

# Lecture 7, Particles in Surface and Water and Exchange of Volatiles between Air and Water

**Conrad (Dan) Volz, DrPH, MPH**

**Bridgeside Point**

**100 Technology Drive**

**Suite 564, BRIDG**

**Pittsburgh, PA 15219-3130**

**office 412-648-8541: cell 724-316-5408: Fax 412-624-3040cdv5@pitt.eduAssistant**

**Professor, Environmental and Occupational Health, University of Pittsburgh, Graduate School of Public Health**

**<http://www.pitt.edu/~cdv5/>; Director-Center for Healthy Environments and Communities<http://www.chec.pitt.edu>;**

**Director, Environmental Health Risk Assessment Certificate Program<http://www.publichealth.pitt.edu/interior.php?pageID=82>**

# Types of Particles

- Mineral- clay aluminosilicates, Iron and manganese hydroxide-approximated density~2.6/cc.
- Organic-plant material, dead bacteria and algal cells as well as decaying aquatic organisms.
- Anthropogenic- sewage biosolids, overflow particles and deposition of industrial emissions. See figure 2-11.

# Particle Settling

- Average settling velocity is approximated by Stokes Law;

$$\omega_f = (2/9)g(p_s/p_f - 1)r^2/\eta_f$$

where  $\omega_f$  is the settling velocity[L/T],  $g$  is acceleration due to gravity,  $p_s$  is solid density and  $p_f$  is fluid density,  $r$  is the particle radius and  $\eta$  is the **kinematic viscosity**(the ratio of the viscosity to the density of the fluid).

**R is meant to be hydrodynamically equivalent diameter (so non-spherical particles can be assessed).**

See figure 2-11 for settling velocities

# Counterbalance of settling and Fickian Processes

- As particles settle they become more concentrated so there is a Fickian transport upward to counteract the downward settling.
- The downward flux density due to settling must equal the upward flux density of diffusion at equilibrium so;

$J_{\text{stokes}} = C \omega_f = J_{\text{fickian}} = D \frac{dC}{dx}$  so by differentiating and rearranging

$C = C_0 e^{-(\omega_f/D)x}$  -the concentration of particles in the water column follows an exponential decay from the bottom upward. **Go over Example 2-3**

# The Air-water Interface

- For volatiles (*i.e.* most solvents and fuels) water-to-air exchange is really the most significant mechanism of removal from surface water. Quite often this removal process is used formally to drive solvents from water through aeration.
- Chemicals in the atmosphere, dependant on concentration can also go from air to water.
- The concentration of a dissolved gas (or vapor) in a surface water at equilibrium with the atmosphere ( $C_{\text{equil}}$ ) is determined by its concentration in air ( $C_a$ ) and its Henry's law constant:  **$C_{\text{equil}} = C_a/H$ ,  $H$  is dimensionless.**
- If the concentration in water ( $C_w$ )  $>$   $C_{\text{equil}}$ , the chemical agent will volatilize into the atmosphere with a flux density given by:  **$J [M/L^2T] = -k_w(C_w - C_a/H)$**  where the gas exchange coefficient ( $k_w$ ),  $[L/T]$  depends on the water flow and air movement above the surface. Flux density is  $-$  into air and  $+$  if into water.
- Note that in the case of volatiles stemming from anthropogenic activity, the term involving  $C_a$  will at least initially be zero and unless atmospheric conditions include low inversions should be essentially thought of as 0 (unless the control volume is small). So the gas exchange coefficient is also called the piston velocity when  $C_a$  is 0.

# The Air-water Interface

- As reality lies somewhere between the conceptualized ideal physical models (*i.e.* the “thin film” and “surface renewal” models) the presently available procedures for estimating flux and/or  $k_w$  purely by calculation are unreliable.
- Thin layer model (figure 2-14)-turbulent diffusion is assumed in both the air and water phases except within a few micrometers from the interface, so transport occurs in this thin stagnant film by molecular diffusion (Ficks first law). Equation 2-32 is the general case and we use 2-29 if  $H$  is  $\gg 0.01$  (most volatile chemicals) and 2-31 if  $H \ll 0.01$  as in the case of PAH or pesticides.
- In the surface renewal model it is assumed that small parcels of water are brought to the surface through turbulence and the average time each parcel spends on the surface determines the gas exchange rate.
- In practice, the best estimates of  $k_w$  are obtained with measurements involving a tracer gas (*e.g.* propane) since the ratio of the gas exchange coefficients of two volatiles can be approximated, but an explicit choice of model must be made.
- In the surface renewal model:  $k_A/k_B = \sqrt{D_A}/\sqrt{D_B}$  (**ratio of the square root of the molecular diffusion constants**)  $\approx \sqrt{[(MW)_B]/[(MW)_A]}$  where the  $D$  are the diffusion coefficients in water and the  $MW$  are the relative molecular masses/weights.
- However, in the case of the thin film model:  $k_A/k_B = D_A/D_B \approx \sqrt{(MW)_B}/\sqrt{(MW)_A}$  where the  $D$  and  $M_r$  are the same

## Ex. 2-6:

Ex. 2-6:

- $k_{TCE}/k_{\text{propane}} = \sqrt{MW_{\text{propane}}}/\sqrt{MW_{\text{TCE}}} = \sqrt{44}/\sqrt{131} \Rightarrow k_{TCE} = (\sqrt{44}/\sqrt{131}) \times 3.0 \times 10^{-3} = 1.7 \times 10^{-3} \text{ {cm/s}}$
- $J = -1.7 \times 10^{-3} \text{ {cm/s}} \times 1.0 \times 10^{-3} \text{ {μg/cm}^3} = \underline{-1.7 \times 10^{-6}} \text{ {μg/cm}^2\text{/s}}$

# Volatilization from Pure Liquids

- This is of concern when a fuel or solvent has been spilled to produce a non-aqueous floating slick on the surface of water or the ground.
- Faster than volatilization of agents dissolved in water as permeation of a “stagnant” film of water at the surface is not required, only a stagnant air film need be overcome.
- The (molar) concentration of the agent at the base of the stagnant air layer (in contact with the spill) is argued to be given by:  $C_a = (PM_w)/RT$  where  $P$  is the vapor pressure,  $M_w$  is the molar mass,  $R$  is the gas constant and  $T$  the absolute temperature.
- The rate of volatilization (flux density) is then given by:
- $J = -k_a C_a = -(D_a/\delta_a) \cdot C_a$
- Where  $k_a$  is the air-side gas exchange coefficient,  $D_a$  the molecular diffusion coefficient of the agent in air and  $\delta_a$  the thickness of the hypothetical film of air;

# Example 2-8

- Benzene VP= 0.12 atm at 20 degrees C.  
Use 2-38 to find the stagnant air film  
[benzene] = 0.4 g/L
- An approximate value for  $ka \approx 3300$   
{cm/hr} [Eq. 2-36]
- [Eq 2-39]  $J = -3300 \text{ {cm/hr}} \times 0.4 \times 10^{-3}$   
{g/cm<sup>3</sup>} = -1.3 g/(cm<sup>2</sup>•hr)

# Volatilization from Pure Liquids

- In practice,  $k_a$  depends quite strongly on the wind velocity and somewhat (for larger slicks) on the size – as advection from upwind contributes to the local concentration, decreasing the concentration gradient at a downwind point.
- Also, the foregoing supposes the spilled agent floats, or does not seep into the ground – but note that halogenated solvents, for example, are more dense than water.

# Relationships involving a first-order process, exponential decay and the half-life:

- $\ln\left(\frac{C}{C_0}\right) = -kt \Rightarrow \ln[C] - \ln[C_0] = -k_1 t$

$$\Rightarrow \ln[C] = \ln[C_0] - k_1 t$$

$$C = C_0 e^{-kt} \quad \text{Exponential decay}$$

Then-Additionally, if  $C_t/C_0 = 0.5$ , then  $\ln(0.5) = -k_1 t_{1/2} \Rightarrow t_{1/2} = 0.693/k_1$

# Reaeration and First-order Processes

- As the air-water gas exchange flux density is proportional to the difference between the concentration (of a given agent) in water ( $C_w$ ) and the equilibrium concentration in air ( $C_w \cdot KH$ ) the difference between the actual and equilibrium concentration in water tends to decay exponentially – like all first-order processes.
- For instance, degassing of some gas (or volatile) from a uniform and steadily flowing stream; when the concentration is  $C_o$  upstream and the atmospheric concentration is negligible, then the concentration downstream is:  $C = C_o \exp(-kr\tau)$  where  $\tau$  the travel time from the upstream to the downstream location and  $kr$  is a gas transfer rate coefficient.
- The coefficient  $kr$  is called a reaeration coefficient if the gas in question is oxygen and is equal to the gas exchange coefficient (*i.e.* the “piston velocity”) divided by the average stream depth.

# First Order Processes in Water

- In still water, the settling of fine particles is counteracted by Brownian motion keeping them suspended; resulting in a concentration gradient of suspended particles that decreases exponentially from the bottom upwards:  $C_x = C_0 \exp(-x \cdot \omega / D)$  where  $\omega$  is the settling velocity,  $D$  is the particle diffusion coefficient and  $x$  is the distance above the bottom.
- Atmospheric  $^{210}\text{Pb}$  (see Table below) is thought to undergo an approximately constant rate of deposition, providing an especially useful means of dating the sediment layers of lakes by measuring the level of residual radioactivity associated with this particular isotope

# Example 2-5

- Letting  $\lambda$  = decay (rate) constant,  $A$  = activity at the sediment depth in question and  $A_0$  = activity at the water-sediment interface, we may write:
- $\ln[A] - \ln[A_0] = -\lambda t \Rightarrow \ln[A/A_0] = -\lambda t$   
 $\Rightarrow -(1/\lambda)\ln[A/A_0] = t$
- $t = -(1/0.031)\ln(2.5/4) = 15$  years
- Sediment accumulation rate =  $10/15 =$   
0.67 cm/yr