

**From:** EHS Assistant <EHSAssistant@eurometaux.be>  
**Subject:** V. Verougstraete : Outcomes ECHA discussion May 21  
**Date:** 23 May 2012 13:09:12 GMT+02:00  
**To:** Violaine Verougstraete <verougstraete@eurometaux.be>  
**Cc:** Hugo Waeterschoot <waeterschoot@eurometaux.be>, Inneke Claes <claes@eurometaux.be>, Araceli Zorrilla Quinza <zorrilla@eurometaux.be>, Anne Heymans <heyman@eurometaux.be>, "Federica Iaccino (federica.iaccino@arche-consulting.be) (federica.iaccino@arche-consulting.be)" <federica.iaccino@arche-consulting.be>, "Katia LACASSE (katia.lacasse@copperalliance.eu)" <katia.lacasse@copperalliance.eu>, "John SCHONENBERGER (john.schonenberger@copperalliance.eu)" <john.schonenberger@copperalliance.eu>, "Daniel VETTER (dv@ebrc.de) (dv@ebrc.de)" <dv@ebrc.de>, "Frederik VERDONCK (frederik.verdonck@arche-consulting.be)" <frederik.verdonck@arche-consulting.be>, Guy Thiran <thiran@eurometaux.be>  
▶ 1 Attachment, 3,2 MB

---

### To the SCC Taskforce

Dear All,

We hope you are all doing fine.

Please find herewith a short update on the discussion we have had with ECHA on the “inorganic UVCB substance ID and assessment” on May 21.

- In terms of **attendance**, there was a significant participation from ECHA representatives, both from the Evaluation and the Substance Identification Units, including several Heads of Unit and Derek Knight, Scientific Adviser, up to 6 pm. All were extremely active in the discussion!
- “Openness”, “Science” and “Pragmatism” are we believe the best qualifiers to describe the **overall ‘meeting mood’**. These are ‘qualities’ we need to take forward in our further work to maintain understanding from both sides
- In terms of **outcomes**: we believe we managed to demonstrate that there is knowledge, experience and a lot of thinking ongoing in the sector on “UVCB assessment”. ECHA also agreed with the idea of a longer workshop where we would present examples (parts of examples) of application of the developed approaches ☺. It is now up to us to contact ECHA with a proposal of date and outline for such a workshop. This workshop shall cover human health and environmental risk assessment, Substance Identification, how to meet data needs, explanations and justification/format of reporting, weight of evidence and data access
- Substance ID and the link with the assessment is a **key aspect** to which we need to pay further attention and time. ECHA also questioned whether we intend to participate in the OECD activity aiming at drafting guidance for Substance identification of UVCBs, in order to ensure consistency (note: this OECD activity is led by ECHA)

We took some –extensive- notes and identified a number of action points we would like to further discuss with you on the 6<sup>th</sup> of June. Those action points were either suggestions from ECHA or actions we identified ourselves while presenting and discussing. Please also find attached the final presentation: we still shortened it a bit more on the plane to Helsinki.

Please do not hesitate to contact us if you have further urgent questions related to the above.

Looking forward to discuss with you on the 6<sup>th</sup> how to make the best use of this opening from ECHA,

Have an excellent day

Katia, Daniel, Frederik, Hugo and Vio



*Inorganic UVCBs: challenges for  
their identification and assessment  
for registration purposes*

Helsinki, May 21 2012

# Background (1)

- Complex Inorganic UVCBs contain varying amounts of metals, metal compounds and/or minerals
- Examples are
  - the naturally occurring mineral ores & concentrates
  - the intermediates produced during the various refining and manufacturing streams of metals (e.g. “refinables”)
  - ...



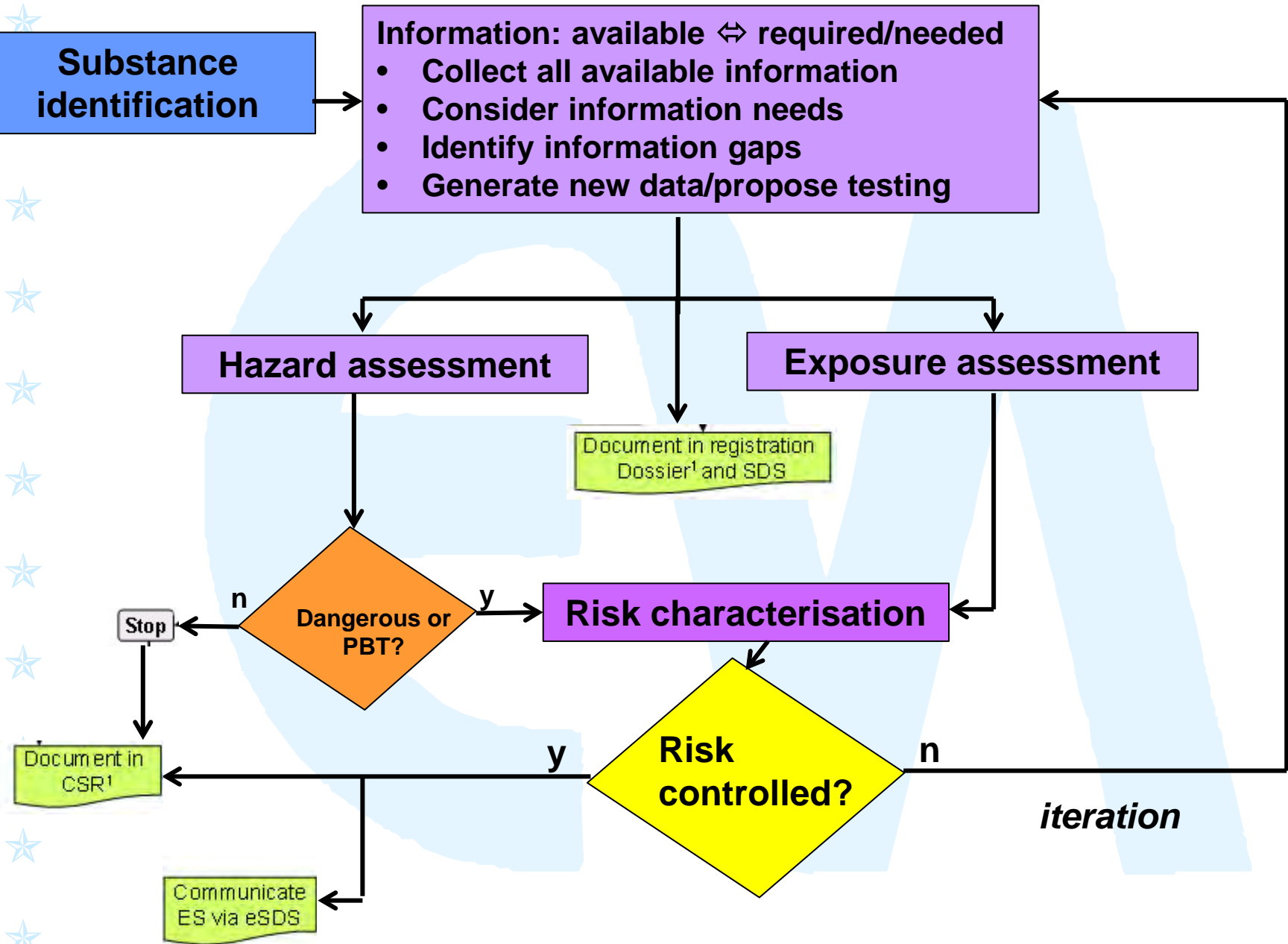
## Background (2)

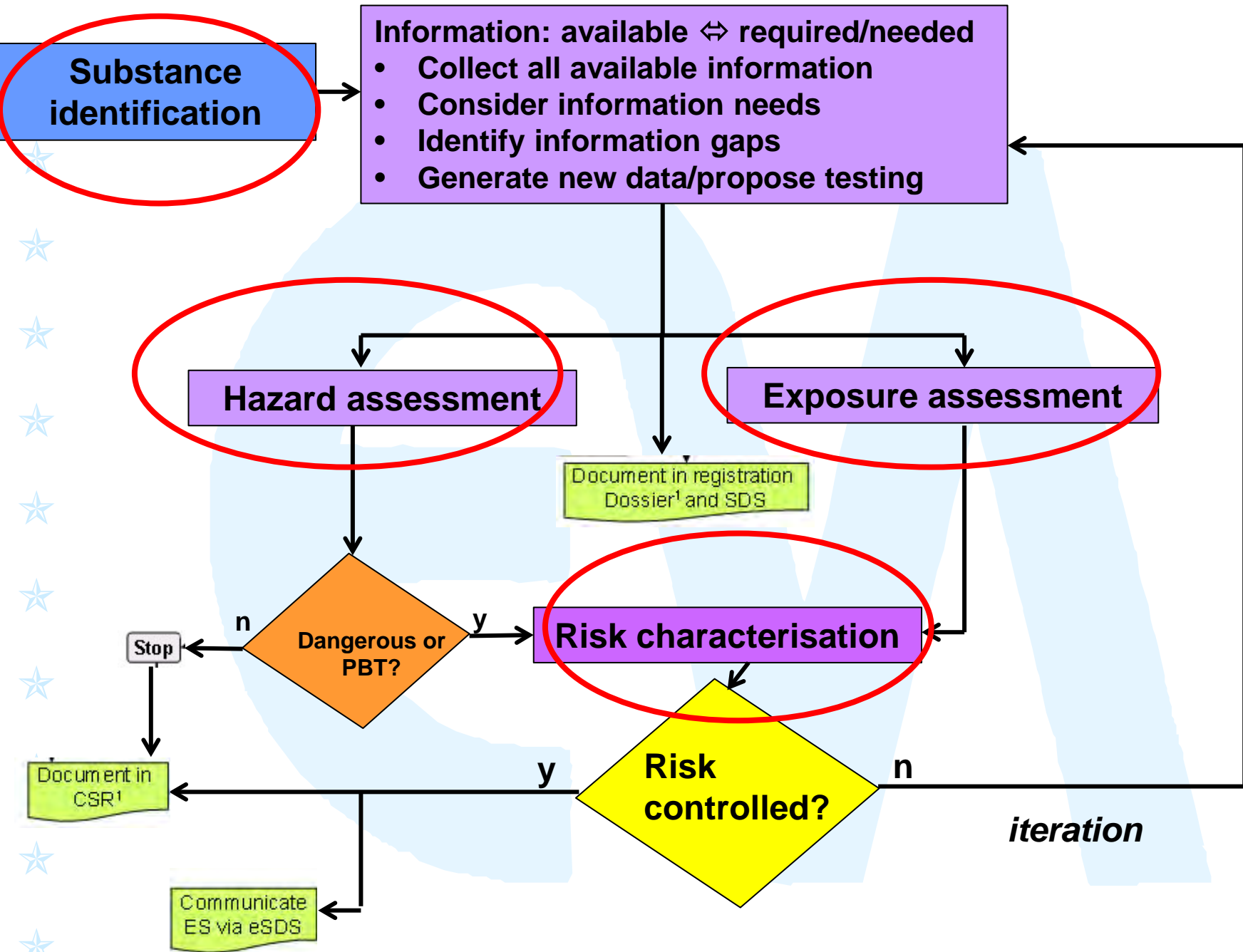
- very complex inorganic materials often composed of 10 or more constituents
- large numbers of streams, covering large parts of the metals refining and recycling sector
- industry explored several options to conduct robust assessments under REACH for UVCBs taking into account existing knowledge, experience, tools,...
- industry needs to roll out the application of these techniques and strategies asap but wants to be sure it has covered all REACH objectives

# Objectives of today

- **exploratory discussion** to exchange views on issues, current state of play with regard to approaches and tools
- **ensuring transparency/brainstorming**
- **plan for a technical workshop** to demonstrate the application of those methodologies/tools to “real cases”
- your comments, questions and alternative concepts are welcomed! 😊

# Draft agenda





Information: available ⇔ required/needed

- Collect all available information
- Consider information needs
- Identify information gaps
- Generate new data/propose testing

**Substance identification**

**Hazard assessment**

**Exposure assessment**

Document in registration Dossier<sup>1</sup> and SDS

Dangerous or PBT?

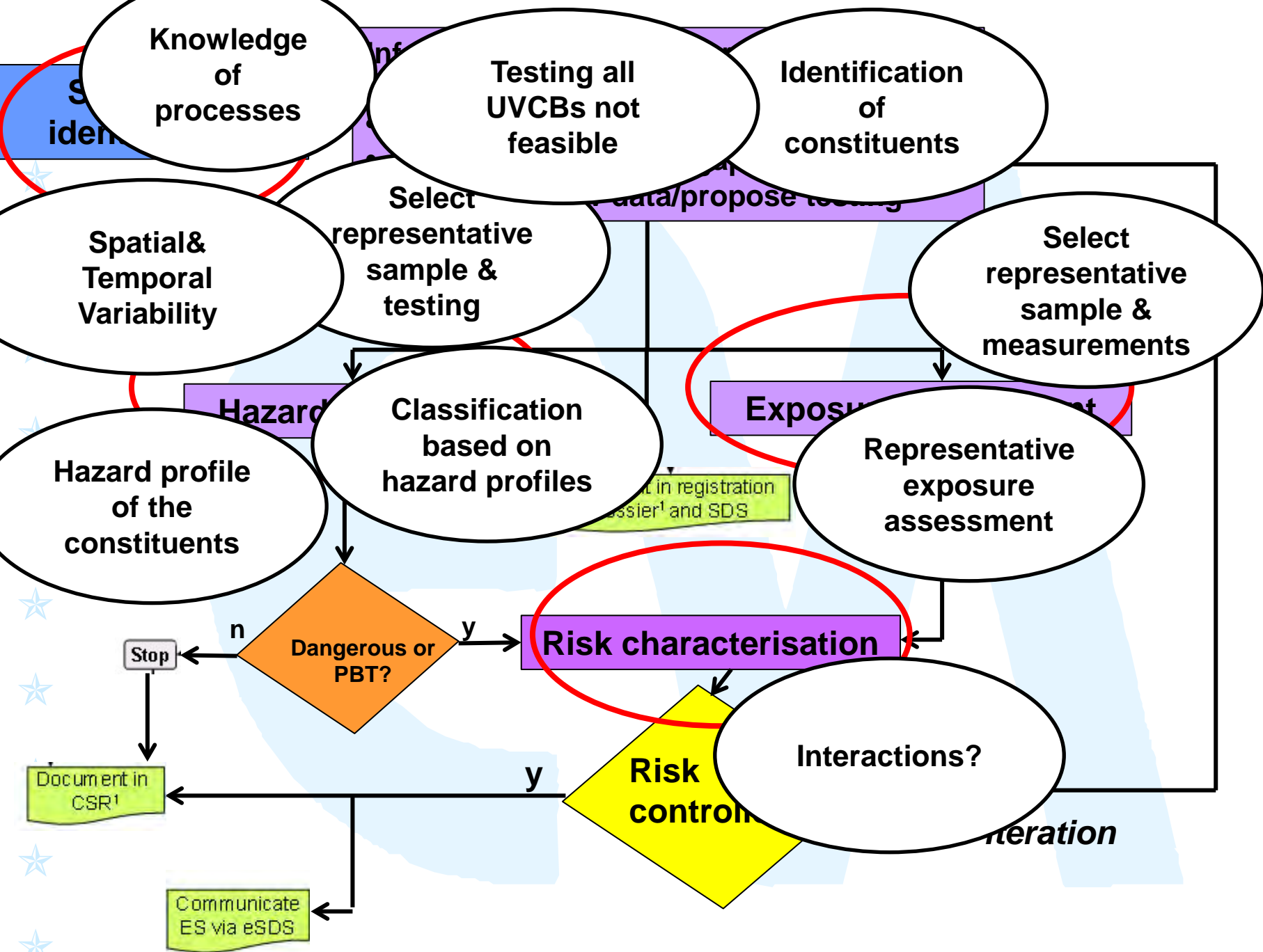
**Risk characterisation**

Risk controlled?

*iteration*

Document in CSR<sup>1</sup>

Communicate ES via eSDS

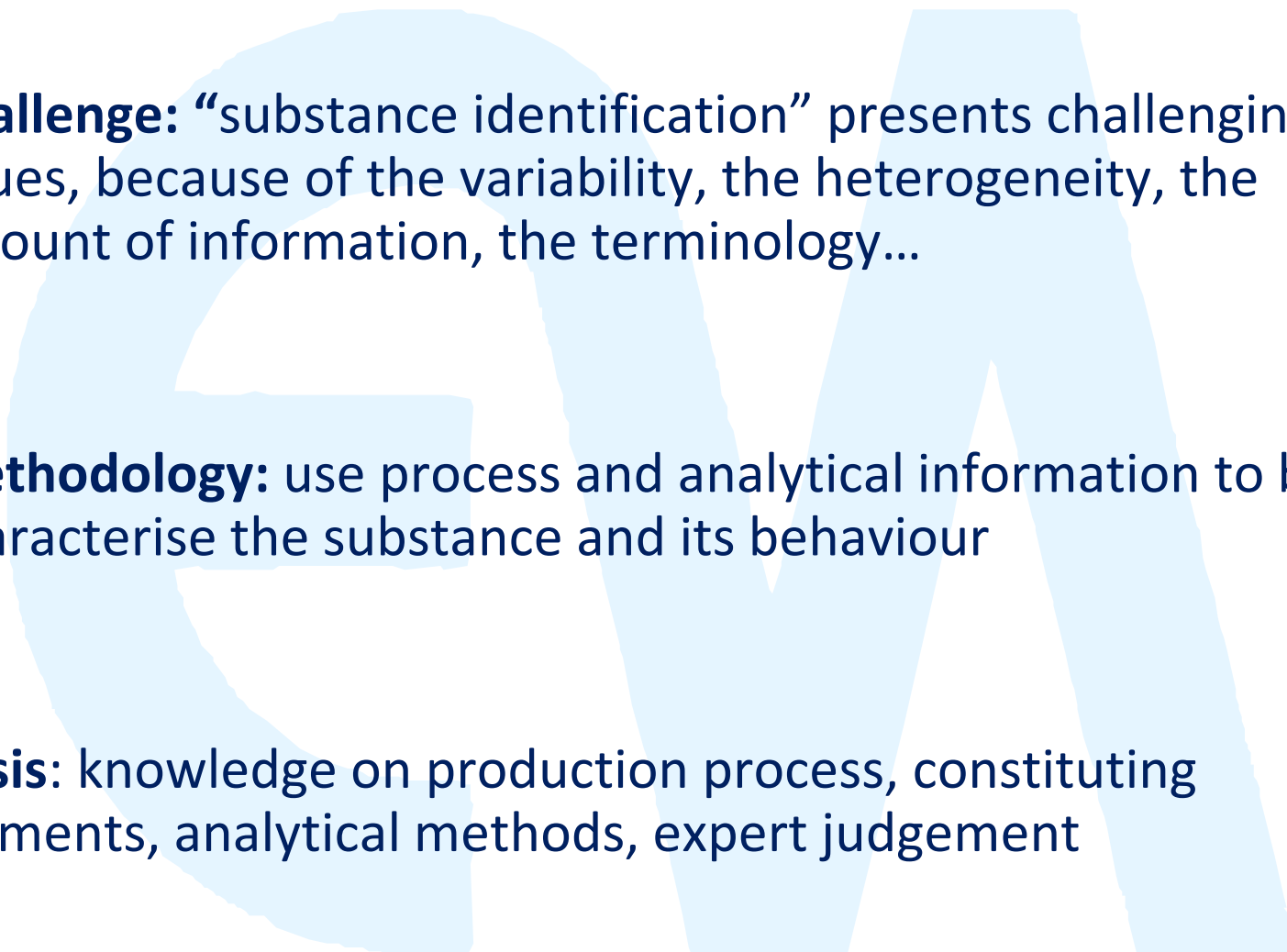


Substance  
identification

Information: available ⇌ required/needed

- Collect all available information
- Consider information needs
- Identify information gaps
- Generate new data/propose testing

# 1. INORGANIC UVCB IDENTIFICATION

- 
- **Challenge:** “substance identification” presents challenging issues, because of the variability, the heterogeneity, the amount of information, the terminology...
  - **Methodology:** use process and analytical information to best characterise the substance and its behaviour
  - **Basis:** knowledge on production process, constituting elements, analytical methods, expert judgement

# Content

Cu

Identification

Characterization: the compositions

Characterization: the properties

Sameness considerations

Analyzing Complex Inorganic UVCBs

Example Copper matte

Conclusion

---

**The identification acc. to REACH and CLP occurs by means of both,**

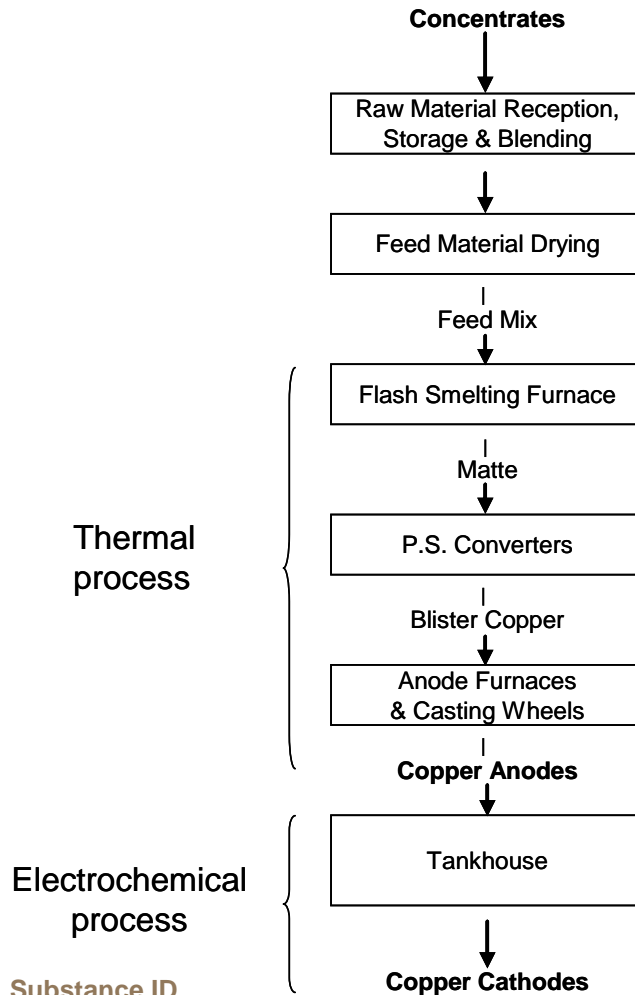
- Its (IUPAC, or internationally accepted) name, and
- Its description

**The description under REACH shall mention identifiers such as**

- the origin or sources of the material (e.g. feedings and production process), and
- the known main constituents

# Example: Copper Production (pyrometallurgy)

Cu



# Characterization: the compositions

Cu

---

**Spatial and temporal heterogeneity and variability in compositions and physical forms →**

## **Chemical (elemental) composition**

- Lists for example, freely dissociated metals that may not actually exist in the material (eg Cu, Fe, S, ...)
- Reflects non-specific analytical procedures (eg AAS)

## **Mineralogical (crystallographic) composition**

- Lists structure and composition in mineralogical form (eg chalcopyrite,...)
- Reflects advanced analytical chemistry (eg advanced X-ray crystallography)

## **Alternatively, refined chemical composition**

- Lists metals, but includes additional information on species and forms present (eg Cu present in the form of metallic inclusion and sulphides, ....)
- Involves expert judgment to select representative sample

---

## Additional information on behavior →

### Physico/chemical properties

- Physical form(s): particle size (distribution), specific surface, density,...
- Oxidation, melting, flammability, ...

### Information on bioavailability

- Aquatic Transformation/Dissolution test (water solubility), Bio elution in body fluid(s), .....



**Same and/or equivalent?**

**The more comprehensive the substance characterization, the more challenging the sameness considerations**

*Is this a fruit, or an apple, or a Boscop, ...*

# Analyzing Complex Inorganic UVCBs

Cu

- **Elemental analysis**
  - Solid samples can be analysed by XRF, Laser Ablation, Arc Emission, Neutron Activation and SEM-EDAX
  - Matrix matching important (e.g. XRF, LA)
  - Solution-based digestion methods (ICP-OES/MS) require complete sample dissolution
  - Quantification of the constituents
- **Mineralogical analysis (speciation)**
  - Relatively more difficult than (chemical) compositional analysis
  - Solid samples can be analysed by XRD, XANES, EXAFS, FTIR, and chemical fractionation & analysis
  - Liquids can be analysed by HPLC/SEC- ICP-MS, ISE, Donnan dialysis, or Ion exchange analysis, etc
- **E-scanning Microscope (SEM)**

# How to characterize in practice?

---

**Analytical techniques used by registrants may vary but:**

- **Robust conventions from mineralogical prospecting exist for reporting compositions**
- **Conceptual framework adopted by registrants is the same**
- **Experienced professionals, familiar with materials and processes**
- **Interpretation based on best statistical calculation packs**
- **Detailed information and explanatory documents provided: exceeding the scope of “only” sameness consideration, and using sophisticated & advanced technologies**

# Example: Copper matte

Cu

---

## Chemical assays:

- by ICP-OES (inductively coupled argon plasma optic emission spectrometer) after total dissolution.
- Cu, Fe, Ni, Pb and As contents were analyzed also by using sequential (H<sub>2</sub>O-, H<sub>2</sub>SO<sub>4</sub>-, KCN- and HNO<sub>3</sub> with KCN- BrMeOH-) dissolutions to distinguish the water soluble copper phases, oxidic copper minerals, secondary copper sulfides and primary copper sulfides.
- SiO<sub>2</sub> content was determined colorimetrically.
- Sulfur and carbon contents were determined by Eltra CS 2000 analyzer.
- The amount of sulfate SO<sub>4</sub> was determined by ion exchange chromatography.

# Example: Copper matte

Cu

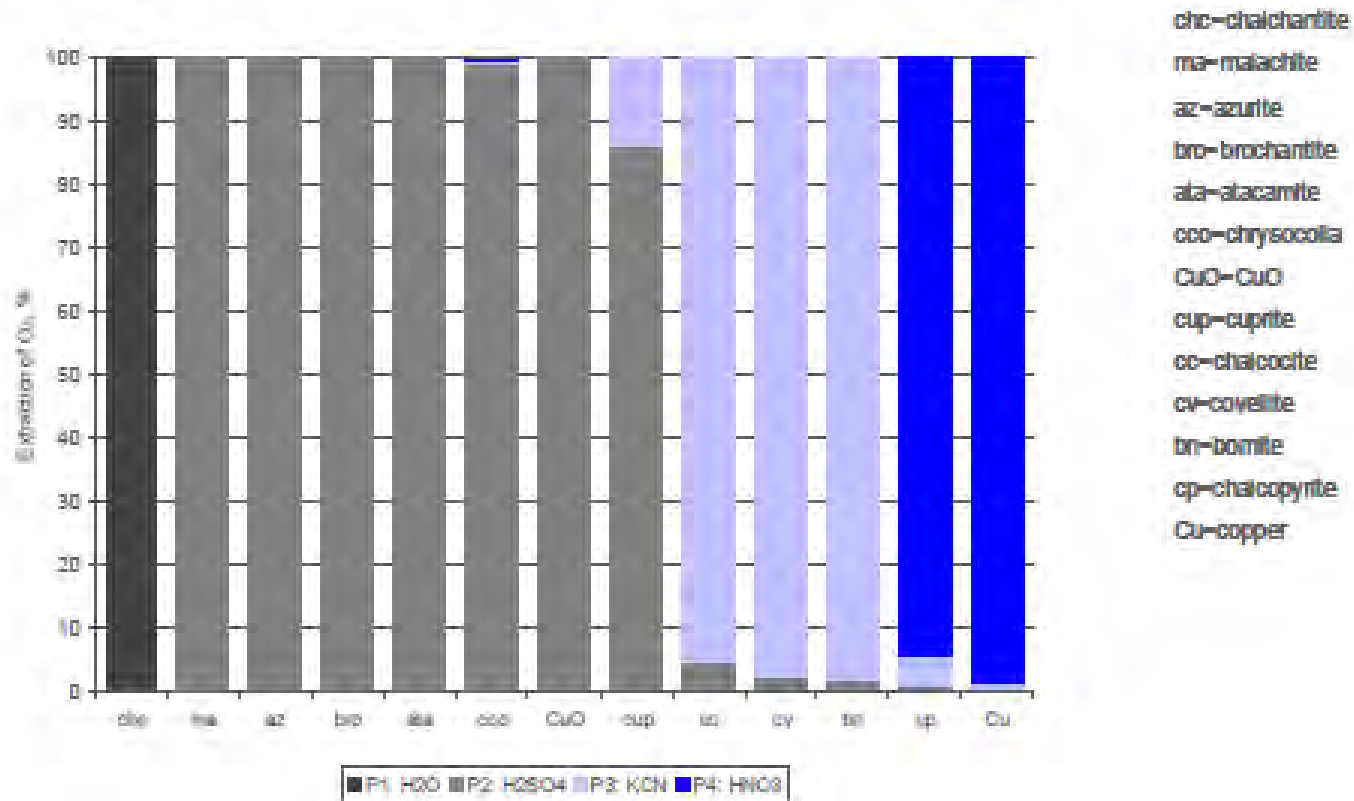


Figure 2: Sequential phase analyzes for copper minerals

# Example: Copper matte

Cu

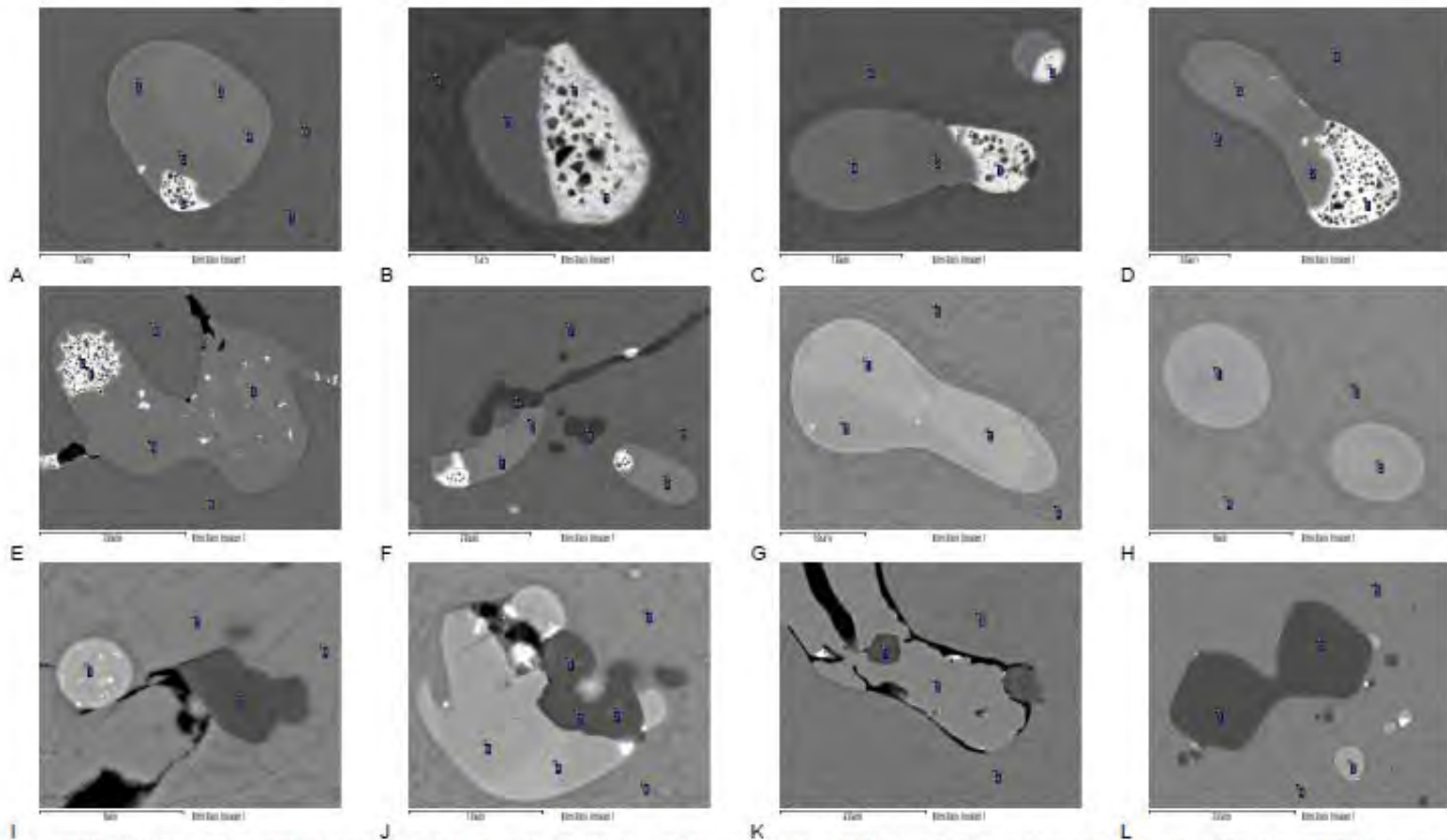
---

## Mineralogical analysis:

- includes consideration from chemical assays results (e.g. sequential dissolutions)
- Additional information from (electronic) microscopy and X-ray Diffraction (XRD)
- Includes Expert judgment and iterative interpretation using various calculation approaches (e.g. Chemical Reaction and Equilibrium Software HSC Chemistry)

# Example: Copper matte

Cu

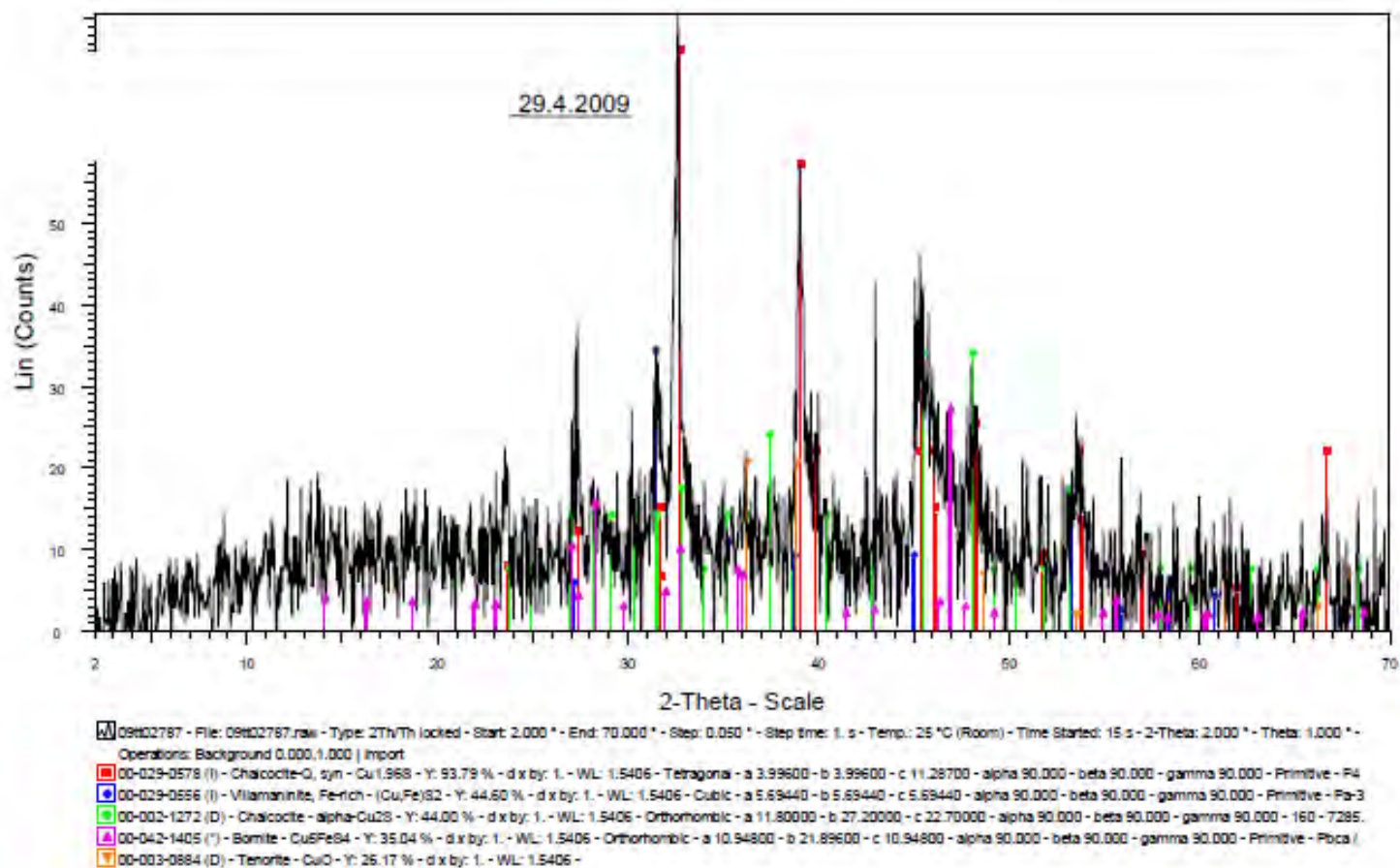


09TT02787, B2\_EF, a-e) metallic copper (1-2, darker grey)- Cu<sub>3</sub>As (3-4, lighter grey) with metallic lead (white) in chalcocitic copper sulfide, f) metallic copper - Cu<sub>3</sub>As-metallic lead inclusions with magnetite veinlet in copper sulfide, g-h) Cu<sub>3</sub>As (1-2)- As-bearing metallic copper inclusion in copper sulfide, i) heterogeneous metallic Cu- Cu<sub>3</sub>As- lead droplet (1) and magnetite (2) in Cu- sulfide (3), j) magnetite (1-3)- Cu<sub>3</sub>As (4-5)- lead-inclusion in Cu- sulfide, k) magnetite (1) in metallic Cu both enclosed in Cu-sulfide, and l) magnetite (1-2) and Cu<sub>3</sub>As (3) inclusions in Cu- sulfide (4-5)

# Example: Copper matte

Cu

## Laboratorioraportti



# Matte identification

Cu

<b>Substance name</b>	copper matte
<b>Trade name</b>	copper matte
<b>EC number:</b>	266-967-8
<b>EC name:</b>	Matte, copper
<b>CAS number (EC inventory):</b>	67711-91-5
<b>IUPAC name:</b>	matte, copper
<b>Description:</b>	Substance resulting from metallurgic processing of primary and secondary sources. The matte is obtained from copper ore/concentrate and recycled materials. It is composed primarily of copper and copper, iron and lead-sulphides with minor sulphides of other metals

**its name**

**its description (production process, feeding materials and resulting composition)**

**→ applicable to all types of copper matte**

# Matte composition

Cu

Constituent	Typical concentration	Concentration range
Copper EC no.: 231-159-6	ca. 55.0 % (w/w)	$\geq 50.0$ — $\leq 80.0$ % (w/w)
Iron EC no.: 231-096-4	ca. 15.0 % (w/w)	$> 1.0$ — ca. 20.0 % (w/w)
Lead EC no.: 231-100-4	$\geq 1.5$ % (w/w)	$\geq 0.9$ — $\leq 6.8$ % (w/w)
Arsenic EC no.: 231-148-6	$< 1.0$ % (w/w)	$\geq 0.06$ — $\leq 1.8$ % (w/w)
Nickel EC no.: 231-111-4	$> 0.5$ % (w/w)	$\geq 0.05$ — $< 1.0$ % (w/w)
Zinc EC no.: 231-175-3	ca. 1.0 % (w/w)	$\geq 0.4$ — $\leq 1.8$ % (w/w)
Silver EC no.: 231-131-3	$< 0.2$ % (w/w)	$\geq 0.0010$ — $\leq 0.7$
Cobalt EC no.: 231-158-0	$> 1.0$ % (w/w)	$\geq 0.1$ — $\leq 2.0$ % (w/w)
Minor constituent	ca. 2.0 % (w/w)	
Oxides	$\leq 3.0$ % (w/w)	
Sulfur EC no.: 231-722-6	ca. 20.0 % (w/w)	ca. 15.0 — ca. 30.0 % (w/w)

## Chemical assays and ICP-OES analysis

Ranges are generic across industry

→ Legal entity specific composition should be within ranges

---

## Selection of representative samples:

- Range in elemental compositions within and across companies assessed
  - Detailed information on the different process conditions evaluated in view of potential differences in resulting mineralogy
  - Expert judgment
- use of standardized sampling protocols

# Mineralogical information

Cu

Sample	09TT02787		09TT02788		09TT07029			
Type	B2		B2		B2			
Mineral composition								
Cu <sub>2</sub> S	Chalcocite	96.39	Cu <sub>5</sub> FeS <sub>4</sub>	Bornite	81.86	Cu <sub>2</sub> S	Chalcocite	95.38
Cu <sub>3</sub> As	Domeykite	3.87	Cu	Copper	10.23	Cu	Copper	1.99
Pb	Lead	0.55	Fe <sub>3</sub> O <sub>4</sub>	Magnetite	4.02	Fe <sub>3</sub> O <sub>4</sub>	Magnetite	1.19
Fe <sub>3</sub> O <sub>4</sub>	Magnetite	0.54	Si(Fe,Al,Ca)O <sub>2-3</sub>	Glass	2.74	Cu <sub>2</sub> O	Cuprite	1.00
Cu	Copper	0.44	ZnS	Sphalerite	0.57	Si(Fe,Al,Ca)O <sub>2-3</sub>	Glass	0.39
			Pb	Lead	0.49	PbS	Galena	0.06
			CuSn	CuSn -alloy	0.08	NiSb	NiSb -alloy	0.04
			NiSn	NiSn -alloy	0.01	Ag	Silver	0.01
Total		101.80	Total		100.00	Total		100.05
Distribution of copper								
Cu <sub>2</sub> S		95.87	Cu <sub>5</sub> FeS		83.41	Cu <sub>2</sub> S		95.99
Cu <sub>3</sub> As		3.59	Cu		10.42	Cu		2.73
Cu		0.53	Fe <sub>3</sub> O <sub>4</sub>		0.09	Cu <sub>2</sub> O		1.27
Fe <sub>3</sub> O <sub>4</sub>		0.02	CuSn		0.08	Si(Fe,Al,Ca)O <sub>2-3</sub>		0.00

**Solid speciation XRF and Sequential Fractionating: the information from the selected (representative) samples is extrapolated to comparable materials**

**Mass balances only!**

# Matte refined composition

Cu

## **Copper Matte (RWC)**

Copper present as Cu oxide (WC Cu(I), 1.04% from total Cu) + sulphides (94,35% from total Cu)

Lead as Pb oxide (WC Pb compounds, 100% from total Pb)

Nickel present as Ni metal (100% from total Ni)

Cobalt (if present) as sulphide (68.27% from total Co) + metal/inclusion (31.73% from total Co)

Other (minor) metal elements: if present, as sulphide (WC, each 100% from total element)

**Species and forms of the constituents determine the (eco) tox profile of the UVCB → For classification purposes, define a Reasonable Worst case distribution pattern for key constituents and use the classifications of these species (mixture rules) and consideration on the form of the UVCB**

**Note: RWC classification may be refined with knowledge of actual release/bio availability profiles of the UVCB (e.g. from T/D test, bio elution test, etc)**

- Density
- Particle size, surface area
- Oxidation and melting
- Water solubility + aquatic transformation/dissolution testing
- Bio-elution profile in body fluid

## Physico-chemical testing

On selected (representative) samples (depending on endpoint to be addressed) → expert judgment required



**Critical factors to determine sameness are name and description**

**Analytical information provided exceeds sameness consideration**

**Additional information on process parameters, etc available in other parts of the registration dossier**

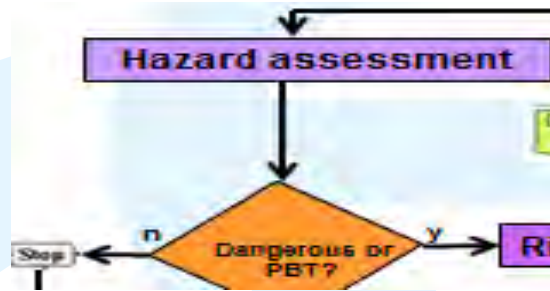
*...no, this is a picture of a fruit, an apple, a Boscop, ...*

# Inquiry issues (1)

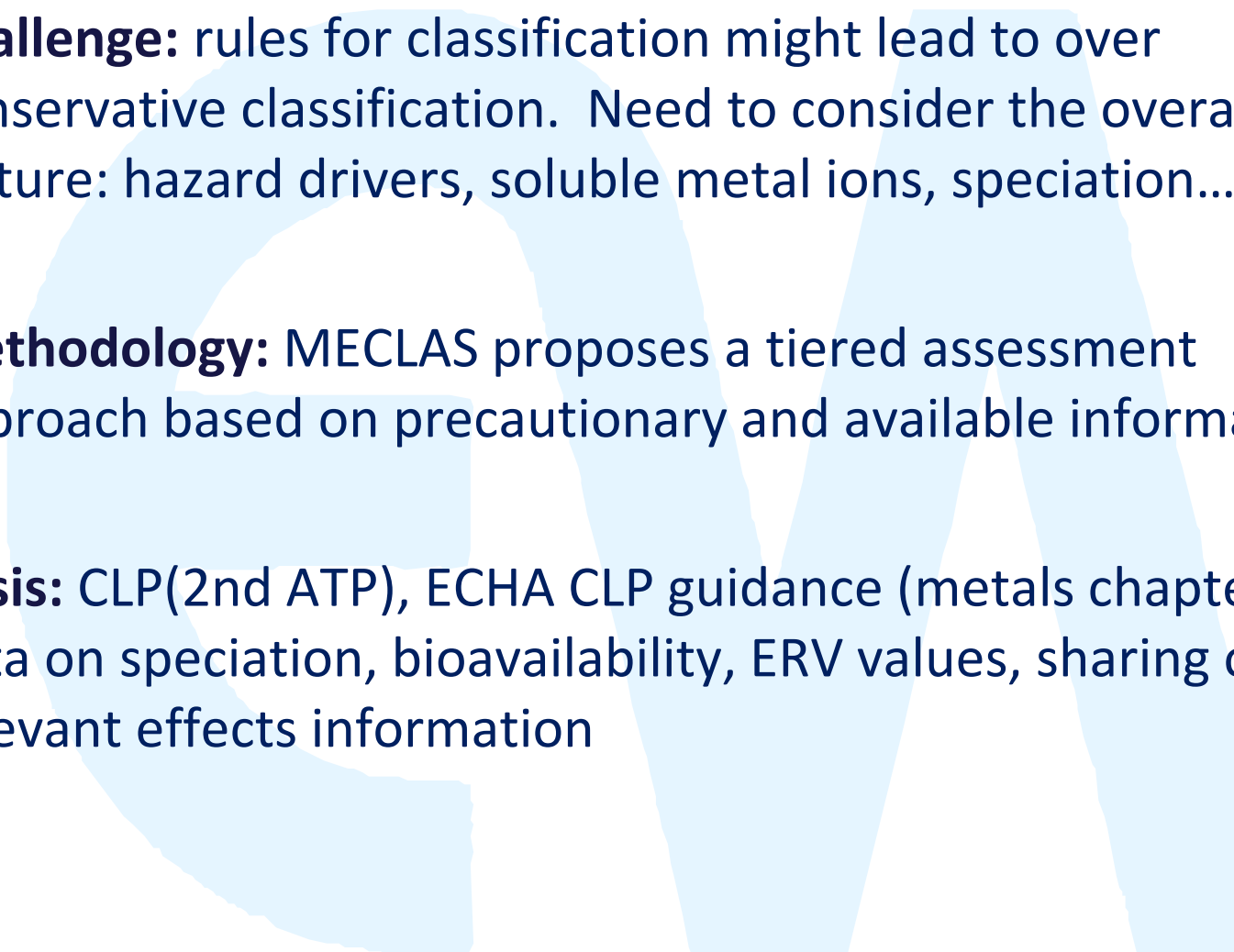
<b>Modification request</b>	<b>UVCB complex inorganic material</b>
<p>Manufacturing process description should include/describe:</p> <ul style="list-style-type: none"><li>• <b>exact origin</b> and the chemical identity of the starting materials,</li><li>• <b>the ratio of the reactants,</b></li><li>• <b>a clearly described chemical process</b></li><li>• <b>process parameters</b> (pH in narrow range, temperature, pressure, etc).</li><li>• the used <b>additives shall not vary</b></li></ul>	<p><b>Requested level of detail is not always possible/feasible</b> because:</p> <ul style="list-style-type: none"><li>• the original materials <b>largely vary also from charge to charge</b> (multiple suppliers, mines etc.).</li><li>• <b>Parameters</b> such as pH, additives, temperature, etc. are <b>not always relevant</b> for NFM UVCBs</li><li>• Many specific terminologies would need to be introduced and explained</li></ul>

## Inquiry issues (2)

Modification request	UVCB complex inorganic material
<p>The <b>XRD spectrum does not confirm the results of the elemental analyses</b> submitted in section 1.4.</p>	<ul style="list-style-type: none"><li>• XRD spectra are covering multiple company elemental analysis. Because of the UVCB character, differences will always occur between elemental analysis and XRD spectra unless taken from the same sample.</li><li>• the <b>whole package of information</b> is taken into account for interpreting XRD results</li></ul>
<p>Create in <b>IUCLID a reference substance for each known constituent (species/mineral)</b> and providing the IUPAC name, numerical identifier molecular/structural formula and weight.</p>	<p>the chemical composition of the complex metals UVCB is <b>preferably analyzed as elements</b> and reported as mass per cent and metallurgical experts recommend the whole package of information is taken into account for interpreting XRD results. Therefore, elements as reference substance</p>



## 2. INORGANIC UVCB HAZARD IDENTIFICATION and CLASSIFICATION

- 
- **Challenge:** rules for classification might lead to over conservative classification. Need to consider the overall picture: hazard drivers, soluble metal ions, speciation...
  - **Methodology:** MECLAS proposes a tiered assessment approach based on precautionary and available information
  - **Basis:** CLP(2nd ATP), ECHA CLP guidance (metals chapters), data on speciation, bioavailability, ERV values, sharing of relevant effects information

# Hazard ID for classification purposes

- **Metal mixtures** obtained by the deliberate mixing of 2 or more components and not interacting like alloys are mixtures and follow the mixture ruling under CLP

- **UVCB and MCS** are considered as substances in respect to CLP, but follow in general the mixture ruling....

- **Alloys are “special mixtures”**: Metal alloys are defined by the CLP as “special preparations” because their (eco)toxicity profile does differ from that of their constituents.

# The soluble metal ion concept

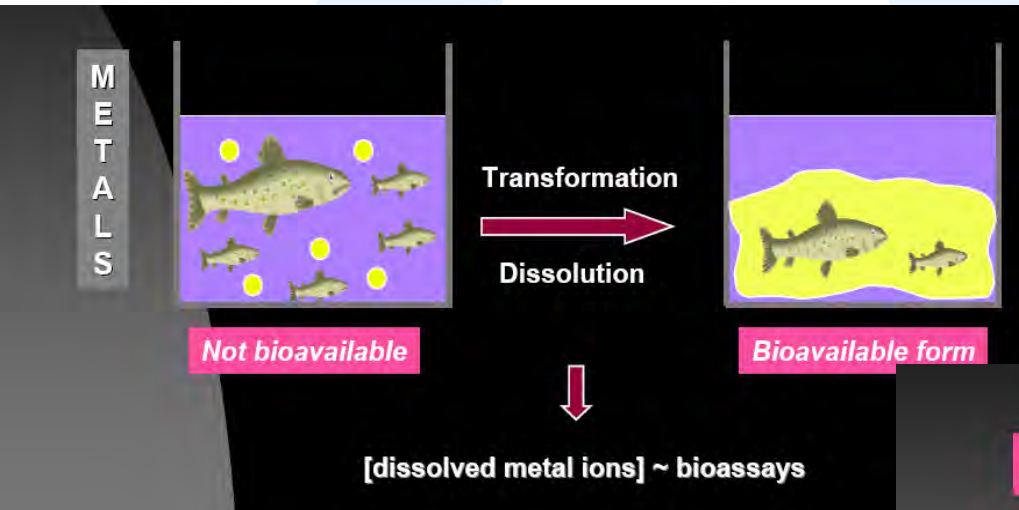
- ☞ Toxicity of most metals is driven by “soluble metal ions”
- ☞ **Toxicity data** are mostly developed on *soluble forms*
- ☞ **Direct toxicity testing** of sparingly soluble or metals is often unreliable due to:
  - Nominal data sets
  - Release determined by surface

OECD/EU therefore recommended to **derive environmental toxicity Reference Values (ERVs) for soluble forms** and to define hazard profile of Sparingly Soluble Metal Compounds & metals using a “**release factor correction**”

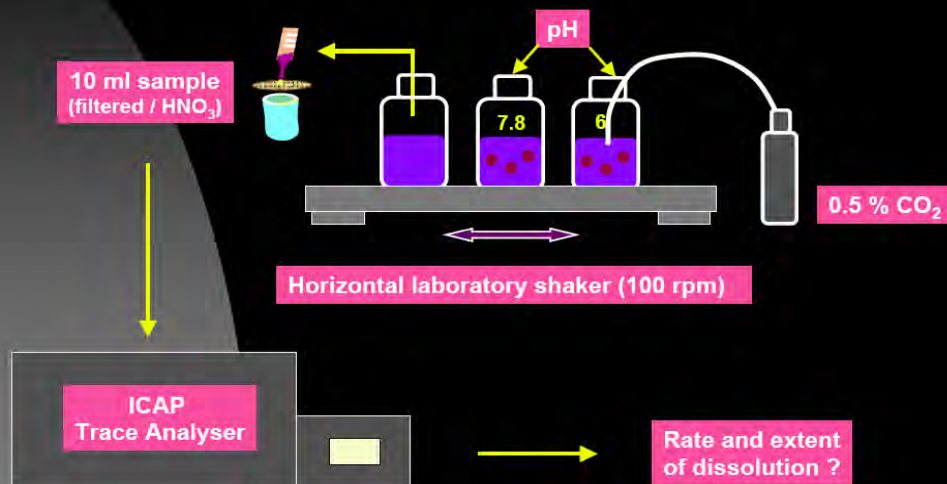
# The soluble metal ion concept (2)

★  
★  
★  
★ **Standard OECD protocol** exists to measure metal release under standard conditions (Transformation dissolution protocol, applies to inorganic metals and metal compounds))

## Test principle



## Test design



## The soluble metal ion concept (3)

### Challenges for UVCB assessment :

- Measure ***all relevant elements*** (all ions that express potential ecotoxicity)
- ***Cut off for analysis*** : minimum classification trigger eventually corrected for M factor
  - Zn : 0,25 %
  - Ag : 0,25 % / 1000
- ***Conditions for the TDp***: pH that releases the highest amount of toxic ions
- ***Combined effect*** : calculate using “mixture ruling”. **UVCB and MCS** are considered as substances in respect to CLP, but follow in general the mixture ruling....

# For UVCBs : Hazard ID based on Classification ruling for complex materials

**T/D test data available**

YES

Concentration at x mg/l loading rate  $\geq$   
*acute/chronic ERV of dissolved form*

YES

**Classify**

NO

**Do not classify**

**Additivity rules :** 
$$\frac{\sum C_i}{L(E)C_{50m}} = \sum_{\eta} \frac{C_i}{L(E)C_{50i}}$$
  $\longrightarrow$  **Classify/not classify**

# Challenges

- ☞ Availability of most recent ERVs and other parameters needed for the hazard id of metal elements
  - Industry initiative for a collective database on all relevant inorganic components
- ☞ Lacking hazard profile for given SSMC
  - Can always be derived from the toxicity profile of the soluble element corrected for TDp
- ☞ Complexity of the hazard calculations and corrections
  - MECLAS : tool developed by industry

# Challenges

- 👉 **Combined effect** of the individual components
  - Calculated based on the Toxic Unit approach
  - Eventually assessed in a validation step for potential synergistic/antagonistic effects
- 👉 **Validation assessment:** Tiered approach recommended in case of expected specific effects
  - Based on Modeling (combined BLMs) (under development)
  - (LT) Testing sensitive representative species and compare with TU calculations (often algae or Ceriodaphnia)
  - Higher tier test if relevant (e.g. Mesocosm)

# Conclusions

Inorganic environmental hazard assessment for UVCBs can be **derived from their composing elements**

**REACH files and ERV values are available** for (almost) all relevant metal elements

Approach is even simpler than for classical read across

**Transformation Dissolution protocol** is basic tool for the hazard assessment strategy for inorganic metal and metal compounds

**Calculations** are based on Toxic Unit approach (accumulation ruling) for hazard assessment

**Validation** is recommended in case additional effects would be expected.

# **MECLAS: facilitating the hazard ID for complex metal materials under CLP**

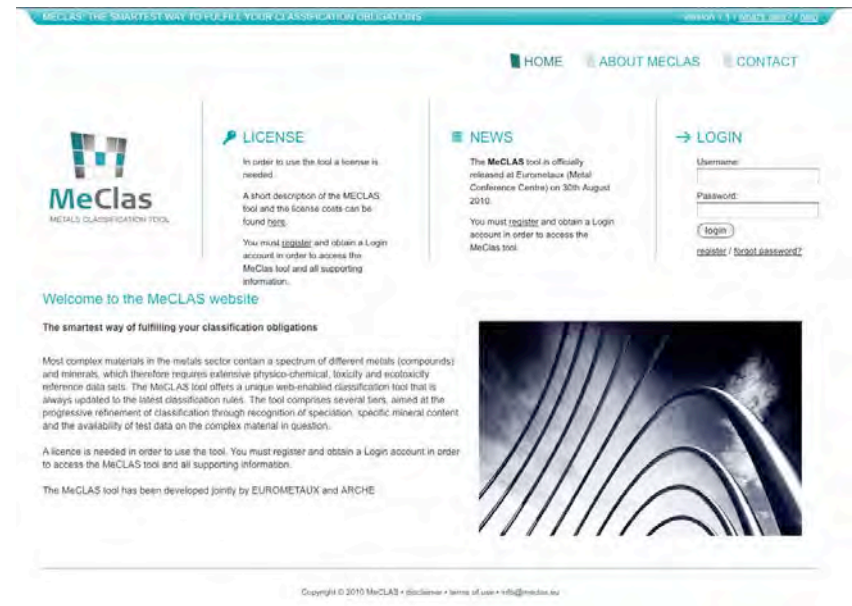
F. Verdonck, H. Waeterschoot,  
M. Vangheluwe, P. Van Sprang,  
I. Vercaigne, L. Claeys, K. Delbeke,  
K. Lacasse & V. Verougstraete

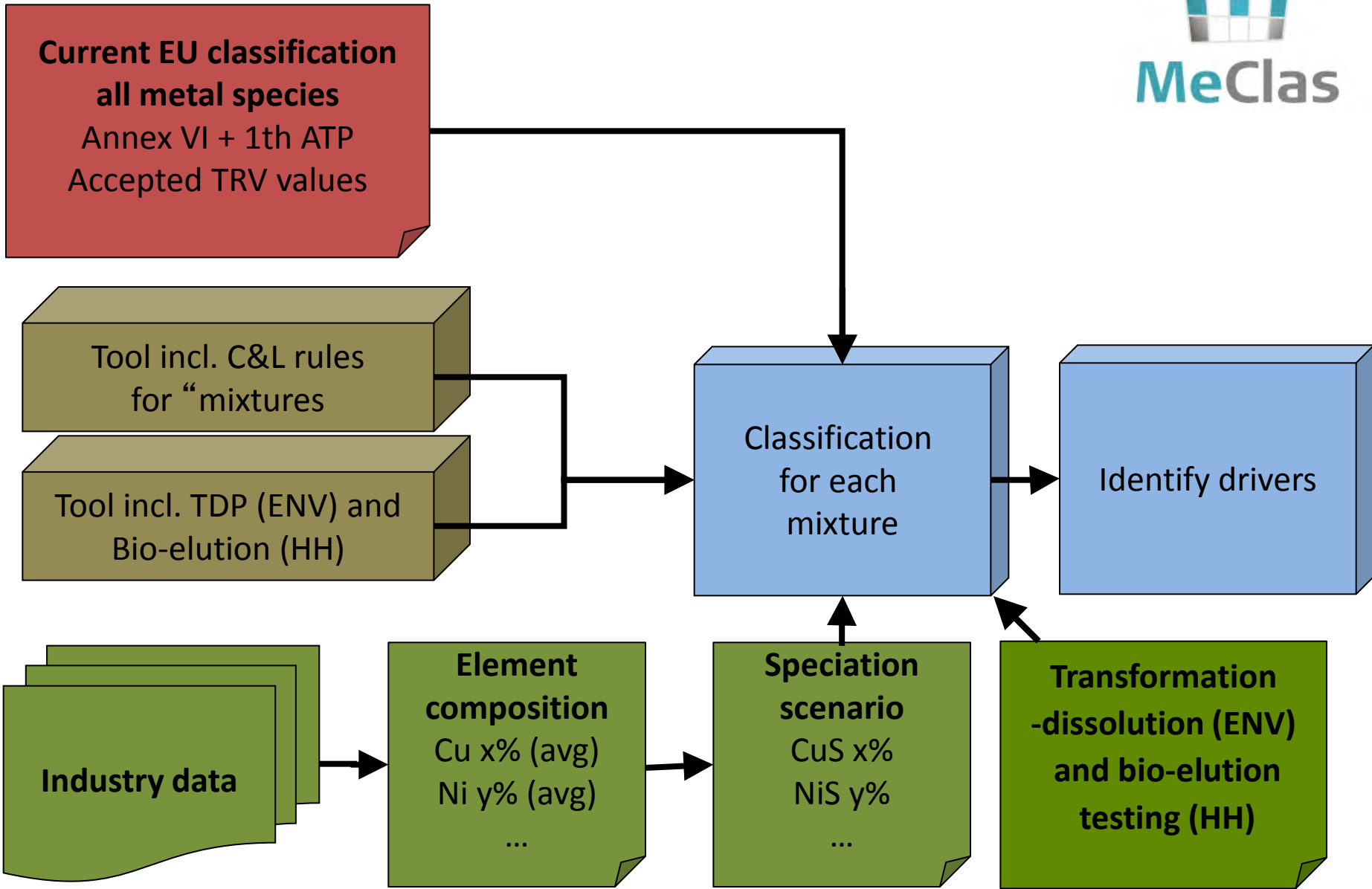
## Replies to a need of the **metals sector**:

- Deal with the **complexity of the Hazard classification** of complex inorganic materials, ores & concentrates, metal mixtures,...
- Covering all legal **EU hazard ID frameworks** ( **CLP** and **DSD** ) (but restricted to toxicity and ecotoxicity endpoints)
- Provide full recognition to metal specific aspects (e.g. **“speciation”**)
- Tiered **hazard assessment approach**, based on available information and typical correction for metals
  - Transformation Dissolution data (ENV)
  - ...

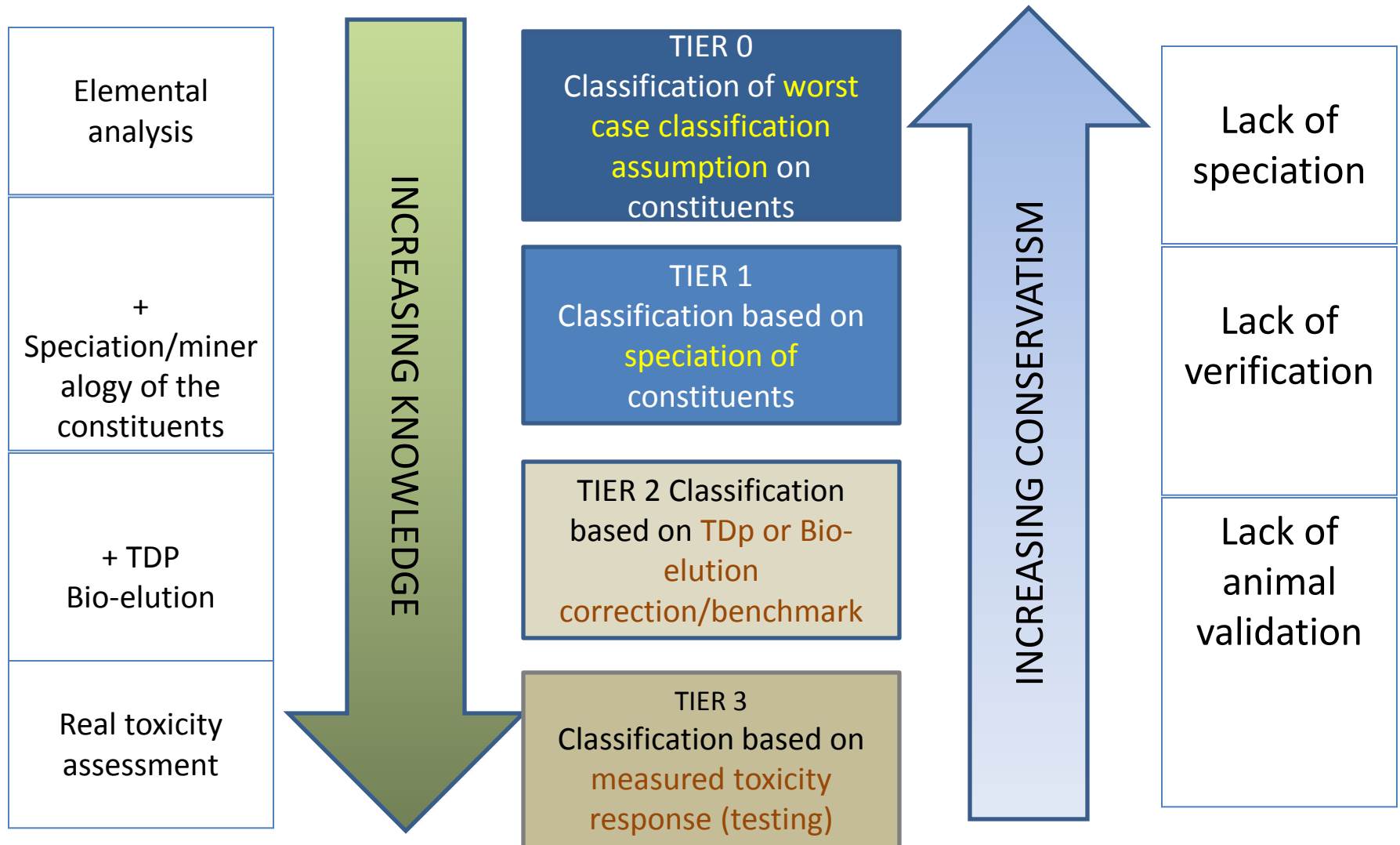
# MECLAS scope

- **Based on the CLP:**
  - Including the 2nd ATP
  - Including the recent “metals guidance” on the CLP, 2nd ATP
- **Applicable to :**
  - Classical mixtures
  - Ores and concentrates
  - UVCBs
  - Alloys
  - ...





# SCHEMATIC OVERVIEW of the TIERED CLASSIFICATION APPROACH FOR COMPLEX MATERIALS



## Elemental Analysis

Cu	TOT	%	0,60	0,54
As	TOT	%	0,00	0,01
Fe	TOT	%	12,20	14,30
Ni	TOT	%	0,03	0,1
Pb	TOT	%	0,28	0,33
Co	TOT	%	0,21	0,2
	BM	%		
Sb	TOT	%	<0,01	<0,01
Sn	TOT	%	<0,01	<0,01
Zn	TOT	%	0,86	0,76
Mo	TOT	%		
Ag	TOT	%	<0,002	<0,002
Se	TOT	%		
Sr	TOT	%		
Te	TOT	%		
Bi	TOT	%		
Cd	TOT	%		
SiO2	KEM	%	45,30	45,50
Al2O3	TOT	%	13,20	13,20
Cr2O3	TOT	%	0,19	0,29
K2O	TOT	%	3,70	2,70
MgO	TOT	%	6,80	7,80
MnO	TOT	%	0,30	0,20
Na2O	TOT	%	1,10	1,20
CaO	TOT	%	11,00	10,00

## Speciation Analysis

% relative to element

% relative to total mixture

Distribution of iron	
CuFeS	0,42
FeCr2O4	1,03
CoFeS	0,19
Cu	0,04
Fe2SiO4	37,89
FeCo	4,91
KAlSiOx	2,09
Si(Fe,Al,Ca)O2-3	11,87
CaSiOx	32,78
ZnFeS	4,22
Fe3O4	4,54
Distribution of zinc	
FeCr2O4	2,56
ZnFeS	53,93
Fe2SiO4	17,88
KAlSiOx	2,26
CaSiOx	14,30
Si(Fe,Al,Ca)O2-3	9,07

CuFeS	Chalcopyrite	0,44
FeCr2O4	Chromite	0,63
CoFeS	Villamaninite	0,08
Cu	Copper	0,26
Fe2SiO4	Fayalite	16,40
FeCo	Fe -alloy	0,67
KAlSiOx	K- Al -silicate	32,11
Si(Fe,Al,Ca)O2-3	Glass	9,65
Pb	Lead	0,11
PbO	Litharge	0,09
PbS	Galena	0,09
CaSiOx	Ca -silicate	37,61
ZnFeS	Sphalerite	1,33
Fe3O4	Magnetite	0,54

Distribution of lead	
Pb	42,78
PbO	31,85
PbS	25,37

Distribution of copper	
CuFeS	49,61
FeCr2O4	0,09
Cu	42,17
FeCo	6,35
KAlSiOx	0,94
Si(Fe,Al,Ca)O2-3	0,84

Reference sample

Company sample

## Elemental Analysis

Cu	TOT	%	0,60	0,54
As	TOT	%	0,00	0,01
Fe	TOT	%	12,20	14,30
Ni	TOT	%	0,03	0,1
Pb	TOT	%	0,28	0,33
Co	TOT	%	0,21	0,2
Sb	TOT	%	<0,01	<0,01
Sn	TOT	%	<0,01	<0,01
Zn	TOT	%	0,86	0,76
Mo	TOT	%		
Ag	TOT	%	<0,002	<0,002
Se	TOT	%		
Sr	TOT	%		
Te	TOT	%		
Bi	TOT	%		
Cd	TOT	%		
SiO2	KEM	%	45,30	45,50
Al2O3	TOT	%	13,20	13,20
Cr2O3	TOT	%	0,19	0,29
K2O	TOT	%	3,70	2,70
MgO	TOT	%	6,80	7,80
MnO	TOT	%	0,30	0,20
Na2O	TOT	%	1,10	1,20
CaO	TOT	%	11,00	10,00

## Speciation Analysis

% relative to element

Distribution of iron

CuFeS	0,42
FeCr2O4	1,03
CoFeS	0,19
Cu	0,04
Fe3SiO4	37,89
FeCo	4,91
KAlSiOx	2,09
Si(Fe,Al,Ca)O2-3	11,87
CaSiOx	32,78
ZnFeS	4,22
Fe3S4	4,54

Distribution of zinc

FeCr2O4	2,56
ZnFeS	53,93
Fe2SiO4	17,88
KAlSiOx	2,26
CaSiOx	14,30
Si(Fe,Al,Ca)O2-3	9,07

Distribution of lead

Pb	2,78
PbO	31,85
PbS	25,37

Distribution of copper

CuFeS	49,61
FeCr2O4	0,09
Cu	42,17
FeCo	6,35
KAlSiOx	0,94
Si(Fe,Al,Ca)O2-3	0,84

## Transformation dissolution Analysis for environment only

### Test principle

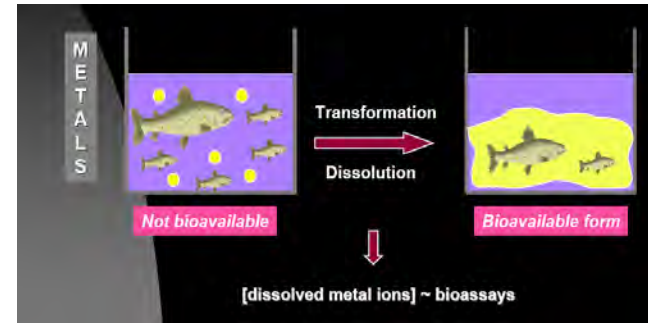


Figure from LISEC

Cu	ug/L	10,10
As	ug/L	0,2
Fe	ug/L	8,20
Ni	ug/L	0,23
Pb	ug/L	0,33
Co	ug/L	0,02
Sb	ug/L	<DL
Sn	ug/L	<DL
Zn	ug/L	<DL
Mo	ug/L	<DL
Ag	ug/L	<DL

Reference sample

Company sample

# Transformation dissolution Analysis

for environment only

## Test principle

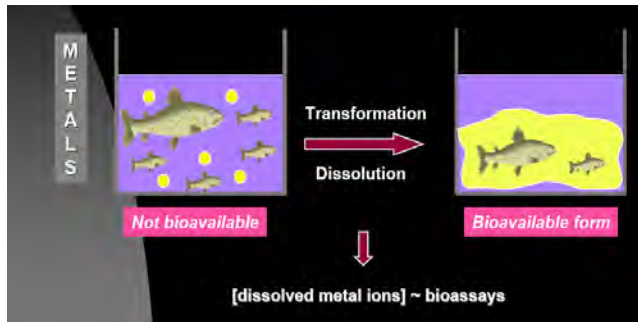


Figure from LISEC

### Released concentration

Cu	ug/L	10,10
As	ug/L	0,2
Fe	ug/L	8,20
Ni	ug/L	0,23
Pb	ug/L	0,58
Co	ug/L	0,02
Sb	ug/L	<DL
Sn	ug/L	<DL
Zn	ug/L	<DL
Mo	ug/L	<DL
Ag	ug/L	<DL



### ERV values

Cu	ug/L
As	ug/L
Fe	ug/L
Ni	ug/L
Pb	ug/L
Co	ug/L
Sb	ug/L
Sn	ug/L
Zn	ug/L
Mo	ug/L
Ag	ug/L



### Toxic unit approach

$$TU \Sigma = \sum_{Me=1}^n TU_{Me}$$

$$TU_{Me} = \frac{Me(aq)}{L(E)C_x}$$

## Calculate classification

Metal mixture:

Version:

Output:

Tier 0

Tier 1

Tier 2

## Output Tier 2

CLP



Endpoint	Classification	Major driver
Acute toxicity-oral	Not classified	/
Acute toxicity-dermal	Not classified	/
Acute toxicity-inhalation	Not classified	/
Skin corrosion/irritation	Not Classified	/
Serious eye damage/eye irritation	Not classified	/
Respiratory or skin sensitisation	Not classified	/
Germ cell mutagenicity	Not classified	/
Carcinogenicity	Not classified	/
Reproductive toxicity	<b>Cat. 1A; H360</b>	lead compounds with the exception of those specified elsewhere in this Annex
Specific target organ toxicity - single exposure	Not classified	/
Specific target organ toxicity - repeated exposure	<b>Cat. 2; H373</b>	lead compounds with the exception of those specified elsewhere in this Annex
Aspiration hazard	Not classified	/
Hazardous to aquatic environment	Not classified	/

Directive 1999/45/EC

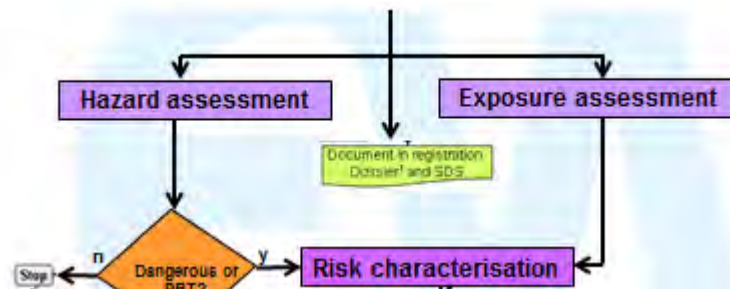


T - Toxic

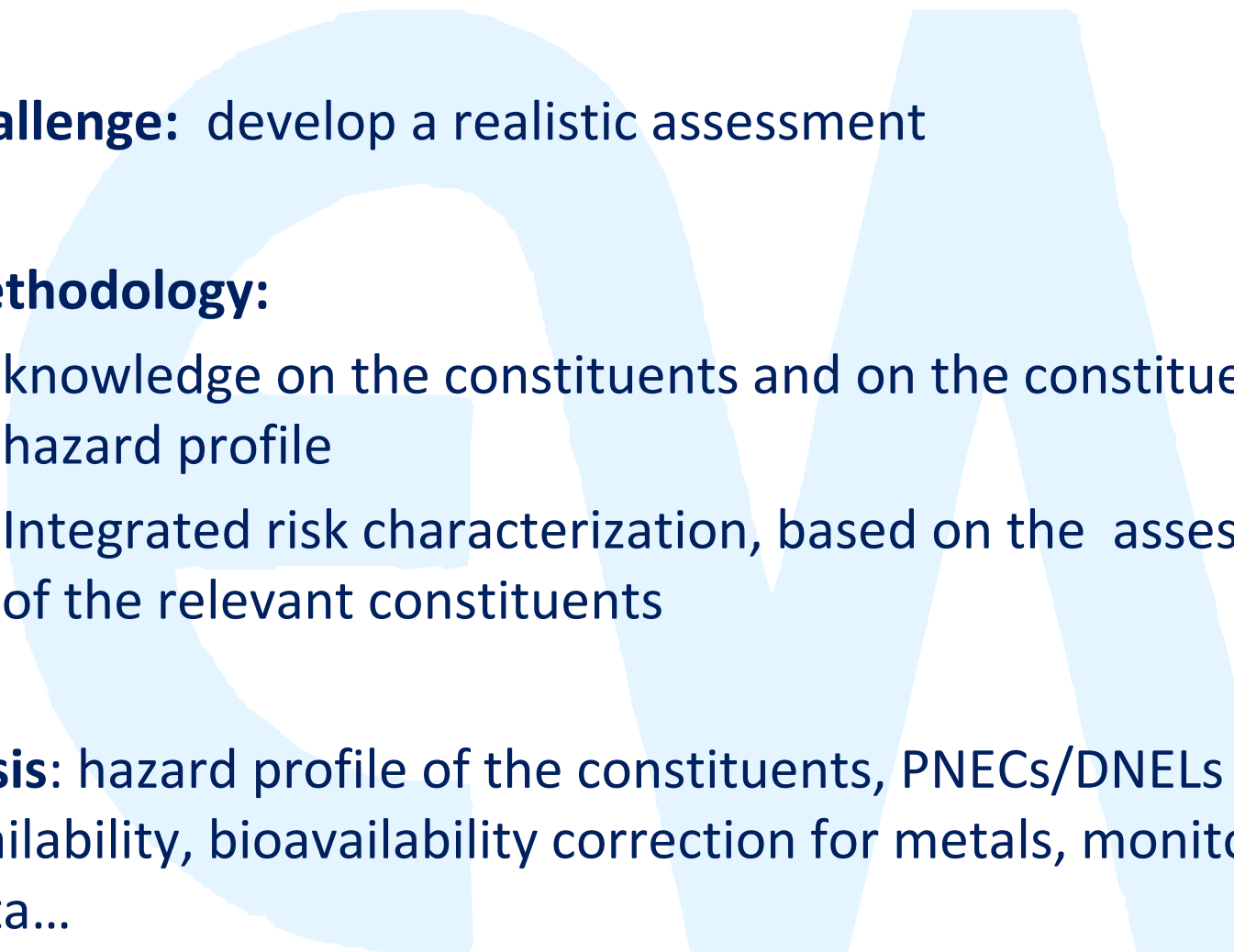
Endpoint	Classification	Major driver
Acute toxicity	Not classified	/
Corrosion	Not classified	/
Irritation	Not classified	/
Respiratory or skin sensitisation	Not classified	/
Germ cell mutagenicity	Not classified	/
Carcinogenicity	Not classified	/
Reproductive toxicity	<b>Repr. Cat. 1; R60/61</b>	lead compounds with the exception of those specified elsewhere in this Annex
Hazardous to aquatic environment	Not classified	/

# Conclusions

- MECLAS is based on CLP (2nd ATP) and metals guidance
- Contains quality controlled TRV values and self-classifications of relevant metal and metal compounds and undergoes continuous updating
- Allows the complex calculations for mixture including all metal specific aspects (TDP, ...)
- Includes a tiered approach based on precautionary and the available information level
- Due to the variable composition, different grades with well defined composition (typical and ranges) and classification entries are derived for one UVCB



### 3. INORGANIC UVCB RISK ASSESSMENT

- 
- **Challenge:** develop a realistic assessment
  - **Methodology:**
    - knowledge on the constituents and on the constituents hazard profile
    - Integrated risk characterization, based on the assessment of the relevant constituents
  - **Basis:** hazard profile of the constituents, PNECs/DNELs availability, bioavailability correction for metals, monitoring data...

# Principles (1)

- Assumption: effects/risk of the UVCB depend on effects/risk of the different constituents
- Issues:
  - huge number of constituents in some UVCB
  - varying relevance for human health risk assessment
- Objective is to perform the **a realistic assessment** to allow safe use, integrating :
  - the effects assessment
  - the exposure assessment
  - risk characterization and management experience;

## Principles (2)

- **Starting point: composition of the intermediate**

- + Existing information on hazard profiles of the constituents (assumption: REACH dossiers for constituents exist)

- + Information on 'industry practice' (process information, exposure pattern, "usual monitoring", operational conditions...), Exposure Scenarios on constituents if meeting criteria

- + Information on bioavailability of constituents from UVCB

## Principles (3)

- Making best use of available information
- Ensuring representativity and coverage of the composition range
- Addressing UVCB specificity: variability and number of constituents

*Need for a **pragmatic and precautionary approach**,  
avoiding extensive assessments, using weight of evidence to  
integrate knowledge coming from all data sources*



# EM

**ENVIRONMENT**



# Content

- ☞ Soluble ion theory
- ☞ Typical properties of CB materials
- ☞ Risk Assessment
- ☞ Outstanding issues

Most key aspects are equal to Hazard section.  
Focus is therefore on the risk assessment part.



# Environmental Risk Assessment of Inorganic UVCBs : strategy

2 subsequent steps :

- PNEC derivation for relevant elements
- Integrated Risk characterization



# PEC/PNEC derivation: strategy identical as for metals :



## PNEC derivation



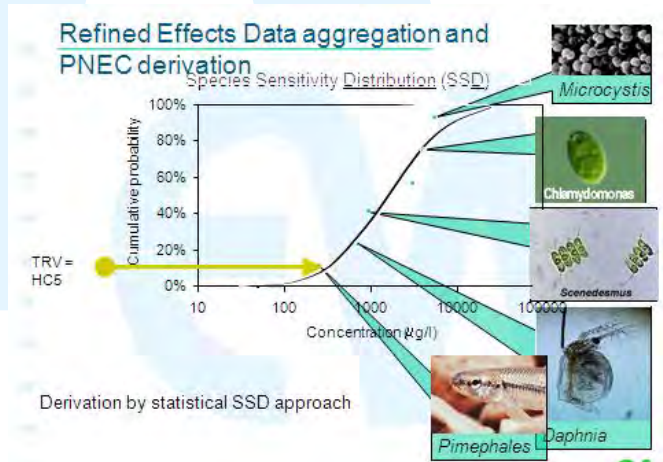
- Determine relevant parameters (elements) (TDp can be helpful in this respect)
- Determine hazard profile of soluble fraction(s) of each relevant metal element individually:
  - Based on chronic tox data sets for metal elements
- Normalise for bioavailability (if relevant)
- Assess PNECs for relevant environmental conditions



## PEC derivation :

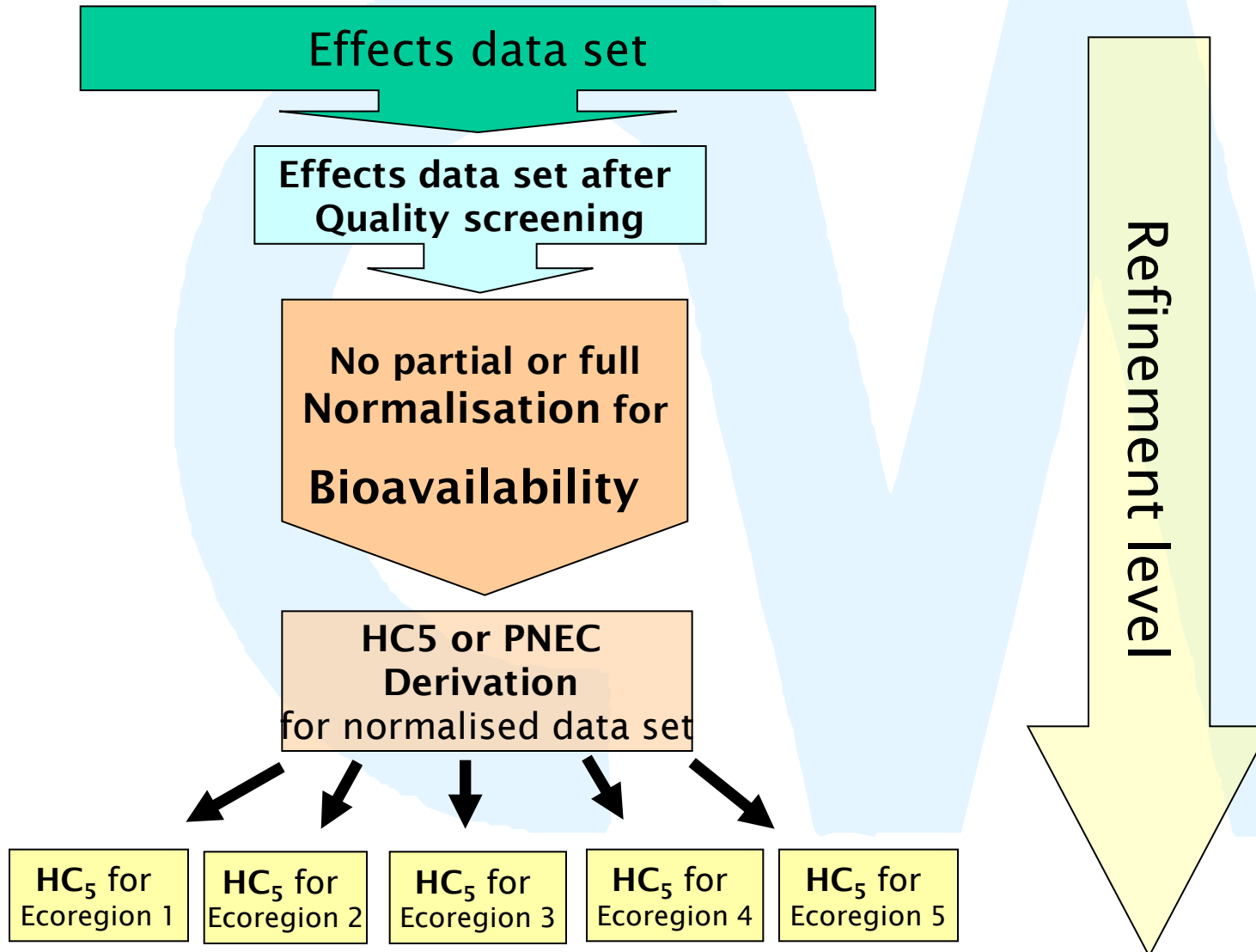


- TIER 1 : model through SPERC
- TIER 2: monitoring data for relevant elements

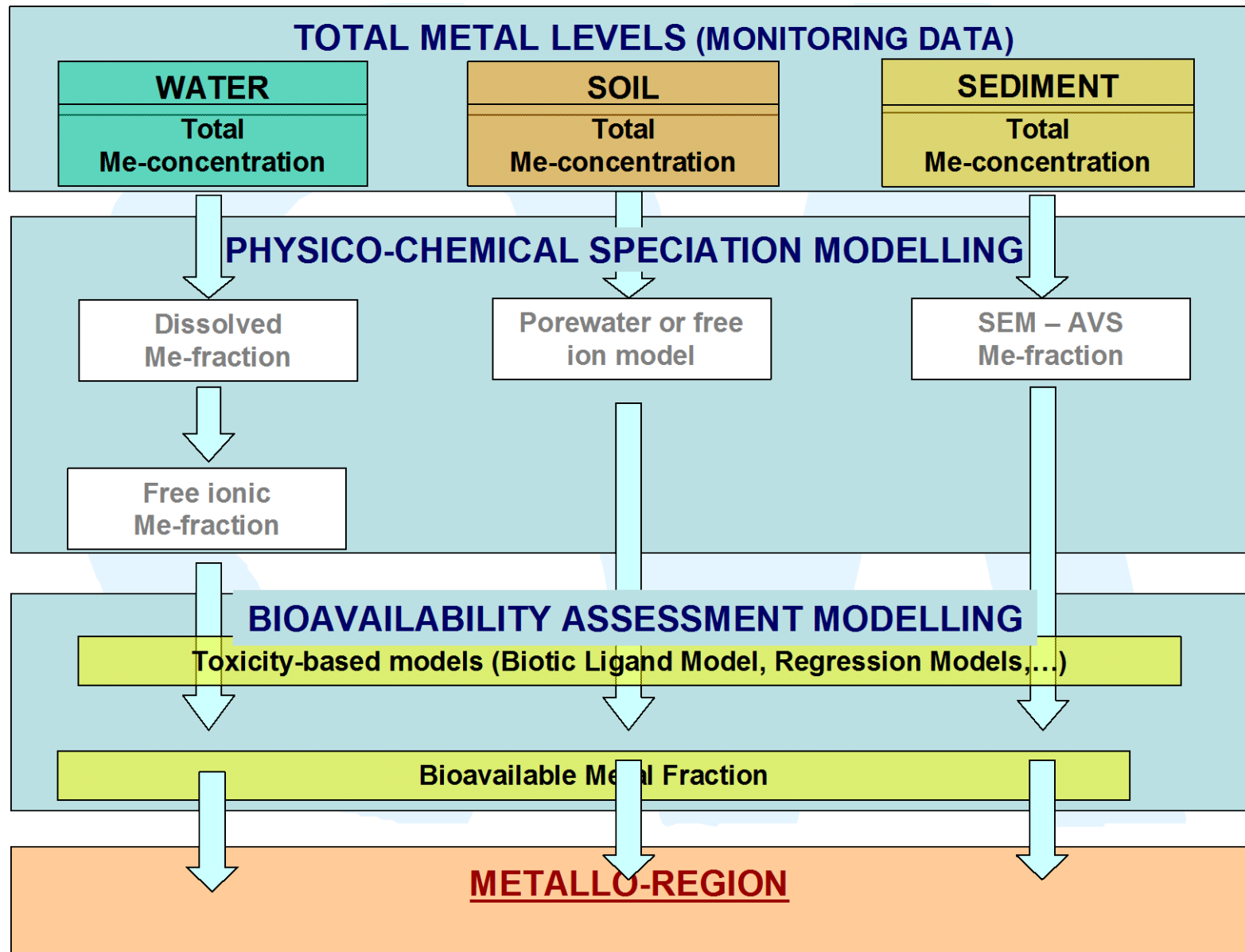


# ENV-Risk Assessment for metals :

*a tiered PNEC approach / element*



# Generic Environmental Risk Assessment Bioavailability correction scheme for metals



# Integrated Risk Characterization

**TIERED approach** driven by refinement of the risk level

**TIER1**

- **Accumulative RCR** of relevant elements, incl. Natural background and regional contributions

**TIER2**

- **Added risk approach** (subtracting natural BG's for all relevant elements, correcting regional contributions, ...) **(Work in Progress)**

**TIER3**

- **Element specific RC** if independent effects can be demonstrated

# Multi-metal regional environmental risk using additivity - FOREGS

	Metal A	Metal B	Metal C	Metal D	Metal E	Metal F	
PEC freshwater (dissolved) $\mu\text{g.L}^{-1}$	0,88	0,093	0,63	1,91	0,01	2,68	
PNEC freshwater (dissolved) $\mu\text{g.L}^{-1}$	7,8	6,5	4,2	3,55	0,19	20,6	
RCR freshwater	0,11	0,01	0,15	0,54	0,05	0,13	<b>0,998</b>

to be updated  
FOREGS

# Challenges

- ❑ Availability of most recent PNECs and other parameters needed for the RISK assessment of the metal elements
  - Industry initiative for a collective database on all relevant inorganic components
- ❑ Monitoring data integrate all emissions of same elements from a site
  - How to define the contribution from the UVCB ?
- ❑ Exposure data reflect contributions from several UVCBs at the plant (intermediates + ores, concept, scraps,etc.).
  - How to define the contribution from the UVCB ?

# Challenges

## ❑ Combined effect of the individual components

- Calculations based on the Toxic Unit approach
- Eventually assessed in a validation step for potential accumulative/synergistic/antagonistic effects

## ❑ Validation assessment: Tiered approach recommended in case of expected element specific/combined effects

- Based on Modeling (combined BLMs) (under development)
- (LT) Testing sensitive representative species and compare with TU calculations (often algae or Ceriodaphnia)
- Higher tier test if relevant (e.g. Mesocosm)

# Conclusions

Inorganic Risk assessment for UVCB's can for the effects part be **derived from their composing elements**

**REACH files and PNEC values are available** for (almost) all relevant metal elements

**PEC assessment** based on monitoring could be complex due to measurement of all element related emission sources

Risk characterization requires a **Tiered approach** to refine the anthropogenic impact related to the UVCB manufacturing or use

**Validation** is recommended in case additional effects would be expected.



# EM



**HUMAN HEALTH**

# Proposal: Stepwise approach (under road-testing):

**Step 1: Identify the “risk driver” for each endpoint, exposure route (driving DNEL + corresponding exposure levels)**



**Step 2: “weight of evidence” approach to ensure coverage of UVCB composition range and representativity**



**Step 3: characterization of the UVCB for each endpoint/exposure route**



**Step 4: consideration of possible additive effects (work in progress)**

★  
★  
★  
★  
★  
★  
★  
★  
★  
★

**Step 1: Identify the “risk driver” for each endpoint, exposure route (driving DNEL + corresponding exposure levels)**





- Aim: complete the table for each exposure pathway, endpoint and exposure duration to which the effect refers

<b>Exposure pattern</b>	<b>DNEL, DMEL</b>
Acute –inhalation systemic effects	
Acute-dermal local effects	
Acute-inhalation, local effects	
Long-term-dermal, systemic effects	
Long-term-inhalation, systemic effects	
Long-term-oral, systemic effects	Not relevant
Long-term-dermal, local effects	
Long-term-inhalation, local effects	

- The “driving DNEL approach” allows this. How? By ranking the DNELs of the constituents, based on a number of inputs and selecting the driving one, using existing tools/data

# Driving DNEL approach (1): inhalation route

- To select “most critical” DNEL by reflecting actual workplace conditions, i.e. exposure conditions
- Exposure in the workplace has basically four determinants:
  1. Substance/material intrinsic emission potential
  2. Process related emission potential
  3. Additional operational conditions & risk management measures
  4. Concentration of constituent in UVCB (as range)
- These determinants are addressed in MEASE on a metal-specific basis
- Weighing factors are derived from MEASE
- Refinements possible with measured data

## ★ Driving DNEL approach (2): inhalation route

★ For **Cold processes**, it is assumed that

- ★ 1. *Substance intrinsic emission potential*
- ★ 2. *Process related emission potential*
- ★ 3. *Additional operational conditions & risk management measures*

★ are **constant\*** for each constituent of the “homogenous” mixture of constituents in the UVCB (\* justification provided in back-up slide)

★ However,

- ★ 4. *Concentration of constituent in UVCB (as range) will vary and is used to weight/rank DNELs for their relevance as risk driver*

# ★ Driving DNEL approach (3): inhalation route

★ For **Hot processes**, only

★ 2. *Process related emission potential*

★ 3. *Additional operational conditions & risk management measures*

★ are **constant\*** for given hot metallurgical processes (\* justification provided in back-up slide)

★ 1. *Substance intrinsic emission potential*: to be considered according to the process temperature/melting point ratio of the individual constituents for weighting of DNELs

★ and

★ 4. *Concentration of constituent in UVCB (as range)* is used to weight DNELs for their relevance as risk driver

# Driving DNEL approach (4): inhalation route

Example: UVCB with 6 constituents: A, B, C, D, E, F

	Percentage [%]	MEASE Ranking weight	DNEL [mg/m <sup>3</sup> ]	Weight * DNEL Ranking value (concentration)
Constituent A	1.2	5	0.07	0.35
Constituent B	3	5	0.5	2.5
Constituent C	0.53	10	0.03	0.3
Constituent D	12	1.7	1	1.7
Constituent E	0.5	10	0.6	6
Constituent F	4	5	0.15	0.75

# Driving DNEL approach (5): inhalation route

Cold processes:

MEASE

Weight \* DNEL

	Percentage [%]	Ranking weight	DNEL [mg/m <sup>3</sup> ]	Ranking value (concentration)	Rank
Constituent A	1.2	5	0.07	0.35	2
Constituent B	3	5	0.5	2.5	5
Constituent C	0.53	10	0.03	0.3	1
Constituent D	12	1.7	1	1.7	4
Constituent E	0.5	10	0.6	6	6
Constituent F	4	5	0.15	0.75	3

# Driving DNEL approach (6):inhalation route

**Hot processes:** PROC 22 (furnace operations), process temperature= 450° C

%ranking  
value \* rank  
temp

	Melting point [°C]	Emission class	Ranking weight temperature	Ranking value (concentration & temperature)	Rank
Constituent A	250	high	1	0.35	1
Constituent B	690	low	7	17.5	5
Constituent C	750	low	7	2.1	4
Constituent D	190	high	1	1.7	3
Constituent E	1200	low	7	42	6
Constituent F	380	medium	2	1.5	2

# Driving DNEL approach (7):inhalation route

For UVCB with 6 constituents: A, B, C, D, E, F

hot process, PROC 22, assessment of acute inhalation?

Exposure pattern	Driving DNEL
Acute –inhalation systemic effects	Constituent A's DNEL
Acute-dermal local effects	
Acute-inhalation, local effects	Constituent B's DNEL
Long-term-dermal, systemic effects	
Long-term-inhalation, systemic effects	Constituent C, DMEL
Long-term-oral, systemic effects	Not relevant
Long-term-dermal, local effects	
Long-term-inhalation, local effects	

Identification of target for exposure level measurement : A

## Driving DNEL approach (8): dermal route

- **Driving DNEL:** basically the same ranking approach
  - Cold processes: Justification: exposure expected to occur to the same dust
  - Hot processes: a different approach is under development (no direct handling): *Work in progress*

# The Driving DNEL approach

## Allows to consider:

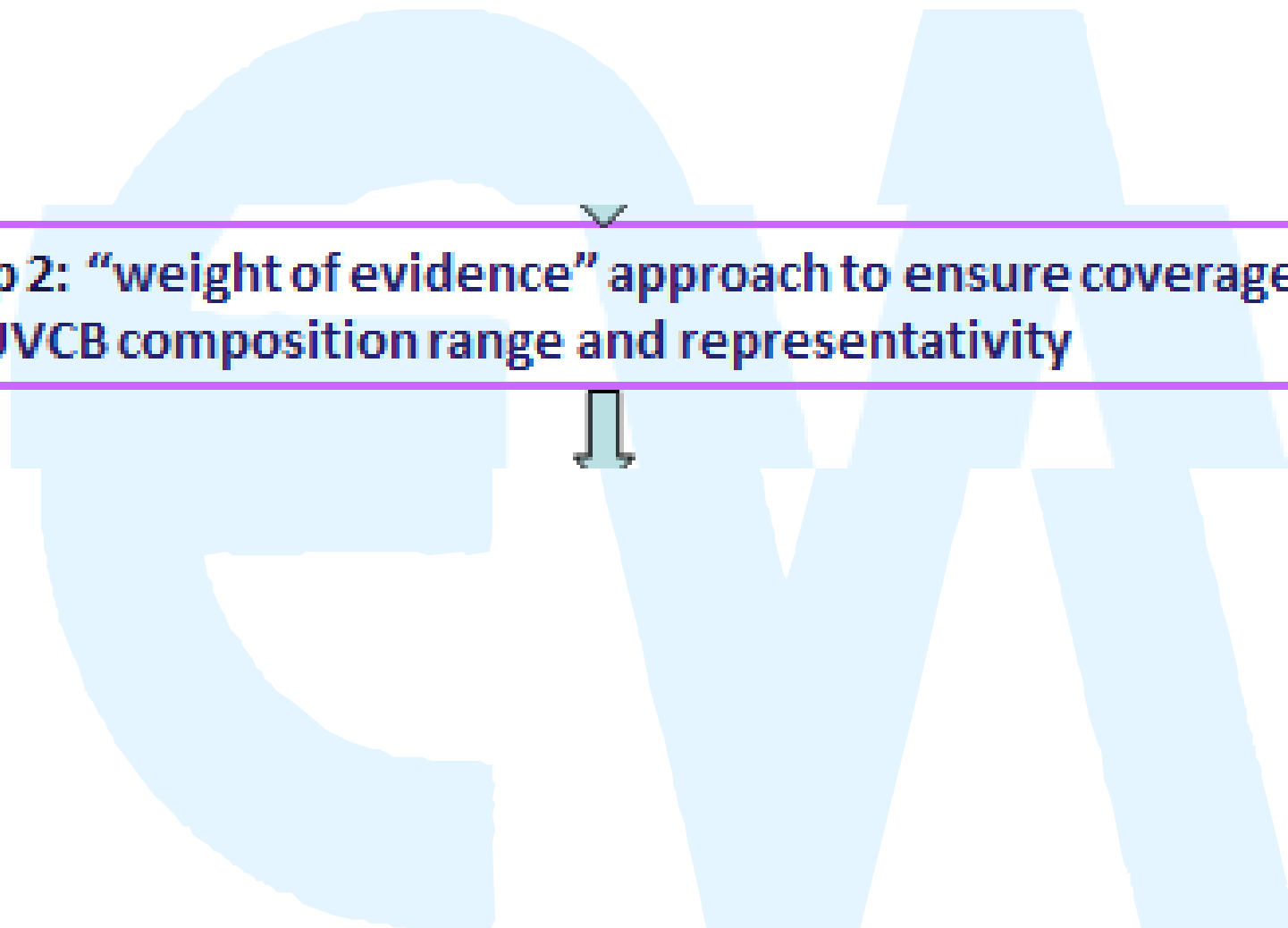
- consideration of variations in content of individual constituents
- selection of individual concentrations of constituents (and associated ranking factors) on a worst-case basis
- assessment of occupational exposure on company-by-company basis

## Requires:

- DNELs, DMELs

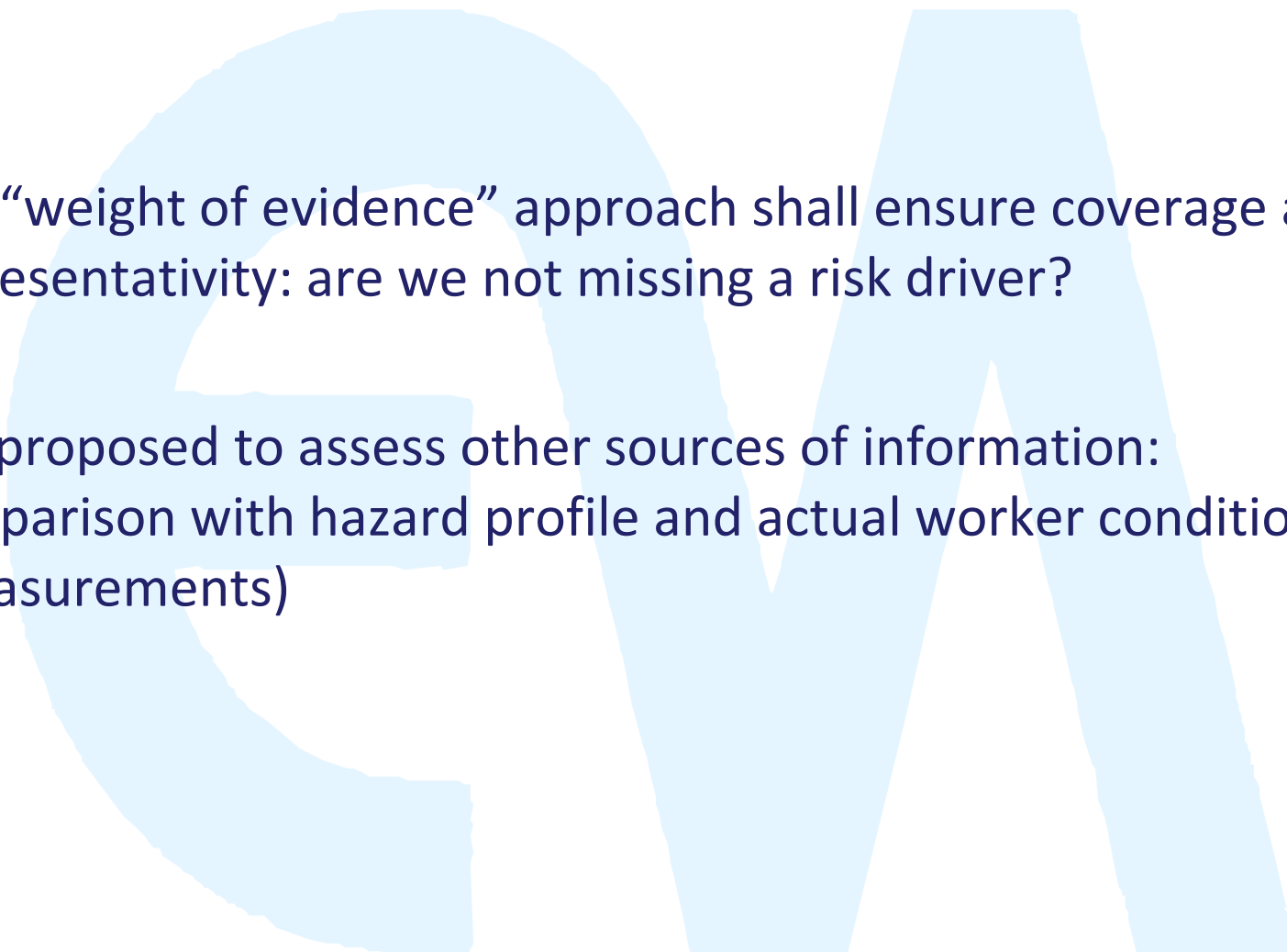
## Work in progress:

- If non-threshold - related effects are involved, qualitative assessment?



**Step 2: “weight of evidence” approach to ensure coverage of UVCB composition range and representativity**

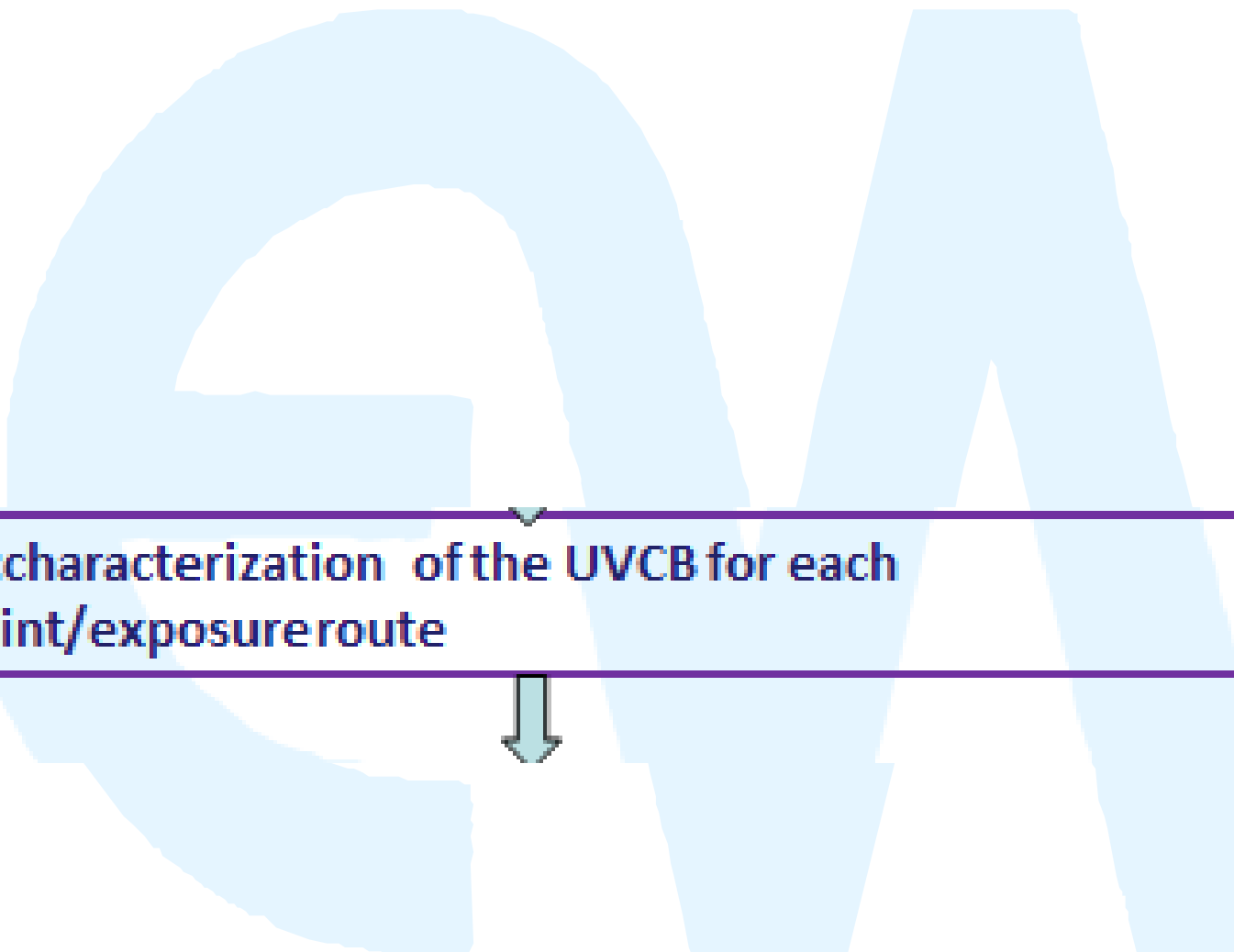




- The “weight of evidence” approach shall ensure coverage and representativity: are we not missing a risk driver?
- It is proposed to assess other sources of information: comparison with hazard profile and actual worker conditions (measurements)



Endpoint + exposure route	Constituent A		Constituent B		Constituent C	
	Speciation:	Conc:	Speciation:	Conc:	Speciation:	Conc:
	Classification	To consider (bioavailability, mode of action)	Classification	To consider (bioavailability, mode of action)	Classification	To consider (bioavailability, mode of action)
Short term, inhalation route (systemic and local effects)	Acute inhalation classification?		Acute inhalation classification?		Acute inhalation classification?	
Short term, dermal route (systemic and local effects)	Acute dermal classification? Irritation?		Acute dermal classification? Irritation?		Acute dermal classification? Irritation?	
Long term, inhalation route (systemic and local effects), oral	Repeated dose classification by Inhalation route ?		Repeated dose classification by Inhalation route ?		Repeated dose classification by Inhalation route ?	
Long term, dermal route (systemic and local effects)	Repeated dose classification by Dermal route ?		Repeated dose classification by Dermal route ?		Repeated dose classification by Dermal route ?	

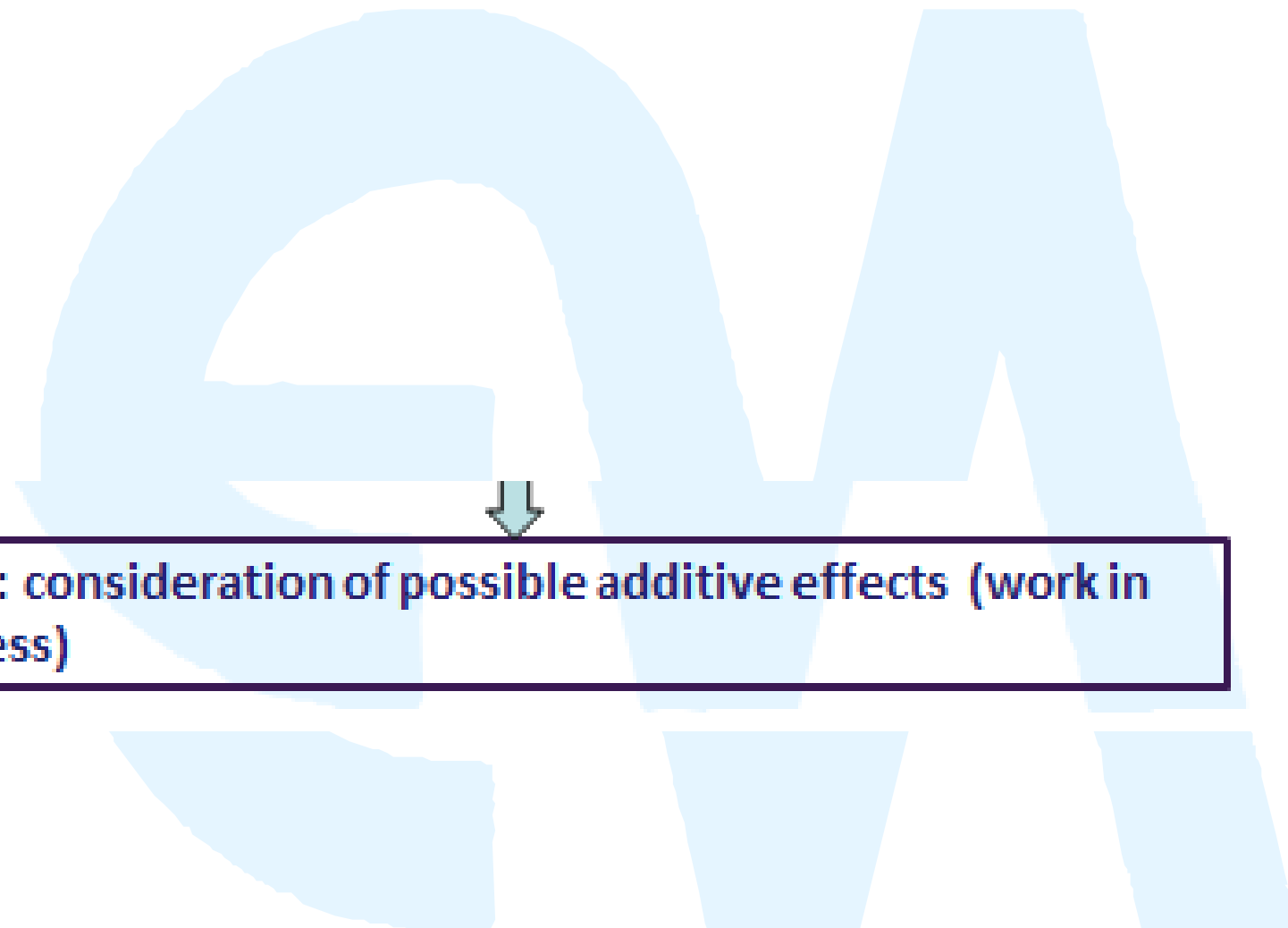


**Step 3: characterization of the UVCB for each endpoint/exposure route**

- Exposure value versus DNEL/OEL for all decisive DNELs/exposure route/endpoint

Exposure pattern	Driving DNEL	Exposure level
Acute –inhalation systemic effects	Constituent A's DNEL	[A]
Acute-dermal local effects	N.R.	
Acute-inhalation, local effects	Constituent A's DNEL	[A]
Long-term-dermal, systemic effects	Constituent B's DNEL	[B]
Long-term-inhalation, systemic effects	Constituent D's DNEL	[D]
Long-term-oral, systemic effects	Not relevant	
Long-term-dermal, local effects	Constituent A's DNEL	[A]
Long-term-inhalation, local effects	Constituent E's DNEL	[E]

- Assessment of uncertainty
- ! This takes into consideration effects of constituents that are independent from each other



**Step 4: consideration of possible additive effects (work in progress)**

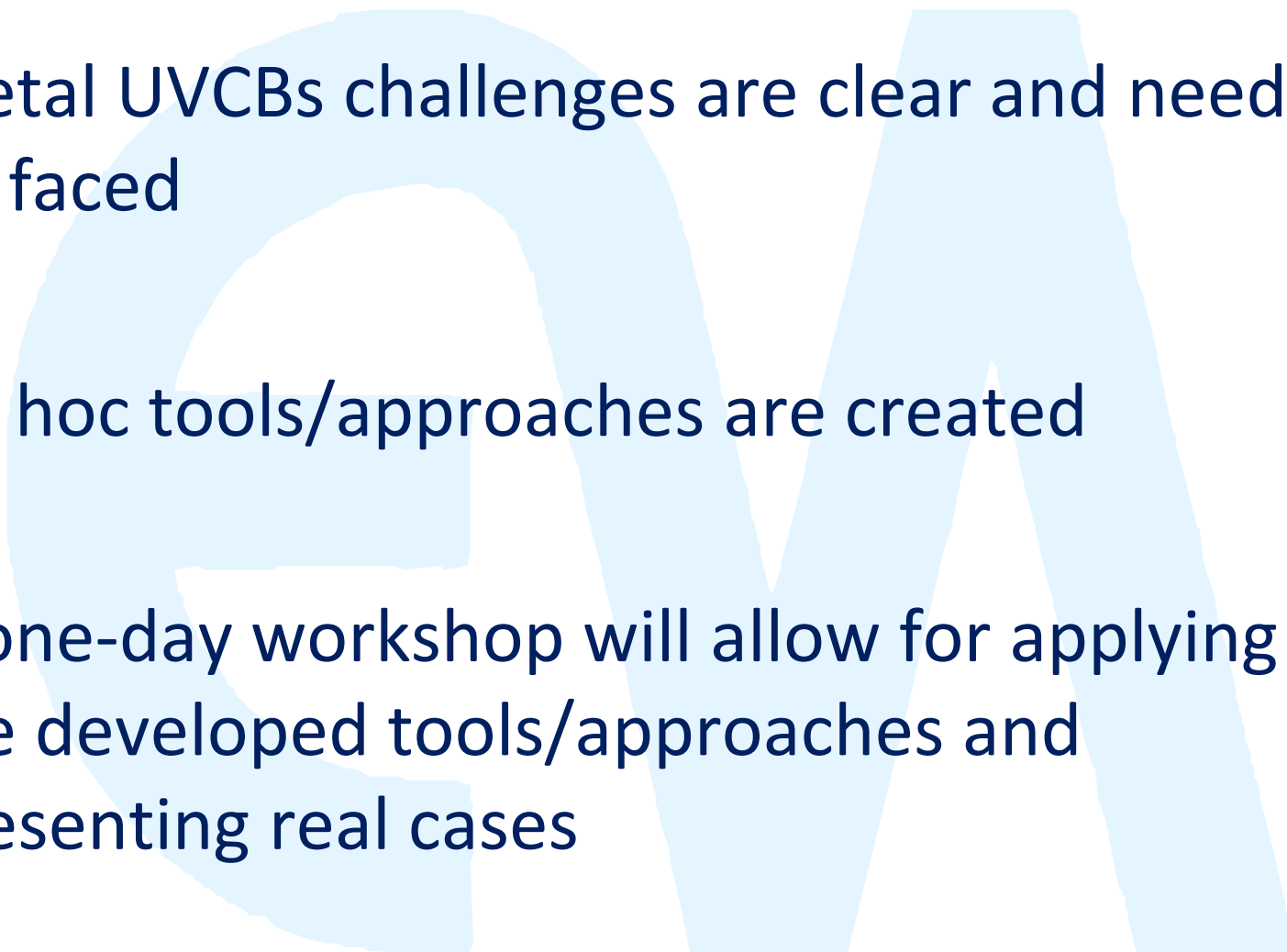
# WORK in PROGRESS

- Need to have a precautionary approach BUT also to allow a reality check and allow refinement with data on e.g. toxicokinetics, mechanism of action showing effects are independent etc.
- Proposal: if additive effects from some constituents are expected/identified, then the lowest DNEL and the SUM of the concentrations of the involved constituents causing the “combined effect” should be used in the decisive DNEL approach (to be tested)



**4. CONCLUSIONS: what's next?**



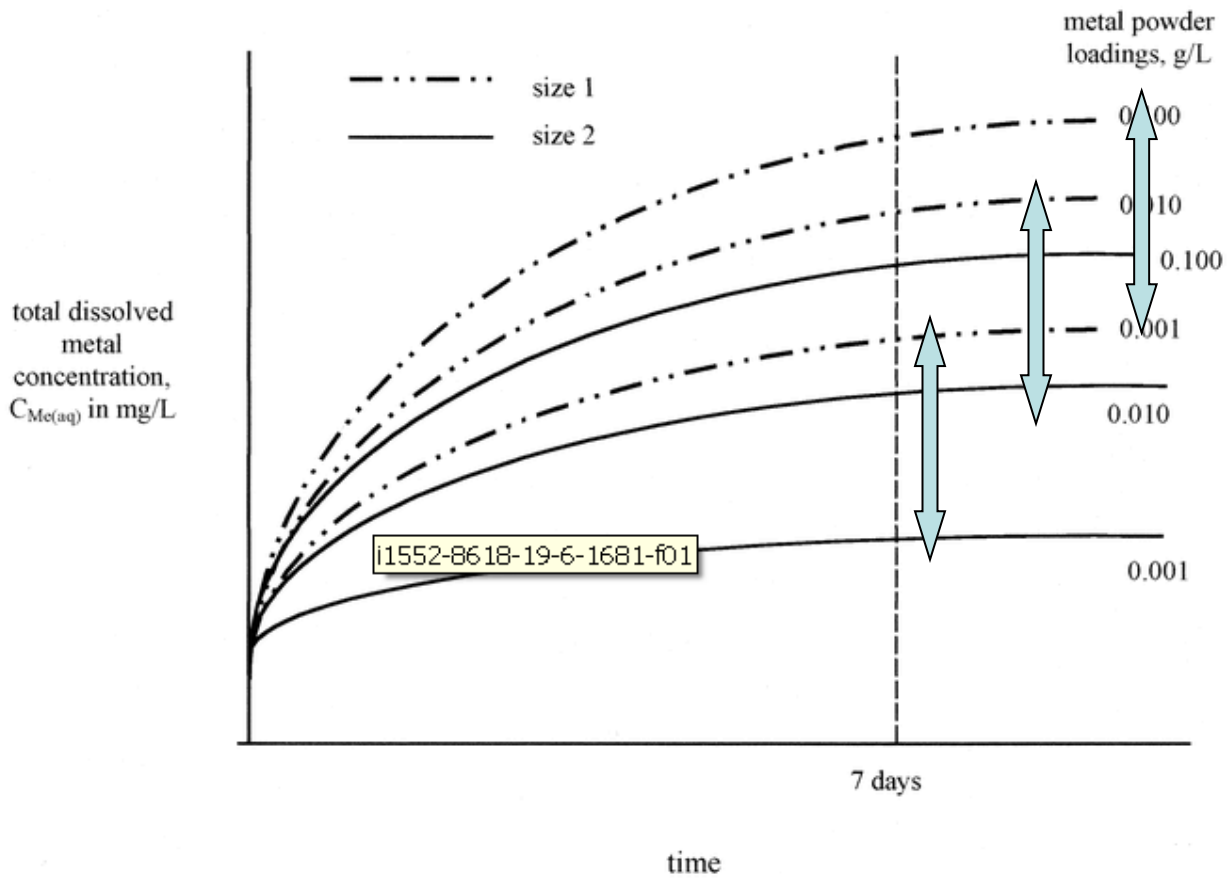
- 
- Metal UVCBs challenges are clear and need to be faced
  - Ad hoc tools/approaches are created
  - A one-day workshop will allow for applying the developed tools/approaches and presenting real cases

EM

**BACK-UP SLIDES**



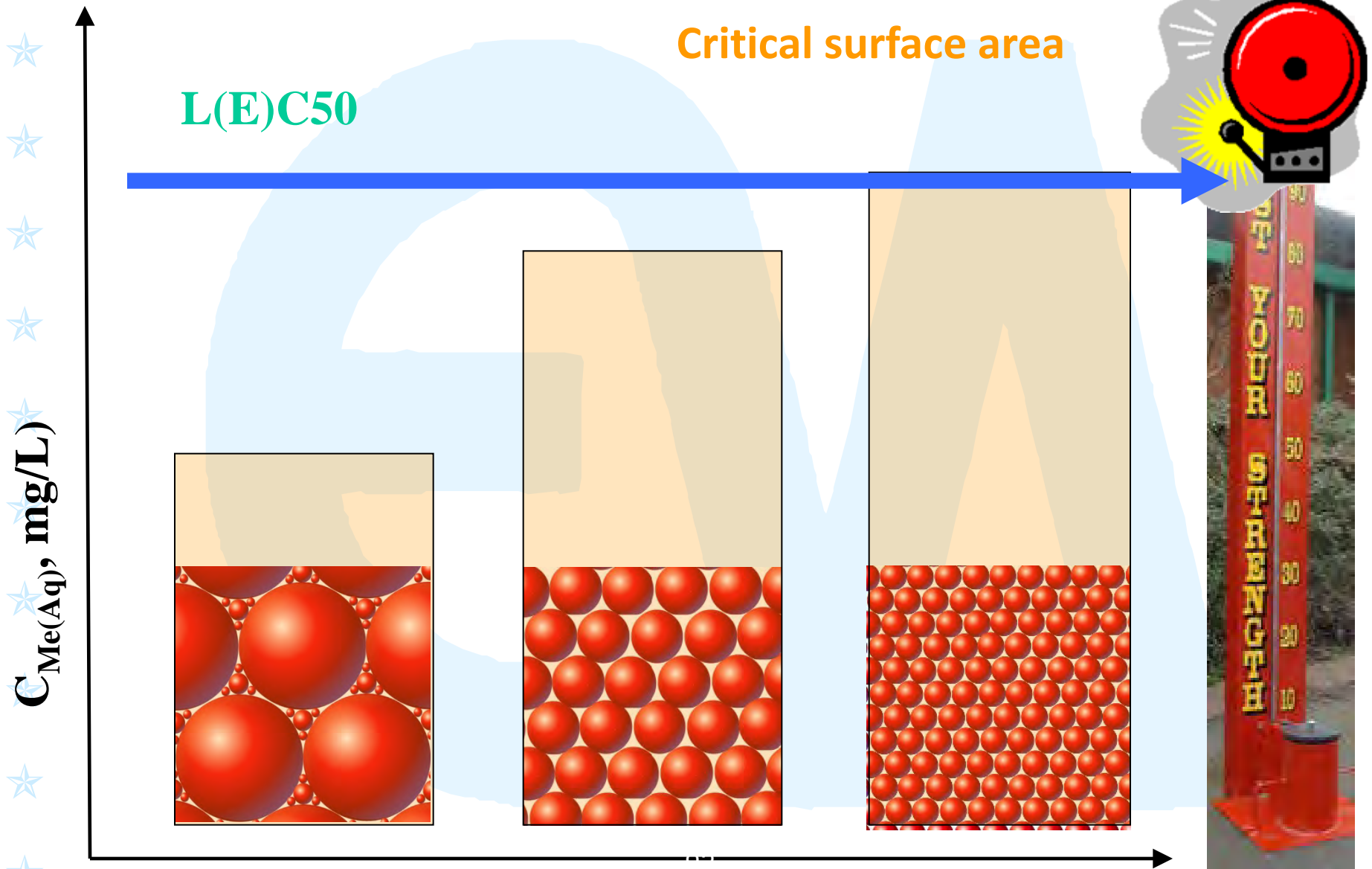
# T/Dp tests results: size matters!



Due to difference in surface area

- Reaction kinetics of two particle sizes of a hypothetical metal powder at three loadings in an aqueous medium, schematic basis

# Differences in surface area matters !!!



Surface area

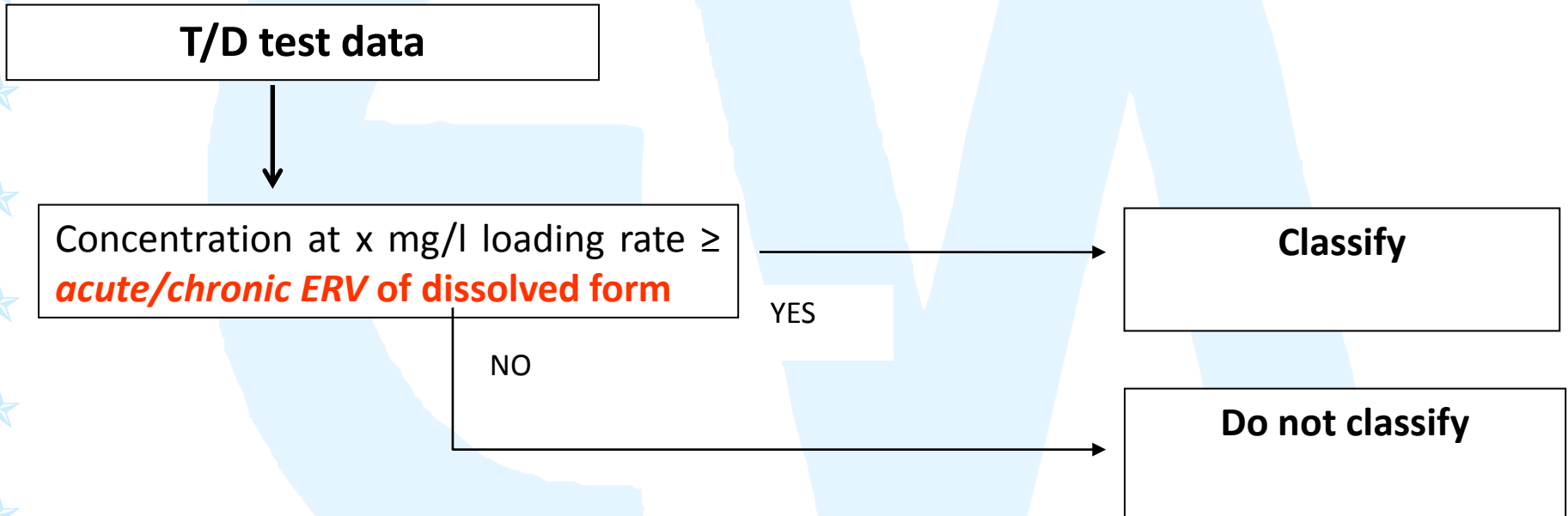
# Hazard ID for classification purposes

- **Metal mixtures** obtained by the deliberate mixing of 2 or more components and not interacting like alloys are mixtures and follow the mixture ruling under CLP

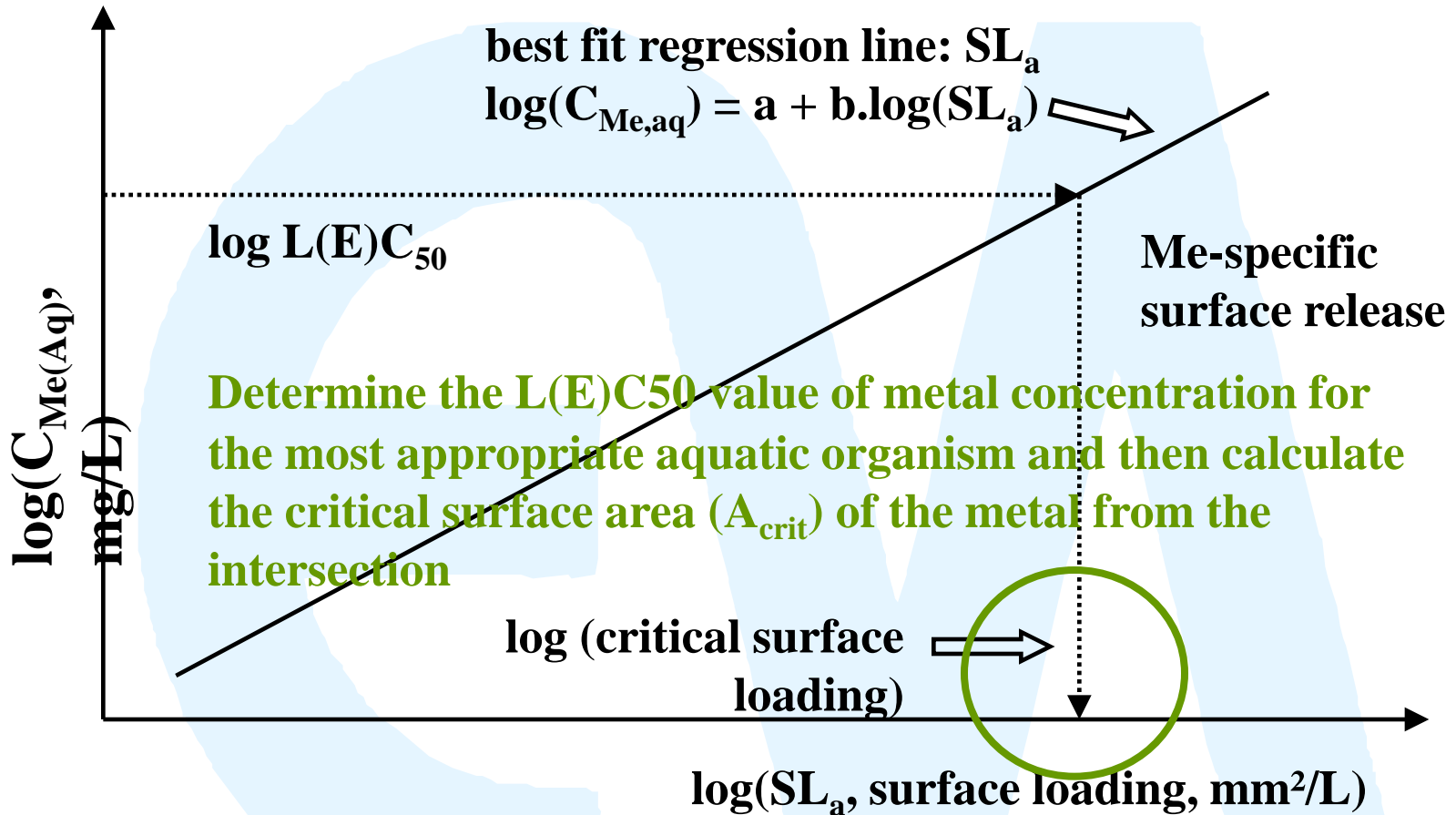
- **UVCB and MCS** are considered as substances in respect to CLP, but follow in general the mixture ruling....

- **Alloys are “special mixtures”**: Metal alloys are defined by the CLP as “special preparations” because their (eco)toxicity profile does differ from that of their constituents.

# Classification rules for sparingly soluble metal containing substances



# Classify on basis of TDp : Determine critical surface loading



surface area loading ( $A$ ,  $\text{mm}^2/\text{L}$ ) = substance specific surface area ( $SA$ ,  $\text{m}^2/\text{g}$ ) \* substance mass loading ( $\text{g/L}$ )

$SA = \text{area (m}^2\text{)/mass (g)}$

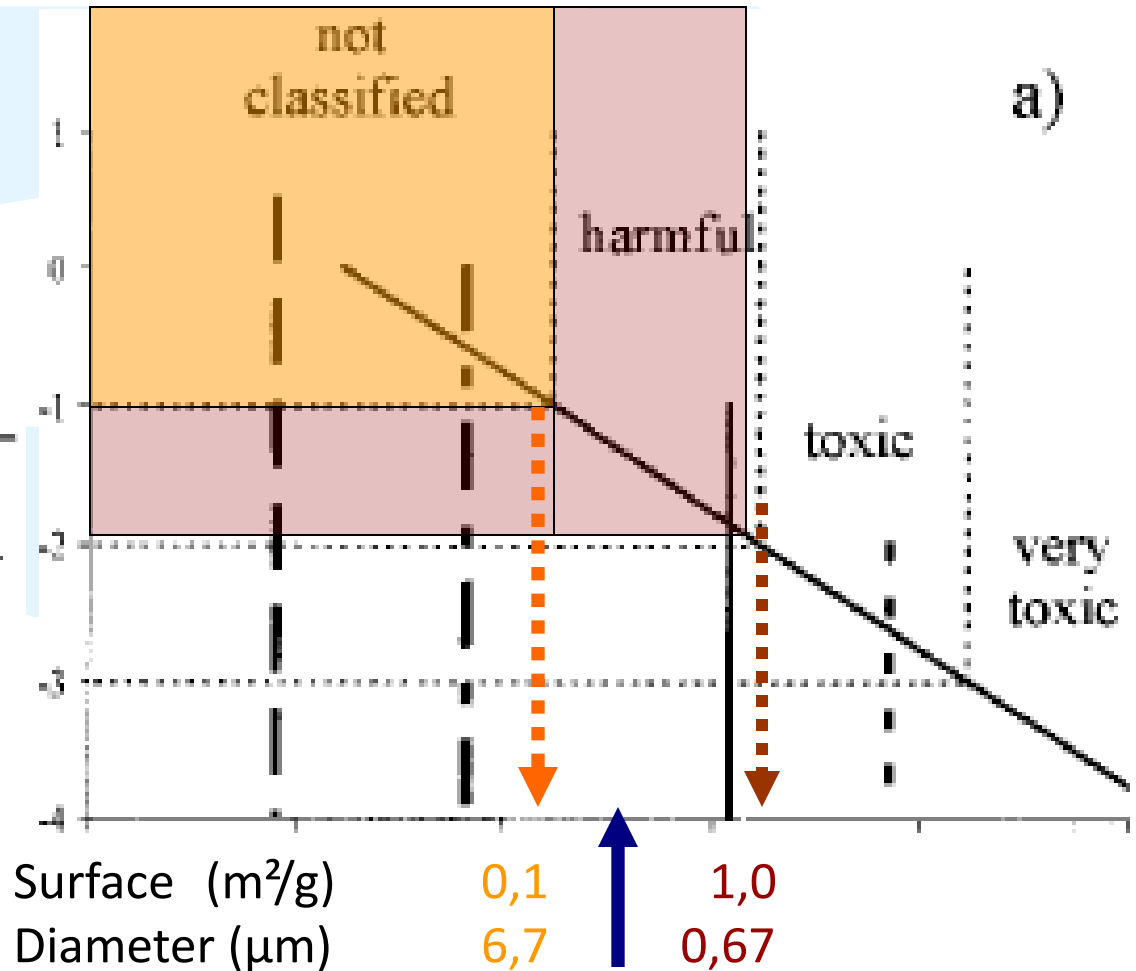
1, 10, 100  $\text{mg/l}$

# An example Ni metal Powder Classification

Ni case

cutoff points in hazard classification

100 mg/L  
10 mg/L  
1 mg/L



For UVCB's this needs to be done for each env. toxic element separately and for the total TU load.

Smallest representative Powder (Surface 0,43 m²/g)

## *Justification cold processes:*

- Generally  $RCR < 1$

(1)  $RCR = EXP / DNEL$  (highest RCR means highest risk)

(2)  $EXP < DNEL$

- For a 1<sup>st</sup> tier assessment in ECETOC TRA or MEASE:

(3)  $EXP = EXP_{initial} * MF_{percentage} * MF_{EPcold} * MF_{RMMs}$

- $EXP_{initial}$  and  $MF_{RMMs}$  are constant for each constituent for a given process (or PROC)

- Cold processes

–  $EP_{cold}$  is constant (e.g. homogenous powder)

– Impact on RCR exclusively comes from  $MF_{percentage}$  considering (1) and (3) **to keep but express simpler**

## *Justification hot processes:*

- Generally  $RCR < 1$ 
  - (1)  $RCR = EXP / DNEL$  (highest RCR means highest risk)
  - (2)  $EXP < DNEL$
- For a 1<sup>st</sup> tier assessment in ECETOC TRA or MEASE:
  - (3)  $EXP = EXP_{initial} * MF_{percentage} * MF_{EPhot} * MF_{RMMs}$
- $EXP_{initial}$  and  $MF_{RMMs}$  are constant for each constituent
- Hot processes
  - Impact on RCR comes from  $MF_{percentage}$  and  $MF_{EPhot}$  considering (1) and (3)

## Driving DNEL approach (4): inhalation route

The proportional contribution of each UVCB constituent to the overall exposure is assessed separately for each constituent of the individual UVCB using Tier 1 tool MEASE and given a weight

Percentage of constituent	Exposure reduction in MEASE	DNEL ranking weights
<1 %	90 %	10.0
1 % - <5 %	80 %	5.0
5 – <25 %	40 %	1.7
25 % - 100 %	0 %	1.0

# Driving DNEL approach (7): inhalation route

## Hot-metallurgical processes

- Emission potential based on ratio Process Temperature/Melting Point

Hot-metallurgical process category	Emission potential and related initial MEASE estimates for inhalation exposure and associated ranking weights					
	low		medium		high	
	estimate	weight	estimate	weight	estimate	weight
PROC 22 (partly closed furnace operations)	1.0	7	3.5	2.0	7	1
PROC 23 (open furnace operations)	0.5	4	1.5	1.3	2	1
PROC 25 (other hot metallurgical processes)	0.5	4	1.0	2.0	2	1
PROC 27a (hot metallurgical powder production processes)	1.0	10	3.5	2.9	10	1

## Limitations of the driving DNEL approach & next steps

- What about bio-monitoring data?
  - In the approach above, it is assumed that relevant DNELs are all derived as external exposure levels
  - For some constituents, DNELs are based on internal exposure (monitored in a specific physiological medium such as Pb in blood, or Cd in urine)
  - On a company level, these constituents are already monitored (national legislations). To integrate those constituents in the driving DNEL approach, the relevant values would have to be converted to an external exposure value
- Additive toxicity of different constituents: (see step 4, not addressed in this step)