Toxics: Volatilization, Photolysis, Hydrolysis and Biodegradation: Recapitulation and Simplified Forms
(Chapra, L41, L42, L43 & L44)
Two film model

- Flux from the bulk liquid to the interface
  \[ J_l = K_l(c_i - c_l) \]

- Flux from the interface to the bulk gas
  \[ J_g = \frac{K_g}{RT_g} (p_g - p_i) \]

- Mass transfer velocities (m/d)

- And the K’s are related to the molecular diffusion coefficients by:
  \[ K_l = \frac{D_l}{z_l} \]
  \[ K_g = \frac{D_g}{z_g} \]

Two film theory (cont.)

- We want to be able to relate flux to bulk air and water concentrations
  - interface concentrations cannot be directly measured
  \[ J = v_i \left( \frac{p_g - c_i}{H_i} \right) \]

- 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
  \[ J_i = K_i (c_i - c_i) \]
  \[ c_i = \frac{J_i}{K_i} + c_i \]

- Now combining, we get:
  \[ p_i = H_e \left( \frac{J_l}{K_l} + c_i \right) \]

\[ p_g - \frac{J_g RT_a}{K_g} = H_e \left( \frac{J_l}{K_l} + c_i \right) \]

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

\[ p_i = \frac{J_g RT_a}{K_g} \]

- And re-arranging
  \[ \frac{\frac{p_g}{H_e} - c_i}{J} = \frac{1}{K_l} + \frac{RT_a}{H_e K_g} \]

- And recall:
  \[ J = v_i \left( \frac{p_g}{H_e} - c_i \right) \]

\[ J = \frac{1}{v_i} \left( \frac{p_g}{H_e} - c_i \right) \]

- Now solving and equating the fluxes, we get (pg. 371 in text):
  \[ \frac{1}{v_y} = \frac{1}{v_i} \left( \frac{p_g}{H_e} - c_i \right) \]

\[ \frac{1}{v_y} = \frac{1}{v_i} + \frac{RT_a}{K_l + H_e K_g} \]

The net transfer velocity across the air-water interface (m/d)
Whitman’s 2 film model (cont.)

- Which can be rewritten as:
  \[ y = \frac{H_c}{H_c + RT_a \left( \frac{K_l}{K_g} \right)} \]

- Now, applying it to toxicants
  - \( p_g = o \)
  - \( c_i = c_d \)

- And converting to the appropriate units:
  \[ J = -v_r c_d \]

\[
\nu \frac{dc}{dt} = -v_r A_i c_d
\]

Volatilization: Parameter estimation

- Liquid film mass transfer coefficient (d⁻¹)
  \[ K_l = K_{l,O_2} \left( \frac{32}{M} \right)^{0.25} \]
  and \[ K_{l,O_2} = K_a H \]

- Gas film mass transfer coefficient (d⁻¹)
  \[ K_g = 168U_u \left( \frac{18}{M} \right)^{0.25} \]

Wind velocity (mps)
Volatilization: lakes

- For lakes, correlations with $K_a$ cannot be used
- Wind velocity ($U_w$) drives liquid phase resistance

$$K_l = 0.17 C_d \left( \frac{D_l}{\nu_l} \right) U_w$$

- Where: $C_d$ is the drag coefficient (~0.001), $D_l$ is the diffusivity of the toxicant in water (0.1 cm$^2$/s)
- This reduces to:

$$K_l \approx 0.0017 D_l U_w$$

Figure 20.4, page 373 in text.
Box and Whisker Plots

- Useful for summarizing non-ideal data distributions

Thickness is proportional to the square root of the number of observations

Lower data range

Upper data range

Lower quartile

Upper quartile

Median

outlier

$x$
Summary of sorption & volatilization effects

- Assume
  - $T_a=283$ K
  - $M=200$ g/mole
  - $U_w = 5$ mph
  - $v_s = 91$ m/yr

![Diagram showing sorption and volatilization effects](image)

**Summary: pesticides**

- Chapra, pg.735
Summary: PCBs

- Chapra, pg.736

Summary: PAHs

- Chapra, pg.736
• To next lecture