SMS-618, Particle Dynamics, Fall 2003 (E. Boss, last updated: 9/22/2003)

Adsorption/desorption (a little beyond the reading material).

'Sorption' is a term describing removal from solution and is a general term for: a. adsorption, b. absorption, and c. precipitation. Adsorption to surfaces is rapid (sec) in contrast to absorption into an aggregate matrix (min/hours). Mathematical description of sorption:

 $q=(mass of material removed from solution)/(mass of solid phase). [<math>\phi$] Partition coefficient:

 $K_d = q/(\text{concentration in solution}) [L^3/M]$

The process of adsorption/desorption controls the distribution of certain chemical between the particulate and dissolved phases. Certain molecules have an affinity to sticking to solids often due to electrical charge interaction. Sorption chemistry controls the behavior of most polar and non-polar organic compounds and heavy metals ions.

Sorption kinetic are fast, and equilibrium is usually assumed between the dissolved fraction and the fraction sorbed. Based on experiment, sorption has been found to obey the Langmuir equation:

$$q = \frac{\Gamma C}{K + C}$$

where C is the concentration in the solution, q is the ratio of adsorbed mass to the particulate mass, K is a constant with units of concentration, and Γ a non-dimensional constant, called the Langmuir isotherm, which provides the value of q for large C. For most toxins in the environment C<<K, and the Langmuir equation simplifies to:

$$q = K_d C$$

Where K_d is the partition coefficient. Typical values for K_d are $10^3 \rightarrow 10^6 l/Kg$.

Source:

Socolofsky A. S., and G. H. Jirka, 2nd edition 2002, Environmental Fluid Mechanics, Part 1: Mass Transfer and Diffusion.

Dissolution and mass transfer:

The conservation equation for a solute is given by

$$\frac{\partial C}{\partial t} + \vec{u}\nabla C = \nabla (D\nabla C), \nabla \equiv \partial/\partial x + \partial/\partial y + \partial/\partial z \tag{1}$$

where \bar{u} is the velocity field ([L T⁻¹]), and *D* the diffusion coefficient ([L² T⁻¹]). We wish to solve this equation for a particle. Let's assume a spherical particles (radius, *r*[L]) suspended in the fluid ($\bar{u} = 0$) and a constant diffusion coefficient *D*=const. around the cell:

$$\frac{\partial C}{\partial t} = D\nabla^2 C, \nabla^2 \equiv \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial}{\partial \phi^2} (2)$$

By invoking spherical symmetry,

$$\frac{\partial C}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right)$$
(3).

The flux of material to/from the cell at any given time $[M L^3 T^{-1}]$ is given by:

$$F = -D \int_{A} \hat{n} \cdot \nabla C dA = -D4\pi r_0^2 \left. \frac{\partial C}{\partial r} \right|_{r=r_0}$$
(4)

where r_0 is the instantaneous radius of the particle.

The volume of the particle is changing as well. Assuming its density stays constant, the mass conservation equation:

$$\frac{\partial m}{\partial t} = \frac{\partial}{\partial t} \left(\frac{4\pi r_0^3}{3} \right) = \rho 4\pi r_0^2 \frac{\partial r_0}{\partial t} = -\alpha F$$
(5)

The mass lost (or gained) is proportional to the flux of material away. When the cell dissolved very slowly, and steady-state can be assumed,

$$C(r) = \frac{r_0(C_0 - C_{ambient})}{r} + C_{ambient}.$$
(6)

A spherical boundary layer forms around the sphere. It turns out that the flux, F, is the same as the steady-state case,

$$F = -4\pi r_0^2 D \frac{\partial C}{\partial r} = 4\pi D r_0 \left(C_0 - C_{ambient} \right), \tag{7}$$

dependent only of the concentration difference between the particle and the dissolved phase. Using (7) within (5), an equation for the change of outer radius as function of time can be retrieved:

$$\frac{\partial m}{\partial t} = \rho 4\pi r_0^2 \frac{\partial r_0}{\partial t} = -\alpha F \to r_0 \frac{\partial r_0}{\partial t} = \frac{D\alpha (C_0 - C_{ambient})}{\rho}$$
(8)

whose solution is:

$$r_0^{2} = R_0^{2} - \frac{2D\alpha(C_0 - C_{ambient})t}{\rho}.$$
(9)

 α is simply a conversion constant from the concentration of solute we are looking at to the material the sphere is made off. Note that many dissolution models assume dr/dt=const...

The particle will disappear in time:

$$t_d = \frac{\rho R_0^2}{2D\alpha (C_0 - C_{ambient})}.$$
(10)

For realism sake, we need to add advection to this model. This will have to wait until we tackle settling velocity, next week.

Resources:

Crank, J., 1975. The mathematics of diffusion. Clarendon Press, Oxford, UK.

Csanady, G. T., 1986. Mass transfer to and from small particles in the sea. *Limnology and Oceanography*, **31**, 237-248.

Karp-Boss, L., E. Boss, and P. A. Jumars, 1996. Nutrient fluxes to planktonic osmotrophs in the presence of fluid motion. *Oceanography and MarineBbiology, an Annual Review*. **34**, 71-107.