"Kinetics of Chemical Reactions in Environmental Systems: Research Needs and Challenges"

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A basic understanding of the kinetics and mechanisms of important reactions and processes (e.g., sorption/desorption, precipitation/dissolution, and redox) in natural systems such as soils and sediments is necessary to accurately determine the speciation, mobility, and bioavailability of contaminants in the environment. Ideally, one should make investigations over a range of spatial and temporal scales and environmental conditions. The rates of these processes can vary over a range of temporal scales ranging from milliseconds to years. In many cases, macroscopic kinetic studies of metal(oid)s, nutrients, radionuclides, and organic chemicals have shown that reaction rates are initially rapid followed by a slow approach to a steady state. The rapid reaction has been ascribed to chemical reactions and film diffusion, while the slow reactions have been attributed to interparticle and intraparticle diffusion, retention on sites of lower reactivity, and surface precipitation. With many metals and organic chemicals it has been shown that desorption is much slower than adsorption and that the longer the contact time (residence time or aging time) between the sorbent and sorbate, the more difficult it is to release the contaminant. This has been ascribed to physical entrapment in pores and to other diffusion phenomena and to surface precipitation. With organic chemicals, the difficulty in desorption has been related to diffusion from rubbery and glassy organic polymeric materials. However, this has not been conclusively proven.

It must be recognized that microscopic conclusions about reaction mechanisms cannot be gleaned from macroscopic investigations. To definitively delineate reaction mechanisms in environmental systems, it is necessary to couple macroscopic, kinetic investigations with molecular scale studies. Ideally, the latter should be conducted in real-time. This paper will review advances in the employment of molecular scale in-situ analytical techniques (e.g., X-ray absorption and Fourier transform infrared spectroscopies), coupled with kinetic investigations, to elucidate mechanisms of environmental contaminants in natural materials. Applications of these techniques to assess metal(loid) and organic chemical sorption/release and natural attenuation processes will be addressed. Future research needs and directions will also be discussed, particularly the need to determine reaction mechanisms of environmentally important processes at the molecular scale in real-time and to measure very rapid reaction processes that are common in natural environments.