**Committee of Experts on the Transport of Dangerous Goods
and on the Globally Harmonized System of Classification
and Labelling of Chemicals**

**Sub-Committee of Experts on the Globally Harmonized
System of Classification and Labelling of Chemicals**

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Implementation of the GHS – Implementation issues

Comments on Annex 3 to ST/SG/AC.10/C.4/2010/15: Hazardous to the aquatic environment examples

Transmitted by the expert from Sweden

Introduction

1.   The expert from Sweden appreciates the work that is done to provide examples on the application of the GHS criteria for classifying mixtures as hazardous to the aquatic environment. Worked out examples are always very important for the guidance on how to apply the criteria.

2.   It seems, however, to be a slight misunderstanding on the application and also a need for a few editorial amendments.

Discussion

Use of the additivity formula

3.   First of all in section 4.1.3.5 (concerning *Classification of mixtures when toxicity data are available for all ingredients or only for some ingredients of the mixture*) it is clarified that ***"The classification of a mixture is based on summation of the concentrations of its classified ingredients."*** and that ***"The percentage of ingredients classified as "Acute" or "Chronic" will feed straight into the summation method."*** (see first para of section 4.1.3.5).

4.   This means that for ingredients with a known classification the additivity formula should not be applied.

5.   Other non-classified ingredients but with adequate toxicity data at hand will first have to be classified before they can be feed into the summation method. It is in this process that a classification can be given to a portion of the mixture (or the whole mixture) based on a calculated combined toxicity of two or more ingredients using the additivity formula. The assigned classification based on the calculated toxicity is then subsequently used in applying the summation method (see para 4.1.3.5.2).

6.   To make full use of this approach requires access to the whole aquatic toxicity dataset and the necessary knowledge to select the best and most appropriate data, which can be a difficult task for company self-classification. Clearly, the best use would be to add up

separately each of the fish toxicity data, the crustacean toxicity data and the algae/aquatic plants toxicity data (or even separate species within these thropic levels) to derive a specific toxicity value for each trophic level (para 4.1.3.5.3).

7.	Para 4.1.3.5.4 which says that *"If a mixture is classified in more than one way, the method yielding the more conservative result should be used"*. This refers to the many ways and difficulties in using the additivity formula. The mixture may end up in different classifications depending on how the additivity formula is being used and then the calculation *yielding the more conservative result should be used*.

8.	Para 4.1.3.5.4 does not refer to a comparison between the summation method at one hand and the additiviy formula on the other. Again, it is the Summation method that shall be used and the additivity formula can be used in classifying non-classified ingredients before feeding these into the summation (see point 3, above).

M-Factor

9.	M-factors may be assigned the portion of two or more previously non-classified ingredients classified together by use of the additivity formula, since this is subsequently used in applying the summation method as if it was a substance.

10.	M-factors, are however, generally not assigned to mixtures.

Revision of the examples

11.	In the annex to this paper, beginning from next page, I have made a number of suggested amendments. I have not considered deleting or adding any of the examples but just made the minimum necessary changes in order to reflect the points I have made above.

12.	In order not to have to correct the word 'chronic' with 'long-term' etc. I have also suggested deleting the words 'acute' and 'chronic' where possible.

13.	An alternative to my suggested amendments would be not to agree on these examples at this stage and to wait with the proposal for inclusion in the training document which is being developed by the UNITAR until further work on the examples has been done.

Annex

Hazardous to the aquatic environment examples

These examples will be proposed for inclusion in the training document which is being developed by the United Nations Institute for Training and Research (UNITAR) (see UN/SCEGHS/19/INF.24, Annex 3):

Example 1

The following example demonstrates application of the acute additivity methods when only acute toxicity data are available for all of the components of a mixture and then applying the summation method. ~~Ingredients 1, 2, and 3 in this mixture are not classified into chronic categories because Ingredients 1, 2, and 3 are ready biodegradable and have experimentally determined bioconcentration factors (BCF) < 500.~~

Ingredient information:

Ingredient	Wt%	Acute toxicity data	$L(E)C_{50}$	~~Classification~~
Ingredient 1	20	Fish (96 hr LC_{50})	0.15	~~Acute 1~~ ~~M-Factor = 1~~
		Crustacea (48 hr EC_{50})	11	
		Algae /aquatic plants (72 or 96 hr ErC_{50})	33	
Ingredient 2	20	Fish (96 hr LC_{50})	12	~~Acute 2~~
		Crustacea (48 hr EC_{50})	1.2	
		Algae /aquatic plants (72 or 96 hr ErC_{50})	43	
Ingredient 3	60	Fish (96 hr LC_{50})	98	~~Acute 3~~
		Crustacea (48 hr EC_{50})	91	
		Algae /aquatic plants (72 or 96 hr ErC_{50})	95	

Answer:

Mixture is Acute Category 1~~, M-Factor 1~~

~~**Additivity formula**~~

Applying the ~~acute~~ additivity formula from 4.1.3.5.2 (a):

$$\frac{\sum C_i}{L(E)C_{50_m}} = \sum_n \frac{C_i}{L(E)C_{50_i}}$$

Where:

C_i	=	concentration of ingredient i (weight percentage);
$L(E)C_{50}$	=	LC_{50} or EC_{50} for ingredient i, in (mg/l);
N	=	number of ingredients, and i is running from 1 to n;
$L(E)C_{50_m}$	=	$L(E)C_{50}$ of the part of the mixture with test data;

Fish $LC_{50Mixture}$ = 100/(20/0.15 + 20/12 + 60/98) = 0.74 mg/l

Crustacea $EC5_{0Mixtur}e = 100/(20/11 + 20/1.2 + 60/91) = 5.22$ mg/l

Algae $ErC_{50Mixture} = 100/(20/33 + 20/43 = 60/95) = 58.73$ mg/l

Classification from additivity method: Category 1, M-Factor 1

~~Summation method~~

This classification based on the calculated toxicity is then subsequently used in applying the summation method

Acute 1:   (Acute 1) x M ≥ 25%

using data from ingredients of the mixture:

(~~20~~100% x 1) = ~~20~~100% (Classified~~Not classified~~)

~~Acute 2:   (M x 10 x Acute 1) + Acute 2 ≥ 25%~~

~~using data from ingredients of the mixture:~~

~~(1 x 10 x 20%) + 20% = 220% (Classified)~~

~~Classification from summation method: Acute Category 2~~

Rationale:

(a)   Classification via application of substance criteria is not possible since acute aquatic toxicity test data was not provided for the mixture as a whole (paragraph 4.1.3.3);

(b)   Classification via the application of bridging principles is not possible since data on a similar mixture was not provided (paragraph 4.1.3.4);

(c)   Classification based on ingredient data for the mixture can be considered (paragraph 4.1.3.5);

(d)   The ingredients are not previously classified and the percentage of the ingredients can therefore not directly be feed into the Summation method (paragraph 4.1.3.5.1);

(~~d~~e)   Adequate toxicity data is available for more than one ingredient so the additivity formulas can be considered (paragraph 4.1.3.5.2);

~~(e)   Classification of the mixture based on the acute summation method should be considered (paragraph 4.1.3.5.5) if the additivity formula is not applied;~~

(f)   Applying the "relevant ingredients" concept from paragraph 4.1.3.1 means that ingredients 1, 2, and 3 will be considered when applying the acute additivity formula (paragraph 4.1.3.5.2 (a)) and the summation method (paragraph 4.1.3.5.5).

~~(g)   Since the mixture was classified in more than one way, the method yielding the more conservative result was used (paragraph 4.1.3.5.4);~~

~~Additivity formula~~

(g)   All ingredients have acute aquatic toxicity data available for all taxonomic groups (i.e. fish, crustacean and algae) so the toxicity was calculated for each taxonomic group and the lowest value (i.e. Fish) was used to determine the classification (paragraph 4.1.3.5.3);

~~Summation method~~

~~(h)   The summation method for acute categories described in paragraph 4.1.3.5.5.3 applies and the cut off value/concentration limits provided in Table 4.1.3 are used for classification.~~

(End of example 1)

Example 2

The following example demonstrates application of the acute and chronic summation methods when classification information is available for some or all of the ingredients of a mixture but the L(E)C₅₀ data upon which classification is based are not available to the classifier of the mixture.

Ingredient information:

Ingredient	Wt%	Acute classification (M-factor)	Chronic classification (M-factor)
Ingredient 1	0.01	Acute 1 (M-factor: 10)	Chronic 1 (M-factor: 10)
Ingredient 2	1.0	Acute 2	Chronic 2
Ingredient 3	25.0	Not classified	Chronic 4
Ingredient 4	68.76	Not classified	Not classified

Answer:

Acute Classification - Not classified because:

Acute 1:   (Acute 1) x M $\geq$ 25%

using data from ingredients of the mixture:

(0.01% x 10) = 0.1% (Not classified)

Acute 2:   (M x 10 x Acute 1) + Acute 2 $\geq$ 25%

using data from ingredients of the mixture:

(10 x 10 x 0.01%) + 1.0% = 2.0% (Not classified)

Acute 3:   (M x 100 x Acute 1) + (10 x Acute 2) + Acute 3 $\geq$ 25%

using data from ingredients of the mixture:

(10 x 100 x 0.01%) + (10 x 1.0) = 20% (Not classified)

Chronic Classification - Category 4 because:

Chronic 1:   (Chronic 1) x M $\geq$ 25%

using data from ingredients of the mixture:

0.01% x 10 = 0.1% (Not classified)

Chronic 2:   (M x 10 x Chronic 1) + Chronic 2 $\geq$ 25%

using data from ingredients of the mixture:

(10 x 10 x 0.01%) + 1.0% = 2% (Not classified)

Chronic 3:   (M x 100 x Chronic 1) + (10 x Chronic 2) + Chronic 3 $\geq$ 25%

using data from ingredients of the mixture:

(10 x 100 x 0.01%) + (10 x 1.0%) = 20% (Not classified)

Chronic 4:   Chronic 1 + Chronic 2 + Chronic 3 + Chronic 4 $\geq$ 25%

using data from ingredients of the mixture:

0.01% + 1.0% + 25.0% = 26.01% (Classified)

Rationale:

(a)   Classification via application of substance criteria is not possible since aquatic toxicity test data was not provided for the mixture (paragraph 4.1.3.3);

(b)   Classification via the application of bridging principles is not possible since data on a similar mixture was not provided (paragraph 4.1.3.4);

(c)   Classification based on ingredient data for the mixture can be considered (paragraph 4.1.3.5);

 (d)   ~~Adequate toxicity data is not available so the additivity formulas cannot be considered (paragraph 4.1.3.5.2);~~

(~~e~~d)   Acute and chronic classification data is available for some of the ingredients of the mixtu~~r~~e and the percentage of these ingredients classified as "Acute" or "Chronic" will feed straight into the summation method~~so the summation method can be considered~~ (paragraph 4.1.3.5.~~5~~1);

Acute classification:

(~~f~~e)   Applying the "relevant ingredients" concept from paragraph 4.1.3.1 means that:

> (i)   The use of expert judgment is necessary to make the "relevant ingredient" decision for ingredient 1 since it is a highly toxic ingredient with an M-factor of 10. In this case it was decided to include the ingredient because its concentration in the mixture (i.e., 0.01%) is still significant given the M factor and the constants used in the Acute 2 and 3 calculations for Acute 1 ingredients;

> (ii)   Ingredient 2 will be included in the calculation because it is in the mixture at a concentration $\geq 1\%$;

(~~g~~f)   The ~~acute~~ summation method approach described in paragraph 4.1.3.5.5.3 applies and the cut-off value/concentration limits provided in Table 4.1.3 are used for classification.

Chronic classification:

(~~h~~g)   Applying the "relevant ingredients" concept from paragraph 4.1.3.1 means that:

> (i)   The use of expert judgment is necessary to make the "relevant ingredient" decision for ingredient 1 since it is a highly toxic ingredient with an M-factor of 10. In this case it was decided to include the ingredient because its concentration in the mixture (i.e., 0.01%) is still significant given the M factor and the constants used in the Chronic 2 and 3 calculations for Chronic 1 ingredients.

> (ii)   Ingredients 2 and 3 will be included in the calculation because they are in the mixture at a concentration $\geq 1\%$.

 (~~i~~h)   The ~~chronic~~ summation method approach described in paragraph 4.1.3.5.5.4 applies and the cut-off value/concentration limits provided in Table 4.1.4 are used for classification.

(End of example 2)

Example 3

The following example demonstrates application of a stepped approach where the additivity formula is used for the part of the mixture that has chronic toxicity data and passing that result into the ~~chronic~~ summation method.

Ingredient information:

Ingredient	Wt%	Chronic toxicity data	NOEC or EC_x	Rapidly degradable	Classification
Ingredient 1	15	NOEC (28 day for fish)	4.1	Yes	<u>not provided</u> ~~Chronic 3~~
		NOEC (21 day for crustacea)	0.13		
Ingredient 2	5	NOEC (for algae)	0.8	No	<u>not provided</u> ~~Chronic 2~~
Ingredient 3	80	~~Data not provided by supplier~~			Chronic 3

Answer:

Mixture is Chronic Category 3

Step 1:

Applying the ~~chronic~~ additivity formula from 4.1.3.5.2 (b):

$$\frac{\sum Ci + \sum Cj}{EqNOEC_m} = \sum_n \frac{Ci}{NOECi} + \sum_n \frac{Cj}{0.1 \times NOECj}$$

where:

C_i =   concentration of ingredient i (weight percentage) covering the rapidly degradable ingredients;

Cj =   concentration of ingredient j (weight percentage) covering the non- rapidly degradable ingredients;

$NOEC_i$ =   NOEC (or other recognized measures for chronic toxicity) for ingredient i covering the rapidly degradable ingredients, in mg/l;

$NOECj$ =   NOEC (or other recognized measures for chronic toxicity) for ingredient j covering the non-rapidly degradable ingredients, in mg/l;

N   =   number of ingredients, and i and j are running from 1 to n;

$EqNOEC_m$ =   Equivalent NOEC of the part of the mixture with test data;

EqNOECm = 20/(15/0.13) + 5/(0.1x 0.8) = 0.11 mg/l

The part of the mixture (i.e., 20%) with Chronic toxicity data (i.e., ingredients 1 and 2) has an EqNOECm of 0.11 mg/l. As the NOEC of the ingredients that are considered not-rapidly degradable have already been multiplied with the factor 0.1 the EqNOECm can now be applied to table 4.1 b (ii) resulting in a classification of Chronic 3.

Step 2:

Ingredient information going into the ~~chronic~~ summation method calculations:

Ingredient	Wt %	Classification
Additivity result – part of mixture with <u>only</u> toxicity data	20	Chronic 3
Ingredient 3	80	Chronic 3

Chronic 1: (Chronic 1) x M $\geq$ 25%

  0% (Not classified)

Chronic 2: (M x 10 x Chronic 1) + Chronic 2 $\geq$ 25%

  using data from the additivity result & ingredients of the mixture:

  (10 x 0%) + 0% = 0% (Not classified)

Chronic 3: (M x 100 x Chronic 1) + (10 x Chronic 2) + Chronic 3 $\geq$ 25%

  using data from the additivity result & ingredients of the mixture:

  (100 x 0%) + (10 x 0%) + 20% + 80% = 100% (Classified)

Rationale:

(a) Classification via application of substance criteria is not possible since acute aquatic toxicity test data was not provided for the mixture (paragraph 4.1.3.3);

(b) Classification via the application of bridging principles is not possible since data on a similar mixture was not provided (paragraph 4.1.3.4);

(c) Classification based on ingredient data for the mixture can be considered (paragraph 4.1.3.5);

(d) <u>The percentage of the ingredient classified as Chronic 3 will feed straight into the summation method (paragraph 4.1.3.5.1);</u>

(~~d~~e) Adequate toxicity data ~~as well as classification results~~ for the <u>other</u> ingredients are available so the additivity formula in combination with the summation method can be considered (paragraphs 4.1.3.5.2 & 4.1.3.5.5.4);

(~~e~~f) Applying the "relevant ingredients" concept from paragraph 4.1.3.1 means that ingredients 1, 2, and 3 will be considered in the calculations (paragraph 4.1.3.5.2 (b));

 (~~f~~g) When applying the additivity formula the preferred method is to calculate the toxicity of this part of the mixture for each ingredient toxicity values that relate to the same taxonomic group (i.e. fish, crustacean or algae) and then to use the highest toxicity obtained (i.e., use the most sensitive of the three groups). However, when toxicity data for each ingredient are not available in the same taxonomic group the data from the most sensitive test organism should be used (paragraph 4.1.3.5.3). In this case ingredient 1's toxicity data for Crustacea is used because it is has the lowest value (i.e. highest toxicity) and ingredient 2's Algae data is used;

(h) Application of the chronic additivity formula results in 20% of the mixture being classified at Chronic Category 3, which is used in the ~~chronic~~ summation method with the classification information provided for ingredient 3;

<div align="center">(End of example 3)</div>

Example 4

The following example demonstrates application of the tiered approach to determining the mixture's classification where acute toxicity data is available on the mixture <u>as a whole </u>as well as on the ingredients, and chronic classification information is only available on the ingredients.

Ingredient information:

Ingredient	Wt%	Acute toxicity data	$L(E)C_{50}$ mg/l	Chronic classification
Ingredient 1	5	LC_{50} (for fish)	12	Chronic 1
		EC_{50} (for crustacea)	18	(M Factor: 1)
		ErC_{50} (algae)	0.9	
Ingredient 2	1.5	LC_{50} (for fish)	40	Chronic 2
		EC_{50} (for crustacea)	25	
		ErC_{50} (algae)	9.5	
Ingredient 3	93.5	LC_{50} (for fish)	> 100	Chronic 4
		EC_{50} (for crustacea)	> 100	
		ErC_{50} (algae)	> 100	

Information on tested mixture:

Acute toxicity data	$L(E)C_{50}$ mg/l
LC_{50} (for fish)	68
EC_{50} (for crustacea)	90
ErC_{50} (algae)	12.5

Answer:

Acute classification - Category 3

Chronic classification - Category 2 because:

Chronic 1: (Chronic 1) x M ≥ 25%

5% x 1 = 5% (Not classified)

Chronic 2: (M x 10 x Chronic 1) + Chronic 2 ≥ 25%

using data from the ingredients of the mixture:

(1 x 10 x 5%) + 1.5% = 51.5% (Classified)

Rationale:

Acute classification:

(a) Classification via application of substance criteria is possible for acute toxicity since acute aquatic toxicity test data was provided for the mixture <u>as a whole </u>(paragraph 4.1.3.3);

(b) The higher toxicity value (from the most sensitive test organism) which in this case is Algae or other aquatic plants is used to classify the tested mixture (paragraph 4.1.3.3.3 (a));

Chronic classification:

(c)   Classification via application of substance criteria is not possible since chronic aquatic toxicity test data was not provided for the mixture <u>as a whole</u> (paragraph 4.1.3.3.4 (a));

(d)   Classification via the application of bridging principles is not possible since data on a similar mixture was not provided (paragraph 4.1.3.4);

(e)   ~~Adequate chronic toxicity data is not available so the chronic additivity formulas cannot be considered (paragraph 4.1.3.5.2 (b));~~

(~~f~~e)   Chronic classification data is available for some <u>or in this case all</u> of the ingredients of the mixture <u>and the percentage of these ingredients will feed straight into the summation method</u> ~~so the summation method can be considered~~ (paragraph 4.1.3.5.~~5~~1);

(~~g~~f)   Applying the "relevant ingredients" concept from paragraph 4.1.3.1 means that ingredients 1, 2, and 3 will be considered when applying criteria in paragraph 4.1.3.5.5;

(~~h~~g)   The chronic summation method approach described in paragraph 4.1.3.5.5.4 applies and the cut-off value/concentration limits provided in Table 4.1.4 are used for classification.

<p align="center">(End of example 4)</p>