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

Examples, Comparison to POPs, and Parameterization

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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

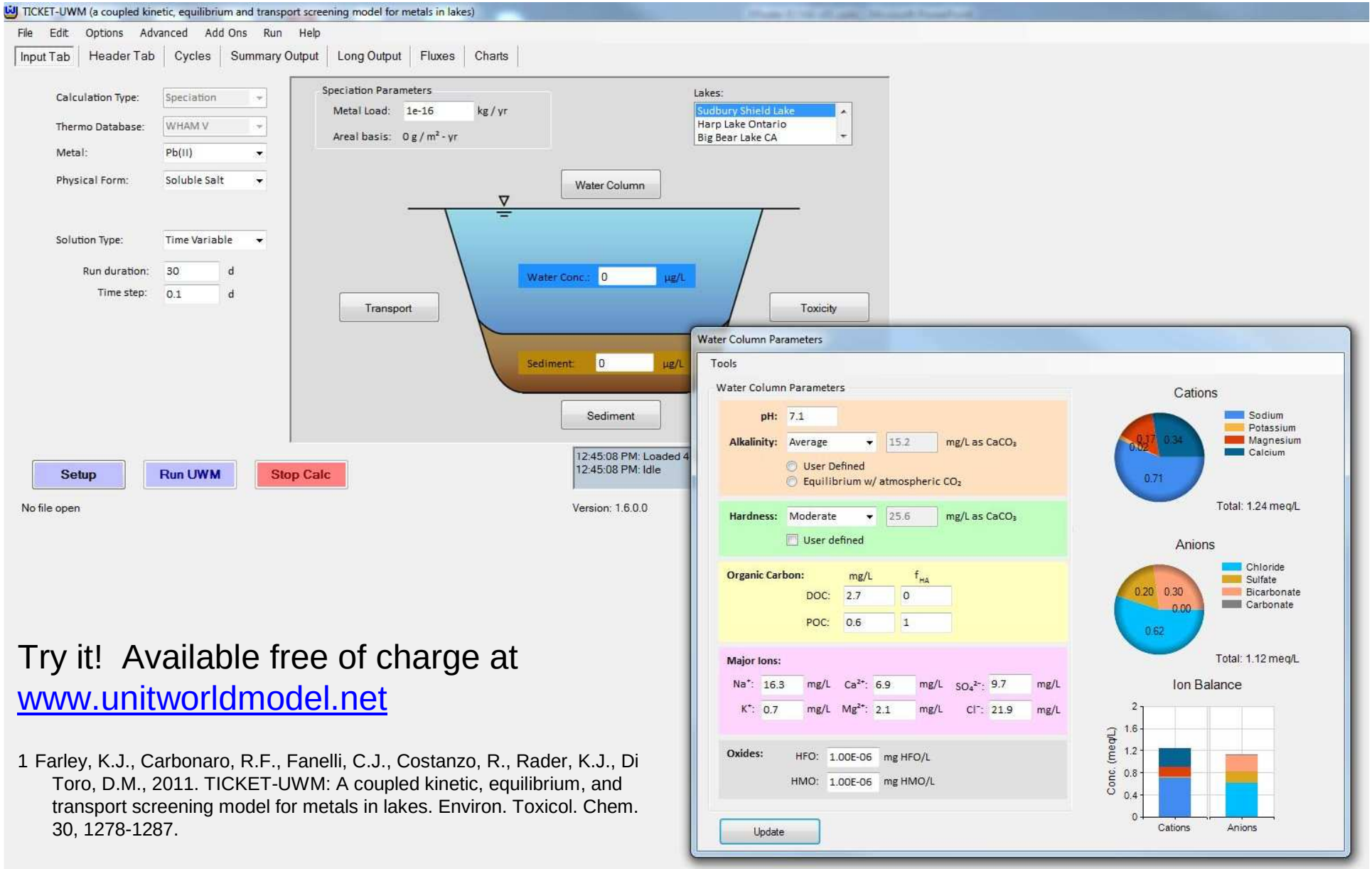
- **Examples** of TICKET-UWM use for metal classification
  - Water column
  - Sediment
- TICKET-UWM calculations with **POPs**
- Discussion of model **parameterization**
- **Performance** assessment example
- **Concluding remarks** on TICKET-UWM application for classification

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-UWM[1] Screenshot

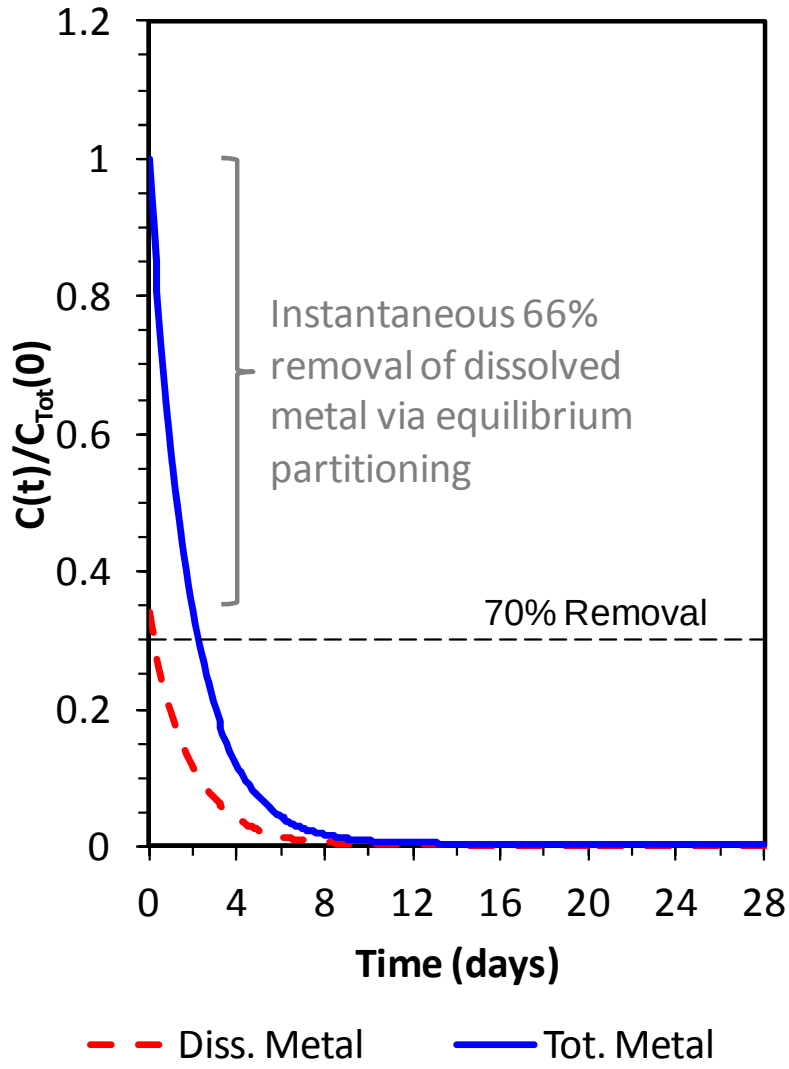


Try it! Available free of charge at www.unitworldmodel.net

1 Farley, K.J., Carbonaro, R.F., Fanelli, C.J., Costanzo, R., Rader, K.J., Di Toro, D.M., 2011. TICKET-UWM: A coupled kinetic, equilibrium, and transport screening model for metals in lakes. Environ. Toxicol. Chem. 30, 1278-1287.

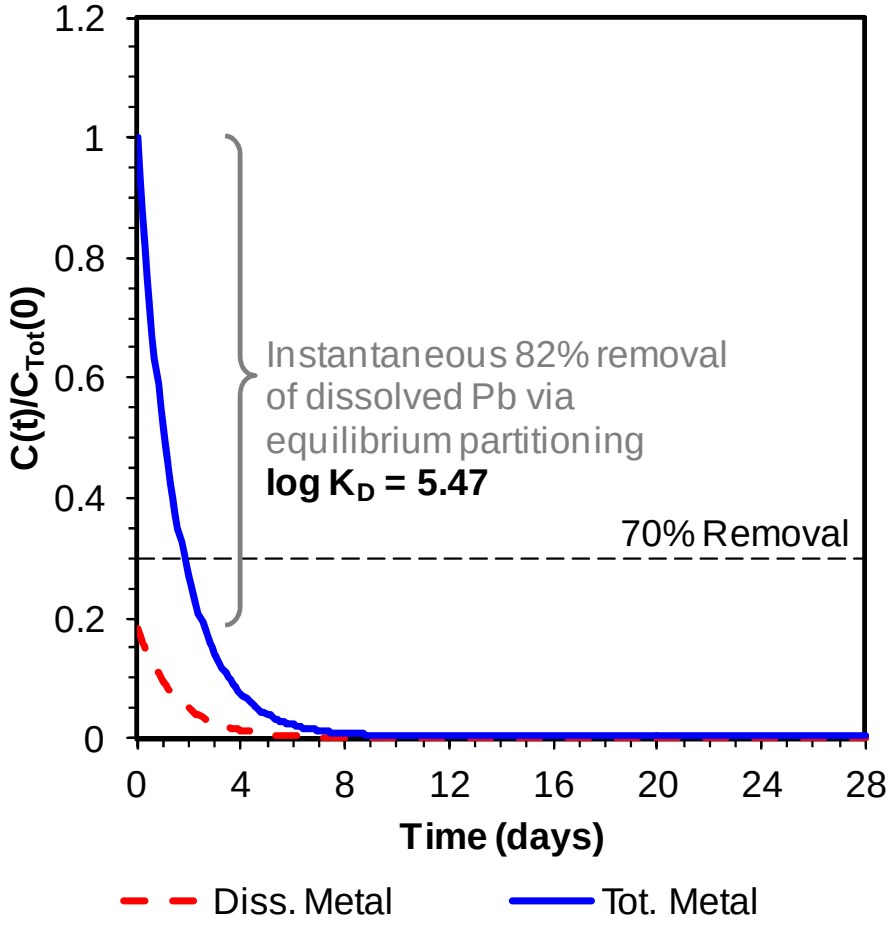
Water Column Partitioning and Sedimentation

- 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***

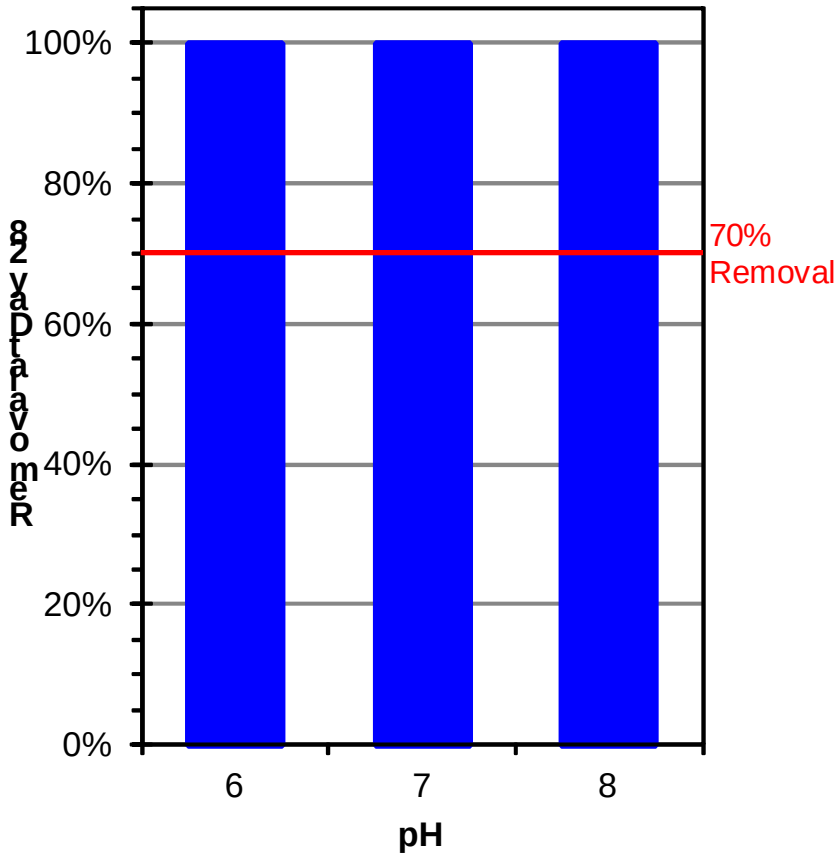


Lead (Pb) Results

Empirical K_D (Constant)



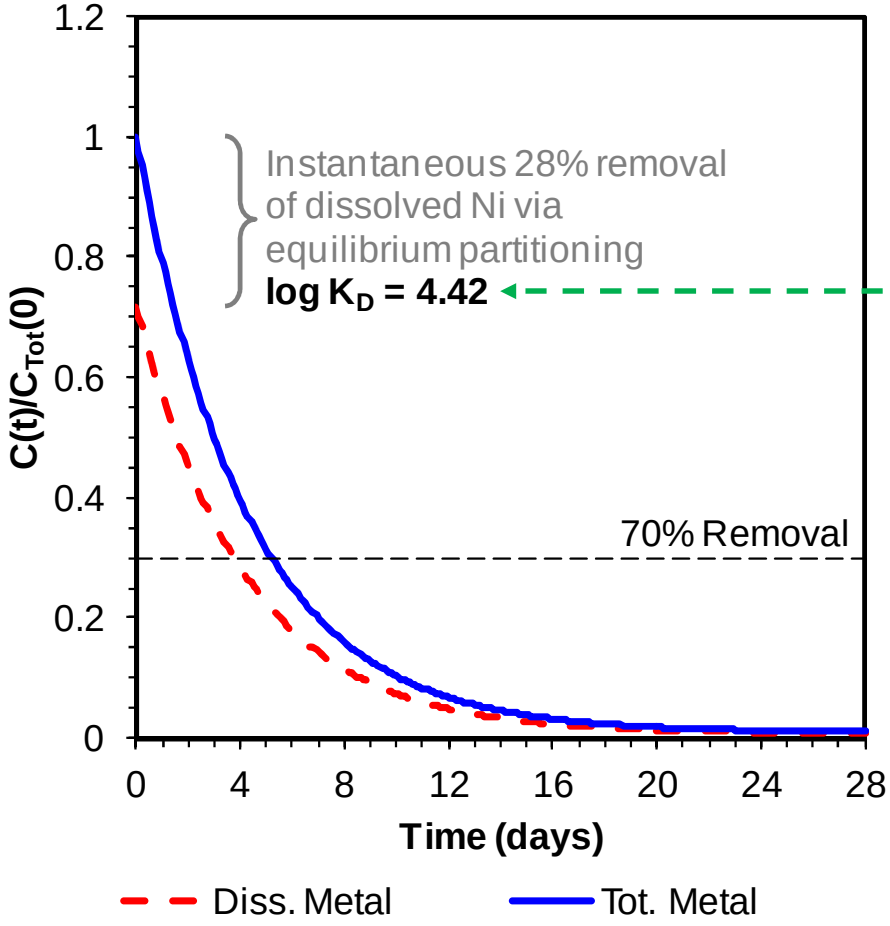
WHAMV K_D (Water chemistry dependant)



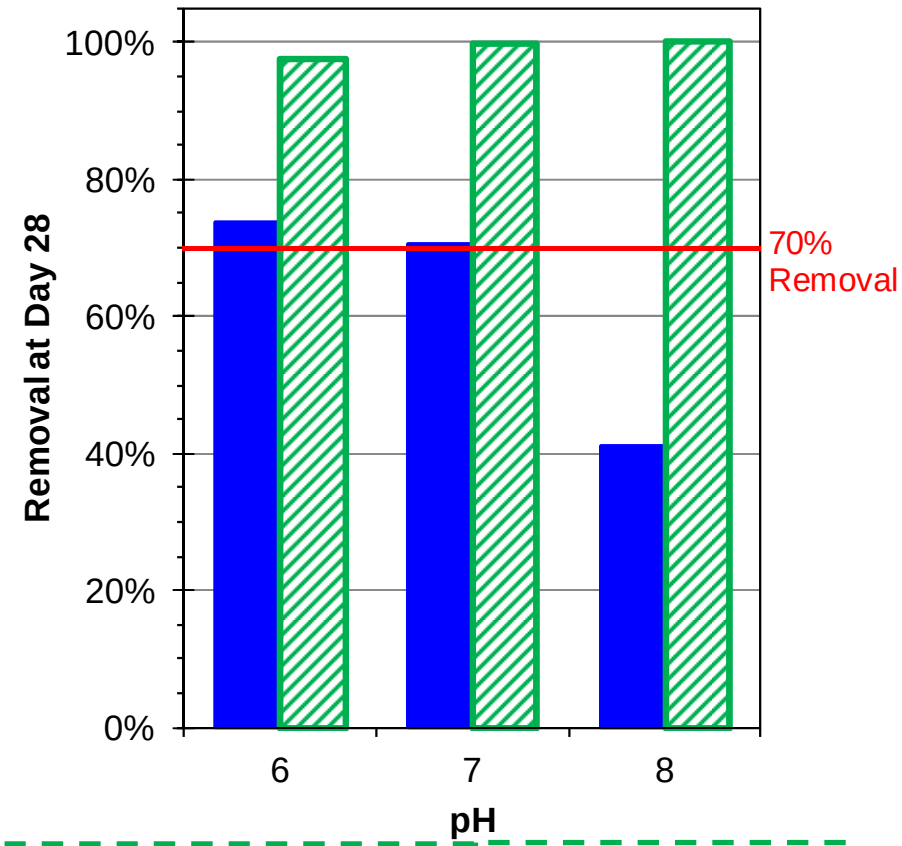
log K_D = 5.28 - 5.97

Nickel (Ni) Results

Empirical K_D (Constant)

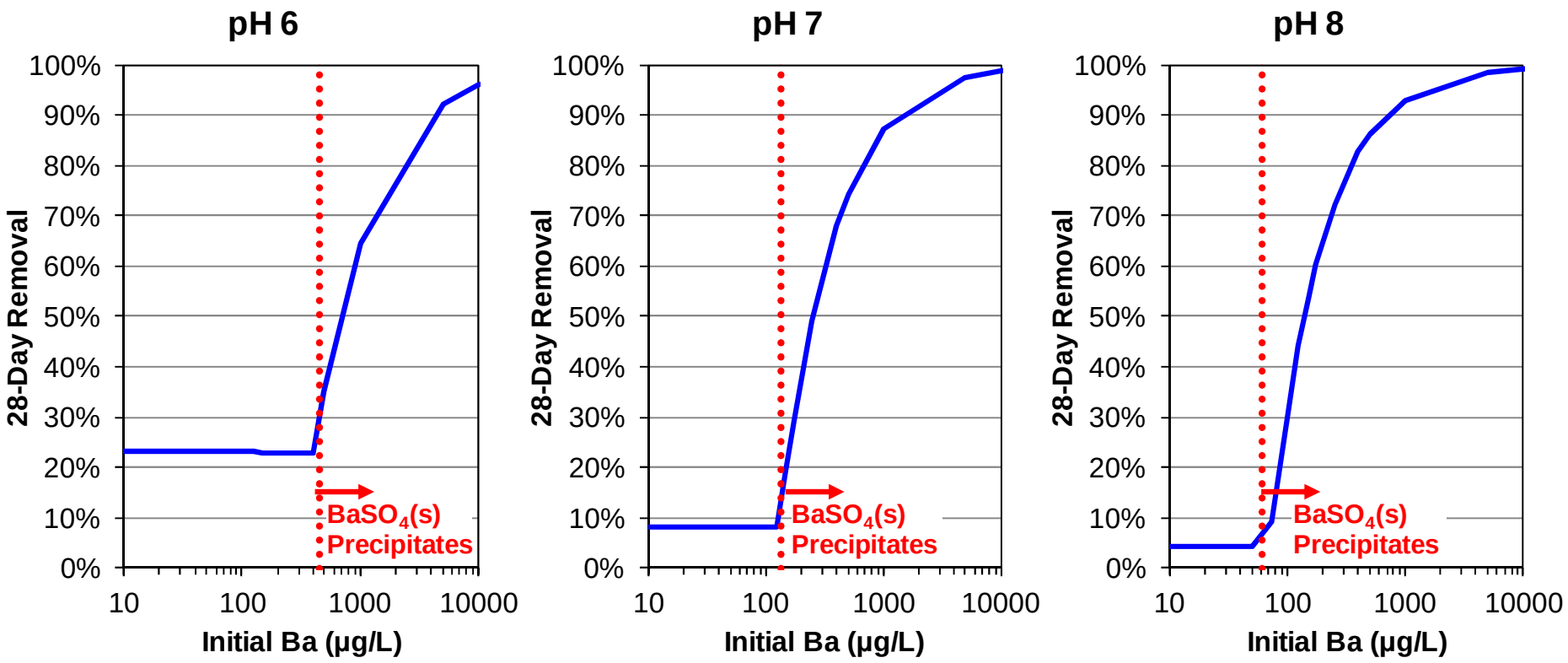


WHAMV K_D (Water chemistry dependant)



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

Barium (Ba) Results



- Below solubility limit of $BaSO_4(s)$ (~75 – 400 µg/L Ba), removal is limited because of weak binding to POC.

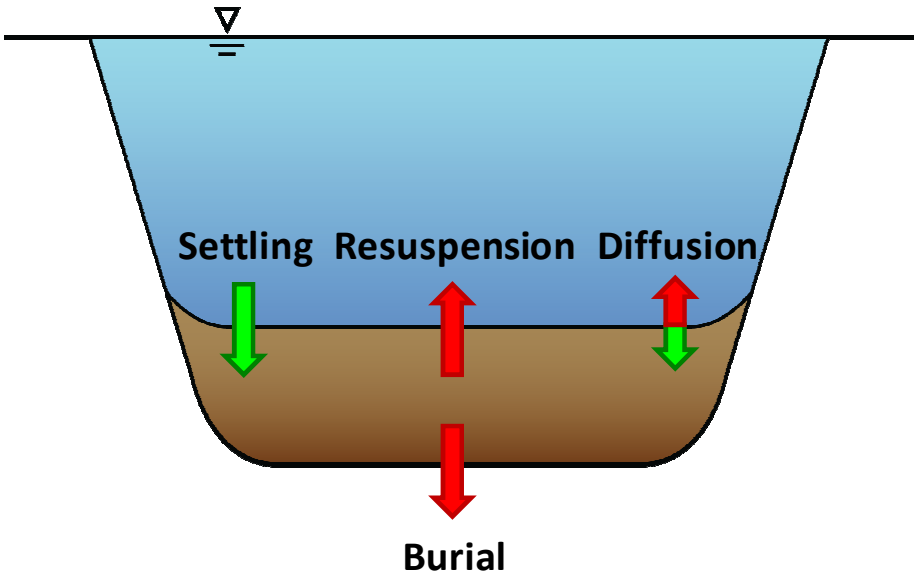
Take Home Messages: Water Column

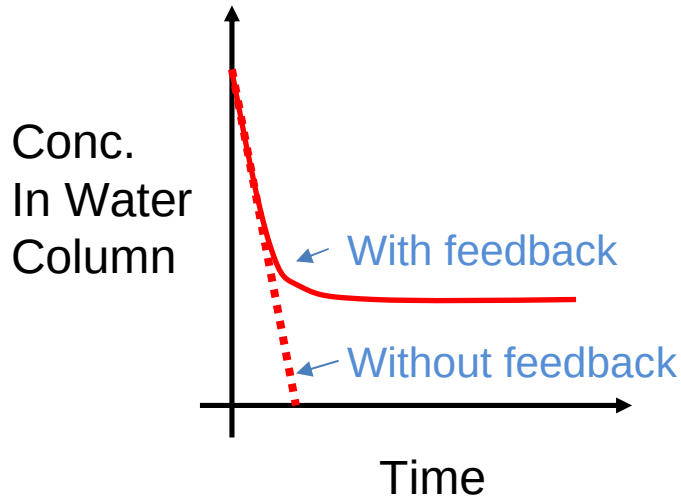
- The “degradation capacity” of metals depends on the extent to which they bind to particles (i.e. particle-reactivity)
  - Elimination from the water column is fast/extensive for highly particle-reactive metals, while non particle-reactive metals remain in the water column.
  - Between those two ends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

- $\mathbf{K_D}$ is a critical factor in removal rate

Transport Between Water Column and Sediment





Water Column Mass Balance

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

Potential feedback mechanisms

$$V(dC/dt) = QC_{in} + W - QC_{out} - v_s A_s C_{part} + v_r A_s C_{part,sed} - k'_f A_s [C_{diss} - C_{diss,sed}]$$

Rate of Accum. of Depletion = $Mass_{inflow}$ + Load – $Mass_{outflow}$ – Settling + Resusp. ± Diffusion

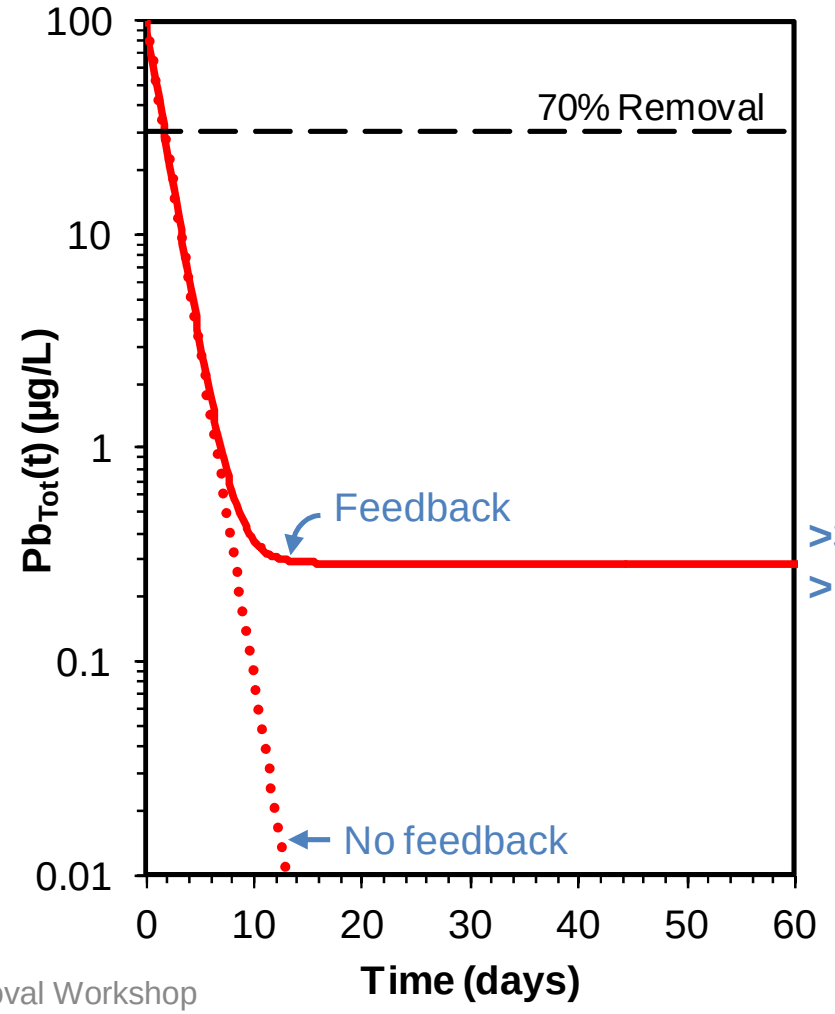
Source *Source* *Sink* *Sink* *Source* *Source/Sink*

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



>300 x lower than initial Pb
>100 x lower than 70% removal conc.

Sediment Results for Select Metals

Scenario		Sequestration Metric		Solid-Phase Speciation
		Sustained 70% removal?	Diffusive Flux	
LEAD	POC and AVS	YES	Into Sediment	100% AVS
	POC, HFO, and HMO	YES	Out of Sediment	Mostly HMO
NICKEL	POC and AVS	YES, after 29 days	Into Sediment	100% AVS
	POC, HFO, and HMO	YES, after 29 days	Out of Sediment	Mostly HFO

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

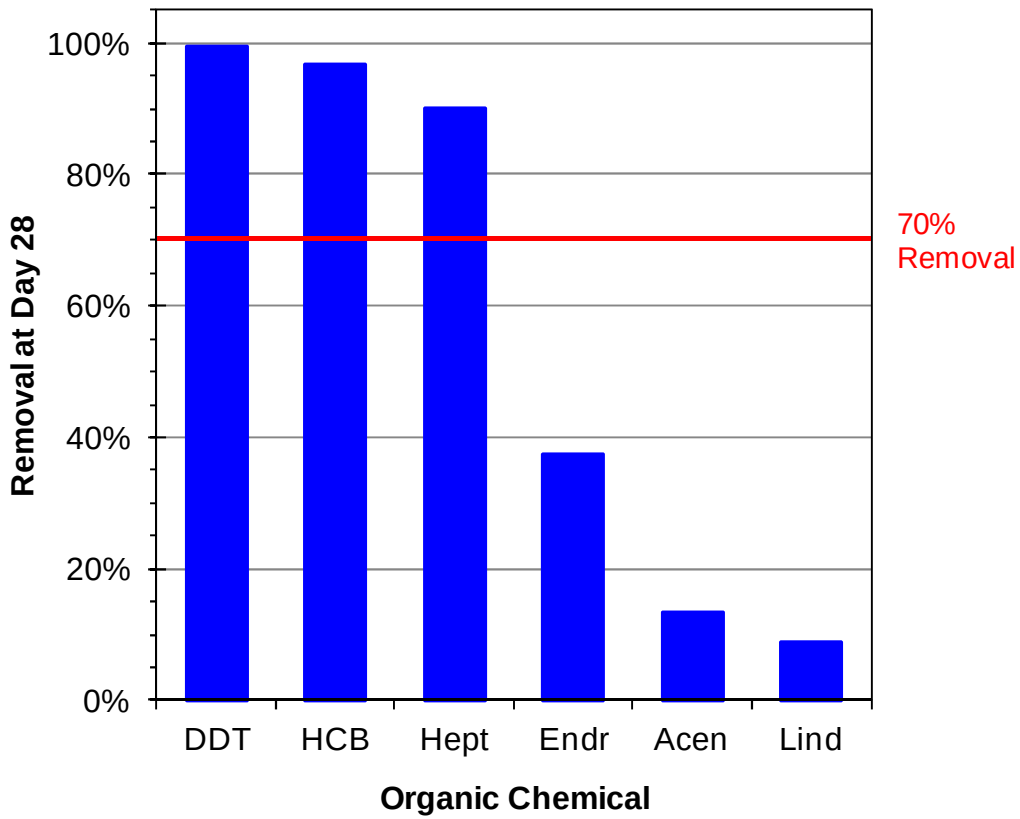
TICKET-UWM Calculations with POPs

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*

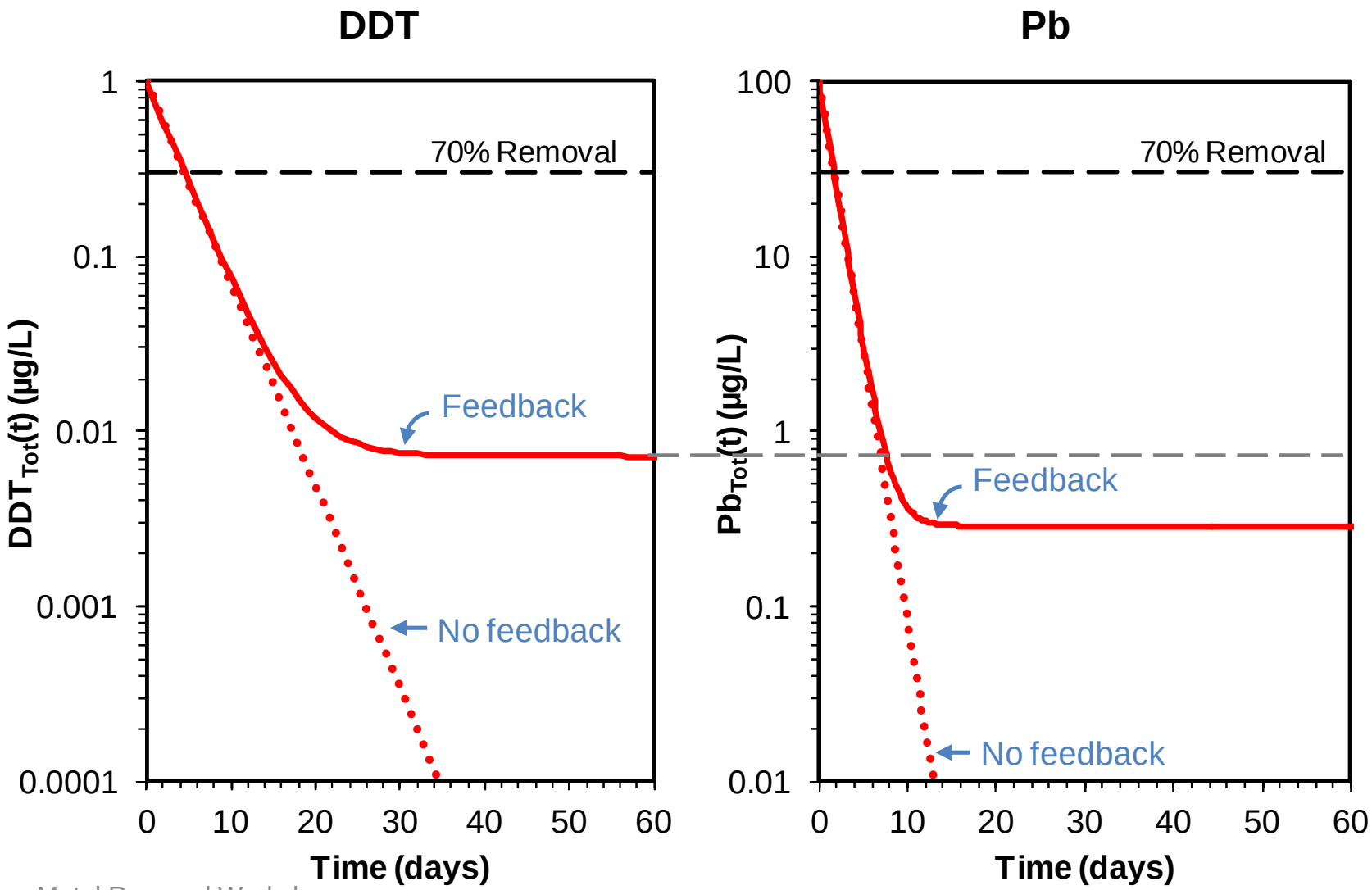
Water Column Partitioning and Sedimentation

Name	Abbr.	Henry's Const. ($Pa \cdot m^3 \cdot mol^{-1}$)	log K_{OW}
4,4'-DDT	DDT	0.14	6
Hexachloro-benzene	HCB	65	5.5
Heptachlor	Hept	38	5.27
Endrin	Endr	1.1	4.5
Acenaphthene	Acen	12.2	3.93
Lindane	Lind	0.29	3.7



No pH effect for organic K_D values →Endr, Acen, Lind will fail 70% removal in 28 day test at pH 6, 7, and 8.

Sediment Results for POPs



Sediment Results for POPs

Scenario	Sequestration Metric		Solid-Phase Speciation
	Sustained 70% removal?	Diffusive Flux	
DDT	YES	Out of Sediment	100% POC
Hexachlorobenzene	YES	Out of Sediment	100% POC
Heptachlor	YES	Out of Sediment	100% POC
Endrin	YES, After 85 days	Out of Sediment	100% POC
Acenaphthene	70% removal not obtained in 1 year	Out of Sediment	100% POC
Lindane	70% removal not obtained in 1 year	Out of Sediment	100% POC

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

Parameter	Source	Value		
Depth, m	EUSES	3		
Settling rate, m/d	EUSES	2.5		
Burial rate, cm/yr	EUSES	0.3		
Resuspension rate , cm/yr	EUSES	2.44		
Diffusive exchange, cm/day	EUSES	0.24		
Sediment f_{oc}	EUSES	0.05		
Sediment solids conc., g/L	EUSES	500		
Active depth, cm	EUSES	3		
AVS, µmol/g	NiPERA, 2009	1		
POC, mg/L	TGD – Part II	1.5		
DOC, mg/L	GHS Annex 10 – T/D	2.0		
pH	GHS Annex 10 – T/D	6.09	7.07	8.00
Alkalinity, mg/L as $CaCO_3$	GHS Annex 10 – T/D	3.85	7.47	37.2
Calcium, mg/L	GHS Annex 10 – T/D	8.0	32.1	80.1
Magnesium, mg/L	GHS Annex 10 – T/D	1.2	4.9	12.1
Sodium, mg/L	GHS Annex 10 – T/D	1.8	3.4	18.0
Potassium, mg/L	GHS Annex 10 – T/D	0.3	1.2	3.02
Sulfate, mg/L	GHS Annex 10 – T/D	4.8	19.2	47.9
Chloride, mg/L	GHS Annex 10 – T/D	14.5	57.8	145

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

Parameter	Source	Value
pH	Flemish dataset	7.56
Ca^{2+}	Flemish dataset	144
Mg^{2+}	Flemish dataset	38.1
Na^{+}, mg/L	Estim. from Flemish dataset	141
K^{+}, mg/L	Estim. from Flemish dataset	6.19
Cl^{-}, mg/L	Flemish dataset	79
SO_4^{2-}, mg/L	Flemish dataset	65
Alkalinity, mg/L as $CaCO_3$	Besser et al., 2010	478
DOC, mg/L	1995 EU sediment data	21
TOC, %	Besser et al., 2010	3.7
HFO, mg HFO/kg	Besser et al., 2010	18,600
HMO, mg HMO/kg	Besser et al., 2010	154
AVS, µmol/g	NiPERA, 2009	1 and 9.1
Porewater [Fe^{2+}], mg/L	Field observations	0.912
Settling rate, m/d	EUSES	2.5
Burial rate, cm/yr	EUSES	0.3
Resuspension rate , cm/yr	EUSES	2.44
Diffusive exchange, cm/day	EUSES	0.24
Sediment solids conc., g/L	EUSES	500
Active depth, cm	EUSES	3

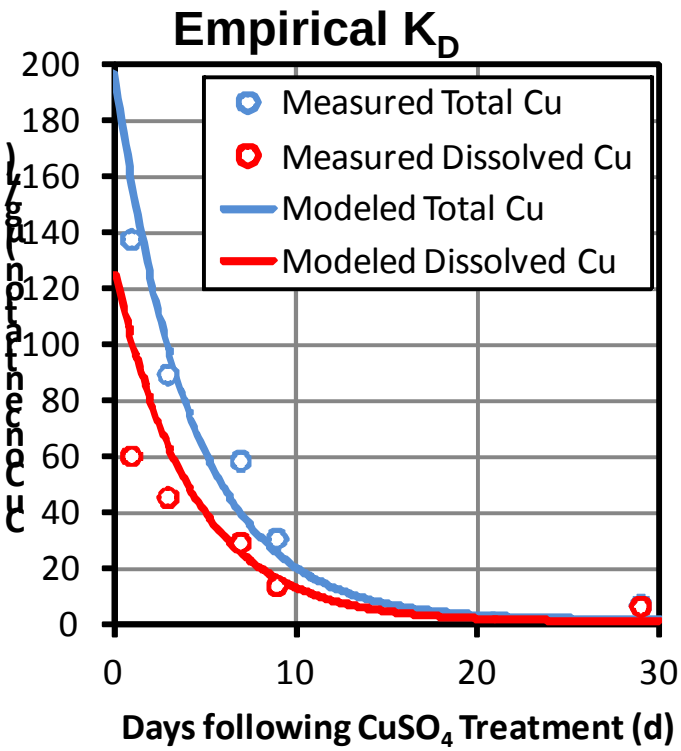
Key Sediment Parameters

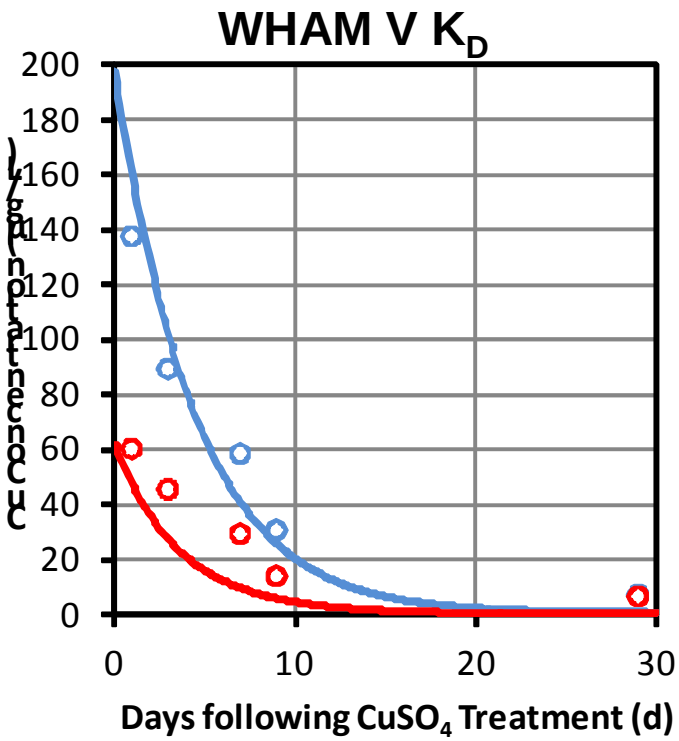
- Physical parameters:
  - Settling, resuspension, burial, diffusion
- Chemical parameters
  - Again, calculated K_D is a function of water chemistry
  - AVS concentration is key
    - At 9.1 µmol/g (~50th P from Flanders dataset), sufficient AVS to bind metals at loading of 1000 µg/L
    - At 1 µmol/g (~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.

1 Van Hullebusch, E., Chatenet, P., Deluchat, V., Chazal, P.M., Froissard, D., Botineau, M., Ghestem, A., Baudu, M., 2003. Copper accumulation in a reservoir ecosystem following copper sulfate treatment (St. Germain Les Belles, France). Water Air Soil Pollut. 150, 3-22.

2 Van Hullebusch, E., Chatenet, P., Deluchat, V., Chazal, P.M., Froissard, D., Lens, P.N.L., Baudu, M., 2003. Fate and forms of Cu in a reservoir ecosystem following copper sulfate treatment (Saint Germain les Belles, France). Journal De Physique Iv 107, 1333-1336.

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