

CHAPTER 3 - Sorption Dynamics of Organic Compounds in Soils and Sediments

- (1) (p. 46) Adsorption - refers to uptake stage of sorption, regardless of mechanism;
Desorption - refers to release stage.
- (2) Sec. 3-1 Slow sorption kinetics
Freundlich eqn used to measure sorption at **equilibrium**:
- $$S = K_d C^n \quad [1]$$
- (3) 1. "Equilibrium constant" obtained as (mg X/g soil) / (mgX/ml) over range of S Conc.
2. Hysteresis where desorptive pathway does not return to zero S at zero C. (Fig. 3-1)
- (4) (p. 49) (1) Resistant - not desorbed during the time of the experiment, but will eventually.
(2) Irreversible - fraction that cannot be recovered in its original form due to transformation (chemical or biological).
5. (p. 49) - Resistant category: = subject of Chapter 3!
(1) Table 3-1 (p. 50), pyrene sorption with incubation time ----->
propose "2-site" model for: (1) fast reaction (min) and (2) slow reaction (hrs, days)
(2) desorption may also follow as pattern of: (1) fast and (2) slow
(3) (p. 53) "Unextractable, bound residues" of pesticides in soil. Research question!
6. (p. 54) Sec. 3-2: Modeling of Sorption Kinetics : Mechanism considerations
(1) Diffusion through bulk water to soil surface
(2) Diffusion through pores of soil to surface of sorbing materials
(3) Diffusion through soil solids (organic matter gels) to sites
(4) Overcoming energy barriers at molecular level to phase transfer or sorption.
7. (p. 54) 3-2.1.1 Diffusion through aqueous solution:
(1) Fick's first law: $F = D \delta C / \delta x$ [2]
(2) Laboratory experiments for batch sorption isotherms: mechanical mixing eliminates diffusion as an important process. Conversely, saturated and unsaturated flow in vadose zone soils, saturated flow in soils and sediments, and laboratory column experiments are cases where advection occurs, but to a lesser degree than a mixed system in a flask!
(3) Advection may be absent altogether: lake bed sediment, small pores of soil particle aggregate, microvoids of soil organic matter or amorphous mineral matter.
(4) Diffusion coefficients in water (D_{H_2O}) at 25C for weak or nonelectrolytes of small molecular size: ca. 0.5 to $1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [$\text{cm}^3/\text{cm}\cdot\text{s}$].
(5) Apparent diffusion coefficient (D_s) for a solute in a porous medium containing solid particles that are inert to the solute:
- $$D_s = \omega D_{H_2O} \quad [4]$$
- where ω is an empirical coefficient to account for solid tortuosity, (0.5 to 0.01).
- (6) Effective diffusion coefficient (D_{eff}) $< D_s$ owing to surface sorption effects:
 D_{eff} will be inversely related to K_d : At high K_d values:
- $$D_{\text{eff}} = \frac{D_s \phi}{\phi + (1 - \phi) \rho_s K_d} \quad [5]$$
- $$D_{\text{eff}} = \frac{D_s \phi}{(1 - \phi) \rho_s K_d} \quad [6]$$

Therefore, as K_d increases, D_{eff} decreases.

(8) (p. 56) 3-2.1.2 Microporosity of Soils

- (1) (p. 57) Fig. 3-4 : Soil aggregate. Pores of 100 - 1000 nm effective diameter can exist between clay domains within microaggregates. Advection of water through pores of this size is slow or nonexistent, therefore transport of solutes is by molecular diffusion.
- (2) Diffusion through micropores may increase sorption times.

(9) (p. 56) 3-2.1.3 Diffusion through organic solids.

- (1) There are little (no) diffusion kinetic studies of sorption to solid soil organic matter.
- (2) (p. 58) Analogy between soil organic matter (gels) and synthetic organic polymers:
- (3) (p. 59) Table 3-3 Diffusion coefficients: 10^{-13} cm² s⁻¹ for benzene in polystyrene. Generally the values in Table 3-3 (diffusion coefficients in polymers) are 2 to 8 orders of magnitude smaller than diffusion coefficients in water.

(10) (p. 61) 3-2.1.4 Activation energies of the sorptive step. Sorption of nonionic organic compounds by partitioning between soil solution and soil organic matter (phyrophobic phase)

1. Sorption is correlated with soil organic matter more than any other factor;
2. Water competes with neutral organics for adsorption to mineral surfaces;
3. Sorption of nonpolar organics does not show competition with other similar organic compounds (as is typical of adsorption on surfaces e.g., activated carbon);
4. Highly hydrophobic organic molecules sorb to dissolved humic and fulvic acids. Similar to surfactant micelles where sorbates dissolve in a microscopic organic phase

(11) (p. 64) 3-2.2 Mathematical approaches to sorption kinetics

- (1) Skip Sec. 3-2.2.1 Nondiffusion Kinetics
- (2) Sec. 3-2.2.2 Diffusion kinetics - important in soil systems!!

$$D_{\text{eff}} = \frac{D_m \phi f(\phi, \tau)}{[(1 - \phi) \rho_s K_d + \phi]} \quad [15]$$

Note inverse relationship between D_{eff} and K_d : See Fig. 3-6 (p. 68).

Engineering implications: (p. 68) Shows sensitivity of D_{eff} to K_d and to other soil variables.

(12) (p. 70) Section 3-3 Implications of Slow Sorption Kinetics

- (1) Sec. 3-3.1 Bioavailability. - Biodegradation occurs in solution phase, therefore, desorption may limit the rate of bioremediation!! Fig. 3-9.
- (2) Sec. 3-3.2 Mass transport -
 - (a) Tailing result of slow sorption
- (3) Sec. 3-3.3 Analytical Methodology - Methodologies are aggressive indicating that rapid sorption and desorption do not occur in "aged" soils.

Engineering implications of this chapter:

- (1) Pump and treat: for "aged" soils and hysteresis, pump and treat systems will not simply "desorb" chemicals from a soil matrix, especially as soil particle size decreases.
- (2) Diffusion is an important process in controlling kinetics of sorption and desorption of organic chemicals in soil systems; "dealing" with this through "pulverization" is one option used on "above-ground" slurry reactors.
- (3) Soil washing technologies have similar factors as those for "pump and treat" with aqueous phases.
- (4) Biodegradation as affected by sorption kinetics and bioavailability

End Chapter 3.

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