Toxics: Photolysis
(Chapra, L42)

Overall decay rate

- $k_1$ is a combination of
  - Hydrolysis ($k_h$)
  - Photolysis ($k_p$)
  - Biodegradation ($k_b$)
  - Any other loss process not otherwise included in the model

- Any of these processes may be affected by sorption
- Photolysis is most commonly attributed to dissolve forms only

$$k_1 = k_h + f_p k_p + k_b$$
Photolysis

- Chemical breakdown initiated by light energy
- Two types
  - Direct photolysis
  - Sensitized (or indirect) photolysis
- Several steps
  - Some solar light reaches water surface
  - Some of this light penetrates to the solute
  - Some of this is absorbed by the solute
  - Some of absorbed light is capable of causing a reaction

Solar Radiation

[Diagram showing solar radiation spectrum with wavelength (nm) on the x-axis and solar radiation on the y-axis, with labels for ultraviolet, visible, and infrared regions and the edge of outer atmosphere and earth's surface marked.]
Attenuation of light through water

- Beer-Lambert’s Law

\[ I(z, \lambda) = I(0, \lambda) e^{-\alpha_d(\lambda)z} \]

- and the attenuation coefficient is from:

\[ \alpha_d(\lambda) = \frac{1}{H} \ln \left( \frac{I(0, \lambda)}{I(H, \lambda)} \right) \]

Measured light intensity with depth

- Lake San Vincente
- Tyler & Smith, 1970
• Average light absorption over depth $H$

$$I = \frac{I(0, \lambda)}{H} \left( 1 - e^{-\alpha(\lambda) H} \right)$$

einsteins/cm$^3$/s
Spectral overlap

- (a) benzene; (b) naphthacene or tetracene

![Graphs showing spectral overlap for benzene and naphthacene or tetracene.]

Absorption of Light

- Attenuation due to background and contaminant

\[ I(\ell, \lambda) = I(0, \lambda)e^{\left[\alpha(\lambda) + \varepsilon(\lambda)c\right]\ell} \]

- Integrating over the depth and isolating on the contaminant we get:

\[ I_{a}(\lambda) = \frac{\varepsilon(\lambda)I(0, \lambda)(1 - e^{-\alpha_{D}(\lambda)H})c}{H\alpha(\lambda)} \]

Molar extinction coefficient (L/mole/cm)
Quantum Yield

• Once absorption occurs, energy is dissipated by:
  • emission of heat
  • emission of light: luminescence
  • contact with another molecule: photosensitization
  • decomposition: direct photolysis

• Fraction following last pathway is quantum yield

\[ \Phi_r(\lambda) = \frac{\text{number of moles transformed}}{\text{total moles of photons of wavelength } \lambda \text{ absorbed}} \]

• And combining with absorption equation:

\[ k_p(\lambda) = \Phi(\lambda)k_a(\lambda) = \Phi(\lambda) \frac{\epsilon(\lambda)I(0,\lambda)(1-e^{-\alpha_p(\lambda)H})}{H\alpha(\lambda)} \]
• To next lecture