

Rapid Removal Information Session

ECHA - Helsinki, 8 February 2019

Summary report

History of the concept and objectives of the session

The GHS and the CLP include the possibility to consider for metals an equivalent concept as rapid degradation for organics. This concept is based on rapid transformation of metal ions from the water column (further called Rapid Removal). At technical level, this concept was for a first time discussed with member states at an ECHA workshop in February 2012, followed by the submission of an extensive data and research package by industry in February 2013 to reply to the concerns and comments raised. The debate has been stalled since then and was identified under MISA as an *outstanding guidance priority for metals* to ensure a harmonised implementation of the chronic environmental endpoint in the registration files. The issue was therefore discussed back-to-back with the MISA workshop on Environmental Endpoints at an information session on the 8 of February 2019. The Rapid Removal workshop was attended by more than 40 experts from ECHA, Member States, independent scientists and Industry and aimed for:

- achieving a level playing field on the understanding and progress made with the concept development on Rapid Removal and
- identifying key issues for further debate to allow making progress with guidance to resolve this open CLP guidance issue on the Rapid Removal of metals, in 2019.

The workshop (please see [agenda](#)) started with a series of presentations on metals behaviour in the water column, methodological aspects related to the Rapid removal and the explanation of the development and experience gained with a measurement tool. This was followed by open discussion to allow participants to share their views on the applicability of the concept and to identify the critical elements for further discussion with the (EU) Member States Competent Authorities on the acceptability of the concept proposals and directions for guidance development.

Introduction by Hugo Waeterschoot (Eurometaux)

The 2012 workshop and its follow-up (the report can be found [here](#)):

- remembered the original meaning of the rapid transformation concept when the GHS was established: as for organics, demonstrate that *exposure to a metal in the water column would be reduced so rapidly that it would prevent that the chronic effects/hazards can be expressed*.
- recognised 3 clear different groups of metals, as a function of fate and potential degradability:
 1. metals that **readily methylate (volatilise)** such as Hg, Se and others. As for organics this removal process should NOT be considered as “rapid transformation” and should not be further considered under guidance development for Rapid Removal
 2. Metals that **rapidly hydrolyse** under relevant aquatic conditions by forming non-toxic chemical forms in the water column such as Al, Fe, Sb, Mo, Al, Sn, Cr and others. These processes appear so quickly that they often hamper ecotox testing and are generally considered as rapidly removing metal ions from the water column.
 3. Metals that **partition and precipitate** from the water column, but for which the “irreversibility” to a non-bioavailable form under relevant environmental conditions, needs to be demonstrated, like Cu, Zn, Ni, Co, Pb and others.
- Identified that the main question to resolve for this “group 3 metals” is to define what happens after the rapid partitioning and precipitation? Does the metal 1) remain unavailable due to the speciation to a form with reduced or any toxicity and 2) the lack of remobilisation under environmentally relevant conditions?
- Recognised that *hydrolysis and precipitation to form unavailable metal species can be a very significant process* that can occur quickly (equivalent to the rate for organics).
- Concluded that the TICKET-Unit World Model (UWM tool) proposed by IND in 2012 to assess the Rapid Removal, was not sufficiently convincing given on its own too risk-based, lacking standardised parameterisation, lacking proof it works for a broad series of metals or for running waters and could potentially also proof rapid degradation for organics.

2012 workshop follow-up

A series of agreed challenges were picked-up as questions by industry for further investigation and replied to in an extensive information and R&D package reported in 2013, concluding that:

1. the TICKET-UWM model can be easily standardised to facilitate a system for hazard classification
2. the most important factors affecting the Rapid Removal efficiency can be assessed in a sensitivity analysis
4. Persistent Organic Pollutants (POPs) remain toxic to the aquatic environment after partitioning and the processes are often reversible; so, the contrary as for metals
5. the UWM model concept works for a broad series of cationic metals providing a gradual comparison in the removal efficiency
6. the standardised UWM model results could be used to derivate the chronic (long-term) environmental classification as demonstrated in a couple of examples

However, the workshop in 2012 and subsequent reactions from member states, indicated that a *measuring tool rather than a model* would be a more transparent way forward to demonstrate the potential for Rapid Removal, especially for assessing mixtures, or UVCBs.

In summary, industry followed up on the concerns and questions that were posed at the 2012 workshop and developed in parallel an experimental approach to check for the partitioning, the irreversibility and strengthening the mechanistic understanding.

Introduction and overview by Jos Mossink (ECHA)

ECHA explained that since the last workshop in 2012 there have been several harmonised classification proposals (CLH) on metals whereby the Risk Assessment Committee of ECHA (RAC) provided “*some consideration*” to the (relevance) of the Rapid Removal properties (e.g. copper containing-substances, silver zinc zeolite, granulated copper and lead).

The CLP text and guidance provides the possibility to apply the Rapid Removal concept (see slide) but the concept is presently not applied yet in the regulatory scheme. Besides the questions raised to industry to provide further arguments supported by examples, to justify the application of the concept of Rapid Removal for other groups of metals than group 2 (see above), the 2012 workshop proposed to establish an *ecotox expert group* to further discuss the concepts and relevant information requirements with examples, however in practice this never happened.



CLP Guidance on 'Rapid Removal'

IV.3 Assessment of environmental transformation

Environmental transformation of one species of a metal to another species of the same metal does not constitute 'degradation' as applied to organic compounds and may increase or decrease the availability and bioavailability of the toxic species. In addition naturally occurring geochemical processes can partition metal ions from the water column while also other processes may remove metal ions from the water column (e.g. by precipitation and speciation). Data on water column residence time, the processes involved at the water – sediment interface (i.e. deposition and re-mobilisation) are fairly extensive for some metals. Using the principles and assumptions discussed above in Section IV.1 of this document, it **may therefore be possible to incorporate this approach into the classification.**

Such assessments are difficult to give guidance for and will normally be addressed on a case-by-case approach. However, the following may be taken into account:

- a. **Changes in speciation** if they are to **non-available forms**, however, the potential for the **reverse change** to occur must also be considered;
- b. Changes to a metal compound which is **considerably less soluble** than that of the metal compound being considered.

Some caution is recommended; see Section IV.1 of this document, the 5th and 6th paragraph.

Comment by ECHA: Please note that in the light of a lack of scientific consensus and continuing discussions on the interpretation of rapid removal from the water column in the context of classification, it has been decided to remove certain parts from the Annex IV for the time being **until agreement on the validity of use of the concept of rapid removal for classification purposes has been reached.**



The presentation further reviewed the outcome of the RAC discussions on the relevance and data availability of the Rapid Removal concept for the 4 CLH proposals that have been submitted since 2012, in general concluding that: *either no convincing case was made in the 4 dossiers, or the information was lacking, or the lack of an assessment scheme did not allow for a justified recognition of the Rapid Removal potential.* It was further proposed that such assessment scheme should preferably be established/recognised at international level.

Therefore, the following questions on the concept require debate at the session and in the future:

- Does the **Rapid Removal concept** apply to all or only to certain types of metals?
- Under which **conditions** is Rapid Removal feasible and relevant?

- Does the **current Transformation/Dissolution protocol (T/Dp) (OECD 29)** address rapid removal, or is an extension T/Dp-Extended (T/DP-E) (see further) a path to follow?
- Are there other relevant means for **addressing environmental transformation** than the T/DP-E?
- Would accepting this concept for metals contradict the system currently applied to organics?

Assessing removal of metals from the water column for chronic environmental hazard classification (by Richard Carbonaro (Manhattan College/Mutch Associates) (Presentation can be found [here](#))

Inorganic compounds and metals “transform” rather than “degrade”, like organics. This is specifically referred to in the UN GHS Annex A9.7.1.5 ‘For inorganic compounds and metals, clearly the concept of degradability, as it has been considered and used for organic substances, has limited or no meaning. Inorganic compounds and metals may be transformed by normal environmental processes to either increase or decrease the bioavailability of the toxic species. Still the concept that a substance... may (not) be rapidly lost from the environment... are as applicable to metals and metal compounds as they are to organic substances”.

This international reference was the base to develop a scientific solution to assess the concept of metal ion removal from the water column in the context of hazard assessment and classification, while providing evidence of metal degradability in terms of removal from the water column via the following subsequent processes: 1) Adsorption to settling particles, 2) Transformation of metals to non-available, non-toxic forms, and 3) Sequestration in sediment that is effectively irreversible (i.e. lack of remobilisation)

The four lines of supporting evidence for the relevancy of a Rapid Removal scheme/tool, equivalent to degradation for organics are based upon:

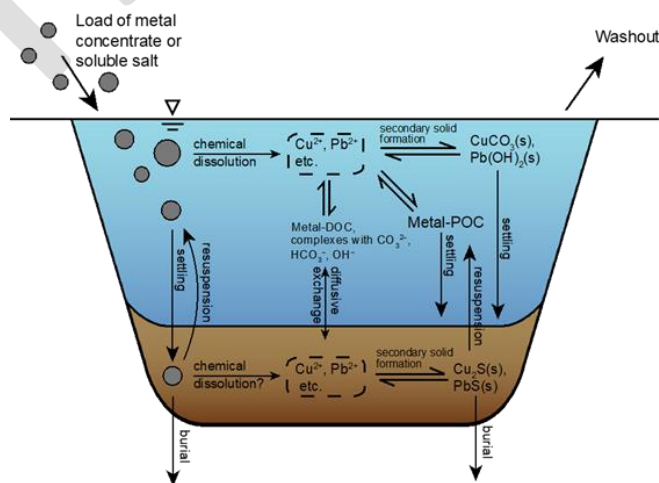
1. The metal intrinsic properties that determine their fate in aquatic systems;
2. Field/laboratory evidence on assessing the fate of dissolved metal ions in aquatic systems;
3. Metal removal/remobilisation under *standardised environmentally relevant conditions using an extended OECD 29 T/DP (T/DP-E) protocol*; and
4. Mechanistic modelling to gain insight into the physico-chemical processes that occur

1. Intrinsic properties of metals:

The TICKET-UWM scheme provided in the picture here aside, illustrates the important processes impacting metals that dictate the extent and time scheme of metal removal, being:

- Chemical (oxidative) dissolution
- Complex formation
- Adsorption
- Precipitation (aging)
- Diffusive exchange
- Settling/resuspension
- Burial

It is however most relevant to carefully consider which of these processes are related to the intrinsic properties of the metal that is being removed from the water column?



Metals do undergo *changes in chemical speciation by: breaking and forming of bonds with significant covalent character with ligands and form* Complex formation by partitioning to DOC, POC, HFO, HMO, etc.; precipitation with sulfide...all these result in changes in chemical speciation as breaking and forming bonds. Organics degradation also involves *covalent bonds but mainly breaking*.

There is however an important distinction between organics and inorganics when they partition to DOC and POC. The interaction of organics with DOC/POC occurs via relatively weak van der Waals forces whilst for metals, via strong covalent bonds. The chemical structure of the organics are therefore not changed when they bind, whereas for metals the formation of covalent bonds changes the chemical structure of the inorganic. Like the degradation of organics, some *metal speciation* changes are rapid and reversible while others possess slow reaction kinetics requiring to assess the rate of the change. Most importantly, the changes in speciation for metals are *predictable from the intrinsic properties* and well known in the scientific literature*. They are based on the known bonding kinetics with functional groups (e.g., -COOH, -OH) on SPM, the settling kinetics was bound. Moreover, the metal reactivity is relatable to their intrinsic properties.

2. Field/Laboratory Studies on Metal Fate

Numerous studies have demonstrated *metal removal in surface waters*, including:

- Di Toro (2001) showing that in near-shore ocean waters, the concentration of metals *predicted* by dilution were orders of magnitude *higher* than observed concentrations which can only be explained by *metal removal*. Sodium is the logic exception.
- Rader (2019) demonstrating that > 70% of added Cu was removed from the water column within 2 weeks of dosing for the majority of toxicity studies
- Di Toro et al. (2001) demonstrating the metal removal efficiency in estuaries, (Cd < Zn < Pb) and this ordering being consistent with the metal K_d values (= intrinsic property)
- Diamond et al. 1990 demonstrating that in mesocosm studies the K_d predicts the removal.

Equally a wealth of literature exists on the binding of metals to specific phases in sediment / substrate, metal removal from sediment pore water, and bioavailability changes in sediment; all most relevant processes in the removal of metals from the water column. Based on experiences from flow through studies the following generic findings on metals can be concluded:

- Sulfides and oxides are the predominant phases responsible for removal of metals
- Cu, Ni, and Zn are strongly partitioned to sediments regardless of the acid volatile sulfide (AVS) and Organic Carbon (OC) contents.
- Metals are increasingly associated with amorphous or crystalline Fe oxides when AVS is lost due to surficial sediment oxidation

3. The Extended T/DP(-E)

The existing Transformation/Dissolution Protocol (T/DP) OECD-29 determines the rate and extent at which a metal, sparingly soluble metal compound, or complex inorganic material may release metal ions to an aqueous environmental medium with standardised composition, not their (subsequent) removal, not at least because it does not contain any substrate. The existing protocol is therefore not sufficient for assessing metal removal from the water column. However, it forms a good basis to provide additional information on the metal removal from the water column. The extension called, extended T/DP-E, was specially developed to measure *the rate and extent of metal removal and irreversibility of the removal* when bringing the metal in contact with substrate.

4. T/DP-E mechanistic model

A numerical model was developed to gain mechanistic insights in the metals' removal mechanisms and processes occurring during the extended part of the T/DP., Only 2 metal-specific parameters were needed to fit the data to the results of the T/DP-E tests (i.e. the adsorption rate constant and the distribution coefficient) indicating that the removal is related to the individual metal's affinity for particles, which is a unique and intrinsic property of the metal.

Metals examples were provided indicating demonstrating that:

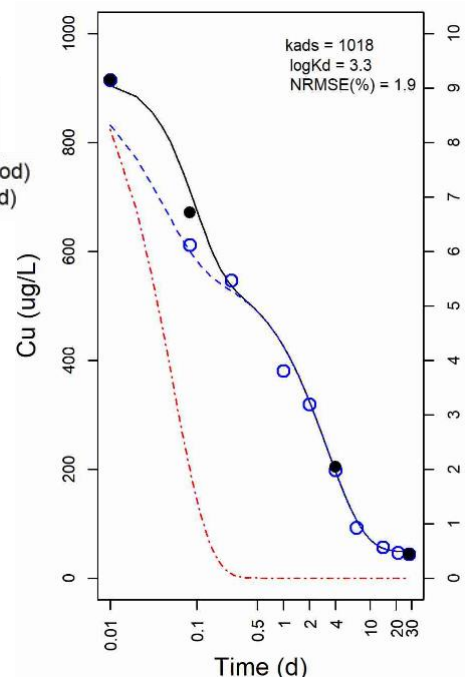
- metal in the water column adsorbs to particles, settling rapidly with the particles
- once particles have settled in the water column (see red dotted line at 0,5 d), dissolved and total metal concentrations are the same
- Most importantly, the metal removal from the water column continue after the particles are settled (see period > 0,5d)
- The model fits short- and long-term experiments with many metals (Ag, Pb, Ni, Zn Cu, Co, and Sr...)

The graph shows quick and sustained removal on Cu.

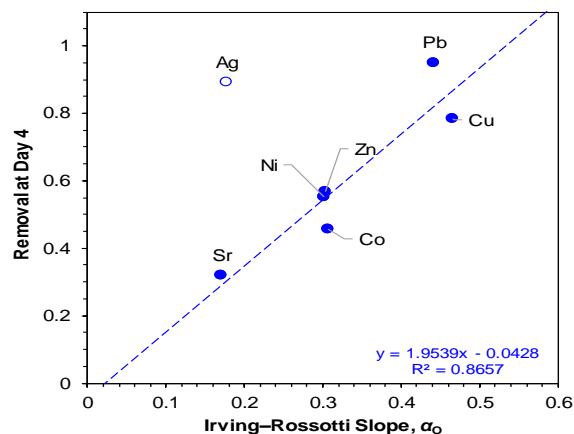
Based on the 4 different lines of evidence and the experimental results, it can be concluded that:

Legend:

- Total Metal
- Dissolved Metal
- WC Total (Mod)
- - - WC Dissolved (Mod)
- . . . WC Substrate (Mod)



- The T/DP-E protocol can discern variations in removal rates related to varying particle affinity of different metals.
- High particle-reactive metals such as Pb have very short half-times in the water column while less particle-reactive Sr achieve very slow removal
- The tendency for metals to bond with functional groups on POC and oxides can be quantified and modelled (e.g. using Irving–Rossotti slopes). This slope is an intrinsic parameter for all metals whereby each metal has a unique value as shown on the graph. Ag is an outlier given the extra strong binding to ligands other than oxygen on the substrate (e.g. sulfur atoms) which are not accounted for.
- the T/DP-E as presently designed is conservative given lacking recognition for additional metal-removal processes that occur in nature: no initial substrate loading, lack of a sediment-water interface lack of recognition for the slower irreversible changes in speciation to more insoluble and non-available forms (soft metal ions: into sulfidic and pyritic solids; hard metals: into hydroxides and oxides)



Conclusively

- Literature show that metals are removed from aquatic systems by naturally occurring processes.
- Removal results from a change in metal speciation that is quantitatively related to the affinity of metal ions for ligands/substrates and are a reflection of the intrinsic properties of metal ions.
- The T/DP-E is a standardised, reproducible method to assess the removal rates for metals under relevant environmental conditions and its validity was demonstrated with data on several metals
- The removal in the T/DP-E could be modelled demonstrating the removal being based on intrinsic properties: (1) Kinetically-controlled adsorption to rapidly-settling substrate particles and (2) Transport to and direct adsorption by the settled substrate particles once they form a layer

[T/DP-E Concept Development by Emily Garman \(Nickel Producers associations\):](#) (presentation can be found [here](#))

[Method Development for Determining the Removal of Metals from the Water Column under Transformation/Dissolution Conditions for Chronic Hazard Classification Philippa Huntsman \(Canadian government, CANMET Mining\)](#) (presentation can be found [here](#))

There is strong scientific understanding and support for the Rapid Removal concept (see previous presentation) allowing it to be modelled. However, regulators indicated that hazard classification best requires a standardised test protocol.

The T/DP Extension (T/DP-E) builds on the T/DP OECD and was specially developed to evaluate and assess the rapid and irreversible removal from the water column recognising that the test should: be conducted under standardised conditions, be repeatable and a measurable outcome, allow comparability among metals and represent some key removal processes in a conservative way. The protocol therefore strikes a balance between key environmental processes and a level of standardisation as relevant for hazard assessment. The objective for the T/DP-E was therefore to build a robust protocol as an extension of the existing OECD 29 T/DP useable at GHS as well as at CLP level.

The T/DP OECD is therefore extended with 2 parts:

- T/DP-E Part 1, to measure binding of metals to a substrate and subsequent settling
- T/DP-E Part 2, to assess the remobilisation of metals following resuspension of substrate

Extension Part 1: measuring the binding of metals to a substrate and subsequent settling:

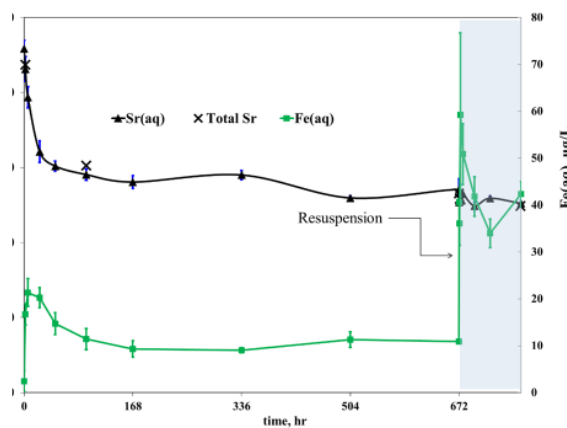
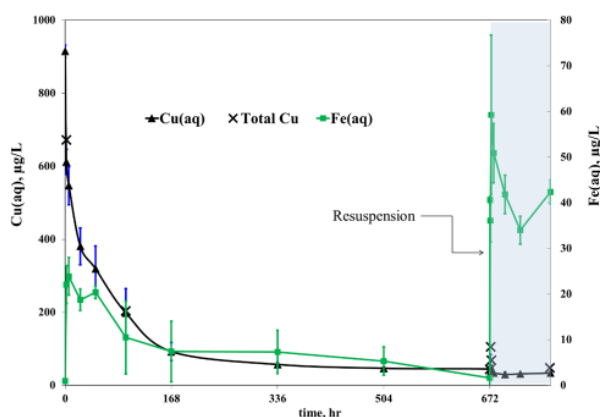
The main elements of the T/DP design and sampling routine were applied to ensure consistency. The main new aspect was the *addition of 10g/L of substrate followed by a minute of energetic agitation*. The 10 g/L loading was based on EUSES (see presentation).

The substrate composition is also critical and was therefore well investigated based on sediment parameters of relevance to metal binding. Based on an extensive European data set on sediments composition (ARCHE 2013) and a preliminary testing program with Nickel, a low binding substrate with a composition of the 10th

percentile for Fe and TOC and a median grain sand was selected. Specific attention for the ability to keep the pH controlled was also part of the assessment criteria.

Extension part 2: assessing the potential remobilisation of metals following resuspension of substrate

After completion of part 1, the flasks are heavily agitated at 150 rpm for 1 hour, to mimic a highly energetic resuspension event. Subsequently the solutions are sampled at regular time intervals over a period of 96h checking for dissolved metal concentrations and relevant parameters (pH, dissolved oxygen concentration, and temperature) as well as the measurement of Fe as a fingerprint of the substrate. Indicative example of dissolution charts covering part 1 removal step (white area) and part 2 resuspension step (grey area) are provided hereunder.



They demonstrate very rapid removal up to more than 90 % in 14ds than levelling off while the agitated resuspension of the substrate does not release the Cu, contrary to the fingerprint metal Fe. To the contrary for strontium the settling and partitioning are limited, with no effect of the resuspension. The removal is even weaker than this given the blank shows this being caused by adsorption to the glass.

Besides these longer-term experiences there is also multiple supportive evidence from other metals (Pb, Ni, Zn,) at shorter timeframes (96 hours).

These results demonstrate that the T/DP-E can be used for standardised rapid removal assessment based on intrinsic properties, in line with the legal requirement of the GHS and CLP. Moreover, the T/DP-E is robust enough to distinguish different rates of removal between different metals and is therefore a suitable tool to assess metal removal in the context of environmental hazard classification.

[Mechanistic understanding of the T/DP-E results by Stijn Baken \(European Copper Association\)](#)

(presentation can be found [here](#))

[Modelling Metal Rapid Removal Experiments for Hazard Classification by Kevin Rader \(Much Associates\)](#)

(presentation can be found [here](#))

Further research conducted at the University of Michigan confirmed the results generated by CANMET by checking for the inter-laboratory repeatability. Additionally, they conducted a sensitivity assessment to evaluate the effect of the selected relevant experimental conditions. 28-day T/DP-E tests with multiple metals using various substrates and examining the impact of several substrate parameters confirmed the robustness of the protocol extension.

Much Associates modelled T/DP-E results aiming to provide a mechanistic insight into the processes controlling metal removal from the water column in T/DP-E experiments. Starting from the CANMET MINING OECD 29 T/DP-E experimental results they developed mass balance equations describing mechanisms of metal removal in the experimental systems. The T/DP-E results could be adequately modelled by using a simple two-layer model representing a water / substrate interface.

The mechanistic modelling results confirmed that for metal that (Rapidly) remove (e.g. Cu fig. on page 4):

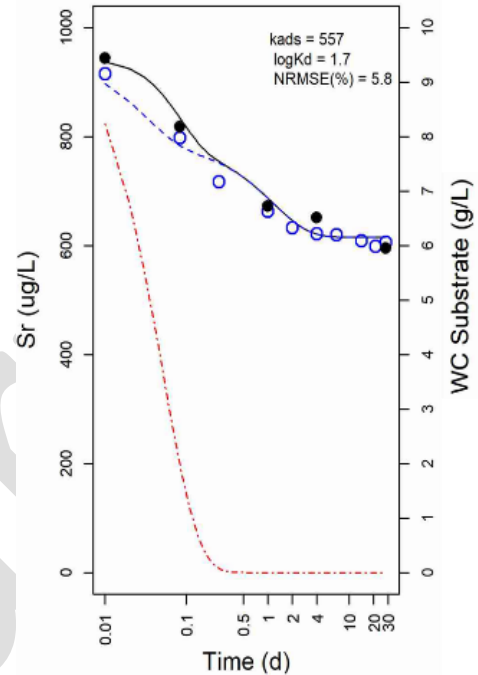
- The added substrate particles settle rapidly in 2-4 hours (log. time scale)
- Part of the dissolved metal fraction adsorbs to particles and settles quickly with the particles
- Once particles have settled from the water column, dissolved and total metal merge: all water column metal is consequently dissolved.
- Metal removal from the water column continues further even after the substrate is settled via transport to and direct adsorption by the settled substrate particles

For metals that *do not* really remove (e.g. strontium (SR)):

- The same mechanisms described for copper play a role for strontium
- The much lower affinity of strontium for particles (lower K_d) and slower adsorption (lower k_{ads}) explain the slow (to no) removal

Legend:

- Total Metal
- Dissolved Metal
- WC Total (Mod)
- - - WC Dissolved (Mod)
- . - . WC Substrate (Mod)



The same model was applied to other metals (Ag, Pb, Ni and Zn) demonstrating the T/DP-E data can be easily fit. *Metal specific intrinsic properties (k_{ads} and K_d) are the only two parameters that were metal specific.*

The model was also successfully applied to the experimental results of the University of Michigan and again the T/DP-E data could be easily fit and explained inclusive the effects of the different substrate types/loadings used.

All this demonstrates that a limited number of metal specific intrinsic properties defines the removal rate and extend.

The impact of different substrate loading regimes (using 10 additions of 1 g/L (instead of 1 addition of 10 g/L)) was evaluated on the suggestion of regulators. As the graph indicates both loading schemes resulted in the same removal after 28 days but the initial rate is logically somewhat different.

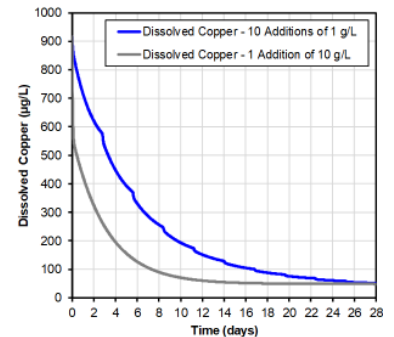
Substrate Loading Results: Copper

1 addition of 10 g/L

- Removal via sedimentation followed by removal via transport to and direct adsorption by settled substrate particles

10 additions of 1 g/L

- Removal by sedimentation is limited; direct adsorption by settled substrate still important



Slower removal but same overall removal extent at day 28

Match Associates, LLC
Environmental Engineers and Scientists

Alternative substrate loading scenarios did not affect the overall removal result after 28-d

Conclusion: the OECD 29 T/DP-E experimental data could be successfully modelled in a relatively simple way, demonstrating the relevant and important processes occurring in the T/DP-E include:

1. Kinetic adsorption of dissolved metals to substrate particles;
2. Settling of particles with adsorbed metals;
3. Dissolved metal transport to and direct adsorption by the settled particles
4. Calibrated metal-specific parameters based on intrinsic parameters like K_d , follow expected trends based on intrinsic properties of the individual metals

Overall question and discussion session

The overall discussion session aimed at collecting further needs for explanation and to identify key issues that would require further debate before specific guidance on metals Rapid Removal could be developed. In general, the issues raised included questions on:

- the mechanistic functioning of the binding of metals to substrates and demonstration of the irreversibility (covalent bounds or not)
- the intrinsic properties of metals that drive the binding (K_ds)
- the laboratory conditions and variance of the T/DP-E
- the difference and/or precedence setting for Persistent Organic Chemicals
- applicability of the Rapid Removal concept: restricted to metals and inorganic metal compounds
- the international relevance and need for standardisation

Questions on the T/DP-E extension itself were limited except on challenging the concept as a whole.

Conclusions

The main aim of the workshop was:

- to raise the understanding by explaining what has been done since the 2012 ECHA technical workshop on the Rapid Removal concept for metals and
- to collect the key issues that would best require further clarification before developing guidance for the Rapid Removal concept should be launched.

The session allowed to identify in this respect the following issues for clarification:

1. The **relevance of particles added** (standard conditions): it would be better to define how the selection of substrate could be standardised.
2. **Inorganics vs. organics** (and extractable fraction). Clarify the difference in nature and strength of the binding. Confirm and clarify the covalent binding for metals and describe how it influences/affects availability (solubility)?
3. Uncertainty about the **speciation of metals in the partitioned phase**. Explain the chemistry of the irreversibility and link this with the absence of ecotoxicity effects.
4. Explain why the **intrinsic properties of metals** related to the binding/speciation that demonstrate the Rapid Removal concept, cannot be applied in the same way to organics.
5. Clarify the **outstanding issues related to the test conditions** of the extended protocol. In particular the relevance of the lack of stirring during the settling phase.

Next steps (only relevant within the EU context)

The debate on the use of the concept in the EU would preferably only start when the listed issues are addressed by further technical responses.

Continue the discussion and debate on how to proceed the concept for hazard classification of metals by the summer.

Participants can still forward technical questions requiring further clarification related to the presentations and suggested T/Dp-E.

ECHA will consider how to conduct the work on the Rapid Removal before it goes to the policy level.