

## Preface

# Biogeochemical controls on the mobility and bioavailability of metals in soils and groundwater

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**Key words.** Trace metal biogeochemistry; terrestrial systems; aquatic systems.

Numerous trace metals have been identified as essential micronutrients for plants and/or microorganisms (including iron, zinc, copper, selenium, and nickel) and as electron acceptors or donors in metabolic processes. At elevated concentrations, however, many of these same metals exhibit significant toxicity and trace metal pollution in soils and groundwater remains one of the most pressing issues in modern environmental science. Arsenic contamination of drinking water, cadmium, copper, lead, and zinc pollution in soils, the transport of radio nuclides over long time scales, and the cycling of mercury are a few examples of important research areas in this context. As a result of their multifaceted biological functions, the significance of metals in the environment will depend on the concentration at which they occur and on environmental factors that control their mobility and bioavailability. The biogeochemical processes that control metal mobility and bioavailability include sorption on mineral and plant surfaces, dissolution, (bio-)mineralization, redox processes, complexation by biogenic or non-biogenic ligands, and biological uptake and derivatization. A wide range of experimental approaches has been used in trace metal related environmental research. It is therefore imperative to foster the discussion of these fundamental processes and approaches among researchers from various fields including plant nutrition, environmental chemistry and microbiology, environmental engineering, agri-

cultural sciences, geochemistry, mineral surface chemistry, and soil chemistry and biology.

The special feature in this issue of *Aquatic Sciences* is based on contributions to a symposium 'Biogeochemical controls on the mobility and bioavailability of metals in soils and groundwater' that was co-organized by Stephan M. Kraemer, Janet G. Hering, Ruben Kretzschmar, and Barbara Sulzberger at Monte Verità, Ascona, Switzerland, March 2–7, 2003. The workshop addressed major advances that have been achieved in recent years including spectroscopic and microscopic studies on mineral surface reactivity and speciation of surface adsorbed ions or molecules, improved understanding of dissolution and precipitation reactions as controlled by surface reactivity and organic ligands, and development of new modeling approaches based on a mechanistic understanding of surface reactions, thermodynamics, and molecular modeling.

An important focus of this workshop was the effect of bio-mineral interactions on micronutrient availability and contaminant fate in soils and groundwater. Mineral surfaces in natural environments are often covered with biofilms or adsorbed biopolymers such as humic substances or polysaccharides. Such polymers can increase or decrease the apparent mineral surface reactivity as observed in sorption or dissolution experiments. Siderophores are an example for biogenic substances that are synthesized and exuded by microorganisms and plants specifically to accelerate mineral weathering and nutrient acquisition. The review by Kraemer in this issue (Kraemer, 2004) explores the mechanisms of siderophore controlled iron oxide dissolution. Microbial cell surfaces are

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Published on Web: March 24, 2004

providing important reactive interfaces for the adsorption of contaminants and nutrients. Biological membranes are sites of uptake, exudation and of a range of enzymatic processes. Claessens et al. (Claessens et al., 2004) clearly demonstrate that these processes need to be taken into account in order to understand the acid base behavior of gram negative cell surfaces.

Redox reactions also play a major role in the biogeochemical cycling of trace metals. Changes in the oxidation state of humic substances in a stratified, ice-covered lake are observed by Fulton (Fulton et al., 2004) using a novel fluorescence-based method. Experiments with fulvic acids isolated from this system demonstrate that they are susceptible to microbial reduction. The authors hypothesize that the pattern in the oxidation state of fulvic acids observed in the near the oxycline in the water column can be attributed to abiotic reaction of reduced humic substances with ferric iron. This study provides an example of the importance of coupling of biotic and abiotic processes.

In natural systems, biogeochemical processes are strongly influenced by physical and chemical heterogeneities on various scales. Evidence for hydrologic control of biogeochemical patterns is investigated by Blodau (Blodau, 2004) in a study of sulfur and iron cycling in a lake receiving acid mining drainage from mine tailings. It is demonstrated that iron and sulfate reduction processes are strongly influenced by changing hydraulic boundary conditions on scales of hundreds of meters.

Ultimately, the understanding of fundamental biogeochemical processes is needed for the accurate and quantitative prediction of the fate and transport of metals on a range of time and length scales. Hence, the development of reactive transport models is a necessary step in order to apply process oriented knowledge to problem solving in critical areas such as sustainable agriculture, water supply, waste disposal (including nuclear waste), site remediation, and risk assessment. Hansen and van Berk (Hansen and van Berk, 2004) demonstrate the use of a reactive controlled material flux model to capture the dynamics of the water quality development in an aquifer which provides drinking water for the city of Hanover, Germany. A conceptual model is developed by stepwise integration of relevant processes. The model is then validated by comparison of the result with an objective function which is derived from a data set spanning close to 40 years of water quality data.

Statistical methods remain useful for efficient and cost-effective risk assessments and for the management

of polluted soils and industrial sites. François et al. (François et al., 2004) propose a model that relates trace metal solubility to physico-chemical parameters of the soils. They express metal solubility as a non-linear function of a set of parameters including pH, texture,  $\text{CaCO}_3$  content, total organic matter content and phosphorus content, using quadratic response surface regression analysis.

These papers represent some of the highlights of the 2003 workshop at Monte Verità. Although they do not span the entire range of the work presented at the workshop, it is our hope that they will provide the reader with an appreciation of the crucial role of biogeochemical processes in trace metal mobility and bioavailability.

As organizers of this workshop, we are most grateful to the Centro Stefano Franscini of the Swiss Federal Institute of Technology for its sponsorship and Mrs. Marianna Berger (CSF) and Mrs. Charlotte Wüstholtz (Institute of Terrestrial Ecology, ETHZ) for their able assistance in coordinating the program. We also thank the session chairs Giovanni Bidoglio, Jim Fredrickson, Geoffrey Gadd, Peter Jaffe, David Kinniburgh, Diane McKnight, Per Persson, Jeremy Semrau, and Alan Stone and the speakers and co-authors for their interest and participation. We thank the contributors to this special issue for their prompt submission of articles and the reviewers for their expertise and timely response. Finally, we would like to thank Barbara Sulzberger and her staff for their support and assistance.

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