Soil Mineral–Microbe-Organic Interactions

Qiaoyun Huang · Pan Ming Huang ·
Antonio Violante (Eds.)

Soil Mineral–Microbe-Organic Interactions

Theories and Applications

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Editors
Dr. Qiaoyun Huang
Huazhong Agricultural
University
Faculty of Resources &
Environment
430070 Wuhan
China, People's Republic
qyhuang@mail.hzau.edu.cn

Dr. Pan Ming Huang
University of Saskatchewan
Dept. Soil Science
51 Campus Drive
Saskatoon SK S7N 5A8
Canada
huangp@sask.usask.ca

Dr. Antonio Violante
Università Napoli Federico II
Dipto. Scienze del Suolo della
Pianta e dell'Ambiente
Via Università, 100
80055 Portici NA
Italy
violante@unina.it

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Preface

Minerals, organic matter and microorganisms are the major solid components in soil systems. These three constituents do not function independently but rather interact with each other constantly at all times and everywhere in the soil ecosystem. The interactions profoundly affect a series of physical, chemical and biological processes of soils including the behavior, transformation and fate of various nutrients and pollutants. The research on these interactions should, thus, be an important issue for Soil and Environmental Scientists. Therefore, the International Society of Soil Science established the Working Group MO in 1990, which was promoted to a new Commission 2.5 Soil Physical/Chemical/Biological Interfacial Interactions of the International Union of Soil Sciences (IUSS) in 2004. To date, the Working Group has sponsored four international symposia and these conferences were held in Edmonton (Canada, 1992), Nancy (France, 1996), Naples (Italy, 2000) and Wuhan (China, 2004), respectively.

The 4th International Symposium on Interactions of Soil Minerals with Organic Components and Microorganisms (ISMOM2004) was the first Inter-Congress Symposium of IUSS Commission 2.5. The conference was cosponsored by the International Union of Pure and Applied Chemistry (IUPAC). Doctors P.M. Huang (Canada), A. Violante (Italy), J. -M. Bollag (USA), J. Berthelin (France), J. Zhou (China) and Q. Huang (China) served in the Symposium Organizing Committee. The meeting attracted 135 delegates from 22 countries and regions in the world including Canada, Chile, China, France, Germany, Hong Kong SAR, India, Indonesia, Iran, Italy, Japan, Kenya, Korea, Malaysia, New Zealand, Russia, South Africa, Thailand, The Netherlands, USA, Venezuela and Zimbabwe. The theme of ISMOM2004 was "Environmental Significance of Mineral-Organic Component-Microorganism Interactions in Terrestrial Systems". The conference program was divided into the following six sessions: (1) Transformation and Dynamics of Pollutants in Soil Environments, (2) Chemical, Biological and Biochemical Processes in the Rhizosphere, (3) Bioavailability of Metals, Nonmetals and Xenobiotics Immobilized on Soil Components, (4) Distribution and Activity of Biomolecules in Terrestrial Systems, (5) Interactions between Soil Microbial Biomass and Organic Matter/Nutrient Transformations, and (6) Impact of Interactions among Soil Mineral Colloids, Organic Matter and Biota on Risk Assessment and Restoration of Terrestrial Ecosystems. There were 2 plenary lectures, 9 invited speakers, 36 oral presentations and 45 posters. Dr. N. Senesi from University of Bari, Italy, presented an IUPAC lecture entitled Metal-Humic

Substance Complexes in Soil. Dr. P. M. Huang from University of Saskatchewan, Canada, who was the founder of Working Group MO and the founding Chair of Commission 2.5 of IUSS, gave a plenary lecture on Physical-Chemical-Biological Interfacial Interactions in Soil Environments.

The 13 chapters in this book are mainly the papers from the plenary and invited speakers of ISMOM2004. They address the state-of-the-art on the theories and applications of the interactions of minerals with organic components and microorganisms in soil environments. The book presents a variety of issues on the fundamental interactions among soil minerals, organic components and microorganisms and their impacts on soil ecosystems. Part I (Chaps. 1–7) addresses the fundamentals of physical-chemical-biological interfacial reactions, the binding and transformation mechanisms of metals, metalloids, biomolecules and organic pollutants as affected by soil organic, inorganic and microbial components. Part II (Chaps. 8–13) deals with the impacts of the interactions of soil components on the dynamics of soil carbon and biomass, the bioavailability of chemicals, and on soil and environmental quality. These chapters present a variety of topics that address issues of the cutting edges of science of the subject matter. We believe that the publication of this ISMOM2004 special book would promote in-depth studies in this field for years to come. The book should be useful for research scientists, professors, graduate students, and consultants working in soil, microbial ecology and environmental sciences.

We wish to extend our gratitude to the many sponsors including the National Natural Science Foundation of China (NSFC) and Organization for the Prohibition of Chemical Weapons (OPCW). We also acknowledge the contributions from many of the Chinese Institutions such as Huazhong Agricultural University, Institute of Soil Science of the Chinese Academy of Sciences, State Key Laboratory of Agricultural Microbiology, and the Key Laboratory of Subtropical Agricultural Resources and Environment.

In addition to this book, volunteered papers presented at ISMOM2004 and accepted after rigorous external review was published as a special issue by the international journal Biology and Fertility of Soils. This special issue serves a companion volume of this IUSS- and IUPAC-sponsored book published by Springer-Verlag.

Editors: Q. Huang
P. M. Huang
A. Violante

About the Editors

Qiaoyun Huang is a professor of Soil Biochemistry at Huazhong Agricultural University, China. He received his Ph.D. degree in soil science at Huazhong Agricultural University. As a visiting scientist, he spent one year (1993–1994) in Department of Soil Science, University of Manitoba, Canada and four months (1997–1998) at University of Naples, Italy. He conducted a two-year (1998–2000) postdoctoral work in Faculty of Agriculture, Yamaguchi University, Japan.

Dr. Huang is currently Director of the Key Laboratory of Subtropical Agriculture and Environment of Ministry of Agriculture, China and Vice Chairman of the Young Scientist Association of Hubei Province. His major research is in the area of soil mineral interactions with biomolecules and microbial transformation of heavy metal in soils. He has published over 90 research articles and book chapters including 35 SCI papers and has been invited as referee for 15 international journals. He serves as a member of the editorial board of the international journal *Applied Soil Ecology* and *The Open Enzyme Inhibition Journal*. He earned an honor of Provincial Distinguished Young Scientist in 2003 and was awarded a second prize by the Ministry of Education of China for the Advancement of Natural Science in 2005.

Dr. Huang is an active participant for international conferences. He gave oral presentations at the 31th Annual Meeting of Clay Mineral Society (Saskatoon, Canada), the Second International Symposium on Interactions of Soil Minerals with Organic Components and Microorganisms (Nancy, France), the 15th and 16th International Symposia on Environmental Biogeochemistry (Wroclaw, Poland and Aomori, Japan), the 17th and 18th World Congress of Soil Science (Bangkok, Thailand and Philadelphia, USA), and the 1st International Symposium on Enzymes in the Environment (Granada, Spain). He presented an invited lecture at the 39th Annual Meeting of Indonesian Society for Microbiology. He was the Chairman of the 4th International Symposium on Interactions of Soil Minerals with Organic Matter and Microorganisms.

P. M. 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 nature and surface reactivity of mineral colloids 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 research papers, book chapters, and 16 books, are fundamental to the development of sound strategies for managing land and water resources.

Dr Huang developed and taught courses in soil physical chemistry and mineralogy, soil analytical chemistry, and ecological toxicology. He has successfully trained and inspired M.Sc and Ph.D. students and postdoctoral fellows, and received visiting scientists from around the globe. He has served on numerous national and international scientific and academic committees. He has also served as a member of many editorial boards such as the *Soil Science Society of America Journal, Geoderma, Chemosphere, Water, Air and Soil Pollution, and Soil Science and Plant Nutrition*. He has served as a titular member of the Commission of Fundamental Environmental Chemistry 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" of the International Union of Soil Science. 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 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.

Antonio Violante is Professor of Agricultural Chemistry at the University of Naples, Italy. He received his Ph. D. in Chemistry at the University of Naples in 1969. He was awarded postdoctoral fellowships from the University of Wisconsin, USA (1967–1977) and the University of Saskatchewan, Canada (1981–1982) and was invited Visiting Professor in the Department of Soil Science, University of Saskatchewan, Canada in 1985, 1992 and 2003.

Dr Violante was Head of the Dipartimento di Scienze Chimico-Agrarie and is Coordinator of the *Doctoral School in Agrobiology and Agrochemistry* of the University of Naples Federico II. He has served on many committees of the Italian Society of Soil Science (President of the Session Soil Chemistry), and Italian Society of Agricultural Chemistry. He is vice-president and liaisons officer of Gruppo Italiano AIPEA. He was the scientific chairman and chief organizer of International and National Congresses.

Dr Violante has contributed to promote research on the interface between soil chemistry and mineralogy and soil biology. The areas of research include the formation mechanisms of Al-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/desorption of nutrients and xenobiotics on/from variable charge minerals and soils and on the factors which influence the sorption and residual activity of enzymes on phyllosilicates, variable charge minerals, organo-mineral complexes, and soils. Dr Violante is the author or co-author of 141 research articles and book chapters. He presented papers at many scientific congresses and Symposia and gave invited lectures at universities and research institutes worldwide. Dr Violante has international research/teaching experience in Canada, the US, Europe, China and Chile. He has trained students for Masters and Ph. D. Degrees and postdoctoral fellows and received visiting scientists from worldwide. He serves on the editorial board of three international journals. He is a Fellow of the Soil Science Society of America and the American Society of Agronomy.

Contributors

Carmine Amalfitano
Dipartimento di Scienze del Suolo della Pianta e dell'Ambiente
Università di Napoli Federico II
Napoli
Italy

Stephen A. Boyd
Department of Crop and Soils
Michigan State University
East Lansing
MI 48824-1325
USA

Qingqiang Chen
State Key Laboratory of Estuarine and Coastal Research
East China Normal University
Shanghai 200062
China

Wenli Chen
Faculty of Life Science and Technology
Huazhong Agricultural University
Wuhan 430070
China

G. J. Churchman
Soil and Land Systems
University of Adelaide
Private Mail Bag 1
Glen Osmond
SA 5064
Australia

Ryoichi Doi
Sakaerat Environmental Research Station
Udom Sap, Wang Nam Khieo
Nakhon Ratchasima Province
30370
Thailand

Yucheng Feng
Department of Agronomy and Soils
Auburn University
AL 36849
USA

Giuseppe Ferrara
Dipartimento di Biologia e Chimica Agroforestale e Ambientale
Università di Bari, Via Amendola
165/A, Bari-70126
Italy

W. P. Gates
Primary Industries Research Victoria
Rutherglen VIC 3685
Australia

Stefania Del Gaudio
Dipartimento di Scienze del Suolo della Pianta e dell'Ambiente
Università di Napoli Federico II
Napoli
Italy

Ji-Dong Gu
Laboratory of Environmental Microbiology and Toxicology
Department of Ecology & Biodiversity
The University of Hong Kong
Pokfulam Road, Hong Kong
China

R. J. Haynes
School of Applied Environmental Sciences
University of KwaZulu-Natal
Pietermaritzburg, Private Bag X01
Scottsville 3200
South Africa

P. M. Huang
Department of Soil Science
University of Saskatchewan
Saskatoon SK
Canada

Qiaoyun Huang
Faculty of Resources and Environment
Huazhong Agricultural University
Wuhan 430070
China

Mantao Jiang
Guangzhou Institute of Geochemistry
Chinese Academy of Sciences
Guangzhou 510640
China

Jaran Jiraphong
Sakaerat Environmental Research Station
Udom Sap, Wang Nam Khieo
Nakhon Ratchasima Province
30370
Thailand

Pramuk Kaeoniam
Sakaerat Environmental Research Station
Udom Sap, Wang Nam Khieo
Nakhon Ratchasima Province
30370
Thailand

Seunghun Kang
Department of Plant, Soil, and Insect Sciences
University of Massachusetts
Amherst, MA 01003
USA

Zhi'an Li
South China Institute of Botany
Chinese Academy of Sciences
Guangzhou 510650
China

Elisabetta Loffredo
Dipartimento di Biologia e
Chimica Agroforestale e
Ambientale
Università di Bari, Via Amendola
165/A, Bari-70126
Italy

Akmal Muhammad
Department of Soil Science and
Soil & Water Conservation,
University of Arid Agriculture
Rawalpindi
Pakistan

Willem Norde
Laboratory of Physical Chemistry
and Colloid Science
Wageningen University
Wageningen
The Netherlands
and
Department of Biomedical
Engineering
University of Groningen
Antonius Deusinglaan
Groningen
The Netherlands

Shaolin Peng
South China Institute of Botany
Chinese Academy of Sciences
Guangzhou 510650
China

Massimo Pigna
Dipartimento di Scienze del
Suolo della Pianta e
dell'Ambiente
Università di Napoli Federico II
Napoli, Italy

Jumlong Placksanoi
Sakaerat Environmental
Research Station
Udom Sap, Wang Nam Khieo
Nakhon Ratchasima Province
30370
Thailand

Marianna Pucci
Dipartimento di Scienze del
Suolo della Pianta e
dell'Ambiente
Università di Napoli Federico II
Napoli
Italy

Nicola Senesi
Dipartimento di Biologia e
Chimica Agroforestale e
Ambientale
University of Bari
Via Amendola 165/A, Bari
Italy

Samai Sewakhonburi
Sakaerat Environmental
Research Station
Udom Sap, Wang Nam Khieo
Nakhon Ratchasima Province
30370
Thailand

Chengde Shen
Guangzhou Institute of
Geochemistry
Chinese Academy of Sciences
Guangzhou 510640
China

Yanmin Sun
Guangzhou Institute of
Geochemistry
Chinese Academy of Sciences
Guangzhou 510640
China

Benny K. G. Theng
Landcare Research
Private Bag 11-052
Palmerston North
New Zealand

Antonio Violante
Dipartimento di Scienze del
Suolo della Pianta e
dell'Ambiente
Università di Napoli Federico II
Napoli
Italy

Baoshan Xing
Department of Plant, Soil and
Insect Sciences
Stockbridge Hall
University of Massachusetts
USA

Jianming Xu
College of Environmental and
Natural Resource Sciences
Zhejiang University
Hangzhou 310029
China

Weixi Yi
Guangzhou Institute of
Geochemistry
Chinese Academy of Sciences,
Guangzhou 510640
China

G. Yuan
Landcare Research
Private Bag 11-052
Palmerston North
New Zealand

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Part I
Fundamentals

1 Soil Physical-Chemical-Biological Interfacial Interactions: An Overview

P.M. Huang

Department of Soil Science, University of Saskatchewan, Saskatoon SK, Canada

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1 Introduction

Soil is the central organizer of the terrestrial ecosystem and its physical, chemical, and biological processes have enormous impacts on ecosystem productivity, services, integrity, and human welfare. On April 21, 2000, the Council of the International Union of Soil Sciences (IUSS) approved the organization of the IUSS scientific structure: D1. Soil in Space and Time, D2. Soil Properties and Processes, D3. Soil Use and Management, and D4. The Role of Soils in Sustaining Society and the Environment. There are four commissions in Division D2: C2.1 Soil Physics, C2.2 Soil Chemistry, C2.3 Soil Biology, and C2.4 Soil Mineralogy. However, physical, chemical, and biological processes are not independent processes but interactive within the soil environment. Soils can be defined as complex interactive biogeochemical reactors, reservoirs of organisms, and a major compartment of the terrestrial ecosystem under the influence of anthropogenic activities.

To improve our scientific knowledge of soil resources and its application to remediation and long-term management, it is of major importance and interest to study soil organization and function, not only through the traditional subdisciplines of soil science but also through interactive approaches. The study of soil physical, chemical, and biological interfacial interactions has to be considered at different scales, namely, from molecular level to field/landscape systems and this approach is essential to stimulating further research to uncover the dynamics and mechanisms of soil processes. Therefore, a new Commission C2.5 Soil Physical/Chemical/Biological Interfacial Reactions was established in Division D2 Soil Properties and Processes within the IUSS structure. Major research thrusts of this new commission include: (1) mineral and biological catalysis and enzyme-mineral interactions leading to humus and organo-mineral complex formation; (2) surface reactions of micro- and macro-biota and biomolecules with soil particles; (3) the effect of soil abiotic and biotic interactive processes on the structure, dynamics, and activities of microbial communities; and (4) ecological impacts of soil abiotic and biotic interactive processes. This last research thrust contains two major topics: (a) porosity formation by structure or organization development; and (b) biogeochemical transformation and transport of chemical and biological components at different temporal and spatial scales.

This paper presents an overview on soil physical-chemical-biological interfacial interactions and the impacts on the terrestrial ecosystem.

2 Role of Organic Substances in the Transformation of Metal Oxides

Metal oxides have a significant role in influencing physical, chemical, and biological properties of soils. They may exist as crystalline minerals, as short-range ordered (SRO) mineral colloids, or as surface coatings on clay minerals and organic matter. Organic compounds influence the formation, transformation, and surface properties of these metal oxides. The SRO Al and Fe oxides are among the most reactive mineral colloids in acidic and neutral soils (Huang et al. 2002; Bigham et al. 2002).

The hydrolysis and polymerization of Al and the subsequent transformation into crystalline phases are strongly influenced by the nature and concentration of natural organics (Huang and Violante 1986; Huang 1988; Krishnamurti et al. 1999, 2004). The influence of organic acids on Al transformation has been studied extensively, with most of the focus on the particular solid phases that form as a result of the perturbation of organic acids (Huang et al. 2002). The influence of a particular organic acid is generally related to the stability constant of the complex that forms with Al (Table 1). Therefore, p-hydroxybenzoic acid, which forms the least stable complex with Al, does not inhibit the crystallization of Al hydroxides. On the other hand, aspartic, tannic, malic, and citric acids increasingly retard crystallization (Fig. 1). In addition to the stability constant of the complex, the concentration of the organic acid is important. At certain low concentrations, which vary with the kinds of organic acids, the presence of some organic acids actually promotes the crystallization of particular $Al(OH)_3$ polymorphs, but above the critical concentration, it disrupts crystallization (Huang and Violante 1986). This is because organic acids replace water molecules that would otherwise coordinate with the Al^{3+} ion. The extent to which this occurs depends on the chemical affinity of the organic acid for the Al, i.e., the stability constant, and its concentration relative to Al. Humic substances also influence the transformation of Al by promoting the formation of microcrystalline boehmite and hampering the formation of more crystalline phases (Kodama and Schnitzer 1980; Singer and Huang 1990). Fulvic acids (FA) and humic acid (HA) resemble aliphatic acids, such as citric and malic acids, in that they contain COOH and aliphatic OH groups. They also resemble tannic acid and quercetin, because they contain phenolic hydroxyl and ketonic C=O groups. Through these functional groups, FA and HA form stable complexes with Al and inhibit the crystallization of Al hydroxides. Through perturbation of crystallization, organic substances have a significant impact on the surface properties of Al transformation products. The presence of organic acids during aging of Al hydroxide gels increases the specific surface of the products up to 30-fold over that of the control, and higher organic acid concentrations result in higher specific surface (Kwong and Huang 1978, 1981). The surface charge characteristics of the products also dramatically change. These intermediate transformation products are the most reactive Al species in influencing physical, chemical, and biological processes of soils and associated environments (Huang et al. 2002).

Table 1. Stability constants of the complexes formed between Al and five organic acids at 25°C (Kwong and Huang 1979a)

Organic acids	Stability constants of the complexes	
	log *K*1	log *K*2
p-hydroxybenzoic acid	1.66	–
Aspartic acid	2.60	–
Tannic acid	3.78	–
Malic acid	5.14	8.52
Citric acid	7.37	13.90

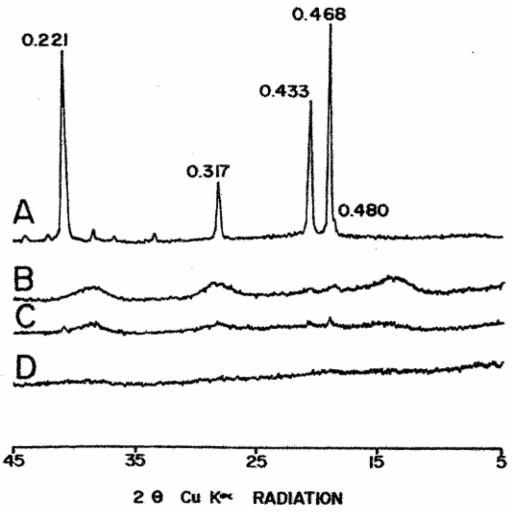

Fig. 1. The x-ray diffraction patterns of hydrolytic precipitation products of Al, showing how four different organic acids influence the transformation to more crystalline phases. The initial Al concentration was 1.1 × 10^{-3}M at an OH/Al molar ratio of 3 and the solution was aged for 40 d at room temperature in the presence of 10^{-4}M organic acid (Kwong and Huang 1979b).

Organic substances also play a very important role in the formation and transformation of Fe oxides in soils (Fig. 2). In soil environments where the amount of organic matter is low, the Fe supplied will form goethite and hematite depending on environmental factors (Schwertmann 1985). As the organic matter content increases, more of the Fe will be complexed with organics resulting in the decrease in Fe activity. The activity of Fe(III) ions is so low that only the solubility product of goethite (10^{-41}–10^{-42}), but not the solubility product of ferrihydrite (10^{-37}–10^{-39}), is exceeded. Consequently, goethite but not the ferrihydrite may form.

Therefore, no hematite will form in an environment where the organic matter is high, since ferrihydrite is deemed a necessary precursor for hematite. This trend is observed generally in soils in the temperate and cool regions as well as in wet depression and surface soils of the subtropical and tropical regions. At a higher content of organic matter, the rate of Fe supply is high and ferrihydrite will form and may survive for pedogenic times. If the content of organic matter is even higher, such as occurs in O horizons or in peaty environments, all of the Fe may be in the form of Fe-organic complexes. The interaction of organic matter with Fe, thus, plays a vital role in influencing the crystallization and speciation of Fe oxides in soil environments (Schwertmann et al. 1986; Cornell and Schwertmann 1996). Furthermore, the fine scale morphology, mean surface roughness, fractal dimension, specific surface, and microporosity of the Fe oxides depend on the concentration of low-molecular-weight organic acids, e.g., citric acid in the solution in which the Fe oxides are formed (Liu and Huang 1999). Surface properties of Fe oxides formed under the influence of organic substances deserve close attention in advancing our understanding of their surface chemistry pertaining to dynamics and transformations of chemical and biological components in soil and related environments (Huang 2004).

3 Influences of Mineral Colloids on Soil Organic Matter Stabilization and Turnover

Soil minerals play a stabilizing role in organic matter. The Al and Fe that complex and stabilize organic matter against microbial decomposition are released from soil minerals during soil formation. The supply rates apparently control the content of soil organic matter to a great extent. This is demonstrated by the relationship between pyrophosphate-extractable C and pyrophosphate-extractable Al plus Fe (Wada 1995).

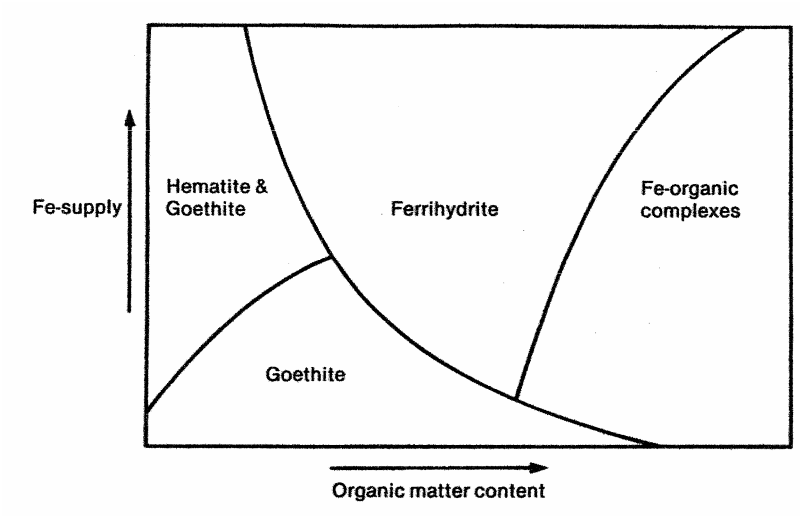

Fig. 2. Tentative schematic representation of the effect of organic matter content and rate of soluble Fe supply on the formation of various Fe forms in soils (Schwertmann et al. 1986).

Torn et al. (1997) investigated interactions between mineralogy and organic C along two natural gradients – of age and of climate – in volcanic soil environments. The total stock of organic C in soil increased with substrate age up to 150 kyr when it was 60 kg m^{-2}, and then decreased to 31 kg m^{-2} over the next four million years (Fig. 3a). Most of the decrease in soil organic C stored in older substrates is attributed to an increase in the turnover of soil organic C, rather than to a decrease in plant productivity. The $\Delta^{14}C$ (‰), which is the turnover time of soil organic matter (i.e., the reciprocal of the decomposition rate), shows that the surface horizons are dominated by fast-cycling organic matter (Fig. 3b). The $\Delta^{14}C$ (‰) values also confirm what is stated above. During the first 150 kyr of soil development, the volcanic parent material weathers to metastable noncrystalline minerals. The amount of noncrystalline minerals increases up to 150 kyr and then declines with greater age (Fig. 3c). In contrast, the amount of more stable crystalline minerals remains low until 150 kyr, then increases steeply (Fig. 3d). Soil organic carbon content follows a similar trend, accumulation to a maximum after 150 kyr, and then decreasing by 50% over the next four millions years (Fig. 3a). The abundance of noncrystalline

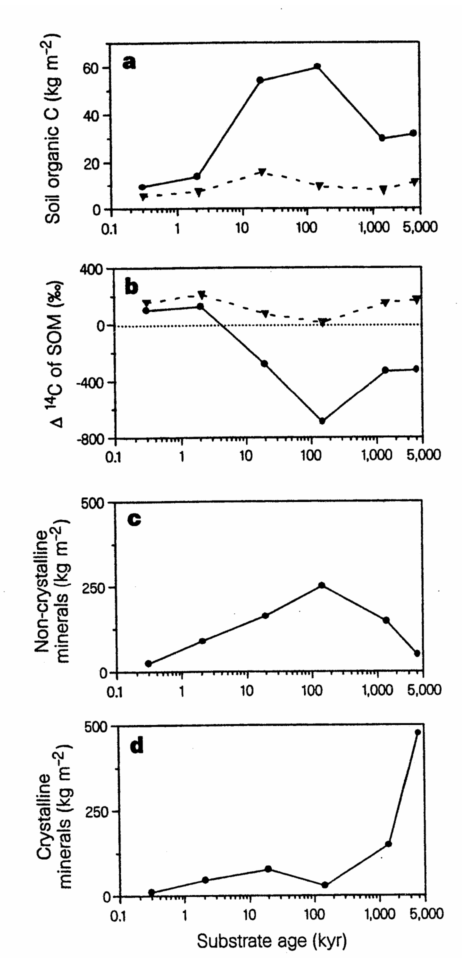

Fig. 3. Soil inventory of carbon in soil organic matter (SOM) **(a)**, $\Delta^{14}C$ of SOM **(b)**, noncrystalline minerals **(c)**, and crystalline minerals **(d)** versus age of soil substrate. Filled circles, total profiles; filled triangle, surface (O and A) horizons (Torn et al. 1997).

minerals accounts for >40% of the variation in organic C content across all the mineral horizons, substrate age, and soil orders. Noncrystalline minerals also strongly influence turnover of soil organic matter. Organic matter $\Delta^{14}C$ is highly and negatively correlated with abundance of noncrystalline minerals (R^2=0.62) except in the oldest site, which has <10% noncrystalline minerals. In contrast, there is no discernible correlation between the abundance of crystalline minerals and C content or turnover time across sites. A positive relationship between noncrystalline minerals and organic

C also exists in soils through the climate gradient. Rasmussen et al. (2005) recently reported significant correlations between Al-humus complexes, and SRO Al mineral species and soil C content, suggesting a chemical protection of organic materials, in addition to the observed physical protection of plant-like material within aggregates. Their results suggest aggregate protection and soil mineral assemblage (namely SRO Al-OH mineral content and Al-humus complex content) significantly control soil C dynamics in the conifer ecosystems. Therefore, soil mineral-organic matter interactions are important in determining the quantity of organic matter stored in soil, its turnover time, and atmosphere-ecosystem carbon fluxes during long-term soil formation.

4 Soil Mineral Catalysis and the Formation of Humic Substances

Humic substances can be synthesized through biotic and abiotic processes. A variety of organic components, such as phenolic compounds, carbohydrates, aldehydes, and nitrogenous substances can participate as starting materials. Soil minerals have the ability to catalyze the abiotic polymerization of phenolic compounds and the polycondensation of phenolic compounds and amino acids and the subsequent formation of humic substances. Kumada and Kato (1970), Wang and Li (1977), and Filip et al. (1977) are among the pioneers in the study of the catalysis of layer silicates on abiotic formation of humic substances through oxidative polymerization of phenolic compounds. Since the early 1980s, Huang and co-workers have studied the sequence of catalytic power of layer silicates and the reaction sites in the polymerization of phenolic compounds and the subsequent formation of humic substances (Shindo and Huang 1985a; Wang and Huang 1986, 1988). Among metal oxides, hydroxides, and oxyhydroxides, Mn oxides are the most powerful catalysts in the transformation of phenolic compounds (Shindo and Huang 1982, 1984). Manganese oxides, which are common in soils, act as Lewis acids that accept electrons from phenolic compounds, leading to their formation of semiquinone and their oxidative polymerization and formation of humic substances. Poorly crystalline aluminosilicates, such as allophane, are common in soils. Allophane has the ability to catalyze the polymerization of polyphenols (Kyuma and Kawaguchi 1964). Even primary minerals have the ability to catalyze the abiotic polymerization of hydroquinone which is a phenolic compound. The sequence of the catalytic power of primary minerals is tephroite > actinolite > hornblende > fayalite > augite > biotite > muscovite ≈ albite ≈ orthoclase ≈ microcline ≈ quartz (Shindo and Huang 1985b).

The Maillard reaction (Maillard 1913) is perceived to be a major pathway in humification because of significant similarities between humic substances and melanoidins (often synthesised *de novo* in microbial cell walls) formed through this pathway involving sugar-amino acid condensations (Ikan et al. 1996). Evershed et al. (1997) reported the presence of characteristic products of the Maillard reaction (alkyl pyrazines) in archaeological plant remains up to 1500 years from Egypt. In spite of the significance of the Maillard reaction, the rates and mechanisms of polycondensation of sugars and amino compounds in nature remains obscure (Ikan et al. 1996). Jokic et al. (2001) reported that birnessite (δ-MnO_2) significantly increases the extent of humification of the glucose-glycine system over the pH range of 6–8 (Fig. 4). The chemical shifts of FA formed in the Maillard reaction systems (Jokic et al. 2001) resemble those of natural humic substances such as soil and stream FAs (Malcolm 1989; Schnitzer 2000). In nature, it is most likely that the polyphenol and Maillard reaction pathways do not occur separately but rather interact with each other. Jokic et al. (2004a) reported that δ-MnO_2, a ubiquitous soil mineral, significantly accelerates humification processes in a system containing glucose, glycine, and catechol at temperatures and pH typical of natural environments. Their data indicate the signicance of linking the polyphenol and Maillard reactions, as promoted by mineral colloids such as δ-MnO_2, into an integrated humification pathway.

5 Interactions of Enzymes with Soil Mineral and Humic Colloids and Impacts on Enzymatic Activity

Extracellular enzymes are rapidly sorbed at mineral and humic colloids in soils and sediments. Mineral colloids have a high affinity for enzymes although that is not always synonymous with the retention of their catalytic ability. On the other hand, humic substances have the ability to sorb and sequester enzymes in such a way as to retain their catalytic activity; they could also strongly inactivate enzyme activity depending on interaction mechanisms.

Mineral colloid-enzyme interactions have been documented (e.g., Theng 1979; Burns 1986; Naidja et al. 2000; Burns and Dick 2002). Besides cation-exchange reactions, adsorption of enzymes by mineral colloids may proceed through ionic, covalent, hydrophobic, hydrogen bonding, and van der Waals forces. When enzymes are adsorbed on mineral colloids, changes in the tertiary structures (i.e., the folding of the helix or

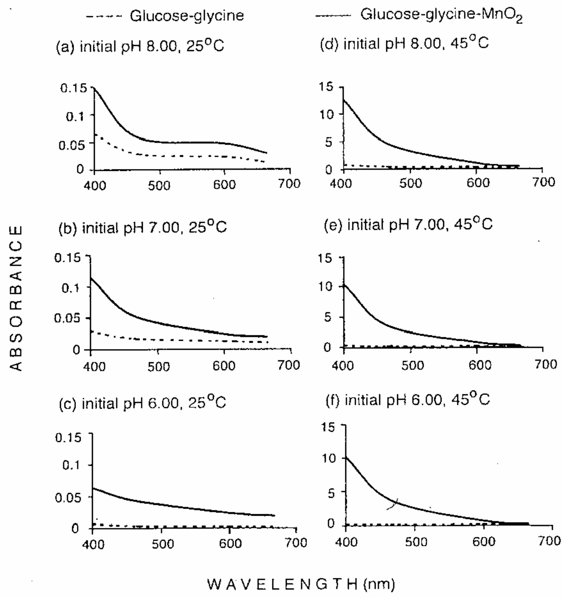

Fig. 4. Absorbance versus wavelength plots in the Maillard reaction between glucose and glycine as influenced by birnessite catalysis. **(a)**, **(b)**, and **(c)**: 30 d reaction period. **(d)**, **(e)**, and **(f)**: 15 d reaction period (Jokic et al. 2001).

coil into a compact, globular molecule stabilized by interfold hydrogen bonding, van der Waals, and hydrophobic interactions) of the enzymes and their active sites decrease the activity of the enzyme or eliminate it altogether (Burns 1986). However, there are notable exceptions to the adsorption-decline in activity rule. Various supports differ in their ability to immobilize enzymes (Table 2). The residual specific activities of laccase and peroxidase immobilized on and/or within all supports including glass beads, montmorillonite, kaolinite, and soil are high. Furthermore, laccase immobilized on montmorillonite shows specific activities that are higher than those of the free enzyme (Table 2). This may be attributed to steric modification of the immobilized enzymes such that the active site becomes more exposed to substrates. Although mineral sorption often stabilizes enzymes against degradation (Tietjen and Wetzel 2003; Kelleher et al. 2004), mineral-bound compounds are unable to diffuse, thereby reducing the encounter rates between enzymes and substrates. Even if some substrates do diffuse to bound enzymes, the active sites may be partially blocked so that enzymatic catalysis is reduced, as evidenced by reductions in the activity of some mineral-sorbed enzymes (Gianfreda et al. 1992). Conversely, mineral-bound C substrates may be physically prevented from entering the active sites of mobile enzymes (Sollins et al. 1996). In addition to the large surface areas of mineral colloids that facilitate sorption, many mineral colloids also contain micropores (Yu et al. 2006) or mesopores or physical structures that can help trap small organic compounds and exclude degradative enzymes (Mayer et al. 2004; Zimmerman et al. 2004a,b). Furthermore, in extreme cases, substrates, enzymes, and microbes may all be present in soils but so strongly bound to mineral surfaces and physically protected that substrate degradation is minimal and enzymatic products are unlikely to reach microbes (Allison 2006a). This scenario may help to explain why the C associated with reactive mineral colloids can be tens of thousands of years old (Torn et al. 1997). The performance of enzymes in the terrestrial ecosystem is, thus, substantially influenced by mineral colloids. The role of SRO oxides, hydroxides, and oxyhydroxides of Al, Fe, and Mn (as well as non soil supports) in influencing enzymatic activity pertaining to the transformation of natural and anthropogenic organics merits increasing attention (Huang 1990, 2004; Naidja et al. 2000; Violante and Gianfreda 2000).

Table 2. Immobilization of a laccase (from *Trametes versicolor*) and a peroxidase (from horseradish) on different supports (Gianfreda and Bollag 1994)

Enzyme and support	Enzymatic activity			
	Protein adsorbed[a] (mg/%)	Units adsorbed[b]	Specific activity[c]	Residual specific activity[d]
Laccase				
Glass beads	0.452/56	28.8	63.7	236
Montmorillonite	0.622/71	19.8	31.8	118
Kaolinite	0.566/64	13.1	23.1	85.5
Soil	0.644/73	15.7	24.4	90.4
Peroxidase				
Glass beads	0.092/17	8.4	91.6	93.8
Montmorillonite	0.224/43	23	102.8	105.2
Kaolinite	0.120/23	9.5	78.9	80.7
Soil	0.162/31	15	92.6	94.8

[a] Difference between proteins initially added to 200 mg of support (0.88 mg laccase and 0.52 mg of peroxidase) and those recovered in the supernatant and washings.

[b] Expressed as μmol O_2 consumed min^{-1} for laccase and μmol guaiacol transformed min^{-1} for peroxidase.

[c] Units adsorbed/protein adsorbed

[d] Calculated as percentage of the specific activity (sa) of the free enzyme (laccase, sa = 27 μmol min^{-1} mg^{-1}; peroxidase, sa = 97.7 μmol min^{-1} mg^{-1}).

It has been reported that soil organic matter can inhibit enzymes (Vuorinen and Saharinen 1996) and enzyme activity may be reduced by adsorption on humic polymers (Gianfreda et al. 1998). Enzyme inhibition by humic substances has been well demonstrated for an oxidoreductase (Pflug 1980; Sarkar and Bollag 1987), a protease (Ladd and Butler 1969), an invertase and a phosphatase (Malcolm and Vaughan 1979). On the other hand, Kang et al. (2002) and Park et al. (2000) reported that, although high concentrations of humic-like polymers tend to inhibit laccase-mediated transformation of xenobiotics (including catechol), low concentrations of humic acid might enhance the enzymatic transformation of phenolic compounds. Furthermore, it has been reported that enzymes can be stabilized against all sorts of impacts (e.g. temperature, solvents, pH, proteases) by soil organic matter (Conrad 1942; Burns 1986; Nannipieri and Gianfreda 1999). Mechanisms proposed to account for the stability of enzymes by soil organic matter include ion exchange, H-bonding, covalent bonding, lipophylic reactions, and entrapment within three-dimensional micelles during organic matter genesis. Enzyme-humic complexes can also be bound to mineral colloids and this may further enhance enzyme stability.

Recent research data of Allison (2006b) suggest that enzyme activity measured in the laboratory represents the sum of active and stabilized enzyme pools. Common soil minerals such as allophane and ferrihydrite, partially determine the size of the stabilized pool. In contrast, humic acid, which is among the most abundant organic components in soil, strongly inactivate enzyme activity, although enzymes incorporated into humics during humic polymer synthesis may be more stable. The functional importance of stabilized enzymes still remains uncertain, and evidence from the literature suggests that the active enzyme pool is more strongly associated with biogeochemical process (Allison 2006b). Future research should address the relative contributions of different enzyme pools to ecosystem function (e.g., Stemmer et al. 1999). Studies measuring bulk enzyme activities in soil should recognize that a large pool of stabilized enzymes could make changes in the active pool more difficult to detect. Compared with bulk soil enzymes, active enzymes probably correlate more closely with soil quality mineralization rates, or disturbance. Therefore, ecosystem models should incorporate multiple pools of enzymes to improve predictions of organic matter decomposition, especially if stabilized enzymes have reduced catalytic efficiency.

6 Influence of Mineral Colloids on the Structure, Dynamics, and Activities of Microbial Communities

Soil is a habitat for myriads of microbes. The microbial biomass constitutes only a very small proportion (<3% of the total organic C in soil). However, it is the most active and dynamic fraction of the living organic pool. Mineral colloids are the most reactive fraction of inorganic components of soils because of their large specific surface areas and high charge density characteristics. Being enriched in ions, water, and organic matter relative to the bulk soil, the surface of mineral colloids serves as a preferred habitat for soil microbes (Theng and Orchard 1995).

The surface of bacterial cells and crystalline clay minerals are both negatively charged. However, bacteria have the propensity for producing extracellular polysaccharides (EPS) which bind simultaneously to cell and clay surfaces through cation bridging involving polyvalent cations (Fig. 5). EPS production aids the retention of bacterial cells within comparatively active biofilm communities at clay (or root) surfaces (Lunsdorf et al. 2000). The predominantly negatively charged mineral colloids in soils are largely coated with hydroxy Al (or Fe) polymers. As a consequence, these coated minerals behave as a positively charged species or display amphoteric characteristics. Therefore, mineral colloids can strongly interact with negatively charged microbial cells in soils. This type of chemical bonding, which is much stronger than cation bridging, is also expected to occur with Al and Fe oxides over the pH range of soils. Microbial cell wall charge characteristics are indeed pH dependent according to the dissociation constants of their exposed cell wall functional groups. The attachment of microbes to SRO mineral colloids and the crystal edges of layer silicates through electrostatic interactions would also be predicted to occur when the soil pH falls below 6 because the net charge of all of these mineral surfaces would then be positive and the surface of all bacteria and fungi would be virtually negatively charged (Theng and Orchard 1995).

In the majority of cases, minerals in topsoils are partially covered with organic materials, especially humic substances, which are to a large extent microbially resistant. The most common mode of mineral colloid-organic material-microorganism interactions may be depicted as follows (Theng and Orchard 1995):

$$[\text{Mineral colloid} — \text{HS}]^{-} \ldots \text{M}^{n+} \ldots [\text{EPS-B}]$$

where HS is humic substances, M is divalent/polyvalent metal cation, EPS extracellular polysaccarides, and B microbes and/or biofilm.

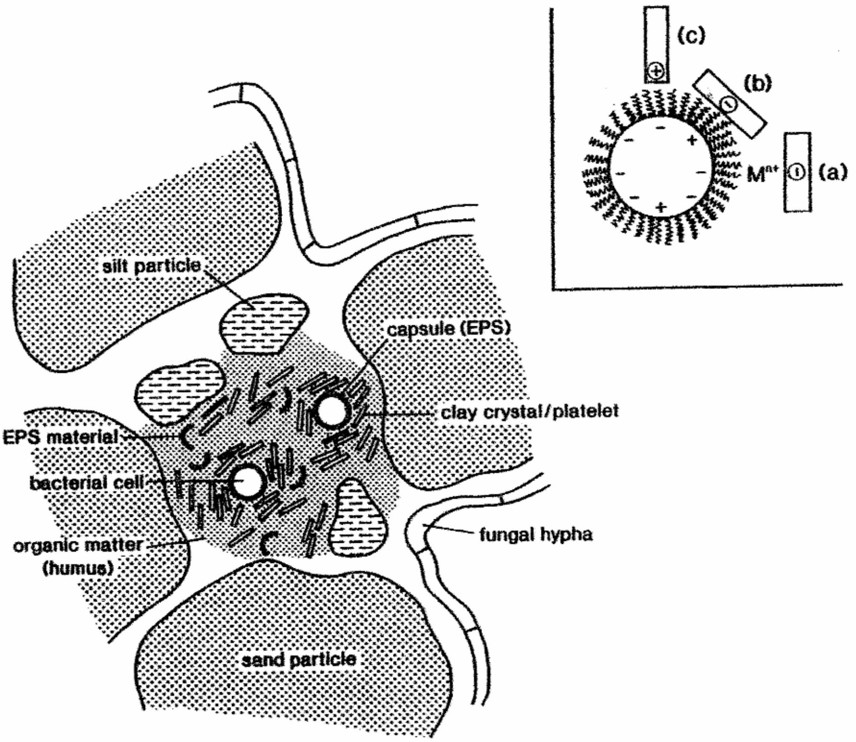

Fig. 5. Diagram illustrating the interaction of bacteria and fungi with mineral particles in a soil aggregate (Theng and Orchard 1995). Bacterial cells with a coat of extracellular polysaccharides (EPS) are enveloped by clay particles. The pore space where clays and bacteria interact, bounded by silt- 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.

In humic-rich calcareous Mollisols, Ca would be the predominant bridging cation. In Andisols, Oxisols, Ultisols and the B horizon of Spodosols, HS largely occur as complexes with Al and Fe, or their respective SRO oxides (Theng et al. 1989; Oades et al. 1989). In soils with little organic matter and in subsoils, mineral colloid-microorganism interactions are largely influenced by the mineralogical composition and pH of the soil. Besides the existing literature (Stotzky 1986, 2002; Theng and Orchard 1995; Huang and Bollag 1999; Huang 2004; Huang et al. 2005) much more research is needed to further understand the mechanisms of surface interactions of mineral colloids with microorganisms.

Mineral colloids can directly or indirectly influence the activity of microorganisms in their immediate vicinity (Stotzky and Burns 1982; Stotzky 1986). The effect of mineral colloids may be positive, negative, or sometimes so small as to escape detection. Mineral colloids have a stimulating effect on the activity of adhering bacteria by keeping the pH of microhabitats within the optimum physiological range for growth. The content and type of mineral colloids are influential in determining the balance between microbial populations in soil. A well-known example is the failure of some fungi to thrive and spread in certain soils (Stotzky 1986). This is largely attributed to the presence of montmorillonite in the suppressive soils. Montmorillonite can serve as a proton sink and is thus able to promote the growth of acid-sensitive bacteria in these soils. This gives bacteria a selective advantage over fungi in competing for available nutrients. Fungal growth and proliferation are, thus, effectively suppressed.

Microbial activity can also be stimulated by mineral colloids through their ability to sorb metabolites that would otherwise have an adverse effect on microbial growth (Filip et al. 1972; Filip and Hattori 1984) This may be due to the toxicity of metabolites, and their feed back repression and, encouraging competitors. Predictably, montmorillonite (CEC ~100 cmol kg^{-1} and specific surface of ~800 m g^{-1}) is more effective than kaolinite and finely ground quarts. Other substances, such as antibiotics and pesticides that are toxic to some microorganisms, can also be adsorbed by the surfaces of mineral colloids (Theng and Orchard 1995; Dec et al. 2002).

Furthermore, adhering microorganisms may benefit from being close to nutrients adsorbed on the surface of mineral colloids (including those concentrated in a cloud in the diffuse double layer). However, the potential substrates may not be readily available or physically accessible (Fletcher 1991) especially if intercalated. Moreover, the addition of mineral colloids to the system beyond a certain concentration may result in a reduction in microbial activity due to restricted diffusion of oxygen and nutrients to microbial cells (Marshall 1971). This is attributable to the progressive enveloping of microbial cells by minerals colloids. Timmis and his co-workers reported a novel interaction between bacteria and clay minerals (Lunsdorf et al. 2000). The biofilms that developed consist of a dense lawn of clay aggregates, each one of which contains one or more bacteria, phyllosilicates, and grains of iron oxides, all held together by bacterial EPS. The clay leaflets are arranged in the form of ‘houses of cards’ and give the aggregates the appearance of ‘hutches’ housing the bacteria. The ‘clay hutches’ may represent a ‘soil microhabit’, a ‘mineral nutrition sphere’,