Frontiers in Assessing the Role of Chemical Speciation and Natural Attenuation on the Bioavailability of Contaminants in the Terrestrial Environment

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SUMMARY
The bioavailability of contaminants in the terrestrial environment is greatly affected by a number of chemical factors and processes including speciation of the contaminant, retention/release rates and mechanisms, pH, and redox conditions. While it is useful to know the total concentration of a contaminant, speciation is critical in affecting its fate, transport, and bioavailability. Traditionally, chemical extraction techniques have been widely employed to provide an indirect assessment of chemical speciation and association of contaminants with various soil components. However, artifacts can often be created, and direct speciation is not achieved. Contaminant retention/release rates and mechanisms also greatly affect its fate and bioavailability. Macroscopic kinetic studies have shown that residence time effects often occur with many metals, metalloids, and organic chemicals. A rapid uptake of sorbate is usually 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 delineate reaction mechanisms of contaminant reactions on soil minerals and in soils, it is necessary to couple macroscopic investigations with molecular scale studies. A large portion of 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) to speciate and elucidate contaminant retention/release mechanisms in soils and on soil components. Applications of these techniques to assess metal and organic chemical sorption/release, natural attenuation processes, and speciation in soil minerals and heterogeneous soils and poultry litter will be addressed. For example, using a variety of molecular and macroscopic scale techniques and approaches, it has been found that metals such as Co, Ni, and Zn can form metal hydroxide surface precipitates in soils over fairly rapid time scales, and that with time, mineral transformations occur which greatly enhances the sequestration of the metal. This could be an important natural attenuation mechanism, significantly affecting the bioavailability of metals. In recent years, micro-focused X-ray absorption spectroscopic and chemical mapping techniques allow one to speciate metal contaminants in soils over square micron scales. Examples and applications will be shown for As speciation in soils and for P speciation of chemically amended poultry litter material. Future research needs and directions will also be assessed.