Waste Management 48 (2016) 24–33

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Assessment of four calculation methods proposed by the EC for waste hazardous property HP 14 'Ecotoxic'

Pierre Hennebert [a,*], Nicolas Humez [b], Isabelle Conche [c], Ian Bishop [d], Flore Rebischung [a]

[a] INERIS (National Institute for Industrial Environment and Risks), BP 2, F-60550 Verneuil-en-Halatte, France
[b] SYPRED (Syndicat Professionnel pour le Recyclage et l'Elimination des Déchets Dangereux), France[1]
[c] SYVED (SYndicat pour la Valorisation et l'Elimination des Déchets), 54, rue Pierre Curie, ZI Les Gâtines, BP 120, 78373 Plaisir CEDEX, France
[d] HazWasteOnline, United Kingdom[2]

ARTICLE INFO

Article history:
Received 8 July 2015
Revised 24 November 2015
Accepted 26 November 2015
Available online 11 December 2015

Keywords:
Ecotoxicity
HP 14
M-factors
European List of Waste

ABSTRACT

Legislation published in December 2014 revised both the List of Waste (LoW) and amended Appendix III of the revised Waste Framework Directive 2008/98/EC; the latter redefined hazardous properties HP 1 to HP 13 and HP 15 but left the assessment of HP 14 unchanged to allow time for the Directorate General of the Environment of the European Commission to complete a study that is examining the impacts of four different calculation methods for the assessment of HP 14. This paper is a contribution to the assessment of the four calculation methods. It also includes the results of a fifth calculation method; referred to as "Method 2 with extended *M*-factors".

Two sets of data were utilised in the assessment; the first (Data Set #1) comprised analytical data for 32 different waste streams (16 hazardous (H), 9 non-hazardous (NH) and 7 mirror entries, as classified by the LoW) while the second data set (Data Set #2), supplied by the eco industries, comprised analytical data for 88 waste streams, all classified as hazardous (H) by the LoW.

Two approaches were used to assess the five calculation methods.

The first approach assessed the relative ranking of the five calculation methods by the frequency of their classification of waste streams as H. The relative ranking of the five methods (from most severe to less severe) is: Method 3 > Method 1 > Method 2 with extended *M*-factors > Method 2 > Method 4. This reflects the arithmetic ranking of the concentration limits of each method when assuming $M = 10$, and is independent of the waste streams, or the H/NH/Mirror status of the waste streams.

A second approach is the absolute matching or concordance with the LoW. The LoW is taken as a reference method and the H wastes are all supposed to be HP 14. This point is discussed in the paper. The concordance for one calculation method is established by the number of wastes with identical classification by the considered calculation method and the LoW (i.e. H to H, NH to NH). The discordance is established as well, that is when the waste is classified "H" in the LoW and "NH" by calculation (i.e. an underestimation of the hazard). For Data Set #1, Method 2 with extended *M*-factors matches best with the LoW (80% concordant H and non-H by LoW, and 13% discordant for H waste by LoW). This method more correctly classifies wastes containing substances with high ecotoxicity. Methods 1 and 3 have nearly as good matches (76% and 72% concordant H and non-H by LoW, and 13% and 6% respectively discordant for H waste by LoW). Method 2 with extended *M*-factors, but 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 limited set of *M*-factors in the CLP. Method 4 is divergent (60% concordant H and non-H by LoW, and 56% discordant for H waste by LoW).

For Data Set #2, Methods 2 and 4 do not correctly classify 24 air pollution control residues from incineration 19 01 07* (3/24 and 2/24 respectively), and should not be used, while Methods 3, 1 and 2 with extended *M*-factors successfully classify 100% of them as hazardous. From the two sets of data,

* Corresponding author.
E-mail address: pierre.hennebert@ineris.fr (P. Hennebert).
[1] www.sypred.fr.
[2] www.hazwasteonline.com.

http://dx.doi.org/10.1016/j.wasman.2015.11.044

Method 2 with extended *M*-factors (corresponding more closely to the CLP methods used for products) matches best with the LoW when the LoW code is safely known, and Method 3 and 1 will deviate from the LoW if the samples contain substances with high ecotoxicity (in particular PAHs). Methods 2 and 4 are not recommended. Formally, this conclusion depends on the waste streams that are used for the comparison of methods and the relevancy of the classification as hazardous for ecotoxicity in the LoW. Since the set is large (120 waste streams) and no selection has been made here in the available data, the conclusion should be robust.

1. Introduction

In 2014, the Member States of the European Union updated the European List of Wastes (LoW) and defined the 15 hazard properties (HP) of wastes with the exception of HP 14 'Ecotoxic' (EC, 2014a,b). This hazard property is the most frequent classifying property as hazardous for waste (Hennebert et al., 2014) if the Classification, Labelling and Packaging of Preparation and Mixtures calculation method (CLP Regulation, 2008), limited to the first two levels of chronic ecotoxicity, but including extended *M*-factors, is used.

To review the different approaches to the assessment of HP 14, (based on the chemical analysis of waste streams), the Directorate General of the Environment of the European Commission's commissioned an assessment of four calculation methods (Call for Tenders: DG ENV, 2014). The four methods differ due to the varying application of hazard statement codes, concentration limits and *M*-factors.

The assessment of the methods is focused on the so-called "mirror entries" in the LoW, that is waste that can be either hazardous or non-hazardous; those that must be assessed for their hazardous properties based on their chemical composition or by biological testing. With "mirror entries", the result of the Call for Tenders will be limited to a ranking of the four methods by their frequency of classification, which is the arithmetic value of their limits of concentration. This ranking, depending on the *M*-factors, is presented below.

This paper is a contribution to the assessment of these four calculation methods, combined with the presentation of a fifth method that applies "extended *M*-factors", i.e. *M*-factors calculated from reviewed EC_{50} and NOEC data for a broader range of inorganic and organic substances, including substances important in waste, like the polyaromatic hydrocarbons (PAHs). Using only the "absolute entries" of the LoW as a reference, and applying the five different classification methods, the methods can be ranked by seeing how closely the results match the LoW classification. To use the LoW as a reference method is a choice of this paper. The correctness of this choice can be argued but we have not found another method. The LoW and hazardous waste classification is political and complex due to links to the CLP (no clear right or wrong approach). Some broader questions as the relevance of the LoW and the speciation of the metallic compounds for proper classification are highlighted. A list of *M*-factors is proposed.

2. Material and methods

2.1. Calculation methods for HP 14, and justification of a method with extended M-factors

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

- **Method 1**:
  $\sum$ c H400 $\geqslant$ 25%, or (100 $\times$ $\sum$ c H410) + (10 $\times$ $\sum$ c H411) + ($\sum$ c H412) $\geqslant$ 25%, or
  $\sum$ c H410 + $\sum$ c H411 + $\sum$ c H412 + $\sum$ c H413 $\geqslant$ 25%
- **Method 2**:
  $\sum$ (c H400 $\times$ *M*) $\geqslant$ 25%, or $\sum$ (*M* $\times$ 10 $\times$ c H410) + $\sum$ c H411 $\geqslant$ 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**:
  $\sum$ c H410 $\geqslant$ 0.1%, or $\sum$ c H411 $\geqslant$ 2.5%, or $\sum$ c H412 $\geqslant$ 25%, or $\sum$ c H413 $\geqslant$ 25%
- **Method 4**:
  $\sum$ (*M* $\times$ c H410) $\geqslant$ 2.5%, or $\sum$ c H411 $\geqslant$ 25%
  The *M*-factors will be determined as per Method 2.

For easier comparison, these methods are presented at Table 1. 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 must be summed. The sum of these ratios is a hazard index. If it is $\geqslant$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 also assessed 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 – level 4 is presented as a "safety net" in the CLP) for waste is argued by an impact assessment (Hennebert and Rebischung, 2012). Another reason is that there is only one final level of hazard for waste (i.e. Hazardous) but there are 4 levels of hazard for products (Ecotoxic acute, Ecotoxic chronic level 1, 2, 3). This approach (Method 2 with extended *M*-factors) has been used in France since 2012.

Calculations written in Excel were used to assess Data Set #1 against the five methods, while the on-line hazardous waste classification software HazWasteOnline™ (www.hazwasteonline.com) was used to analyse Data Set #2.

The LoW is taken in this paper as the reference method. This implies that the wastes used in the LoW are all classified as hazardous for HP 14. In practice, this cannot be established with absolute certainty. There is no account of how various types of waste with absolute entries in the LoW have been allocated as hazardous or non-hazardous. There is no information available about how waste has been classified as hazardous or non-hazardous in LoW, and in particular for HP 14. The match or concordance for a given

Table 1
Classification methods for HP 14 by calculation proposed the DG ENV of the EU. For acute or chronic ecotoxicity, the concentrations of the substances with the relevant hazard statement code (HSC) are summed vertically according to each rule.

Method	∑ HSC	Acute	Chronic			
		(Rule 1)	(Rule 1)	(Rule 2)	(Rule 3)	(Rule 4)
3	H400 Aquatic Acute 1	–				
	H410 Aquatic Chronic 1		0.10%			
	H411 Aquatic Chronic 2			2.50%		
	H412 Aquatic Chronic 3				25%	
	H413 Aquatic Chronic 4					25%
1	H400	25%				
	H410		0.25%	25%		
	H411		2.50%	25%		
	H412		25%	25%		
	H413			25%		
2	H400	$25/M_{acute}$ %				
	H410		$2.5/M_{chronic}$ %			
	H411		25%			
	H412					
	H413					
4	H400	–				
	H410		$2.5/MCLP_{chronic}$ %			
	H411			25%		
	H412					
	H413					

calculation method is established by the number of wastes with a classification identical to 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 also be considered. Erroneous classification of non-hazardous waste as hazardous can also be problematic, but, for the clarity of the paper, will not be handled here.

2.2. Waste and waste composition data

Data Set #1 has 32 different waste streams with known LoW codes. For three wastes with mirror entries, an entry has been chosen based on independent information. The bauxite residue (waste stream #46) has been washed and dried in press filter and amended with gypsum to bring the pH to 8.5, to allow plants to grow on it (Hennebert et al., 2014). For this waste stream, the non-hazardous mirror entry code has been used. In contrast, for two sulphidic mine tailings waste streams (#64 and #66), that have been without vegetation for 60 years and produce acid mine drainage (pH 3.5 and 2.8), the hazardous mirror entry has been selected. Most of the wastes have been analysed according to AFNOR XP X30-489 "Determination of elements and substances in waste" which is being discussed as a European standardization Work Item submitted to formal vote (CEN/TC 292, 2015). This approach will give a reasonable approximation as to the composition of the waste undergoing hazardous waste classification and can also be used for Seveso classification, Water Framework Directive classification, transport regulation, and occupational health and safety requirements. Please be aware that hazard classification with incomplete analytical data is misleading.

For Data Set #1, the analytical mass balances (sum of all measured concentrations) were better than 90%. Some of these wastes were presented in Hennebert and Rebischung (2013). When the concentration of a substance is below its limit of quantification (LOQ), the LOQ has been used as the concentration. The concentrations are expressed in terms of 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 conversion using the relevant moisture content correction.

Data Set #2 comprises a set of laboratory results from 88 different waste streams. The original analytical data were supplied by the professional body representing the French eco-industries (SYVED, SYPRED, CNPA). The 88 waste streams have been analysed exhaustively (AFNOR XP X30-489) but for practical reasons only results for volatile and semi-volatile compounds, petroleum products, and heavy metals are used here (not PAH concentrations). Among these, results for 208 substances have been excluded from the assessment because they are not documented in the CLP. The mass balance for the remaining analysed concentrations has a mean value of 7.8% (with one sample reaching 78%), covering 179 substances and metals (including 13 heavy metals) where they were detected. Across the whole of Data Set #2, there were only 34 common substances (including the 13 metals). The classification results presented below are hence not "absolute" results, but they can be used to compare the calculation methods.

2.3. Speciation of mineral elements to mineral substances

In waste, classification by chemical composition depends in part on the hypothesis of speciation of the different metals into the concentrations of actual metal compounds. Chemical classification is routinely hampered by this speciation question. Where the CLP 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 typically poorly defined in terms of the exact chemical form of the substances that they contain. Lack of information on the chemical form of a metal required for speciation can lead to the use of "worst case" metal compound, which is a poor measure of hazardousness, and a possible classification as hazardous (Hennebert and Weltens, 2014). A presentation of the different available methods with a step-wise method (depending on the concentration of the metal) can be found in AFNOR FD X30-494 (2015) and in an Annex of Hennebert and Rebischung (2015).

A first step to avoid expensive speciation work is to use "worst case with information" approach, i.e. (1) to suppose that a particular metal is in its most hazardous form in the waste, and (2) that it can realistically be present in the waste. "Simple" metal compounds with only one ecotoxic element are used rather than more complex metal compounds (i.e. sodium chromate instead of lead chromate). A list of such substances can be found for all HPs in Hennebert and Rebischung (2015). That list has been used here for HP 14. For the 12 heavy metals, the species used here are presented at Tables 7.1 and 7.2.

Table 2
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%	0.25% + 25%	0.25% + 25%	0.25% or 25%

It must be remembered that the "exact" classification of one waste stream should not use the total content of metal with the worst case compound, but the content of each metallic compound (silicate, embedded species as catalyst in a polymer matrix, soluble forms…) and its hazard statement code. In particular, CLP addresses aquatic ecotoxicity, and terrestrial ecotoxicity is not assessed. For ecotoxicity, according to ECHA's Guidance on the application of the CLP criteria (2011), a substance must be dissolved (in water) in order to be available for an ecotoxicological response or to migrate into the environment and subsequently pose a potential hazard.

For the purpose of this paper (Which method matches best with the LoW?), those considerations are not a major obstacle.

2.4. M-factors

In the CLP, multiplying factors for the concentrations of the substances that produce biological effects in tests at concentration <1 mg/L are used to calculate the hazard for the aquatic environment. Table 3.1 of Annex VI of the CLP has a (limited) 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 (EC_{50}) if it is <1 mg/L, <0.1 mg/L, <0.01 mg/L, etc.) and for chronic ecotoxicity (depending on the concentration with no observed effect (NOEC) if it is <0.1 mg/L, <0.01 mg/L, <0.001 mg/L, etc.) (CLP 2008 ATP 02). Tables of *M*-factors can be found in Hennebert and Rebischung (2013, updated in 2015).

2.5. Arithmetic comparison of the calculation methods for HP 14

To give an insight about the proposition of DG ENV (2014) and the proposition of a fifth method, the five calculation methods can tentatively be classified by increasing concentration limit, taking into account the following observations:

a. A waste classified as acute ecotoxic is also classified as chronic ecotoxic (empirical result not presented for this set of data, other data in Hennebert et al., 2014). The reverse is not true. This statement cannot be verified if the waste contains hazardous degradable substances that have an acute *M*-factor greater than a chronic *M*-factor. This is the case for some PAH: benzo[k]fluoranthene, M_{acute} = 100, $M_{chronic}$ = 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 codes 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 number of substances with these hazard statements codes in Table 3.1 of Annex VI CLP (H412: 431 substances, and H413: 254 substances) for H412 are mainly related to 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 sulphide. With a 25% cumulative concentration, these materials will not be *a priori* material that the waste holder wishes to discard, but rather a resource which the holder 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 five calculation methods for chronic ecotoxicity H410 and H411 depend on the value of the chronic *M*-factor. If a mean chronic *M*-factor is hypothesized, and if that *M*-factor is in the CLP Annex VI, a classification by increasing concentration limit can be set (Table 2). 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 upwards.
d. For hazardous metal compounds and other substances, Annex VI of CLP contains only *M*-factors for pesticides and nickel compounds. For other metals 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 inventory. 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 3.

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.

Table 3
Comparison of 5 classification methods for HP 14 by calculation for hazardous elements and substances (heavy metals, PAHs, $M \geqslant 10$, extended *M*-factors).

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

Table 4
Classification of 32 waste streams by the European List of Waste (LoW) and by 5 calculation methods (H = hazardous, NH = non-hazardous, M = mirror entry of the LoW) (Data Set #1).

N	Waste	LoW	LoW	M3	M1	M2 +ext. M	M2	M4
13	Municipal Solid Waste Incinerator (MSWI) fly ash	19 01 05*	H	H	H	H	H	H
14	Air Pollution Control (APC) residue industrial waste #1	19 01 07*	H	H	H	H	H	H
16	Industrial waste bottom ash	19 01 11*	H	H	H	H	H	H
19	Packages and materials #2	19 12 11*	H	H	H	H	H	H
28	Hydrocarbon #1	13 07 03*	H	H	H	H	H	H
58	Sulfidic acid mine residue Pb Zn Cd	01 03 04*	H	H	H	H	H	H
67	MSWI APC 3	19 01 07*	H	H	H	H	H	H
59	APC residue from animal meal incineration	19 01 07*	H	H	H	H	H	NH
10	Wastes from transport tank cleaning, mixed sludge of food and chemical transport	16 07 09*	H	H	H	H	NH	NH
11	MSWI Air pollution control (APC) residue, bicarbonate process	19 01 07*	H	H	H	H	NH	NH
12	MSWI APC residue, lime process	19 01 07*	H	H	H	H	NH	NH
43	APC residue from municipal waste after solid fuel, metals and organic matter separation	19 01 07*	H	H	H	H	NH	NH
63	Treated wood containing hazardous substances	17 02 04*	H	H	H	H	NH	NH
66	Acid-generating tailings from processing of sulphide ore	01 03 04*	H	H	H	H	NH	NH
17	Metallic dust from aluminum industry	10 03 19 *	H	H	NH	NH	NH	NH
64	Waste from physical and chemical processing of metalliferous minerals Cu Zn	01 03 07*	H	NH	NH	NH	NH	NH
-								
1	Municipal waste - Organic fraction separately collected	20 01 08 or 20 02 01	NH	NH	NH	NH	NH	NH
46	Bauxite residue	01 03 09	NH	NH	NH	NH	NH	NH
57	Demolition concrete 2	17 01 01	NH	NH	NH	NH	NH	NH
4	Compost from mixed municipal waste, fraction < 30 mm after crushing	19 05 01 or 20 03 01	NH	H	NH	NH	NH	NH
8	Sludges from treatment of urban waste water	19 08 05	NH	H	NH	NH	NH	NH
5	Non-composted organic fraction of municipal wastes < 30 mm after crushing.	19 05 01	NH	H	H	NH	NH	NH
3	Mixed municipal waste, fraction > 30 mm after crushing	19 05 01 or 20 03 01	NH	H	H	H	NH	NH
68	Ferrous metal dust and particles	12 01 02	NH	H	H	H	NH	NH
65	End-of-life tyres, crushed 4 mm	16 01 03	NH	H	H	H	H	H
-								
44	Surface treatement - sludges and filter cakes	11 01 09* or 11 01 10	M	H	H	H	H	H
45	Bottom ash and slag from municipal waste after solid fuel, metals and organic matter separation - maturated and pretreated	19 01 11* or 19 01 12	M	H	H	H	H	H
61	Boiler dust from animal meal incineration	19 01 15* or 19 01 16	M	H	H	H	H	NH
60	Bottom ash from animal meal incineration	19 01 11* or 19 01 12	M	H	NH	NH	NH	NH
6	Active landfill leachate containing hazardous substances or landfill leachate other than those mentioned in 19 07 02	19 07 02* or 19 07 03	M	NH	NH	NH	NH	NH
7	Closed landfill leachate containing hazardous substances or landfill leachate other than those mentioned in 19 07 02	19 07 02* or 19 07 03	M	NH	NH	NH	NH	NH
9	Sludges from landfill leachate, after evapo-concentration	19 02 05* or 19 02 06	M	NH	NH	NH	NH	NH

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.

3. Results and discussion

Classification of Data Set #1

The results for the 32 waste streams are presented at Table 4, ordered by method with decreasing corresponding score with the LoW. The scores are presented in Table 5.

One criterion to measure the relative ranking of the five calculation methods can be to assess the number of waste streams that each method classifies as hazardous. The order (Table 5) is Method 3 (25/32) > Method 1 (21/32) > Method 2 with extended *M*-factors (20/32) > Method 2 (12/32) > Method 4 (10/32). This result corresponds to the arithmetic ranking by concentration limits for chronic ecotoxicity in case of mean $M = 10$ (Table 2).

A more complete approach is to look for "absolute" matching of both H and NH waste (Table 5).

Method 2 with extended *M*-factors is the most concordant and second best (equal with Method 1) in terms of not matching the LoW entry.

The other calculation methods then rank in the order of concentration limits set forth above, with decreasing performance.

Methods 1 and 3 are in good agreement with the LoW. They have low concentration limits (Method 1: 0.25%; Method 3: 0.1%) but do not classify correctly in relation to the LoW for wastes containing substances with high chronic *M*-factors (>10), in particular:

Table 5
Synthesis of classification of 32 waste streams by the European List of Waste (LoW) and by 5 calculation methods (Data Set #1).

Calculation method	Hazardous (H) or Non-Hazardous NH) or Mirror entry (M) LoW	H by calculation method	NH by calculation method	Matching classification (25 samples)	Calculated NH but H by LoW (16 samples)
2 with extended M-factors	H	14	2	20 wastes = 80%	2 wastes = 13%
	NH	3	6		
	M	3	4		
1	H	14	2	19 wastes = 76%	2 wastes = 13%
	NH	4	5		
	M	3	4		
3	H	15	1	18 wastes = 72%	1 waste = 6%
	NH	6	3		
	M	4	3		
2 with CLP M-factors	H	8	8	16 wastes = 64%	8 wastes = 50%
	NH	1	8		
	M	3	4		
4	H	7	9	15 wastes = 60%	9 wastes = 56%
	NH	1	8		
	M	2	5		

Table 6
Waste streams, number of European List of Waste entries (all waste are estimated hazardous), number of samples, number of samples assessed hazardous by different calculation methods (ranked by decreasing number of samples calculated as hazardous) (Data Set # 2).

Waste	LoW codes concerned	Samples	Method 3	Method 1	Method 2 extended	Method 2	Method 4
Solid		43	40	34	33	4	2
Industrial APC[a] residue, bicarbonate	1	3	3	3	3		
Industrial APC residue, lime	1	1	1	1	1		
Industrial APC, filter dust	1	3	3	3	3	2	1
MSWI APC residue, bicarbonate	1	4	4	4	4		
MSWI APC residue, lime	1	6	6	6	6	1	1
MSWI APC, fly ash	1	7	7	7	7		
Packages and materials	2	6	6	3	3		
Pasty waste, organic	36	13	10	7	6	1	
Liquid		45	18	17	15	15	11
Cooling fluid	10	3					
Hydrocarbons, incineration	49	10	3	3	1	1	1
Hydrocarbons, recovery	49	6	1	1	1	1	1
Liquid, biological treatment	142	3					
Liquid, evapo-concentration	35	3					
Liquid, evapo-incineration	35	1					
Liquid, incineration	23	2	1	1	1	1	
Liquid, physico-chemical treatment	142	5	2	2	2	2	2
Oil, engine	2	5	5	5	5	5	2
Oil, hydraulic, recovery	10	3	3	3	3	3	3
Solvents, halogenated	26	4	3	2	2	2	2
Total		88	58	51	48	19	13
Ratio H samples/total samples (%)			66	58	55	22	15

[a] Air pollution control.

– Metals: 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 from the chemical or metallurgical industry, petroleum products and combustion residues, pesticides packaging, and soils, sludges and contaminated sediments. Only some of the wastes were analysed for PAHs, which explains the differences in ranking.

In Data Set #1, there is a PAH, benz(a)anthracene in waste stream #28, and a pesticide, chlorpyrifos, in waste stream #19.

Method 2, which utilises only the harmonised *M*-factors published in the CLP, is less concordant (i.e. lower ranking). As the same method with extended *M*-factors gives the best performance, the poorer performance of this method clearly comes from the limited set of *M*-factors.

Method 4 is poorly concordant or even divergent.

Classification of Data Set #2

Table 7.1
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 (using the mass fraction of the element in the substance) (Method 2 ext. *M*-factors) (%)
Hg	(1)	CLP	1000	0.025	0.02
Cd	(1)	CLP	100 (2)	0.25	0.15
As	(1)	CLP	10	2.50	1.33
Co	Cobalt oxide 1307-96-6	CoO	10	2.50	1.97
Cr(VI)	(1)	CLP	10	2.50	0.91
Cu	Copper chloride	$CuCl_2$	10 (3)	2.50	1.18
Pb	(1)	CLP	10	2.50	2.07
Zn	Zinc chloride	$ZnCl_2$	10	2.50	1.20
Mn	Potassium permanganate 7722-64-7	$KMnO_4$	1	25.00	8.69
Ni	Nickel chloride	$NiCl_2$	1	25.00	8.81
Se	(1) /hyp. Lead selenate	$PbSeO_4$	1	25.00	5.64

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 EC_{50} = 0.0034 mg/L. Lower EC_{50} values (0.0009 mg/L, *M* = 1000) are also reported.
(3) Based on EC_{50} = 0.011 mg/L. A lower value of EC_{50} can be found in a European Commission – European Voluntary Risk Assessment Report (EU-VRAR) report but it is proposed to use this value instead.

Table 7.2
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 H410 (other elements have no HSC 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	0.01
Hg	(1)	CLP	100	0.025	0.02
As	(1)	CLP	10	0.25	0.13
Co	Cobalt oxide 1307-96-6	CoO	10	0.25	0.20
Cr(VI)	(1)	CLP	10	0.25	0.09
Cu	Copper chloride	$CuCl_2$	10	0.25	0.12
Pb	(1)	CLP	10	0.25	0.21
Se	(1) /hyp. Lead selenate	$PbSeO_4$	10	0.25	0.06
Zn	Zinc chloride	$ZnCl_2$	10	0.25	0.12
Ag	Silver nitrate 7761-88-8	$AgNO_3$	1	2.50	1.59
Mn	Potassium permanganate 7722-64-7	$KMnO_4$	1	2.50	0.87
Ni	Nickel chloride	$NiCl_2$	1 (2)	2.50	0.88

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.

The 88 waste streams in Data Set #2 are representative of the main industrial hazardous waste streams in Europe (Table 6). The assumptions used to assess the chemistry of these waste streams are the usual ones, either assuming a standard composition or a composition based on a particular treatment process and are not necessarily chemically exact. The number of entries in the LoW per waste type is presented in Table 6. Waste from incineration processes are specifically identified (corresponding to one entry in the LoW), but the other wastes are mixtures of different wastes, created during collection and treatment processes (corresponding to as many as 142 entries in the LoW). All the entries are hazardous. All the wastes of this data set are therefore classified by the LoW as hazardous. It is not known which entries were classified as hazardous due to just the hazard property 'Ecotoxic' or for any other hazard property (e.g. HP 7 carcinogenic). The number of waste streams classified as hazardous by each method is also presented in Table 6.

Solid wastes are more frequently classified as hazardous than are liquid wastes. If the number of LoW entries increases (waste streams originating from other industries or processes), the frequency of a hazardous outcome decreases. While some liquid wastes are not classified, the most classified liquid wastes are engine oils, hydraulic oils and halogenated solvents.

The methods are ranked in Table 6 by decreasing number of samples classified as hazardous: 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 2).

The six incineration waste types (24 waste streams) are air pollution residues (APC) from industrial or municipal solid waste incineration (MSWI). They have a highly soluble fraction and contain heavy metals epurated from the fumes. They correspond to 19 01 07*. They are recognized by experts as ecotoxic and have received a hazardous entry in the LoW due to (in part) this ecotoxic hazard. Methods 3, 1 and 2 with extended *M*-factors successfully classify these 24 waste streams as hazardous. Methods 2 and 4 fail to classify them as hazardous, and should not be used.

The remaining Method 3, 1 and 2 with extended *M*-factors give exactly the same assessment results except for four of the waste streams: packages and materials, organic pasty waste, hydrocarbons for incineration and halogenated solvents. For these 33 waste streams, Method 1 classifies 22 of them as hazardous, Method 3

Table 7.3
Some EC_{50} and M_{acute}-factors of organic substances. *Source*: Portal of chemical substances, INERIS http://www.ineris.fr/substances/fr/.

CAS#	Substance	EC_{50} (min mg/L)	M_{acute}
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	Disulphoton	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
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

classifies 15, and Method 2 with extended *M*-factors classifies 12 of them as hazardous. The analytical data are from different waste streams (many LoW entries) and it is not known as to the extent by which they have been classified as ecotoxic by experts establishing the LoW and/or by the other hazard properties.

Metals and substances triggering classification for the Method 2 with extended M-factors

With respect to the waste streams in Data Set #1, the metal elements (worst case hypothesis) that triggered a hazardous classification were Zn (19 times for 32 samples), Cu (11), Hg (7), Pb (7), Co (5), Cd (4), Cr(VI) (4), and Ni (2). For organics, it was benz[a]anthracene (H400 $M = 100$ and H410 $M = 1$), and the pesticide chlorpyrifos (H400 $M = 10{,}000$ and H410 $M = 10{,}000$).

With respect to the waste streams in Data Set #2 (with the more limited analysis), the elements (worst case hypothesis) that triggered a hazardous classification were Zn (42 times for 88 samples), Cu (34), Pb (31), Cd (24), Hg (13), Ni (2), Cr(III) (1) and Cr(VI) (1), while concentrations of As (H400 $M = 10$ and H410 $M = 10$), Se (H400 $M = 1$ and H410 $M = 10$) and Sb (H411) compounds were too low to be significant. For organics, it was heptane, octane, cyclohexane, dipentene, 1,2,4-trimethylbenzene, 1,1-dichloro-1-fluoroethane, 1,2,4-trichlorobenzene and diesel fuel (gasoil), that contributed to the hazardous classifications.

Additional tables of M-factors (Tables 7.1–7.4)

In Table 3.1 of Annex VI of the CLP, "harmonised" M_{acute}-factors of 212 substances are supplied, mainly pesticides, nickel salts and compounds, cobalt sulphate, oxide and carbonate, benz[a]anthracene and dibenz[a]anthracene (PAHs) and other rare organic or metal compounds. There are 63 substances with $M_{acute} = 1$ (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 *M*-factors are proposed for metal elements ("heavy metals", worst case hypothesis) and organic substances, **covering the major cases in waste** (from Hennebert and Rebischung, 2015; Andres, 2013), in addition to the *M*-factors in Table 3.1 of Annex VI of CLP (Tables 7.1–7.4), eight "heavy metals" H400 elements have M_{acute}-factors and nine H410 elements have $M_{chronic}$-factors ("worst case" hypothesis). They have been used in this study. About one hundred organic substances that have been encountered in waste have *M*-factors; this number includes the pesticides.

4. Conclusions

Analysis of two data sets has allowed the relative ranking of the five methods (frequency of classification from a set of compositions) to be assessed. The results correspond to what can be expected from an arithmetic approach, and depend on the presence of hazardous substances and the use of their *M*-factors:

– From Data Set #2 (88 H waste streams), not taking into account PAHs data but including heavy metals data, Method 3, 1 and 2 with extended *M*-factors give exactly the same assessment results for 55 of the waste streams (not all classified as H), and diverge for 33 waste streams data sets gathered from four waste types: packages and materials, organic pasty waste, hydrocarbons for incineration and halogenated solvents. Methods 2 and 4 classify less waste as hazardous. The ranking

Table 7.4
EC_{50} and M_{acute}-factor, NOEC and $M_{chronic}$-factor of organic substances. *Source*: Andres (2013).

CAS	Substance	Lowest EC_{50} [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	
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					

(decreasing number of calculated H waste) is Method 3 > Method 1 > Method 2 with extended *M*-factors > Method 2 > Method 4. This result corresponds to the arithmetic comparison of the five classification methods for HP 14 by calculation, using the hypothesis that the mean chronic *M*-factor = 10.
- From Data Set #1, with data including PAHs and heavy metals, the same ranking of the methods is obtained.

Additionally, the methods can be ranked by absolute concordance with the LoW with Data Set #1 and the air pollution control residue of Data Set #2. From Data Set #1, Method 2 with extensive *M*-factors:

- matches best with the LoW (80% concordant H and non-H by LoW, and 13% discordant for H waste by LoW in Data Set #1);
- correctly classifies waste containing cadmium, mercury ($M_{chronic}$ = 100), polycyclic aromatic hydrocarbons – PAHs (frequently M_{acute} = 100, $M_{chronic}$ = 10), pesticides (frequently M_{acute} and $M_{chronic}$ = 1000 or 100) and in general the substances with high ecotoxicity.

Methods 1 and 3 are similar in terms of matching (76% and 72% concordant H and non-H by LoW, and 13% and 6% respectively discordant for H waste by LoW), but they will not correctly classify waste containing substances with high ecotoxicity (in particular the PAHs frequently encountered in waste). Method 2 which is 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 limited set of *M*-factors. Method 4 is divergent (60% concordant H and non-H by LoW, and 56% discordant for H waste by LoW).

From Data Set #2, Methods 2 and 4 don't correctly classify the 24 air pollution control residues and should not be used.

From the two sets of data, Method 2 with extended *M*-factors (corresponding more closely to the CLP methods used for products) matches best with the LoW when the code is known, and Method 3 and 1 will deviate from the LoW if the samples contain substances with high ecotoxicity (in particular PAHs). Methods 2 and 4 are not recommended.

Acknowledgement

This research is financially supported by the Ministère de l'Ecologie et du Développement Durable, France.

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