

BIOPHYSICO-CHEMICAL PROCESSES OF HEAVY METALS AND METALLOIDS IN SOIL ENVIRONMENTS

Edited by

**ANTONIO VIOLANTE
PAN MING HUANG
GEOFFREY MICHAEL GADD**



A JOHN WILEY & SONS, INC., PUBLICATION

**BIOPHYSICO-CHEMICAL
PROCESSES OF HEAVY
METALS AND METALLOIDS
IN SOIL ENVIRONMENTS**



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PREFACE

Pollution induced by heavy metals and metalloids in soils is a serious environmental problem because, in comparison with the atmosphere and water, the soil environment has a much lower ability to recover from toxic effects. In soil, trace elements potentially toxic to plants and other living organisms are involved in chemical and biological reactions such as solution and surface complexation, precipitation, sorption–desorption, and oxidation–reduction. These elements interact with a series of clay minerals, humic substances, metal oxides, microorganisms, extracellular enzymes, biopolymers, and other organic and inorganic ligands. Their behavior depends on chemical and physicochemical as well as biological processes and their interactions with microbial activities. These physicochemical–biological interactions would influence the transfer of these elements from the inorganic and organic soil constituents to the soil solution and to plants and contaminate the terrestrial food chain, thus endangering human and animal health. Biogeochemical processes operating in soil environments that affect the fate, behavior, and bioavailability of metals and metalloids are currently an area of active research.

As a recognition of the importance of biophysico-chemical processes of metals and metalloids in soil environments, we initiated the first volume of the IUPAC–Wiley book series “Biophysico-Chemical Processes in Environmental Systems.” This volume, which consists of 15 chapters, is organized into three parts: Fundamentals of Biotic and Abiotic Interactions of Trace Metals and Metalloids with Soil Components; Transformations and Dynamics of Metals and Metalloids as Influenced by Soil–Root–Microbe Interactions; and Speciation, Mobility, and Bioavailability of Metals and Metalloids and Restoration of Contaminated Soils.

This book, contributed by a multidisciplinary group of soil and environmental scientists, provides the scientific community with a critical evaluation of the state of the art on the fundamentals of reactions and processes of these elements in soil environments, their speciation, mobility, bioavailability, and toxicity and their impact on the development of innovative restoration strategies. The book is an

important guide to scientists interested in environmental sciences, soil chemistry and mineralogy, soil biochemistry, soil microbiology, and plant nutrition and physiology as related to understanding the biophysico-chemical processes of these pollutants in soil environments. The latest advances in spectroscopy to study various aspects of heavy metal and metalloid interactions with soil inorganic and organic components are also reviewed critically and addressed clearly. The authors are scientists who are experts in their fields and the chapters have been reviewed critically by at least two external referees. We wish to thank all of the referees, who generously contributed their time and talent to maintain the high quality of this volume. We also express our thanks to the staff of IUPAC and John Wiley & Sons for their invaluable support and cooperation in the publication of the book.

A. VIOLANTE
P. M. HUANG
G. M. GADD

SERIES PREFACE

Scientific progress is based ultimately on unification rather than fragmentation of knowledge. Environmental science is the fusion of physical and life sciences. Physical, chemical, and biological processes in the environment are not independent but rather, interactive processes. Therefore, it is essential to address physical, chemical, and biological interfacial interactions to understand the composition, complexity, and dynamics of ecosystems. Keeping separate these domains, no matter how fruitful, one cannot hope to deliver on the full promise of modern environmental science. The time is upon us to recognize that the new frontier in environmental science is the interface, wherever it remains unexplored.

The Division of Chemistry and the Environment of the International Union of Pure and Applied Chemistry (IUPAC) has recently approved the creation of an IUPAC-sponsored book series entitled *Biophysico-Chemical Processes in Environmental Systems* to be published by John Wiley & Sons, Hoboken, NJ. This series addresses the fundamentals of physical–chemical–biological interfacial interactions in the environment and the impacts on (1) the transformation, transport, and fate of nutrients and pollutants; (2) food chain contamination and food quality and safety; and (3) ecosystem health, including human health.

The book *Biophysico-Chemical Process of Heavy Metals and Metalloids in Soil Environments* is Volume I of this newly created Wiley–IUPAC series. The transformation of metals and metalloids is influenced by physicochemical–biological interfacial interactions. The impacts of these interactive processes are especially important in the rhizosphere, which is the bottleneck of the contamination of the terrestrial food chain, and in the location near the decomposition of biological residues. In contrast to classical books which focus largely on separate physical, chemical, and biological processes, this book is unique in integrating the frontiers of knowledge on both fundamentals and impacts of interfacial interactions of physical, chemical, and biological processes pertaining to the transformation, transport, bioavailability, and toxicity of metals and metalloids in soil environments.

This book can be used as an advanced reference book on biophysico-chemical processes of metals and metalloids in soils and related environments for senior undergraduate and graduate students in soil and environmental sciences. It is an essential reference for chemists and biologists studying environmental systems. It will serve as a useful resource book for instructors, research scientists, professional consultants, and others working on environmental and ecological systems.

SERIES EDITORS

P. M. HUANG

N. SENESI

ABOUT THE EDITORS

Antonio Violante is professor of soil chemistry at the Department of Soil, Plant and Environmental Sciences, University of Naples Federico II, Italy, where he has been actively involved in research and teaching since 1970. He received his academic degree in chemistry from the University of Naples in 1969. He spent two sabbatical years at the University of Wisconsin, Madison (1976–1977) and the University of Saskatchewan, Saskatoon, Canada (1981–1982) and was invited to serve as a visiting professor in the Department of Soil Science at the University of Saskatchewan in 1985, 1992, and 2003. He was Head of the Dipartimento di Scienze Chimico-Agrarie from 1994 to 1999 and is coordinator of the Doctoral School in Agrobiology and Agrochemistry.

Dr. Violante has taught courses in agricultural chemistry, soil chemistry, and soil fertility for undergraduate students and in environmental biogeochemistry and soil mineralogy for Ph.D. students. He has trained many M.S. and Ph.D. students and postdoctoral fellows and has received visiting scientists worldwide. Three of his students have received awards for their theses in soil chemistry.

He has contributed to research on the interface between soil chemistry and mineralogy and soil biology. His special areas of research include the formation mechanisms of aluminum hydroxides and oxyhydroxides, the surface chemistry and reactivities of short-range-ordered precipitation products of Al and Fe, the influence of biomolecules on the sorption and desorption of nutrients and xenobiotics on and from variable charge minerals and soils, the factors that influence the sorption and residual activity of enzymes on phyllosilicates, variable charge minerals, organomineral complexes, and soils and the chemistry of arsenic in soil environments.

Dr. Violante has served on many committees of the Italian Society of Soil Science (president of the session on soil chemistry) and the Italian Society of Agricultural Chemistry. He is vice-president and liaison officer of Gruppo Italiano AIPEA. He has been the scientific chairman and chief organizer of international and national congresses.

Dr. Violante is the author or coauthor of 167 refereed research articles and book chapters and invited reviews, and has coedited six books. He has also presented papers at many scientific congresses and symposia and has given invited lectures at universities and research institutes worldwide. He has international research and teaching experience in Canada, the United States, Europe, China, and Chile. He is a Fellow of the Soil Science Society of America and American Society of Agronomy.

Pan Ming Huang received his Ph.D. degree in soil science at the University of Wisconsin, Madison, in 1966. He is professor emeritus of soil science at the University of Saskatchewan, Saskatoon, Canada. His research work has significantly advanced the frontiers of knowledge on the formation chemistry and nature and surface reactivity of mineral colloids, organic matter, and organomineral complexes of soils and sediments and their role in the dynamics, transformations, and fate of nutrients, toxic metals, and xenobiotics in terrestrial and aquatic environments. His research findings, embodied in over 300 refereed scientific publications, including nine research papers published in *Nature* and others in leading journals, book chapters, and books, are fundamental to the development of sound strategies for managing land and water resources.

He has developed and taught courses in soil physical chemistry and mineralogy, soil analytical chemistry, and ecological toxicology. He has trained and inspired M.Sc. and Ph.D. students and postdoctoral fellows, and has received visiting scientists from all over the world. He has served on numerous national and international scientific and academic committees. He has also served as a member of many editorial boards, including those of the *Soil Science Society of America Journal*; *Geoderma*; *Chemosphere*; *Water, Air and Soil Pollution*; *Soil Science and Plant Nutrition*; and *Pedosphere*. He has served as a titular member of the Division of Chemistry and the Environment of the International Union of Pure and Applied Chemistry and is the founding chairman of the Working Group MO, "Interactions of Soil Minerals with Organic Components and Microorganisms," and the founding chair of Commission 2.5, "Soil Physical/Chemical/Biological Interfacial Reactions," of the International Union of Soil Sciences. He received the Distinguished Researcher Award from the University of Saskatchewan and the Soil Science Research Award from the Soil Science Society of America. He is a Fellow of the Canadian Society of Soil Science, the Soil Science Society of America, the American Society of Agronomy, the American Association for the Advancement of Science, and the World Innovation Foundation.

Geoffrey Michael Gadd is an international leader in the field of metals and microorganisms and is well known for research that has advanced understanding of cellular and physicochemical mechanisms underlying microbial–metal transformations, and their environmental and biotechnological significance, especially in relation to metal and radionuclide geomicrobiology. He holds a personal chair in microbiology at the University of Dundee and has served as Head of the Department of Biological Sciences, Head of the Division of Environmental and

Applied Biology, and as deputy research director of the School of Life Sciences; currently, he is Head of the Division of Molecular and Environmental Microbiology. Several scientific societies have recognized Professor Gadd's research through specific awards (e.g., the Berkeley Award of the British Mycological Society, the Charles Thom Award of the Society for Industrial Microbiology), and he is a Fellow of the Linnean Society, the Institute of Biology, the American Academy of Microbiology, and the Royal Society of Edinburgh. From 2004 to 2006 he served as president of the British Mycological Society (the first to serve a three-year term of office) and is currently convener of the Environmental Microbiology Group of the Society for General Microbiology. He has contributed to the vitality of his field via significant contributions to many professional societies and national and international editorial boards, advisory groups, and committees. Professor Gadd has published over 190 refereed scientific papers, over 40 edited books (two as sole editor), and over 35 invited book chapters.

PART I

FUNDAMENTALS OF BIOTIC AND ABIOTIC INTERACTIONS OF METALS AND METALLOIDS WITH SOIL COMPONENTS

1

IMPACTS OF PHYSICOCHEMICAL–BIOLOGICAL INTERACTIONS ON METAL AND METALLOID TRANSFORMATIONS IN SOILS: AN OVERVIEW

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1.1. INTRODUCTION

Soil, geoderma, is the “skin” of planet Earth and the central organizer of the terrestrial ecosystem. It is a life-sustaining material which is a structurally porous and biologically active medium that has evolved over time on continental land surfaces. This material is formed and continues to develop through weathering processes driven by geological, biogeochemical, topological, climatic, chronological, and anthropogenic influences.

Soils are complex interactive biogeochemical reactors, reservoirs of organisms (microorganisms, protozoans, and nematodes), and major compartments of the terrestrial ecosystem. Minerals, organic components, and organisms are among major solid components of soils. These components are not separate entities but rather, form a unified system whose members are constantly in association with each other in the environment (Huang and Schnitzer, 1986; Huang et al., 1995; Banfield and Nealson, 1997). The association of microorganisms with soil mineral and organic colloids is depicted in Figure 1.1. Interactions among the components have an enormous impact on the physics, chemistry, and biology of soil and surrounding ecosystems (Huang, 2002). However, physical, chemical, and biological processes are not independent but rather, interactive processes in soil environments. A fundamental understanding of physical, chemical, and biological interfacial interactions in soil is essential in restoring, enhancing, and sustaining ecosystem productivity, services, and integrity and for establishing soil’s impact on human welfare. In view of the mineral–organic component–organism interactions and interactive physical, chemical, and biological processes in the terrestrial ecosystem, a commission on Soil Physical/Chemical/Biological Interfacial Reactions was created within the structure of the International Union of Soil Sciences in 2004.

The transformation of metals and metalloids in the environment is influenced by physicochemical–biological interfacial interactions. The impact of these interactive interfacial processes on metal and metalloid transformations is especially important in the rhizosphere (Huang and Germida, 2002; Huang and Gobran, 2005) and near the decomposition of plant residues (Huang and Schnitzer, 1986), where the types and concentrations of substrates are different from those of the bulk soil because of enhanced biological activity. In the rhizosphere, root exudation leads to colonization by various populations of bacteria, fungi, protozoans, and nematodes. The distribution of microorganisms with distance from the root is illustrated in Figure 1.2. Plant–microbe interactions result in intense biological processes in the rhizosphere. These intense biological processes, in turn, affect physicochemical reactions in the rhizosphere. Physicochemical properties that can be different in the rhizosphere include acidity, concentration of complexing biomolecules, redox potential, ionic strength, moisture, and nutrient status. In the rhizosphere, it is difficult to separate the effects of microbial activity on the chemistry of metals and metalloids from the effects of plant root activity. Microorganisms act in a fashion similar to that of plant roots in that they can accumulate metals and metalloids through uptake and adsorption as well as mobilizing them through the action of microbial exudates, diffusates, and excretions.

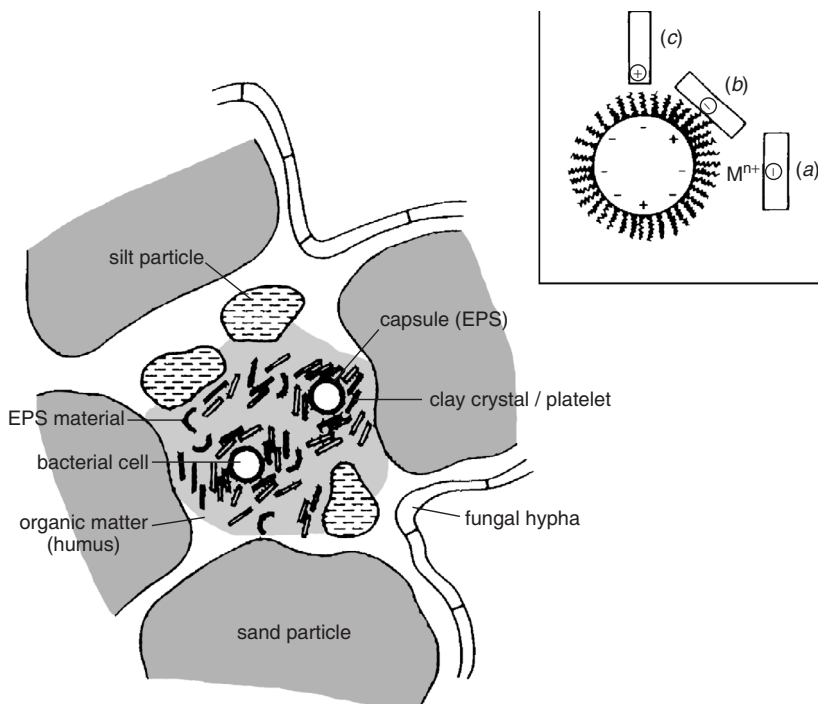


Figure 1.1. Interaction of bacteria and fungi with mineral particles in a soil aggregate. Bacterial cells with a coat of extracellular polysaccharides (EPSs) are enveloped by clay particles. The pore space where clays and bacteria interact, bounded by silt- and sand-size particles, is relatively enriched in organic matter, including EPS residues. Fungal hyphae are attached to the outside surface of an aggregate. Inset shows an enlarged view of a bacterial cell with its complement of EPS. At normal soil pH conditions, the cell has a net negative surface charge. Most clay particles adhere to the cell surface by bridging through polyvalent cations, represented by M^{n+} (a), although some may be attached directly by electrostatic interactions, either in face-to-face (b) or edge-to-face (c) association. (From Theng and Orchard, 1995.)

The total rhizosphere environment is governed by an interacting trinity of the soil, the plant, and the organisms associated with the root (Lynch, 1990a,b), as illustrated in Figure 1.3.

Therefore, the role of physicochemical–biological interfacial interactions in controlling the transformation, transport, fate, and toxicity of metals and metalloids in soil and surrounding environments, especially the rhizosphere, which is the bottleneck of contamination of the terrestrial food chain, deserves increasing attention. In this chapter we present an overview of this emerging and extremely important area of science, to advance our knowledge of the interface between physicochemical and biological reactions and processes in the environment.

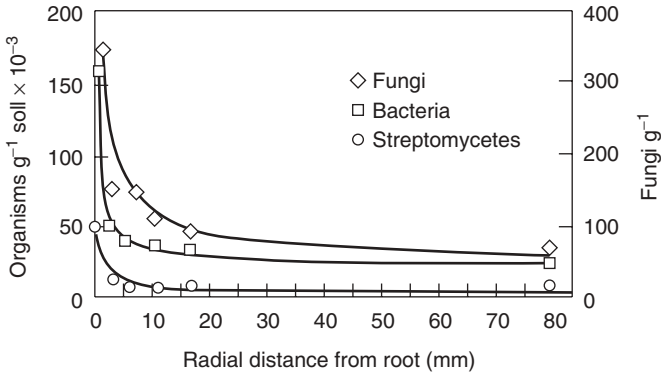


Figure 1.2. Distribution of organisms with distance from the roots of 18-day-old lupin (*Lupinus angustifolius* L.). (From Rovira and Davey, 1974.)

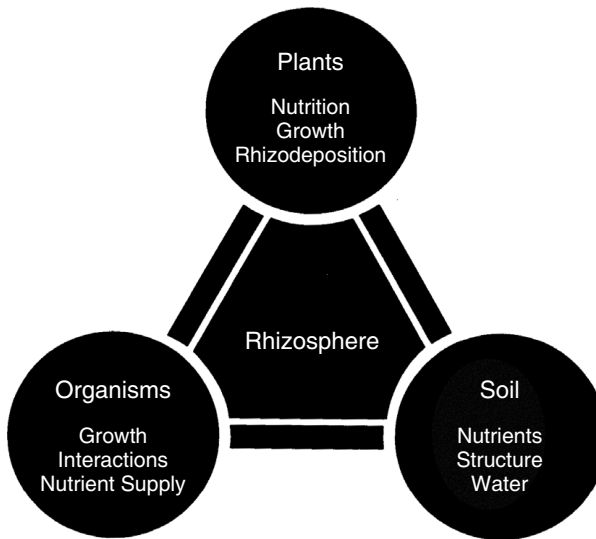


Figure 1.3. Rhizosphere trinity. The total rhizosphere environment is determined by an interacting trinity of the soil, the plant, and the organism associated with the roots. (From Lynch, 1990a.)

1.2. MINERAL–ORGANIC MATTER–MICROORGANISM INTERACTIONS IN SOIL ENVIRONMENTS

Interactions of soil minerals with organic matter and microorganisms exert a vital role in the formation of short-range-ordered metal oxides, humic substances, mineral colloid–humic complexes, aggregates, and the structure and porosity of soils. These nonliving and living reactive components and the structural stability

and associated nanoporosity of soils control the transformation, transport, fate, and toxicity of metals and metalloids in the environment.

1.2.1. Formation of Short-Range-Ordered Metal Oxides

Short-range-ordered Al and Fe oxides, especially nanoparticles, are indeed among the most reactive components of acidic and neutral soils (Bigham et al., 2002; Huang et al., 2002). In addition to humic substances, biomolecules, which are present in root exudates, microbial metabolites, and decomposition products of biological tissues play a very significant role in influencing the formation and transformation of these metal oxides and the resulting alteration of their surface properties pertaining to the speciation, transport, fate, and toxicity of metals and metalloids in soil environments (Huang and Violante, 1986; Schwertmann et al., 1986; Sposito, 1996, 2004; Huang and Wang, 1997; Huang et al., 2002; Violante et al., 2002; Huang, 2004). Details of this issue are treated by Violante et al., in Chapter 5.

As the third most abundant element on Earth's surface (after O and Si), Al is a major element in all mineral soils. There are only a few crystalline Al oxides, hydroxides, or oxyhydroxides, and only one, gibbsite, occurs to any great extent in soils. Aluminum, however, also forms a series of highly reactive soluble species and poorly crystalline to noncrystalline mineral colloids (Figure 1.4). The mode depicted in the figure incorporates multiple reaction paths. Reaction path I is believed to be common when systems are neutralized rapidly within seconds or hours. Under these conditions, little or no Al_{13} polynuclear species $[AlO_4Al_{12}(OH)_{24}(H_2O)_{7+}]^{12}$ forms; the formation of $Al(OH)_3$ nuclei is rapid, and gibbsite appears within days or weeks of aging. Reaction paths II and III both involve the formation of Al_{13} . Reaction path II is applicable when systems are neutralized relatively slowly compared with reaction path I. The individual Al_{13} ions can remain in solution for months to years, but eventually they transfer by one of the three pathways. If no Al_{13} nuclei are present, the soluble Al_{13} ions can slowly dissociate into Al^{3+} ions and deposit onto $Al(OH)_3$ nuclei (path IIa). These soluble Al_{13} may also aggregate and form Al_{13} nuclei (path IIb). If some Al_{13} nuclei are already present, the remaining Al_{13} ions can be deposited on them within weeks and months (path IIc). Path III is applicable when Al_{13} forms under conditions that promote the rapid formation of Al_{13} aggregates via an anion bridging mechanism (i.e., outer-sphere associations). These aggregates rearrange themselves rapidly into Al_{13} nuclei. The Al_{13} nuclei in paths IIb, IIc, and III then transform into a poorly ordered phase, microcrystalline boehmite (pseudoboehmite), which then transforms into gibbsite. The relative importance of each pathway depends greatly on reaction conditions. These soluble Al species and poorly ordered to noncrystalline Al species formed in the reaction pathways are highly reactive and thus important in influencing reactions and processes in the environment. The transformation of Al via the various pathways described above are strongly influenced by the nature and concentration of solution inorganic and organic ions and solid-state ions such as clay minerals and humic substances

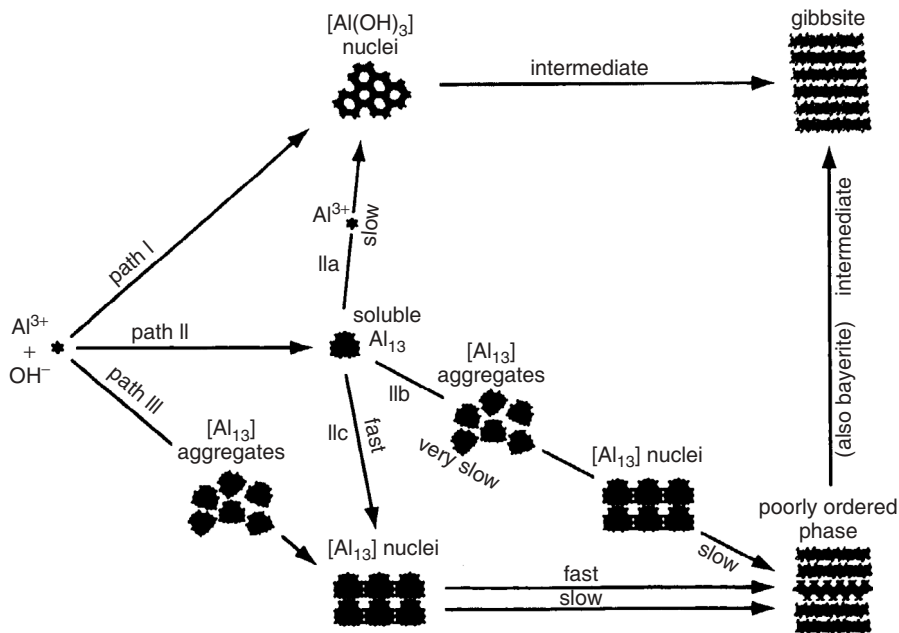


Figure 1.4. Reaction scheme proposed for Al hydroxide mineral formation from hydrolyzed Al solution. (Modified from Bertsch and Parker, 1996; Huang et al., 2002.)

(Huang and Violante, 1986, Huang, 1988; Bertsch and Parker, 1996; Krishnamurti et al., 1999, 2004; Huang et al., 2002).

Organic substances such as fulvic acid (FA) and humic acid (HA) and many low-molecular-mass organic acids (LMMOAs) form stable complexes with Al and disrupt the crystallization of Al hydroxides and thus promote the formation of short-range-ordered (SRO) Al hydroxides (Kwong and Huang, 1975, 1979a,b, 1981; Lind and Hem, 1975; Kodama and Schnitzer, 1980; Violante and Huang, 1985; Singer and Huang, 1990; Violante et al., 2002; Colombo et al., 2004). Organics greatly influence the surface properties of Al transformation products. For instance, the presence of organic acids during aging of Al hydroxide gels for 40 days increases the specific surface of the precipitation products up to 30-fold over that of the control and higher acid concentrations results in higher specific surfaces (Table 1.1). The surface charge characteristics of the precipitation products are also altered dramatically (Figure 1.5). These SRO transformation products of Al should thus exert substantial influence on the adsorption–desorption, transformation, and dynamics of metals and metalloids in the environment.

Interactions of soil minerals with organic substances and microorganisms have a great impact on the formation and transformation of SRO Fe oxides (Schwertmann et al., 1986; Cornell and Schwertmann, 2003). Microorganisms may influence Fe transformation through reduction and oxidation reactions. Soil