Metal Classification using a Unit World Model (TICKET-UWM)

Examples, Comparison to POPs, and Parameterization

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Workshop: Validity of the Use of the Concept of “Rapid Removal”
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Objectives

• Demonstrate that long-term effects can be successfully evaluated for metals in line with the guidance in the metals section of the UN-GHS and the EU-CLP

• Provide examples of metal removal and remobilization potential assessments and discuss most critical model parameters

• Compare removal behavior of persistent organic pollutants (POPs) using model simulations similar to those used for metals

• Provide full transparency on the parameterization of the TICKET-UWM model as used for hazard screening
Presentation Outline

• **Examples** of TICKET-UWM use for metal classification
  – Water column
  – Sediment

• TICKET-UWM calculations with **POPs**

• Discussion of model **parameterization**

• **Performance** assessment example

• **Concluding remarks** on TICKET-UWM application for classification
Metal Classification Examples
Principles of TICKET-UWM Assessment

- Use TICKET-UWM to assess removal of soluble metal salts from the water column resulting from changes of speciation and subsequent precipitation:
- This entails simulation of:
  1. Removal of soluble metal salts from the water column through speciation transformations and sedimentation of particulate metal AND
  2. Metal fate in sediments including metal speciation transformations and remobilization potential in sediments (as indicated by sediment feedback and diffusive fluxes)
- Model parameterization is standardized for use in hazard classification schemes based on GHS
TICKET-UWM¹ Screenshot

Try it! Available free of charge at www.unitworldmodel.net

Water Column Partitioning and Sedimentation

- Spike of soluble metal salt into water column
- pH 6, 7, and 8
- Binding phases: DOC and POC
- Starting concentrations between chronic ERVs and 1000 µg/L
- Partitioning description
  - WHAM V-calculated
    - Water chemistry-dependant
    - *Variable $K_D$*
  - Empirical $K_D$
    - Linear partitioning
    - *Constant $K_D$*

Instantaneous 66% removal of dissolved metal via equilibrium partitioning
70% Removal

![Graph showing partitioning](image-url)
Lead (Pb) Results

**Empirical $K_D$ (Constant)**

Instantaneous 82% removal of dissolved Pb via equilibrium partitioning

$log K_D = 5.47$

**WHAMV $K_D$ (Water chemistry dependant)**

70% Removal

$log K_D = 5.28 - 5.97$
Nickel (Ni) Results

**Empirical $K_D$ (Constant)**

- Instantaneous 28% removal of dissolved Ni via equilibrium partitioning
- $\log K_D = 4.42$

**WHAMV $K_D$ (Water chemistry dependant)**

- 70% Removal
- $\log K_D = 3.16 - 3.61$
- $\log K_D = 3.95 - 5.30$

**Removal at Day 28**

- Default: $\log K_D = 3.16 - 3.61$
- No Ca/Mg Competition: $\log K_D = 3.95 - 5.30$

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Barium (Ba) Results

- Below solubility limit of $\text{BaSO}_4(s)$ (~75 – 400 µg/L Ba), removal is limited because of weak binding to POC.
Take Home Messages: Water Column

• The “degradation capacity” of metals depends on the extent to which they bind to particles (i.e. particle-reactivity)
  – Elimination from the water column is fast/extensive for highly particle-reactive metals, while non particle-reactive metals remain in the water column.
  – Between those two ends there is a scaling of affinities and removal capacities

• Since model-predicted $K_D$ values may deviate from empirical values, it is important to consider model results with both empirical and WHAM V-predicted solid-solution distribution in hazard classification

• $K_D$ is a critical factor in removal rate
**Transport Between Water Column and Sediment**

Water Column Mass Balance:

\[ V\frac{dC}{dt} = QC_{in} + W - QC_{out} \]

Rate of Accum. of Depletion:

\[ \text{Mass}_{\text{inflow}} + \text{Load} - \text{Mass}_{\text{outflow}} \]

In non flow through (batch) system w/ spike loading, these terms = 0

- Settling
- Resusp.
+ Diffusion

Potential feedback mechanisms:

\[ v_s A_s C_{part} - v_r A_s C_{part,sed} - k_r A_s [C_{diss} - C_{diss,sed}] \]

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Sediment Speciation and Remobilization Potential

• Spike at acute ERV, 100 and 1000 µg/L
• 365-day simulation
• Sediment speciation calculation:
  – Binding phases:
    • Oxic sediment: POC, HFO, and HMO
    • Anoxic sediment: POC and AVS
  – AVS oxidizes immediately upon resuspension (= worst case)
• Remobilization assessment metrics:
  – Is water column conc. maintained below 70% removal benchmark?
  – Direction of diffusive flux
  – Speciation transformations
Sediment Results for Select Metals

Example of feedback effect (resuspension and diffusion) : Pb

[Graph showing Pbₜₐₜ(t) (µg/L) over time (days) with 70% Removal and feedback and no feedback conditions.]

- >300 x lower than initial Pb
- >100 x lower than 70% removal conc.
# Sediment Results for Select Metals

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Sequestration Metric</th>
<th>Solid-Phase Speciation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sustained 70% removal?</td>
<td>Diffusive Flux</td>
</tr>
<tr>
<td><strong>LEAD</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>POC and AVS</td>
<td>YES</td>
<td>Into Sediment</td>
</tr>
<tr>
<td>POC, HFO, and HMO</td>
<td>YES</td>
<td>Out of Sediment</td>
</tr>
<tr>
<td><strong>NICKEL</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>POC and AVS</td>
<td>YES, after 29 days</td>
<td>Into Sediment</td>
</tr>
<tr>
<td>POC, HFO, and HMO</td>
<td>YES, after 29 days</td>
<td>Out of Sediment</td>
</tr>
</tbody>
</table>
Take Home Messages: Sediment

• Feedback from sediment generally has limited impact on attainment and sustainment of low metal concentrations in the water column following dosing

• Model-predicted metal precipitation as metal sulfides maintains diffusive flux directed into the sediment
TICKET-UWM Calculations with POPs
Persistent Organic Pollutants (POPs)

- **Concern:** “Rapid degradation” approach for metals could indicate POPs are rapidly degraded
- Use TICKET-UWM to perform removal/remobilization calculations for select organics analogous to those made for metals
- Persistent Organic Pollutants (POPs*) and other Organics Chemicals
  - DDT*
  - Hexachlorobenzene*
  - Heptachlor*
  - Endrin*
  - Acenaphthene
  - Lindane*
Water Column Partitioning and Sedimentation

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbr.</th>
<th>Henry’s Const. (Pa·m³·mol⁻¹)</th>
<th>log $K_{OW}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4'-DDT</td>
<td>DDT</td>
<td>0.14</td>
<td>6</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>HCB</td>
<td>65</td>
<td>5.5</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>Hept</td>
<td>38</td>
<td>5.27</td>
</tr>
<tr>
<td>Endrin</td>
<td>Endr</td>
<td>1.1</td>
<td>4.5</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>Acen</td>
<td>12.2</td>
<td>3.93</td>
</tr>
<tr>
<td>Lindane</td>
<td>Lind</td>
<td>0.29</td>
<td>3.7</td>
</tr>
</tbody>
</table>

No pH effect for organic $K_D$ values $\rightarrow$ Endr, Acen, Lind will fail 70% removal in 28 day test at pH 6, 7, and 8.
Sediment Results for POPs

DDT

Pb

Time (days)

0 10 20 30 40 50 60

DDT_{tot}(t) (\mu g/L)

0 0.001 0.01 1

70% Removal

Feedback

No feedback

Time (days)

0 10 20 30 40 50 60

Pb_{tot}(t) (\mu g/L)

0 0.1 1

70% Removal

Feedback

No feedback
## Sediment Results for POPs

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Sequestration Metric</th>
<th>Diffusive Flux</th>
<th>Solid-Phase Speciation</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDT</td>
<td>Sustained 70% removal? YES</td>
<td>Out of Sediment</td>
<td>100% POC</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td>YES</td>
<td>Out of Sediment</td>
<td>100% POC</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>YES</td>
<td>Out of Sediment</td>
<td>100% POC</td>
</tr>
<tr>
<td>Endrin</td>
<td>YES, After 85 days</td>
<td>Out of Sediment</td>
<td>100% POC</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>70% removal not obtained in 1 year</td>
<td>Out of Sediment</td>
<td>100% POC</td>
</tr>
<tr>
<td>Lindane</td>
<td>70% removal not obtained in 1 year</td>
<td>Out of Sediment</td>
<td>100% POC</td>
</tr>
</tbody>
</table>
Take Home Messages: POPs

• Some POPs can also “degrade” to levels representing > 70% removal from the water column, **BUT:**
  – Exclusively due to partitioning to POC
  – Model-predicted diffuse flux is **out** of the sediment into the water column
  – Unlike metals, no speciation transformation to a less (or non) toxic form
Discussion of Model Parameterization
# Water Column - UWM Model Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth, m</td>
<td>EUSES</td>
<td>3</td>
</tr>
<tr>
<td>Settling rate, m/d</td>
<td>EUSES</td>
<td>2.5</td>
</tr>
<tr>
<td>Burial rate, cm/yr</td>
<td>EUSES</td>
<td>0.3</td>
</tr>
<tr>
<td>Resuspension rate, cm/yr</td>
<td>EUSES</td>
<td>2.44</td>
</tr>
<tr>
<td>Diffusive exchange, cm/day</td>
<td>EUSES</td>
<td>0.24</td>
</tr>
<tr>
<td>Sediment f_{oc}</td>
<td>EUSES</td>
<td>0.05</td>
</tr>
<tr>
<td>Sediment solids conc., g/L</td>
<td>EUSES</td>
<td>500</td>
</tr>
<tr>
<td>Active depth, cm</td>
<td>EUSES</td>
<td>3</td>
</tr>
<tr>
<td>AVS, µmol/g</td>
<td>NiPERA, 2009</td>
<td>1</td>
</tr>
<tr>
<td>POC, mg/L</td>
<td>TGD – Part II</td>
<td>1.5</td>
</tr>
<tr>
<td>DOC, mg/L</td>
<td>GHS Annex 10 – T/D</td>
<td>2.0</td>
</tr>
<tr>
<td>pH</td>
<td>GHS Annex 10 – T/D</td>
<td>6.09  7.07  8.00</td>
</tr>
<tr>
<td>Alkalinity, mg/L as CaCO₃</td>
<td>GHS Annex 10 – T/D</td>
<td>3.85  7.47  37.2</td>
</tr>
<tr>
<td>Calcium, mg/L</td>
<td>GHS Annex 10 – T/D</td>
<td>8.0  32.1  80.1</td>
</tr>
<tr>
<td>Magnesium, mg/L</td>
<td>GHS Annex 10 – T/D</td>
<td>1.2  4.9  12.1</td>
</tr>
<tr>
<td>Sodium, mg/L</td>
<td>GHS Annex 10 – T/D</td>
<td>1.8  3.4  18.0</td>
</tr>
<tr>
<td>Potassium, mg/L</td>
<td>GHS Annex 10 – T/D</td>
<td>0.3  1.2  3.02</td>
</tr>
<tr>
<td>Sulfate, mg/L</td>
<td>GHS Annex 10 – T/D</td>
<td>4.8  19.2  47.9</td>
</tr>
<tr>
<td>Chloride, mg/L</td>
<td>GHS Annex 10 – T/D</td>
<td>14.5  57.8  145</td>
</tr>
</tbody>
</table>
Key Water Column Parameters

- Physical parameters:
  - Water depth
  - Settling velocity
- Chemical parameters
  - In WHAM models, calculated $K_D$ is a function of water chemistry
  - pH, DOC, POC, hardness cations
## Sediment - UWM Model Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Source</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>Flemish dataset</td>
<td>7.56</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>Flemish dataset</td>
<td>144</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>Flemish dataset</td>
<td>38.1</td>
</tr>
<tr>
<td>Na$^+$, mg/L</td>
<td>Estim. from Flemish dataset</td>
<td>141</td>
</tr>
<tr>
<td>K$^+$, mg/L</td>
<td>Estim. from Flemish dataset</td>
<td>6.19</td>
</tr>
<tr>
<td>Cl$^-$, mg/L</td>
<td>Flemish dataset</td>
<td>79</td>
</tr>
<tr>
<td>SO$_4^{2-}$, mg/L</td>
<td>Flemish dataset</td>
<td>65</td>
</tr>
<tr>
<td>Alkalinity, mg/L as CaCO$_3$</td>
<td>Besser et al., 2010</td>
<td>478</td>
</tr>
<tr>
<td>DOC, mg/L</td>
<td>1995 EU sediment data</td>
<td>21</td>
</tr>
<tr>
<td>TOC, %</td>
<td>Besser et al., 2010</td>
<td>3.7</td>
</tr>
<tr>
<td>HFO, mg HFO/kg</td>
<td>Besser et al., 2010</td>
<td>18,600</td>
</tr>
<tr>
<td>HMO, mg HMO/kg</td>
<td>Besser et al., 2010</td>
<td>154</td>
</tr>
<tr>
<td>AVS, µmol/g</td>
<td>NiPERA, 2009</td>
<td>1 and 9.1</td>
</tr>
<tr>
<td>Porewater [Fe$^{2+}$], mg/L</td>
<td>Field observations</td>
<td>0.912</td>
</tr>
<tr>
<td>Settling rate, m/d</td>
<td>EUSES</td>
<td>2.5</td>
</tr>
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<td>EUSES</td>
<td>3</td>
</tr>
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</table>
Key Sediment Parameters

- Physical parameters:
  - Settling, resuspension, burial, diffusion

- Chemical parameters
  - Again, calculated $K_D$ is a function of water chemistry
  - AVS concentration is key
    - At 9.1 µmol/g (~50th P from Flanders dataset), sufficient AVS to bind metals at loading of 1000 µg/L
    - At 1 µmol/g (~10th P from Flanders dataset), sufficient AVS to bind metals at loading of 100 µg/L
Performance Assessment Example
Model Performance Testing
Saint Germain les Belles Reservoir CuSO$_4$ treatment$^{1,2}$

- Data were fit with settling velocities between 0.68 and 1.02 m/d
  - Lower than EUSES but still consistent with range for POC
- Empirical K$_D$ (10$^{4.48}$ L/kg from Cu RA doc) more consistent w/ observations than WHAM-predicted values.
- K$_D$ and settling velocity are critical to water column removal.

Concluding Remarks

- **TICKET-UWM** represents a useful tool for evaluating metal “degradation” in the aquatic environment in a standard way and in line with GHS-CLP criteria.

- Examples demonstrate different metals have different “degradation capacity.”

- The “degradation capacity” of metals depends on the extent to which they bind to particles (i.e. particle-reactivity).
  - Elimination from the water column is fast/extensive for highly particle-reactive metals, while non particle-reactive metals remain in the water column.

- Model allows for empirical or WHAM V-calculated $K_D$ values to be used.
Concluding Remarks

- Some **POPs** can also “degrade” to levels representing > 70% removal from the water column, **BUT**:  
  - Exclusively due to partitioning to POC  
  - Model-predicted diffuse flux is *out of the sediment into the water column*  
  - Unlike metals, no speciation transformation to a less (or non) toxic form

- **TICKET-UWM**:  
  - Is promising and provides selective degradation assessments  
  - Relevancy of test model performance against real world data is recommended (available for some metals)

- **Degradation assessment of metals**: a *weight of evidence* approach is recommended using the UWM and eventually available confirming field evidence