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

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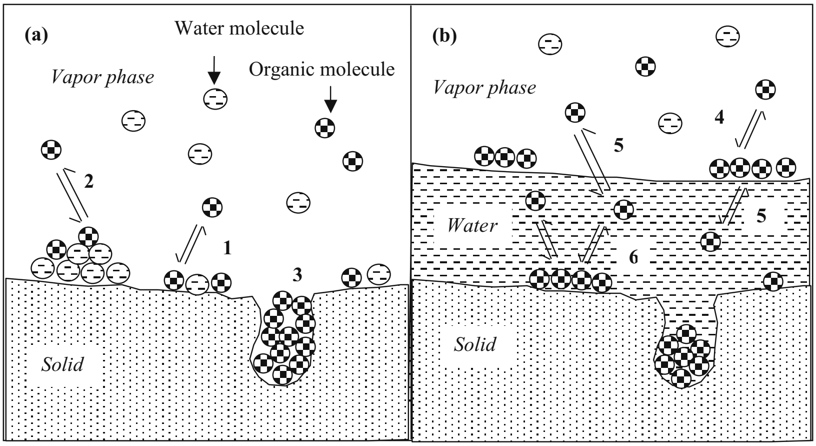

Figure 4.1. Vapor sorption (a) with less than a monolayer of water molecules on the surface, (b) with a film of water on the surface; Mechanisms: 1 – direct solid–gas sorption; 2 – sorption onto water molecules; 3 – condensation; 4 – sorption at the gas–water interface; 5 – dissolution; 6 – solid–water 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.

$$\frac{\Gamma}{\Gamma_{\mathrm{m}}} = \frac{c\left(\frac{P}{P_{\mathrm{o}}}\right)}{\left(1 - \frac{P}{P_{\mathrm{o}}}\right)\left(1 + \frac{P}{P_{\mathrm{o}}}(c-1)\right)} \tag{4.1}$$

where Γ is the amount of sorbate adsorbed per unit surface area (g/m^2), Γ_{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 ($P/P_{\mathrm{o}} > 0.35$). 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

Table 4.1. Examples of solid–gas sorption coefficients onto dry soils

Soil type	Organic carbon content (%)	Surface area (m^2/g)	Solid–gas partition coefficients, K'_d (cm^3/g)	Solid–water partition coefficient, K_d (cm^3/g)
Rhineback[a]	3	82.5	1,377	1.41
Harford[a]	1.6	44.0	1,669	0.96
Gila[a]	0.4	98.5	1,831	0.3
Montmorillonite[a]	0.02	733	23,300	0.31
Iron Oxides[b]	N/A	273	15,840	N/A
Kaolinite[b]	N/A	10	440	N/A
Aquifer Soil[c]	0.1	18.7	1,464	0.1
Yolo[c]	1.1	80.6	3,401	0.58

[a] Ong and Lion (1991a)
[b] Shimizu et al. (1992)
[c] Peterson et al. (1995)
N/A – not available

properties of the sorbate and sorbent. Most of these equations relate the adsorption coefficients to the enthalpies of vaporization, enthalpies of adsorption, and saturation vapor pressures (e.g., Goss and Schwarzenbach, 1998; Goss and Schwarzenbach, 1999). However, these equations do not consider the effects of moisture or humidity on the sorption of VOCs. Typical solid–vapor partitioning coefficients, K'_d, for trichloroethylene (TCE) on oven-dried soils are presented in Table 4.1. As a comparison, the aqueous solid–water partitioning coefficients, K_d, are also presented.

In a moist environment, the mass of VOC sorbed is less than the mass of VOC sorbed on oven-dried surfaces due to competition for sorption sites between water molecules and VOCs (Call, 1957; Chiou and Shoup, 1985; Rhue et al., 1989; Ong and Lion, 1991b; Thibaud et al., 1992; Goss, 1993; Storey et al., 1995). The charged surfaces of minerals and soils have a higher affinity or preference for water molecules than the hydrophobic vapor compounds. Figure 4.2 shows the impact of different relative humidities on the sorption of TCE onto alumina.

Assuming that the mass of VOC sorbed for each process is additive, the mass of VOC sorbed can be written as:

$$\begin{aligned}\text{Total mass sorbed} = {} & \text{Mass sorbed at the solid–water interface}\\ & + \text{Mass dissolved in the liquid phase}\\ & + \text{Mass sorbed at the gas–water interface}\\ & + \text{Mass sorbed at the solid–gas interface}\\ & + \text{Condensation into pores}\end{aligned}$$

If sufficient moisture is present on the surface of the soil, the mass sorbed at the solid–gas interface can be neglected. Ignoring condensation, the vapor partitioning

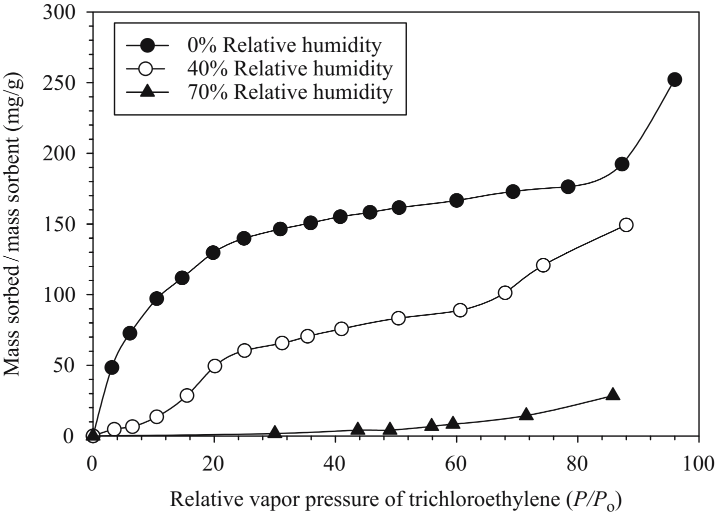

Figure 4.2. Effect of relative humidity on trichloroethylene adsorption on alumina

coefficient, K'_{d} can be written as:

$$K'_{\mathrm{d}} = \frac{K_{\mathrm{d}}}{K_{\mathrm{H}}} + \frac{\theta}{K_{\mathrm{H}}\gamma_{\rho}} + \frac{K_{\mathrm{iw}}A}{M} \tag{4.2}$$

where K_{d} is the solid–gas partition coefficient (m^3/g), K_{H} is the dimensionless Henry's law constant, θ is the moisture content (in fraction), K_{iw} is water–gas partition coefficient (m) for sorption at water–gas interface (g), A is the water–gas interfacial area (m^2), γ is the aqueous activity coefficient, and M is the mass of sorbent (g). Applying the above equation and using the number of monolayers of water coverage instead of the moisture content, Ong and Lion (1991c) were able to generalize the impact of moisture on the solid–gas sorption. Figure 4.3 plots the total mass partitioned onto the soil less the mass sorbed at the solid–water interface (represented by the term, $K_{\mathrm{d}}/K_{\mathrm{H}}$) versus the number of monolayers of water on the surface. As shown in Figure 4.3, Ong and Lion found that for oven-dried minerals, direct adsorption onto the solid surface of the minerals for TCE was a controlling factor. From oven-dried to one monolayer coverage of water, direct sorption was evident with strong competition from water for adsorption sites. The adsorption coefficient was found to decrease by several orders of magnitude. Between a monolayer and six layer of water molecules coverage, likely interactions include sorption of TCE onto surface bound water and limited TCE dissolution into the sorbed water with some salting out effects caused by the sorbed water structure. Beyond six monolayer of water molecules, TCE dissolution into the condensed water, obeying Henry's Law, and partitioning at the solid–water interface were evident. At this moisture level, water behaves like bulk water on the surface of the soil for the dissolution of VOC vapors (Ong and

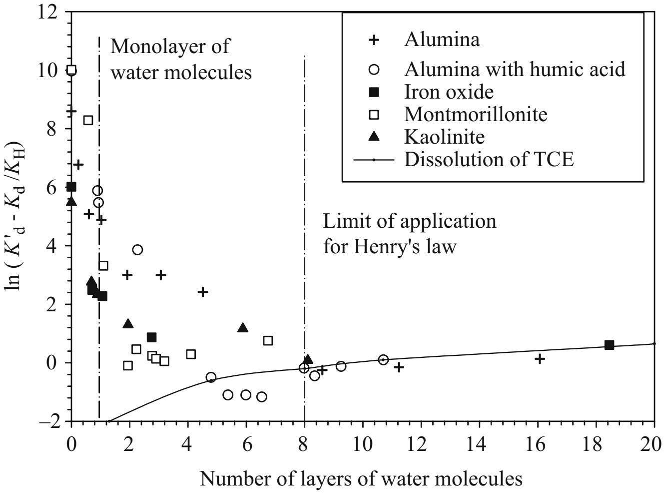

Figure 4.3. Impact of water molecules on mineral surfaces on trichloroethylene vapor sorption and the applicability of Henry's law (adapted from Ong and Lion, 1991c)

Lion, 1991c). The number of monolayers of water on the surface as presented in Figure 4.3 was based on surface area measurement using the ethylene glycol method. If the surface areas of the minerals were determined by the BET nitrogen method, the number of monolayers of water coverage when Henry's Law becomes applicable will be approximately eight monolayers. Similar results were obtained by Petersen et al. (1995) using toluene and TCE as the vapor sorbates.

In the work by Ong and Lion (1991c), they concluded that sorption at the water–gas interface was negligible. However, there are evidence that sorption at the water–gas interface may be significant. Valsaraj and Thibodeaux (1992) showed that model predictions based on the dissolution of VOCs into organic matter underpredicted the mass sorbed from gas phase. Therefore, the assumption that vapor sorption at high relative humidity behaves like aqueous phase sorption and dissolution into the water may be too simplistic and may not take into account other sorption processes such as sorption at the water–gas interface. Mass balance calculations by Thibaud et al. (1992) on the sorption of toluene and chlorobenzene onto an EPA standard soil at a relative humidity of 87%, clearly showed that aqueous phase sorption and dissolution into the water could not account for the mass sorbed from the vapor phase. Pennell et al. (1992) found that sorption of p-xylene at the water–gas interface may account for up to 50% of the total mass adsorbed from the vapor phase. Similarly, Hoff et al. (1993a, b) estimated that the water–gas interface may be responsible for up to 50% of the observed sorption of alkanes in aquifer material. Mass balances conducted by Conklin et al. (1995) on their experimental data showed that up to 60% of the total mass of p-xylene sorbed in their experiments may be at the water–gas interface. A recent review indicated that vapor sorption at the water–gas interface in soils may

Table 4.2. Examples of correlations for the sorption of vapors at the water–gas interface

Equation	Nomenclature	Reference
$\Gamma = -(p/RT)(\mathrm{d}\gamma/\mathrm{d}p)$	Γ – surface excess (mol cm^{-2}) γ – surface tension p – partial pressure R – universal gas constant T – temperature	Gibbs equation (as presented in Chattoraj and Birdi, 1984)
$\log K_{IW} = -5.53 + 0.2735 I_x$	K_{IW} – water–gas partition coefficient, I_x – first order molecular connectivity index	Valsaraj (1988)
$\log K_{IW} = -8.58 - 0.769 \log C_W^s$	K_{IW} – water–gas partition coefficient (m) C_W^s – saturated solubility of the VOC	Hoff et al. (1993b)
$\ln K_{IW} = A^* - (\Delta H_s/R)(1/T - 1/323.15) - C(100 - RH)(3)$ where $A^* = -0.615 \ln vp + 7.86\text{ß} - 5.80$ $C = -0.054\beta - 0.00070\,mR - 0.0041\mu + 0.00061\,\Delta H_s = 3.20 \ln vp - 50.2\beta - 55.0.$	K_{IW} – water–gas partition coefficient (m), vp – vapor pressure (pascal), β – hydrogen bond acceptor, mR – molar refraction, μ – dipole momentum, ΔH_s – heat of adsorption (kJ mol^{-1}) R – universal gas constant (kJ mol^{-1}K^{-1})	Goss (1994)

be a dominant retention mechanism depending on the moisture content (Costanza and Brusseau, 2000). Obviously as the moisture content approaches saturation the water–gas interface (A) available will be reduced resulting in insignificant sorption at the water–gas interface. It must be pointed out that VOCs with high aqueous solubility would prefer to be in the aqueous phase rather than at the water–gas interface. TCE has an aqueous solubility of 1100 mg/L which is higher than the solubility of p-xylene (198 mg/L). Therefore it is probable that because of the physical characteristic of the TCE used by Ong and Lion (1991c), sorption at the water–gas interface was found to be negligible.

Several researchers have proposed correlations for the estimation of mass sorbed at the water–gas interface (see Table 4.2). Sorption at the water–gas interface can be modeled using the Gibbs equation where the surface excess is determined by the change in the surface tension with varying vapor pressure. The equations proposed by Goss (1994) imply that for a VOC with high saturated solubility and high vapor pressure vapors such as TCE, the air–water partition coefficients would be low and that the VOC that are most likely to be sorbed at water–gas interface are those with a high β, hydrogen bond acceptor, value.

Most vapor sorption studies were conducted using a single VOC in competition with water for sorption sites. There are only a few studies investigating sorption of multiple vapors under unsaturated zone conditions even though many different VOCs may be found at a typical contaminated site. For simplicity sake, it is assumed that each VOC behaves independently and does not affect the other (Baehr and Corapcioglu, 1987; Nye et al., 1994). This assumption which may be true for aqueous phase sorption of hydrophobic VOCs (Chiou et al., 1988) but may not be true for vapor phase sorption under dry conditions. For soils with low moisture conditions, VOCs may compete with each other for adsorption sites while on the other hand, sorption of one class of VOC may be enhanced by another class of VOC. If a condensed VOC phase is formed, this phase, in turn, may act as a medium in which other hydrophobic VOCs may partition into. Lindner (1990) showed that certain types of VOCs would compete for sorption sites onto moist minerals while, in some cases, sorption of some types of VOCs were enhanced. The work done by Lindner was for low concentrations ($P/P_o < 2\%$) and the VOCs used were chlorinated solvents and components of fuel. Nye et al. (1994) investigated the sorption of m-xylene and n-dodecane vapors on air-dried and oven-dried soil. They found that on air-dried soil the addition of a second component increased the sorption of the first for all relative vapor pressures. However, work done by Amali et al. (1994) showed that the ternary system of TCE, toluene and water did not indicate any increase in the sorption of one of the VOCs in the presence of the other compounds.

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