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INERIS

maîtriser le risque
pour un développement durable

Study to assess the impacts of different classification approaches for hazard property "H 14" on selected waste streams

Workshop

Brussels, 20th April 2015

European Commission

Agenda

Part I

Context & objectives of the project

Context of the project

Regulatory framework governing classification of waste in the EU

Decision 2000/532/EC

List of Waste (LoW)

Common encoding of waste characteristics, for purposes including **classification of hazardous wastes**

Article 2

Wastes classified as hazardous are those considered to display one or more of the 15 properties listed in **Annex III to the WFD**

Directive 2008/98/EC*

Annex III

Defines the 15 properties that render waste hazardous: H1 to H15; among which **H14 "ecotoxic"**.

200 waste codes in mirror pairs: the unique basis for choosing the hazardous or non-hazardous entry is **Annex III of the WFD**

Definition of mirror pairs:

Pairs of entries of the LoW of which one waste may be classified as hazardous or non-hazardous depending on the type and concentration of the hazardous substances it contains.

Waste codes	Name of waste
19 01 11*	Bottom ash and slag containing dangerous substances
19 01 12	Bottom ash and slag other than those mentioned in 19 01 11

*The Waste Framework Directive (WFD)

Context of the project

A strong link with chemical legislation

Annex III to the WFD
Defines the 15 properties that render waste hazardous

Criteria

Dangerous Substance Directive Annex VI
R-phrases

e.g. R50 : very toxic to aquatic organisms

Dangerous Preparation Directive Annex VI
Limit values

Progressively being repealed by the CLP and REACH Regulation (1st June 2015)

Tests

Dangerous Substance Directive Annex V
Also: relevant CEN notes

Test Method Regulation (EC) 440/2008
Takes over all test methods from Annex V of the DSD

However :

- At EU level, no guidelines or recommendations exist for a specific methodology for the assessment of H 14.
- As a result, H 14 is assessed in different ways throughout Member States.

Context of the project

A need to review and harmonise H 14 approaches

- Review of LoW and WFD in 2008 by a WG : priority on review of hazardous properties

- H-Criteria 1- 15 renamed HP 1-15
- Strict alignment on CLP (concentration limit, M-Factors)

- Issues raised by the alignment on CLP
- Changes in amounts of waste classified as hazardous
- Disagreements on strategy to adopt
- Proposal to ignore concentration limits & M-Factors, or Chronic 3&4 categories
- No agreement reached

Objectives of the project

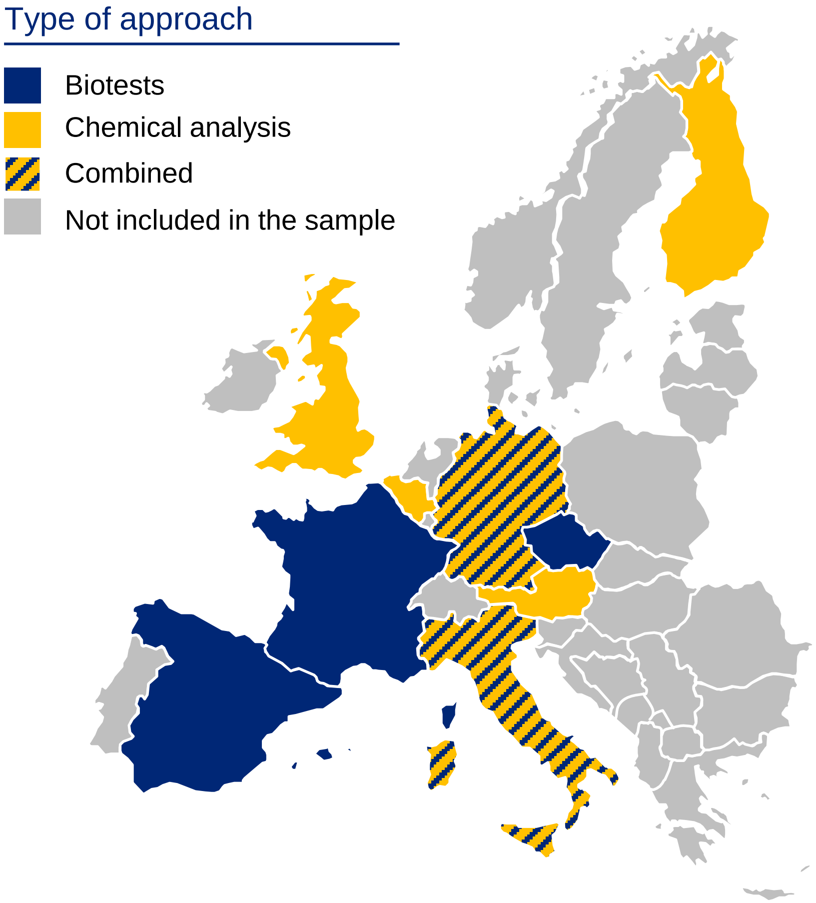
- Documenting the strategies of a sample of Member States regarding assessment of HP 14
- Assessing the implications for Member States and the industry of the implementation of 4 different options of calculation methods for HP 14 assessment
  - calculation methods proposed by the Commission based on outcomes of the WG
- The identification of the potential limits of the proposed methodologies and recommendations

Part II

Approaches in nine Member States

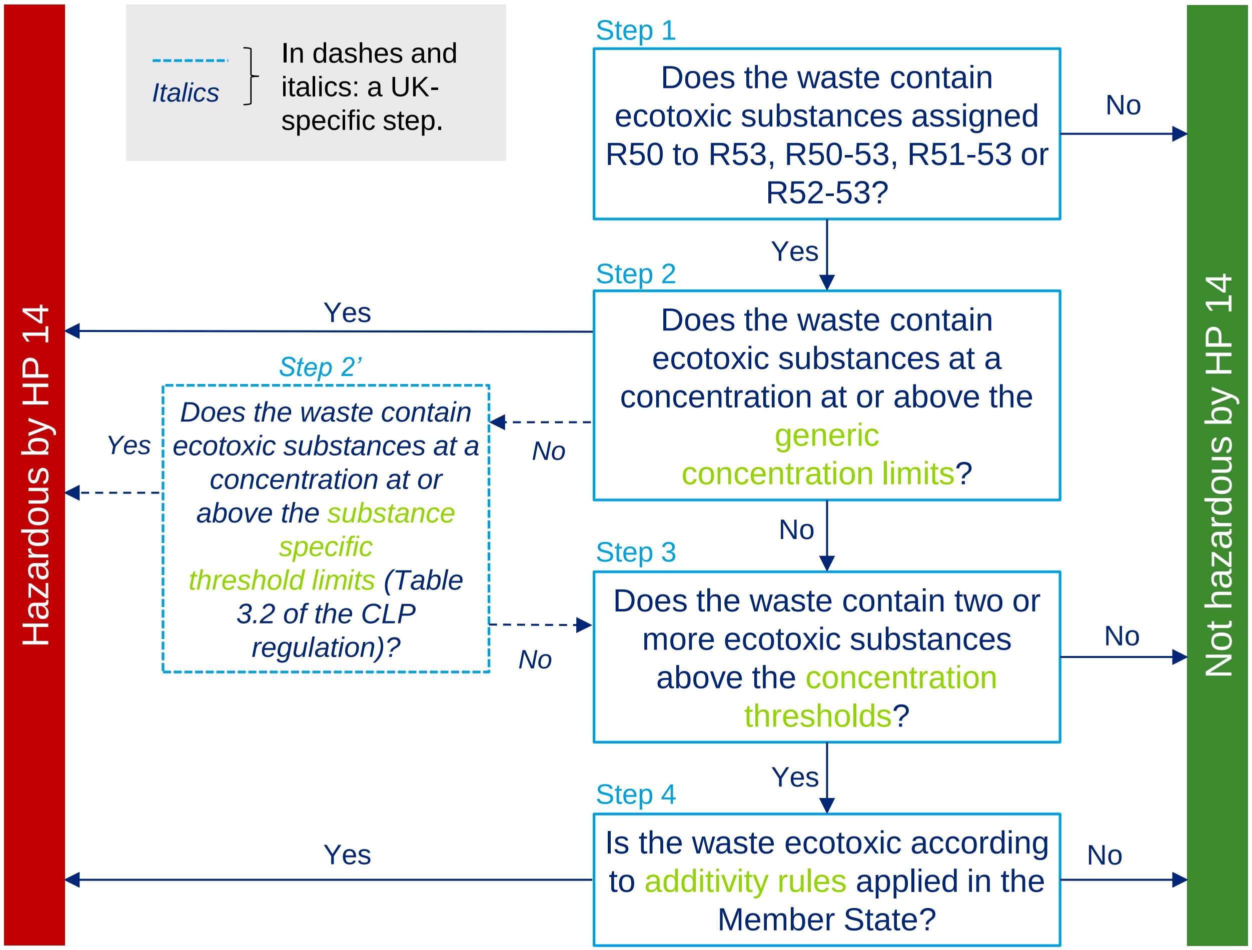
Approaches in nine Member States
Overview

	Law	Guidelines
Austria	✗	
Belgium		✗
Czech Republic	✗	✗
Finland		✗
France		✗
Germany		✗
Italy	✗	
Spain	✗	✗
UK		✗



Approaches in nine Member States

Based on chemical analyses: the DPD as a reference



Approaches in nine Member States

Based on chemical analyses: Member States apply different additivity rules

Member State(s)	Conditions
Finland, UK and Italy	$\sum\left(\frac{P_{R50\text{-}53}}{0.25}+\frac{P_{R51\text{-}53}}{2.5}+\frac{P_{R52\text{-}53}}{25}\right) \geq 1$ Or $\sum(P_{R50}+P_{R50\text{-}53}) \geq 25$ Or $\sum P_{R52} \geq 25$ Or $\sum(P_{R53}+P_{R50\text{-}53}+P_{R51\text{-}53}+P_{R52\text{-}53}) \geq 25$
Belgium	$\sum(P_{R50\text{-}53}) \geq 2.5$ Or $\sum(P_{R51\text{-}53}) \geq 25$ Or $\sum(P_{R50}) \geq 25$ Or $\sum(P_{R59}) \geq 0.1$

Member State(s)	Conditions
Germany[1]	$\sum(P_{R50\text{-}53}) \geq 0.25$ Or $\sum(P_{R51\text{-}53}) \geq 2.5$ Or $\sum(P_{R52\text{-}53}) \geq 25$ Or $\sum(P_{R59}) \geq 0.1$
Where P_{RX} is the total concentration of substances classified as RX, expressed in w/w %.	

Approaches in nine Member States

Based on chemical analyses: advantages and drawbacks

- Easy and satisfactory for well-defined waste samples.
- Lower cost compared to approaches based on biotests.
- In particular, strategies based on the DPD are clear and align directly with chemical risk phrase classification systems
- The Austrian strategy, partly based on classification according to the ADR, is easier to apply than DPD-based approaches and costs less because the classification according to the ADR is required anyway if the waste is transported.
- Specific advantage of the British strategy: the most complete.
  - Includes more recent legislation; and
  - Provides a more finely tuned approach.

- Limited information and uncertainties regarding the composition of waste:
  - heterogeneity of waste samples can make determination of composition difficult.
  - suitable methods to identify organic substances in waste are lacking
  - the application of worst-case scenarios when the composition of waste is not sufficiently known leads to an overestimation of the waste hazard
- The applicability of methodologies provided in the DPD and the CLP for the assessment of waste is not straightforward and has not been evaluated.

Approaches in nine Member States

Based on biotests: batteries (aquatic)

Organism	Standard	Member States					
		CZ	FR(i)	FR(h)	ES	DE	IT
D. Magna (acute)	ISO 6341	x	x	x	x	x	x
D. Magna (chronic)	ISO 10706					x	
V. fischeri	ISO 11348		x	x	x	x	x
P. subcapitata	ISO 8692		x	x		x	x
L. minor	ISO 200795					x	
S. alba	Czech guidelines	x					
P. reticulata	ISO 7346-2	x					
C. dubia	ISO 20665		x				
B. Calicyflorus	ISO 20666		x				

FR(i): Initial approach in France, as recommended by the FNADE
FR(h): Hydrid approach in France, combining initial strategy and German strategy

Approaches in nine Member States

Based on biotests: batteries (aquatic) – example of *D. magna*

No harmonisation of thresholds (value and unit).

Organism	Standard		Member States				
			FR	ES	DE	IT	CZ
D. Magna (acute)	ISO 6341	Expression of results	EC50				
		Test duration	24h or 48h			48h	
		Threshold	10mL/L (i.e. 1% v/v)	10% (v/v)	10% (v/v)	750 mg/L	10% (v/v)

Approaches in nine Member States

Based on biotests: batteries (terrestrial)

Organism	Standard	Member States					
		CZ	FR(i)	FR(h)	ES	DE	IT
E. fetida (acute)	ISO 11268-1		x			x	
E. fetida (chronic)	ISO 17512-1			x		x	
L. sativa	ISO 11269-2		x				
A. globiformis	ISO 18187			x		x	
L. minor	ISO 200795					x	
B. rapa	ISO 11269-2			x		x	
F. candida	ISO 11267					x	

In Italy and the Czech Republic, members of the scientific community recommend the use of terrestrial tests in the assessment of HP 14.

Approaches in nine Member States

Based on biotests: preparing waste samples

Preparing waste samples is a key step for the assessment of ecotoxicity, as test results can be highly variable depending on the protocol.

Member State	Standard	Scope	Description
Czech Republic	EN 14735	raw wastes or water extracts	Necessary steps to be performed before carrying out ecotoxicity tests on wastes: taking of the sample, transport, storage of wastes and to define preparation.
France	EN 12457 - 2	water extracts	Leaching - Compliance test for leaching of granular waste materials and sludge. One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction)
Germany	EN 12457 - 2	water extracts	See France
	DIN 19528	water extracts	Leaching of solid materials - Percolation method for the joint examination of the leaching behaviour of inorganic and organic substances
Italy	EN 14735	raw wastes or water extracts	See Czech Republic
Spain	EN 12457 - 2	water extracts	See France

Approaches in nine Member States

Based on biotests: advantages and drawbacks

- Mirror well the effects of:
  - all bioavailable contaminants, including their potential interactions (additive, synergistic and antagonistic);
  - pollutants in complex matrices, which cannot be determined by chemical analysis
- Are sensitive to many water soluble substances, thus being relevant to the assessment of wastes
- Test batteries containing only a few assays can be cheap and simple

- The lack of legally-fixed and harmonised threshold values.
- Some hold the view that animal testing of solid wastes raises ethical concerns.
- Some test batteries only include aquatic tests

Approaches in nine Member States

Combined approaches

In Germany and Italy, assessment of HP 14 follows a **tiered approach**:

- If the composition of the waste sample can be sufficiently known through chemical analysis, then classification according to HP 14 is done following the DPD method

Italy	Germany
$\sum\left(\frac{P_{R50\text{-}53}}{0.25}+\frac{P_{R51\text{-}53}}{2.5}+\frac{P_{R52\text{-}53}}{25}\right) \geq 1$	$\sum(P_{R50\text{-}53}) \geq 0.25$
Or	Or
$\sum(P_{R50}+P_{R50\text{-}53}) \geq 25$	$\sum(P_{R51\text{-}53}) \geq 2.5$
Or	Or
$\sum P_{R52} \geq 25$	$\sum(P_{R52\text{-}53}) \geq 25$
Or	Or
$\sum(P_{R53}+P_{R50\text{-}53}+P_{R51\text{-}53}+P_{R52\text{-}53}) \geq 25$	$\sum(P_{R59}) \geq 0.1$
Where P_{RX} is the total concentration of substances classified as RX, expressed in w/w %.	

- If the composition of the waste is unknown or complex, biotests are applied.

• good complementarity • Recently been investigated by researchers as a promising alternative to the status quo regarding the assessment of HP 14 in the EU	• it has been noticed in the UK that the results of the two approaches (chemical analysis and biotests) are often different and lead to different classification of the waste.

Questions

Coffee break

Part III

Calculations methods: results and assessment

Overview of data sent by the Members states

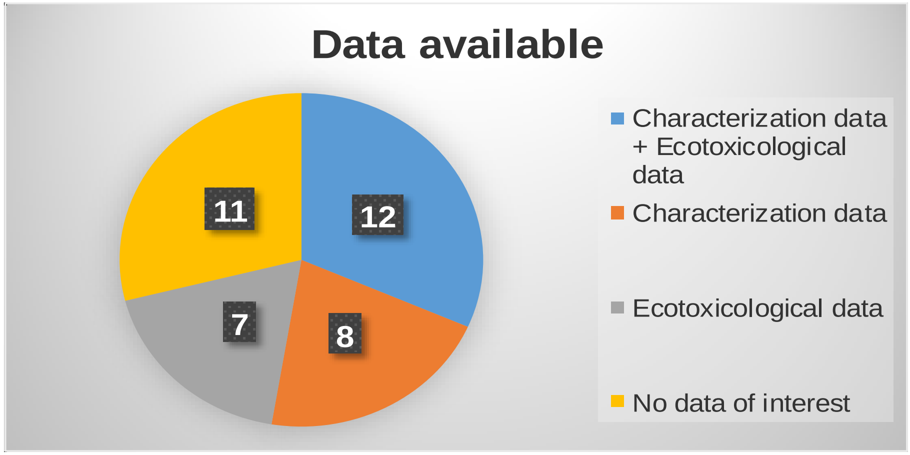
Six member states have responded positively to our solicitations

Member states	Filled database	Reports	Characterization data	Ecotoxic-ological data	Waste code
Belgium		x	(5)		19 01 12 19 01 14
Finland	x		(1)	x	19 01 14
Germany		x	(9)	x	08 01 13* 06 05 03 19 01 12 12 01 14* 19 01 13* 19 10 04 19 08 13*
Italy	x			x	17 05 03* / 17 05 04 19 01 11* 19 01 13* / 19 01 14
Sweden	x		(6)	x	19 01 11* / 19 01 12 19 01 13* / 19 01 14
United Kingdom		x	(20)		19 01 11* / 19 01 12

Overview of data from publications

Bibliographic data:

- 18 publications
- 15 reports
- 4 databases
- 1 website



Only 11 references report waste code ***(+ 4 references with probable code identified)***

Sludges from paint or varnish *08 01 13* / 08 01 14 (1)*
Sludges and filter cakes *11 01 09* / 11 01 10 (1)*
Flue-gas dust *10 03 19* / 10 03 20 (1)*
Packaging *15 01 10* / 15 01 11 (1)*
Soil and stones *17 05 03* / 17 05 04 (6)*
Bottom ash and slag *19 01 11* / 19 01 12 (2)*
Fly ash *19 01 13* / 19 01 14 (1)*
Sludges from waste water treatment plants *19 08 11* / 19 08 12 (1)*
Sludges from other treatment of industrial waste water *19 08 13* / 19 08 14 (1)*
Bottom ash and slag *19 01 11* / 19 01 12 (5)*
Other wastes from mechanical treatment of waste *19 12 11* / 19 12 12 (1)*

Data from publications/reports: 70 % of references without waste code

Characterization data collection on the selected pairs

Waste code	Description	Characterization data (sample)	
		Waste code mentionned	Probable waste code
06 05 02* / 06 05 03	sludges from on-site effluent treatment	1	-
08 01 13* / 08 01 14	sludges from paint or varnish	3	-
10 03 19* / 10 03 20	flue-gas dust	1	-
11 01 09* / 11 01 10	sludges and filter cakes	1	-
12 01 14* / 12 01 15	machining sludges	2	-
15 01 01 / 15 01 02 / 15 01 10*	packaging	1	-
17 05 03* / 17 05 04	soil and stones	3	7
19 01 11* / 19 01 12	bottom ash and slag	27	9
19 01 13* / 19 01 14	fly ash	7	-
19 08 11* / 19 08 12	sludges from biological treatment of industrial waste water	3	1
19 08 13* / 19 08 14	sludges from other treatment of industrial waste water	2	-
19 10 03* / 19 10 04	fluff-light fraction and dust	1	-
19 12 11* / 19 12 12	other wastes (including mixtures of materials) from mechanical treatment of waste	1	-
		57	17

Difficulties and limitations

Limitations according to characterization data

- Only concentrations of elemental compounds in most of the cases (mainly metallic elements)

- Non exhaustive characterization data

  - *Chemical speciation not identified*
  - *Data on organic compounds rarely available*
  - *Data for a group of compounds (sum of PAH compounds, nitroaromatic compounds,…)*
  - *A significant fraction of the waste could be not identified (≈ 95 to 99.9 % w/w)*
  - *Only few weight by weight percentage data (mainly mg/kg concentration)*

Limitations according to waste code identification

- Several characterization data are not associated to a waste code
- Many waste code are possible for a single denomination (e.g. bottom ash)

Limitations due to protocols, pre-treatment, test method,…

- Not always mentioned or briefly described
- Characterization data only available on eluate (aqueous extract)

CLP Regulation (1272/2008/EC)

Regulation (EC) N°1272/2008 of the European Parliament and of the Council of 16 December 2008 **on classification, labelling and packaging of substances and mixtures**, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) N°1907/2006

- Implements Globally Harmonized System (GHS) of classification and labelling in the EU
- To identify all the physical, toxicological and **ecotoxicological properties** of substances/mixtures as placed on the market (elemental compound was not considered, except for few metals)
- Hazard based only
- Elements of classification
  - Hazard class and category *(e.g. Aquatic Acute Toxicity, category 1)*
  - Hazard statement *(e.g. H400 :Very toxic to aquatic life)*
  - M factor
  - GHS Pictogram 
- Two kind of classification
  - Harmonized classifications which were adopted by the EU
  - Notified classifications which were proposed by industrial (significant disparity between notifiers)
- Mixtures are always self-classified

CLP Regulation (1272/2008/EC)

Specificity for aquatic environmental hazards of mixtures (M factor)

- Acute 1 and Chronic 1 highly toxic components contribute to the toxicity of the mixture even at a low concentration and shall be given increased weight in classification of mixtures.
- Multiplying factors based on ecotoxicological data (L(E)C50 or NOEC values) are determined
- M factor is reported, if available, in harmonised and notified classification

Acute toxicity	M factor	Chronic toxicity	M factor	
$L(E)C_{50}$ value mg/l		NOEC value mg/l	NRD ([a]) components	RD ([b]) components
$0,1 < L(E)C_{50} \leq 1$	1	$0,01 < NOEC \leq 0,1$	1	—
$0,01 < L(E)C_{50} \leq 0,1$	10	$0,001 < NOEC \leq 0,01$	10	1
$0,001 < L(E)C_{50} \leq 0,01$	100	$0,0001 < NOEC \leq 0,001$	100	10
$0,0001 < L(E)C_{50} \leq 0,001$	1 000	$0,00001 < NOEC \leq 0,0001$	1 000	100
$0,00001 < L(E)C_{50} \leq 0,0001$	10 000	$0,000001 < NOEC \leq 0,00001$	10 000	1 000
(continue in factor 10 intervals)		(continue in factor 10 intervals)		

([a]) Non-rapidly degradable.
([b]) Rapidly degradable.

CLP Regulation (1272/2008/EC)

M factor among harmonised classification

M factor	Number of compounds
M = 10	69
M = 100	49
M = 1,000	32
M = 10,000	10
M = 100,000	1
M = 1,000,000	1

Entries identified in n°1272/2008/EC regulation and the Adaptations to Technical Progress (ATP 1, 2, 3, 5 and 6) among 4,552 substances with harmonised classification

Feasibility of the calculation methods

Worst case consideration

- Based on the elemental compounds concentrations
  - Selection of the worst case based on harmonized classification
    - ✓ Consideration of the metal classification if available, or,
    - ✓ Consideration of the salt with the most severe classification
  - Difficulties associated to the worst case selection (e.g. lead chromate if only one of these elements is present in the waste)
  - Presence of the salt/compound in a waste lead to higher molecular weight and then higher concentration in the waste
- Probable underestimation : organic compounds not considered, significant fraction of waste not identified
- Only based on harmonized classification
- M factor not always available and mainly based on the soluble fraction
- Hazardous to the ozone layer : hazard rarely identified (only 4 substances with harmonized classification)

Example of worst case consideration

Harmonised classification for cobalt compounds

Substance	Index Number	EC Number	CAS Number	Classification	M-Factor
cobalt oxide	027-002-00-4	215-154-6	1307-96-6	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	10
cobalt sulfide	027-003-00-X	215-273-3	1317-42-6	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	10
cobalt dichloride	027-004-00-5	231-589-4	7646-79-9	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	10
cobalt sulfate	027-005-00-0	233-334-2	10124-43-3	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	10
cobalt acetate	027-006-00-6	200-755-8	71-48-7	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	10
cobalt nitrate	027-009-00-2	233-402-1	10141-05-6	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	10
cobalt carbonate	027-010-00-8	208-169-4	513-79-1	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	10
cobalt lithium nickel oxide	028-058-00-2	442-750-5	-	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
zinc hexacyanocobaltate(III), tertiary butyl alcohol/polypropylene glycol complex	027-007-00-1	425-240-7	-	Aquatic Chronic 2 H411	-
tetrazinc(2+)bis(hexacyanocobalt(3+))diacetate	030-015-00-8	440-060-9	-	Aquatic Chronic 2 H411	-
reaction mass of: pentasodium bis[6-anilino-3,5'-disulfonatonaphthalene-2-azobenzene-1,2'-diolato]cobaltate(III) tetrasodium [6-anilino-3,5'-disulfonatonaphthalene-	611-177-00-4	444-290-0	508202-43-5	Aquatic Chronic 3 H412	-
cobalt	027-001-00-9	231-158-0	7440-48-4	Aquatic Chronic 4 H413	-
complex of cobalt(III)-bis(N-phenyl-4-(5-ethylsulfonyl-2-hydroxyphenylazo)-3-hydroxynaphthylamide), hydrated (n H2O, 2<n<3)	027-008-00-7	427-390-9	-	-	-
cobalt nickel oxide	028-043-00-0		12737-30-3	-	-
cobalt nickel dioxide	028-043-00-0	261-346-8	58591-45-0	-	-
cobalt nickel gray periclase C.I. Pigment Black 25 C.I. 77332	028-043-00-0	269-051-6	68186-89-0	-	-
cobalt dimolybdenum nickel octaoxide	028-057-00-7	268-169-5	68016-03-5	-	-

Worst cases

Example of worst case consideration
Harmonised classification for zinc compounds

Substance	Index Number	EC Number	CAS Number	Classification	M-Factor
ziram (ISO) zinc bis dimethyldithiocarbamate	006-012-00-2	205-288-3	137-30-4	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	100
trizinc diphosphide zinc phosphide	015-006-00-9	215-244-5	1314-84-7	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	100
zinc bis(dibutyldithiocarbamate)	006-081-00-9	205-232-8	136-23-2	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
zinc bis(diethyldithiocarbamate)	006-082-00-4	238-270-9	14324-55-1	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
zinc chloride	030-003-00-2	231-592-0	7646-85-7	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
dimethylzinc	030-004-00-8	208-884-1	544-97-8	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
diethylzinc	030-004-00-8	209-161-3	557-20-0	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
zinc oxide	030-013-00-7	215-222-5	1314-13-2	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
benzothiazole-2-thiol	613-108-00-3	205-736-8	149-30-4	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
+ 9 compounds with the same classification (Aquatic Acute/Chronic 1 H400 /H410)					
mancozeb (ISO) manganese ethylenebis(dithiocarbamate) (polymeric) complex with zinc salt	006-076-00-1	-	8018-01-7	Aquatic Acute 1 H400	10
propineb (ISO) polymeric zinc propylenebis(dithiocarbamate)	006-091-00-3	-	9016-72-2	Aquatic Acute 1 H400	-
diamminediisocyanatozinc	030-005-00-3	401-610-3	-	Aquatic Acute 1 H400	-
vanadium(IV) oxide hydrogen phosphate hemihydrate, lithium, zinc, molybdenum, iron and chlorine-doped	015-162-00-8	407-350-7	-	Aquatic Chronic 2 H411	-
zinc 2-hydroxy-5-C13-18alkylbenzoate	607-183-00-1	402-280-3	-	Aquatic Chronic 2 H411	-
+ 9 compounds with the same classification (Aquatic Chronic 2 H411)					
aluminium-magnesium-zinc-carbonate-hydroxide	030-012-00-1	423-570-6	169314-88-9	Aquatic Chronic 4 H413	-
zinc salts, fatty acids, C16-18 and C18 unsaturated, branched and linear	607-692-00-9	446-470-4	-	Aquatic Chronic 4 H413	-

Worst cases

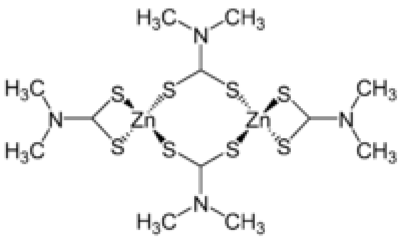
Presence of zinc phosphide in waste is questionable

Example of worst case consideration

Harmonised classification for zinc compounds

Worst case consideration: two compounds (H400, H410, M factor = 100)

- Zinc phosphide (rodenticide) (Zn_3P_2)
- Ziram (fungicide, complex organic compound)



Presence in waste is questionnable (examples)

- Ziram
  - *In case of incineration, ziram is degraded into elemental compounds*
  - *In soil, ziram seems to be rapidely degraded (half-life = 2-7 days)*
- Zinc phosphide
  - *In dry soils, zinc phosphide was reported to dissipate with a half-lives of one month or longer; in moist soils dissipation half-lives were less than one week*
  - *Zinc phosphide would may be hydrolysed (rate of hydrolysis is dependent on the pH)*

Selection of worst case could be difficult and could have a significant impact on waste classification

Second choice for worst case ➔ zinc oxide (M factor = 1)

Overview of the four calculation methods

Method 1	Method 2
IF: $c\,(H420) \geq 0.1\%$ OR $\Sigma\, c(H400) \geq 25\,\%$ OR $(100 \times \Sigma c\ H410) + (10 \times \Sigma c\ H411) + (\Sigma c\ H412) \geq 25\%$ OR $\Sigma\, c\ H410 + \Sigma\, c\ H411 + \Sigma\, c\ H412 + \Sigma\, c\ H413 \geq 25\,\%$ → waste hazardous	IF: $c\,(H420) \geq 0.1\%$ OR If $c\,(H400) \geq 0.1/M\%$ and $\Sigma\,(c\ H400 \times M) \geq 25\,\%$ OR If $c\,(H410) \geq 0.1/M\%$ and $c\,(H411) \geq 1\%$ and $\Sigma\,(M \times 10 \times c\ H410) + \Sigma\, c\ H411 \geq 25\%$ → waste hazardous
Method 3 IF: $c\,(H420) \geq 0.1\%$ OR $\Sigma\,(c\ H410) \geq 0.1\,\%$ OR $\Sigma\,(c\ H411) \geq 2.5\,\%$ OR $\Sigma\,(c\ H412) \geq 25\,\%$ OR $\Sigma\,(c\ H413) \geq 25\,\%$ → waste hazardous	**Method 4** IF: $c\,(H420) \geq 0.1\%$ OR $\Sigma\,(c\ H410) \geq 2.5/M\,\%$ OR $\Sigma\,(c\ H411) \geq 2.5\,\%$ → waste hazardous

- **Method 3 and 4 :**
  Acute category 1 (H400) classification not considered
- **Method 2 and 4 :**
  Chronic category 3 and 4 (H412/H413) not considered
  Only method that allows M factor consideration: usually the most severe in case of factor M availability

Overview of the four calculation methods

Cut-off values comparison

Concentrations required to consider the waste as hazardous (assumption that M factor = 1)

Hazard statement	Cut –off values			
	Method 1	Method 2	Method 3	Method 4
H420	0.1 %	0.1 %	0.1 %	0.1 %
H400	25 %	25 %	NC	NC
H410	0.25 %	COMBINED HAZARD	0.1 %	**2.5 %**
H411	2.5 %	COMBINED HAZARD	2.5 %	**25 %**
H412	25 %	NC	25 %	NC
H413	25 %	NC	25 %	NC

NC: Not considered

COMBINED HAZARD: $\sum c(H410) \geq 0.1\ \%$ ***AND*** $\sum c(H411) \geq 1\ \%$ ***AND*** $\sum (10 \times c(H410)) + \sum c(H411) \geq 25\%$

Example of calculation according to the 4 methods (German Ring test results)

Bottom ash from municipal waste (19 01 11* / 19 01 12)

Element	Concentration	Worst case selection	Classification	M factor
Cd	6.6 mg/kg	cadmium (pyrophoric)	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
As	7.4 mg/kg	arsenic	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
Co	19 mg/kg	cobalt sulfate	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	10
Cr	212 mg/kg	sodium chromate	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
Cu	6,500 mg/kg	copper chloride copper (I) chloride	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
Hg	37 mg/kg	mercury	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
Mn	800 mg/kg	potassium permanganate	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
Ni	211 mg/kg	nickel sulfate	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
Pb	1,623 mg/kg	Lead sulphate	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
V	42 mg/kg	divanadium pentaoxide vanadium pentoxide	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-
Zn	2,639 mg/kg	trizinc diphosphide zinc phosphide	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	100

➔ ***relevance of the presence of zinc phosphide in the waste (M factor = 100) ?***

Example of calculation according to the 4 methods (German Ring test results)

Different concentration according to the consideration of element/compound

Compound	Worst case selection	% w/w (element)	% w/w (compound)
Cd	cadmium	0.0007%	-
As	arsenic	0.0007%	-
Co	cobalt sulfate	0.0019%	0.005%
Cr	sodium chromate	0.0212%	0.066%
Cu	copper chloride copper (I) chloride	0.6500%	1.377%
Hg	mercury	0.0037%	-
Mn	potassium permanganate	0.0800%	0.230%
Ni	nickel sulfate	0.0211%	0.055%
Pb	lead sulphate	0.1623%	0.237%
V	divanadium pentaoxide vanadium pentoxide	0.0042%	0.007%
Zn	trizinc diphosphide zinc phosphide	0.2639%	0.347%

unknown fraction of waste ≈ 97.7 % w/w

Example of calculation according to the 4 methods (German Ring test results)

Calculation based on % w/w (compound)

METHOD 1

∑ c(H400) ≥ 25 %	OR	[100 x ∑ c(H410)] + [10 x ∑ c(H411)] ≥ 25 %
2,3459%		**234,59%**

METHOD 2

∑ c(H400) ≥ 0.1/M %	AND	∑ c(H400) x M ≥ 25 %
zinc phosphide ≥ 0.001 %		**36,75%**

METHOD 3

∑ c(H410) ≥ 0.1 %
2,35%

METHOD 4

∑ c(H410) ≥ 2.5/M %
zinc phosphide ≥ 0.025 %

→ Hazardous waste

Example of calculation according to the 4 methods (German Ring test results)

Calculation based on % w/w (compound)

METHOD 1

∑ c(H400) ≥ 25 %	OR	[100 x ∑ c(H410)] + [10 x ∑ c(H411)] ≥ 25 %
2,3274%		**232,74%**

METHOD 2

∑ c(H400) ≥ 0.1/M %	AND	∑ c(H400) x M ≥ 25 %
23.7 > 1		2,37%

METHOD 3

∑ c(H410) ≥ 0.1 %
2,33%

METHOD 4

∑ c(H410) ≥ 2.5/M %
0.95 < 1

With zinc oxide consideration (M factor = 1)

Method 1 & 3

↓

Hazardous waste

Example of calculation according to the 4 methods (UK EAHW, Hazardous Waste, 2013)

Soil and stones (17 05 03* / 17 05 04)

Compound	Concentration	Worst case selection‡	Classification	M factor	% w/w (compound)
Cyanide (total)	320 mg/kg	sodium cyanide	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-	0.06%
Arsenic	530 mg/kg	diarsenic trioxide	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-	0.07%
Cadmium	782 mg/kg	cadmium carbonate	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-	0.12%
Copper	400 mg/kg	copper(I) oxide	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-	0.05%
Lead	1,620 mg/kg	lead sulphate	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-	0.24%
Nickel	297 mg/kg	nickel carbonate	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-	0.06%
Zinc	1,446 mg/kg	zinc oxide	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-	0.18%
Benzo[a]pyrene	0.23 mg/kg	-	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-	0.00002%

unknown fraction of waste ≈ 99.2 % w/w

Asbestos, Antimony, barium, Hexavalent chromium, Mercury, Molybdenum, PCBs, Selenium were analyzed for but not detected in this sample

*‡ worst case selected by UK EAHW. Same classification priority as worst case selected for bottom ash example, except for zinc ➔ **relevance of the presence of zinc phosphide in the waste ?***

Example of calculation according to the 4 methods (UK EAHW, Hazardous Waste, 2013)

Soil and stones (17 05 03* / 17 05 04)

% w/w (compound)

METHOD 1

∑ c(H400) ≥ 25 %	OR	[100 x ∑ c(H410)] + [10 x ∑ c(H411)] ≥ 25 %
0,77%		**77,24%**

METHOD 2

∑ c(H400) ≥ 0.1/M %		∑ c(H400) x M ≥ 25 %
7.71 > 1	AND	0.77 % < 25 %

METHOD 3

∑ c(H410) ≥ 0.1 %
0.77 % > 0.1 %

METHOD 4

∑ c(H410) ≥ 2.5/M %
0.31 < 1

Method 1 & 3

↓

Hazardous waste

Example of calculation according to the 4 methods (German ring test results)

Soil and stones (17 05 03* / 17 05 04)

Compound	CAS	Classification	M-factor	Concentration (mg/kg)	Concentration (% w/w)
Naphthalene	91-20-3	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-	n.d.	n.d.
Acenaphthylene	208-96-8	NC*	-	n.d.	n.d.
Acenaphthene	83-32-9	Aquatic Acute 1 H400* Aquatic Chronic 1 H410*	-	7.18	0.0007%
Fluorene	86-73-7	Aquatic Acute 1 H400* Aquatic Chronic 1 H410*	-	4.16	0.0004%
Phenanthrene	85-01-8	Aquatic Acute 1 H400* Aquatic Chronic 1 H410*	1*	69.1	0.0069%
Anthracene	120-12-7	Aquatic Acute 1 H400* Aquatic Chronic 1 H410*	-	23.4	0.0023%
Fluoranthene	206-44-0	Aquatic Acute 1 H400* Aquatic Chronic 1 H410*	-	181.6	0.0182%
Pyrene	129-00-0	Aquatic Acute 1 H400* Aquatic Chronic 1 H410*	10*	146	0.0146%
Benz[a]anthracene	56-55-3	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	100	87.2	0.0087%
Chrysene	218-01-9	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-	69.4	0.0069%
Benzo[b]fluoranthene	205-99-2	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-	78.6	0.0079%
Benzo[k]fluoranthene	207-08-9	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-	31	0.0031%
Benzo[a]pyrene	50-32-8	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	-	59	0.0059%
Dibenz[ah]anthracene	53-70-3	Aquatic Acute 1 H400 Aquatic Chronic 1 H410	100	9.37	0.0009%
Benzo[ghi]perylene	191-24-2	Aquatic Acute 1 H400* Aquatic Chronic 1 H410*	-	34.7	0.0035%
Indeno[1,2,3-cd]pyrene	193-39-5	NC*	-	35.2	0.0035%

n.d. : not determined
NC : Not classified for environmental hazard (according to notified classification)
***** : according to notified classification

unknown fraction of waste ≈ 99.9 % w/w

Example of calculation according to the 4 methods (German Ring test results)

Soil and stones (17 05 03* / 17 05 04)

METHOD 1

∑ c(H400) ≥ 25 %	OR	[100 x ∑ c(H410)] + [10 x ∑ c(H411)] ≥ 25 %
0,08%		8,01%

METHOD 2

∑ c(H400) ≥ 0.1/M %	AND	∑ c(H400) x M ≥ 25 %
Benz[a]anthracene > 0.001 %		1.17 % < 25 %

METHOD 3

∑ c(H410) ≥ 0.1 %
0.08 % < 0.1 %

METHOD 4

∑ c(H410) ≥ 2.5/M %
0.47 < 1

Non-hazardous waste
(but only PAH data available)

Overview of calculation results for characterisation data available (17 05 03* / 17 05 04)

17 05 03* / 17 05 04 - Soil and stones

Source of characterisation data	Result for Method 1	Result for Method 2	Result for Method 3	Result for Method 4	Presence of compounds with M factor
Ring test (Germany)	Non hazardous	Non hazardous	Non hazardous	Non hazardous	Yes
Waste Classification Report (HazWasteOnline)	Non hazardous	Non hazardous	Hazardous	Non hazardous	Yes
EAHW, Hazardous Waste (united Kingdom)	Hazardous	Non hazardous	Hazardous	Non hazardous	No
Publication Gudrun M., et al (2000) Soil contaminated with mineral oil (LMKW1)	Non hazardous	Non hazardous	Hazardous	Non hazardous	Generic entries like "sum of PAH" or "sum of nitroaromatics" don't allowed M factor identification
Publication Gudrun M., et al (2000) Soil contaminated with mineral oil (SPMKW1)	Non hazardous	Non hazardous	Hazardous	Non hazardous	
Publication Gudrun M., et al (2000) Soil containing nitroaromatics, PAH and heavy metals (HTNT1)	Hazardous	Non hazardous	Hazardous	Non hazardous	
Publication Gudrun M., et al (2000) Soil containing nitroaromatics (CTNT1a)	Non hazardous	Non hazardous	Hazardous	Non hazardous	
Publication Gudrun M., et al (2000) Soil contaminated with PAH and chromium (SPAK1a)	Hazardous	Non hazardous	Hazardous	Non hazardous	
Publication Gudrun M., et al (2000) Soil containing heavy metals (R1)	Hazardous	Non hazardous	Hazardous	Non hazardous	
Publication Koci V., et al (2010) Soil contaminated with PAH and inorganic salts	Hazardous	Non hazardous	Hazardous	Non hazardous	Yes but generic entry "sum of PAH" doesn't allowed M factor identification

- Classification of waste as hazardous with method 3 is related to the consideration of Acute Toxicity category 1 (H410) and the low cut-off value (0.1 %)
- For method 1, for some characterisation data, results could be very close to the cut-off value of 0.25 %

Key aspects for discussion

- **Several limitation according to characterization data = possible underestimation of waste classification**
  - *Data on organic compounds rarely available*
  - *Data for a group of compounds (e.g. sum of PAH compounds, nitroaromatic compounds,…): difficulties for worst case consideration*
  - *A significant fraction of the waste could be not identified (≈ 95 to 99.9 % w/w)*
  - *Several compounds didn't have harmonised classification and/or M factor determination*

- **Importance of the worst case selection**
  - *Identification of worst case according to:*
    - *Harmonised classification (including M factor)*
    - *Molar mass*

Difficulties associated to the relevance of worst case in waste considered (e.g. zinc phosphide)

- **Availability of waste code essential for comparison**

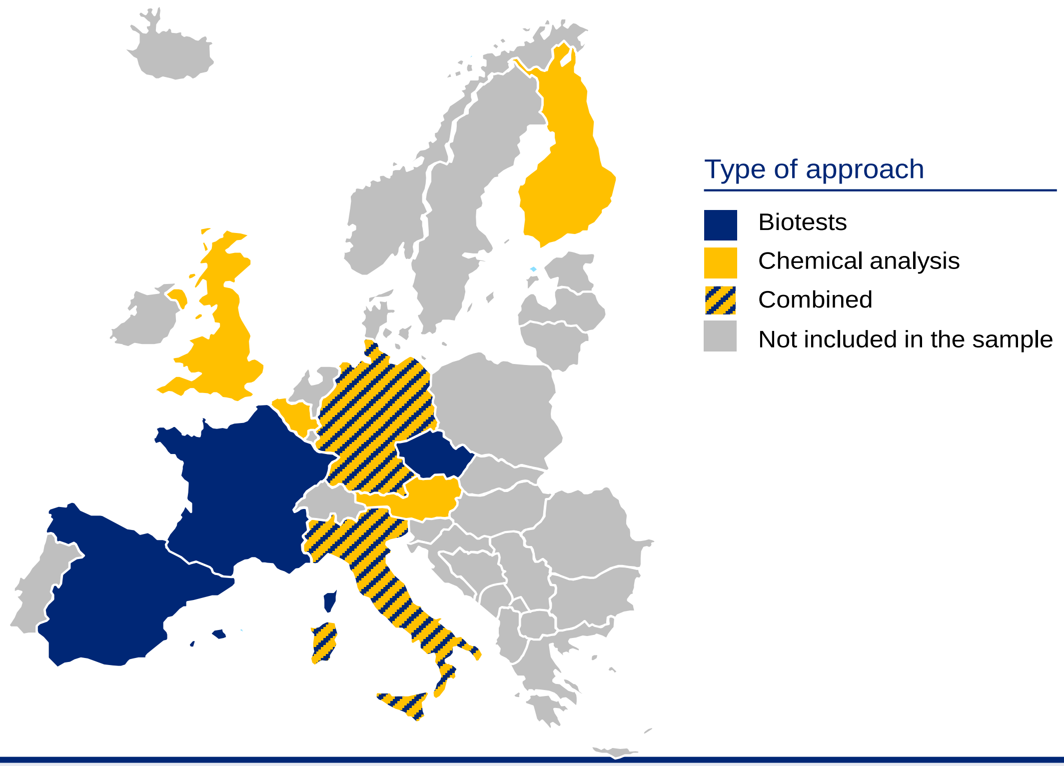
Discussion

Part IV

Possible combination of chemical analysis and biotests?

Reminder

Approaches for the assessment of HP 14 in the nine studied Member States



Germany and Italy are the only Member States proposing a combined approach

Reminder

Batteries of tests used in Member States

Member State	Aquatic tests: Organism	Aquatic tests: Standard	Terrestrial tests: Organism	Terrestrial tests: Standard
Czech Republic	*Daphnia magna* *Sinapis alba* *Desmodesmus subspicatus* *Poecilia reticulata*	ISO 6341 Czech guidelines ISO 8692 ISO 7346-2	None	
France (initial strategy)[1]	*Daphnia magna (acute)* *Vibrio fischeri* *Pseudokirchneriella subcapitata* *Ceriodaphnia dubia* *Brachionus calyciflorus*	ISO 6341 *ISO 11348-3* NF EN ISO 8692 NF ISO 20665 NF ISO 20666	*E. fetida (acute)* *Lactuca sativa*	*ISO 11 268-1* *ISO 11269-2*
France (hybrid strategy combining initial strategy and German strategy)	*Daphnia magna (acute)* *Vibrio fischeri* *Pseudokirchneriella subcapitata*	ISO 6341 *ISO 11348-3* *NF EN ISO 8692*	*E. fetida (avoidance)* *Avena sativa / Brassica rapa* *Arthrobacter globiformis*	*ISO 17512-1* *ISO 11269-2* *ISO/DIS 18187*

Member State	Aquatic tests: Organism	Aquatic tests: Standard	Terrestrial tests: Organism	Terrestrial tests: Standard
Spain	*Vibrio fischeri* *Daphnia magna*	*ISO 11348* ISO 6341	None	
Germany	*Daphnia magna (acute)* *Daphnia magna (chronic)* *Vibrio fischeri* *Pseudokirchneriella subcapitata / Desmodesmus subspicatus* *Lemna minor*	ISO 6341 ISO 10706 *ISO 11348-1/2/3* *NF EN ISO 8692* *ISO 20079*	*E. fetida* *E. fetida (chronic)* *Brassica rapa* *Arthrobacter globiformis* *Folsomia candida (chronic)*	ISO 17512-1 ISO 12 268-1 *ISO 11269-2* ISO/DIS 18187 *ISO 11267*
Italy	*Daphnia magna (acute)* *Vibrio fischeri* *Pseudokirchneriella subcapitata and Desmodesmus subspicatus*	ISO 6341 *ISO 11348* *ISO 8692*	None	

Invertebrate
Plant
Micro-organisms

Algae
Fish
} Acute and chronic endpoints

Available data for both biotests and characterisation on the selected pairs

Waste code	Description	Data (sample)	
		Waste code mentionned	Probable waste code
06 05 02* / 06 05 03	sludges from on-site effluent treatment	1	-
08 01 13* / 08 01 14	sludges from paint or varnish	2	-
11 01 09* / 11 01 10	sludges and filter cakes	1	-
12 01 14* / 12 01 15	machining sludges	2	-
17 05 03* / 17 05 04	soil and stones	3	6
19 01 11* / 19 01 12	bottom ash and slag	18	9
19 01 13* / 19 01 14	fly ash	7	-
19 08 11* / 19 08 12	sludges from biological treatment of industrial waste water	3	1
19 08 13* / 19 08 14	sludges from other treatment of industrial waste water	1	-
19 10 03* / 19 10 04	fluff-light fraction and dust	1	-
19 12 11* / 19 12 12	other wastes (including mixtures of materials) from mechanical treatment of waste	1	-
		40	16

Test battery and proposed threshold values considered to classify wastes

Test	Proposal of threshold values	Duration	Standard
Inhibition of the mobility of *Daphnia magna* (**Dap**)	EC50 ≤ 10%	48 h	ISO 6341
Inhibition of the light emission of *Vibrio fischeri* (Luminescent bacteria test) (**Vib**)	EC50 ≤ 10%	30 min	ISO 11348-3
Fresh water algal growth inhibition test with unicellular green algae (**Alg**)	EC50 ≤ 10%	72 h	ISO 8692
Solid contact test using the dehydrogenase activity of *Arthrobacter globiformis* (**Art**)	EC50 ≤ 10%	2 h	ISO/DIS 18187
Effects on the emergence and early growth of higher plants (*Avena sativa*, *Brassica napus*) (**Ave, Bra**)	EC50 ≤ 10%	14 d	ISO 11269-2
Avoidance test with earthworms (*Eisenia andrei/fetida*) (**Ear**)	EC50 ≤ 10%	48 h	ISO 17512-1

Comparison of waste classification according to chemical composition and experimental approach

Waste	Waste Code	Chemical approach				Experimental approach						
						Aquatic tests			Terrestrial tests			
		M 1	M 2	M 3	M 4	Dap	Vib	Alg	Arthr.	Ave	Bra	Ear
Soil contaminated with heavy metals	17 05 03* / 17 05 04	HW	HW	HW	HW	NH	HW	HW	HW	HW	NH	NH
PAH contaminated soil	17 05 03* / 17 05 04	NH	NH	NH	NH	NH	NH	NH	NH	NH	NH	NH
Bottom ash #1	19 01 11* / 19 01 12	HW	HW	HW	HW	HW	NH	HW	HW	NH	NH	HW
Bottom ash #2	19 01 11* / 19 01 12	NH	NH	HW	NH	NH	NH	NH	NH	NH	NH	HW
Bottom ash #3	19 01 11* / 19 01 12	HW	NH	HW	NH	HW	HW	NH	NH	NH	NH	NH
Fly ash	19 01 13* / 19 01 14	HW	HW	HW	NH	HW	NH	NH	HW	HW	HW	HW

- **Result obtained from battery of aquatic and battery of terrestrial tests are generally consistent (except for bottom ash #2)**
- **Given to the specificity of each test, combination of tests is mandatory to obtain a relevant answer**
- **Method 3 is the only one method consistent with experimental approach**

→ *Preliminary results for 6 wastes (further results are needed, work in progress)*

Possible combination of chemical and experimental approaches?

- **According to CLP rules**

The approach for classification of aquatic environmental hazards is tiered, and is dependent upon the type of information available for the mixture itself and for its components. Elements of the tiered approach include:

- ✓ *classification based on tested mixtures;*
- ✓ *classification based on bridging principles;*
- ✓ *the use of 'summation of classified components' and/or an 'additivity formula'*.

- **Alternative approach**

- ✓ Step 1: summation method
- ✓ Step 2 : experimental approach (if waste is not classified according to step 1)

  If the composition of the waste is unknown or complex, biotests are applied. The testing strategy includes a test battery with terrestrial and aquatic tests

Debate and wrap up

Thank you for your attention.

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