Lecture #12

Application of TLM & TVs to sediments.

\[ TLM \quad C_{Lj}^+ = K_{LW_i} C_{Wi}^+ \]  
Species j chemical i

\[ \text{For species } i \quad C_{L}^+ = K_{LW_i} C_{W_i}^+ \]
\[ \log K_{LW_i} = 0.945 \log K_{OW_i} \]
\[ \Rightarrow C_{W_i}^+ \quad \text{(eq. LC50)} \]

Mixtures: Toxic Units \( TU_i \) = \( \frac{C_{Wi}^+}{C_{W_i}^+} \)

Common mode of action \( TU = \sum_i TU_i \)

\( TU = 1 \) 50% effect (LC50)

\( EqP / Sediments / \)

\( (\text{mmol/kg dry wt}) \quad C_s^+ = K_p C_{W_i}^+ \) (mmol/L)

\( K_p = \text{partition coeff. sediment} + \text{pore water} \) (L/kg dry wt)

For hydrophobic, neutral organic chemicals

\( K_p = f_{oc} K_{oc_i} \quad / \quad f_{oc} > 0.5 \% \)

\( \log K_{oc_i} = 0.00078 + 0.986 \log K_{OW_i} \)

Definition \( C_{S,OC_i} = \frac{C_s^+}{f_{oc}} = K_{oc_i} C_{W_i}^+ \) (mmol/kg OC)
Sediment Toxic Units

\[ TU_i = \frac{c_{Wi}^*}{c_{Wc}^*} = \frac{c_{S,oc_i}^*/K_{oc_i}}{c_{S,oc_i}^*/K_{oc_i}^*} = \frac{c_{S,oc_i}^*}{c_{S,oc_i}^*/K_{oc_i}^*} \]

\[ TLW : c_L^* = K_{LW_i} c_{Wc}^* / c_{Wc}^* = \frac{c_L^*}{K_{LW_i}} \]

\[ c_{S,oc_i}^* = K_{oc_i} c_{Wc}^* = \frac{K_{oc_i} c_L^*}{K_{LW_i}} \]

\[ \Rightarrow c_{S,oc_i}^* = \frac{K_{oc_i}}{K_{LW_i}} c_L^* \]

\[ \log c_{S,oc_i}^* = \log K_{oc_i} - \log K_{LW_i} + \log c_L^* \]

\[ = 0.00028 + 0.986 \log K_{oc_i} - (0.945 \log K_{oc_i}) + \log c_L^* \]

\[ = 0.00028 + 0.038 \log K_{oc_i} + \log c_L^* \]

\[ TU_i = \frac{c_{S,oc_i}^*}{c_{S,oc_i}^*} \]

\[ TU = \sum_i TU_i \]

\[ \% \text{ mortality} \]

\[ 50\% \]

Multiple chemicals

\[ TU = \sum_i TU_i \]

\[ \log TU \]
Approximation

\[ \log C_{S, OC}^* = 0.00028 + 0.038 \log K_{OW_i} + \log C_L^* \]

\[ C_{S, OC}^* = 10^{0.64} C_L^* \]

\[ \log K_{OW_i} \approx 1.09 \]

\[ C_{S, OC}^* \approx 1.3 C_L^* \rightarrow \begin{align*}
1 & \rightarrow 3 \\
5 & \rightarrow 1.55
\end{align*} \]

Independent of chemical

\[ T_U = \frac{C_{S, OC}_i}{C_{S, OC}^*} = \frac{C_{S, OC}_i}{1.3 C_L^*} \]

Mixture:

\[ T_U = \sum_{i} \frac{C_{S, OC}_i}{1.3 C_L^*} = \frac{1}{1.3 C_L^*} \sum_{i} C_{S, OC}_i \]

\[ \text{Example: } C_L^* = 10 \text{ nmol/g lipid} \]

\[ C_{S, OC}^* = 1.3 \times (10 \text{ nmol/g OC}) \]

Note: Sum of all the chemicals in sediment OC normalized.
Variations in Copper LC50 Due to Variations in Water Chemistry

Estuarine Diatom Exposed to Copper (Thalassiosira pseudonana)

Figure 2. Growth rate of closter 3H vs the negative log of the total copper concentration in M-62 seawater media containing 0.10 mM Cu at pH 7.7 to 8.7. Results are from experiments 1-5. Error bars represent the standard deviation for least squares linear regression of growth curves.

Figure 3. Growth rate of closter 3H vs Cu2+ in M-62 seawater culture media containing 1.0 mM Cu for the pH range 7.7 to 8.7. Individual points are from experiments 1-5. The Cu2+ error bars represent variation in Cu2+ caused by changes in culture pH.

[from Sunda and Guillard 1976, J. Mar. Res. 34:511-529]
Copper Speciation in Fresh Water

\[ \text{DOC} = 0.01 \text{ mg/L } \text{Cu}_f = 18 \text{ ug/L} \]

\[
\begin{align*}
\text{Cu}^{2+} & \quad \text{CuSO}_4 \\
\text{CuHCO}_3^- & \quad \text{Cu-DOC} \\
\text{CuOH}^- & \quad \text{CuO} \\
\text{CuCO}_3 & \\
\text{Cu(OH)}_2 & \quad \text{pH}
\end{align*}
\]

Toxic: \[ \text{Cu}^{2+} + \text{HCO}_3^- \rightarrow \text{CuHCO}_3^+ \] (Non-toxic)

\[
\begin{align*}
\text{Ca}^{2+} + \text{Cu}^{2+} & \rightarrow \text{Ca} \cdot \text{Cu}^{4+} \quad \text{(No)}
\end{align*}
\]

Copper LC50 - Cutthroat Trout

<table>
<thead>
<tr>
<th>Alkalinity ((\sim) HCO(_3^))</th>
<th>Low Hardness</th>
<th>Medium Hardness</th>
<th>High Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>LC50 (umol/L)</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Low</td>
<td>1</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Medium</td>
<td>2</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>High</td>
<td>3</td>
<td>6</td>
<td>5</td>
</tr>
</tbody>
</table>

Chakourakis, C., R.C. Russo, and R.V. Thurston,
Toxicity of copper to Cutthroat Trout (Salmo clarki) under different conditions of alkalinity, pH and hardness.
\[
\begin{align*}
\uparrow & \quad \text{Ca}^{2+} \quad \text{Ca}^{2+} \\
\downarrow & \quad \text{Cu}^{2+} \quad \text{Ca}^{2+} \\
\text{Ca}^{2+} \quad \text{HCO}_3^- & = \quad \text{HCO}_3^- \quad \downarrow \\
\text{add Ca}, \text{ what happens.} & =
\end{align*}
\]
Pagenkopf Gill Surface Interaction Model (1983)

The ideas:

- Only $[\text{Cu}^{2+}] + [\text{CuOH}^+] + [\text{Cu(OH)}_2] = \alpha_{\text{Cu}}\text{Cu}_T$ is bioavailable.

- Hardness competes with inorganic copper at the gill:

  \[
  \text{Ca}^{2+} + \text{Cu} - \text{BL} \rightarrow \text{Cu}^{2+} + \text{Ca} - \text{BL} \\
  K_H (?)
  \]

  Effective Toxic Conc. \[ \rightarrow \text{ETC} = \frac{\alpha_{\text{Cu}}\text{Cu}_T}{1 + K_H[M]} \]

  \[
  M = \text{Hardness cations}
  \]

The Gill Surface Interaction Model (GSIM)

Pagenkopf (1983)

Copper, Rainbow Trout

![Graph showing LC50 and ETC values across pH levels](image)
Playle and Dixon (1993)
FHM TCu = 17 ug/L

![Graph showing gill Cu (µg Cu·g⁻¹ wet tissue) vs. free Cu⁺⁺ (µM) with data points and a trend line.]

![Graph showing 120-Hour Juvenile Rainbow Trout Mortality (%) vs. 24-Hour Gill Cu (nmol/g wet weight) with data points and a trend line.]
Fig. 2. Measured copper accumulation on fathead minnow gills from Playle et al. [12] and biotic ligand model (BLM) predictions as a function of cupric ion concentration.
Fig. 5. Relationship of copper LC50s to variations in dissolved organic carbon (DOC) concentration. The lines are drawn by eye to represent the data. (A) LC50 expressed as the concentration of total dissolved copper. (B) LC50 expressed as the concentration of the free ion activity of copper. (C) LC50 expressed as the concentration of the copper sorbed to the gill. The LC50s in (B) and (C) are calculated using the Windermere humic aqueous model (WHAM) and the biotic ligand model from the concentrations of total copper and the other relevant aqueous species (Table 1). Data from Erickson [39].
Fig. 7. Relationship of copper LC50s to variations in pH. The lines are drawn by eye to represent the data. (A) LC50 expressed as the concentration of total dissolved copper. (B) LC50 expressed as the concentration of the free ion activity of copper. (C) LC50 expressed as the concentration of the copper sorbed to the gill. The LC50s in (B) are the measured copper activities using a specific ion electrode. The LC50s in (C) are calculated using the biotic ligand model (BLM) from the concentrations of total copper and the other relevant aqueous species (Table 1). Data from Erickson [39].
Water Effect Ratio

Site Water
Copper Concentration (µg/L)
0 100 200 400 600 1600

Lab Water
Copper Concentration (µg/L)
0 100 200 400 800 1600

Vert Test Dose Response:
Site Water
Lab Water

Mortality (%) vs Copper (µg/L)

Site Water LC50 = 400 µg/L
Lab Water LC50 = 200 µg/L

Therefore:
WER = 400/200 = 2

Site Specific WQC = WER x WQC

Fig. 8: The impact concentrations of total organic carbon (TOC), total of the essential for dissolved organic carbon in the application of basic, regular chab, alkalinity, hardness, and pH, to laboratory water, NAP, exposure water (10%), and the percentage of effluent differences in operation water (Table 1). Data from Dussault (47).
Fig. 9. Method of calculating the LC50 using the biotic ligand model. Relationship of copper concentration sorbed on the gill and dissolved copper as computed using the biotic ligand model (BLM) for laboratory water and 75% effluent.