Updated: 28 December 2015

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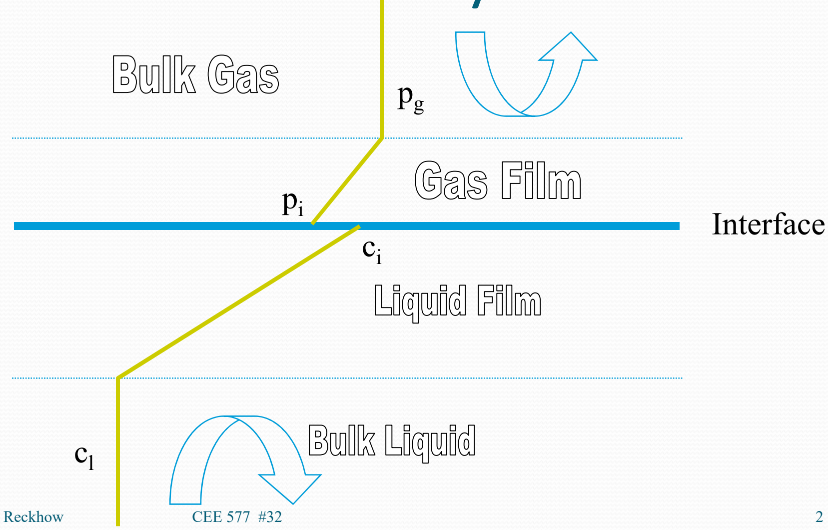
CEE 577: Surface Water Quality Modeling

Lecture #32

Toxics: Volatilization, Photolysis, Hydrolysis and Biodegradation: Recapitulation and Simplified Forms

(Chapra, L41, L42, L43 & L44)

The two film theory



Two film model

- Flux from the bulk liquid to the interface

$$J_l = K_l (c_i - c_l)$$

- Flux from the interface ot the bulk gas

Mass transfer velocities (m/d)

$$J_g = \frac{K_g}{RT_a}(p_g - p_i)$$

  - And the K's are related to the molecular diffusion coefficients by:

$$K_l = \frac{D_l}{z_l} \qquad K_g = \frac{D_g}{z_g}$$

Two film theory (cont.)

- We want to be able to relate flux to bulk air and water concentrations
  - interface concentrations cannot be directly measured

$$J = v_v \left(\frac{p_g}{H_e} - c_l \right)$$

- to do this we must substitute expressions for the interface concentrations

Whitman's 2 film model (cont.)

- According to Henry's law: $p_i = H_e c_i$
- And relating this back to the bulk concentration

$$J_l = K_l(c_i - c_l)$$

$$c_i = \frac{J_l}{K_l} + c_l$$

- now combining, we get:

$$p_i = H_e\left(\frac{J_l}{K_l} + c_l\right)$$

$$J_g = \frac{K_g}{RT_a}(p_g - p_i)$$

$$p_i = p_g - \frac{J_g RT_a}{K_g}$$

$$p_g - \frac{J_g RT_a}{K_g} = H_e\left(\frac{J_l}{K_l} + c_l\right)$$

Whitman's 2 film model (cont.)

- And re-arranging

$$\frac{\left(\frac{p_g}{H_e} - c_l\right)}{J} = \frac{1}{K_l} + \frac{RT_a}{H_e K_g}$$

- And recall:

$$J = v_v\left(\frac{p_g}{H_e} - c_l\right) \rightarrow \frac{1}{v_v} \equiv \frac{\left(\frac{p_g}{H_e} - c_l\right)}{J}$$

- now solving and equating the fluxes, we get (pg. 371 in text):

$$\frac{1}{v_v} = \frac{1}{K_l} + \frac{RT_a}{H_e K_g}$$

The net transfer velocity across the air-water interface (m/d)

Whitman's 2 film model (cont.)

- Which can be rewritten as: $$v_v = K_l \frac{H_e}{H_e + RT_a\left(K_l/K_g\right)}$$
  - H_e: Contaminant specific
  - $RT_a\left(K_l/K_g\right)$: Environment specific
- Now, applying it to toxicants
  - $p_g \cong 0$
  - $c_l = c_d$

or $$v_v = K_l \frac{K_g H_e'}{K_l + K_g H_e'}$$

Where, $H_e' = H_e/RT$
Unitless Henry's Law Const

- And converting to the appropriate units:

$$J = -v_v c_d$$

$$V\frac{dc}{dt} = -v_v A_s c_d$$

Volatilization: Parameter estimation

- Liquid film mass transfer coefficient (m/d)

$$K_l = K_{l,O_2}\left(\frac{32}{MW}\right)^{0.25} \quad \text{and} \quad K_{l,O_2} = K_a H$$

MW: Compound molecular weight

- Gas film mass transfer coefficient (m/d)

$$K_g = 168 U_W \left(\frac{18}{MW}\right)^{0.25}$$

or $$K_g = 346 U_W (MW)^{-0.25}$$

U_W: Wind velocity (mps)

Volatilization: lakes

- For lakes, correlations with K_a cannot be used
- Wind velocity (U_w in m/s) drives liquid phase resistance

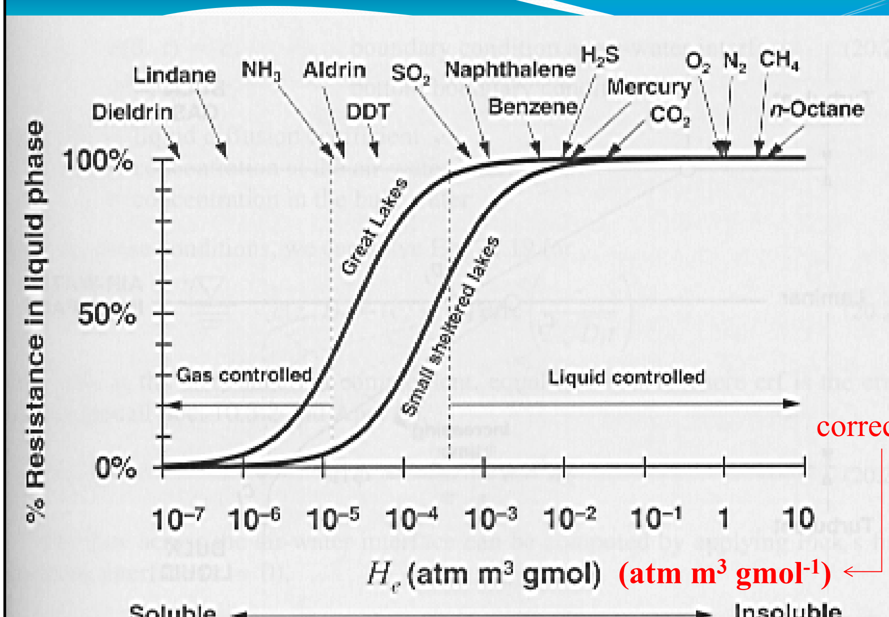
$$K_l = 0.17 C_d \left(\frac{D_l}{\nu_l} \right) U_w$$ For K_l in m/d

  - Where: C_d is the drag coefficient (~0.001), D_l is the diffusivity of the toxicant in water, and ν_l is the kinematic viscosity of water (0.01 cm²/s)
  - This reduces to: $$K_l \approx 0.017 D_l U_w$$ For K_l in m/s

$$K_l \approx 1470 * D_l U_w$$ For K_l in m/d

From Thomann & Mueller, 1987

Thus, the 0.017 coefficient essentially has the units: s/cm².



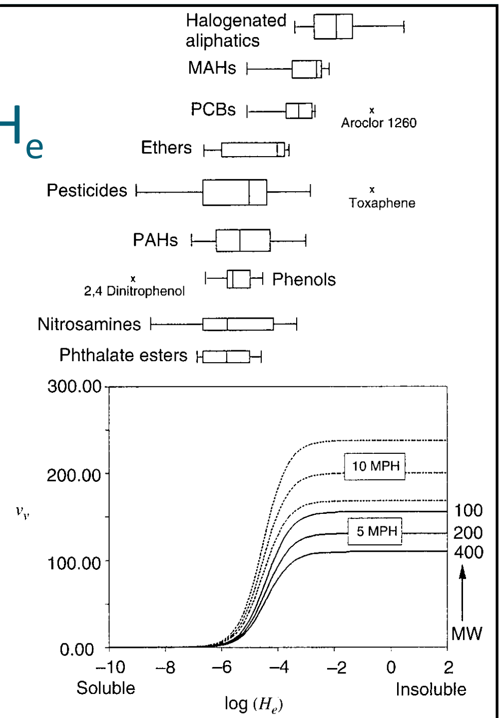
correction

(atm m³ gmol⁻¹)

Figure 20.4, page 373 in text.

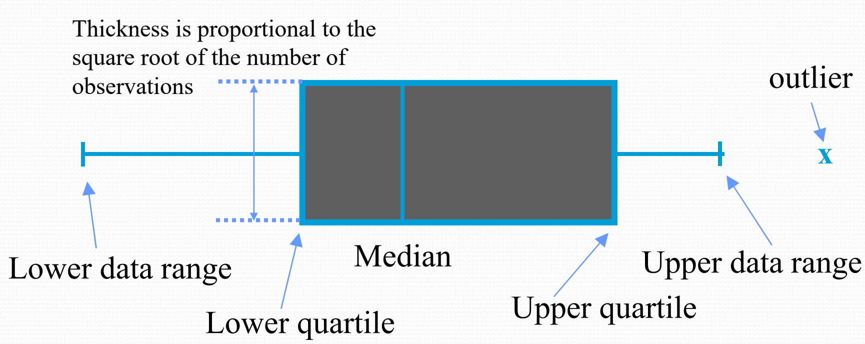
Effect of U_w and H_e

- Chapra, pg. 730



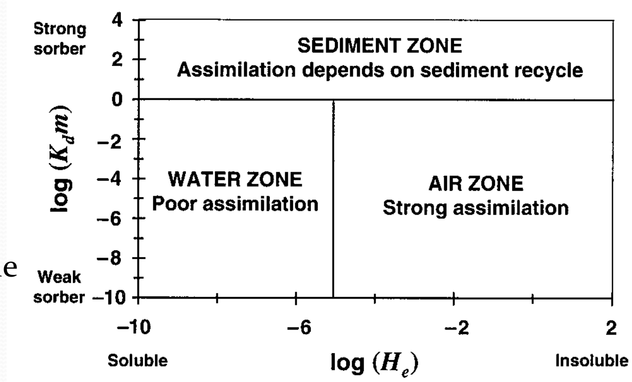
Box and Whisker Plots

- Useful for summarizing non-ideal data distributions



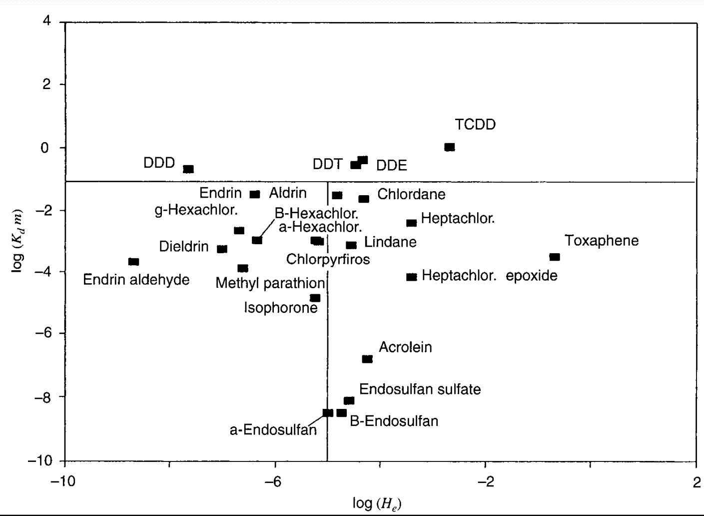
Summary of sorption & volatilization effects

- Assume
  - T_a=283 K
  - M=200 g/mole
  - U_w = 5 mph
  - v_s =91 m/yr
- Assimilation refers to general rate of removal



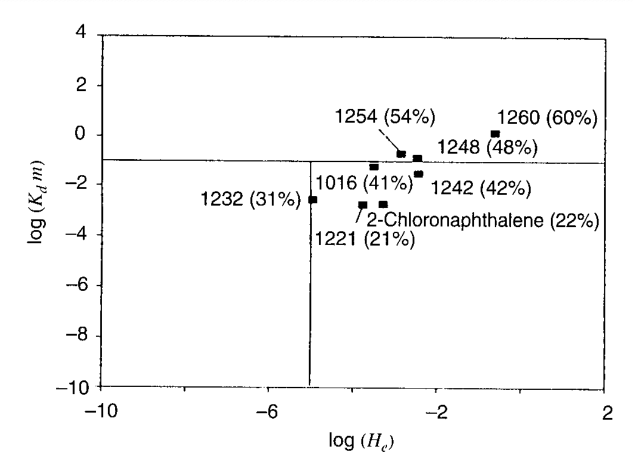
Summary: pesticides

- Chapra, pg.735



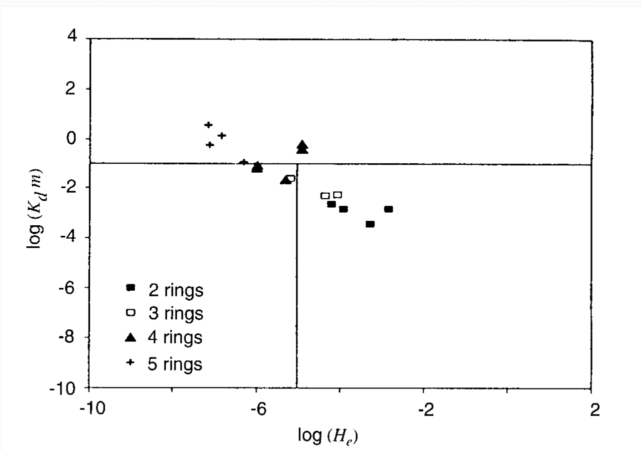
Summary: PCBs

- Chapra, pg.736



Summary: PAHs

- Chapra, pg.736



- To next lecture