Eurometaux

METALS: AT THE HEART OF EUROPE

RAPID REMOVAL of metals from the WATER COLUMN

The applicability of the concept for the environmental classification of metals

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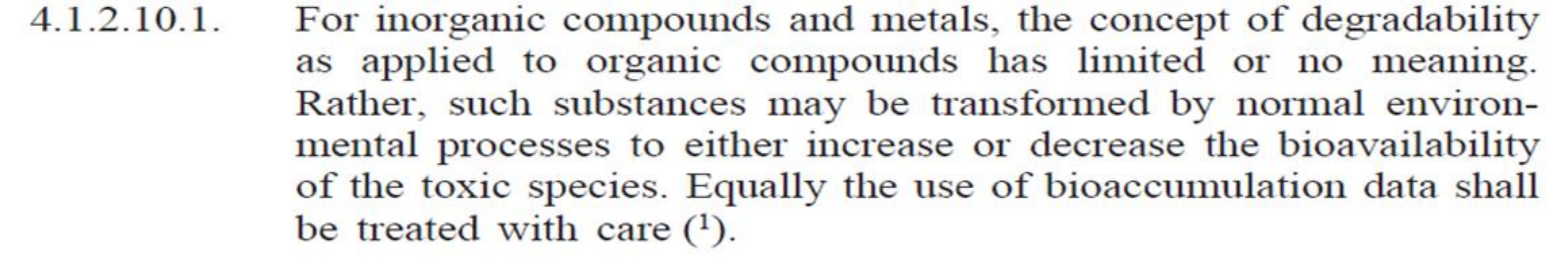
GHS

- What to learn for metals from the GHS?
  - There is **a need to develop a concept for the Rapid Degradation for metals** in the aquatic column (cf. 9.7.1.5)
  - Data on **Rapid Degradation can only be used** where it is demonstrated that once partitioned they should be speciated to a non-toxic form that cannot be resuspended to a level of concern (cf. 9.4.2.4)
  - **Guidance is needed for metals** on how to use data obtained by employing non-standard test methods (cf. 9.1.12)
  - **Multiple line of evidences** that demonstrate Rapid Removal can be used in defining Rapid Degradability (cf. 4.1.1.6.2)
  - It **needs to be demonstrated that the metal may be transformed** by normal environmental processes to either increase or decrease the bioavailability of the toxic species (cf. 9.1.7.5)

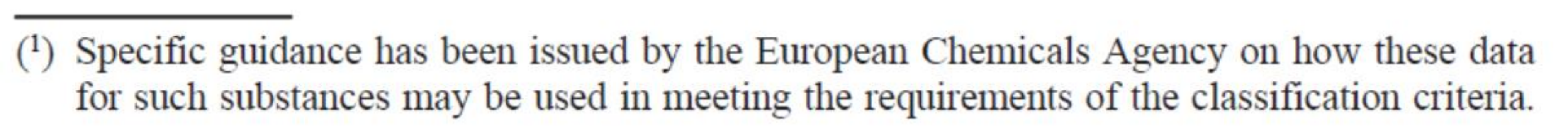
CLP

The reason for the concept development



4.1.2.10.1. For inorganic compounds and metals, the concept of degradability as applied to organic compounds has limited or no meaning. Rather, such substances may be transformed by normal environmental processes to either increase or decrease the bioavailability of the toxic species. Equally the use of bioaccumulation data shall be treated with care (1).

So, why are we here today?



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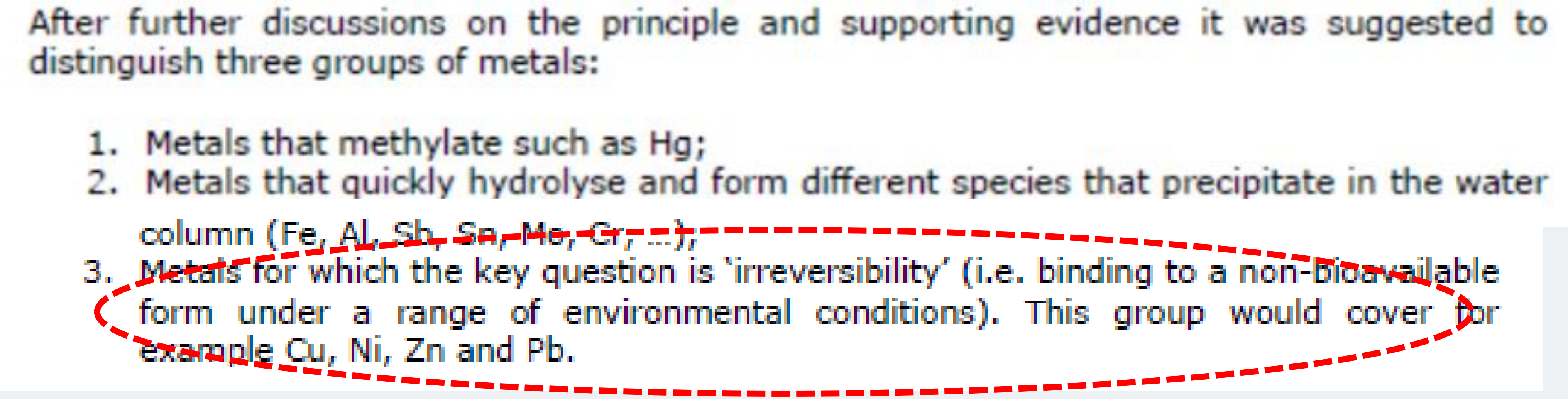
(1) Specific guidance has been issued by the European Chemicals Agency on how these data for such substances may be used in meeting the requirements of the classification criteria.

Conclusions from the February 2012 workshop

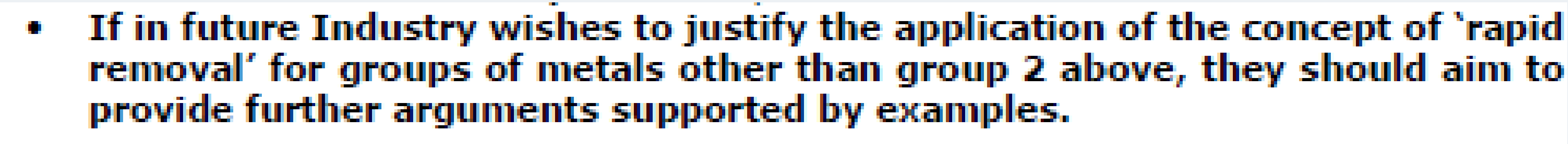
- Focus today is on “TYPE 3 metals”



After further discussions on the principle and supporting evidence it was suggested to distinguish three groups of metals:

1. Metals that methylate such as Hg;
2. Metals that quickly hydrolyse and form different species that precipitate in the water column (Fe, Al, Sb, Sn, Mo, Cr, ...);
3. Metals for which the key question is ‘irreversibility’ (i.e. binding to a non-bioavailable form under a range of environmental conditions). This group would cover for example Cu, Ni, Zn and Pb.

- The chair concluded:



- **If in future Industry wishes to justify the application of the concept of ‘rapid removal’ for groups of metals other than group 2 above, they should aim to provide further arguments supported by examples.**

And thus, the metals sector

- considered **need for demonstrating**:
    - Measuring **Removal rate over time** under standard conditions
    - **Speciation** to non-soluble chemical forms
    - **Lack of resuspension** under normal conditions

- used “**Multiple lines-of-evidence”:**
    - Literature on field/lab removal mechanisms
    - Metal-specific models (TICKET-UWM)
    - **Classification tool** *(Extension of OECD Transformation Dissolution protocol)*

Development of a Rapid Removal measuring tool built on OECD guidance (OECD TG 29)

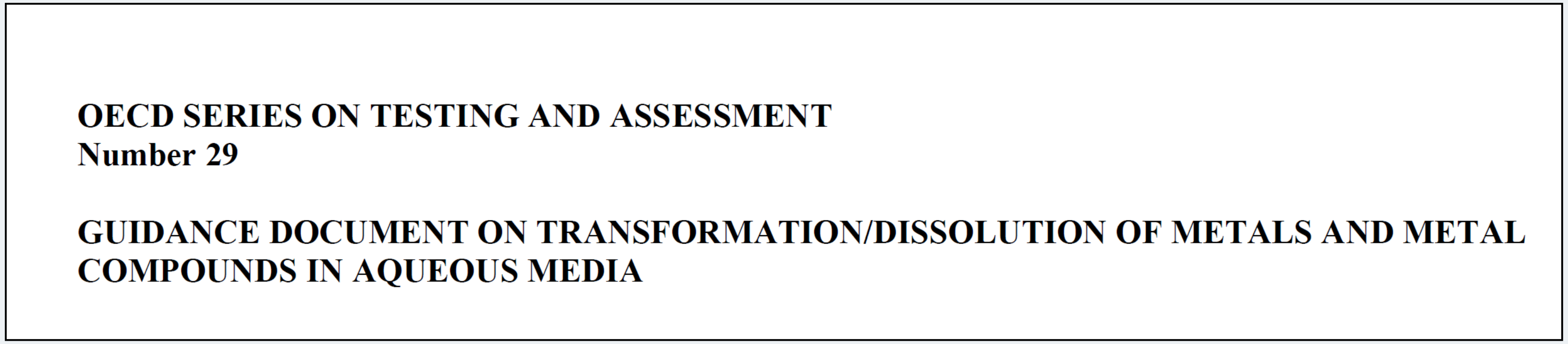
Scope

Rapid Removal concept provides “guidance”on the **METALS SECTION** of the GHS/CLP

- This section is NOT APPLICABLE to non-metals and also organo-metals are excluded
- Focus is on metals that partition and precipitate, but for which the “irreversibility” *(i.e. binding to a non-bioavailable form under a range of environmental conditions*) needs demonstration (Type 3 metals)
- It AIMS at providing guidance for the equivalent of *rapid degradation of organics*, to metals to assess the CHRONIC ENVIRONMENTAL classification categories ONLY
  - If Rapidly Removed either the M factor or the chronic env cat 1 or 2 shift one step
- It does NOT AIM to substitute or being a surrogate for the persistency assessment (e.g. REACH), nor the bioaccumulation potential
- It focusses on demonstrating transformation by normal environmental processes to either increase or decrease the bioavailability of the toxic species
- For classification purposes, the pH range for metals hazard assessment is defined as pH 5,5-8 (see TDp conditions)

Measuring tool: *Concept development*

- Starting point: Build on established experimental test methods for hazard assessment of metals (Transformation Dissolution protocol T/DP OECD TG 29)



OECD SERIES ON TESTING AND ASSESSMENT
Number 29

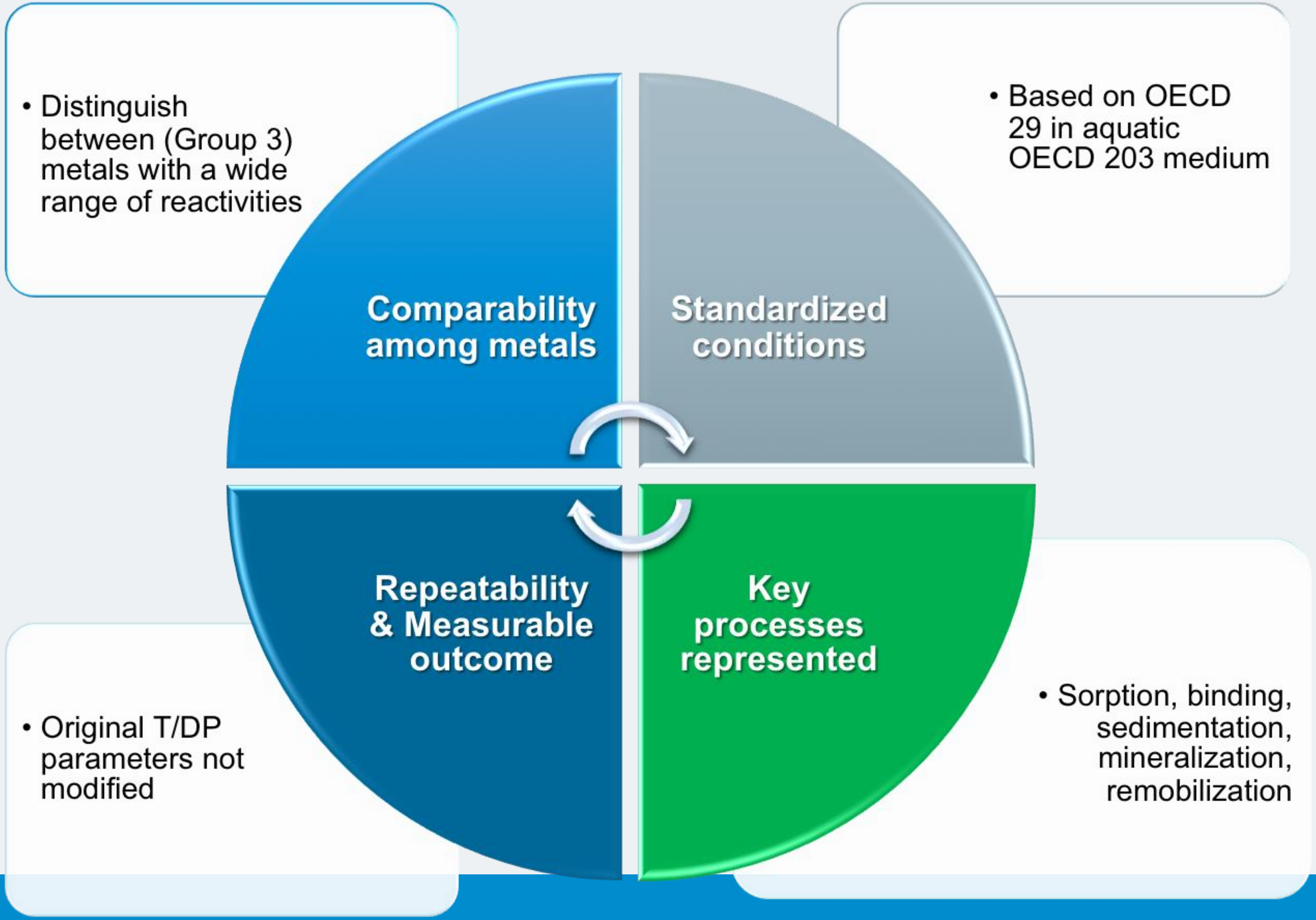
GUIDANCE DOCUMENT ON TRANSFORMATION/DISSOLUTION OF METALS AND METAL COMPOUNDS IN AQUEOUS MEDIA

- **T/DP** measures rate and extent metals and Sparingly Soluble Metal Compounds (SSMCs) can produce metal ions in aqueous media under standard lab conditions

- **T/DP Extension** (T/DP-E) developed and assessed:
  - T/DP-E Part 1: Binding to a substrate with settling
  - T/DP-E Part 2: Remobilization following resuspension

Pillars of T/DP-E

The T/DP-E assesses metal removal in a uniform, repeatable, and comparative way



Comparability among metals

- Distinguish between (Group 3) metals with a wide range of reactivities

Standardized conditions

- Based on OECD 29 in aquatic OECD 203 medium

Key processes represented

- Sorption, binding, sedimentation, mineralization, remobilization

Repeatability & Measurable outcome

- Original T/DP parameters not modified

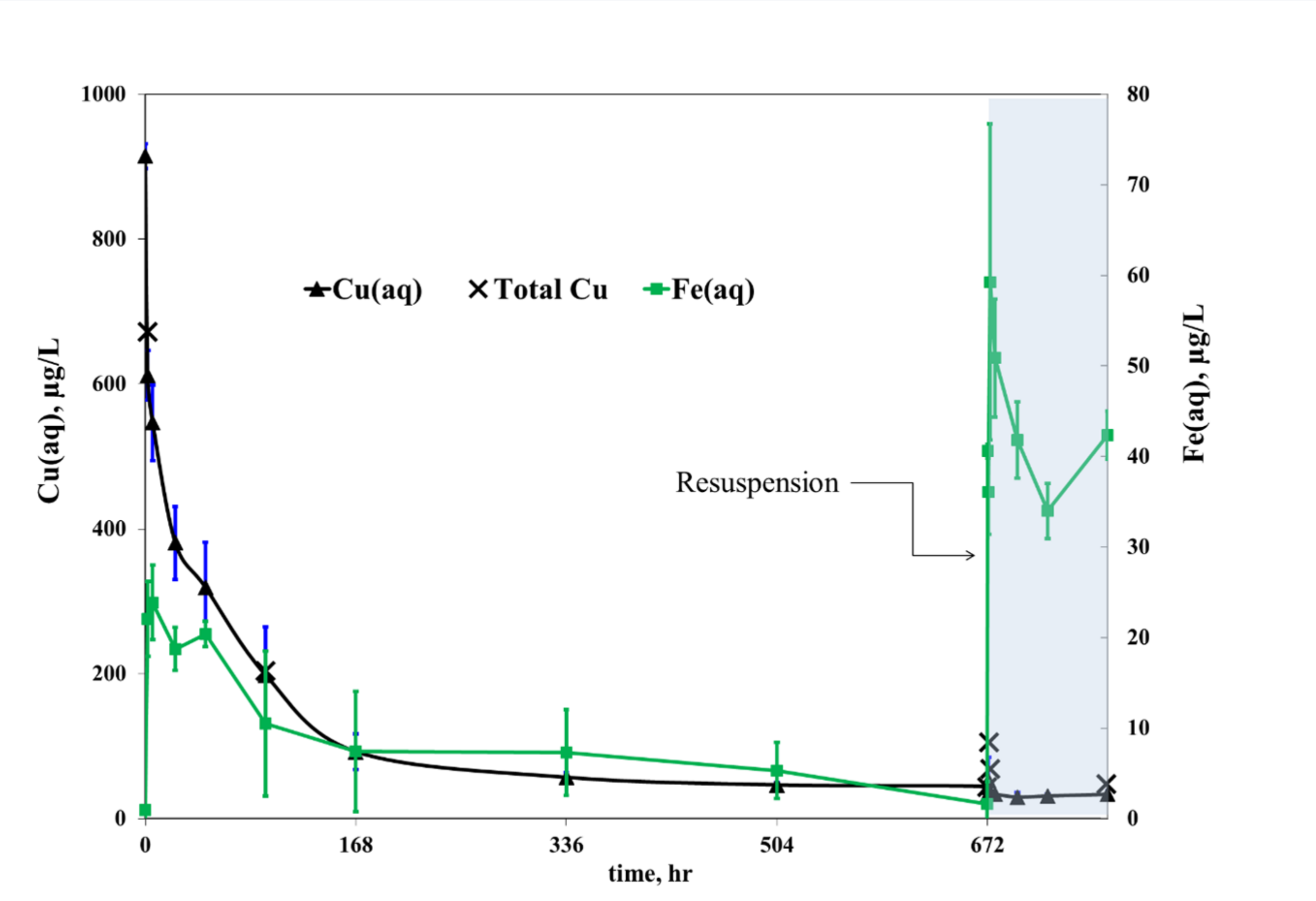
Copper: an example of a metal that is *rapidly removed*

PART 1: 28 day removal

- Cu removal (blue line) from 1000 to < 100 µg/l in 28 days
- Fe from the particulates (green line)

PART 2: Resuspension

- Cu does not remobilise
- Fe remobilises



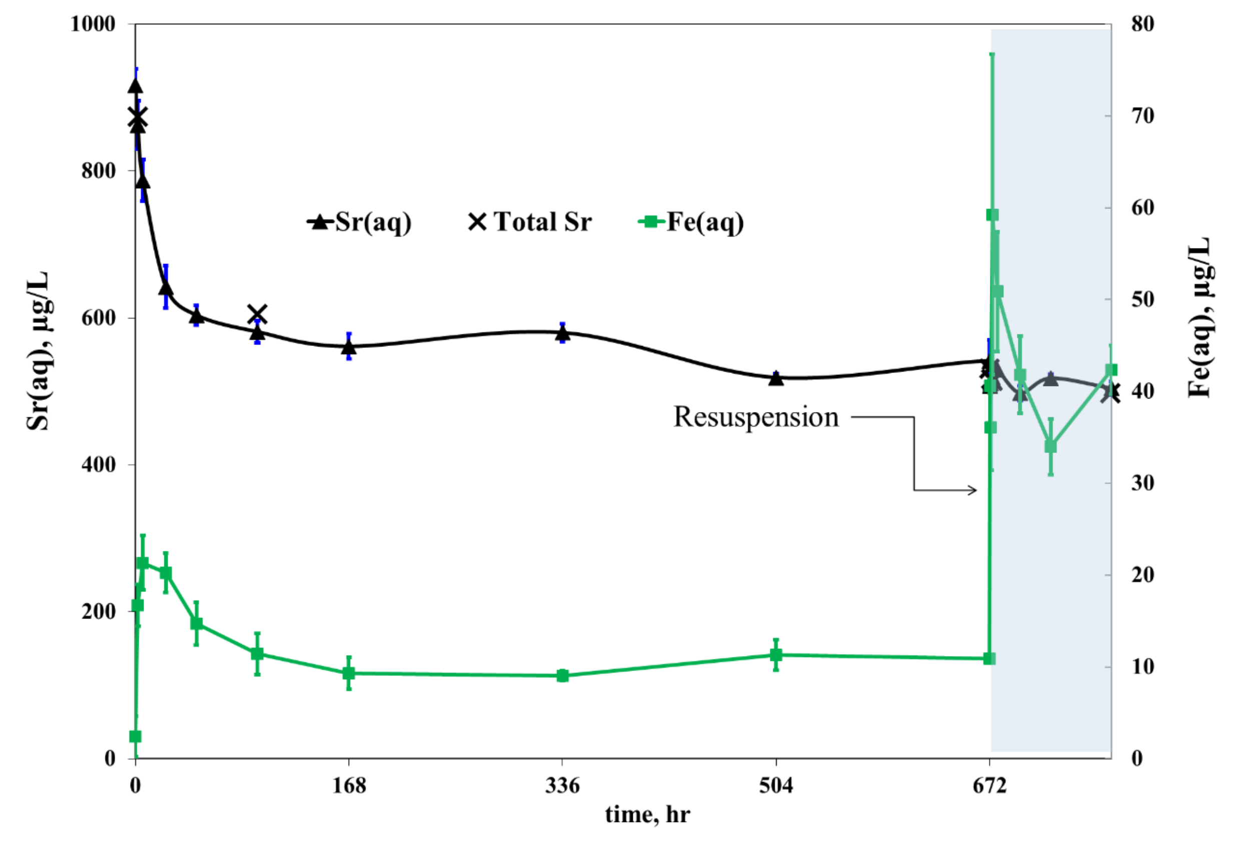
Strontium as an example of a metal *failing rapid removal*

PART 1: 28 day removal

- Sr removal (blue line) from 1000 to +/- 600 µg/l in 28 days (mostly adsorbed to glassware)
- Fe from particulates (green line)

PART 2: Resuspension

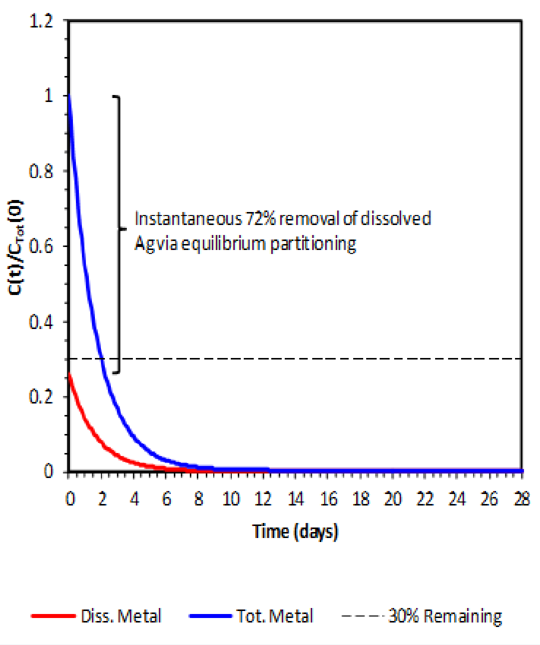
- Sr does not remobilise
- Fe remobilises

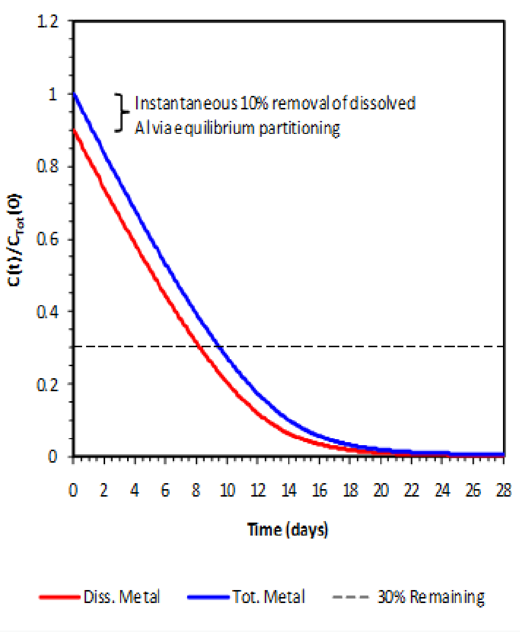


MULTIPLE LINES OF EVIDENCE all concluding the same

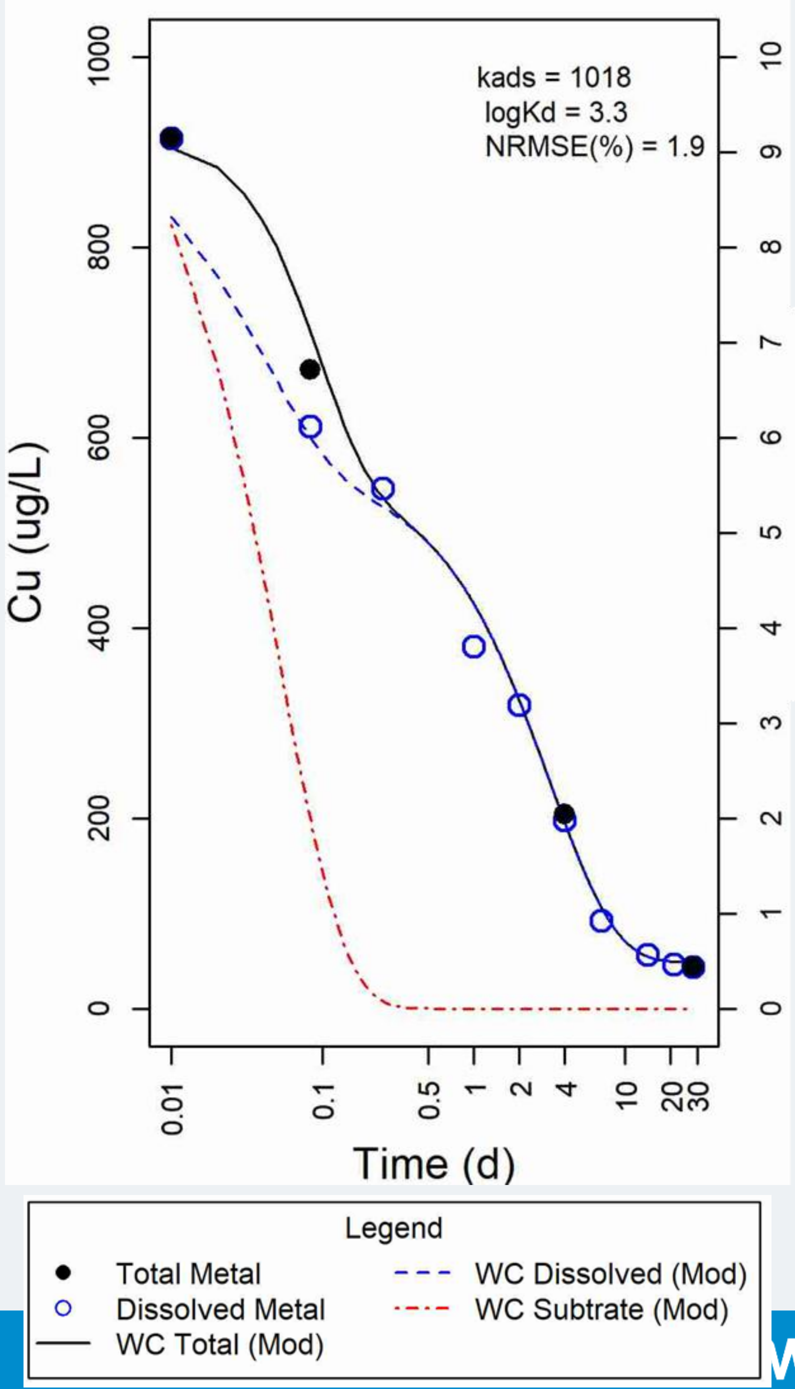
- TD/P-E nicely modelled with **kinetic sorption dispension model** (see graph)

- TD/P-E results are in line with **TICKET-Unit World Model predictions**





- Observations in TDp-E similar to **field observations** (e.g. lake studies in background information)



Briefing papers to clarify questions from February 2019 workshop

1. Partitioning and Removal of Metals and Organics

- **METALS:** partitioning and precipitation of dissolved ions to PM results **in new covalent bonds** and speciation change
- **ORGANICS:** degradation involves **breaking covalent bonds**, which may result in detoxification
- *Metal partitioning to PM and/or precipitation can be analogous to degradation of organics*

BUT:

- **For ORGANICS**: Partitioning to PM occurs *via van der Waals interactions*. Molecule remains identical at the chemical level.
- **For METALS:**
  - Removal correlated to Irving-Rossotti slope, an intrinsic property,
  - Literature and TDP-E show sediment resuspension does not cause long-term remobilization of metals to overlying water.

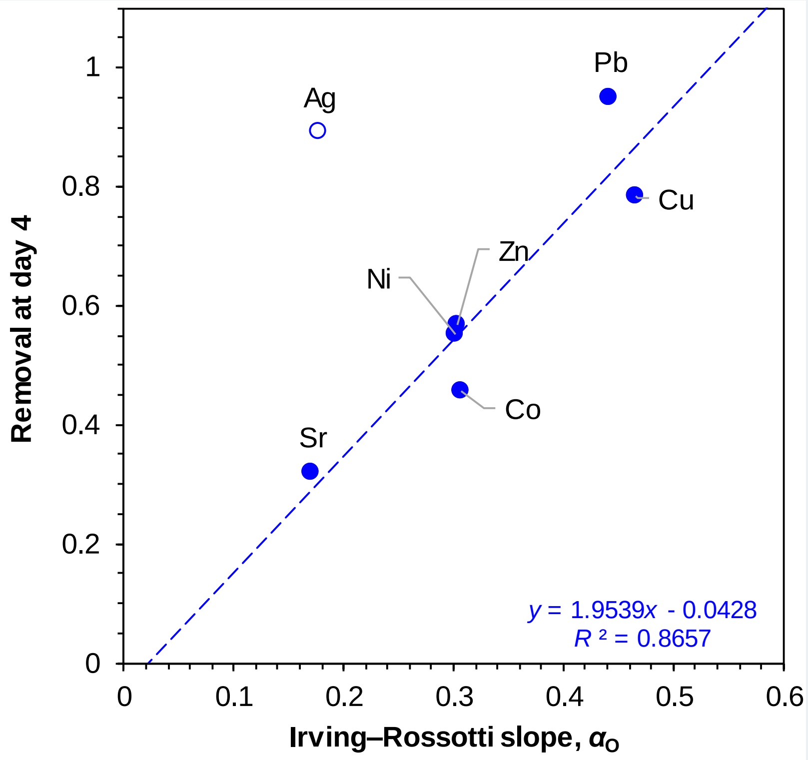


Figure A1. Relationship between removal of metal observed at day 4 of the CanmetMINING experiments and the Irving-Rossotti slope (α_O). Data point for Ag is excluded from the regression.

Conclusion: *Partitioning of organics, cannot be considered equivalent to metal binding and removal*

2. Outstanding Aspects of the Extended Transformation-Dissolution Protocol

Q1: Selection of Representative Substrate

- Metal binding is related to substrate properties (Fe, Al, Mn, organic carbon, and fine particles)
- Criteria based on iron and organic carbon content can identify a suitable substrate (basis = 10th percentile of EU sediments).

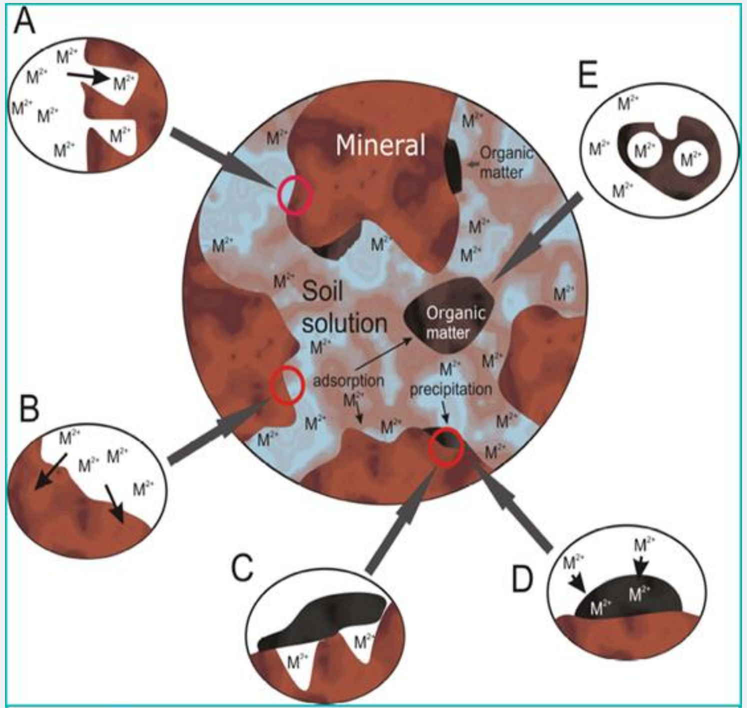
Q2: Impact of Stirring

- T/DP-E developed without stirring during settling phase,
- Modelling & testing confirmed that stirring accelerates metal removal, because kinetic convection-diffusion of dissolved metal ions towards particles is faster

T/DP-E conditions can therefore be considered **as RWC** compared to normal environmental conditions, relevant to ENV. Classification for metals

3. Fate, speciation and long-term toxicity in sediments

- Metals entering aquatic compartment
    - ➢quickly adsorb to SS and settle
    - ➢making sediment the main environmental sink for metals
- Fate of metals bound to particles
    - ➢is key to understand potential exposure (bioavailability)
- Ageing (diagenesis) redistributes adsorbed metals
    - ➢to the interior of organic and mineral substrates
    - ➢resulting in increased stability on sorption sites
- Pore water is dominant route eliciting toxic effects.
    - ➢dietary uptake shown to be minor toxicity route, and decreases through time.
- Particle associated metal
    - ➢is buried through time.



A. Diffusion in micro-pores
B. Inclusion in crystal structure of sediment minerals
C. Occlusion by Fe/Mn (oxy) hydroxides precipitates
D. Precipitation on sediment surface
E. Occlusion in organic matter

Conclusions

Conclusions

- **Guidance** on Rapid Removal is needed to complete the chronic environmental classification scheme for metals under GHS & CLP

- **Rapid Removal** for “type 3 metals”, can be assessed by the removal of *dissolved metals in the water column* by:
  - Partitioning followed by speciation to non-bioavailable form
  - Demonstrating the relative irreversibility of resuspension

- The GHS scheme only applies to metals while **metal removal is substantially different from organics** as covalent boundings are formed under relevant environmental conditions

- **T/Dp-E measures** removal and lack of resuspension of metals in a standardised way, meeting the requirements of the GHS

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