

Advances in elucidating biogeochemical processes in soils: it's about scale and interfaces

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Abstract

Contributions in biogeochemical research have immensely benefited humankind, including enhanced food production and the quality of our environment. This overview paper focuses on recent breakthroughs in elucidating biogeochemical processes in soils and other natural materials and delineates frontiers for the present decade and beyond. Frontiers will undoubtedly involve multiple spatial and temporal scale investigations, elucidation of reactions at biological, chemical, and physical interfaces, and the use of advanced in situ technologies in combination with interdisciplinary research.

Keywords: molecular scale, macroscopic scale, temporal scale, biogeochemical processes, surface spectroscopy

I. Introduction

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, 2004).

With the advent of state-of-the-art analytical techniques, some of which are synchrotron-based (e.g., X-ray absorption fine structure spectroscopy, XAFS) one can elucidate reaction mechanisms at small scale. This has been one of the major advances in the earth and environmental sciences over the past decade. Undoubtedly, the molecular characterization of microenvironments and interfacial reactions will become increasingly significant in understanding the interactions between chemistry, physics, and biology in natural environments.

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The use of small scale techniques in environmental research has resulted in a new multidisciplinary field of study that 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, and the atmosphere at the molecular level (Sparks, 2002, 2004). There are a number of areas in the geosciences where the application of molecular environmental science is resulting in major frontiers. These include: 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; development of predictive models; effective remediation and waste management strategies; and risk assessment. Some of these frontier areas will be discussed in the paper.

2. Results and Analysis

Over the past 15 years, major advances have occurred in elucidating sorption mechanisms at the mineral/water interface. From these studies one can conclude that sorption of alkali and alkaline earth elements primarily occurs via outer-sphere complexes while for most other cations and anions, such as most heavy metals and oxyanions, inner-sphere sorption complexes result. Sorption of metals such as Co, Cr, Mn, Ni, and Zn on mineral components and soils can result in the formation of metal hydroxide precipitate phases (Scheidegger *et al.*, 1997). The formation of these phases could be an important mechanism for sequestering metals in soil and water environments such that they are less mobile and bioavailable.

In the remaining section of this paper, I will focus on the use of advanced micro-focussed synchrotron-based techniques to speciate metals in contaminated soils. Other frontier topics that will be covered in the oral presentation will include mineral/ microbe and plant/soil interfacial reactions. Standard XAS techniques probe an area of several square mm. However, the most reactive sites in soils have particle sizes in the micrometer range and metal speciation may vary over regions of a few $100 \mu\text{m}^2$. Therefore, the derived structural information may be only an average of several contaminant species. With the advent of third generation synchrotron radiation facilities, which afford enhanced spatial resolution ($<5 \mu\text{m}$) and sensitivity, one can speciate metals in soils using micro-XAS and determine elemental distributions and associations using micro-X-ray fluorescence (micro-XRF) spectroscopy. An example of the use of these techniques is shown in Figure 1 from the research of Nachtegaal *et al.* (2004). They investigated the speciation, distribution, and association of Zn and its relation to mobility and bioavailability of Zn in a non-remediated and a remediated smelter contaminated soil from Belgium. Overall, the researchers found that there were no significant differences in Zn speciation between samples of the two soils. Thirty percent of Zn was in smelter related minerals, mainly willemite, 10% of Zn was chemisorbed to Fe- and Mn-oxides, and 60% of Zn was incorporated into newly formed mixed Zn-Al layered double hydroxides (LDH) in the non-remediated and Zn-phyllsilicates in the remediated soil. Macroscopic desorption and biosensor studies were conducted on the soils to assess bioavailability of Zn. At the pH of the soils (6.4-6.7), these studies showed that the presence of the LDH phases greatly diminished the bioavailability of Zn in the soils. Desorption of Zn, and consequently bioavailability, was enhanced at lower pHs. The results of this investigation indicate that at higher pHs the formation of (mixed) metal hydroxide precipitates could be an important means of sequestering toxic metals such as Zn, as well as Co and Ni, in the soil environment.

