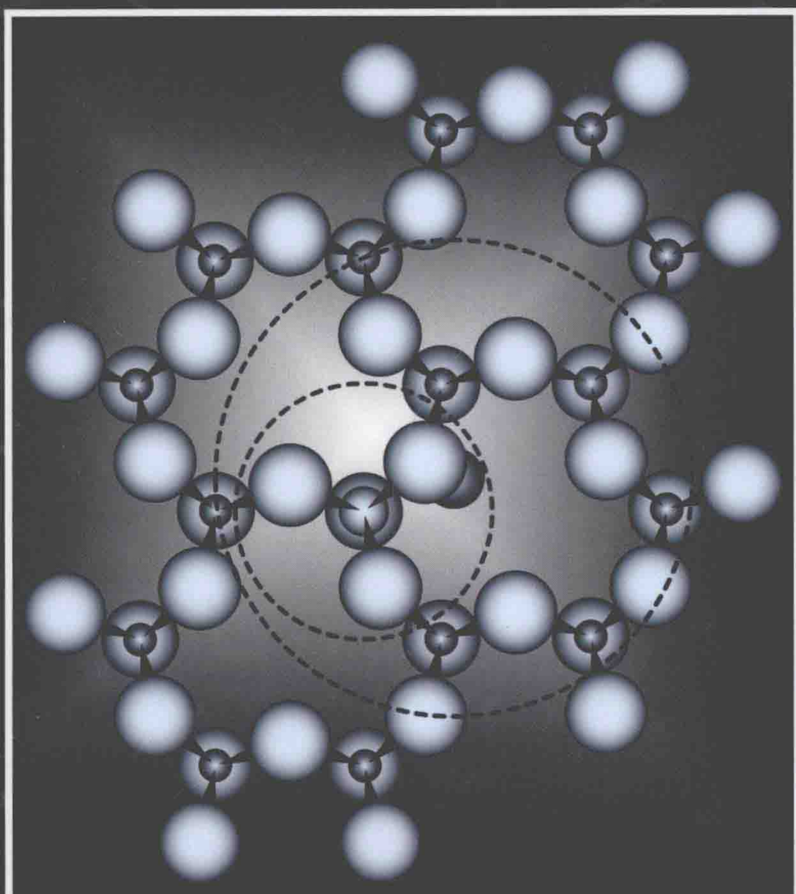
SECOND EDITION

SOIL and WATER CHEMISTRY

An Integrative Approach



MICHAEL E. ESSINGTON

CRC Press
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SECOND EDITION

SOIL and WATER CHEMISTRY

An Integrative Approach

Dedicated to my girls, Nina, Erin, and Meghan

Preface to the Second Edition

It has been more than 10 years since the first edition of *Soil and Water Chemistry: An Integrative Approach* was published. At that time, and during the years that followed, the idea of preparing a second edition was simply unpalatable. Indeed, the birthing pains remained ever fresh and I continually resisted the pressure from the folks at CRC Press to produce a second edition. I also felt that I had placed all that I knew into the first edition and, therefore, had nothing substantially new to offer. Furthermore, the production of a second edition without providing some substantial change or addition to the original text (with the exception of cover art) was not a practice I wished to follow. But the passage of time has a way of softening one's perspectives and remembrances, and those nagging birthing pains of the first edition faded. I had also amassed (with input from my peers and students) a large list of errors that required attention, as well as suggestions for inclusions in a second edition.

One of the primary driving forces for the production of the second edition was to correct errors and to improve readability. Relative to the former, it is my hope that I have done this without producing additional errors. I am indebted to the many who have read the text with a critical eye and who have shared their error findings with me. Most notably, I thank George Vance at the University of Wyoming, who routinely made it a class project to find errors in the text. In addition to the many minor textual modifications and the inclusion of new figures and tables, there are a number of notable additions to the text that are consistent with the topics I cover in my undergraduate- and graduate-level soil chemistry courses.

In Chapter 1 (Soil Chemical Environment: An Overview), I have added an extensive section that details the sources, speciation, and the general behavior of the elements in soils. I owe a debt of gratitude to the late Philip M. Jardine, who reviewed this textual addition, providing valuable feedback and encouragement. In Chapter 2 (Soil Minerals), I have expanded the section on crystal structure, updated the phyllosilicates classification scheme, included the sepiolite–palygorskite group, and expanded the x-ray diffraction section. In Chapter 5 (Soil Water Chemistry), a discussion of surface runoff losses of phosphorus from soil is included, as is a description of the inductively coupled argon plasma–mass spectroscopy (ICP-MS) analytical technique for determining elemental concentrations in soil solution. The chapter "Oxidation–Reduction Reactions in Soils" (Chapter 9 in the first edition) has been included in this edition as Chapter 7 and has been expanded to include a section on the influence of redox processes on the soil chemistry of nonelectroactive elements. The repositioning of this chapter places the topic in line with the flow of topics in my undergraduate soil chemistry course. Chapter 8 (Surface Chemistry and Adsorption Reactions) includes a description of the electrokinetic phenomenon and investigates the influence of temperature on adsorption. Chapter 12 (Chemical Thermodynamics Applied to Soil Systems) is a new addition to the text that is patterned after my lecture notes from the soil physical chemistry courses taught by Garrison Sposito and my advanced soil chemistry course. The principles of thermodynamics are applied throughout this text to characterize and predict soil chemical processes such as ion speciation, mineral solubility, and ion exchange equilibria. Chapter 12 provides a preamble to those discussions.

During the preparation of the first edition of this text, I had intended to produce a solutions manual to the exercises. However, the publisher felt the manual would not be a worthwhile addition to the text. Although my pleas at the time fell on deaf ears, it became readily apparent through the years that a solutions manual would indeed be a valuable addition which would not only provide students with insight into the mechanics of solving problems but also provide faculty with a time-saving tool (readily available answers to the exercises). Therefore, for the second edition, I have expanded the exercise sections in each chapter by incorporating additional problems, and I have prepared a solutions manual that not only provides the answers to the questions, but also details the problem-solving steps. In addition to these inclusions, there are a small number of modifications that I hope will have improved the overall quality of the text. First, I'm hopeful that the index will be substantially improved over that of the first edition. Second, I have included a color insert of figures. For the most part, I have colorized the phyllosilicate structures that appear in Chapter 2.

As with the first edition, the production of this book would not have been possible without input from the many students that I have mentored throughout the years. Although they have come to call this book the "Black Bible" (attributed to the black cover art and their indelible view that the book was created to torment them), it is for them, and for those who follow, that this book is written. I hope this book satisfies your needs as students and professionals in the soil and environmental sciences. Many of my students have also provided an abundance of material for this text; most notable among these have been Darlene Allred, Robert Anderson, William Holden, Jessica Journey, Yul Roh, Dibyendu "Dibs" Sarkar, Sloane Smith, Melanie Stewart, Jennifer Suba, and Kalyn Vergeer. For your contributions to this book, I am most grateful.

Finally, I am blessed with three daughters. When informed that I was going ahead with the second edition, the oldest stated, "So, we're not going to see you for another two years," while the youngest simply wanted to know if her name would be in it again (on the dedication page). While the preparation of the first edition of this text truly devoured every waking moment of my life for more than two years, the development of this second edition has not been all-consuming. It is true that the modification of existing text is a whole lot simpler than writing a book from scratch, thus requiring less time. However, I prefer to believe that I've learned that no project is more important than spending time with my girls.

Michael E. Essington
Knoxville, Tennessee

Preface to the First Edition

Soil and Water Chemistry: An Integrative Approach was written to meet the needs of undergraduate and first-year master's students in soil and environmental chemistry courses. The book may also serve as a reference for professionals in the soil sciences and allied disciplines. The discipline of soil chemistry, or its contemporary counterpart, environmental soil chemistry, examines the chemical and mineralogical characteristics of the soil environment and the chemical processes that distribute matter between the soil solid, solution, and gaseous phases. Essentially, a soil chemistry course and this book offer a basic understanding of the complexity of the natural system that occupies an exceedingly thin layer of the Earth's surface. Traditionally, the application of chemical principles to the study of soils has been limited to agronomic systems, and primarily to the behavior of agrichemicals. However, it is well established that as a discipline soil chemistry is not limited to describing the processes that control the availability of nutrients to plants. Indeed, the chemical properties and processes that control the behavior of nutrients and pesticides in soils are the same as those that operate on a vast array of inorganic and organic substances that are outside the purview of production agriculture.

Recent texts in soil chemistry, those published in the last decade, have attempted to embrace the environmental aspects of the discipline, as evidenced by their various titles (e.g., *Environmental Soil Chemistry*, *Environmental Chemistry of Soils*, and *Environmental Soil and Water Chemistry: Principles and Applications*). Topically, *Soil and Water Chemistry: An Integrative Approach* continues the *environmental* trend established by its predecessors. However, my intent is to focus on the needs of undergraduate students in soil chemistry and allied disciplines and offer a balanced presentation of the chemical processes operating in soils.

This book contains more information and topic coverage than an instructor might cover in a single semester and introduces some topics that may be too advanced for an undergraduate course. This extensive coverage is by design. I envision that it will allow instructors the latitude to choose their own *essential* topics while providing additional information or a more advanced treatment for others. This book also contains more than 300 original figures and approximately 90 tables to help make the material more accessible. I have also reviewed some of the more common methodologies and analytical techniques used to characterize soil chemical properties. In addition, each chapter contains several examples that illustrate problem-solving techniques.

Each chapter concludes with a section containing numerous exercises. The problems are not esoteric, nor do they require advanced training in soil chemistry to begin to formulate a solution. Each problem has at one time or another appeared in one of my problem sets. They are tested, relevant, and doable, but ask more of students than to simply (or not so simply) generate a number. It may be inevitable that the path to complete a computation or series of computations is tortuous, but this tortuosity should not blind the student to the purpose of determining a numerical answer. It is important for students to understand concepts and to recognize that the answers to their computations have physical meaning. I have attempted to include exercises that embody both traits: compute an answer and discuss its significance.

This book has its roots in the undergraduate course I offer in environmental soil chemistry. This is a required course for the environmental and soil sciences major and is perhaps the last technically oriented course these students will take during their undergraduate experience. I have high expectations of students, particularly with respect to the amount of information retained from prerequisite courses. However, I am also a pragmatic person and recognize that materials introduced in an organic chemistry course taken as a sophomore may have long since been relegated to the *recycle bin* of the mind. The information is there, it just needs to be restored. As with my course in environmental soil chemistry, this textbook begins with an overview of the soil environment and the chemical processes that operate to distribute matter between the soil solid, solution, and atmosphere. Students are then introduced to the concept of speciation, and they are presented with a list of common oxidation states and species for nearly every element as it might exist in the soil solution (with the exception of aqueous complexes). I do not specifically discuss units, unit conversions, or mass transfer computations in lecture (e.g., if an X g mass of soil is extracted with Y mL of water and the water contains Z mg L^{-1} of element A, what is the concentration of A in the soil, in mg kg^{-1}?). Instead, I rely on problem sets to refresh and restore this information. However, I am annually queried, "Where was I supposed to have learned how to do this?" I now recognize that three years or more of college has not prepared students for this important rudimentary capability. Therefore, these topics are also covered in Chapter 1. Also introduced in Chapter 1 is the concept of spatial variability and spatial statistics. We often discuss the elemental composition of soils in soil chemistry courses, indicating that for every element there is a mean and median value and a range of concentrations observed in the soils of the world. Soil chemical properties are spatially variable on a local scale as well; they change with location on a landscape and depth in a profile.

Chapters 2 through 4 are devoted to soil solids. Chapter 2 (Soil Minerals) begins by discussing the *glue* that bonds atoms together in mineral structures and the rules that describe how these atoms are arranged in 3D space (Pauling's rules). The remainder of the chapter describes the silicates, emphasizing the phyllosilicates, and the hydrous metal oxides. Finally, x-ray diffraction and its application to identifying clay minerals are discussed. Chapter 3 (Chemical Weathering) focuses on clay mineral transformations. This chapter also (re)introduces a very important capability that must be mastered by any individual in a chemistry-based course or discipline: balancing chemical reactions. Chapter 4 (Organic Matter in Soil) examines the organic component of the soil solid phase. The reader is (re)introduced to the organic functional groups and structural components that occur in soil organic matter. The distinction between nonhumic and humic substances is drawn, as well as the mechanisms for isolating humic substances. The nonhumic substances are described, as are their transformations from biomolecules to humic substances. The chemical and (pseudo)structural characteristics of the humic substances are also discussed.

One of the largest chapters in this book is Chapter 5 (Soil Water Chemistry). It begins by discussing chemical characteristics of water, the universal solvent, and ends by examining some important analytical methods used to determine the concentrations of dissolved substances in soil solutions. These topics, and those in between, constitute a course in water chemistry and reflect my belief that the aqueous chemistry of a substance dictates its fate and behavior. The nonideality of soil solutions, hydration–hydrolysis, Lowry–Brønsted and Lewis acidity and basicity, aqueous complexation, geochemical modeling, and soil solution sampling methods are topics that are addressed with detail and rigor. Chapters 6 through 8 examine the processes that distribute matter between the soil solid and solution phases. In Chapter 6 (Mineral Solubility), the soil solid and solution characteristics that control the precipitation and dissolution of soil minerals are examined. This chapter also examines the influences of temperature and impurities in soil minerals on mineral stability and the compositions of soil solutions. Chapter 7 (Surface Chemistry and Adsorption Reactions) rivals Chapter 5 in size and scope. Adsorption and partitioning reactions are the principal mechanisms by which all organic solutes and many inorganic substances are retained in soils (the other mechanism is precipitation). The chapter describes soil surfaces and identifies the inorganic and organic functional groups that react with solutes to form surface species. The chapter also examines those factors that influence the reactivity of soil surface functional groups and applies surface- and solute-specific information to predict adsorption behavior (surface complexation modeling). The descriptive models that are commonly employed to provide an empirical characterization of adsorption are also examined (e.g., Langmuir and Freundlich isotherm models). Although ion exchange is also an adsorption process (or is it—are all adsorption processes ion exchange processes?), it is standard practice to discuss exchange phenomena separately from adsorption.

This is done in Chapter 8 (Cation Exchange). This chapter focuses on the history, methods of characterizing the soil's capacity to exchange cations, the qualitative characteristics of cation exchange, and the techniques to quantify exchange behavior.

Oxidation–reduction processes in soils are examined in Chapter 9 (Oxidation–Reduction Reactions in Soils). Although this topic is introduced in a later chapter, this should not be taken to imply that the redox behavior of an element is of minor importance. Quite the contrary, the redox status of an environment is a master chemical variable (along with pH) that directly dictates the fate and behavior of redox-sensitive elements, which in turn may influence the chemistry of other soil constituents. Methods for determining soil redox status, reduction–oxidation sequences in soils, and the redox chemistry of chromium, selenium, and arsenic are discussed. The two final chapters (Chapters 10 and 11) are devoted to topics of regional interest: Acidity in Soil Materials and Soil Salinity and Sodicity. The genesis, characterization, management, and chemical properties of these differing soil systems are discussed. I have also included case studies that examine the reclamation of pyritic acid mine spoils and sodic mine spoils.

I am deeply appreciative to the many individuals who donated their time and expertise to the preparation of this book. John Sulzycki at CRC Press planted the *textbook bug* and gave me the opportunity to bring this project forward. He also provided encouragement and continued to demonstrate confidence that I would complete this project, even after I missed several deadlines. Julia Nelson critically reviewed every chapter with a keen eye. Her critiques were thorough and immeasurably improved the clarity of the manuscript and caught my many typos, misspellings, and grammatical errors. I am deeply indebted to her for her efforts. I am also indebted to Gary Pierzynski, George Vance, April Ulery, Dean Hesterberg, and Malcolm Sumner for their highly constructive reviews and suggestions. I applaud their selfless contribution to the discipline of soil and water chemistry and to the education of future *Earth* scientists and technicians by giving their time and expertise. I was buoyed by their positive feedback and by their desire to see a book that has utility for students and professionals. Finally, I have made every effort to produce a text that is complete for the intended audience and conceptually sound. I also recognize that no book is without errors. For the errors that remain, I hope they are few in number and minor in magnitude. If errors are discovered, or if you as the reader have comments and suggestions that would improve future editions of this book, please bring them to my attention. I welcome your input.

In addition to the individuals mentioned who helped shepherd this book from manuscript to reality, there are many people who have mentored me and provided me with the tools, insight, and drive necessary to complete this book. First and foremost is a fellow soil scientist who steered me away from a major in biology and toward the soil science curriculum at New Mexico State University. The late Edward Essington uttered these words during a job fair while I was still a senior in high school: "Get a degree that will allow you to do more than wait tables when you graduate." I took his advice. I thank George O'Connor and Al Page for their continual encouragement and support throughout my career, and Shas Mattigod and Garrison Sposito who set the bar for me many years ago. Finally, without the students whom I have directed or who have taken my soil chemistry courses, this book would not have come to fruition. Their research has provided an abundance of material for this text, and their response to the materials in the lecture notes has been instrumental in the production of this book. You all have my gratitude.

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Michael E. Essington is professor of soil and water chemistry in the Institute of Agriculture at the University of Tennessee in Knoxville. In addition to teaching courses in soil chemistry and clay mineralogy, his special research interests center on the role of aqueous speciation in environmental chemistry, with particular emphasis on trace element adsorption and precipitation phenomena. These interests have resulted in more than 200 publications and technical reports. Dr. Essington received his BSc in agriculture from New Mexico State University in 1980 and his PhD in soil science from the University of California, Riverside, in 1985. He was a research scientist at the Western Research Institute in Laramie, Wyoming, from 1985 to 1990 and has been at the University of Tennessee since then. He is a member of the Soil Science Society of America, the American Society of Agronomy, Sigma Xi, and Gamma Sigma Delta. He is a fellow of the Soil Science Society of America and the American Society of Agronomy. Dr. Essington's professional activities include serving as an associate editor and technical editor for the *Soil Science Society of America Journal* and as soil chemistry division chair and member of the board of directors for the Soil Science Society of America.

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