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Book Review

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

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Wiley- IUPAC Series on Biophysico-Chemical Processes in Environmental Systems, P. M. Huang and N. Senesi, Series Editors.
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Soil pollution is one of the most relevant phenomena, which is mainly result of anthropogenic activity, also cumulating the pollutant from air and water through dry and wet deposition.

Pollution induced by heavy metals and metalloids in soil 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 potentially toxic elements to plants and other living organisms can be involved in chemical and biological reactions, such as solution and surface complexation, precipitation, sorption-desorption, oxidation-reduction. In addition, these elements interact with soil components (minerals, humic substances, metal oxides, microorganisms, extracellular enzymes, biopolymers, ligands, depending on physico-chemical and biological conditions in the soil.

Biogeochemical processes from soils affect the fate behaviour and bioavailability of metals and metalloids in soils.

The book reveals the importance of biophysico-chemical processes of metals and metalloids in soil environments.

This work is the result of the contribution of a multidisciplinary group of soil and environmental scientists and offers to the scientific community 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 the first volume of a newly created Wiley-IUPAC Series. In contrast with classical books focused on separate physical and biological processes, the present book integrates the frontiers of knowledge on both fundamentals and practical aspects on interactions of physical, chemical and biological processes, in relation with transformation, transport, bioavailability, toxicity of metals and metalloids in soil environments.

The book is structured into three parts, each of them including some chapters, written by specialists which provide the scientific community with a critical evaluation of various aspects of the book topics.

Part I, "Fundamentals of biotic and abiotic interactions of metals and metalloids with soil components" contain six chapters, which deal with:

- impact of phyico-chemical-biological interactions on metals and metalloid transformations in soils;
- transformation and mobilization of metals, metalloids and radionuclides by microorganisms;
- kinetics and mechanisms of sorption-desorption in soils;
- spectroscopic techniques for studying metal-humic complexes in soil;
- factors affecting the sorption-desorption of trace elements in soil;
- modeling adsorption of metals and metalloids by soil components.

Chapter 1, written by P.M. Huang, presents an overview on role of physicochemical-biological interfacial interactions in controlling the transformation, transport, fate and toxicity of metals and metalloids in soil and surrounding environments, especially rhizosphere, considered to be the terrestrial food chain. The analysis considers all these aspects as an emerging and important area of science and approaches them to advance the knowledge of the interface between physicochemical and biological reactions and processes in the environment, which are not independent but rather, interactive with each other. These interactions govern the mechanism of transformations, speciation, dynamics, bioavailability, toxicity and fate of metals and metalloids in soil and related environments.

A special attention is done to mineral-organic-microorganisms interactions in soil environment which involve formation of short-range-ordered metal oxides, formation of humic substances and organomineral complexes, formation of aggregates and the relation with porosity. Other issues envisage: solution complexation reactions, oxidation reactions, sorption-desorption reactions and precipitation dissolution reactions of metals and metalloids, microbe mediated metal and metalloids release from soil particles, microbial sorption and uptake of metals and metalloids, biomineralization of metals and metalloids and fine-grained mineral development. Also, impacts on the terrestrial ecosystems are evaluated considering global ion cycling, geomedical problems, ecotoxicological problems, biodiversity, risk assessment, management and restoration of soil environment.

Chapter 2, authored by G. M. Gadd outlines some aspects of the transformation and mobilization of metals by microorganisms in relation to the soil environment, and evidences that metal-microbe interactions are important in several soil contexts, in the biogeochemical cycling of metals, associated elements and nutrients and plant productivity. These interactions are also important for many natural microbial and microbe-plant processes, in the area of bioremediation. It is highlighted that laboratory and short-term field experimentation may provide extensive information on changes in metal speciation, microbial communities, soil structure and composition. The author outline the major mechanisms by which microorganisms can affect metal transformation and draw attention to their significance in the soil, especially regarding metal mobility, biogeochemical cycling and plant nutrition and remediation technologies for contaminated habitats.

Chapter 3, written by M. J. Borda and D. L. Sparks put together some of the results reported in the recent literature on sorption-desorption to establish the state of the art and the future experimental challenges that face scientists working in the research area.

The authors focus on the limitations of equilibrium-based approaches in understanding systems that are kinetically controlled and the importance of using and developing techniques able to assess sorption-desorption reactions at high spatial and temporal resolution. The current methods for assessing sorption-desorption are discussed, including macroscopic and molecular-scale approaches leading to a new description of soil chemical processes.

Chapter 4, (authors: N. Senesi and E. Loffredo) develops some analysis on spectroscopic techniques for studying metal-humic complexes in soil. First, complexation capacity, stability constants, modeling and models are discussed as preliminary knowledge in the application of spectroscopic techniques to study metal-humic complexes in soils. Then, some techniques are approached: ultraviolet-visible spectroscopy, fluorescence spectroscopy, infrared spectroscopy, electron spin resonance or electron paramagnetic resonance spectroscopy, Mössbauer spectroscopy, nuclear magnetic resonance, synchrotron-based X-ray absorption spectroscopy. Also, a variety of separation and non-separation methods are shortly presented, which have been used to speciate metal ions in the presence of humic substances (HS), assess complexity of HS and calculate conditional stability constants and quotients of metal-HS complexes.

Chapter 5 (authors: A. Violante, G. S. R. Krishnamurli, M. Pigna) provides information on the current state of knowledge about the factors that affect the mobility of trace elements in soil environments. Special attention is given to the influence of inorganic and organic ligands, including nutrients and root exudates, on the sorption-desorption processes of trace elements in cationic and anionic forms on or from soil components is affected by many factors such as pH, nature of the sorbents, redox reactions, presence and concentration of organic and inorganic ligands, including humic and fulvic acids, root exudates and nutrients.

Also, sorption of trace elements onto soil components is analyzed considering trace elements in cationic form as well as in anionic form. Desorption of trace elements is discussed based on desorption kinetics and bioavailability, effect of residence time on desorption.

Chapter 6 (authors: S. Goldberg and L. J. Griscenti) presents several of the most common models applied for describing metal and metalloid ions adsorption by soil components.

It describes empirical models used in soil chemistry, together with their limitations. Also, chemical models used to describe metal adsorption on soil minerals are presented and their advantages over empirical models are discussed.

Methods for establishing adsorption mechanisms and surface speciations are analyzed, as well as the limitations and approximations in the application of chemical models to natural systems.

Part II, "Transformations and dynamics of metals and metalloids as influenced by soil-root-microbe interactions" include four chapters, which provide information on:

- biochemistry of metals and metalloids at the soil-root interface;
- biogeochemical process controlling the cycling of arsenic in soils and sediments,
- microbial oxidation and reduction of iron in the root zone and influences on metal mobility;
- the complexity of aqueous complexation: the case of aluminium – and iron III – cetrate.

Chapter 7 (authors: P. Hinsinger, F. Courchesue) define the spatial and temporal characteristics of the rizosphere and relate these to major physical processes that govern the transport of water and trace elements at the soil-root interface. Various types of biogeochemical gradients that occur in the rizosphere are covered, such as: elemental concentration, pH, pCO_2, pO_2, redox potential, organic ligand concentrations, which alter the speciation and ultimately determine the mobility and bioavailability of heavy metals and metalloids at soil-root interface. The direct role of plant roots are focused as well as the role of rhysosphere microorganisms, including symbionts (mycorrizal fungs).

Some of the key terms and concepts are defined and presented in an attempt to establish their meaning and to acknowledge the range of meanings available in the scientific literature.

Chapter 8, authors: S. Fendorf, M. J. Herbel, K. J. Tufans, B. D. Kocar, focuses on biogeochemical processes controlling the cycling of arsenic in soils and sediments. Arsenic retention on soil solids is critical for regulating the dissolved concentrations of this hazardous element, thus helping to limit its exposure to living organisms and migration within environment. In the chapter content, some fundamental aspects on processes controlling the cycling of arsenic in soils and sediments are analyzed: aqueous chemistry of arsenic, arsenic retention in soils and sediments (adsorption processes, precipitation of arsenic phases), desorption of arsenic in soils and sediments (ion displacement, desorption of arsenite compared to desorption of arsenate), biogeochemical processes (arsenate reduction – detoxification and respiration, arsenic desorption on anaerobiosis (desorption on metal reduction and desorption on iron and arsenic reduction).

Chapter 9, written by: S. C. Neubauer, D. Emerson and J. P. Megonigal, focuses on the physiology, ecology and biogeochemistry of the aerobic and anaerobic microbes involved in the rhisosphere of wetland plants. The wetland rhisosphere is considered as an interface between oxic and anoxic environment, so that it is a site where microbial reactions can cycle iron between oxidized and reduced forms. The sequestration of metals and metalloids can reduce the availability of the potentially toxic elements (Cr, Pb, Cu, Zn, As, Si). Microbial processes help iron cycle rapidly between oxidized and reduced forms, but the role of microbes in the exchange of elements between iron plaque and soil has not received sufficient study. There are many important yet unanswered questions about the role that microbes play in plant-microbe-soil systems to influence the transformation and distributions of metals and metalloids.

Chapter 10 (author: M. E. Essington) examines citrate aqueous metal complexation, with specific emphasis on the complexation of Fe (III) and Al. Citrate is a naturally occurring ligand, with a widespread occurrence in nature. It is a chelate exuded by plant roots and having the effect of enhancing the phytoavailability of Fe, while detoxifying Al. The chapter content brings into question the ability to predict the influence of citrate, on the soil chemistry of metals. Chemical models of metal-citrate aqueous complexation are studied: aluminium – citrate interactions (Öhman model, Motekaotis and Martell model, Gregor and Powell model, Venturimi and Berthon model, Harris model, Lakatos model and related spectroscopic studies, Essington model). Also, iron (III) – citrate interactions are analyzed based on several models (Field, Königsberg, Essington). It is concluded that, at present, the most appropriate mechanism for predicting the impact of citrate on Al and Fe(III) aqueous speciation is to select a specific chemical model and employ the model unmodified.

Part III, "Speciation mobility and bioavailability of metals and metalloids and restoration of contaminated soils" contains five chapters which examine fundamentals and applications in the field of mobility and remediation of contaminated soils:

- chemical speciation and bioavailability of trace metals;
- fractionation and mobility of trace elements in soils and sediments;
- sources and mobility of metallic radio-nuclides in soil system;
- remediation of metal-contaminated soils;
- phosphate-induced lead immobilization in contaminated soils (mechanism, assessment, field application).

Chapter 11, (authors: G. S. R. Krishnamurti, R. Haidu) refers to chemical speciation and bioavailability of trace metals, since the mobility, bioavailability and toxicity of chemicals depend not simply on their concentration but critically, on their form. Classical speciation based on thermodynamic models and solution speciation is discussed.

Speciation and bioavailability from the basis of any risk assessment and risk-based management process. The lack of appropriate techniques t estimate this parameters can lead to significant difficulty in setting up of policies on contaminated site management and remediation.

Chapter 12, written by P. S. Fedotov and M. Miro, details the fundamental principles of equilibrium-based sequential extraction. The ability to elucidate soil-phase associations for trace elements is discussed in detail, as is their adaptability for testing the accessibility of anionic species (metalloid compounds from targeted soil – sediment compartments). Special emphasis is paid to relevant aspects for appropriate sampling and sample preparation which might affect the quality of fractionation result. Novel techniques for in-situ sampling of soil solution directly from the solid substrate with minimum disturbance of the sampling site are also addressed.

Chapter 13, (authors: S. Staunton, C. S. Haudin, G. Wang, G. Shaw) illustrates some similarities and differences between the behaviour of metallic radionuclides and other metals in soil systems. It also summarizes some basic principles to show the hazards associated with radionuclides give a brief inventory of the metals that may exist in soil system and also a concise description of the behaviour of some of the more common and most widely studied radioactive metals.

Chapter 14, written by: M. Gräfe and R. Naidu, is an overview on the remediation of metal contaminated soils. Depending on the severity of contamination, heavy metals could be extremely toxic to both the environment and human health. A number of physical, chemical and biological technologies have been developed to remediate metal – contaminated soils. The remediation technologies discussed in this chapter refer to: biological technologies (bioremediation, phytoremediation), chemical technologies (electrokinetics, in situ soil flushing, monitored natural attenuation, solidification and stabilization, permeable reactive barriers, soil washing), physical technologies (in situ capping, excavation, soil mixing), thermal technologies (incineration, vitrification).

Major challenges for the remediation of metal-contaminated soils are highlighted.

Chapter 15, (authors: R. Melamed, L. Q. Ma) review current knowledge on the mechanisms and assessment of P-induced Pb immobilization in situ and water. Mechanisms include sorption, cation substitution, chemical precipitation which may occur simultaneously and/or sequentially. Field application of P amendments in a Pb-contaminated soil is also addressed. The information gathered should be useful for field application of this in situ remediation technology.

The complexity of kinetics in various systems was discussed and the data shown encourage further research to identify the reactions occurring in the system.

Each chapter ends with a comprehensive list of References.

Considering the whole content and information included, this book can be used as an advanced reference book on biophysico-chemical processes of metals and metalloids in soils and related environment for students and scientists.

It can be a very useful guide to the PhD students and scientists interested in environmental science and engineering, soil chemistry, mineralogy, biochemistry and microbiology as well as plant nutrition and physiology in relation with soil and biophysico-chemical processes.

Finally, the book is “an authoritative, core reference … on soil contamination by heavy metals and metalloids

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