# Ecotox classification for substances and mixtures under CLP

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- 1. Classification drivers
- 2. The Environmental Classification system: *from*DSD to 2nd ATP of the CLP
- 3. Labelling requirements
- 4. Data "rich" substances and the Metals' annex of the CLP
- 5. Mixtures classification and M factors
- 6. Hazardous for the Ozon layer

### 1. Classification drivers

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# 1. Classification drivers for the environment under DSD, GHS & CLP

Classification drivers for ecotoxicity:

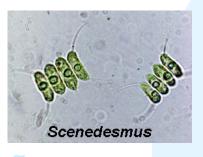
ü *Toxicity*: short or chronic toxicity

ü Absence of "degradability" to define long-term effects

ü Potential for "bioaccumulation"

### 1. Classification drivers for the environment under DSD and CLP

### How is this measured?



### ü Toxicity:

- û *Lowest EC50* for reference species representing the different throfic levels (fish, daphnia and algae)
- û *Lowest NOEC* for reference species



### ü Absence of degradation:

- û ½ Lifetime of Bio- or photodegradation
- û And for metals "Removal from the watercolumn"



### ü Bioaccumulation:

û Bioaccumulation Factor (BCF) (for organics: often as log Kow)

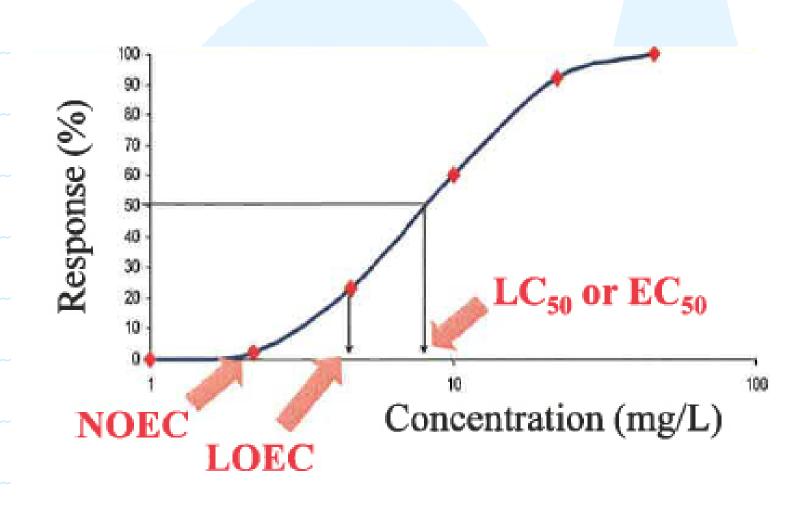
### 1. Deriving ecotoxicity values - Data selection

### « Quality criteria - Data hierarchy

The best quality data & most sensitive as basis for the classification

- Type of test (standard tests (e.g. OECD) preferred for classification)
- Standard species preferred but non-standard species can be used in case of equivalent endpoints
- 3. Relevancy of test medium (natural & artificial media, conditions related to transformation/dissolution media for classification)
- 4. Relevancy of test substance (solubility, impurities, metabolites)

# 1. Toxicity assessment : concentration-effect response



# 2. The environmental classification system from DSD/DPD over GHS to CLP (2<sup>nd</sup> ATP)

# 2. The system DSD classification scheme (Dir.67/548)



EC50	R phrases	<b>Hazard Label</b>	
Mg/I	Label		
< 1	R50 <b>N</b>	Very Toxic to Aquatic Env.	
< 1 Not rapidly biodegradable and/or BCF>500	R50/53 N	Very Toxic to Aquatic Env. Can cause long term effects	
Ø1 < 10 Not rapidly biodegradable and/or BCF>500	R51/53 <b>N</b>	Toxic to Aquatic Env. Can cause long term effects	
Ø10 < 100  Not rapidly biodegradable and/or BCF>500	R52/53	Harmful to Aquatic Env. Can cause long term effects	
Expected chronic effects	R53	Can cause long term effects	

### 2. UN-GHS Classification Categories

GHS Class EU DSD and R-Code		Hazard Label in the EU		
Acute I	and N-code	Very Toxic to Aquatic Env.		
Acute I & Chronic I		Very Toxic to Aquatic Env Can cause long term effects		
Acute II & Chronic II		Toxic to Aquatic Env. Can cause long term effects		
Acute III & Chronic III		Harmful to Aquatic Env. Can cause long term effects		
Chronic I, II or III		Can cause long term effects		
Chronic IV (safety net)		Can cause long term effects		

CHRONIC toxicity assessment CRITERIA based on NOECS

### **EU-CLP** Classification Categories

CLP Class		Hazard Label in the EU		
_ Acute I		Very Toxic to Aquatic Env.		
	Chronic I	Very Toxic to Aquatic Env. Can cause long term effects		
Thus no acute 2	Chronic II	Toxic to Aquatic Env. Can cause long term effects		
or 3	Chronic III	Harmful to Aquatic Env. Can cause long term effects		
~	Chronic IV	Can cause long term effects		

### 2. Changes introduced by 2nd ATP

#### **CLP**

 Chronic tox = <u>acute</u> tox <u>corrected for fate</u> properties (bio-accumulation potential and bio-degradation)

Acute M factor

### CLP incl. 2nd ATP

- Chronic tox = based <u>on real</u>
   <u>chronic data</u> or in absence the surrogate scheme
- Chronic classification categories depending on potential for degradation
- Acute and Chronic M factor

### 2. Lack of Chronic data

### **ACUTE TOXICITY**

- à Acute 1
  - ü L(E)C<sub>50</sub> (Fish, Daphnia, Algae) < 1mgL
- à Acute 2
  - $\ddot{u}$  L(E)C<sub>50</sub> (Fish, Daphnia, Algae) > 1 but < 10mgL
- à Acute 3
  - $\ddot{u}$  L(E)C<sub>50</sub> (Fish, Daphnia, Algae) > 10 but < 100mgL

## FATE (surrogate scheme)

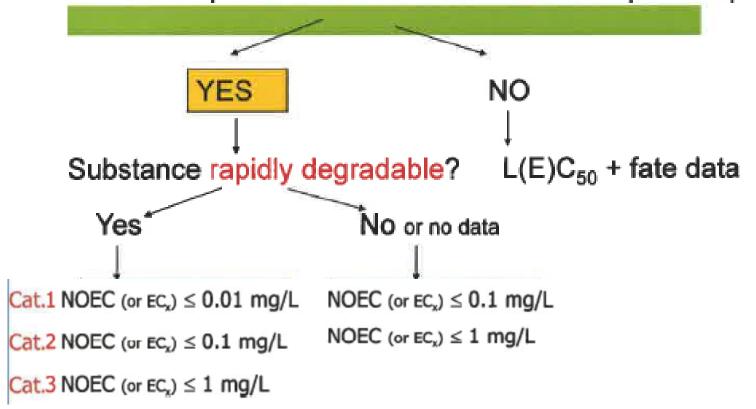
- à Rapid degradation:
  - ü 70% degradability in 28 d
- à Bioconcentration
  - ü fish > 500 or
  - ü Log Kow < 4

### 2. CLP from 2nd ATP on

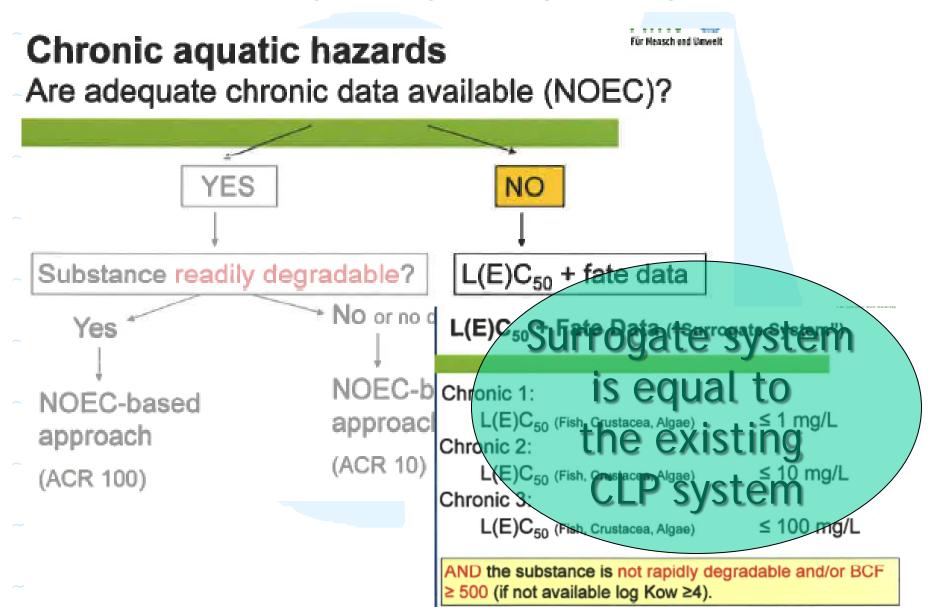
### Chronic aquatic hazards

Für Mensch und Umwellt

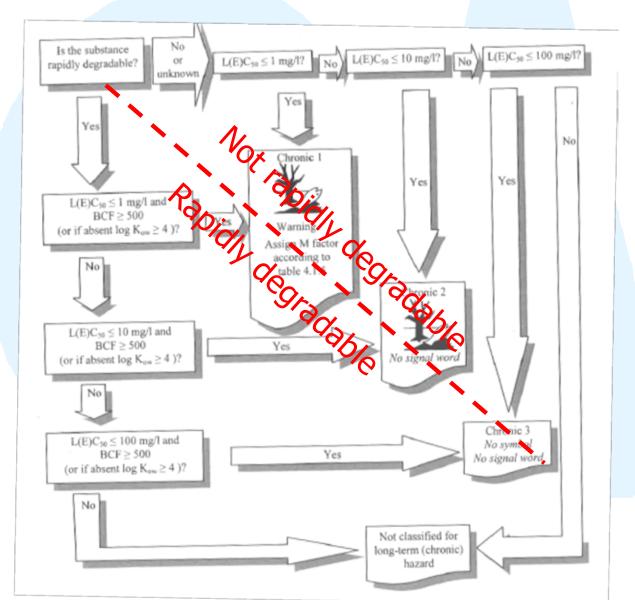
Are adequate chronic data available (NOEC)?



### 2. CLP from 2nd ATP on



### Surrogate approach No chronic info available



# 3. Labeling for the environmental endpoint

### 3. Labelling

ACUTE 1
CHRONIC 1 and 2



WARNING (not for C2)

CHRONIC 3 and 4

No pictogram

### 3. Labelling: Hazard statements

- Very toxic to aquatic life (H400)
- Very toxic to aquatic life with long lasting effects (H410)
- C2 Toxic to aquatic life with long lasting effects (H411)
- C3 Harmful to aquatic life with long lasting effects (H412)
- C4 May cause long lasting harmful effects to aquatic life (H413)

### 3. Labelling: Precautionary statements

Avoid release to the environment (P273)

Collect spillage (P391)

Dispose of contents/container to ... (P501)

. . .

### Massive versus other forms



# 4. Specific Environmental classification aspects for data rich and metals/alloys/inorganics

# Data rich and "metal" issues and guidance

- à Data rich substances:
  - ü Scientifically unfair to take to "lowest toxicity reference"
- à For metals: "ion" causes often the toxicity
  - ü Nominal testing of insoluble substances not allowed
- à Metals have specific particularities
  - ü Solubility differs for different "physical forms"
  - ü "Metal surface" corresponds with loadings
- à Need for specific approaches:
  - ü Measure release rate and equilibrium to read across between ion and Poorly Soluble Metal Compounds or Metals

### Classification strategy for metals

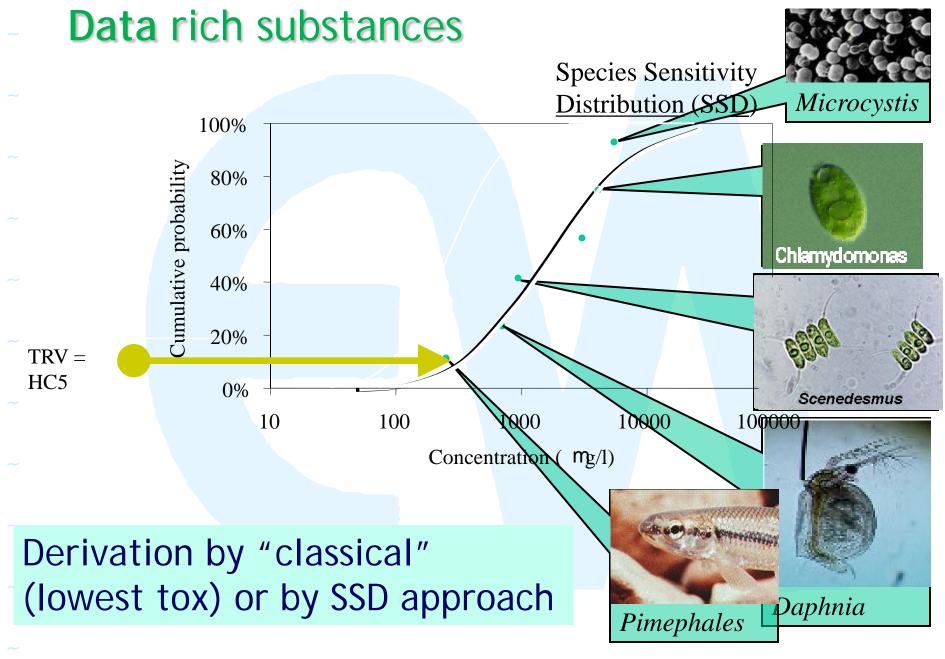
- 1. Assessment approach for effects data
- 2. Guidance on interpreting *BCF* and rapid degradation
- 3. Assessment tool for release rate and equilibrium (TDp)
- Classification strategy for metals and metal compounds

## Classification example Data selection- lowest value vs species mean

Test organism	L(E)C <sub>50</sub> (μg/l)				
	pH:	pH:	pH: >7.5-	All pHs	
	5.5-6.5	>6.5-7.5	8.5		
Algae					
R. subcapitata					
n	2	3	12	17	
Min.	152.0	32.0	12.9	12.9	
Max.	194.0	163.1	245.3	245.3	
Geometric mean	171.7	76.0	61.8	72.3	

#### In case of data rich substances:

-Use geometric mean when 4 or more effects data for same species and same endpoint, under comparable test conditions

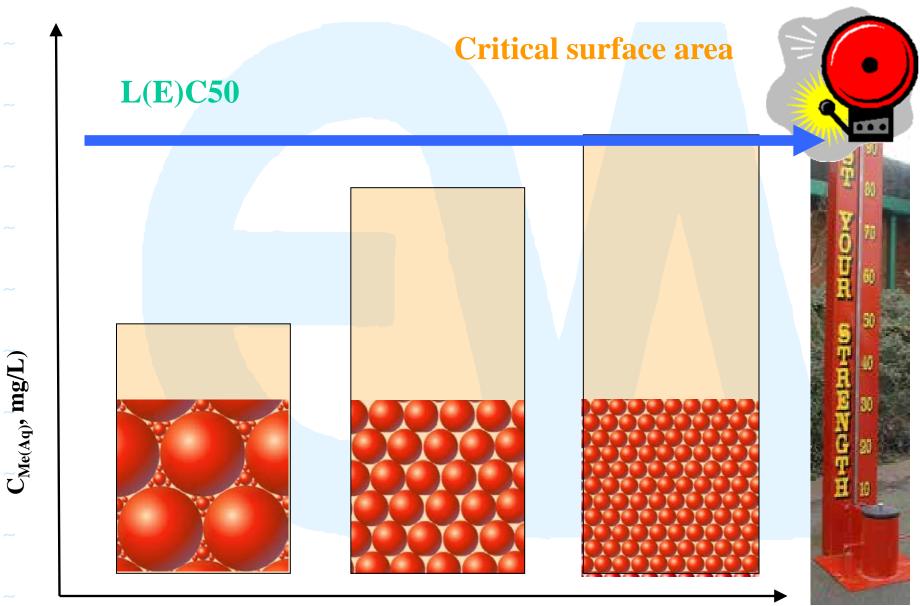


# Environmental Classification of metals and metal (compounds)

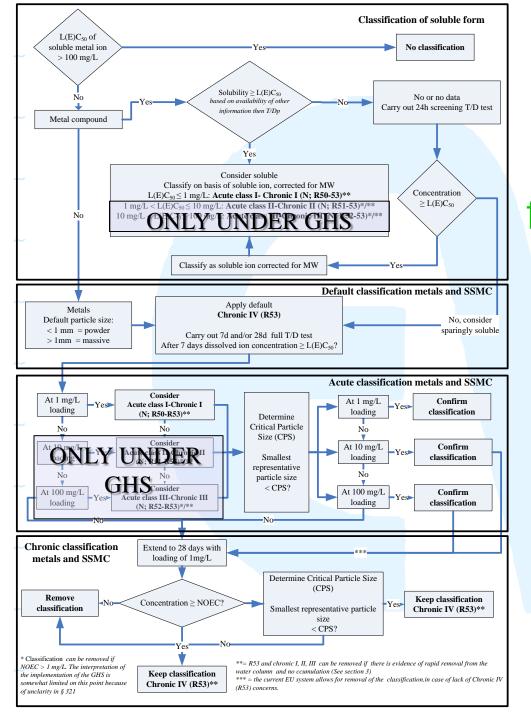
### PRINCIPLES:

- Soluble metal compounds :
  - All classified cf. toxicity metal ion
  - Classification corrected for "molecular weight"
- Metals and Insoluble metals :
  - Classification based on READ ACROSS comparing
    - Ion toxicity
    - Potential of the metal SSMC to release enough ions

### Differences in surface area matters !!!

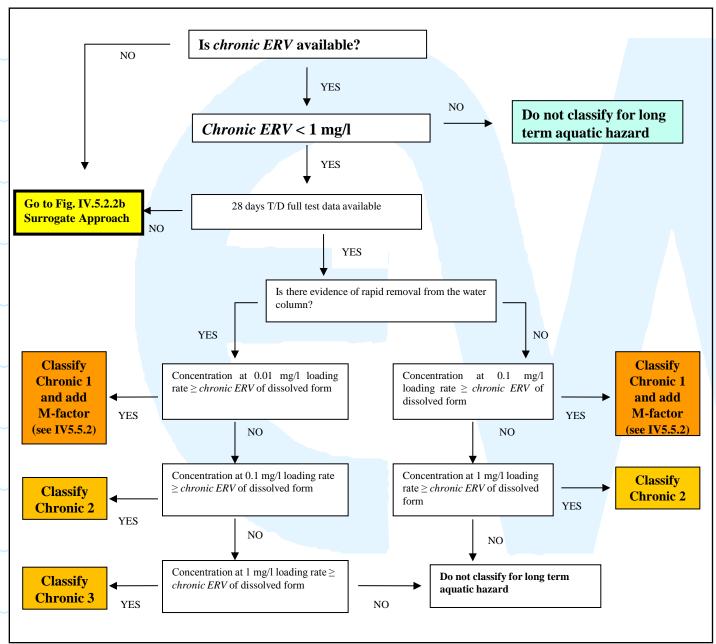


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### Classification strategy for metals and alloys

CLP scheme for chronic endpoint



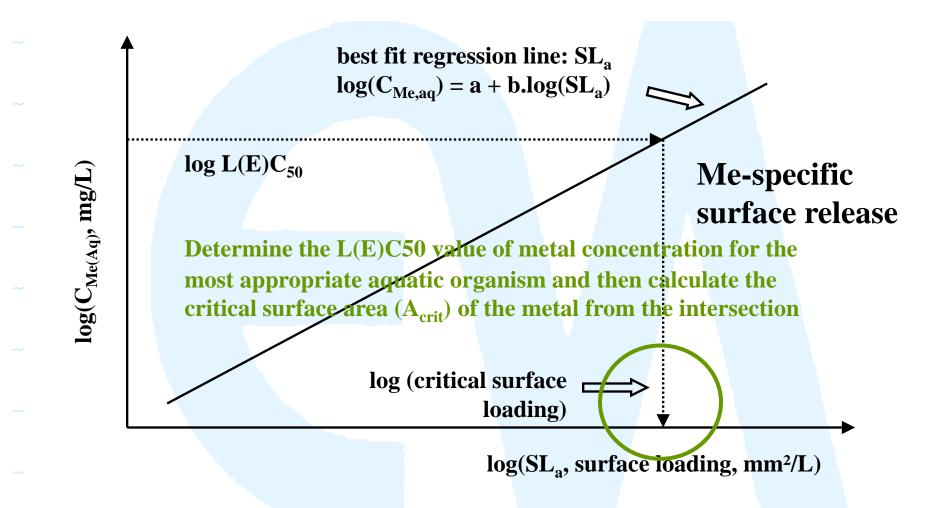
### Transformation Dissolution testing

### **PRINCIPLES**

- à 24h screening test
  - ü for metal salts to proof different solubility and
  - ü determine pH dependency
- à Full test
  - ü 7 d at pH that dissolves most
    - û Used to classify for acute
    - û Doses to be tested for DSD/GHS: 1, 10 and 100 mg/l
    - û Doses to be tested for CLP: 1 mg/l
  - ü 28 d at pH that dissolves most
    - û Used to classify for chronic
    - û Doses to be tested for DSD: 1 mg/l
    - û Doses to be assessed\* for CLP 2nd: 1, 0,1 and 0,01 mg/l

<sup>\*</sup> can be calculated

### Classify on basis of TDp: Determine critical surface loading

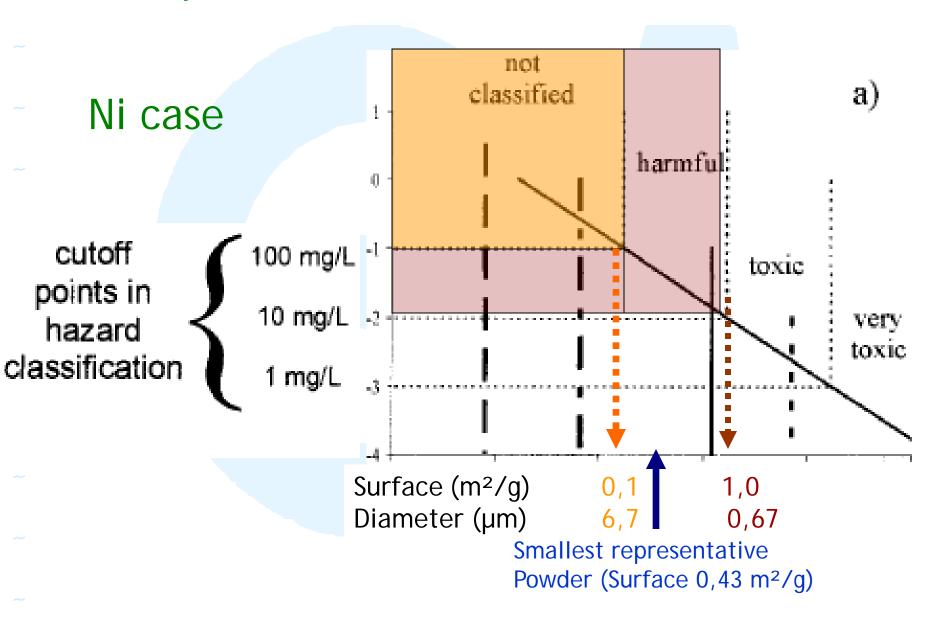


surface area loading (A, mm²/L) = substance specific surface area (SA, m²/g) \* substance mass loading (g/L)

 $SA = area (m^2)/mass (g)$ 

1, 10, 100 mg/l

### An example Ni metal Powder Classification



# Classification for metal compounds MW correction: only SOMETIMES !!!

### Classification:

ü Reference ecotoxicity of the metal ion μg Me/L & Molecular weight correction (MWC) if relevant

### When is MWC relevant?

- ü Metal (ion) : MWC = 1
- ü Soluble metal compound : MWC correction
- ü Poorly soluble ion: MWC correction included in TDp test (100 mg/l loading of poorly compound)
- à The same actually applies when a WAF method is used for organics!!

### Metal Powder/Massive Env. Classification : example of Ni : *Conclusions*

WITHOUT TDp evidence: based on "read across from ion tox"

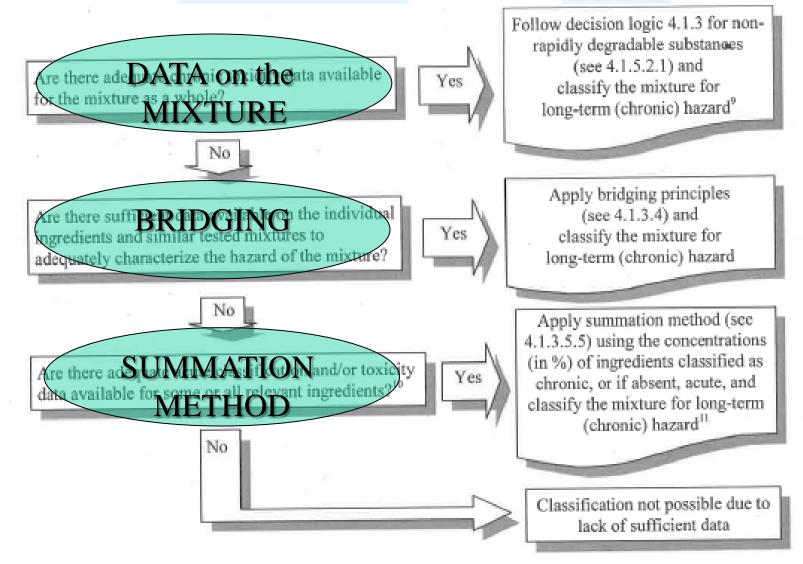
- à Ni powder and Ni metal classified as ACUTE 1!!!!
- à Ni metal massive classified as CHRONIC 4 !!!

WITH TDp evidence: based on "dissolution kinetics"

- à Ni powder classified as ACUTE 3 under DSD and no classification under CLP if raid removal is recognised
- à Ni massive NOT classified !!!

### 5. Classification of mixtures

# 5. Classification of mixtures for the environmental endpoint



# 5. How to classify mixtures?

## à By testing the mixtures :

- ü Expensive and "not possible" for alloys and sparingly soluble metals and inorganics since nominal testing is NOT allowed
- ü The GHS foresees ONLY a testing possibility in TDp water (not a WAF approach)

## à By bridging principles :

- ü A preparation very close to the one under assessment
- ü Not recommended (when / for metals) composition does not predict release

## à By applying "calculation rules":

- ü "Summation rule" for Mixtures
- ü "Additivity rule" for mixtures that are substances under REACH/CLP (inorganic UVCB's)

# 5. Are test data available on similar mixtures or individual components?

## **USE BRIDGING RULES**

- <u>Dilution</u>: if diluent has an equivalent or lower aquatic hazard classification then resulting mixture same classification as original mixture
- <u>Batching</u>: where a batch of a mixture is produced under a controlled process than the hazards of each new batch are equivalent to the previous batch
- Substantially similar mixtures: each mixture contains an additional ingredient which is not identical but are present in equivalent concentrations and same hazard category

## 5. M factor correction

- à Applied to substances classified as "acute 1" and/or "chronic 1"
- à Corrects for the very high ecotoxic potential is > 10 x as the cut-off for that category
- à Is applied to correct the cut-off to calculate the hazard ID for mixtures

**NEW**: TDp can be used to correct the M factor based on "differential release" for massive forms

## 5. The M-factor under CLP

1	Annex I: 4.1.3.5.5.5.1.			
	<b>Table 4.1.3</b>			
1	Multiplying factors for highly toxic components of mixtures			
	L(E)C <sub>50</sub> value mg/l	Multiplying factor (M)		
	$0.1 < L(E)C_{50} \le 1$	1		
	$0.01 < L(E)C_{50} £ 0.1$	10		
-	$0.001 < L(E)C_{50} £ 0.01$	100		
	$0.0001 < L(E)C_{50} £ 0.001$	1 000		
	$0.00001 < L(E)C_{50} £ 0.0001$	10 000		
	(continue in factor 10 intervals)			

M-factor is used to classify preparations for highly ecotoxic substances and must be communicated through the SDS

### 5. The M Factor under 2nd ATP

Annex I: Table 4.1.3

#### Multiplying factors for highly toxic components of mixtures

Acute toxicity	M factor	Chronic toxicity	M factor	
L(E)C <sub>50</sub> value mg/l		NOEC value mg/l	NRD <sup>a</sup> components	RD <sup>b</sup> components
$0.1 < L(E)C_{50} \le 1$	1	0,01 < NOEC ≤ 0,1	1	-
$0.01 < L(E)C_{50} \le 0.1$	10	0,001 < NOEC ≤ 0,01	10	1
$0,001 < L(E)C_{50} \le 0,01$	100	0,0001 < NOEC ≤ 0,001	100	10
$0,0001 < L(E)C_{50} \le 0,001$	1000	0,00001 < NOEC ≤ 0,0001	1000	100
$0,00001 < L(E)C_{50} \le 0,0001$	10000	0,000001 < NOEC < 0,00001	10000	1000
(continue in factor 10 intervals)		(continue in factor 10 intervals)		

a Non-rapidly degradable

## This could lead to different Hazard categories if:

A-C ratio is < 10 or > 100

b Rapidly degradable



# WARNING!!!



## For substances on Annex VI:

- Rule 1: The hazard classification of Annex VI must be used
  - unless a higher CI category is required based on "new evidence"
- Rule 2: Not all endpoints may have been covered and M factors were often not taken over;
   So this responsibility maintains with the registrant
  - Be especially careful with M factors (acute and chronic)

# 5. How to classify preparations?

# Classification of a mixture for chronic (long term) hazards, based on summation of classified components

Sum of components classified as:	Mixture is classified as:	
Chronic Category ≥ 25 %	Chronic Category 1	
(10 ' Chronic Category 1) +	Chamina Catagory 2	
Chronic Category $2 \ge 25 \%$	Chronic Category 2	
(100 ' Chronic Category 1) + (10 '		
Chronic Category 2)	Chronic Category 3	
+ Chronic Category 3 ≥ 25 %		
Chronic Category 1 + Chronic		
Category 2 + Chronic Category 3	Chronic Category 4	
+ Chronic Category 4 ≥ 25 %		

# 5. M-factor application to preparations

# Classification of a mixture for chronic (long term) hazards, based on summation of classified components

Sum of components classified as:	Mixture is classified as:
Chronic Category 1 ' $M \ge 25 \%$	Chronic Category 1
(M ′ 10 ′ Chronic Category 1) + Chronic Category 2 ≥ 25 %	Chronic Category 2
(M ′ 100 ′ Chronic Category 1) + (10 ′ Chronic Category 2) + Chronic Category 3 ≥ 25 %	Chronic Category 3
Chronic Category 1 + Chronic Category 2 + Chronic Category 3 + Chronic Category 4 ≥ 25 %	Chronic Category 4

# 5. "Additivity" versus "Summation"

## **Summation**

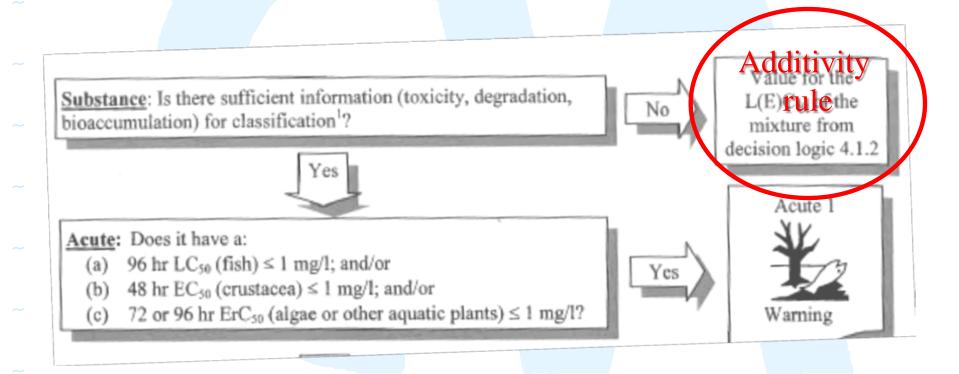
- Based on % of substance classified in a given category
- Relevant for **ALL MIXTURES**

## **Additivity**

 Based on L(E)C50 of each component

 ONLY for SUBSTANCES than contains several components (with known or partly known classification

# "Additivity" versus "summation"



### www.meclas.eu

MECLAS: THE SMARTEST WAY TO FULFILL YOUR CLASSIFICATION OBLIGATIONS

version 1.1 / what's new? / help









#### LICENSE

In order to use the tool a license is needed.

A short description of the MECLAS tool and the license costs can be found here.

You must register and obtain a Login account in order to access the MeClas tool and all supporting information.

#### ■ NEWS

The MeCLAS tool is officially released at Eurometaux (Metal Conference Centre) on 30th August 2010.

You must register and obtain a Login account in order to access the MeClas tool.



register / forgot password?

#### Welcome to the MeCLAS website

The smartest way of fulfilling your classification obligations

Most complex materials in the metals sector contain a spectrum of different metals (compounds) and minerals, which therefore requires extensive physico-chemical, toxicity and ecotoxicity reference data sets. The MeCLAS tool offers a unique web-enabled classification tool that is always updated to the latest classification rules. The tool comprises several tiers, aimed at the progressive refinement of classification through recognition of speciation, specific mineral content and the availability of test data on the complex material in question.

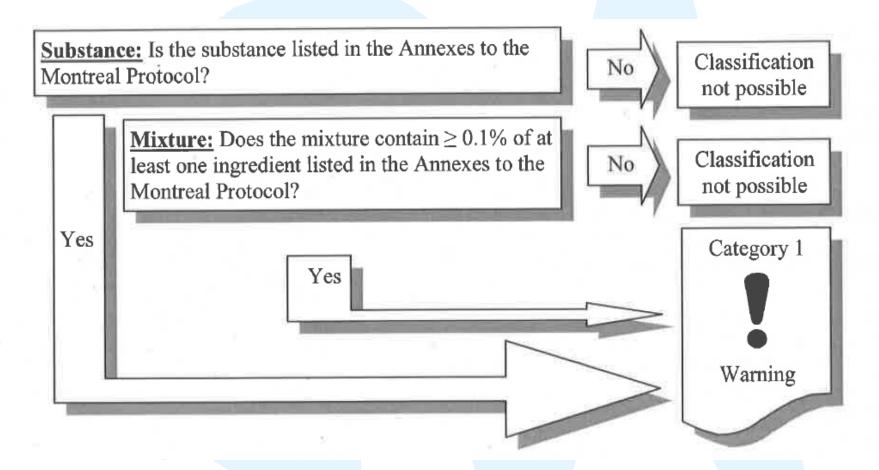
A licence is needed in order to use the tool. You must register and obtain a Login account in order to access the MeCLAS tool and all supporting information.

The MeCLAS tool has been developed jointly by EUROMETAUX and ARCHE



# 6. Hazardous for the Ozon layer

# Hazardous for the Ozon layer



For substances on the Montreal protocol list

# Examples on ENV. Mixtures classification



# Example: an inorganic mixture

## Poorly soluble metal compound with:

- Acute & chronic toxicity data on the components,
- With or without: Transformation/Dissolution data at 7 d's and at 28 d's on the alloy
- With or without of evidence of Rapid removal from the water column.

# Example: a mixture with known tox but no rapid degradation

### DATA:

- Substance 1 : NOEC : 4 μg/l, 5% in mixture
- Substance 2 : NOEC : 40 μg/l, 10% in mixture
- Substance 3: no chronic tox; 85% in mixture

### Classification:

- -(5% \* 10) + (10% \* 1) = 60%
- > 25%, so Chronic 1

# Example: a mixture with known tox AND rapid degradation

### **DATA:**

- Substance 1 : NOEC : 4 μg/l, 5% in mixture
- Substance 2 : NOEC : 40 μg/l, 10% in mixture
- Substance 3: no chronic tox; 85% in mixture

### Classification:

- (5% \* 1) + (10% \* 1) = 15 %
- > 2,5 but < 25% but, so Chronic 2

# Example 3: mixture 1 (glass) with known tox and TDp and non-degradable

## **DATA:**

- Subst. 1: NOEC: 4 μg/l, 5% in mixt., TDp: 2μg/l at 1mg/l
- Subst. 2: NOEC: 40 μg/l,10% in mixt., TDp: 80μg/l at 1mg/l

8µg/l at 0,1 mg/l

Subst. 3: no chronic tox; 85% in mixture

# Classification: of GLASS powder (special mixture)

- Subst. 1 : TDp < NOEC: not taken forward for Cl</li>
- Subst. 2 : TDp > NOEC: taken forward for Cl
- If No Rapid degradability: Chronic 3
- If Rapid degradability: no classification

# Questions: to train your brains

- à When do I need to **analyse for concentrations of** constituents in a mixture below 0,25 %?
  - ü ANSWER: When an M factor of 10 or more is applied!
    - û Eg Silver ions M factor 1000x requires a concentration cut off of 0,00025%
- à Are there conditions when I classify for the environment even when "no acute" nor "chronic" classification category can be applied?
  - ü ANSWER: YES chronic 4 can be applicable IF
    - û No chronic/acute data are available for the 3 throphic level nevertheless there is "grounds for concern"
    - û For metals/inorganics when massives are not tested for TDp while the soluble ion is classifiable

# Questions: to train your brains (2)

- a Can I always apply an acute/chronic ecotox test to a mixture to define the appropriate hazard category?
  - ü ANSWER: Mostly possible BUT not always!
    - û NOMINAL testing is NOT allowed
    - û REMINDER: vertebrate testing under REACH requires a Testing Proposal (Substances)
- à Can I apply the accumulation rule on a UVCB substance?
  - ü ANSWER: YES because a SUBSTANCE (not a MIXTURE)
- à When do I not need to correct for the Molecular Weight of a/the ingredient(s)?
  - ü ANSWER: when a WAF or a TDp result is used on an insoluble given the loading of the test already accounts for the MW!