CHAPTER 4

SOLID/GAS PARTITIONING

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Some of the earliest environmentally related studies on sorption of vapors onto soils involved pesticides, herbicides and fumigants. In these studies, the objective was to assess the extent and effects of adsorption on the performance of the pesticides (Hance, 1965). Over the last two decades, information on adsorption of pesticides onto soils is being complimented with information on adsorption of volatile organic compounds (VOCs) from poor management of waste disposal sites, landfills and leaking underground storage tanks. Soils in the unsaturated zone are generally coated with a film of water as the air pores of the unsaturated zone is saturated with water at a relative humidity greater than 99%. The amount of water retained by soil is a function of soil grain size, pore sizes, pore volume distribution, and the total surface area. Soils with very low or dry surfaces are generally found only on the surface of the ground (1–2 cm from the surface) and soils in arid regions. Moisture content in the unsaturated zone may be assumed to be approximately close to field capacity.

Vapor partitioning may be visualized as follows; under moist conditions, VOCs from the vapor phase distribute into soil matrices by (i) sorption at the gas-water vapor interface, (ii) dissolution into the aqueous phase, (iii) adsorption onto the mineral surface from the aqueous phase, (iv) partitioning into the organic matter from the aqueous phase, and (v) condensation of VOCs into pores. Under very low moisture conditions, typically of surface soils, direct sorption onto the mineral and direct partitioning into organic matter from the gas phase may occur in competition with water molecules or sorption may occur on top of the sorbed water molecules. Figure 4.1 illustrates the various mechanisms.

Sorption of VOCs onto oven-dried soils (typically surface soils) has been found to be greatly affected by the external surface area of the soil (Call, 1957; Jurinak, 1957; Jurinak and Volman, 1957; Chiou and Shoup, 1985; Rhue et al., 1988; Ong and Lion, 1991a; Ong and Lion, 1991b). For low concentrations typically encountered in ambient conditions, partitioning into solid phase may be characterized by a linear partition coefficient. However for high concentrations or vapor pressures that are
Figure 4.1. Vapor sorption (a) with less than a monolayer of water molecules on the surface, (b) with a film of water on the surface; Mechanisms: 1 – direct solid–gas sorption; 2 – sorption onto water molecules; 3 – condensation; 4 – sorption at the gas–water interface; 5 – dissolution; 6 – solid–water sorption close to vapor saturation pressures as typically found in the areas with nonaqueous phase liquids, the adsorption isotherms for oven-dried soils are generally curvilinear in nature. The Brunauer-Emmett-Teller (BET) equation presented below is usually used to model the sorption phenomenon.

\[ \frac{\Gamma}{\Gamma_m} = \frac{c \left( \frac{P}{P_o} \right)}{\left(1 - \frac{P}{P_o}\right) \left(1 + \frac{P}{P_o c - 1}\right)} \]  

(4.1)

where \( \Gamma \) is the amount of sorbate adsorbed per unit surface area (g/m\(^2\)), \( \Gamma_m \) is the monolayer of sorbate adsorbed per unit surface area (g/m\(^2\)), \( c \) is a constant related to the energy of adsorption, \( P \) is the vapor pressure of sorbate (mm Hg) and \( P_o \) is the saturated vapor pressure of the sorbate (mm Hg). Sorption of organic vapors to soils typically exhibits a type II curve with hysteresis at high relative vapor pressures (\( P/P_o > 0.35 \)). The hysteresis generally indicates the occurrence of multilayer sorption and/or vapor condensation in pores (Call, 1957; Jurinak, 1957; Jurinak and Volman, 1957; Chiou and Shoup, 1985; Rhue et al., 1988; Ong and Lion, 1991b). Some researchers have proposed that sorption of VOCs onto dry soil may be considered as consisting of two fractions, that is, the mineral fraction which behaves as a conventional solid adsorbent and the organic matter fraction which acts as a partition medium (Boyd et al., 1988; Chiou et al., 1988). Under very dry conditions, the mineral surface area available for sorption is usually much larger than the organic carbon content present, making surface adsorption reactions more likely to dominate vapor uptake than partitioning into organic matter (Rhue et al., 1988).

Efforts have been made to correlate the linear gas–solid adsorption coefficients for sorption of various VOCs on different surfaces with various thermodynamic