Contribution of France to the « Study to asses the impacts of different classification approaches for hazard property « H14 » on selected waste streams »

SUMMARY

The Member States of the European Union have in 2014 updated the list of waste and defined the 15 hazard properties (HP) of wastes except for HP14 'Ecotoxic'. Four calculation methods for HP 14 are assessed till June 2015 in a Call for Tenders of the Directorate General of the Environment of the European Commission. The comparison of these 4 calculation methods uses only "mirror entries" of the European List of Waste (LoW).

This paper is a contribution of France to the assessment of these 4 calculation methods, with the presentation of results of a 5th one, which corresponds to method 2 using "extended M-factors". A data set of 25 absolute samples[1] from different origin (16 "absolute" hazardous (H) and 9 "absolute" non-hazardous (NH) by LoW) is used to complete the comparison based on "mirrors entries" of the LoW. These 16 hazardous wastes studied here are supposed to be hazardous especially for the hazardous property HP14.

The result of the classification results allow to forward a relative ranking of the methods by the frequency of classification as H. **The ranking is method 3 > method 1 > method 2 with extended M-factors > method 2 > method 4.** The same ranking can be obtained by a simple arithmetic comparison of concentrations limits when Mchronic = 10 (Table 1).

Method 2 with extensive M-factors matches best with the European list of waste (80% concordant H and non-H by LoW, and 13% discordant for H waste by LoW). **It classifies safely waste containing substances with high ecotoxicity**. **Methods 1 and 3 have nearly as good matching** (76% and 72%) concordant H and non-H by LoW, and 13% and 6% respectively discordant for H waste by LoW). Method 2 with M-factors limited to the M-factors published in the CLP has insufficient concordance (64% concordant H and non-H by LoW, and 50% discordant for H waste by LoW). As the same method with extended M-factors gives the best performance, the lower performance is due to the limitation of the M-factor. Method 4 is divergent (60% concordant H and non-H by LoW, and 56% discordant for H waste by LoW).

Usually, methods 2 and 4 don't classify many hazardous wastes by the LoW in the data set. The experimental approach shows that calculation **methods 1, 3, and 2 with extended M factors have a good concordance with biotest results.**

1. INTRODUCTION

The Member States of the European Union have in 2014 updated the list of waste (EC 2014a) and defined the 15 hazard properties (HP) of wastes (EC 2014b) except for HP14 'Ecotoxic'. This hazard property is the most frequent classifying property for waste (Hennebert et al 2014) if the Classification, Labelling and Packaging of Preparation and Mixtures calculation method (CLP Regulation 2008), limited to two levels of chronic ecotoxicity, but including extended M-factors, is used.

Four calculation methods are assessed till June 2015 in a Call for Tenders of the Directorate General of the Environment of the European Commission (DG ENVIRONMENT 2014). They differ by the hazard statement codes, the concentration limits, and the use of M-factors. The assessment is focused on so-called "mirror entries" in the European List of Waste (LoW), that is waste that can be either hazardous or non-hazardous, and that must be assessed for their hazard properties by chemical composition or by tests.

This paper is a contribution to the assessment of these 4 calculation methods, with the presentation of results of a 5th one, using "extended M-factors".

M-factors calculated from reviewed EC50 and NOEC of a broader range of mineral and organic substances, including substances important in waste, like polycyclic aromatic carbons (PAH). Using "absolute entries" instead of "mirrors entries" of the LoW as a reference, the different classification methods by calculation can be ranked for matching with the LoW classification.

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1 It is not all absolute entries as listed in the LoW ; some mirrors entries have also been integrated, and a positioning in one of the entries was performed from knowledge of the waste.

2. ISSUES OF THE CALCULATION METHODS

2.1 Calculation methods considered for HP 14

The different calculation methods (named Method 1 to 4) in the Call for Tenders are:

- Method 1 :
  Σ c H400 ≥ 25 %, or (100 x Σc H410) + (10 x Σc H411) + (Σc H412) ≥ 25 %, or
  Σ c H410 + Σ c H411 + Σ c H412 + Σ c H413 ≥ 25 %
- Method 2 :
  Σ (c H400 × M) ≥ 25 %, or Σ (M × 10 × c H410) + Σ c H411 ≥ 25 %
  The cut-off value for consideration in an assessment for Aquatic Acute 1 and Aquatic Chronic 1 is 0.1/M %; and for Aquatic Chronic 2 is 1%. The M-factors will be determined as follows:
  For substances for which M-factors have been established in Table 3.1, Annex VI of the CLP Regulation, those multiplying factors shall apply. For substances for which no M-factors have been established in Annex VI, a multiplying factor M = 1 shall apply.
- Method 3 :
  Σ c H410 ≥ 0.1 %, or Σ c H411 ≥ 2.5 %, or Σ c H412 ≥ 25 %, or Σ c H413 ≥ 25 %
- Method 4 :
  Σ (M × c H410) ≥ 2.5 %, or Σ c H411 ≥ 25 %
  The M-factors will be determined as Method 2.

2.2 Speciation of mineral elements to mineral substances for calculation

Classification by chemical composition depends in waste on hypothesis of speciation of elemental concentrations into mineral chemical substances. The chemical classification is hampered in routine by this question. Where the CLP regulation is mainly focused on chemicals and formulations consisting of pure substances and mixtures of pure substances, the waste regulation covers a wide range of materials which are poorly defined in terms of the chemical form of the substances they contain. Lack of information on the chemical form of substances (speciation) could lead to the use of “worst case” hypothesis, a poor surrogate for hazardousness, and a possible delisting as hazardous (Hennebert and Weltens 2014). A presentation of the different available methods with a step-wise method (depending on the concentration of the element) can be found in AFNOR FD X30-494 (2015) and in an Annex of Hennebert and Rebishung (2015).
A first step to avoid expensive speciation work is to use “worst case with information” calculations, for instance to suppose that the element is in the most hazardous form in the waste, and that can realistically be present in the waste. “Simple” substances with one ecotoxic element are used rather than more complex substances (for instance sodium chromate instead of lead chromate). List of such substances can be found for all HPs in Hennebert and Rebischung (2015).

2.3 M-factors

For easier comparison, the calculation methods are presented in the left part of Table 4. For each method, each rule of classification is written as a column in the Table. To assess HP 14, each concentration of a substance with the hazard statement code must be divided by concentration limit specified in the table, and the ratios mut be summed. The sum of these ratios is a hazard index. If it is ≥ 1, the waste is hazardous for this rule of classification. If it is <1, the waste is considered as non-hazardous for that rule.
We have used also a fifth method (named Method 2 with extended M-factors). The limitation of hazard assessment to chronic ecotoxicity of level 1 and 2 (not taking into account level 3 of CLP regulation – level 4 is presented as a “safety net” in the CLP regulation) for waste is argued by an impact assessment (Hennebert and Rebishung 2012). Another reason is that there is only one final level of hazard for waste (Hazardous) but there are 4 levels of hazard for products (Ecotoxic acute, Ecotoxic chronic level 1, 2, 3). This method is used in France since 2012.

In the CLP regulation, multiplying factors of the concentrations of the substances that produce biological effects in tests at concentration < 1 mg/L are used to calculate the hazard for aquatic environment. The Table 3.1 of Annex VI of the CLP regulation has a (restricted) list of M-factors. The M-factors should be calculated for each substance for acute toxicity (depending on the concentration having 50% of biological effect EC50 if < 1 mg/L, < 0.1 mg/L, < 0.01 mg/L, …) and for chronic ecotoxicity (depending on the concentration with no observed effect NOEC if < 0.1 mg/L, < 0.01 mg/L, < 0.001 mg/L, …) (CLP regulation 2008 ATP 02). Tables of extended M-factors can be found in Hennebert and Rebischung (2013, updated in 2015).

3. ARITHMETIC COMPARISON OF THE CALCULATION METHODS FOR HP 14

To give an insight about the proposition of DG Environment and the proposition of a fifth method, the five calculation methods can temptatively be classified by increasing concentration limit, taking into account the following observations:

a. A waste classified for acute ecotoxicity is always classified for chronic ecotoxic (empirical results not shown for this set of data, other data in Hennebert et al. 2014). The reverse is not true. That statement could not be verified if the waste contains hazardous degradable substances that can have a acute M-factor greater than a chronic M-factor. This is for instance the case for some PAH: benzo[k]fluoranthene, Macute = 100, Mchronic = 10; anthracene, 100 and 10 respectively; fluoranthene, 100 and 10; pyrene, 10 and 10; phenanthrene, 10 and 1). Excepted for these cases, the comparison of methods may therefore be limited to chronic ecotoxicity;

b. References to hazard statement code (HSC) H412 and H413 do not play a practical role in the classification of waste, because the cumulative concentrations must achieve 25% and such concentrations are unlikely to be present in the waste. The substances with these hazard statements codes (H412: 431 substances, and H431: 254 substances) in Table 3.1 of Annex VI CLP regulation are mainly for H412 synthetic organic chemicals, and the minerals tin chloride and powdered nickel (excluding rare substances), and for H413 elements and substances containing Ni, Co, Se, U, Tl and cadmium sulfide. With 25% cumulative concentration, these materials will not be a priori material that the holder wishes to discard, but rather a resource which he will seek to use due to their technical or commercial value. Comparing methods can therefore be confined to the limits of concentration of H410 and H411 substances;

c. The arithmetic ranking concentration limits of the 5 calculation methods for chronic ecotoxicity H410 and H411 depends on the value of chronic M-factor.
If a mean chronic M is hypothetized, and if that M factor is in the CLP regulation Annex VI, a classification by increasing concentration limit can be set (Table 1). The exact classification will depend on the presence of substances with chronic M-factor > 10. The rank of Methods 2 and 4 can in that case move forward.

Table 1: Arithmetic comparison of 5 classification methods for HP 14 by calculation, with hypothesis that mean chronic M-factor = 10 (concentration limits for H410 and H411 substances).

Method 3	Method 1	Method 2 with ext. M-factors ($M_{chronic}$=10)	Method 2 with CLP M-factors ($M_{chronic}$=10)	Method 4 ($M_{chronic}$=10)
0.1%	0.25% + 2.5%	2.5/M% + 25%	2.5/M% + 25%	2.5/M% or 25%

d. For hazardous elements and substances, the Annex VI of CLP regulation contains only M-factors for pesticides and nickel substances. For other elements and substances, and mixtures of them, the producer must provide ecotoxicological data and self-classification (including M-factors) to register its product in the REACH repository. Reviewed tables of M-factors are given in this paper. A comparison of concentration limits for heavy metals and PAHs (frequently encountered in waste) with or without M-factors is given in Table 2.

Table 2: Comparison of 5 classification methods for HP 14 by calculation for hazardous elements and substances (heavy metals, PAHs, M ≥ 10, extended M-factors)

<table>
<tr><td>Elements/substances</td><td>M_{acute}-factor (not in CLP Annex VI)</td><td>$M_{chronic}$-factor (not in CLP Annex VI)</td><td colspan="5">Concentration limits (lowest sum of substances with H400 or sum of substances with H410 hazard statement code)</td></tr>
<tr><td></td><td></td><td></td><td>Method 3</td><td>Method 1</td><td>Method 2</td><td>Method 4</td><td>Method 2 with extended M-factors</td></tr>
<tr><td>Hg (worst case)</td><td>1000</td><td>100</td><td rowspan="6">0.1%</td><td rowspan="6">0.25%</td><td rowspan="6">2.5%</td><td rowspan="6">2.5%</td><td>0.025%</td></tr>
<tr><td>Cd (worst case)</td><td>100</td><td>100</td><td>0.025%</td></tr>
<tr><td>As, Co, Cr(VI), Cu, Pb, Zn (worst case)</td><td>10</td><td>10</td><td>0.25%</td></tr>
<tr><td>Benzo[k]fluoranthene, anthracene, fluoranthene</td><td>100</td><td>10</td><td>0.25%</td></tr>
<tr><td>Pyrene</td><td>10</td><td>10</td><td>0.25%</td></tr>
<tr><td>Benz[a]anthracene</td><td>100</td><td>1</td><td>0.25%</td></tr>
</table>

If one waste contains As, Co, Cr(VI), Cu, Pb, Zn and PAHs, the ranking of the methods will be (from most severe to less severe): method 3 > method 1 = method 2 with extended M-factors > method 2 > method 4.

If one waste contains in addition significant concentrations of Hg and Cd, the ranking of the methods will be: method 2 with extended M-factors > method 3 > method 1 > method 2 > method 4.

4. RESULTS OF THE CLASSIFICATION BY THE 5 CALCULATION METHODS AND BIOTESTS

The set of 25 samples studied comes from different origin was used (Table 3). Most of them have been analysed according to AFNOR XP X30-489 “Determination of elements and substances in waste”. That method is discussed as a European standardization Work Item submitted to formal vote (CEN/TC 292 2015). The method gives a full knowledge of the waste to be characterized and classified. The results can be used for waste hazard classification, Seveso classification, transport regulation, and occupational health and safety requirements. Please be aware that hazard classification with uncomplete analytical data is misleading.

The analytical mass balances (sum of all measured concentrations) were > 90%. Some of these wastes have been presented in Hennebert et al. (2013). When a concentration of a substance is below its limit of quantification (LOQ), the LOQ has been used as the concentration. The concentrations are expressed on dry matter for solid waste and on raw mass (including water) for liquid waste. The hazard indexes can be expressed on dry matter or on raw mass by simple conversion with the moisture content.

The LoW is taken in the comparison methodology as a reference method. This implies that the wastes used here are classified as hazardous for HP 14 in the LoW. However, in practice, this can not be established with absolute certainty but it is supposed considering of the typology of the 16 hazardous wastes studied.
The concordance for one calculation method is established by the number of waste with identical classification by the considered calculation method and the LoW (H/H, NH/NH). The discordance is established as well, and the case where the waste is classified “H” in the LoW and “NH” by calculation (under-estimation of the hazard) will be considered.

The 25 results are presented at Table 3, ordered by method with decreasing matching with the Low. The correspondence score are presented at Table 4, and a synthesis at Table 5.

Table 3: Classification of the classification of 25 wastes by assigned code of the LoW and by 5 calculation methods and biotests (H = hazardous, NH = non-Hazardous, noting = not evaluate)

N	Waste	LoW code[2]	LoW	M3	M1	M2 +ext. M	M2	M4	biotests[3]
1	Municipal Solid Waste Incinerator (MSWI) fly ash	19 01 05*	H	H	H	H	H	H	
2	Air Pollution Control (APC) residue industrial waste	19 01 07*	H	H	H	H	H	H	
3	Industrial waste bottom ash	19 01 11*	H	H	H	H	H	H	
4	Packages and materials	19 12 11*	H	H	H	H	H	H	H
5	Hydrocarbon	13 07 03*	H	H	H	H	H	H	H
6	Sulfidic acid mine residue Pb Zn Cd	01 03 04*	H	H	H	H	H	H	H
7	Solid wastes from gas treatment	19 01 07*	H	H	H	H	H	H	H
8	APC residue from animal meal incineration	19 01 07*	H	H	H	H	H	NH	H
9	Wastes from transport tank cleaning, mixed sludge of food and chemical transport	16 07 09*	H	H	H	H	NH	NH	
10	MSWI Air pollution control residue, bicarbonate process	19 01 07*	H	H	H	H	NH	NH	
11	MSWI APC residue, lime process	19 01 07*	H	H	H	H	NH	NH	H
12	APC residue from municipal waste after solid fuel, metals and organic matter separation	19 01 07*	H	H	H	H	NH	NH	H
13	Treated wood containing hazardous substances	17 02 04*	H	H	H	H	NH	NH	H
14	Acid-generating tailings from processing of sulphide ore	01 03 04*	H	H	H	H	NH	NH	H
15	Metallic dust from aluminum industry	10 03 19 *	H	H	NH	NH	NH	NH	H
16	Waste from physical and chemical processing of metalliferous minerals Cu Zn	01 03 07*	H	NH	NH	NH	NH	NH	H
17	Municipal waste - Organic fraction separately collected	20 01 08 or 20 02 01	NH	NH	NH	NH	NH	NH	
18	Bauxite residue	01 03 09	NH	NH	NH	NH	NH	NH	H
19	Demolition concrete	17 01 01	NH	NH	NH	NH	NH	NH	H
20	Compost from mixed municipal waste, fraction < 30 mm after crushing	19 05 01 or 20 03 01	NH	H	NH	NH	NH	NH	
21	Sludges from treatment of urban waste water	19 08 05	NH	H	NH	NH	NH	NH	
22	Non-composted organic fraction of municipal wastes < 30 mm after crushing,	19 05 01	NH	H	H	NH	NH	NH	
23	Mixed municipal waste, fraction > 30 mm after crushing	19 05 01 or 20 03 01	NH	H	H	H	NH	NH	H
24	Ferrous metal dust and particles	12 01 02	NH	H	H	H	NH	NH	H
25	End-of-life tyres, crushed 4 mm	16 01 03	NH	H	H	H	H	H	H

4.1 Comparison of calculation methods and the LoW

Table 4: Comparison of the classification of 25 wastes by the European list of waste and by 5 calculation methods (H = hazardous, NH = non-Hazardous with assigned code)

[2] The waste codes which are mentioned in this column are those have been assigned within the European list of Waste (LoW) as defined in Decision 2014/955 and also according to the knowledge of the wastes concerned. So there may be some divergence of interpretation between this proposal to assign an "absolute entry" code and that is proposed in the guide "Guidance Document on the definition and classification of hazardous waste" in Annex A. This "absolute entry" waste code assignment within that Table 3 was carried out based on the nature of the waste and the expertise of Ineris.

[3] The biotests used and the results are described below at the section "Comparison of biotests and calculation methods". Only 16 biotests could have been realised of the 25 samples of wastes studied.

HP 14 Calculation Methods						Hazardous or Non Hazardous with assigned code	H or NH by method		Matching classification (25 samples)	Calculated NH but H with assigned code (16 samples)
Method 3						LoW \ Method 3	H	NH	18	1
∑	Acute	Chronic				H	15	1	72%	6%
H400						NH	6	3		
H410		0.10%								
H411			2.50%							
H412				25%						
H413					25%					
Method 1						LoW \ Method 1	H	NH	19	2
∑	Acute	Chronic				H	14	2	76%	13%
H400	25%					NH	4	5		
H410		0.25%	25%							
H411		2.50%	25%							
H412		25%	25%							
H413			25%							
Method 2						LoW \ M2 + ext. M-factors	H	NH	20	2
∑	Acute	Chronic				H	14	2	80%	13%
H400	$25/M_{acute}$ %					NH	3	6		
H410		$2.5/MCLP_{chronic}$ %								
H411		25%								
H412						LoW \ Method 2 CLP	H	NH	16	8
H413						H	8	8	64%	50%
						NH	1	8		
Method 4						LoW \ Method 4	H	NH	15	9
∑	Acute	Chronic				H	7	9	60%	56%
H400						NH	1	8		
H410		$2.5/MCLP_{chronic}$ %								
H411			25%							
H412										
H413										

Table 5: Concordance of methods (synthesis)

Method	Method 2 with extended M-factors	Method 1	Method 3	Method 2	Method 4
Matching with assigned code (H/H, NH/NH)	80%	76%	72%	64%	60%
Mismatching: H with assigned code and NH by calculation	13%	13%	6%	50%	56%

A relative ranking can be the decreasing number of samples classified as hazardous ; the order (Table 4) is :

method 3 > method 1 > method 2 with extended M-factors > method 2 > method 4

This result corresponds to the arithmetic ranking by concentration limits for chronic ecotoxicity in case of mean M=10 (Table 1).
A more complete approach is to look for “absolute” matching of both H and NH waste (Table 4, Table 5).

Method 2 with extended M-factors is the most concordant with the LoW, and the second (with Method 1) in rank of mismatching.

The other calculation methods then rank in the order of concentration limits set forth above, with decreasing performance.
Methods 3 and 1 have a good agreement with the LoW. They have low concentration limits (method 3: 0.1%; Method 1: 0.25**%) but do not classify correctly in relation to the LoW waste containing substances with high chronic M-factors (> 10):**

- Mineral substances: compounds of Hg and Cd (chronic M = 100)
- Organic substances: PAHs and pesticides (chronic M = 100 to > 1000).

The wastes that may contain these substances are **wastes of the chemical or metallurgical industry, petroleum products and combustion residues, pesticides packaging, and soils, sludges and contaminated sediments**. Some tested wastes contain PAHs, which explains the differences in ranking.

In the set of waste, there is a PAH, benz(a)anthracene in sample 5, and a pesticide, chlorpyrifos, in sample 4 (Table 3).

Method 2 with M-factors of CLP regulation provides a lower ranking correspondence. As the same method with extended M-factors gives the best performance, the lower performance of this method clearly **comes from the limitation of the M-factor.**

Method 4 is little concordant or even divergent with the LoW.

4.2 Comparison of biotests and calculation methods

The “harmonized” experimental approach, consisting of three aquatic ecotoxicity tests and three terrestrial ecotoxicity tests (Table 6) was applied to 16 of the 25 wastes selected in this study.

Table 6 : Test battery and threshold values proposed to assess the HP 14 property

Type of test	Test	Duration	Standard	Proposal of Threshold value
Aquatic Tests	Inhibition of the mobility of *Daphnia magna*	48 h	NF EN ISO 6341	EC 50 < 10%
	Inhibition of the light emission of *Vibrio fischeri* (Luminescent bacteria test)	30 min	NF EN ISO 11348-3	EC 50 < 10%
	Fresh water algal growth inhibition test with unicellular green algae (*Pseudokirchneriella subcapitata*)	72 h	NF EN ISO 8692	EC 50 < 10%
Terrestrial Tests	Solid contact test using the dehydrogenase activity of *Arthrobacter globiformis*	2 h	ISO/DIS 18187	EC 50 < 10%
	Effects on the emergence and early growth of higher plants (*Avena sativa, Brassica rapa*)	18 j	NF ISO 11269-2	EC 50 < 10%
	Avoidance test with earthworms (*Eisenia andrei/fetida*)	48 h	NF ISO 17512-1	EC 50 < 10%

Table 7 : described results of biotests and comparison with the calculation methods and the LoW

Waste	LoW Code	Classification according to calculation methods					Classification according to harmonized experimental approach						
							Aquatic tests			Terrestrial tests			
		M2+ext. M	M1	M2	M3	M4	Daph	Vib	Alg	Arthr.	Oat	Turnip rape	Earthworm avoidance
Acid-generating tailings from processing of sulphide ore	01 03 04*	H	H	NH	H	NH	NH	NH	H	NH	NH	NH	NH
Sulfidic acid mine residue Pb Zn Cd	01 03 04*	H	H	H	H	H	NH	H	H	H	H	NH	NH
Waste from physical and chemical processing of metalliferous minerals Cu Zn	01 03 07*	NH	NH	NH	NH	NH	NH	NH	NH	H	NH	NH	NH
Metallic dust from aluminium industry	10 03 19*	NH	NH	NH	H	NH	H	NH	H	H	H	H	H
Hydrocarbon	13 07 03*	H	H	H	H	H	NH	NH	NH	NH	H	H	H
Treated wood containing hazardous substances	17 02 04*	H	H	NH	H	NH	H	NH	H	H	NH	NH	NH
Solid wastes from gas treatment	19 01 07*	H	H	H	H	H	H	NH	H	H	H	H	H
APC residue from municipal waste after solid fuel, metals and organic matter separation	19 01 07*	H	H	NH	H	NH	NH	H	H	H	H	H	H
MSWI APC residue, lime process	19 01 07*	H	H	NH	H	NH	H	NH	H	H	H	H	H
APC residue from animal meal incineration	19 01 07*	H	H	H	H	NH	H	NH	H	H	H	H	H
Packages and materials	19 12 11*	H	H	H	H	H	H	H	H	H	H	H	H
Bauxite residue	01 03 09	NH	NH	NH	NH	NH	NH	NH	NH	NH	NH	NH	H
Ferrous metal dust and particles	12 01 02	H	H	NH	H	NH	NH	NH	H	NH	NH	NH	H
End-of-life tyres, crushed 4 mm	16 01 03	H	H	H	H	H	NH	NH	NH	H	NH	NH	NH
Demolition concrete	17 01 01	NH	NH	NH	NH	NH	NH	NH	NH	H	NH	NH	H
Mixed municipal waste, fraction >30 mm after crushing	19 05 01	H	H	NH	H	NH	NH	H	NH	H	NH	H	NH

The classification rule is as follows : only one positive result among the different tests[4] that compose the test battery “harmonized” experimental approach rank a waste as “hazardous” for the Ecotoxic property. In view of these results[5], the biotests are (with the limits of concentration described above), more stringent than calculation methods. Biotests rank in fact all the 16 wastes which has been tested.
These results also show that the reference of the LoW could be compared with the reality of biotests, relevant to evaluate this property HP14 "Ecotoxic", hazardous for the environment. Moreover, for these 16 wastes which results are available by biotests, the 3 most relevant calculation methods M1, M2 and M3 extended with M factors, lead to the same conclusion for 15 of the 16 wastes. For these 16 wastes, method 3 is a little bit more ranking, but there is a good concordance between biotests and the 3 calculation methods (Methods 3, 1 and 2 with extended M factors) which rank respectively 13 and 12 samples as hazardous whereas biotests rank the 16 samples. However, there are two samples which are not classified as “hazardous” neither by the LoW, nor any calculation method, but which are by biotest. Maybe, concentration limits of the “harmonised” battery could be refined with wastes which are sure to not contain hazardous substances and so which are sure to be not Ecotoxic.

5. CONTRIBUTION OF ADDITIONNAL TABLES OF “EXTENDED” M-FACTORS

In Table 3.2 of Annex VI of CLP regulation, “harmonised” Macute-factors of 212 substances are supplied, mainly pesticides, nickel salts and substances, cobalt sulphate, oxide and carbonate, benz[a]anthracene and dibenz[a]anthracene (PAHs), other rare organic or mineral substances. There are 63 substances with Macute = 1 (62 nickel substances and one pesticide), 67 substances with M = 10, 46 substances with M = 100, 29 substances with M = 1000, 6 substances with M = 10 000 and one substance with M = 1 000 000 (deltamethrin).

Tables of additional “extended” M-factors are proposed here for mineral elements (“heavy metals”, worst case hypothesis) and organic substances, covering the major cases in waste (from Hennebert and Rebishung 2015, Andres 2013), in addition to the M-factors in Table 3.2 of Annex VI of CLP REGULATION. Height “heavy metals” H400 elements have Macute-factors and nine H410 elements have Mchronic-factors (“worst case” hypothesis). They have been used in this study. About hundred organic substances that have been encountered in waste have M-factors, with taking into account the pesticides.
These proposals could be a basis of reflexion for an harmonized list of extended M-factors for wastes in the EU.

Table 8: M-factors and concentration limit per substance and per elements (realistic worst case approach) for HP 14 acute and chronic

Elements (worst case) with hazard statement code H400 (other elements have no HSC H400)

Element	Worst case substance, CAS#	Formula	M_{acute}-factor	HP 14 acute Concentration limit /substance (Method 2 ext. M-factors)	Worst case Concentration limit /element (Method 2 ext. M-factors)
Hg	(1)	CLP	1000	0.025%	0.0204%
Cd	(1)	CLP	100 (2)	0.25%	0.1473%
As	(1)	CLP	10	2.50%	1.3297%
Co	Cobalt oxide 1307-96-6	CoO	10	2.50%	1.9663%
Cr(VI)	(1)	CLP	10	2.50%	0.9066%
Cu	Copper chloride	$CuCl_2$	10 (3)	2.50%	1.1816%
Pb	(1)	CLP	10	2.50%	2.0703%

[4] Two species were used in the test on emergence and early growth of higher plants, leading to obtain 7 responses for each waste.

[5] For these results, 2 sampling (“Solid wastes from gas treatment” and “MSWI APC residue, lime process”) have no adjustment of the pH of the eluate.

Zn	Zinc chloride	$ZnCl_2$	10	2.50%	1.1995%
Mn	Potassium permanganate 7722-64-7	$KMnO_4$	1	25.00%	8.6911%
Ni	Nickel chloride	$NiCl_2$	1	25.00%	8.8124%
Se	(1) / hyp. Lead selenate	$PbSeO_4$	1	25.00%	5.6374%

HYP: HYPOTHESIS OF SUBSTANCE

(1) GENERIC HAZARD STATEMENT CODE OF CLP. CONVERSION OF ELEMENT TO SUBSTANCE BASED ON ALL THE SUBSTANCES WITH THAT ELEMENT IN THE CLP
(2) BASED ON EC50 = 0.0034 MG/L. LOWER EC50 VALUES (0.0009 MG/L, M= 1000) ARE ALSO REPORTED.
(3) Based on EC50 = 0.011 mg/l. A lower value of EC50 can be found in a European Commission - European Voluntary Risk Assessment Report (EU-VRAR) report but it is proposed to use this value instead

Substances with hazard statement code H410

Element	Worst case substance	Formula	$M_{chronic}$-factor	HP 14 Min. Concentration limit /substance (Method 2 ext. M-factors)	Worst case Concentration limit /element (Method 2 ext. M-factors)
Cd	(1)	CLP	100	0.025%	0.0147%
Hg	(1)	CLP	100	0.025%	0.0204%
As	(1)	CLP	10	0.25%	0.1330%
Co	Cobalt oxide 1307-96-6	CoO	10	0.25%	0.1966%
Cr(VI)	(1)	CLP	10	0.25%	0.0907%
Cu	Copper chloride	$CuCl_2$	10	0.25%	0.1182%
Pb	(1)	CLP	10	0.25%	0.2070%
Se	(1) / hyp. Lead selenate	$PbSeO_4$	10	0.25%	0.0564%
Zn	Zinc chloride	$ZnCl_2$	10	0.25%	0.1199%
Ag	Silver nitrate 7761-88-8	$AgNO_3$	1	2.50%	1.5875%
Mn	Potassium permanganate 7722-64-7	$KMnO_4$	1	2.50%	0.8691%
Ni	Nickel chloride	$NiCl_2$	1 (2)	2.50%	0.8812%

HYP: HYPOTHESIS OF SUBSTANCE

(1) GENERIC HAZARD STATEMENT CODE OF CLP. CONVERSION OF ELEMENT TO SUBSTANCE BASED ON ALL THE SUBSTANCES WITH THAT ELEMENT IN THE CLP
(2) BASED ON NOEC = 0.011 MG/L. A LOWER VALUE OF NOEC CAN BE FOUND IN A EUROPEAN COMMISSION - EUROPEAN VOLUNTARY RISK ASSESSMENT REPORT (EU-VRAR) REPORT BUT IT IS PROPOSED TO USE THIS VALUE INSTEAD

Organic substances: Some EC50 and Macute factors

CAS#	Substance	EC50 min mg/l	Macute
191-24-2	Benzo(g,h,i)perylene	0.0005	1000
107-02-8	Acrolein	0.007	100
110-30-5	N,N'-ethylenedi (stearamide)	0.0023	100
118-74-1	Hexachlorobenzene	0.005	100
120-12-7	Anthracene	0.0017	100
207-08-9	Benzo(k)fluoranthene	0.0012	100
298-04-4	Disulfoton	0.0041	100
3194-55-6	1,2,5,6,9,10 Hexabromocyclododecane	0.0027	100
50-32-8	Benzo(a)pyrene	0.005	100
608-73-1	Hexachlorocyclohexane	0.009	100
6742-54-7	Undecylbenzene	0.01	100
77-47-4	Hexachlorocyclopentadiene	0.0035	100
85535-85-9	Alcanes, C14-17 chloro	0.0061	100
106325-08-0	Epoxyconazole	0.0147	10
106-47-8	4-Chloroaniline	0.0563	10
107-64-2	Dimethyldioctadecylammonium chloride	0.0563	10
1113-02-6	Omethoate	0.026	10
121158-58-5	Dodecylphenol, mixed isomers (branched)	0.018	10
123-31-9	Hydroquinone	0.052	10
129-00-0	Pyrene	0.027	10
140-66-9	para-tert-octylphenol	0.014	10
143390-89-0	Kresoxim methyl	0.0167	10
1643-20-5	Dodecyldimethylamine oxide	0.0195	10
210555-94-5	4-dodecylphenol, branched	0.017	10

CAS#	Substance	EC50 min mg/l	Macute
25376-45-8	Diaminotoluene	0.041	10
301-12-2	Oxydemeton-methyl	0.026	10
3926-62-3	Sodium chloroacetate	0.028	10
79-11-8	Monochloroacetic acid	0.027	10
84649-84-3	C12-14, Alkyldimethylamines	0.026	10
85-01-8	Phenanthrene	0.0195	10
85535-84-8	Alkanes, C10-13, chloro	0.015	10
87-86-5	Pentachlorophenol	0.0122	10
88-85-7	2-sec-butyl-4,6-dinitrophenol	0.039	10
95-31-8	N-tert-butylbenzothiazole-2-sulphenamide	0.091	10

Source: Portal of chemical substances, INERIS http://www.ineris.fr/substances/fr/

CAS	Substance	Lowest EC50 [mg/L]	M_{acute}-factor	H400	Lowest NOEC [mg/L]	Degradable.	$M_{chronic}$-factor	H410	H411	H412
2921-88-2	Phosphorothioic acid, diethyl (-trichloro-pyridinyl) ester	0.00001	10000	H400	0.00006	no	1 000	H410		
34256-82-1	Acetamide, 2-chloro-N-(ethoxymethyl)- N-(2-ethyl-6-methylphenyl)-	0.00052	1000	H400	0.00006	no	1 000	H410		
118-74-1	Benzene, hexachloro-	0.005	100	H400	0.00013	no	100	H410		
609-046-00-1	Trifluralin	0.012	10	H400	0.0003	no	100	H410		
207-08-9	Benzo[k]fluoranthene	0.0011	100	H400	0.00027		10	H410		
120-12-7	Anthracene	0.0012	100	H400	0.0012	no	10	H410		
206-44-0	Fluoranthene	0.009	100	H400	0.0012	no	10	H410		
129-00-0	Pyrene	0.02	10	H400	0.0012	no	10	H410		
87-68-3	hexachloro-13-butadiene	0.06	10	H400	0.004	no	10	H410		
608-93-5	Benzene, pentachloro-	0.1	10	H400	0.01	no	10	H410		
85509-19-9	Flusilazole	1.2			0.003	no	10	H410		
56-55-3	Benz[a]anthracene	0.0018	100	H400	0.0012		1	H410		
85-01-8	Phenanthrene	0.02	10	H400	0.01		1	H410		
112-41-4	1-Dodecene	22			0.004		1	H410		
872-05-9	Decene	22			0.01		1	H410		
112-18-5	1-Dodecanamine, N,N-dimethyl-	0.014	10	H400	0.02				H411	
793-24-8	Benzenediamine,(-dimethylbutyl)-phenyl-	0.03	10	H400	0.02				H411	
81406-37-3	Fluroxypyr 1-methylheptyl ester	0.04	10	H400	0.02				H411	
20020-02-4	Naphthalene, 1,2,3,4-tetrachloro-	0.07	10	H400	0.1				H411	
1928-43-4	Acetic acid, (2,4-dichlorophenoxy)-, 2-ethylhexyl ester	0.23	1	H400	0.02				H411	
101-21-3	Chlorpropham	0.43	1	H400	0.02				H411	
87-61-6	123-trichlorobenzene	0.33	1	H400	0.03				H411	
86-73-7	Fluorene	0.41	1	H400	0.03				H411	
83-32-9	Acenaphthene	0.12	1	H400	0.04				H411	
103-23-1	Hexanedioic acid, bis(2-ethylhexyl) ester	0.23	1	H400	0.04				H411	
115-86-6	Triphenyl phosphate	0.4	1	H400	0.04				H411	
120-82-1	124-trichlorobenzene	0.45	1	H400	0.04				H411	
15299-99-7	Napropamide	0.68	1	H400	0.05				H411	

CAS	Substance	Lowest EC50 [mg/L]	M_{acute}-factor	H400	Lowest NOEC [mg/L]	Degradable.	$M_{chronic}$-factor	H410	H411	H412
103-24-2	Nonanedioic acid, bis(2-ethylhexyl) ester	0.07	1	H400	0.06				H411	
95-94-3	Benzene, 1,2,4,5-tetrachloro-	0.32	1	H400	0.06				H411	
128-37-0	Butylated Hydroxytoluene	0.17	1	H400	0.07				H411	
56-23-5	Carbon Tetrachloride	0.25	1	H400	0.07				H411	
85-68-7	benzyl butyl phtalate	0.49	1	H400	0.08				H411	
84-74-2	dibutyl phtalate	0.35	1	H400	0.1				H411	
100-44-7	Benzyl chloride	0.39	1	H400	0.1				H411	
91-20-3	Naphtalene	0.8	1	H400	0.12					H412
92-52-4	Biphenyl	0.3	1	H400	0.17					H412
108-70-3	Benzene, 1,3,5-trichloro-	0.4	1	H400	0.2					H412
106-46-7	14-dichlorobenzene	0.7	1	H400	0.2					H412
106-43-4	4-chlorotoluene	0.96	1	H400	0.32					H412
119-47-1	Phenol, methylenebis[(-dimethylethyl)-methyl-	1	1	H400	0.34					H412
88-06-2	Phenol, 2,4,6-trichloro-	0.41	1	H400	0.5					H412
95-50-1	12-dichlorobenzene	0.66	1	H400	0.63					H412
112-53-8	1-Dodecanol	0.97	1	H400	0.73					H412
131-17-9	1,2-Benzenedicarboxylic acid, di-2- propenyl ester	0.23	1	H400	1.16					
36653-82-4	1-Hexadecanol	0.4	1	H400	100					

Source: Andres 2013.

6. CONCLUSIONS

The data set of these 25 wastes allow a relative ranking of the 5 methods challenged (frequency of classification from a set of composition).
The ranking (decreasing number of calculated H waste) is method 3 > method 1 > method 2 with extended M-factors > method 2 > method 4.

Additionnaly, the methods can be ranked by concordance with the assigned codes by the LoW. In the context of this methodology, **method 2 with extensive M-factors:**

- **matches best with the European list of waste** (80% concordant H and non-H by LoW, and 13% discordant for H waste by LoW);
- **classifies safely** waste containing cadmium, mercury (Mchronic = 100), polycyclic aromatic hydrocarbons – PAHs (frequently Macute = 100, Mchronic = 10), pesticides (frequently Macute and Mchronic = 1000 or 100) **and in general the substances with high ecotoxicity**.

Methods 1 and 3 have nearly as good matching (76% and 72% respectively concordant H and non-H by LoW, and 13% and 6% respectively discordant for H waste by LoW), but they will not classify safely waste containing substances with high ecotoxicity (in particular PAHs frequent in waste).
Method 2 with M-factors limited to the M-factors published in the CLP has insufficient concordance (64% concordant H and non-H by LoW, and 50% discordant for H waste by LoW). As the same method with extended M-factors gives the best performance, the lower performance is due to the limitation of the M-factor. Method 4 is divergent (60% concordant H and non-H by LoW, and 56% discordant for H waste by LoW).
The methods 2 and 4 don't classify many hazardous wastes by the LoW in the 25 wastes studied.

Moreover, the results of biotests put forward that there is a good concordance between the 3 calculation methods 3, 1 and 2 with extended M factors. Biotests could be refined but it seems relevant to asses the Ecotoxic property with biotest results too. Anyway, the experimental approach could be refined (number of tests, threshold values).

In Conclusion, it seems that method 2 with extended M factors has a near performance than methods 1 and 3 but **method 2 with extended M factors is more relevant because it classifies safely waste which contain substances with high ecotoxicity, associated with exhaustive M factors**.

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