THE CHEMISTRY OF ORGANIC CONTAMINANT TRANSPORT IN SOILS

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The transport of organic contaminants in surface soils and subsoils is an important and complex issue in environmental science. Contaminant transport in the terrestrial environment embodies aspects of soil physics relating to the movement of water, soil microbiology relative to the persistence of contaminants under various environmental conditions, and soil chemistry. This paper will focus on the soil chemistry of organic contaminants by summarizing their sorptive interactions with soil components, and how sorption can be purposely enhanced or reduced. The ability to manipulate contaminant sorption in soils may be critical to the successful implementation of several environmental remediation technologies.

SORPTION OF ORGANIC CONTAMINANTS BY SOILS

Sorption of organic contaminants by soils may occur via a variety of mechanisms including:

1. *Physical adsorption:* Van der Waals forces as the major cause for surface condensation.
2. *Chemisorption:* chemical bond formation, complexation, and cation/anion exchange.
3. *Partition:* solubilization of solutes into the interior network of the sorbent.

In considering contaminant sorption, it is important to distinguish adsorption and partitioning as sorptive mechanisms. Adsorption refers to the condensation of a vapor or solute on the surface or interior pores of a solid (e.g., soil), the important point being that it is a surface phenomena. In contrast, partitioning refers to the dissolution of the sorbed material into an organic phase. This is a process of solubilization analogous to the partitioning of a solute between water and an immiscible organic solvent phase such as octanol or hexane. As distinct sorptive mechanisms, adsorption and partitioning manifest different characteristics. Adsorption is characterized by high equilibrium heats of sorption, nonlinear sorption isotherms and adsorbate competition in multisolute systems. Partitioning is characterized by low and constant equilibrium heats of sorption, linear isotherms, noncompetitive sorption and a dependence (inverse) of the magnitude of sorption on the water solubility of the solute (1, 2).

The uptake of nonionic-organic compounds (NOCs) from water by soils shows a strong dependence on the organic matter content of soil. This is now a well established fact in soil science. The uptake of NOCs can be represented mathematically by the Freundlich equation:

$$x/m = KC^{1/n} \qquad [1]$$

where x/m is the amount of solute sorbed per unit weight of soil, C is the equilibrium concentration of the solute in water and K is the sorption or partition coefficient. A plot of x/m versus C yields a sorption isotherm, and n is a constant describing the linearity of the isotherm. For many NOCs, it has been observed that n is ~1, i.e., linear isotherms are observed over a wide range of relative solute solubilities (C divided by the solute water solubility, S_w). The slope of such linear isotherms corresponds to the sorption coefficient K which is a simple ratio of the concentration of the solute in soil to its concentration in water at equilibrium.

Through a series of studies, it has now been determined that the K values normalized on the basis of the organic matter (OM) content of soil converge to a relatively constant value for a variety of soils and sediments (1–3). Thus an organic matter normalized sorption coefficient, $K_{om} = K/f_{om}$, can be defined where f_{om} is the fractional organic matter content of the soil or sediment. For practical purposes, K_{om} is now viewed as a constant independent of sediment or soil properties and dependent only on the nature of the compound, primarily its water solubility. The important practical result is that once the K_{om} value is determined on a single soil, K values on other soils can be estimated accurately by simply knowing their organic matter contents. It is important to remember that the K value defines the actual distribution of the contaminant between soil and water, and hence determines its potential for leaching.

The observed relationship between soil organic matter content and the sorption of NOCs has enhanced our ability to predict contaminant mobility in soils and subsoils. This predictive capability was further enhanced through the development of empirical regression equations relating K_{om} values to octanol-water partition coefficients (K_{ow}) and solute water solubility. A variety of such equations exist and are of the form (3):

$$\log K_{om} = 0.904 \log K_{ow} - 0.779 \qquad [2]$$

$$\log K_{om} = -0.729 \log S_w + 0.001 \qquad [3]$$

These types of predictive equations are useful because K_{ow} and S_w values are generally available for most NOCs. It is important to realize that the accuracy of such predictive equations is improved when they are confined to a structural class of compounds such as chlorinated aromatic hydrocarbons or polyaromatic hydrocarbons (4).

Despite the development of these empirical relationships and predictive capabilities, until recently there was no firm conceptualization of the sorptive mechanism for NOC-soil organic matter interactions. In 1979, two papers (5, 6) independently described the basic elements of a sorptive mechanism for NOC-soil organic matter interactions commonly referred to as solute partitioning. Basically this view of sorption holds that soil organic matter functions as a partition medium which solubilizes NOCs. In this fashion soil organic matter functioned like a bulk phase organic solvent, and solutes would distribute themselves between water and soil organic matter based on their solubilities in each phase.

To complete he picture of soil as a sorbent for NOCs, Chiou et al. (7) viewed soil as a dual sorbent consisting of mineral and organic matter; the former functioning as a conventional solid adsorbent and the latter as a partition medium. In aqueous systems, water would either hydrate the polar mineral surfaces (e.g., Fe and Al oxides) or the exchangeable cations of soil clays. Because these interactions were energetically more fa-