model</i>	413
18.3	<i>Time Variable Model</i>	426
18.4	<i>Effect of pH</i>	439
	<i>Appendix 18A: MACSYMA</i>	449
19	<i>Manganese II: Overlying Water-Sediment Interaction</i>	453
19.1	<i>Introduction</i>	453
19.2	<i>Model Formulation</i>	456
19.3	<i>Time Variable Model</i>	464

19.4	<i>Calibration</i>	467
	<i>Appendix 19A: MACSYMA</i>	475
20	<i>Iron Flux Model</i>	479
20.1	<i>Introduction</i>	479
20.2	<i>Iron Chemistry</i>	479
20.3	<i>Model Configuration</i>	482
20.4	<i>Application to Onondaga Lake</i>	485
20.5	<i>Application to the Croton Reservoir</i>	501
20.6	<i>Model Framework</i>	503
20.7	<i>Summary</i>	506
21	<i>Cadmium and Iron</i>	509
21.1	<i>Introduction</i>	509
21.2	<i>Toxicity of Metals</i>	510
21.3	<i>Model Structure</i>	511
21.4	<i>Model Framework</i>	512
21.5	<i>Solution Method</i>	520
21.6	<i>Applications</i>	521
21.7	<i>Conclusions</i>	535
	<i>Appendix 21A: Partitioning Equations</i>	536
A.1	<i>FeS Partitioning</i>	536
A.2	<i>Cadmium Partitioning</i>	537
	<i>Appendix 21B: MACSYMA</i>	539
	<i>Appendix A: Data Tables</i>	541
A.1	<i>Chesapeake Bay</i>	542
A.2	<i>MERL</i>	542
A.3	<i>Lake Champlain</i>	543
	<i>Appendix B: Computer Program</i>	567
	<i>Nomenclature</i>	581
	<i>Bibliography</i>	593
	<i>Index</i>	613

# *Preface*

Sediments are an important feature of natural water bodies. The physical, chemical, and biological processes that take place are critically influenced by their presence. A primary interaction is the exchange of solutes between the sediment and the overlying water. The flux – the transport of mass – of dissolved and particulate chemical species to and from the sediments are important components of the chemical and biological cycles that take place. For example, the consumption of dissolved oxygen by organic matter that settles to the sediment in the spring is usually the primary cause, or at least an important cause, of summertime oxygen depletion in the bottom waters of lakes and estuaries. The cycling of nutrients and metals are controlled to a significant extent by processes in sediments. In particular the degree to which they are either trapped or transformed in sediments determines the extent to which they continue to interact with the water column. Dissolved nutrients are returned to the water column where they can be reused by the biological community. Dissolved toxic metals that recycle to the water column are almost always more toxic than their particulate counterparts in the sediment. It is the degree of remobilization that determines the extent to which materials stored in sediments: e.g., organic matter, inorganic phosphorus, toxic and non-toxic metals, become available to interact chemically and biologically in the water column. It determines the extent to which the consequences of historical discharges to water bodies – the materials stored in the sediments – can still exert an influence.

This book addresses the problem of mathematically modeling the processes in sediments that determine the extent to which materials that settle to the sediment are recycled to the water column. It is the flux of materials to and from the water

column that is the primary focus of this book. The substances considered are the nutrients: ammonia, nitrate, phosphate, and silica; dissolved oxygen; and the metals: calcium, manganese, iron, and cadmium. They were chosen primarily because of their importance in water quality problems: eutrophication and its consequences (N, P, Si), low dissolved oxygen with its attendant severe biological impacts; excessive concentrations of toxic metals (Mn, Cd), and for their importance to other processes (Ca, Fe).

The modeling philosophy employed is one of parsimony,\* sometimes referred to as Occam's razor.† Thus, for the most part, we adopt a two-layer rather than a many-layer representation of the sediment. Also we approximate some complex processes with empirical formulations in order to proceed, and then evaluate the consequences. An important component of the model building exercise is the constant reliance on high quality, large data sets, the sources of which are specifically acknowledged below. In fact, most of the effort is spent in an interplay of model formulations and data comparisons.

The mathematical methods employed are algebraic equations for the steady state models, and ordinary differential equations for the time variable models, for which an appendix is provided. With the exception of a few illustrative solutions, the differential equations are approximated by finite differences and solved numerically. A unique feature is the use of MACSYMA, a symbolic computational program to produce analytical solutions of the algebraic equations. This is such a useful, powerful, and necessary technique that a brief introduction to MACSYMA programming is included in an appendix. In addition, the actual MACSYMA inputs and outputs are listed throughout the book. This should provide an excellent starting point for developing a facility with this most useful of tools. The majority of the more complex models, especially the metals models, could not have been developed without this aid.

Also included in the appendices are the data used for the model calibrations and applications. It is likely that the data will ultimately prove to be more enduring, as the models are superseded. No small effort is required to assemble large data sets – not to mention the effort to collect them – so these tables should prove to be useful in themselves. The FORTRAN code for the steady state model is also provided. It can be used for applications of the model to other data sets and to provide the basis for the development of improved and more general models.

The book is divided into six parts and two appendices, listed below. Part I, comprising the first two chapters, presents the necessary background information: the physical, chemical and biological facts that are directly relevant to sediment processes. Mass balance models are introduced and applied to simplified situations. The mathematical and MACSYMA appendices conclude the presentation.

\*“Everything should be made as simple as possible, but not simpler.” Albert Einstein (1879–1955)

†“Entities should not be multiplied unnecessarily.” William of Occam (1300–1439)

Part		Part	
I	Preliminaries	IV	Time Variable Model
	1. Properties of Sediments		12. Diagenesis
	2. Model Formulation		13. Mass Transport
II	Nutrients	V	Model Calibration
	3. Ammonia		14. Chesapeake Bay
	4. Nitrate		15. MERL, LI Sound, Lake Champlain
	5. Steady State Model		16. Steady State and Time Variable Behavior
	6. Phosphorus	VI	Metals
	7. Silica		17. Calcium and Alkalinity
III	Oxygen		18. Manganese I
	8. Oxygen Equivalents		19. Manganese II
	9. Sulfide		20. Iron
	10. Methane		21. Cadmium and Iron
	11. Sulfide and Methane	A	Data Tabulations
		B	Computer Program

Part II, comprising five chapters, presents the steady state models for nutrients. Ammonia and nitrate flux models are considered in Chapters 3 and 4. A general steady state model is formulated and analyzed in Chapter 5. Phosphate and silica flux models are considered in Chapters 6 and 7. Of particular interest is the failure of the phosphate model to reproduce observed anaerobic flux rates, which points directly to a time variable effect.

The four chapters of Part III are devoted to modeling oxygen fluxes. Modeling sediment oxygen demand (SOD) has been a preoccupation of mine for many years. The chapters chronicle the progression of models from a formulation that focuses solely on oxygen equivalents (Chapter 8), to the explicit consideration of the oxidation of reactive intermediates: sulfide (Chapter 9) which predominates in marine sediments, and methane (Chapter 10) in freshwater sediments. Chapter 11, which considers both by explicitly modeling sulfate uptake, concludes the presentation.

All the models in Parts II and III are steady state models. They are very instructive and quite successful in some cases. However, modeling the seasonal variation of fluxes requires a time variable formulation. Part IV begins with Chapter 12 that presents the kinetic model for the organic matter diagenesis. The “three G” model of Westrich and Berner\* is used, which divides the organic matter into three reactivity classes in order to model properly the differing time scales of organic matter mineralization. Chapter 13 presents the structure of the time variable version of the

\*Berner (1980), Westrich and Berner (1984)

model. Included are the formulation for particle mixing due to benthic organisms (bioturbation), and the use of a benthic stress surrogate in order to include the effect of low (or zero) dissolved oxygen on the benthos.

Part V presents the calibration and applications of the model. The calibration of the time variable model to the Chesapeake Bay data set is presented in Chapter 14. In Chapter 15 the model is applied to three additional data sets, initially with no change in any of the model parameters. For the MERL data set, the model succeeds and fails in interesting ways, pointing to the strengths and weaknesses of the model and the price that is paid for simplicity. Two smaller but still instructive data sets are examined, Long Island Sound and Lake Champlain. The latter is an application of the model to a freshwater lake. The chapter concludes with a summary table of all the model parameters used in each application, together with sets from other applications. There is almost no variation with the exception of the phosphate partitioning coefficients, which points out the need for a more general formulation. Part V ends with Chapter 16 that revisits the steady state model, applying it to all the data sets, and using it to perform a number of sensitivity investigations. It ends by examining what controls the time to steady state for the time variable model, a question of great practical importance when the model is being used to examine remedial alternatives as part of a coupled water column-sediment model.

Part VI presents the models for metal fluxes. These are considerably more complex than the nutrient flux models because of the changing redox states for manganese and iron. Both oxidized and reduced manganese and iron need to be modeled explicitly. As a prelude, a simple model of calcium and alkalinity flux is considered in Chapter 17. The novel feature is explicitly considering calcium carbonate formation. This produces the first nonlinear set of algebraic equations for which MACSYMA is required. Manganese fluxes were also measured during the MERL experiments, which were analyzed in Chapter 15, and a model is formulated and applied to these observations in Chapters 18 and 19. In Chapter 18 the normal progression is followed, a steady state model followed by a time variable analysis. The influence of pH on the oxidation rate of Mn(II) is examined. In Chapter 19, an explicit model of the overlying water column is included with the same oxidation kinetics. This is an interesting model, since the coupled behavior is most instructive. This is followed by an iron flux model in Chapter 20, which is calibrated using field data from a lake and a reservoir.

Chapter 21 presents a model for cadmium in sediments. Unlike the preceding models, it is no longer two-layer, but rather examines the vertical distribution of sediment and pore water constituents. It focuses on the oxidation of cadmium sulfide and the liberation of dissolved cadmium to the pore water as well as the overlying water. The motivation for its construction is to aid in understanding the toxicity of metals in sediments. It uses a multilayered structure and it is the most complex of the models discussed.

The book concludes with two appendices that contain tabulations of the calibration data, a listing of the sediment flux model, and a listing of the mathematical nomenclature. The flux data from the Chesapeake Bay stations are tabulated. Pore water data from a much earlier study are also included. The MERL nutrient addition

study data including the manganese data, and the Lake Champlain data complete the presentation.

I hope this book will be of use to anyone with an interest in sediments. It provides an exposition of sediment flux models for the water quality modeling community. It can be thought of as the next step to books that discuss surface water quality modeling: Thomann and Mueller (1987), Schnoor (1996), and Chapra (1997).

DOMINIC. M. DI TORO  
Englewood, NJ and Wellfleet, MA

# *Acknowledgments*

Many colleagues and friends have been involved with the work presented in this book. The first sediment flux model was constructed as part of the Lake Erie Eutrophication model (Di Toro, 1980) in response to a question by our EPA project officer Nelson Thomas, an old sediment oxygen demand (SOD) hand himself: “And when the phosphorus loading to the lake changes, what are you going to do about the SOD?” The result was the oxygen equivalents model for SOD.

The close relationships with my colleagues and friends at the Department of Environmental Engineering at Manhattan College contributed greatly to my development and this work. My mentor and dear friend, the late Donald J. O’Connor, who trained and inspired a generation of environmental engineers and water quality modelers, suggested that we embark on building what are now called eutrophication models. His wide-ranging interests, rigorous approach to problems, and the primacy of data in model building, were lessons we all learned by his example. My long-time friend and colleague, Robert V. Thomann, played a critical role as a careful and insightful critic and collaborator. His scholarship and authorship of two books were an accomplishment to be emulated. I had the good fortune and privilege of being the youngest member of this group. I owe a debt of gratitude to Don and Bob. I hope this book is a small payment.

My recent appointment to the Donald J. O’Connor Chair of Environmental Engineering has enabled me to complete this project. I thank the contributors, the college administration, and the faculty of the department: Kevin Farley, Scott Lowe, John Mahony, Jim Mueller, and Rob Sharp, for their support.

Part of my professional life has been spent at the consulting firm HydroQual, and its predecessor firm, Hydrosience. My former and present colleagues Alan Blumberg, Charlie Dujardin, Jim Fitzpatrick, Tom Gallagher, Ed Garland, Jim Hallden, Bill Leo, John Mancini, Tom Mulligan, Paul Paquin, Karl Scheible, John St. John, and the rest of the members of the firm have helped in many ways.

The models that are the subject of this book have been developed during the conduct of various projects. The methane oxidation model was constructed as part of the Milwaukee River Comprehensive Study (SWRPC, 1987) in response to measurements of gas fluxes that indicated the importance of methane as the endproduct of diagenesis and the inadequacy of the oxygen equivalents assumption for this situation. My colleagues Paul Paquin and Thomas Gallagher at HydroQual, Inc. and I struggled with this model for some time. The data collected by David A. Gruber (Milwaukee Metropolitan Sewerage District) was central to its development (Di Toro et al., 1990).

The Chesapeake Bay project, sponsored by the Chesapeake Bay Program Office of the US Environmental Protection Agency and the US Army Corps of Engineers, provided the opportunity for the next developments. Much of contents of Chapters 3–7, 9, and 12–14 are from that effort. The importance of sulfide as an intermediate in oxygen consumption reaction was apparent. The presence of sulfide as a solid phase as well as in pore water clearly invalidated the oxygen equivalents idea. Perhaps the biggest impetus was the failure of a summer steady state water column model, which had no interactive sediment model, to respond to loading reductions in a sensible way – that is, to respond at all. The coupled water column-sediment eutrophication model was then developed (Cercio and Cole, 1993) with the two layer sediment flux model providing the sediment fluxes (Di Toro and Fitzpatrick, 1993). My colleagues James Fitzpatrick at HydroQual and Carl Cercio at the US Army Engineer Waterways Experiment Station (WES) were of great help. Kai-Yuan Yang (HydroQual), Mark Dortch, and Don Robey (WES) also helped with moral and program support. Ongoing commentary and advice was provided by Michael Kemp and Walter Boynton (University of Maryland). The members of the technical review committee were: Robert Thomann (Manhattan College), Donald Harleman (MIT), and Jay Taft (Harvard University), who also aided in the development.

The success of this modeling effort is due in no small measure to the excellent and comprehensive experimental data sets used in the development and calibration. They are the result of the efforts of scientists who developed the methods for reliably measuring sediment fluxes and applied these techniques in a systematic and comprehensive way. Their efforts are specifically acknowledged and appreciated: Walter Boynton, Michael Kemp, Jeffery Cornwell, and Peter Sampou (University of Maryland's Center for Estuarine and Ecosystem Studies), Jonathan Garber (EPA Research Laboratory, Narragansett, RI), and David Burdige (Old Dominion University). An older pore water data set collected under the supervision of Owen Bricker (then with the Maryland Geological Survey) was very useful.

The application of the sediment flux model to the MERL data set was sponsored by an NSF research project at Manhattan College. The support, generous coopera-

tion, and insights of Candace Oviatt and Scott Nixon (University of Rhode Island, Graduate School of Oceanography) are gratefully acknowledged.

The manganese and iron models were developed as part of the Water Quality Research Program at WES (Di Toro et al., 1998). Chapters 17–20 are based on this work. Carl Cerco was the project officer and provided his usual generous and insightful support. My colleagues Jim Fitzpatrick and Richard Isleib (HydroQual) and Scott Lowe (Manhattan College) participated in this study and provided their usual high level of professional help. The MERL manganese data were collected and provided to the author by Carlton D. Hunt of Battelle Ocean Services, Duxbury, MA. These were unpublished data, generously provided from his personal notebooks. A special thanks for a wonderful data set.

The cadmium and iron model (Chapter 21) is based on research sponsored by a US EPA Office of Water Cooperative Agreement and by a National Institutes of Environmental Health Sciences Superfund Hazardous Substances Basic Research Program project. My coworkers John D. Mahony (Manhattan College), David J. Hansen and Walter J. Berry (EPA Research Laboratory, Narragansett, RI) and project officers Chris Zarba and Mary Reiley (EPA) provided necessary support and data with which to build the model. Additional data were kindly provided by Ed Leonard (EPA Research Lab, Duluth MN), Karsten Liber (University of Saskatchewan), Landis Hare, and Andre Tessier (University de Quebec), all of whom are thanked.

A number of colleagues read various portions of the manuscript and provided useful suggestions: Kevin Farley and John Mahony (Manhattan College); Ferdi Hellweger, Richard Isleib, and Paul Paquin (HydroQual); and Steve Chapra (Tufts University). A special note of thanks to John Mueller who read the entire manuscript with great care and devotion to detail.

The final acknowledgments are to my parents: my father, Michael, who was my first inspiration, and my mother Josephine. And, lastly, my deepest gratitude to my wife Marilyn and our children Jennifer and Joseph, who have contributed to this effort in more ways than they know.

D.M.D.