

Jianming Xu
Pan Ming Huang
Editors

Molecular Environmental Soil Science at the Interfaces in the Earth's Critical Zone



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With 132 figures

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Preface

Resource depletion and environmental problems are challenging the world for its sustainability. The theme of the International Symposium of Molecular Environmental Soil Science at the Interfaces in the Earth's Critical Zone (ISMESS) is of special significance for understanding environmental pollution and global change processes. The Critical Zone (CZ) is the system of coupled chemical, biological, physical, and geological processes operating together to support life at the Earth's surface. Further advance on the frontiers of knowledge on this subject matter requires scientists to cross disciplines and scales to integrate understanding of processes in the CZ, ranging in scale from the environmental mineral-organism-humus-water-air interfaces to the impact on the globe and humankind. These fundamental interactive processes in the CZ have an enormous impact on ecosystem productivity, services, and integrity, and on human welfare.

Carbon is a major component of soils. Globally, the mass of soil organic carbon is more than that of carbon in living matter and in the atmosphere combined. However, the CO₂ emission from the soil to the atmosphere is the primary mechanism of soil carbon loss. Agricultural practices and land use conversion contribute substantially (approx. 32%) to the total anthropogenic CO₂ emission. Soil organo-mineral-microbe interactions affect carbon turnover and sequestration. Our understanding of the role of mineral colloids in carbon transformation, dynamics, and sequestration in the environment would contribute to developing innovative management strategies to minimize its impact on climate change.

The interfacial interactions at the soil-plant(root)-microbe interface (rhizosphere) profoundly affect the physicochemical and biological processes such as transformation, fate, and toxicity of heavy metals and organic pollutants. Microbial population in the rhizosphere can be 10~100 times larger than the population in the bulk soils. Therefore, the rhizosphere is bathed in root exudates and microbial metabolites and the chemistry and biology at the soil-root interface is governed by biotic (plant roots, microbes) and abiotic (physicochemical reactions) interactions, and thus differs significantly from those in bulk soil. Little is known about the physicochemical and biological interfacial interactions in the rhizosphere, especially at the molecular level. The dynamics, transformations, bioavailability, and toxicity of metal pollutants and anthropogenic organics should be influenced enormously by the chemistry and biology of the rhizosphere.

Nanoparticles are discrete nanometer (10⁻⁹ m) scale assemblies of atoms. A significant fraction of atoms are exposed on surfaces rather than contained in the particle interior of nanoparticles. The biogeochemical and ecological impacts of nanomaterials are some of the fastest growing areas of research today, with not only vital scientific but also environmental, economic, and societal consequences. Little is known about the distribution, formation, transformation, structural and surface chemistry of environmental nanoparticles and their biogeochemical and ecological impacts.

Material cycling and energy flow processes are affected both by abiotic and biotic factors, which affect ecosystem integrity and the environmental quality. However, there are great knowledge gaps on how and to what extent the processes are affected by the interfacial interactions of environmental nanoparticles, especially at the molecular level. The research on this subject matter should, therefore, be an issue of intense interest on a global scale for years to come.

The objective of this symposium is to provide a forum for the interactions and communication of soil chemists, mineralogists, microbiologists, and physicists with allied scientists including pure chemists, biologists, environmental scientists, ecologists, and ecotoxicologists to address the current state-of-the-art on "Molecular Environmental Soil Science". The main sessions of the symposium were: 1) The Role of Mineral Colloids in Carbon Turnover and Sequestration and the Impact on Climate Change; 2) Biogeochemical Interfacial Reactions and the Transformation, Transport and Fate of Vital and Toxic Elements; 3) Anthropogenic Organics, Crop Protection and Ecotoxicology; 4) Environmental Nanoparticles: Distribution, Formation, Transformation, Structural and Surface Chemistry, and Biogeochemical and Ecological Impacts; and 5) Environmental Processes & Ecosystem Health. Two eminent scientists of the International Union of Pure and Applied Chemistry (IUPAC)

were invited to serve as Plenary Lecturers (IUPAC Lecturers) and 18 world renowned leading scientists were invited to give lectures in the 5 sessions of the symposium.

The symposium was held in Zhejiang University, Hangzhou, China on October 10-14, 2009. Zhejiang University, founded in 1897, is a key comprehensive university whose academic and research endeavors cover eleven disciplines, namely philosophy, literature, history, education, science, economics, law, management, engineering, agriculture and medicine. The University now has 112 specialties for undergraduate studies, and it is entitled to confer masters degrees in 317 programs and doctoral degrees in 283 programs. Under its administration there are 14 National Key Laboratories, 2 National Engineering Research Centers and 3 National Engineering Technology Centers. Besides, it has set up 35 national key specialties and 43 post-doctor stations. Soil Science in Zhejiang University is the National Key Discipline of China.

The participants of this symposium represent five continents: Asian delegates from China, Iran, Pakistan, Vietnam, D.P.R. Korea and R.O. Korea; European scientists from Austria, Belgium, France, Italy, the UK, Russia and Spain; Australasian participants from both Australia and New Zealand; delegates from the USA, Canada and Brazil in the Americas; and representatives from Egypt, Kenya and South Africa on the African continent.

It is the first time to hold such an international symposium in China. The IUPAC Project Committee has contributed to funding the symposium under the program for conferences on New Directions in Chemistry. The Project Committee noted that the Conference identifies, and builds on, the need to view and understand the CZ at the molecular level. It will provide a novel interface that will facilitate the integration of contributions from traditionally separate disciplines. It will add a molecular and nanoparticle dimension to a field of endeavor that has traditionally been viewed on a different scale (dimension). It will identify and focus on emerging challenges for research that will be predominantly cross-discipline in nature. It will help to secure the appreciation of the relevance of chemistry to this field that is of utmost importance to sustain humankind. Therefore, it is hoped that the symposium would lead to identification of gaps in knowledge and as such to provide future research directions and promote research on soil processes at the interfaces at the molecular level in the Earth's Critical Zone. It is expected to advance the frontiers of knowledge on biophysico-chemical processes in soil and related environmental systems and their biogeochemical and ecological impacts and also to promote education in this extremely important and challenging area of science for years to come.

The book of proceedings is composed of extended abstracts that present new ideas, methods, findings, and experiences on the 5 sessions of the symposium. All the extended abstracts have been subject to peer review by external referees, by International Scientific Committee members of the symposium, and by the editors of the proceedings. On behalf of the Organizing Committee, we would like to thank members of the International Scientific Committee and the authors for their invaluable collaboration. Special thanks are extended to our sponsors: The International Union of Soil Sciences, The International Union of Pure and Applied Chemistry, Organization for the Prohibition of Chemical Weapons, National Natural Science Foundation of China, Soil Science Society of China, Y.C. Tang Disciplinary Development Fund, Zhejiang University, Zhejiang Provincial Natural Science Foundation of China, and Zhejiang Provincial Key Laboratory of Subtropical Soil and Plant Nutrition. Valuable personal time of Mr. Jianjun Wu, Dr. Yan He, concerning the careful revising, typesetting and proof-checking of this book is also greatly acknowledged.

Dr. Jianming Xu
Chair of the Organizing Committee
ISMESS 2009

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Co-Chair of the Organizing Committee
ISMESS 2009

August 2009

Contents

Plenary Lectures by IUPAC Scientists (1)

Advances in the Use of Synchrotron Radiation to Elucidate Environmental Interfacial Reaction Processes and Mechanisms in the Earth's Critical Zone

Donald Lewis Sparks (3)

Microbial Role in Global Biogeochemical Cycling of Metals and Metalloids at the Interfaces in the Earth's Critical Zone

Geoffrey Michael Gadd (5)

Session 1 The Role of Mineral Colloids in Carbon Turnover and Sequestration and the Impact on Climate Change (9)

Soils as Source and Sink of Environmental Carbon Dioxide

Rattan Lal (11)

Impacts of Mineral Colloids on the Transformation of Biomolecules and Physical and Chemical Protection of Soil Organic Carbon

Pan Ming Huang † (13)

Unravelling the Biogeochemical Cycles of Carbon and Nutrients in Forest Ecosystems: Innovative Approaches with Advanced Stable Isotope and NMR Techniques as well as Soil Chemical and Physical Methods

Zhihong Xu (17)

Effects of Soil Management from Fallow to Grassland on Soil Microbial and Organic Carbon Dynamics

Yuping Wu, Sarah Kemmitt, Jianming Xu, Philip C Brookes (20)

Effect of Long-term Fertilization on the Sequestration Rate of Physical Fractions of Organic Carbon in Red Soil of Southern China

Minggang Xu, Xiaogang Tong, Xiujun Wang (23)

Abiotic Catalysis of the Maillard and Polyphenol-Maillard Humification Pathways by Soil Clays from Temperate and Tropical Environments

Ailsa Ghillaine Hardie, James Joseph Dynes, Leonard Myrell Kozak, Pan Ming Huang † (26)

Effect of Organic Matter Application on CP-MAS-¹³C-NMR Spectra of Humic Acids from a Brown Soil

Sen Dou, Kai Li (29)

The Composition and Organic Carbon Distribution of Organo-mineral Complex in a Black Soil as Influenced by Land-use Change and Long-term Fertilization

Xiaozeng Han, Xueying Hou, Haibo Li (32)

Characterization of Dissolved Organic Matter Derived from Rice Straw at Different Decay Stages

Hualin Chen, Jiangmin Zhou (35)

Organic Fertility of Severely Eroded Soils: Effect of Organic and Inorganic Fertilization and Cropping Patterns

Wiqar Ahmad, Farmanullah Khan, Muhammad Naeem (38)

Session 2 Biogeochemical Interfacial Reactions and the Transformation, Transport and Fate of Vital and Toxic Elements (41)

- Role of Biomolecules in Influencing Transformation Mechanisms of Metals and Metalloids in Soil Environments
Antonio Violante (43)
- Biogeochemical Processes of Arsenic in Paddy Soils
Yongguan Zhu, Wenju Liu, Guilan Duan, Paul Williams, Guoxin Sun (47)
- Soil Microorganism-mineral-organic Matter Interactions and the Impact on Metal Mobility
Jacques Berthelin (49)
- Rhizosphere Processes and Management for Improving Nutrient Use Efficiency and Crop Productivity
Fusuo Zhang, Jianbo Shen, Jingying Jing, Long Li, Xinpeng Chen (52)
- Effect of Soil Hg Stress on Expression of Heat Shock Protein Gene in Springtail *Folsomia Candida*
Yurong Liu, Yuanming Zheng, Yu Da, Jizheng He (55)
- Antimony, Arsenic and Other Toxic Elements in the Topsoil of an Antimony Mine Area
Xiangqin Wang, Mengchang He, Jianhong Xi, Xiaofei Lu, Jun Xie (58)
- Microcalorimetric and Potentiometric Titration Studies on the Adsorption of Copper by *P. putida* and *B. thuringiensis* and Their Composites with Minerals
Linchuan Fang, Peng Cai, Pengxiang Li, Wei Liang, Qiaoyun Huang (62)
- Sorption, Transformation and Migration of Zn in Some Soils with Percolated Water Regime
Galina Vasilievna Motuzova, Natalia Jurievna Barsova (66)
- Speciation and Biochemical Transformations of Sulfur and Copper in Rice Rhizosphere and Bulk Soil—XANES Evidence of Sulfur and Copper Associations
Huirong Lin, Jiyan Shi, Bei Wu, Jianjun Yang, Yingxu Chen, Yidong Zhao, Tiandou Hu (69)
- Population Dynamics of Ammonia Oxidizing Bacteria and Archaea and Relationships with Nitrification Rate in New Zealand Grazed Grassland Soils
Hong Jie Di, Keith C. Cameron, Jupei Shen, Jizheng He, Chris S. Winefield, Maureen O'Callaghan, Saman Bowatte (72)
- Plant Clonal Systems as a Strategy for Nitrate Pollution Removal in Cold Latitudes
Derong Lin, Lijiang Hu, Hong You, Dipayn Sarkar, Baoshan Xing, Kalidas Shetty (75)
- Effect of Ionic Strength on Specific Adsorption of Ions by Variable Charge Soils: Experimental Testification on the Adsorption Model of Bowden *et al.*
Renkou Xu, Jun Jiang, Cheng Cheng (78)
- Estimation of the Electrostatic Repulsive Force among Charged Clay Particles in Aqueous Systems
Hang Li, Jie Hou, Xinmin Liu (81)
- Kinetics of As(III) and Cr(III) Oxidation by OH-birnessites with Various Average Oxidation States (AOSs)
Xionghan Feng, Jiali Xu, Fan Liu, Wenfeng Tan (85)
- Adsorption/Desorption Kinetics of Zn in Soils: Influence of Phosphate
H. Magdi Selim, Keli Zhao, Lixia Liao, Jianming Xu (88)
- Bioavailability and Redistribution of Trace Metals in Soil Washed with a Sulfosuccinamate Formulation
Maria del Carmen Hernández-Soriano, Aránzazu Pea, Maria Dolores Mingorance (91)
- Fractions of Cd, Zn and Their Correlation with Soil Black Carbon in Contaminated Soils Affected by a Smelting Furnace
Ling Liu, Na Li, Longhua Wu, Zhu Li, Jinping Jiang, Yugen Jiang, Xiya Qiu, Yongming Luo (94)
- Formation of the Metal Complexes between Protoporphyrin IX and Divalent Metal Cations in the Environment
Chi-In Jung, Jeong-Im Yang, Chul-Ho Park, Jee-Bum Lee, Hyoung-Ryun Park (97)

- The Impact of Urban Activities on Heavy Metal Distribution and Bioavailability Index in Selected Tropical Urban Soils
John Onam Onyatta, Charles Kibii Chepkwony, Peter Olengo Ongoma (100)
- Nitrate Accumulation as Affected by Nitrogen Fertilization and Foliar Application of Micronutrients in Rocket Plant
Ayman Mohamed El-Ghamry (103)
- Fractions of Heavy Metals in Paddy Fields and Their Spatial Relationship to Rice Plant
Keli Zhao, Xingmei Liu, Jiachun Shi, Jianming Xu (110)
- Competitive Sorption of Nickel and Cadmium in Soils
Lixia Liao, Amitava Roy, Gregory Merchan, H. Magdi Selim (112)
- Interaction Effect between P and K Fertilization on Faba Bean Plant (*Vicia faba* L.) Grown under Salt Affected Soils
Mohamed Rida Abd EL-Hady Mohamed Ebrahim, Adel Mohamed Abd EL-Hameed Abd EL-Mohsen (115)
- Design of a POSS-modified Zeolite Structure and the Study of the Enhancement of Ammonia-nitrogen Removal from Drinking Water
Derong Lin, Lijiang Hu, Qun Zhang, Hong You (118)
- Study on Immobilizing Soil Exogenous Lead Using Phosphate Rock
Guanjie Jiang, Hongqing Hu, Yonghong Liu, Chang Yang, Haizheng Yang (121)
- Long-term Fertilizer Application Alters the Balance and Vertical Distribution of Phosphorus in a Calcarosol
Dang Thanh Vu, Caixian Tang, Roger Armstrong (124)
- Nitrate Nutrition But Not Rhizosphere pH Enhances Zinc Hyperaccumulation in *Thlaspi caerulescens* (Prayon)
Alison C Monsanto, Gaelle Ng Kam Chuen, Yaodong Wang, Caixian Tang (127)
- Adsorption of Phosphate and Arsenate on New Al₁₃-Oxalate Precipitate: Spectroscopic and Macroscopic Competitive Adsorption Investigations
Jing Liu, Fenghua Zhao (130)
- Short-term Changes of pH Values and Aluminium Activity in Acid Soils after the Application of Nitrogen Fertilizers
Hejie Pi, Qingru Zeng, Zhaohui Jiang, Jianyu Liao, Xiaoyou Feng, Yulin Sun (134)
- Transformation of Nitrogen and Its Effects on Metal Elements by Coated Urea Application in Soils from South China
Zhaohui Jiang, Qingru Zeng, Hejie Pi, Bohan Liao, Xiaoyou Feng, Yulin Sun (137)
- Impacts of Copper on Rice Growth and Yield as Affected by Pig Manure
Jianjun Wu, Xiuling Yu, Zaffar Malik, Hao Chen, Jianming Xu (141)
- The Effects of Several Amendments on Forms of Lead and Its Uptake by Two Cultivars of *Brassica Chinensis* in an Acid Red Soil
Xia Li, Jiachun Shi, Jianming Xu, Jianjun Wu (144)
- Does Iron Plaque Improve the Uptake and Translocation of Lead by Broad-leaf Cattail in Lead-contaminated Soils
Shunqin Zhong, Jianming Xu, Jiachun Shi, Jianjun Wu (148)
- The Influence of Zn²⁺ and Mn²⁺ on Pb²⁺ Adsorption Behaviors of Birnessite
Fan Liu, Wei Zhao, Wenfeng Tan, Xionghan Feng (151)
- Removal of Arsenite in Water Using Biogenic Schwertmannite as Adsorbent
Yuehua Liao, Jianru Liang, Lixiang Zhou (154)
- Wien Effect Measurements in Soil Colloidal Suspensions: A Novel Method for Characterizing the Interactions between Charged Particles and Counter Ions
Yujun Wang, Dongmei Zhou, Chengbao Li, Haowen Zhu, Wei Wang, Jun Zhou (157)
- Can Zn, Ca and Sulfate Amendments Affect Cadmium Uptake in Rice (*Oryza sativa* L.)
Linfei Hu, Jianming Xu, Jianjun Wu, Murray B. McBride (161)

Dynamics of As Species in the Interface of Soil and Rice Roots under Three Water Regimes

Wenju Liu, Lina Chen, Ying Wang (164)

Extra Supply of Calcium Is Not Required for Maximal Root Growth in the Nitrate and Phosphorus-rich Patch in an Acid Soil

Chandrakumara Weligama, Caixian Tang, Peter W.G. Sale, Mark K. Conyers, De Li Liu (167)

Effect of Natural Acid Peat Application on the Phytoextraction of Cadmium from Contaminated Soils

Iksong Ham, Jianming Xu, Linfei Hu, Pan Ming Huang † (170)

Session 3 Anthropogenic Organics, Crop Protection and Ecotoxicology (179)

Interaction of Anthropogenic Organic Chemicals with Organic Matter in Natural Particles

Joseph J. Pignatello (181)

Decontamination of Soils through Immobilization of Anthropogenic Organics by Biotic and Abiotic Catalysts

Jean-Marc Bollag (182)

Effects of “Aging” on Bioreactive Chemical Retention, Transformation, and Transport in Soil

Hwei Hsien Cheng, William C. Koskinen (184)

Interaction of Bt toxin with Organo-mineral Surfaces and Consequences for Its Fate in the Environment

Nordine Helassa, Sylvie Noinville, Philippe Déjardin, Jean-Marc Jano, Hervé Quiquampoix, Siobhán Staunton (187)

Microbial and Abiotic Interactions between Transformation of Reducible Pollutants and Fe(II)/(III) Cycles

Fangbai Li, Shungui Zhou, Xiaomin Li, Chunyuan Wu, Liang Tao (190)

Assessment of Availability of Phenanthrene and Pyrene in Aging Soil

Wanting Ling, Yuechun Zeng, Yanzheng Gao, Xuezhu Zhu (193)

Levels, Distributions and Profiles of Polychlorinated Biphenyls in Paddy Fields from Two Towns in a Typical Electronic Waste Recycling Area of Eastern China

Xianjin Tang, Chaofeng Shen, Wenli Liu, Congkai Zhang, Yingxu Chen (196)

Phytoremediation of Contaminated Soils with Polycyclic Aromatic Hydrocarbons and Its Ecologically Enhanced Techniques

Shiqiang Wei (200)

The Contribution of Rhizosphere to Remediation of Polycyclic Aromatic Hydrocarbons (PAHs) and Their Toxicity in Soil: Evaluating with Sequential Extraction and Toxicity Risk

Bin Ma, Huaihai Chen, Yan He, Jianming Xu (203)

Spectral Studies of the Toxin of *Bt* Adsorbed by Minerals

Qingling Fu, Hongqing Hu, Shouwen Chen, Li Huang, Qiaoyun Huang, Tongmin Sa (207)

Genotypic Differences in Responses of Wheat (*Triticum durum*) Roots to Oxytetracycline

Zhaojun Li, Xiaoyu Xie, Alin Song, Ruihuan Qi, Fenliang Fan, Yongchao Liang (210)

Dynamics of Dissolved Organic Carbon in the Rhizosphere of Ryegrass (*Lolium multiflorum* L.) Induced by PCBs Pollution

Na Ding, Malik Tahir Hayat, Yan He, Haizhen Wang, Jianming Xu (213)

Dynamic Behavior of Persistent Organic Pollutants in Soil and Their Interaction with Organic Matter

Malik Tahir Hayat, Jianming Xu, Na Ding, Tariq Mahmood (217)

Effect of Crude Water Extract of *Fructus Gleditsiae Sinensis* on the Removal of Phenanthrene and Pyrene from Contaminated Soils

Ran Wei, Jun Wang, Hongyu Yang, Yi Chen, Peifen Liu, Jinzhi Ni (223)

Distribution Pattern, Sources and Potential Risks of Polycyclic Aromatic Hydrocarbons in Urban Soils of Fuzhou City, China

Jinzhi Ni, Xiaoyan Li, Juan Guo, Jun Wang, Hongyu Yang, Ran Wei (226)

Thermal Degradation of Chlorotetracycline in Animal Manure and Soil
Mingkui Zhang, Huimin Zhang (229)

Enhancement of Atrazine Degradation in Paddy Soils by Organic Amendments
Chaolan Zhang, Jianming Xu, Bin Yao (232)

Session 4 Environmental Nanoparticles: Distribution, Formation, Transformation, Structural and Surface Chemistry, and Biogeochemical and Ecological Impacts (241)

Soil Science at the Nanoscale: A New View of Structure, Stability, and Reactivity
Patricia A. Maurice (243)

Environmental and Colloidal Behavior of Engineered Nanoparticles
Baoshan Xing (246)

Humic Substances as Natural Nanoparticles Ubiquitous in the Environment
Nicola Senesi (249)

Degradation of Organochlorine Compounds Using Zero Valent Iron (ZVI) Nano Particles Impregnated in Hydrophobic Modified Bentonite
Sandro Froehner, M. Maceno, E.C. Da Luz, K.S. Machado, F. Falcão (251)

Effect of Electrolyte on Adsorption/Desorption of Cu^{2+} on Nano-particle Mn Oxide
Wenfeng Tan, YuanPeng Wang, Fan Liu, Xionghan Feng (255)

Sorption of Selected Organic Compounds in Two Black Carbon Particles
Yang-hsin Shih, Po-Hsin Su (258)

Adsorption and Inhibition of Butyrylcholinesterase by Different Nanoparticles
Zhenyu Wang, Kai Zhang, Jian Zhao, Fengmin Li, Dongmei Gao, Baoshan Xing (262)

Characterization of Soil Clay Minerals Using Mid-infrared Spectroscopy
Changwen Du, Guiqin Zhou, Jing Deng, Jianmin Zhou (265)

Investigation Mechanism of MTBE on Wall of Carbon Nanotube (CNT) to Other Products from Air-groundwater (in Environment): MNDO
Leila Mahdavian, Mahmoud Raouf (269)

Extraction of Nanoparticles from Argosols and Ferrosols
Wenyan Li, Jianming Xu, Pan Ming Huang † (275)

Surface and Adsorption Characteristics of Black Carbon from Different Sources
Mingkui Zhang, Zhaoyun Liu (279)

A High-resolution TEM Investigation of Nanoparticles in Soils
Rui Zhu, Shenggao Lu (282)

Adsorption and Desorption of Tylosin on the Colloidal Fractions of Black Soil
Chunhong Wang, Aifang Xue, Wei Liang, Peng Cai, Qiaoyun Huang (285)

Session 5 Environmental Processes and Ecosystem Health (289)

Spatial and Temporal Dimensions of Environmental Processes in Soils—An Integrated Approach
Winfried E.H. Blum (291)

Emission, Fate and Exposure Risk of Polycyclic Aromatic Hydrocarbons in China
Shu Tao, Yanxu Zhang (293)

How Do Microbial Extracellular Enzymes Locate and Degrade Natural and Synthetic Polymers in Soil
Richard G. Burns (294)

Influence of Solution Composition on the Exfoliation of Organic Matter from a Model Soil System	<i>Charisma Lattao, Robert L. Cook</i> (298)
Transfer of Soil Nickel to Crops in Suburban Areas and Their Healthy Risk in Fujian Province, Southeast China	<i>Dan Luo, Yanhui Chen, Guo Wang</i> (301)
Transformation Dynamics and Memory Effect of Soil Amino Sugars Amended with Available Substrates	<i>Hongbo He, Xudong Zhang</i> (304)
Evaluating the Maturity and Quality of Solid Waste Compost through Phospholipid Fatty Acid Biomarkers	<i>Ghulam Jilani, Jianming Xu, Yuping Wu, Zhongzhen Liu</i> (307)
Effects of Depleted Uranium on Soil Microbial Activity: A Bioassay Approach Using ¹⁴ C-labeled Glucose	<i>Rizwan Ahmad, David L. Jones</i> (311)
Is the Alkalinity within Agricultural Residues Soluble	<i>Clayton R Butterly, Jeffrey A Baldock, Jianming Xu, Caixian Tang</i> (314)
Soil Micro-interfaces Control the Fate of Pollutants in Soil Environment	<i>Jizheng He, Yuanming Zheng</i> (317)
Soil Microbial Biomass and pH as Affected by the Addition of Plant Residues	<i>Yunfeng Wang, Ling Zhou, Jianjun Wu, Clayton R Butterly, Caixian Tang, Jianming Xu</i> (320)
Changes of Soil Enzyme Activities in the Process of Karst Forest Degradation in Southwest China	<i>Fang Liu, Shijie Wang, Xiuming Liu, Yuansheng Liu, Jian Long</i> (323)
Effect of <i>cry1Ab</i> Gene Transformation on the Microbial Mediated Decomposition of Rice Residues under Intensive Rice Cropping System	<i>Haohao Lu, Weixiang Wu, Yingxu Chen</i> (325)
Characterization of Microbial Community and Phosphorus-releasing Bacteria in the Sediments of a Eutrophic Shallow Lake, Eastern China	<i>Yichao Qian, Yingxu Chen, Jiyan Shi, Liping Lou</i> (328)
Carbon Compounds Differ in Their Effects on Soil pH and Microbial Respiration	<i>Fatima Rukshana, Clayton R Butterly, Jianming Xu, Jeffrey A Baldock, Caixian Tang</i> (331)
Effects of Soil Water Content on Soil Microbial Biomass and Community Structure Based on Phospholipid Fatty Acid Analysis	<i>Yuping Wu, Yan He, Haizhen Wang, Jianming Xu</i> (334)
Effects of Cadmium and Mercury alone and in Combination on the Soil Microbial Community Structural Diversity	<i>Min Liao, Haijun Zhang, Shouna Yu, Chengli Chen, Changyong Huang</i> (337)
Author Index	(343)

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**Plenary Lectures by IUPAC
Scientists**

Advances in the Use of Synchrotron Radiation to Elucidate Environmental Interfacial Reaction Processes and Mechanisms in the Earth's Critical Zone

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Abstract: The employment of bright light sources generated at synchrotrons has greatly advanced our understanding of important environmental interfacial (mineral/water, mineral/microbe, plant/soil) reaction processes in the soil, environmental, and geological sciences over the past two decades. This plenary paper will provide background on principles and types of synchrotron radiation techniques with an emphasis on the use of synchrotron-based X-ray absorption spectroscopy (XAS), X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD) and microtomography to elucidate speciation of contaminants in heterogeneous soils, surface precipitation phenomena, mechanisms of rapid redox transformations, microbial transformations on mineral surfaces, air and terrestrial emanated particulate reactivity and composition, and metal reactivity and speciation in hyperaccumulator plants.

Keywords: Biogeochemical processes; Environmental interfaces; Molecular scale; Spatial and temporal scales; Surface spectroscopy

Introduction and Discussion

It has become increasingly recognized that to accurately predict and model fate/transport, toxicity, speciation, bioavailability, and risk assessment of plant nutrients, toxic metals, oxyanions, radionuclides, and organic chemicals in the Earth's Critical Zone, we must have fundamental information at multiple spatial and temporal scales, and our research efforts must be multidisciplinary and interdisciplinary. The critical zone is "the heterogeneous, near surface environment in which complex interactions involving rock, soil, water, air and living organisms regulate the natural habitat and determine the availability of life sustaining resources" (NRC, 2001). The critical zone is an interfacial region of mass and energy flux comprising terrestrial, lacustrine, and marine components of the continental crust and is one of two primary loci of life

on Earth and for most of human activity. The critical zone is comprised of an array of spatial scales, ranging from the atomic to the global, and temporal scales, ranging from seconds to eons. The physical, chemical, and biological processes within the critical zone mediate exchange of mass and energy which is required for biomass productivity, chemical recycling, and water storage. The critical zone is the most heterogeneous and abstruse portion of the entire Earth (NRC, 2001). If we are going to sustain the planet for human habitation we must understand the physical, chemical, and biological processes and reactions in the critical zone over a range of spatial and temporal scales (NRC, 2001; Hochella, 2002; Sparks, 2002).

With the advent of state-of-the-art, *in-situ*, analytical techniques, some of which are synchrotron-based (e.g., X-ray absorption spectroscopy, XAS) one can elucidate reaction mechanisms at small spatial and

rapid temporal scales. The use of small scale techniques in environmental research has resulted in a multi-disciplinary field of study that environmental and geoscientists are actively involved in-molecular environmental science. Molecular environmental science can be defined as the study of the chemical and physical forms and distribution of contaminants in soils, sediments, waste materials, natural waters, plants, and the atmosphere at the molecular level (Sparks, 2002). Since the first use of XAS in 1987 (Hayes *et al.*, 1987) to study selenate and selenite complexation at the goethite/water interface, there have been a multitude of studies using bulk XAS to determine sorption mechanisms of metal(loids) and radionuclides on mineral surfaces over a range of reaction conditions. With the development of third and fourth generation light sources that afford brighter light and greater spatial resolution, scientists are able to use micro-focused XAS and X-ray fluorescence (XRF) spectroscopy to determine the speciation, distribution, and association of contaminants at the micron scale in heterogeneous soils, biosolids, particulates, and plants. These techniques, along with synchrotron-based X-ray diffraction (XRD), microtomography, and Quick XAS, have opened up research frontiers in a number of areas that will be covered in this plenary talk including speciation of contaminants, which is essential for understanding release mechanisms, spatial resolution, chemical transformations, toxicity, bioavailability, and ultimate impacts on human health; mechanisms of microbial transformations at mineral/metal(loid) interfaces; mechanisms of rapid redox transformations, air and terrestrial emanated particulate reactivity and composition, and metal uptake and speciation in hyperaccumulator plants.

Summary and Conclusions

To successfully address and fund the major research needs in the area of environmental interfacial biogeochemistry, multidisciplinary and interdisciplinary and multifaceted approaches must be carried out. Geochemists, soil scientists, chemists, physicists, biologists, ecologists, and engineers must and will increasingly collaborate. Arguably, one of the major research leitmotifs in the 21st century will be the study of biological effects on geochemical reactions and processes at environmental interfaces in the critical zone. This provides us with a unique opportunity to combine our expertise with that of molecular biologists. We must also employ an array of multiple, molecular scale techniques over a range of temporal scales in combination with macroscopic approaches and computational modeling to solve complex scientific questions related to the Earth's environment.

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Microbial Role in Global Biogeochemical Cycling of Metals and Metalloids at the Interfaces in the Earth's Critical Zone

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Keywords: Microorganisms; Biogeochemical cycling; Metals; Metalloids; Minerals; Geomicrobiology

Microorganisms are intimately involved in many processes of fundamental importance to geology, and these include biotransformations of metals and minerals, as well as related substances like metalloids, and metal radionuclides (Gadd *et al.*, 2005; Gadd, 2007). Such processes are involved in bioweathering, mineral dissolution and formation, and soil formation and development. Integral to all mechanisms are interactions with metals, and microorganisms are intimately involved in metal biogeochemistry with a variety of processes determining mobility, and bioavailability (Gadd, 2005; 2008). The balance between metal mobilization and immobilization varies depending on the organisms involved, their environment, and physico-chemical conditions. Metal mobilization can arise, e.g. from leaching mechanisms, complexation by metabolites, and methylation where this results in volatilization. Immobilization can result from sorption, transport and intracellular sequestration or precipitation as a variety of "organic" and inorganic biominerals, e.g. oxalates (fungi), carbonates, phosphates and sulfides (Sayer *et al.*, 1999; Burford *et al.*, 2003, 2006). Sorption can be markedly affected by the presence of clay minerals, and clay mineral-biomass aggregates exhibit differing metal binding characteristics (Morley and Gadd, 1995; Gadd, 2009). This may be an important soil process as well as in epi- and endolithic microbial communities that are ubiquitous and associated with a wide variety of rocks and minerals (Burford *et al.*, 2003). In addition, reduction of higher-valency species may effect mobilization, e.g. Mn(IV) to Mn(II), or immobilization,

e.g. Cr(VI) to Cr(III).

Metal-mineral-microbe interactions can be considered an important topic within the framework of geomicrobiology, which can simply be defined as the roles of microbes in geological processes. Key topics within the geomicrobiology framework include biogeochemical cycling of the elements, mineral formation, mineral degradation (which can include such subjects as bioweathering and biocorrosion, as well as processes leading to soil and sediment formation), and the transformations of metals, metalloids and radionuclides. Apart from being important in natural environments, these processes can have beneficial or detrimental consequences in a human context. Bioremediation refers to the application of biological systems to the clean-up of organic and inorganic pollution with bacteria and fungi being the most important organisms in this context for breakdown, degradation, reclamation or immobilization of pollutants. In contrast, similar microbial activities may result in degradation and spoilage of natural and synthetic materials, rock and mineral-based building materials, acid mine drainage with accompanying metal pollution, biocorrosion of metals, alloys, and related substances, and adverse effects on radionuclide speciation, mobility and containment.

Metals exhibit a range of toxicities towards microorganisms, depending on physico-chemical factors, speciation etc, and while toxic effects can arise from natural processes in the soil, toxic effects on microbial communities are more commonly

associated with anthropogenic contamination or redistribution of toxic metals in aquatic and terrestrial ecosystems. Such contamination can arise from aerial and aquatic sources, as well as agricultural practices, industrial activity, and domestic and industrial wastes. In some cases, microbial activities can result in remobilization of metals from other wastes and transfer into aquatic systems. It is commonly accepted that toxic metals, and their chemical derivatives, metalloids, and organometals can have significant effects on microbial populations and almost every index of microbial activity can be affected. However, metal toxicity is greatly affected by the physico-chemical nature of the environment and the chemical behaviour of the particular metal species in question. Despite apparent toxicity, many microorganisms survive, and flourish in apparently metal-polluted locations and a variety of mechanisms, both active and incidental, contribute to tolerance (Gadd and Griffiths, 1978). All mechanisms depend on some change in metal speciation leading to decreased or increased mobility. Such metal transformations between soluble and insoluble phases are also at the heart of metal biogeochemistry, thus providing a direct link between microbial responses and element cycles. Thus, interactions of microorganisms with metals are extremely important and underpin many aspects of biogeochemistry, geomicrobiology and soil science.

In terrestrial environments, fungi serve as neglected but important geochemical agents (Gadd, 1993; 1999; 2006; 2007). Fungi promote rock weathering and contribute to the dissolution of mineral aggregates in soil through excretion of H^+ , organic acids and other ligands, or through redox transformations of mineral constituents. We have found that the main mechanism of metal mobilization from insoluble metal minerals is a combination of acidification and ligand-promoted dissolution: if oxalic acid is produced the production of metal oxalates can occur. Fungi can therefore also play an active or passive role in mineral formation through precipitation of secondary minerals, e.g. oxalates, and through the nucleation of crystalline material onto cell walls that can result in the formation of biogenic micro-fabrics within mineral substrates. Such interactions between fungi and minerals are of importance to biogeochemical cycles including those of C, N, S and P. We have shown that fungi may play an important role in the transformation of micro-fabrics in limestone ($CaCO_3$) and dolomite

($CaMg(CO_3)_2$) and have produced direct evidence of mineralized fungal filaments with secondary carbonates. Experiments have shown that fungi can precipitate calcite ($CaCO_3$) and whewellite (calcium oxalate monohydrate, $CaC_2O_4 \cdot H_2O$). We have examined elemental profiles of adjacent layers from a sandstone outcrop to find out whether differences in mineralogical composition influenced fungal and bacterial diversity. Culture-independent molecular approaches were used in combination with geochemical analyses, community-level physiological profiling and environmental scanning electron microscopy. A DNA-based community fingerprinting approach (ARISA: automated ribosomal intergenic spacer analysis) combined with construction of fungal and bacterial rRNA gene clone libraries (internal transcribed spacer) was used to assess community structure. Molecular data was combined with X-ray diffraction and X-ray fluorescence to identify those chemical properties that influenced community structure. It was found that sandstone supports a varied microbial diversity and community ribotype profiles differed between mineralogically-distinct sandstones in close proximity to each other (Gleeson *et al.*, 2005; 2006). Canonical correspondence analysis (CCA) illustrated relationships between certain ribotypes and particular chemical elements with Al, Na and Ca appearing to have a considerable impact on microbial community structure. Such molecular and statistical methods provide a powerful tool for resolving rock-inhabiting bacterial and fungal communities, and their relationship to the mineral nature of the substrate.

Other processes that can determine metal bioavailability are important microbially-catalyzed reactions of the natural sulfur cycle. Chemolithotrophic leaching by sulfur/sulfide-oxidizing bacteria can result in mobilization from polluted soil matrices, while sulfide production by SRB can result in precipitation of soluble metals as insoluble sulfides, with other redox transformations also being mediated by these organisms, e.g. Cr(VI) to Cr(III) (Smith and Gadd, 2000). We have found metals such as Cd, Co, Cr, Cu, Mn, Ni and Zn can be efficiently leached from contaminated soils, and removed from solution by SRB. In addition, SRB can reduce metalloid oxyanions such as selenite to elemental selenium (Hockin and Gadd, 2003; 2006). We have found that SRB, growing as a biofilm, can mediate formation of elemental sulfur in the presence of selenite. The

indirect, enzymatically-mediated coprecipitation of sulfur and selenium is a generalised ability among SRB, arising from sulfide biogenesis, and can take place under low redox conditions and in the dark (Hockin and Gadd, 2003).

This presentation will detail the above examples of metal-mineral transformations by microorganisms, and discuss their biogeochemical and applied relevance. For bioremediation, solubilization of metal contaminants provides a means of removal from soils, sediments, and solid industrial wastes. Alternatively, immobilization processes may enable metals to be transformed *in situ* and are particularly applicable to removing metals from aqueous solution. Specific highlighted examples in this presentation will include fungal degradation and transformations of copper and lead-containing minerals, depleted uranium and uranium oxides, fungal biodeterioration of concrete (which has implications for storage of radioactive waste), metal sulfide precipitation and reduction of metalloids oxyanions to elemental forms by sulfate-reducing bacteria. The overall aim of the presentation is to emphasise the important diversity of microbial roles in biogeochemical cycling and transformations of metals and related elements in the Earth's critical zone.

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Session 1

The Role of Mineral Colloids in Carbon Turnover and Sequestration and the Impact on Climate Change

Soils as Source and Sink of Environmental Carbon Dioxide

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World soils contain 2500 Pg C to 1-m depth, comprising of 1500 Pg of soil organic C (SOC) and 950 Pg of soil inorganic C (SIC) (Houghton, 2007; Lal, 2004). Therefore, the soil C pool is 3.1 times more C than the atmospheric pool (800 Pg and increasing at the rate of 4.1 Pg C·yr⁻¹) and 4.0 times the biotic pool (620 Pg and decreasing at the rate of 1.6 Pg C·yr⁻¹). The current global C budget comprises anthropogenic emissions of 8.0 Pg C·yr⁻¹ from fossil fuel combustion and cement manufacture, and 1.6 Pg C·yr⁻¹ from deforestation, biomass burning and soil cultivation. Of the total emission of 11.5 Gt C E (including CO₂, CH₄ and N₂O) in 2000, 14% (1.6 Pg) were those due to agricultural activities and 18% (2.1 Pg) from land use conversion. Thus, land use and agriculture contribute about one-third (32%) of total anthropogenic emissions. Confirmed sinks include atmospheric absorption of 4.1 Pg C·yr⁻¹, oceanic uptake of 2.3 Pg C·yr⁻¹, and a land sink of about 1.5 Pg C·yr⁻¹ (WMO, 2008). Thus, there is an unknown terrestrial sink of about 1.7 Pg C·yr⁻¹.

Atmospheric concentration of CO₂ has increased from 280 mg·L⁻¹ in the pre-industrial era to about 382 mg·L⁻¹ by volume, or 582 mg·L⁻¹ by mass in 2008. In total, the atmosphere contains approximately 0.01% of the C present in the atmosphere-ocean-upper earth crust system (Oelkers and Cole, 2008). World soils and terrestrial ecosystems have been the source of atmospheric CO₂ ever since the dawn of agriculture about 10,000 years ago, and of CH₄ since the domestication of animals and cultivation of rice paddies about 5,000 years ago (Ruddiman, 2005). Terrestrial ecosystems (soils and vegetation) may have contributed as much as 320 Pg C from pre-historic era to 1850 (Ruddiman, 2005) and about 158 Pg C from 1850 to 2006 (Canadell *et al.*, 2007).

Presently, terrestrial ecosystems and agricultural activities contribute about 1.6 Pg C as CO₂ and 3.7 Pg CE (including CO₂, CH₄ and N₂O) (Koonin, 2008). In comparison, fossil fuel combustion have contributed 292 Pg C between 1750 and 2002, and is projected to contribute an additional 200 Pg C between 2003 and 2030 (Holdren, 2008). Therefore, world soils have been historically a major source of atmospheric CO₂. Most agricultural soils have lost 25% to 75% of their SOC pool, and the magnitude of loss is more on severely eroded/degraded than slight or un-degraded soils.

The process of transfer of atmospheric CO₂ into other long-lived pools (geologic, oceanic, terrestrial), called C sequestration, is widely considered an option to mitigate the climate change (Broecker, 2008; Oelkers *et al.*, 2008; Lal, 2008). Sequestration of CO₂ into terrestrial ecosystem (soils, trees) is based on the natural process of photosynthesis. The terrestrial biosphere annually photosynthesizes about 120 Pg C into the biomass. However, almost all of it is returned back to the atmosphere either through plant respiration or soil respiration. Yet, global C budget can be effectively balanced even if merely 8% to 10% of the photosynthesized C is retained in the biosphere.

Conversion to a restorative land use (perennial land use such as forest cover, permanent pastures) and adoption of recommended management practices (RMPs) on agricultural soils can create a positive soil C budget. There is a wide range of RMPs, and no one technology is universally applicable under diverse soils and ecoregional conditions. Some examples of RMPs for cropland include no-till farming with crop residue mulch and cover cropping, use of complex crop rotations including agroforestry, adoption of integrated nutrient management (INM) techniques

including use of biofertilizers (e.g., manure, compost, biological N fixation, mycorrhizae), application of soil amendments (e.g., biochar, soil conditioners), and soil water management (e.g., drip irrigation, water harvesting and recycling). Similarly, RMPs for grazing lands include sowing of improved forage species, controlled grazing with low stocking rate, fire management, water conservation, etc.

The rate of SOC sequestration in agricultural soils is about 0.1 to 1.5 Mg C·ha⁻¹·yr⁻¹ depending on climate, soil type, land use and management. The rate is more in cool and humid than in warm and dry regions, and more in heavy-textured than light-textured soils. The potential of C sequestration in terrestrial ecosystems (soils and trees) is about 3 Pg C·yr⁻¹ for the next 25 to 50 years. It is equivalent to a total drawdown of about 50 mg·L⁻¹ of atmospheric CO₂ (Hansen *et al.*, 2008).

There are numerous co-benefits of C sequestration in soils. Improvement in soil quality increases use-efficiency of input and crop yields. Thus, soil C sequestration is essential to advancing global food security. Other ancillary benefits include increase in biodiversity, improvement in quality of natural waters and decrease in non-point source pollution, and increase in aesthetic value of ecosystems. Soil C sequestration, being a cost-effective (McKinsey and Co., 2008) and a natural process, is a win-win situation. It is a bridge to the future, until non-C or C-neutral fuel sources take effect.

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Impacts of Mineral Colloids on the Transformation of Biomolecules and Physical and Chemical Protection of Soil Organic Carbon

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Abstract: Soil mineral colloids, along with enzymes, have the ability to catalyze the transformation of biomolecules, which are from biological residues, root exudates, and biological metabolites, to relatively recalcitrant humic substances (HS). Virtually all HS in a wide range of soils are bound to mineral colloids, especially short-range ordered (SRO) Al and Fe (oxy) hydroxides because of their large specific surface area, high density of reactive sites, and surface reactivity. Soil mineral-HS complexes may anchor unstable plant constituents by various adsorptive forces and/or chemical binding. Highly degradable proteins, for example, may be protected against rapid biodegradation by their nucleophilic addition to mineral complexes. Besides chemical protection, mineral colloids have the ability to interact with biomolecules and microorganisms to form microaggregates. Furthermore, organic substances serve as intracolloid binding agents leading to the formation of macroaggregates through biogenic aggregation processes. The vast majority (90%) of soil organic C (SOC) in surface soil is located within aggregates. Undecomposed biological materials have turnover times in terms of years. Turnover times of occluded SOC increase with decreasing aggregate size. SOC in macroaggregates has turnover times in terms of decades and the turnover times are about centennials for SOC in microaggregates. Turnover times of chemically protected SOC through binding to mineral surfaces usually approach millennia. Therefore, mineral colloids play a vital role in governing the transformation and turnover of soil organic matter and the impact on climate change.

Keywords: Mineral colloids; Biomolecules; Humification; Recalcitrance; Occlusion; Aggregation; Complexation; Chemical protection

Introduction

The stocks of organic matter in soils result from the balance between inputs and outputs of SOC within the below-ground environment. Inputs are primarily controlled by net primary productivity; outputs are dominated by the efflux of CO₂ from the soil surface, although methane CH₄ efflux and hydrological leaching of dissolved organic and inorganic and particulate organic C compounds can also be important (Davidson and Janssens, 2006). During the turnover process of organic C, biomolecules are transformed to more recalcitrant HS through enzymatic and mineral catalysis (Hardie *et al.*, 2009a; Huang and Hardie,

2009). HS and some of the relatively unstable biological residues, root exudates, and microbial metabolites may become physically protected in the interior of soil aggregates. Furthermore, these biologically derived organic components may become sorbed onto surfaces of mineral colloids, especially SRO Al and Fe (oxy) hydroxides, thus chemically protected. Therefore, the pivotal role of mineral colloids in the transformation and turnover of SOC can be addressed in terms of (1) abiotic catalysis of the transformation of biomolecules to HS, (2) physical protection through occlusion of SOC in aggregates, and (3) chemical protection through sorption of SOC on the surface of mineral colloids.

Formation of HS

There is a large volume of work documenting the polycondensation and polymerization of simple biomolecules (e.g., polyphenols, amino acids, and sugars), as catalyzed by soil minerals and enzymes, leading to the formation of HS (Shindo and Huang, 1982; Wang and Huang, 1986; Bollag *et al.*, 1998; Huang and Hardie, 2009). Because these catalysts are ubiquitous in soil environments and the substrate biomolecules are readily available from the continuous decomposition of biological residues, root exudates and microbial metabolite, it is certain that these reactions occur in the natural environment. HS is relatively recalcitrant compared to labile biomolecules (e.g., polysaccharides and protein). There is ample evidence that the biotic community is able to degrade any organic matter of natural origin. Therefore, the recalcitrance of organic matter is less important in later stages of decomposition. However, the HS formed through abiotic and biotic catalyses would interact with very reactive mineral colloids to form very stable mineral-humic complexes as addressed below. It is well established that HS is largely associated with mineral particles in a wide range of soils (Huang and Hardie, 2009).

Physical Protection

Nearly 90% of SOC in surface soils is located within aggregates (Jastraw *et al.*, 1996) with 20% to 40% of SOC in intra-microaggregates (Carter, 1996). Turnover times of occluded SOC increase with decreasing aggregate size. Turnover times were about 15 to 50 years for SOC stored in macroaggregates and 100 to 300 years for SOC in microaggregates (Puget *et al.*, 2000; Six *et al.*, 2000; John *et al.*, 2005). SOC is stabilized by different aggregate formation processes, biogenic aggregation in macroaggregates and physicochemical interactions of mineral colloids with organic substances and microorganisms in microaggregates. Biogenic aggregation is a relatively transient process within the active and intermediate SOC pools and is sensitive to management practices. Occlusion of SOC within microaggregates, especially

in the <20 μm is operative over long time scales controlled by pedogenic processes (von Lützow *et al.*, 2006). Mineral colloids, thus, have a vital role in influencing the turnover of SOC through the formation of aggregates.

Chemical Protection

Early experimental evidence such as the work of Allison *et al.* (1949) has led many authors (e.g., Tate and Theng, 1980; Oades *et al.*, 1989) to suggest that the impact of clays on C stabilization will change as a function of clay mineralogy. Soil mineral colloids, especially SRO Al and Fe (oxy)hydroxides have the ability to complex with SOC (Huang and Hardie, 2009) and control the turnover rate and storage of SOC (Torn *et al.*, 1997; Rasmussen *et al.*, 2005). Chemical protection of SOC against decomposition through adsorption with mineral surfaces has received increasing attention over the past two decades and has been identified as the most likely mechanism to achieve centennial and millennial protection of SOC (Kögel-Knabner *et al.*, 2008). However, a detailed mechanistic understanding at a molecular level of why sorption of SOC to soil minerals decreases decomposition rates of SOC is lacking. Furthermore, HS, which is formed through mineral and enzymatic catalyses and subsequently bound to mineral surfaces to form mineral-humic complexes, may anchor and encapsulate unstable biomolecules by various adsorption processes or chemical binding (Bollag *et al.*, 1998; Huang and Hardie, 2009). Any biomolecules intimately associated with HS that cannot be separated effectively by chemical and physical methods may be considered as humic components (Sutton and Sposito, 2005).

Therefore, many unstable biological constituents may survive in mineral-humus complexes in the environment for a significant length of time. Most recently, it has been shown that mineral catalysis not only promotes the formation of HS from biomolecules but also the genesis of carbonates such as rhodochrosite (MnCO_3) (Hardie *et al.*, 2009b). This indicates the vital role of mineral catalysis in abiotic carbonate formation from biomolecules, which contributes to C sequestration in natural environments.

Conclusions

Transformations of biomolecules from biological residues, root exudates, and microbial metabolites under enzymatic and mineral catalyses as influenced by climatic factors and anthropogenic activity are important processes contributing to the turnover of SOC. Tissue chemistry, i.e., recalcitrance of biological materials is less important at the late stage of decomposition of SOC. Physical protection by occlusion of SOC in aggregates, which are formed by interactions of mineral colloids with nonliving organic matters and microorganisms, accounts for turnover times of decades and centennials. Chemical protection by bonding of SOC to mineral surfaces to form mineral colloid-humus complexes accounts for the turnover times of millennials. Therefore, pedogenic processes of mineral weathering transformations control the strength of bonding and the amount of SOC stored in the terrestrial ecosystem. It is thus challenging to understand at a molecular level the mechanisms of bonding SOC to mineral surfaces and how they would govern turnover and stabilization of SOC. This is of fundamental importance in developing innovative land resource management strategies to sequester C in the terrestrial ecosystem.

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Unravelling the Biogeochemical Cycles of Carbon and Nutrients in Forest Ecosystems: Innovative Approaches with Advanced Stable Isotope and NMR Techniques as well as Soil Chemical and Physical Methods

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Abstract: Long-term impacts of global climate change (GCC) and local forest management on important biogeochemical cycles of carbon (C) and nutrient cycling in the soil-plant ecosystems are complex and difficult to assess, particularly under gradually and continuously rising atmospheric carbon dioxide concentration [CO_2] and warming in the real world with multiple limiting factors. In this presentation, we highlight the recent developments and applications of advanced stable isotope, nuclear magnetic resonance (NMR) and bio-molecular techniques, in an integrated approach with innovative rhizosphere and tree ring methods, for improving our understanding and management of above- and below-ground C and nutrient cycling processes in forest ecosystems, particularly in response to GCC and local management practices as well as mitigation / adaptation strategies. The opportunities and limitations of these techniques for investigating C and nutrient cycling processes in forest ecosystems are discussed, in the context of both short- and long-term impacts on the above- and below-ground processes. Improved understanding and knowledge of environmental fingerprints of the biogeochemical cycles embedded in tree rings can be effectively used to account for long-term forest productivity and C stocks at local, regional and global scale in response to the future GCC and management options.

Keywords: C and nutrient cycling; Global climate change; Acid deposition; Forest management; Above- and below-ground processes; Integrated approach; Stable isotope; NMR; Bio-molecular technique; Rhizosphere; Tree ring growth

Global Climate Change and Forest Management

Over the last century, atmospheric [CO_2] has increased globally by nearly 30% and temperature by approximately 0.6 °C, and these trends are projected to continue more rapidly (Xu and Chen, 2006; Xu *et al.*, 2009), particularly with more extreme climatic conditions. The impacts of GCC on future structure, composition, and C and nutrient cycling in forest ecosystems deserve particular attention and further research. Little is known about the impacts of GCC and forest management on plant-soil-microbe interactions. Plant-soil-microbe interactions mainly occur in the rhizosphere, which is defined as the zone

of soil that is affected by the root activity of any plant species. The rhizosphere is suggested here as the “hotspot” for plant-soil-microbe interactions the most chemically and biologically active microsite in soil, and represents a complex integrated ecosystem. The ecology in the underworld, particularly below-ground processes and their interactions with above-ground processes, has been highlighted (Science 304, 11 June 2004). There is growing need for improving the understanding and management of important below-ground processes. Understanding rhizosphere C and nutrient cycling processes in relation to rising [CO_2] and temperature is crucial for predicting the response of forest ecosystems to GCC (Xu and Chen, 2006; Xu *et al.*, 2009).