Eurometaux

METALS: AT THE HEART OF EUROPE

RAPID REMOVAL of metals from the WATER COLUMN
Follow-up after the 2012, Helsinki, workshop

Eurometaux, 8 February 2019

Al Cu Ni Pb Zn Au Ag Pt Sb Be Si Co Mo V Sn Pd Ru Re Os Ir W Ta Ge Se Ga Cr Mg

Outcome of the 2012 workshop

A distinction between **3 groups of metals** as a function of fate and potential degradability:

1. Metals that **readily methylate:**
   - such as Hg, Se and others
   - They volatise so should as organic materials NOT be considered as “rapidly degrading”
2. Metals that **rapidly hydrolyse** under a range of relevant aquatic conditions and that form different non-toxic chemical forms that quickly precipitate in the water column:
   - such as Fe, Sb, Mo, Al, Sn, Cr and others
   - processes go so quickly that they even hamper ecotox testing
3. Metals that **partition and precipitate** like the previous group, but for which the “irreversibility” (*i.e. binding to a non-bioavailable form under a range of environmental conditions*) needs to be demonstrated:
   - such as Cu, Zn, Ni, Co, Pb and others.

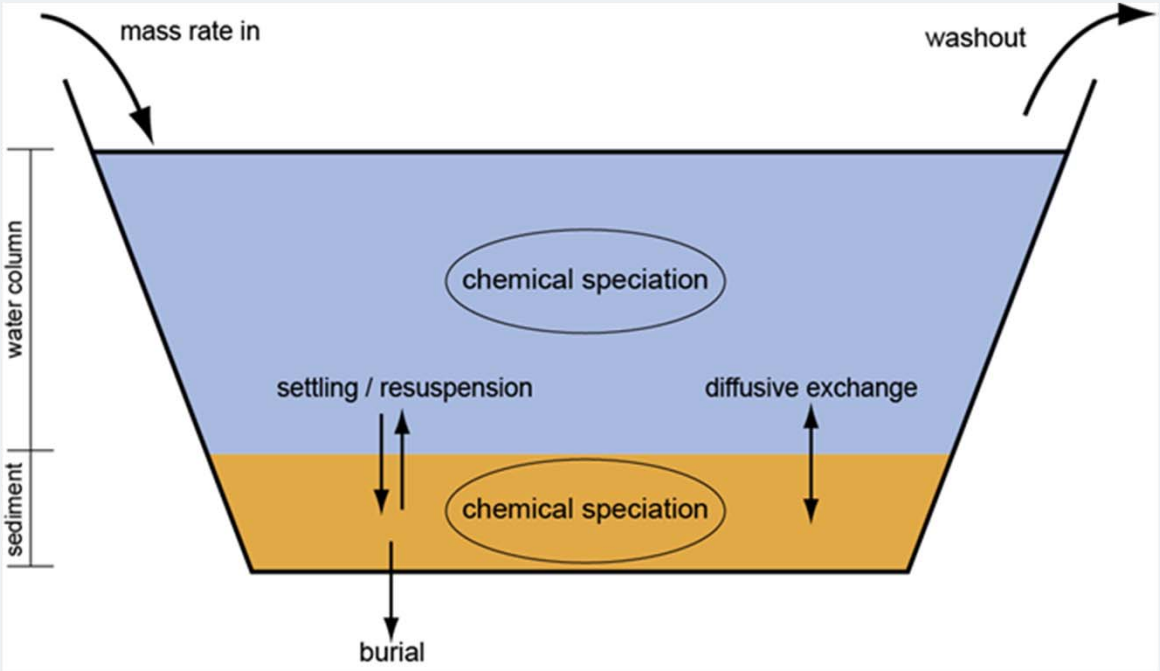
Outcome of the 2012 workshop

- *"hydrolysis and precipitation to form different species"*
  - *is a very significant removal process for their removal from the aquatic system.*
- *When these processes occur very quickly*, they **can** be taken into account for hazard classification, considering:*
  - *that the hazard assessment should consider the properties of the newly produced metal-species"*
  - the rate and "irreversibility" of the toxic substance removal from the aquatic compartment
  - **equivalent to the rate for organics*
- *The **TICKET-UNIT Model** may be too much Risk based for use in Rapid Removal demonstration*

CONCLUSION: before considering the ***relevance for Rapid Removal***, *more information is required on partitioning (rates and conditions) and on binding to particles in order to define "irreversibility" under a range of environmental conditions relevant for hazard identification.*

The Ticket Unit World Model

Conceptual model for the TICKET Unit World Model for Metals in Lakes:



TICKET-UWM software is available free of charge at http://unitworldmodel.net/

Questions raised at the workshop for follow-up

5 Questions considered as critical:

1. The performance of the TICKET UWM model to prove RR is ***based on standard parameters including abiotic conditions***.
   - EUSES standard lake parameterization was used to ***standardize the system for hazard ID***.
   - do these standard conditions ensure sufficient protection of the EU aquatic environment?

2. What **are the standard parameters** that have an impact on the RR assessment?
   - ***Carry out a sensitivity analysis on the most important factors*** to demonstrate the nature and extent of their impact, and demonstrate this by examples

3. ***Persistent Organic Pollutants*** can also partition. However, they remain toxic to the aquatic environment and should not be candidates for rapid removal.
   - Demonstrate that the TICKET-UWM model prediction for POPs indicates a difference in comparison with metals in that a non-toxic species is formed?

Questions raised at the workshop for follow-up

5 Questions considered as critical:

4. ***Expanding experience with the UWM model***:
   - the model's functionality has so far been proven for a limited series of metals - mostly divalent cationic metals.
   - A valid model would require broader validity (type of waters)
   - need to extend experience significantly to other (type) of metals

5. ***Apply the UWM model to one or more examples,*** including the impact on the derivation of chronic (long-term) environmental classification

BUT more importantly: is the UWM the right way forward? Would *a more experimental approach* not be more convincing?

Follow-up on the 2012 workshop questions

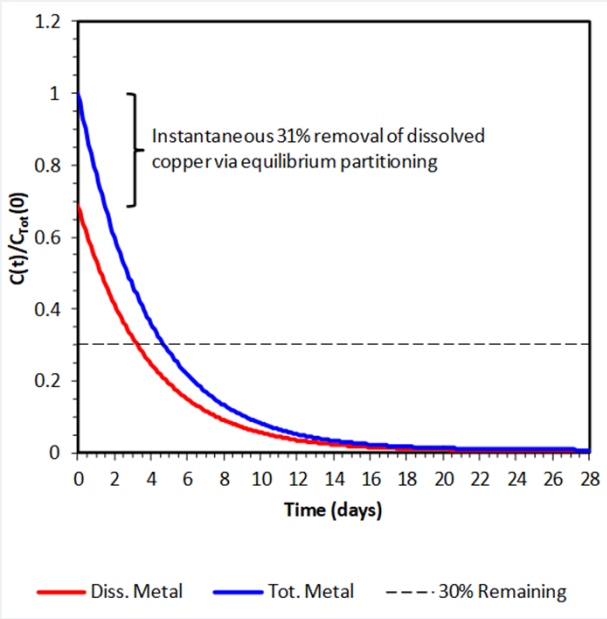
Extending the dataset to other metals and conduct a sensitivity analysis for critical parameters (Q2 & Q4):

The TICKET-UWM was used to measure the:

- removal of a long series of soluble metal salts from the water column through speciation transformations and sedimentation of particulate metal, and
- metal speciation transformations in and remobilization potential from settled material.

Demonstrating (lack of) RR could be demonstrated for Zn, Cu, Ni, Co, As, Sr, Mo, Cd, Ag, … **SO THE MODEL WORKS for metals** in general and can differntiate those that

Sensitivity analysis of parameters that influence the removal rate (loading, depth, …) and resuspension was demonstrated by several cases



Follow-up on the 2012 workshop questions

Rapid Removal assessment of POPs with the TICKET-UWM model (Q 3)

- The more hydrophobic organic chemicals are the more they can exhibit > 70% removal from the water column in 28 days.
- However, for organics, there is no change in speciation towards a nontoxic form. Unlike metals, there is no speciation transformation to a less (or non-) toxic form.
- The UWM model-predicts that the diffusive flux is directed out of the sediments in case of resuspension, which is quite the opposite as for metals.

Follow-up on the 2012 workshop questions

An extensive set of reports was provided in Feb 2013 providing answers to the Q's

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EUROPEAN ASSOCIATION OF METALS
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Environmental Engineers and Scientists
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THE RAPID REMOVAL ASSESSMENT OF METALS AND METAL COMPOUNDS: AN UPDATE OF THE STATUS IN RESPONSE TO THE OUTCOME OF THE ECHA WORKSHOP OF 8TH FEBRUARY 2012,

BY HUGO WAETERSCHOOT, KATRIEN DELBEKE AND WILLIAM ADAMS

Introduction

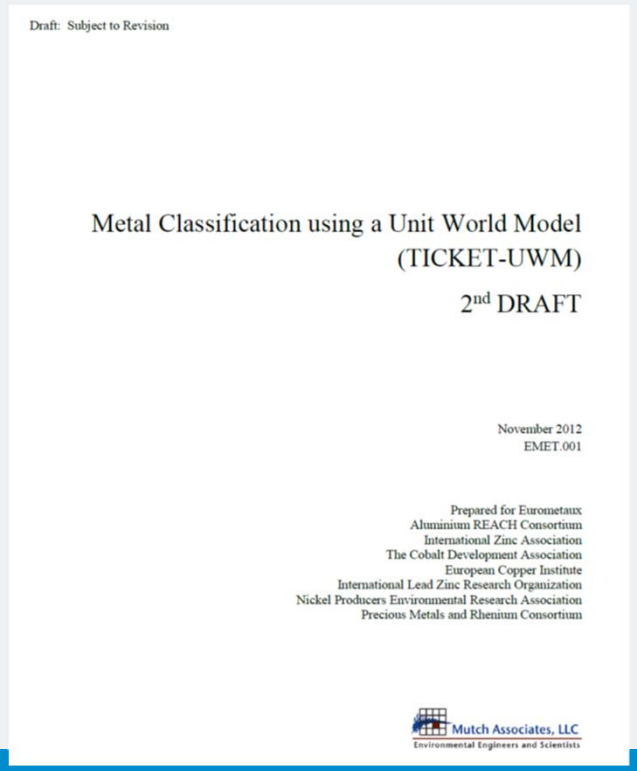
The 2nd ATP to the CLP introduced the chronic (long-term) environmental toxicity endpoint as defined by the 3rd version of the UN-GHS into the EU hazard classification and labelling scheme. The GHS and EU scheme include in this respect the concept of degradation whereby a rapid degradation from the water column results in different classification cut-off values and categories. For metals and inorganic metal compounds, the rapid and irreversible removal from the water column has been proposed as equivalent to the rapid degradation concept for organics. This concept, based on chemical speciation, partitioning, precipitation and transformation of toxic metal species to non-toxic forms, required guidance and a demonstration of experience to review its relevance and acceptability.

An extensive update of the CLP metals guidance was developed during 2011. The guidance included in this respect a provision allowing a demonstration of "the removal from the water column" to assess the "lack of persistence" or "lack of degradation of metal ions" responsible for the expression of toxicity of metals and metal compounds. The draft guidance section on metals includes a proposal to apply the "rapid degradation principle for organics" measured as a 70 % removal rate in 28 days in a comparable way for metals from laboratory and field experiments or by using a recently developed model, the TICKET-Unit World Model (UWM). The application of a standard model facilitates the assessment of Rapid Removal from the water column in a standardised way for hazard classification under CLP and GHS.

The ECHA PEG CLP guidance group accepted the principle behind the proposed use of rapid removal from the water column for metals; however, they felt that the model should first be reviewed before the guidance could include this reference in the ECHA CLP guidance. This resulted in ECHA's organizing a briefing and discussion workshop in Helsinki on the status and performance of the TICKET-UWM model for this purpose on February 8, 2012.[1]

[1] Tableau Input Coupled Kinetic Equilibrium Transport - Unit World Model

ECHA UWM model workshop follow-up report Page 1



Draft: Subject to Revision

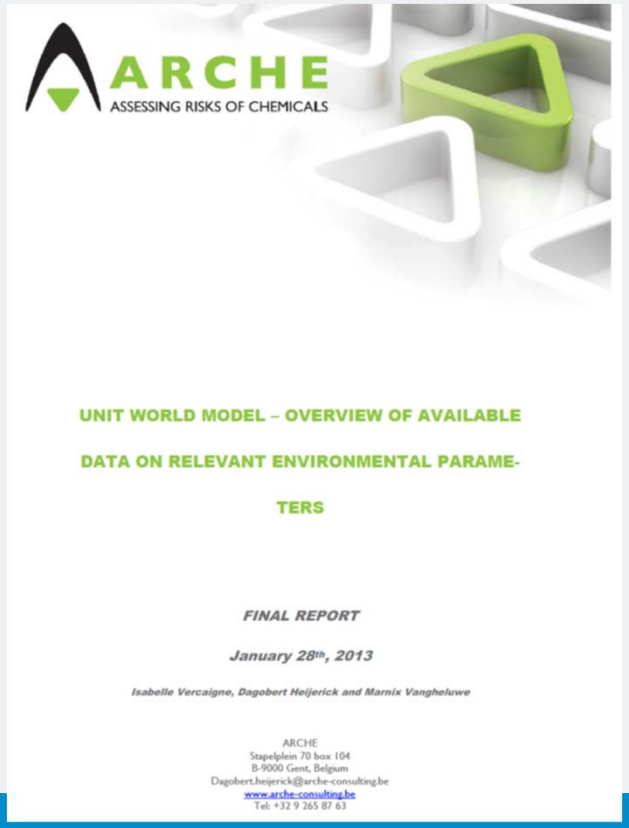
Metal Classification using a Unit World Model (TICKET-UWM)

2nd DRAFT

November 2012
EMET.001

Prepared for Eurometaux
Aluminium REACH Consortium
International Zinc Association
The Cobalt Development Association
European Copper Institute
International Lead Zinc Research Organization
Nickel Producers Environmental Research Association
Precious Metals and Rhenium Consortium

Mutch Associates, LLC
Environmental Engineers and Scientists



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ASSESSING RISKS OF CHEMICALS

UNIT WORLD MODEL – OVERVIEW OF AVAILABLE DATA ON RELEVANT ENVIRONMENTAL PARAMETERS

FINAL REPORT

January 28th, 2013

Isabelle Vercaigne, Dagobert Heijerick and Marnix Vangheluwe

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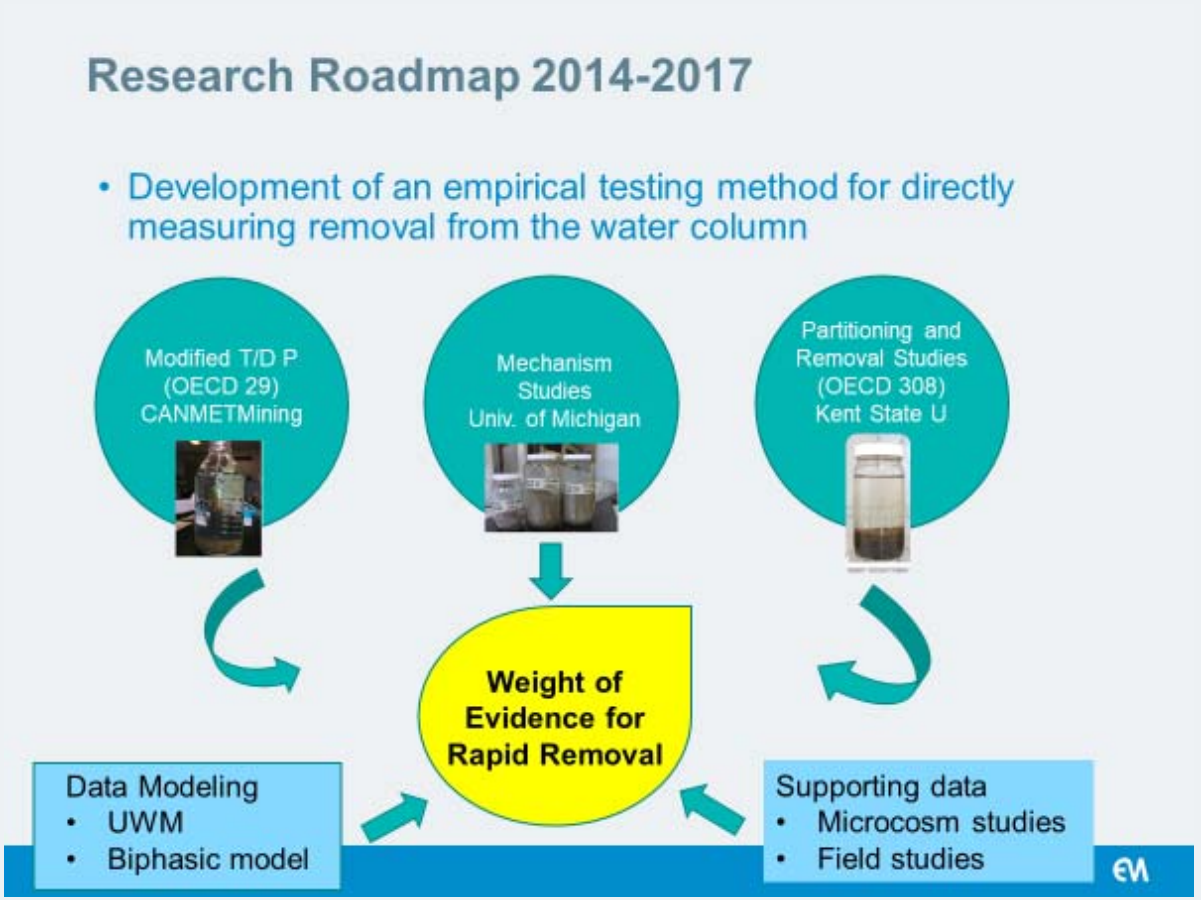
A more experimental approach….



A more experimental approach…

This is how the TDp-E was born

- Assess removal and remobilization using standardized conditions
- Extend T/DP in 2 parts
  1) 28 d experiment to assess binding of metals to substrate and settling rates
  2) Assess remobilization event with 4 d tracking post event
- Methodological variables tested
  - CO_2 delivery (pH maintenance)
  - Ionic strength variation of OECD 203 medium
  - Agitation time after initial substrate loading
  - Binding affinity of substrates
  - Substrate source and loading quantity
  - Substrate pre-incubation and condition