Contaminant Geochemistry

Interactions and Transport in the Subsurface Environment

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Part V
Transformations and Reactions of Contaminants in the Subsurface

After reaching the subsurface, contaminants are partitioned among the solid, liquid, and gaseous phases. A fraction of the contaminated gaseous phase is transported into the atmosphere, while the remaining part may be adsorbed on the subsurface solid phase or dissolved into the subsurface water. Contaminants dissolved in the subsurface aqueous phase or retained on the subsurface solid phase are subjected, over the course of time, to chemical, biochemical, and surface-induced degradation, which also lead to formation of metabolites.

In many cases, the subsurface is contaminated by a mixture of toxic chemicals with components having different physical and chemical properties. Therefore, a contaminant undergoes transformations controlled by the properties of each substance, the characteristics of the subsurface, and the ambient conditions. Physicochemically mediated and biologically mediated degradation are the main processes involved in such transformations.

From an environmental point of view, the transformation of contaminants is not restricted to molecular changes. Rather, we also must consider all deviations from the original properties of a contaminant that may be relevant to its behavior in the subsurface. For example, in addition to degradation-induced transformation, contaminants may change their physicochemical characteristics as a result of specific reactions with other natural or anthropogenic chemicals found in the subsurface environment. To be more specific, complexation of a contaminant with existing natural ligands may lead to a change in its solubility, thus affecting its transport and redistribution in the vadose zone. The volatilization of high vapor pressure compounds from a mixture of immiscible (NAPL) contaminants, such as petroleum products, leads to changes in the retention or transport behavior of remaining constituents.

As a first approximation, we consider the main subsurface transformation processes to comprise reactions leading to chemical transformation or degradation and metabolite formation in the liquid phase or the solid-liquid interface and reactions resulting in complexation of chemicals, which in turn lead to a change in their physicochemical properties.

The upper part of the subsurface is characterized by enhanced biological activity. Therefore, contaminant transformation in this zone proceeds mainly by microbial processes, which are often faster than chemical ones. In the deeper subsurface,

biological activity often is reduced and, therefore, degradation proceeds abiotically, at a much slower rate. It should be emphasized, however, that contaminant transformation is related mainly to the formation of metabolites with properties different than those of the parent material (sometimes more polar, more soluble in water, and even more toxic), which may reach the groundwater. Even though abiotic and biologically mediated contaminant transformation may occur simultaneously in the subsurface aqueous solution and in the solid-liquid interface, they are discussed separately for didactic purposes.

Environmental conditions cause changes in the initial properties of organic and inorganic contaminants and affect their persistence in the subsurface. Relevant external factors include temperature and solar radiation, while the principal subsurface properties include water chemistry, the surface properties of the solid phase, and bioactivity. In Part V, we focus on research findings that illustrate abiotic and biologically mediated degradation of individual contaminants occuring in the liquid phase and at the solid-liquid interface, as well as examples of multiple-component contaminant transformation.