

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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Item 2 (c) of the provisional agenda

Updating of the Globally Harmonized System of Classification
and Labelling of Chemicals (GHS) – Environmental hazards

Request for nominations for a technical correspondence group to align the Annex 9 (section 9.7) and Annex 10 on the Transformation Dissolution protocol to the generic environmental hazard guidance

**Transmitted by the International Council on Mining and Metals
(ICMM)**

Background

1. Reference is made to the report of the Sub-Committee of Experts on its 20th session (ST/SG/AC.10/C.4/40, paras. 20 and 21) and to its programme of work for 2010/2011 (ST/SG/AC.10/C.4/40, Annex II, section 3 (a) (ii)).

Introduction

Long-term hazard assessment for metals and metal compounds

2. Amending the strategy for metals and metal compounds to include the long-term aquatic assessment is feasible, technical in nature and not overly complex given that chronic toxicity data are typically abundantly available for metals and that the Transformation/Dissolution tool (T/Dp Protocol) can be applied in the same way as it is for the acute hazard assessment. No new concepts or principles are needed to implement this update in Annex 9 section A9.7 and Annex 10 as parallel application to the acute environmental hazard assessment can be drawn. It is therefore suggested that a specific *technical correspondence group* could develop the update and guidance accordingly based on the experience in the EU.

3. Indeed the mining and metals industry, in cooperation with the European Chemicals Agency (ECHA), has completed a redrafting of the European Union guidance for the implementation of the third revised edition of the GHS under the Classification, Labelling and Packaging Regulation (CLP Regulation), which includes an updated classification strategy, scheme and guidance for metals and metal compounds. This European Union guidance is expected to be approved by mid-2011.

4. It is well recognised that GHS introduction in European Union legislation for the environmental hazard endpoints is not identical to the original third revision of the GHS,

given that Acute 2 and 3 are hazard classes that do not exist in the European Union system. This however, does not impede the review suggested here since it is focussed on long-term hazard assessment exclusively and in the European Union this is nearly identical to the GHS system.

5. The representative of ICMM would therefore invite **all Sub-Committee experts wishing to participate in the work of the correspondence group to review Annex 9 section A9.7 and Annex 10 of the GHS, to contact him.**

Proposed scope and organisation of the work

Scope

6. The correspondence group will review Annex 9 section A9.7 on the Classification of Metals and Metal Compounds as well as Annex 10 on the Transformation-Dissolution of Metals and Metal Compounds in Aqueous Media for inclusion under the next revised edition of the GHS. This would ensure the classification strategy, guidance and tools on metals and metal compounds are in line with the long-term aquatic classification scheme introduced by the third revised edition.

7. The main changes that are required to amend the present acute hazard categories towards the long-term aquatic classification endpoint for metals and metal compounds include:

- (a) For Annex 9, section A9.7:
 - (i) extension of the classification strategy (see figure A9.7.1 in Annex I) and guidance for metals, and poorly soluble metal compounds towards the long-term aquatic classification endpoint. Figure IV.5.3.2a, (see Annex II) from the European Union guidance provides an overview of the section to be included in Annex 9, section A9.7
 - (ii) extension of the effects data interpretation for data rich substances, to the long-term aquatic classification endpoint
 - (iii) review of the application of M-factors for the acute and long-term aquatic classification endpoint
 - (iv) potential additional guidance on the demonstration of “rapid removal” from the water column
- (b) For Annex 10: extension of the Transformation Dissolution protocol (TDp) to lower doses (0.1 and 0.01 at 28 days) - which could include testing and modelling guidance

8. Given the complexity on the interpretation of the use of acute and chronic Transformation Dissolution data and equivalent effects data, it is also suggested to *include some examples* demonstrating the application of section A9.7 of Annex 9 under the GHS scheme.

9. The draft EU proposal on the metals environmental classification system prepared by an ECHA expert group including representatives from the mining and metals sector as well as the examples developed for this purpose are enclosed in Annex 3 and 4 of this document. These proposals are presently under review by an EU Partner Expert Group and approval is expected by mid-2011.

Organisation of the work

10. The **Sub-Committee is invited** to nominate experts for the revision of Annex 9, section 9.7 and Annex 10 in line with the long-term aquatic classification endpoint as introduced by the third revised edition of the GHS.

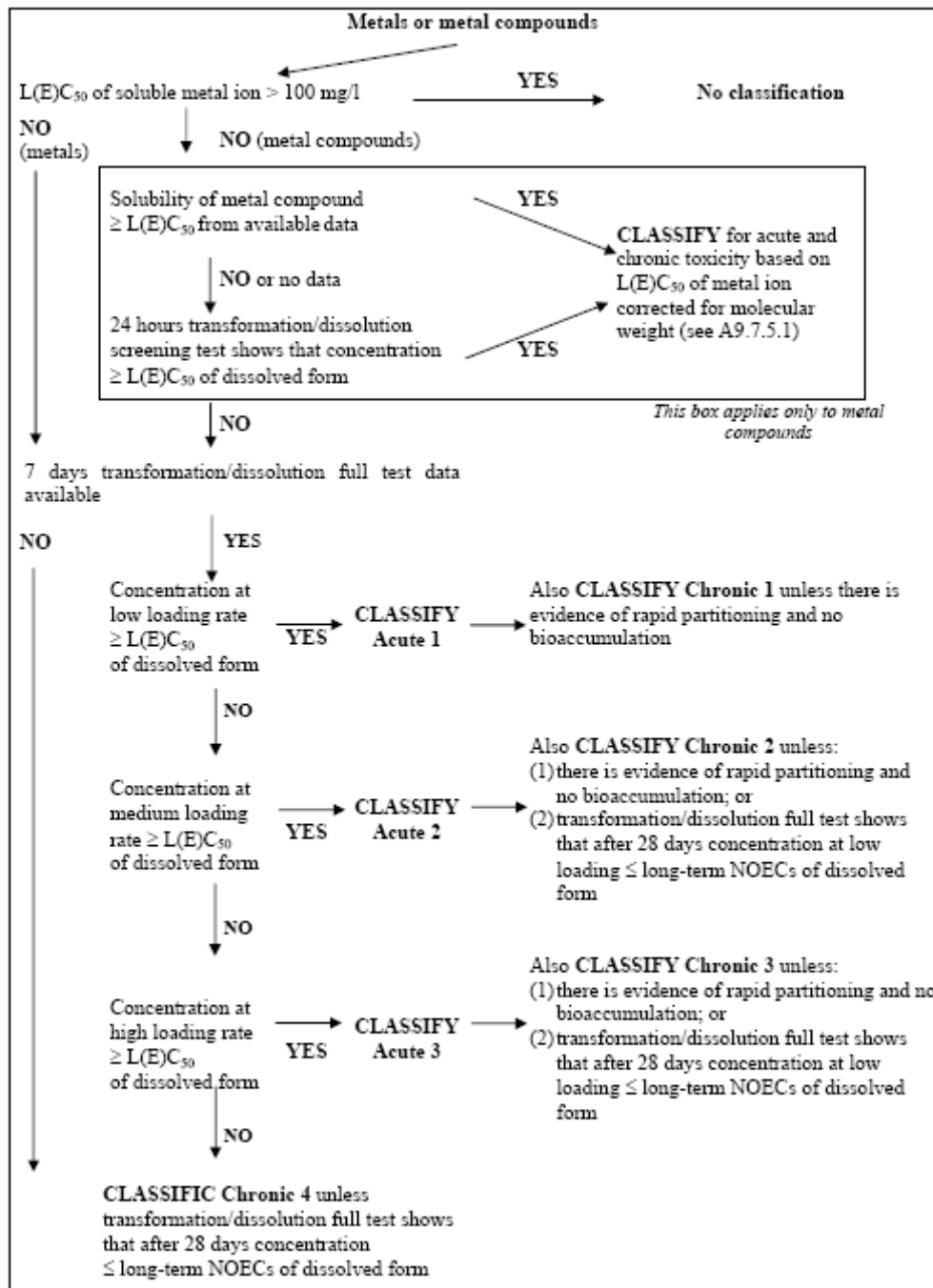
11. **ICMM will provide** a proposed draft update of section 9.7 of Annex 9 of the GHS, based on the experience with the EU CLP guidance (once approved), for consideration by the correspondence group.

12. **The correspondence group will:**

- (a) review the proposed draft update of section 9.7 of Annex 9 of the GHS
- (b) review the suggested amendments for Annex 10 of the GHS
- (c) review some indicative examples that can be used to illustrate the guidance
- (d) organise a written technical discussion round starting on 1 June and organise a conference call to discuss and review the suggested changes
- (e) Submit a proposal for consideration of the Sub-Committee at its 22nd session.

Annex I

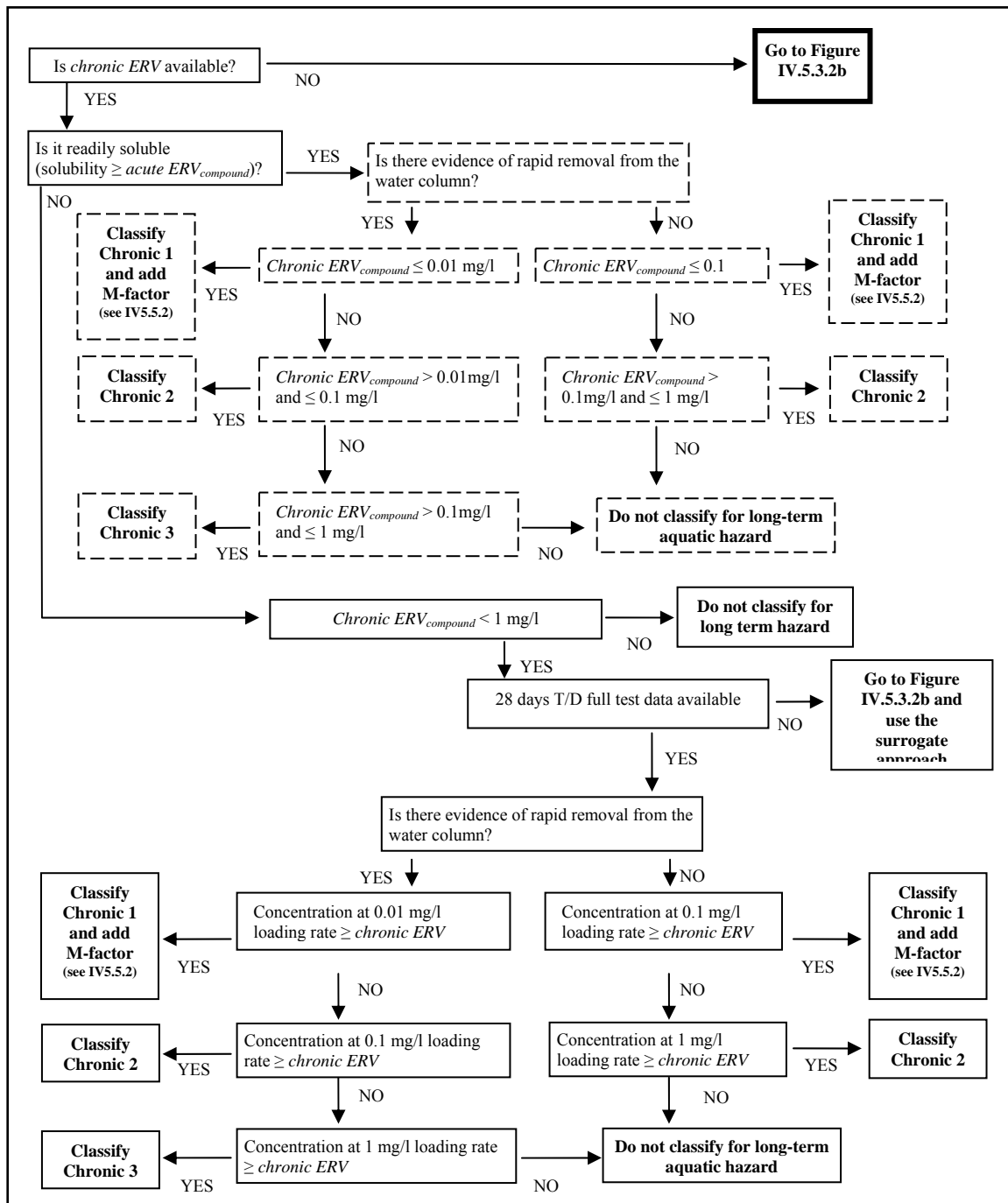
Figure A9.7.1 (GHS Rev.3): Classification strategy for metals and metal compounds



Annex II

EU-CLP guidance (updated version under review by the Partner Expert Group)

Figure IV.5.3.2a: Classification strategy for determining long-term aquatic hazard for metal compounds



Annex III

Guidance on the application of the CLP criteria

1 **Guidance on the Application of the CLP Criteria**

2

3 **Version as prepared by experts (May 1) in response to the 3rd update of the GHS and**
4 **under review by Partner Expert Group.**

5

1 **Metal and metal compounds**

4.1.2.10. Inorganic compounds and metals

4.1.2.10.1. For inorganic compounds and metals, the concept of degradability as applied to organic compounds has limited or no meaning. Rather, such substances may be transformed by normal environmental processes to either increase or decrease the bioavailability of the toxic species. Equally the use of bioaccumulation data shall be treated with care*.

4.1.2.10.1. Poorly soluble inorganic compounds and metals may be acutely or chronically toxic in the aquatic environment depending on the intrinsic toxicity of the bioavailable inorganic species and the rate and amount of this species which enter solution. All evidence must be weighed in a classification decision. This would be especially true for metals showing borderline results in the Transformation/Dissolution Protocol.

(*) Specific guidance has been issued by the European Chemicals Agency on how these data for such substances may be used in meeting the requirements of the classification criteria.”

2 **Annex IV** provides the detailed guidance on the classification of metals and metal
3 compounds.

4 The guidance on classification of alloys and complex metal containing materials is limited so
5 far. More guidance is needed (see also **Annex IV 5.5.1**).

6

1 IV ANNEX IV: METALS AND INORGANIC METAL COMPOUNDS

2 IV.1 Introduction

3 The harmonised system for classifying chemical substances is a hazard-based system, and the
4 basis of the identification of hazard is the aquatic toxicity of the substances, and information
5 on the degradation and bioaccumulation behaviour (OECD 1998). Since this document deals
6 only with the hazards associated with a given substance when the substance is dissolved in
7 the water column, exposure from this source is limited by the solubility of the substance in
8 water and bioavailability of the substance to organisms in the aquatic environment. Thus, the
9 hazard classification schemes for metals and metal compounds are limited to the acute and
10 long term hazards posed by metals and metal compounds when they are available (i.e. exist
11 as dissolved metal ions, for example, as M^+ when present as $M-NO_3$), and do not take into
12 account exposures to metals and metal compounds that are not dissolved in the water column
13 but may still be bioavailable, such as metals in foods. This section does not take into account
14 the non-metallic ion (e.g. CN^-) of metal compounds which may be toxic. For such metal
15 compounds the hazards of the non-metallic ions must also be considered.

16 Also organometal compounds may be of concern given they may pose bioaccumulation or
17 persistence hazards. Organometals do not dissociate or dissolve in water as the metal ion, as
18 metals and inorganic metal compounds do. Organometals (e.g. methyl mercury or tributyltin)
19 that do not release metal ions are thereby excluded from the guidance of this section and
20 should be classified according to the general guidance provided in section 4. Metal
21 compounds that contain an organic component but that dissociate easily in water or dissolve
22 as the metal ion should be treated in the same way as metal compounds and classified
23 according to this annex (e.g. zinc acetate).

24 The level of the metal ion which may be present in solution following the addition of the
25 metal and/or its compounds, will largely be determined by two processes: the extent to which
26 it can be dissolved, i.e. its water solubility, and the extent to which it can react with the media
27 to transform to water soluble forms. The rate and extent at which this latter process, known as
28 “transformation” for the purposes of this guidance, takes place can vary extensively between
29 different compounds and the metal itself, and is an important factor in determining the
30 appropriate hazard class. Where data on transformation are available, they should be taken
31 into account in determining the classification. The Protocol for determining this rate is
32 available as Annex 10 to the UN GHS.

33 Generally speaking, the rate at which a substance dissolves is not considered relevant to the
34 determination of its intrinsic toxicity. However, for metals and many poorly soluble inorganic
35 metal compounds, the difficulties in achieving dissolution through normal solubilisation
36 techniques are so severe that the two processes of solubilisation and transformation become
37 indistinguishable. Thus, where the compound is sufficiently poorly soluble that the levels
38 dissolved following normal attempts at solubilisation do not exceed the available $L(E)C_{50}$, it
39 is the rate and extent of transformation, which must be considered. The transformation will be
40 affected by a number of factors, not least of which will be the properties of the media with
41 respect to pH, water hardness, alkalinity, temperature etc. In addition to these properties,
42 other factors such as the size and, in particular, the specific surface area of the particles which
43 have been tested, the length of time over which exposure to the media takes place and, of
44 course the mass or surface area loading of the substance in the media will all play a part in
45 determining the level of dissolved metal ions in the water. Transformation data can generally,

1 therefore, only be considered as reliable for the purposes of classification if conducted
2 according to the standard protocol in Annex 10 to UN GHS. This protocol aims at
3 standardising the principal variables such that the level of dissolved ion can be directly
4 related to the loading of the substance added. It is this loading level which yields the level of
5 metal ion equivalent to the available L(E)C₅₀ or NOEC/EC₁₀ that can then be used to
6 determine the acute or long-term hazard category appropriate for classification. The testing
7 methodology is detailed in Annex 10 to the UN GHS. The strategy to be adopted in using the
8 data from the testing protocol, and the data requirements needed to make that strategy work,
9 are described in Annex IV.2, IV.3 and in more detail in Annex IV.5 of this document.

10 In considering the classification of metals and metal compounds, both readily and poorly
11 soluble, recognition has to be paid to a number of factors. As defined in Annex II, section
12 II.1, the term “degradation” refers to the decomposition of organic molecules. For inorganic
13 compounds and metals, clearly the concept of degradability, as it has been considered and
14 used for organic substances, has limited or no meaning. Rather, the substance may be
15 transformed by normal environmental processes to either increase or decrease the
16 bioavailability of the toxic species. Equally, the log K_{ow} cannot be considered as a measure of
17 the potential to accumulate. Nevertheless, the concept that a substance, or a toxic
18 metabolite/reaction product may not be rapidly lost from the environment and/or may
19 bioaccumulate, are as applicable to metals and metal compounds as they are to organic
20 substances.

21 Speciation of the soluble form can be affected by pH, water hardness and other variables, and
22 may yield particular forms of the metal ion which are more or less toxic. In addition, metal
23 ions could be made non-available from the water column by a number of processes (e.g.
24 mineralisation and partitioning). Sometimes these processes can be sufficiently rapid to be
25 analogous to degradation in assessing chronic (long-term) aquatic hazard. However,
26 partitioning of the metal ion from the water column to other environmental media does not
27 necessarily mean that it is no longer bioavailable, nor does it necessarily mean that the metal
28 has been made permanently unavailable.

29 Information pertaining to the extent of the partitioning of a metal ion from the water column,
30 or the extent to which a metal has been or can be converted to a form that is less toxic or non-
31 toxic is frequently not available over a sufficiently wide range of environmentally relevant
32 conditions, and thus, a number of assumptions will need to be made as an aid in
33 classification. These assumptions may be modified if available data show otherwise. In the
34 first instance it should be assumed that the metal ions, once in the water, are “not rapidly
35 partitioned” from the water column. Underlying this is the assumption that, although
36 speciation can occur, the species will remain available under environmentally relevant
37 conditions. This may not always be the case, as described above, and any evidence available
38 that would suggest changes to the bioavailability over the course of 28 days, should be
39 carefully examined.

40 The term “Rapid removal” is a more accurate description for metals in this respect because,
41 partitioning (e.g. by precipitation and especially speciation processes) can lead to the non
42 available form and the elimination of metals from the water column.

43 The bioaccumulation of metals and inorganic metal compounds is a complex process and
44 bioaccumulation data should be used with care. The application of bioaccumulation criteria
45 will need to be considered on a case-by-case basis taking due account of all the available
46 data.

1 A further assumption that can be made, which represents a cautious approach, is that, in the
2 absence of any solubility data for a particular metal compound, either measured or calculated,
3 the metal compound will be assumed to be sufficiently soluble to cause toxicity at the level of
4 the ecotoxicity reference value (ERV), being the acute ERV (expressed as L(E)C₅₀), and/or
5 the chronic ERV (expressed as the NOEC/EC_x or an HC₅ for extensive data sets) and thus
6 may be classified in the same way as other soluble salts of the metal. Again, this is clearly not
7 always the case, and it may be wise to generate appropriate solubility data. Absence of
8 solubility data on the metallic form for a metal for which the soluble salts are classified for
9 the environment, will therefore lead to a default classification due to potential hazard
10 concerns.

11 This Annex IV deals with metals and inorganic metal compounds. Within the context of this
12 guidance document, metals and metal compounds are characterised as follows:

- 13 (a) metals (M⁰) in their elemental state are not soluble in water but may transform to yield
14 the available form (eg Fe⁰ will not dissolve as such but the Fe⁰ molecules present at
15 the surface of a massive/powder will be first transformed into Fe²⁺ or Fe³⁺ compounds
16 prior to their solubilisation). This means that a metal in the elemental state may react
17 with water or a dilute aqueous electrolyte to form soluble cationic or anionic products,
18 and in the process the metal will oxidise, or transform, from the neutral or zero
19 oxidation state to a higher one;
- 20 (b) in a simple metal compound, such as an oxide or sulphide, the metal already exists in
21 the oxidised state, so that further metal oxidation is unlikely to occur when the
22 compound is introduced into an aqueous medium.

23 Organo-metals are therefore outside the scope of this section.

24 While oxidisation may not change, interaction with the media may yield more soluble forms.
25 A sparingly soluble metal compound can be considered as one for which a solubility product
26 can be calculated, and which will yield a small amount of the available form by dissolution.
27 However, it should be recognised that the final solution concentration may be influenced by a
28 number of factors, including the solubility product of some metal compounds precipitated
29 during the transformation/dissolution test, e.g. aluminium hydroxide.

30 **IV.2 Application of aquatic toxicity data and solubility data for classification**

31 **IV.2.1 Interpretation of aquatic toxicity data**

32 Ecotoxicity data of soluble inorganic compounds are used and combined to define the
33 toxicity of the metal ion under consideration. The ecotoxicity of soluble inorganic metal
34 compounds is dependent on the physico-chemistry of the medium, irrespective of the original
35 metal species released in the environment. Reading across metal compounds can therefore be
36 conducted by comparing the soluble metal ion concentration (µg Me/L) causing the
37 ecotoxicity effect and translating this towards the compound under investigation. A molecular
38 weight correction of the ecotoxicity reference value may be required to classify soluble metal
39 compounds (MW soluble substance/MW metal ion¹). Poorly soluble metal compounds do not
40 require Molecular weight correction given the amount used for Transformation Dissolution
41 already recognises this into the loading calculation. The comparison is therefore directly done

¹ Note that this calculation needs to be adjusted to reflect the stoichiometry of the compound, for example for Zn₃(PO₄)₂ the MW metal would be multiplied by three.

1 by comparing the soluble fraction measured after Transformation Dissolution with the
2 ecotoxicity reference values of the soluble metal ion. (based on the UN GHS, 2009).

3 When evaluating ecotoxicity data, the general guidance on the weight of evidence (see
4 section 4.1.3.6 of this document) is also applicable to metals.

5 The term adequacy covers here both the *reliability* (inherent quality of a test relating to test
6 methodology and the way that the performance and results of a test are described) and the
7 *relevance* (extent to which a test is appropriate to be used for the derivation of an ecotoxicity
8 reference value) of the available ecotoxicity data:

9 Under the reliability criteria, metal specific considerations include the description of some
10 abiotic parameters in the test conditions for enabling the consideration of the bioavailable
11 metal concentration and free metal ion concentration:

12 - *Description of the physical test conditions:* further to the general parameters (O₂, T°,
13 pH, ...) abiotic parameters such as dissolved organic carbon (DOC), hardness,
14 alkalinity of the water that govern the speciation and hence the metal bioavailability is
15 required. A proper description of culture conditions related to the level of essential
16 metals is required to avoid artefacts due to acclimatisation/adaptation (see also below)

17 - *Description of test materials and methods:* to calculate the free metal ion
18 concentration with speciation models the concentrations of dissolved major ions and
19 cations like Al, Fe, Mg, Ca... are required

20 - *Concentration-effect relationship; hormesis:* sometimes an increased performance in
21 growth or reproduction is seen at low metal doses that exceed the control values,
22 referred to as hormesis. Such effects can be important especially for major trace
23 nutrients such as Fe, Zn and Cu but can also occur with a wide variety of non-
24 essential substances. In such cases, positive effects should not be considered in the
25 derivation of acute ERV's and especially chronic ERV's, likely other models than the
26 conventional log-logistic dose-response model should be used to fit the dose-response
27 curve and consideration should be given to the adequacy of the control diet/exposure.
28 Due to the essential nutritional needs, caution is needed with regards to extrapolation
29 of the dose-response curve (eg to derive an acute ERV) below the lowest tested
30 concentration.

31 Under the relevancy criteria, certain considerations need to be made, related to the relevancy
32 of the test substance and to acclimatisation/adaptation:

33 - *Relevance of the test substance:* soluble metal salts should be used for the purpose of
34 classification of inorganic metals/metal compounds. The ecotoxicity adapted from
35 organic metal compounds exposure should not be used.

36 - *Acclimatisation/adaptation:* For essential metals, the culture medium should contain a
37 minimal concentration not causing deficiency for the test species used. This is
38 especially relevant for organisms used for long term toxicity tests where the margin
39 between essentiality and toxicity may become small. As an example, for algae,
40 deletion of the strong complexing agent EDTA from the medium may result in iron
41 deficiency.

42 Aquatic toxicity studies carried out according to a recognised protocol should normally be
43 acceptable as valid for the purposes of classification. Annex I should also be consulted for
44 generic issues that are common to assessing any aquatic toxicity data point for the purposes
45 of classification.

46

1 **IV.2.1.1 Metal complexation and speciation**

2 The toxicity of a particular metal in solution, appears to depend primarily on (but is not
3 strictly limited to) the level of dissolved free metal ions and the physico-chemistry of the
4 environment. Abiotic factors including alkalinity, ionic strength and pH can influence the
5 toxicity of metals in two ways: (i) by influencing the chemical speciation of the metal in
6 water (and hence affecting the availability) and (ii) by influencing the uptake and binding of
7 available metal by biological tissues. For the classification of metals,
8 Transformation/Dissolution is carried out over a pH range. Ideally both T/D and ecotoxicity
9 data are compared at a similar pH since both parameters will vary with pH. However, the
10 majority of ecotoxicity tests are performed at the higher pH range (i.e. > pH 7.5) and
11 ecotoxicity data obtained at lower pH are often scarce. Bioavailability and speciation models
12 (e.g. respectively Biotic Ligand Models and WHAM (Tipping, 1994), as discussed below)
13 may allow to normalise ecotoxicity data obtained at a given pH to other pH values, relevant
14 to the T/D data. The applicability of the bioavailability models to the biological species for
15 which data are available must be evaluated. Guidance on the Bioavailability correction for
16 metals can be found in IR/CSA Annex R.7.13.2).

17 Where chemical speciation is important, it may be possible to model the concentrations of the
18 different chemical forms of the metal, including those that are likely to cause toxicity.
19 Analysis methods for quantifying exposure concentrations, which are capable of
20 distinguishing between the complexed and uncomplexed fractions of a test substance, may
21 not always be available or economic.

22 Complexation of metals to organic and inorganic ligands in test media and natural
23 environments can be estimated from metal speciation models. Speciation models for metals,
24 including pH, hardness, DOC, and inorganic substances such as MINTEQ (Brown and
25 Allison, 1987), WHAM (Tipping, 1994) and CHESS (Santore and Driscoll, 1995) can be
26 used to calculate the uncomplexed and complexed fractions of the metal ions.

27 Alternatively, and when available for the metal, the Biotic Ligand Model (BLM), allows, for
28 the calculation of the acute and/or chronic ERV's of the metal ion, for different pH values,
29 through integration of metal speciation and its interaction with the organism. The BLM
30 model has at present been validated for a number of metals, organisms, and end-points
31 (Santore and Di Toro, 1999). The models and formula used for the characterisation of metal
32 complexation in the media should always be clearly reported, allowing for their translation
33 back to natural environments (OECD, 2000). In case a metal-specific BLM is available
34 covering an appropriate pH range, a normalised comparison of aquatic toxicity data can be
35 made using the entire effects database for different reference pH values.

36

37 **IV.2.2 Interpretation of solubility data**

38 When considering the available data on solubility, their validity and applicability to the
39 identification of the hazard of metal compounds should be assessed. In particular, the pH and
40 the medium in which the data were generated should be known.

41

42 **IV.2.2.1 Assessment of existing data**

43 Existing data will be in one of the three forms: *for soluble, insoluble metal compounds and*
44 *the metallic form*. For some well-studied metals, there will be solubility products and/or
45 solubility data for the various inorganic metal compounds. It is also possible that the pH

1 relationship of the solubility will be known. However, for many metals or metal compounds,
2 it is probable that the available information will be descriptive only, e.g. poorly soluble or
3 resulting from the water solubility test form the OECD 105 physico-chemical water
4 dissolution test. Unfortunately there appears to be very little (consistent) guidance about the
5 solubility ranges for such descriptive terms. Where these are the only information available it
6 is most probable that solubility data will need to be generated using the
7 Transformation/Dissolution Protocol (Annex 10 to the UN GHS).

9 **IV.2.2.2 Screening T/D test for assessing solubility of metal compounds**

10 In the absence of solubility data, a simple “Screening Test” for assessing solubility, based on
11 the high rate of loading (100 mg/l) for 24 h and rigid stirring conditions, should be used for
12 metal compounds as described in the Transformation/Dissolution Protocol (Annex 10 to the
13 UN GHS). The function of the screening test is to identify those metal compounds which
14 undergo either dissolution or rapid transformation such that they are indistinguishable from
15 soluble forms and hence may be classified based on the dissolved ion concentration and those
16 who dissolves slowly and can be assessed in the same way as the metallic form. Where data
17 are available from the screening test detailed in the Transformation/Dissolution Protocol, the
18 maximum solubility obtained over the tested pH range should be used. Where data are not
19 available over the full pH range, a check should be made that this maximum solubility has
20 been achieved by reference to suitable thermodynamic speciation models or other suitable
21 methods (see section IV.2.1.1 of this document). It should be noted that this test is only
22 intended to be used for inorganic metal compounds. Metals should immediately be assessed
23 at the level of the full T/D test.

25 **IV.2.2.3 Full T/D test for assessing solubility of metals and metal compounds**

26 The Full Transformation Dissolution test should be carried out at the pH² that maximises the
27 concentration of dissolved metal ions in solution and that expresses the highest toxicity..

28 Based on the data from the Full Test, it is possible to generate a concentration of the metal
29 ions in solution after 7 days for each of the three loadings (i.e. 1 mg/l as “low”, 10 mg/l as
30 “medium” and 100 mg/l as “high loading”) used in the test. If the purpose of the test is to
31 assess the long-term hazard of the substance, then the loadings³ should be 0.01 mg/l, 0.1 mg/l
32 or 1 mg/l depending on the removal rate and the duration of the test being extended to 28
33 days.

² The UN-GHS transformation/dissolution protocol specifies a pH range of 6-8.5 for the 7days test and 5.5 to 8 .5 for the 28 days test. Considering the difficulty in carrying out transformation/dissolution tests at pH 5.5, the OECD only validated the test in the pH range of 6-to 8.5.

³ The standard protocol in Annex 10 to UN GHS presently only foresees a long-term loading rate of 1 mg/l and lower loading rates may not even be practically feasible for each case. While TDp testing at lower loading rates is in principle the best way forward it is technically often not feasible for the lower chronic loading rates. Extensive experience with the T/D protocol demonstrated that reliable predictions can be made for other loading rates. In order to make maximal use of existing Transformation Dissolution data, the 28 days results for the lower chronic loading rates (0,1 and 0,01 mg/l) can therefore be derived by extrapolation from TDp evidence from other loading rates. Such read across should be justified on a case by case basis and supported by reliable information on the T/D at different loading rates, e.g. over 7 and/or 28 days. It should be noted that the relationship between loading rate and dissolved metal concentration may well not be linear. Therefore extrapolation of T/D data to lower loadings should preferably be made by using the equations of section A10.6.1 of the UN-Annex 10 transformation dissolution protocol or alternatively by extrapolating in a precautionary way.

The UN announced to change/update Annex 10 in the near future to bring it better in line with the chronic classification strategy an aim that is already anticipated in this guidance note for the CLP.

1 IV.2.3 Comparison of aquatic toxicity data and solubility data

2 A decision on whether or not the substance is classified will be made by comparing aquatic
3 toxicity data and solubility data. Depending on the available data two approaches can be
4 followed.

5 1) When only a *limited dataset* is available existing data should be taken together
6 irrespective of whether the toxicity and dissolution data are at the same pH and the
7 lowest data point should give the basis for classification (this should be used as the
8 default approach). This default approach may lead to the lowest toxicity data point
9 compared with the highest Transformation Dissolution result each derived at different
10 pH levels..

11 2) When a more *extensive toxicity/dissolution dataset* is available, a split of the acute and
12 chronic ecotoxicity reference values can be performed according to their pH used
13 during T/D test. The worst case classification entry across pHs should be used based
14 on comparing TDp data with relevant ecotox data across the pH range. Meaning that
15 toxicity data and transformation data are in this case always compared at the same pH.

16 This split of the effects data into pH classes would apply in an equal way to the acute and the
17 long-term effects data sets.

18 IV.3 Assessment of environmental transformation

19 Environmental transformation of one species of a metal to another species of the same metal
20 does not constitute “degradation” as applied to organic compounds and may increase or
21 decrease the availability and bioavailability of the toxic species. In addition naturally
22 occurring geochemical processes can partition metal ions from the water column while also
23 other processes may remove metal ions from the water column (e.g. by precipitation and
24 speciation). Data on water column residence time, the processes involved at the water –
25 sediment interface (i.e. deposition and re-mobilisation) are fairly extensive for some metals.
26 Using the principles and assumptions discussed above in **section IV.1** of this document, it
27 may therefore be possible to incorporate this approach into the classification.

28 Such assessments are difficult to give guidance for and will normally be addressed on a case-
29 by-case approach. However, the following may be taken into account:

30 (a) Changes in speciation if they are to non-available forms, however, the potential
31 for the reverse change to occur must also be considered;

32 (b) Changes to a metal compound which is considerably less soluble than that of the
33 metal compound being considered.

34 Some caution is recommended; see **section IV.1** of this document, the 5th and 6th paragraph.

35 Laboratory tests evaluating changes of metal species to less soluble metal species,
36 laboratory/mesocosm studies, and field data and/or supported by relevant models could be
37 useful in evaluating removal of soluble metal species through precipitation/speciation
38 processes over a range of environmentally relevant conditions.

39 IV.4 Bioaccumulation

40 While log Kow is a good predictor of BCF for certain types of organic compounds e.g.
41 nonpolar organic substances, it is irrelevant for inorganic substances such as inorganic metal
42 compounds because metals, in contrast to organic substances, are not lipophilic and are not

1 passively transported through cellular membranes. Uptake of metal ions occurs through
2 active processes.

3 The mechanisms for uptake and depuration rates of metals are very complex and variable and
4 there is at present no general model to describe this. Instead the bioaccumulation of metals
5 according to the classification criteria should be evaluated on a case-by-case basis using
6 expert judgement.

7 While BCFs are indicative of the potential for bioaccumulation there may be a number of
8 complications in interpreting measured BCF values for metals and inorganic metal
9 compounds. For most metals and inorganic metal compounds the relationship between water
10 concentration and BCF in aquatic organisms is inverse, and bioconcentration data should
11 therefore be used with care. This is particularly relevant for metals that are biologically
12 essential. Metals that are biologically essential are actively regulated in organisms in which
13 the metal is essential. Removal and sequestration processes that minimise toxicity are
14 complemented by an ability to up-regulate concentrations for essentiality. Since nutritional
15 requirement of the organisms can be higher than the environmental concentration, this active
16 regulation can result in high BCFs and an inverse relationship between BCFs and the
17 concentration of the metal in water. When environmental concentrations are low, high BCFs
18 may be expected as a natural consequence of metal uptake to meet nutritional requirements
19 and can in these instances be viewed as a normal phenomenon. Also, while a metal may be
20 essential in a particular organism, it may not be essential in other organisms. Therefore,
21 where the metal is not essential or when the bioconcentration of an essential metal is above
22 nutritional levels, special consideration should be given to the potential for bioconcentration
23 and environmental concern.

24 Non-essential metals are also actively regulated to some extent and therefore also for non-
25 essential metals, an inverse relationship between the metal concentration and the external
26 concentration may be observed (McGeer et al., 2003).

27 Consequently for both essential and non-essential elements, measured BCFs decline as
28 external concentration increases. When external concentrations are so high that they exceed a
29 threshold level, or overwhelm the regulatory mechanism, this can cause harm to the organism

30 BCF and BAF may be used to estimate metal accumulation by:

31 a) Considering information on essentiality and homeostasis of metals/ metal compounds. As a
32 result, of such regulation, the “bioaccumulative” criterion is not applicable to these metals.

33 b). Assessing bioconcentration factors for non-essential metals, should preferably be done
34 from BCF studies using environmentally relevant concentrations in the test media.

35 **IV.5 Classification strategies for metals and metal compounds**

36 **IV.5.1 Introduction**

37 Notice! *Acute and Long Term hazard assessment* are assessed individually.

38 For determination of long-term hazards preference should be given in applying the approach
39 based on chronic toxicity data. Such evidence is often frequently available for the
40 bioavailable forms of metals.

41 The schemes for the determination of acute and long term aquatic hazards of metals and
42 metal compounds are described below and summarised diagrammatically in the figures:

43 IV.5.2.1 (acute hazard classification of metals),

- 1 IV.5.2.2 (a and b) (long-term hazard of metals);
- 2 IV.5.3.1 (acute hazard classification of metal compounds);
- 3 IV.5.3.2 (a and b) (long-term hazard of metal compounds).

4 There are several stages in these schemes where data are used for decision purposes. It is not
5 the intention of the classification schemes to generate new ecotoxicity data. In the absence of
6 valid data, it will be necessary to use all available data and expert judgement.

7 In the following sections, the reference to the acute and chronic ERV's refer to the data
8 point(s) that will be used to select the hazard category(ies) for the metal or metal compound.

9 When considering acute and chronic ERV's data for metal compounds, it is important to
10 ensure that the data point to be used as the justification for the classification is expressed in
11 the weight of the molecule of the metal compound to be classified. This is known as
12 correcting for molecular weight. Thus while most metal data is expressed in, for example,
13 mg/l of the metal (ion), this value will need to be adjusted to the corresponding weight of the
14 metal compound. Thus:

15 Acute ERV_{compound} = acute ERV of the metal compound = acute ERV of metal ion x
16 (Molecular weight of metal compound /atomic weight of the metal).

17 Chronic ERV_{compound} = chronic ERV of the metal compound = chronic ERV of metal ion x
18 (Molecular weight of metal compound /atomic weight of the metal).

19

20 **IV.5.2 Classification strategies for metals**

21 Notice! Acute and Long Term hazard assessment are assessed individually for metals.

22 **IV.5.2.1 Classification strategy for determining acute aquatic hazard for metals**

23 The scheme for the determination of *acute* aquatic hazard for metals are described in this
24 section and summarised diagrammatically in Figure IV.5.2.1.

25 Where *the acute ERV* for the metal ions of concern is greater than 1 mg/l the metals need not
26 be considered further in the classification scheme for acute hazard.

27 Where the acute ERV for the metal ions of concern is less than or equal to 1 mg/l
28 consideration must be given to the data available on the rate and extent to which these ions
29 can be generated from the metal. Such rate and extend data, to be valid and useable should
30 have been generated using the Transformation/Dissolution Protocol (Annex 10 to UN GHS)
31 for a 7d period.

32 Where 7d data from the Transformation/Dissolution protocol are available, then the results
33 should be used to classify, according to the following rule:

34

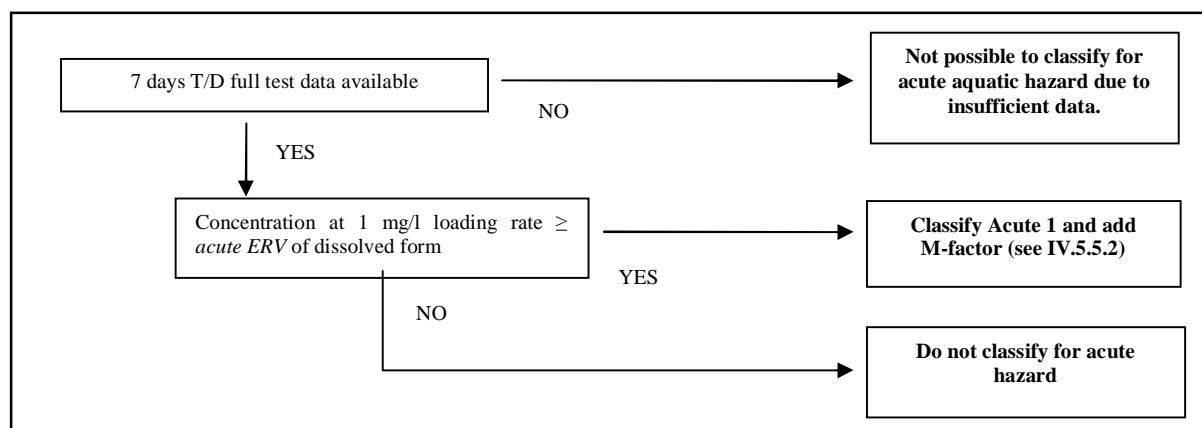
35 Classify the metal as **Category Acute 1** if the dissolved metal ion concentration after a
36 period of 7 days (or earlier for a significant time period) at a loading rate of 1 mg/l
37 exceeds that of the acute ERV, an M-factor must also be established as part of this
38 classification (see IV 5.5.2).

39

40

41

1 **Figure IV.5.2.1** Classification strategy for determining *acute* aquatic hazard for metals.



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5 **IV.5.2.2 Classification strategy for determining long-term aquatic hazard for metals**

6 The scheme for the determination of *long-term* aquatic hazard for metals are described in this
7 section and summarised diagrammatically in Figures IV.5.2.2 (a and b).

8 Metals can be classified for long term aquatic hazards:

- 9 1) using chronic reference data when available; or
10 2) using the surrogate approach in absence of appropriate chronic toxicity reference data.

11

12 In case relevant chronic ecotoxicity data (chronic ERV) are available the approach comparing
13 chronic ERV with 28 days transformation/dissolution reference should be applied as
14 described under IV.5.2.2.1 while otherwise the surrogate approach (see IV.5.2.2.2) should be
15 followed.

16

17 **IV.5.2.2.1 Approach based on available chronic toxicity reference data**

18 Where *the chronic ERV* for the metal ions of concern is greater than 1 mg/l, the metals need
19 not be considered further in the classification scheme.

20 Where the chronic ERV for the metal ions of concern is less than or equal to 1 mg/l
21 consideration must be given to the data available on the rate and extent to which these ions
22 can be generated from the metal. Such rate and extend data, to be valid and useable should
23 have been generated using the Transformation/Dissolution Protocol (Annex 10 to UN GHS)
24 for a 28 d period.

25 Where such T/Dp data are unavailable the surrogate approach should be applied (see section
26 5.2.2.2). Where 28d data from the Transformation/Dissolution protocol are available, then,
27 the results should be used to aid classification according to the following rules:

- 28 a) **Classify** the metal as **Category Chronic 1** if the dissolved metal ion concentration
29 obtained at a loading rate of 0.1 mg/l is greater than or equal to the chronic ERV, an
30 M-factor must also be established as part of this classification (see IV.5.5.2); or
31 b) **Classify** the metal as **Category Chronic 2** if the dissolved metal ion concentration
32 obtained at a loading rate of 1 mg/l is greater than or equal to the chronic ERV.

1 If there is evidence of rapid removal from the water column and

2 c) **Classify** the metal as **Category Chronic 1** if the dissolved metal ion concentration
3 obtained at a loading rate of 0.01 mg/l is greater than or equal to the chronic ERV, an
4 M-factor must also be established as part of this classification (see IV 5.5.2). ; or

5 d) **Classify** the metal as **Category Chronic 2** if the dissolved metal ion concentration
6 obtained at a loading rate of 0.1 mg/l is greater than or equal to the chronic ERV; or

7 e) **Classify** the metal as **Category Chronic 3** if the dissolved metal ion concentration
8 obtained at a loading rate of 1 mg/l is greater than or equal to the chronic ERV.

9

10 Do not classify for long-term hazard if the dissolved metal ion concentration obtained from
11 the 28 day Transformation/Dissolution test at **a loading rate of 1 mg/l** is less than the chronic
12 ERV of the metal ion.

13

14 **IV.5.2.2.2 The surrogate approach**

15 Where the acute ERV for the metal ions of concern is less than or equal to 100 mg/l
16 consideration must be given to the data available on the rate and extent to which these ions
17 can be generated from the metal. Such rate and extend data, to be valid and useable should
18 have been generated using the Transformation/Dissolution Protocol (Annex 10 to UN GHS)
19 for a 7d period.

20 Where such T/Dp data are unavailable, i.e. there is no clear data of sufficient validity to show
21 that the transformation to metal ions will not occur; the safety net classification (Category
22 Chronic 4) should be applied if.

23 Where T/Dp data are available classification should be according to the following rules:

24 (a) **Classify** the metal as **Category Chronic 1** if the dissolved metal ion concentration
25 obtained from the 7 day transformation test at the low loading rate (1 mg/l) is
26 greater than or equal to the acute ERV, an M-factor must also be established as
27 part of this classification (see IV.5.5.2).;

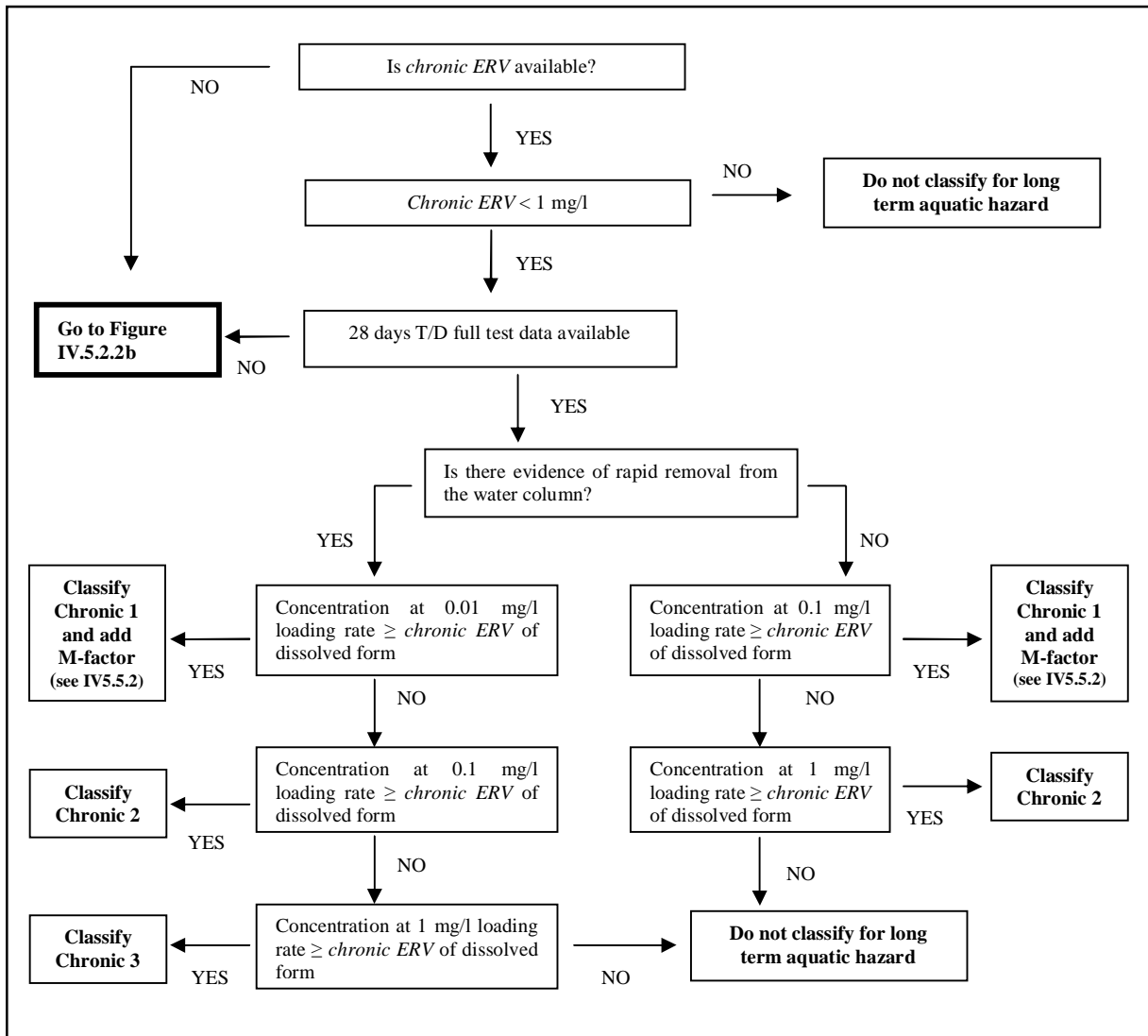
28 (b) **Classify** the metal as **Category Chronic 2** if the dissolved metal ion concentration
29 obtained from the 7 day transformation test at the medium loading rate (10 mg/l)
30 is greater than or equal to the acute ERV;

31 (c) **Classify** the metal as **Category Chronic 3** if the dissolved metal ion concentration
32 obtained from the 7 day transformation test at the high loading rate (100 mg/l) is
33 greater than or equal to the acute ERV.

34 (d) **Classify** the metal as **Category Chronic 4** if the dissolved metal ion concentration
35 obtained from the 7 day transformation test at the high loading rate (100 mg/l) is
36 lower than the acute ERV.

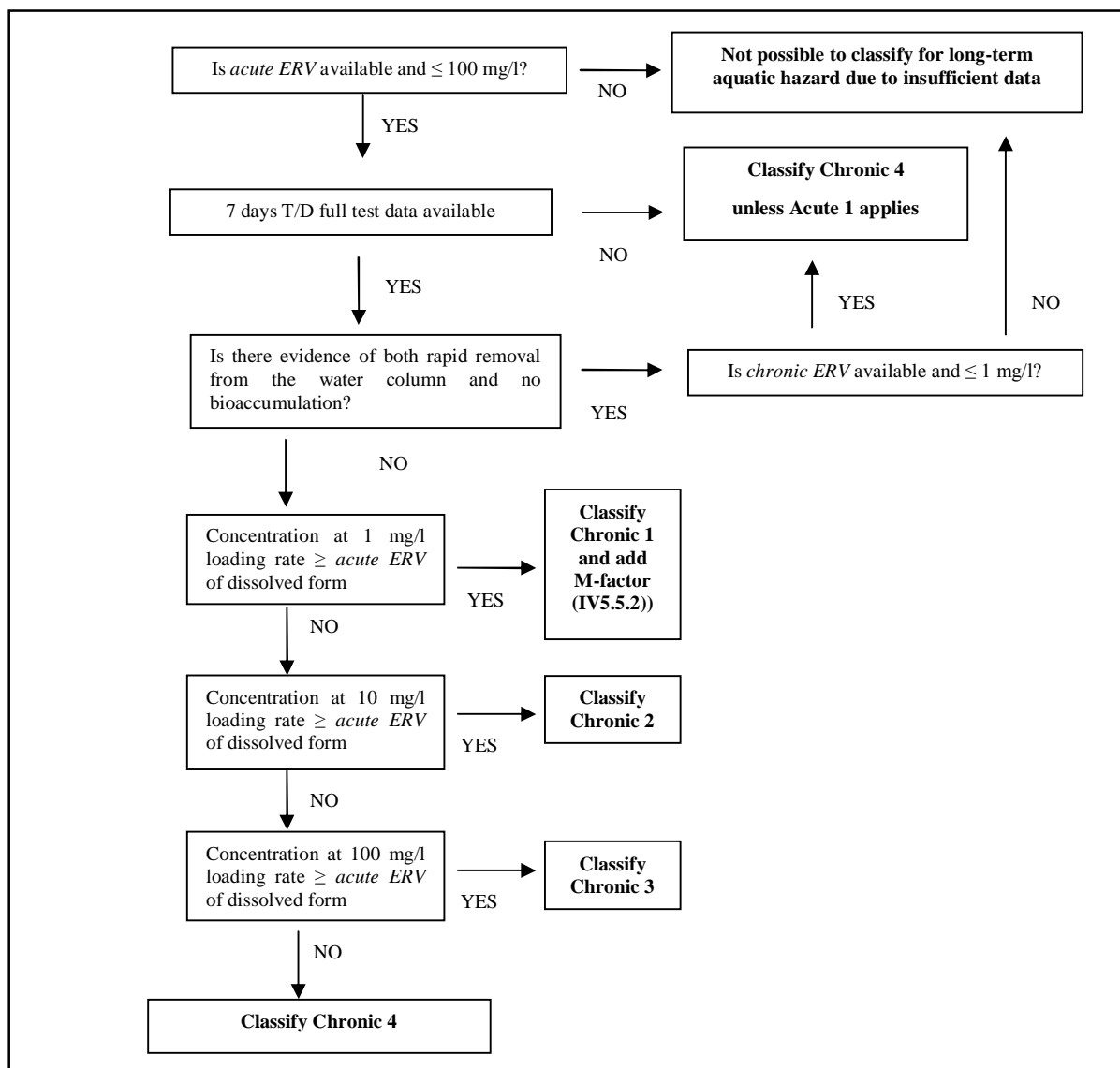
37

1 **Figure IV.5.2.2a** Classification strategy for determining long-term aquatic hazard for metals.



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1 **Figure IV.5.2.2b** Classification strategy for determining long-term aquatic hazard for metals
 2 in absence of appropriate chronic toxicity reference and/or T/Dp data.



3

4 **IV.5.3 Classification strategies for metal compounds**

5 Notice! Acute and Long Term hazard assessment are assessed individually for metal
 6 compounds.

7 A metal compound will be considered as *readily soluble* if:

- 8 - the water solubility (measured through a 24-hour Dissolution Screening test or
- 9 estimated e.g. from the solubility product) is greater or equal to the acute ERV of the
- 10 dissolved metal ion concentration; or
- 11 - If such data are unavailable, i.e. there are no clear data of sufficient validity to show
- 12 that the transformation to metal ions will not occur;

13 Care should be exercised for metal compounds whose solubility is close to the acute toxicity
 14 reference value as the conditions under which solubility is measured could differ significantly
 15 from those of the acute toxicity test. In these cases the results of the Dissolution Screening
 16 Test are preferred.

1 Metal compounds that have lower water solubility than the acute ERV through a 24-hour
2 Dissolution Screening test or estimated from the solubility product, are considered as **poorly**
3 **soluble metal compound**.

4 **IV.5.3.1 Classification strategies for determining acute aquatic hazard for metal** 5 **compounds**

6 The scheme for the determination of *acute* aquatic hazard for metal compounds are described
7 in this section and summarised diagrammatically in Figure IV.5.3.1.

8 Where the acute ERV for the metal ions of concern corrected for the molecular weight of the
9 compound (further called as *acute ERV_{compound}*) is greater than 1 mg/l, the metal compounds
10 need not to be considered further in the classification scheme for acute hazard.

11 Where the acute ERV_{compound} for the metal ions of concern is less than or equal to 1 mg/l,
12 consideration must be given to the data available on the rate and extent to which these ions
13 can be generated from the metal compound. Such data, to be valid and useable should have
14 been generated using the T/D (Annex 10 to UN GHS).

15 **Readily soluble metal compounds**

16 Classify the metal compound as **Category Acute 1** if the acute ERV_{compound} ≤ 1 mg/l, an
17 M-factor must also be established as part of this classification (see IV.5.5.2).

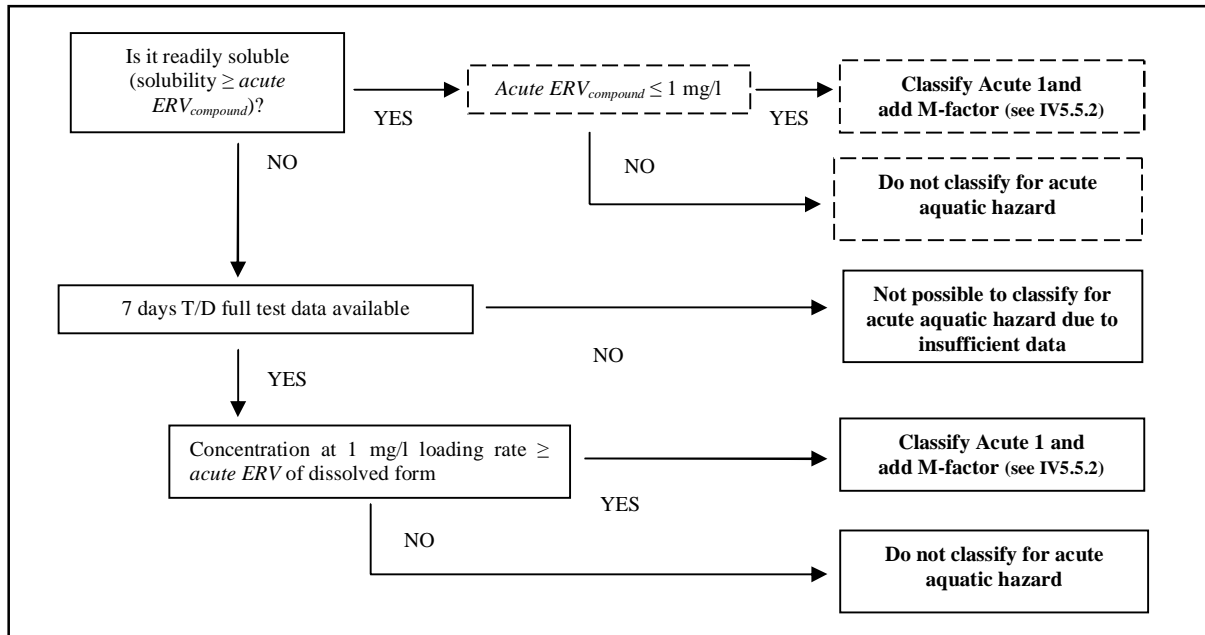
18 **Poorly soluble metal compounds**

19 Where 7d data from the Transformation/Dissolution protocol are available, then the results
20 should be used to classify sparingly soluble metal compounds, according to the following
21 rule:

22 Classify the metal compound as **Category Acute 1** if the dissolved metal ion
23 concentration after a period of 7 days (or earlier for a significant time period) at a
24 loading rate of 1 mg/l exceeds that of the acute ERV, an M-factor must also be
25 established as part of this classification(see IV.5.5.2).

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1 **Figure IV.5.3.1** Classification strategy for determining acute aquatic hazard for metal
 2 compounds.



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1 **IV.5.3.2 Classification strategy for determining long-term aquatic hazard for metal**
2 **compounds**

3 The scheme for the determination of *long-term* aquatic hazard for metal compounds are
4 described in this section and summarised diagrammatically in Figures IV.5.3.2 (a and b).

5 Metal compounds can be classified for long term aquatic hazards:

- 6 1) using chronic reference data when available; or
7 2) using the surrogate approach in absence of appropriate chronic toxicity reference data.

8
9 In case relevant chronic ecotoxicity data (chronic ERV) are available the approach comparing
10 chronic ERV of the dissolved metal ion with release data of 28 days
11 transformation/dissolution, should be applied as described under IV.5.3.2.1 while otherwise
12 the surrogate approach (see IV.5.3.2.2) should be followed.

13

14 **IV.5.3.2.1 Approach based on available chronic toxicity reference data**

15 Where the chronic ERV for the metal ions of concern corrected for the molecular weight of
16 the compound (further called as *chronic ERV_{compound}*) is greater than 1 mg/l, the metal
17 compounds need not to be considered further in the classification scheme for long-term
18 hazard.

19 **Readily soluble metal compounds**

20 Readily soluble metal compounds are classified on the basis of chronic ERV of the dissolved
21 metal ion, corrected for the molecular weight of the compound (further called as chronic
22 ERV_{compound}).

23 If there is no evidence of rapid removal from the water column

- 24 a) Classify the metal compound as Category Chronic 1 if the chronic ERV_{compound} ≤ 0.1
25 mg/l, an M-factor must also be established as part of this classification (see IV.5.5.2);
26 or
27 b) Classify the metal compound as Category Chronic 2 if the chronic ERV_{compound} >
28 0.1mg/l and ≤ 1 mg/l.

29 If there is evidence of rapid removal from the water column

- 30 c) **Classify** the metal compound as **Category Chronic 1** if the chronic ERV_{compound} ≤
31 0.01 mg/l, an M-factor must also be established as part of this classification (see
32 IV.5.5.2); or
33 d) **Classify** the metal compound as **Category Chronic 2** if the chronic ERV_{compound} >
34 0.01mg/l and ≤ 0.1 mg/l; or
35 e) **Classify** the metal compound as **Category Chronic 3** if the chronic ERV_{compound} >
36 0.1mg/l and ≤ 1 mg/l.

37

38

1 **Poorly soluble metal compounds**

2 Where *the chronic ERV* for the metal ions of concern is greater than 1 mg/l, the metals need
3 not be considered further in the classification scheme.

4 Where the chronic ERV_{compound} is less than or equal to 1 mg/l consideration must be given to
5 the data available on the rate and extent to which these ions can be generated from the metal
6 compound. Such rate and extend data, to be valid and useable should have been generated
7 using the Transformation/Dissolution Protocol (Annex 10 to UN GHS) for a 28d period.

8 Where 28d T/Dp data are unavailable, the surrogate approach should be applied (see section
9 5.3.2.2).

10 Where 28d data from the Transformation/Dissolution protocol are available, then classify
11 according to the following rules:

12 a) **Classify** the metal compound as **Category Chronic 1** if the dissolved metal ion
13 concentration obtained from the 28 day transformation test at a loading rate of 0.1
14 mg/l is greater than or equal to the chronic ERV, an M-factor must also be established
15 as part of this classification (see IV.5.5.2); or

16 b) **Classify** the metal compound as **Category Chronic 2** if the dissolved metal ion
17 concentration obtained from the 28 day transformation test at a loading rate of 1 mg/l
18 is greater than or equal to the chronic ERV.

19 If there is evidence of rapid removal from the water column and

20 c) **Classify** the metal compound as **Category Chronic 1** if the dissolved metal ion
21 concentration obtained from the 28 day transformation test at a loading rate of 0.01
22 mg/l is greater than or equal to the chronic ERV, an M-factor must also be established
23 as part of this classification (see IV.5.5.2); or

24 d) **Classify** the metal compound as **Category Chronic 2** if the dissolved metal ion
25 concentration obtained from the 28 day transformation test at a loading rate of 0.1
26 mg/l is greater than or equal to the chronic ERV; or

27 e) **Classify** the metal compound as **Category Chronic 3** if the dissolved metal ion
28 concentration obtained from the 28 day transformation test at a loading rate of 1 mg/l
29 is greater than or equal to the chronic ERV.

30

31 Do not classify for long-term hazard if the dissolved metal ion concentration obtained from
32 the 28 day Transformation/Dissolution test at a loading rate of 1 mg/l is less than the chronic
33 ERV of the dissolved metal ion.

34

35 **IV.5.3.2.2 The surrogate approach**

36

37 **Readily soluble metal compounds**

38 In absence of relevant chronic toxicity data, and unless there is evidence of both rapid
39 removal from the water column and evidence of no bioaccumulation (see sections IV.3 and
40 IV.4), **Readily soluble metal compounds** are classified as:

41 a) **Category Chronic 1** if the acute ERV_{compound} ≤ 1 mg/l, an M-factor must also be
42 established as part of this classification (see IV.5.5.2); or

- 1 b) **Category Chronic 2** if the chronic ERV_{compound} > 1mg/l and ≤ 10 mg/l; or
2 c) **Category Chronic 3** if the chronic ERV_{compound} > 10mg/l and ≤ 100 mg/l.

3

4 **Poorly soluble metal compounds**

5 Where the acute ERV_{compound} is less than or equal to 100 mg/l consideration must be given to
6 the data available on the rate and extent to which these ions can be generated from the metal.
7 Such rate and extend data, to be valid and useable should have been generated using the
8 Transformation/Dissolution Protocol (Annex 10 to UN GHS) for a 7d period.

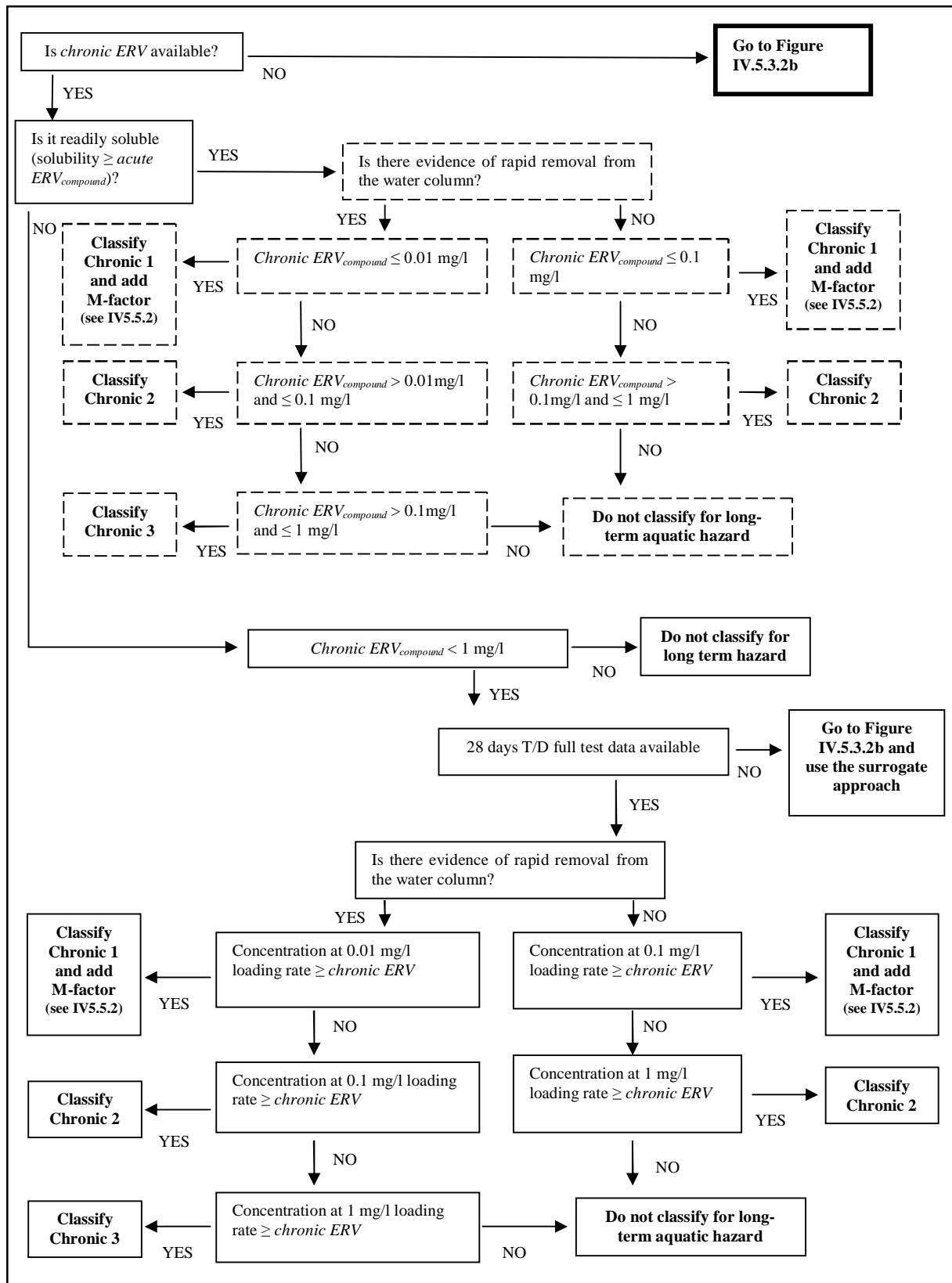
9 Where such 7d T/Dp data are unavailable, i.e. there is no clear data of sufficient validity to
10 show that the transformation to metal ions will not occur; the safety net classification
11 (Category Chronic 4) be applied.

12 Where T/Dp data are available but relevant chronic ERV is are absent, the results should be
13 used to aid classification according to the following rules:

- 14 a) **Classify** the metal compound as **Category Chronic 1** if the dissolved metal ion
15 concentration obtained from the 7 day transformation test at the low loading rate (1
16 mg/l) is greater than or equal to the acute ERV, an M-factor must also be established
17 as part of this classification(see IV.5.5.2);
- 18 b) **Classify** the metal compound as **Category Chronic 2** if the dissolved metal ion
19 concentration obtained from the 7 day transformation test at the medium loading rate
20 (10 mg/l) is greater than or equal to the acute ERV;
- 21 c) **Classify** the metal compound as **Category Chronic 3** if the dissolved metal ion
22 concentration obtained from the 7 day transformation test at the high loading rate (100
23 mg/l) is greater than or equal to the acute ERV.
- 24 d) **Classify** the metal compound as **Category Chronic 4** if the dissolved metal ion
25 concentration obtained from the 7 day transformation test at the high loading rate (100
26 mg/l) is lower than the acute ERV.

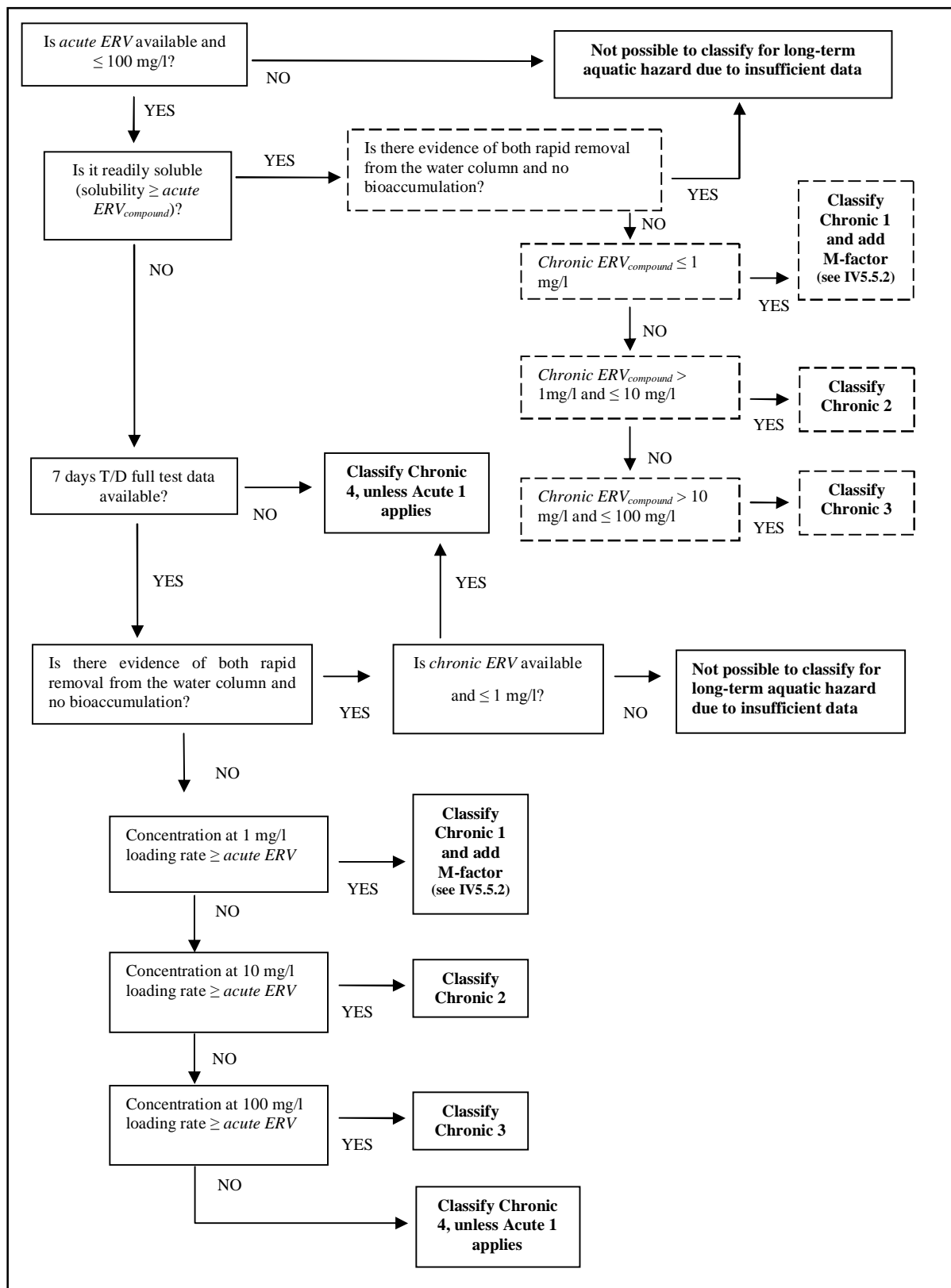
27

1 **Figure IV.5.3.2a** Classification strategy for determining long-term aquatic hazard for metal
 2 compounds.



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4

1 **Figure IV.5.3.2b** Classification strategy for determining long-term aquatic hazard for metal
 2 compounds in absence of appropriate chronic toxicity reference and/or T/Dp data.



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1 IV.5.4 Particle size and surface area

2 Surface area is a crucial parameter in that any variation in surface area tested may cause a
3 significant change in the levels of metals ions released in a given time-window. Thus, particle
4 size or surface area is fixed for the purposes of the transformation test, allowing the
5 comparative classifications to be based solely on the loading level. Normally, the
6 classification data generated would have used the smallest particle size marketed to determine
7 the extent of transformation. There may be cases where data generated for a particular metal
8 powder are not considered as suitable for classification of the massive forms. For example,
9 where it can be shown that the tested powder is structurally a different material (e.g. different
10 crystallographic structure) and/or it has been produced by a special process and is not
11 generally generated from the massive metal, classification of the massive can be based on
12 testing of a more representative particle size or surface area, if such data are available. The
13 powder may be classified separately based on the data generated on the powder. However, in
14 normal circumstances it is not anticipated that more than two classification proposals would
15 be made for the same metal.

16 Metals with a particle size smaller than the default diameter value of 1 mm can be tested on a
17 case-by-case basis. One example of this is where metal powders are produced by a different
18 production technique or where the powders give rise to a higher dissolution (or reaction) rate
19 than the massive form leading to a more stringent classification.

20 The particle sizes tested and/or used for classification and labelling depend on the substance
21 being assessed and are shown in the table below:

Type	Particle size	Comments
Metal compounds	Smallest representative size sold	Never larger than 1 mm
Metals – powders	Smallest representative size sold	May need to consider different sources if yielding different crystallographic/morphologic properties
Metals – massive	1 mm	Default value may be altered if sufficient justification

22 Massives will usually be tested as 1 mm particles. Alternatively, the T/D testing of materials
23 with different surface area's may result in highly reliable dissolution kinetic equations that
24 allows to define the "Critical Particle Diameter" (CPD) for appropriate loadings for the acute
25 and long-term hazard assessment .

26 For most metals and some metal compounds, it is possible, using the
27 Transformation/Dissolution Protocol (Annex 10 to UN GHS), to obtain a correlation between
28 the concentration of the metal ion after a specified time interval as a function of the surface
29 area loadings of the forms tested. Such correlations should be established for the relevant pH
30 ranges as specified in the protocol. In such cases, it could then be possible to estimate the
31 level of dissolved metal ion concentration at a given pH of the metal with different particles,
32 using the critical surface area approach [Skeaff *et. al.* (2000)]. From this correlation and a
33 linkage to the appropriate toxicity data at corresponding pH level, it is possible to determine a
34 "Critical Surface Area" (CSA) of the substance that delivers the L(E)C₅₀ to the dissolution
35 medium and then to convert the CSA to a Critical Particle Diameter (CPD) (see example).
36 This CPD at appropriate mass loadings for acute and long-term hazard assessment can then
37 be used to:

- 1 - determine the classification category of powders based on the finest representative
- 2 powder on the market and
- 3 - determine an accurate classification of the massive metal by applying a 1 mm
- 4 (default) diameter

5

6 Within the CSA Approach an equation is developed to predict metal ion release (based on

7 previously measured metal ion release from different loadings of the metal), which is

8 correlated to measured surface area, and a corresponding calculated equivalent particle

9 diameter. The basis of the CSA Approach is that ***the release of metal ions is dependent on***

10 ***the surface area of the substance***, with this release being predictable once the relationship

11 has been established. The CSA as the surface area loading (mm²/l) to a medium that delivers

12 a selected ecotoxicity reference value to that medium. The term SA is the measured specific

13 surface area (m²/g) of the metal sample. The measured specific critical surface area (SA_{crit})

14 (m²/g) is the measured specific surface areas for the corresponding low, medium and high

15 loadings which are associated with the respective acute and long term aquatic toxicity

16 classification categories in the classification scheme for metals and metal compounds. A

17 typical equation for this relationship for a given substance, aquatic medium, pH and retention

18 time is:

$$\log (C_{Me(aq)}, \text{ mg/l}) = a + b \log(A_{meas})$$

19

20 C_{Me(aq)} = total dissolved concentration of metal ion (mg/l) at a particular length of test time

21 (*i.e.* 168 hours for acute toxicity transformation testing) under certain conditions (*i.e.* pH,

22 specified medium, etc.), as determined by transformation/dissolution testing of different

23 surface area loadings

24 *a, b* = regression coefficients

25 A_{meas} = initial surface area loading (mm²/l) [equals (measured specific surface area, SA, in

26 m²/g) X (substance mass loading in g/l) X 10⁶], where SA was measured with the BET

27 nitrogen adsorption-desorption technique.

29 **IV.5.5 Classification of mixtures of metals and metal compounds**

30 Simple composed metal or metal compound mixtures should be handled as mixtures and

31 classified according to the mixtures rules described in Section 4.1.4 given they normally

32 express toxicity as a function of their composing ingredients. Ores and concentrates and

33 UVCB inorganics are considered as substances in respect to CLP, but follow in general the

34 mixture ruling. to determine their classification unless specific ecotoxicity data are available

35 for the mineral(s) under consideration.

36 The metals Industry developed classification tools that allow for the hazard ID and

37 environmental classification of those more complex mixtures like ores and concentrates,

38 UVCB intermediates and others are substances by integrating all aspects of this guidance

39 with mineralogical information and other typical metal properties.

40 Metal alloys are defined by the CLP as “special preparations” because their (eco)toxicity

41 profile does differs from that of their constituents. Further ruling on how to assess the

42 environmental hazard classification of alloys and other complex metal containing materials is

43 provided hereunder.

45 **IV.5.5.1 Classification of alloys and complex metal containing materials**

1 Metal alloys, or alloy manufacturing products are not simple mixtures of metals or metal
2 compounds, since the alloy has clearly distinctive properties compared to a classical mixture
3 of its metal components. Justified by their intrinsic properties, the solubility properties can
4 differ substantially from what is observed for each individual constituent in that alloy (eg the
5 rate and extend of metals release from pure metals are different from the ones from alloys).
6 The rate and extend to which the ingredient of the alloy react with the media to transform to
7 water soluble forms can be measured in the same way as with metals (by using the OECD
8 Transformation/Dissolution test (Annex 10 to UN GHS)). However, alloys often react slowly
9 and to a very limited extent, making the application of the T/D protocol more complex.
10 Special care should be taken in this respect to the detection limit and the accurate
11 determination of the measured surface. Initial testing of alloys, using the T/D protocol, shows
12 that this can be useful but **further additional guidance on this aspect is recommended.**

13 More complex metals or metal compounds containing inorganic substances like e.g. ores and
14 concentrates are not simple mixtures of metals or metal compounds. Justified by their
15 intrinsic properties, the solubility properties can differ substantially from what is observed for
16 each individual constituent of that complex substance (e.g. the rate and extent of metals
17 release from e.g. ores/concentrates are different from the ones from simple metals). All these
18 materials are typically not readily soluble in any aqueous medium. In addition, these
19 materials are often heterogeneous in size and composition on a microscopic/macrosopic
20 scale. Therefore, adequate amounts of the material could be used to evaluate the extent to
21 which the substances can be dissolved, i.e. its water solubility and/or the extent to which the
22 metals can react with the media to transform to water soluble forms e.g. through
23 Transformation/Dissolution tests. Additional guidance on this aspect is needed for complex
24 metal mixtures.

25

26 An **ecotoxicity validation step** may be important for alloys and complex metal containing
27 materials (e.g. ores, concentrates, slags), where binding of the metal to biotic and biological
28 binding sites will in many cases be competitive. Therefore the “additivity mode” is not
29 necessarily valid and additional information may be relevant.

30 Therefore, information from ecotoxicity validation steps could be useful in cases where a
31 significant uncertainty is associated with the existing toxicity data. This ecotoxicity validation
32 should have been derived from tests using most sensitive species at dissolved ion
33 concentrations equivalent to those measured in the T/D medium. However, information from
34 ecotoxicity testing directly in the T/D medium is not recommended because the composition
35 of this medium is unlikely to meet the requirements for standard test media to ensure proper
36 survival and/or reproduction. Therefore, ecotoxicity tests should have been conducted in
37 standard media dosed at metal concentration equivalent to the concentration level actually
38 measured in the T/D medium.

39

40 **IV.5.5.2 M-factor application for metal mixtures and alloys**

41 For appropriate classification of metal mixtures, Ecotoxicity Reference Values (ERVs) for
42 the metal ion(s) or metal compounds contained in the mixture are used to derive cut-off
43 values for mixtures. If these ERVs is/are below the lowest dose level (e.g. 1mg/L for acute
44 toxicity or 0,1 mg/L or 0,01 mg/l for respectively Chronic toxicity without and with
45 demonstration of removal), an appropriate acute or Chronic M-factor is needed. This M-
46 factor derived for the metal or metal compound is then used to ensure the mixture containing
47 the metal compound is appropriately classified.

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For *soluble metal compounds* M-factors are applied as for organic substances (see table IV.5.5.2).

For poorly soluble metal compounds and metals M-factors can be estimated from the ratio of the soluble metal ions concentrations obtained from Transformation Dissolution (at respectively 7 d or 28 d's for a loading of 1 mg/l) and the ERV of the dissolved metal ion taking the considerations mentioned in I.V.2.3 into account. If this ratio is:

- below 10 then an M-factor of 1 should be applied
- ≥ 10 and < 100 then the M-factor would be 10,
- ≥ 100 and < 1000 then the M-factor would be 100,

Continue in factor 10 intervals

Table IV.5.5.2: M-factors for inorganic substances.

Acute ERV (mg/L)	Multiplying factors (M)
0,1 < Acute ERV < 1	1
0,01 < Acute ERV < 0,1	10
0,001 < Acute ERV < 0,01	100
0,0001 < Acute ERV < 0,001	1000
Continue in factor 10 intervals	10000

Chronic ERV (mg/L)	Multiplying factors (M)	
	No rapid removal	Rapid removal
0,01 < Chronic ERV < 0,1	1	1
0,001 < Chronic ERV < 0,01	10	1
0,0001 < Chronic ERV < 0,001	100	10
0,00001 < Chronic ERV < 0,0001	1000	100
Continue in factor 10 intervals		

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Annex IV

Decision on classification: examples for metals and metal compounds

1 **IV.7 Decision on classification: examples for metals and metal compounds**

2

3 List of examples:

4 • Example A: Soluble metal compound with acute and chronic toxicity data and
5 evidence of rapid removal from the water column (Me₂ (SO₄)₂).

6 • Example B: Poorly soluble metal compound with acute and chronic toxicity data,
7 Transformation/Dissolution data at 7 days (low loading rate) and 28 days (low,
8 medium and high loading rates) and evidence of rapid removal from the water
9 column.

10 • Example C: Poorly soluble metal compound with acute and chronic toxicity data
11 equal to example B, Transformation/Dissolution data at 7 days (low loading rate) and
12 at 28 days (only low and medium loading rates) and no evidence of Rapid removal
13 from the water column.

14 • Example D: Metal in powder and massive form with acute and chronic toxicity data
15 and Transformation/Dissolution data at 7 days (low, medium and high loading rates)
16 and at 28 days (only the high loading rate) and evidence of rapid removal from the
17 water column.

18 ○ *Explanatory note to Example D - Critical Surface Area (CSA) Approach.*

19 • Example E: Hazard classification of a soluble metal salt: the case of removal through
20 speciation in the water column.

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1 **Example A: Soluble metal compound with acute and chronic toxicity data and evidence**
 2 **of rapid removal from the water column (Me₂ (SO₄)₂).**

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DATA ELEMENTS	Value	Test method ((EC) No. 440/2008) or OECD guideline / remarks
Transformation dissolution protocol evidence		
<u>Screening test (24 h) at 100 mg/l loading</u>	pH 6 : 6240 µg/l pH 8 : 840 µg/l	Metals TDp, non-GLP
<u>7 d TDp test</u>	Not applicable	
<u>28 d TDp test</u>	Not applicable	
MWT of the metal ion versus compound	60 / 312	
Acute aquatic toxicity of metal ion¹		
<u>Fish:</u> <i>Oncorhynchus mykiss:</i>	120 µg/l (96 h LC ₅₀) at pH 7,8 106 µg/l (96 h LC ₅₀) at pH 7,8 104 µg/l (96 h LC ₅₀) at pH 7,8 78 µg/l (96 h LC ₅₀) at pH7,8 <i>(species mean: 102 µg/l at pH 7,8)</i>	C.1. / static, GLP C.1. / static, non-GLP C.1. / static, GLP C.1. / static, non-GLP
<u>Crustacea</u> <i>Daphnia magna:</i>	180 µg/l (48 h EC ₅₀) at pH 8	C.2. / static, non-GLP
<u>Algae/aquatic plants</u> <i>Scenedesmus subspicatus:</i>	154 µg/l (72 h ErC ₅₀) at pH 8	C.3. / static, GLP
<i>Lemma gibba:</i>	670 µg/l (7 d ErC ₅₀) at pH 8	C.26. / semi-static, GLP
Chronic aquatic toxicity²		
<u>Fish:</u> <i>Danio rerio:</i> Marine Fish	24 µg/l (28 d NOEC) at pH 6 87 µg/l (28 d NOEC) at pH 8 1414 µg/l (28 d EC10)	OECD 210 / 28 d flow-through, non-GLP OECD 210 /28 d flow through, GLP) OECD 210 /28 d flow through, GLP)
<u>Crustacea:</u> <i>Daphnia magna:</i> Marine decapoda	37 µg/l (21 d EC ₁₀) at pH 7.8 8.6 µg/l (21 d NOEC) at pH 6.4 1612 µg/l (21 d NOEC)	C.20. / semi-static, GLP C.20./semi-static non-GLP Non standard test

¹ Tests performed with readily soluble salts such as metal sulphates and metal chlorides.

² Tests performed with readily soluble salts such as metal sulphates and metal chlorides.

<u>Algae/aquatic plants:</u> <i>Scenedesmus subspicatus:</i>	21.6 µg/l (72 h NOEC) at pH 8 8.7 µg/l (72 h NOEC) at pH 6.2	C.3. / static, GLP C.3. / static, non-GLP
Degradation (evidence of rapid degradation)		
<u>Rapid removal</u>	The speciation of the metal compound in water to form insoluble and non classifiable ³ forms for aquatic hazard, is low (12% within 28 days).	Based on literature data and empirical reaction kinetics
Bioaccumulation		
Bioconcentration factor in fish	+/- 200 at NOEC level	

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2 **Aquatic hazard assessment, conclusions and comments:**

3 Transformation Dissolution :

- 4 • The substance passes the 24 h screening TDp test at pH 6 given the dissolution at a
5 loading of 100 mg/l is 6240 µg/l > acute ERV of the soluble ion being 102 µg/l at pH 7.8.

6 Acute aquatic toxicity:

- 7 • The acute ecotoxicity reference value is driven by the Fish data. No data are available for
8 the low pH end.
9 • The acute ERV for the metal compound is $102 * (312/(2*60)) = 265 \mu\text{g/l}$.

10 Degradation (evidence of rapid removal from the water column):

11 Since the speciation of the metal compound in water to form insoluble and non classifiable
12 forms⁴ (for aquatic hazard is low (12% removal of the soluble species within 28 days
13 corresponding), this cannot be considered as rapid removal from the water column. The
14 substance can consequently **not** be considered for classification purposes as rapidly
15 degradable.

16 Chronic aquatic toxicity:

- 17 • The chronic aquatic ecotoxicity reference toxicity value based on the lowest of the
18 available toxicity values is slightly below 10 µg/l for Daphnia magna at pH 6,4 for the
19 metal ion.
20 • The chronic ERV for the metal compound is $8.6 * (312/(2*60)) = 22.4 \mu\text{g/l}$.

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22 **Aquatic hazard classification and, where applicable, established M-factor(s):**

- 23 • Acute (short-term) aquatic hazard: category Acute 1, M-factor: 1

³ To speciate to non-bioavailable and non-classifiable form(s) for aquatic hazard as to fulfil the requirements for rapid removal means that the potential for the reverse change to occur has been considered, and assessed as negligible.

⁴ To speciate to non-bioavailable and non-classifiable form(s) for aquatic hazard as to fulfil the requirements for rapid removal means that the potential for the reverse change to occur has been considered, and assessed as negligible.

- 1 • Long-term aquatic hazard: category Chronic 1, M-factor: 1

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3 **Reasoning:**

4 Acute aquatic hazard

- 5 • The acute ecotoxicity reference value is driven by the Fish data. A species mean of 102
6 $\mu\text{g/l}$ for the metal ion, is calculated for *Oncorhynchus mykiss* given 4 or more toxicity
7 data for the same species under comparable conditions are available.

- 8 • Acute aquatic hazard expressed as the ERV for the metal compound after molecular
9 weight correction $\leq 1 \text{ mg/l}$. M-factor is 1 given the acute ERV is between 1 and 0.1 mg/l.

- 10 • The molecular weight correction recognises that 2 metal ions are included.

- 11 • The substance passes the 24 h screening dissolution test by comparing acute toxicity data
12 at pH 7.8 with TDp data at pH6 given an acute toxicity data set at pH 6 is lacking and the
13 chronic data indicate more toxic behaviour of the metal at the lower pH end.

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15 Long-term aquatic hazard:

- 16 • Adequate information on chronic toxicity (all 3 trophic levels) is available allowing long-
17 term hazard classification (no use of the surrogate approach).⁵

- 18 • Marine toxicity data are not included in the chronic ERV assessment given far less
19 sensitive as fresh water toxicity references and data for 3 trophic levels for the freshwater
20 are available

- 21 • The *Daphnia magna* reference at pH6 is the lowest and determines the chronic ERV.

- 22 • A molecular weight correction is applied to the substance recognising that 2 metal ions
23 are included.

- 24 • Rapid removal cannot be demonstrated given the lack of sufficient speciation to the non-
25 bioavailable form in 28 d.

- 26 • The M-factor of 1 is based on the chronic ERV of 22 $\mu\text{g/l}$ (so between 0.01 and 0.1 mg/l.)
27 without rapid removal.

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⁵ In absence of adequate chronic toxicity data for all trophic levels, the subsequent step is to combine two types of information, i.e. chronic info for the trophic level with such data and acute aquatic toxicity data and environmental fate information for lacking info on trophic levels. For details see section 4.1.3.3 and Table 4.1.0.

1 **Labelling elements based on the classification:**

Element	Code
GHS Pictogram	GHS09
Signal Word	WARNING
Hazard Statement	H400, H410 → H410 ⁶
Precautionary statement(s)	P273, P391, P501

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⁶ In accordance with CLP Article 27, the hazard statement H400 may be considered redundant on the label and therefore not included on the label because hazard statement H410 also applies, see section 4.1.6 of this document.

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Example B: Poorly soluble metal compound with acute and chronic toxicity data, Transformation Dissolution data at 7 days (low loading rate) and 28 days (low, medium and high loading rates) and evidence of rapid removal from the water column.

DATA ELEMENTS	Value	Test method ((EC) No. 440/2008) or OECD guideline / remarks
Transformation dissolution protocol evidence		
<u>Screening test (24 h) at 100 mg/l loading</u>	pH 6 : 74 µg/l pH 8 : 34 µg/l	Metals TDp, non-GLP
<u>7 d TDp test</u> at 1 mg/l loading	pH 6 : 50 µg/l pH 8 : 16 µg/l	Metals TDp, non-GLP Metals TDp, non-GLP
<u>28 d TDp test</u> at 1 mg/l loading	pH 6: 182 µg/l pH 8: 71 µg/l	Metals TDp, non-GLP Metals TDp, non-GLP
at 0,1 mg/l loading	pH 6: 18 µg/l pH 8: 7 µg/l	Metals TDp, non-GLP Metals TDp, non-GLP
at 0,01 mg/l loading	pH 6: 2 µg/l pH 8: < 1 (DL)	
MWT of the metal ion versus compound	60 / 91	
Acute aquatic toxicity of metal ion⁷		
<u>Fish:</u> <i>Oncorhynchus mykiss:</i>	186µg/l (48 h LC ₅₀) at pH 7 120 µg/l (96 h LC ₅₀) at pH 7.8 106 µg/l (96 h LC ₅₀) at pH 7.8 104 µg/l (96 h LC ₅₀) at pH 7.8 78 µg/l (96 h LC ₅₀) at pH 7.8 <i>(species mean for 4 values : 102 µg/l at pH 7.8)</i> 78 µg/l (96 h LC ₅₀) at pH 6.4	C.1. / static, non-GLP C.1. / static, GLP C.1. / static, non-GLP C.1. / static, GLP C.1. / static, non-GLP
<u>Crustacea</u> <i>Daphnia magna:</i>	180 µg/l (48 h EC ₅₀) at pH 8	C.2. / static, non-GLP

⁷ Tests performed with readily soluble salts such as metal sulphates and metal chlorides.

		106 µg/l (48 h EC ₅₀) at pH 8	
<u>Algae/aquatic plants</u>	<i>Scenedesmus subspicatus</i> :	154 µg/l (72 h ErC ₅₀) at pH 8 78 µg/l (72 h ErC ₅₀) at pH 6	C.3. / static, GLP
	<i>Lemna gibba</i> :	670 µg/l (7 d ErC ₅₀) at pH 8	C.26. / semi-static, GLP
Chronic aquatic toxicity⁸			
<u>Fish</u> :	<i>Danio rerio</i> :	24 µg/l (28 d NOEC) at pH 6 87 µg/l (28 d NOEC) at pH 8	OECD 210 / 28 d flow-through, non-GLP OECD 210 /28 d flow through, GLP)
<u>Crustacea</u> :	<i>Daphnia magna</i>	37 µg/l (21 d EC ₁₀) at pH 7.8 8.6 µg/l (21 d NOEC) at pH 6.4	C.20. / semi-static, GLP C.20. / semi-static, non-GLP
<u>Algae/aquatic plants</u> :	<i>Scenedesmus subspicatus</i> :	21.6 µg/l (96 h NOEC) at pH 8 8.7 µg/l (72 h EC ₁₀) at pH 6.2	C.3. / static, GLP C.3. / static, non-GLP
Degradation (evidence of rapid degradation)			
<u>Rapid removal</u>		The speciation of the metal compound in water to form insoluble and non classifiable ⁹ forms for aquatic hazard is high (>90% removal of the soluble species within 28 days)	Based on literature data and empirical reaction kinetics.
Bioaccumulation			
	Bioconcentration factor in fish	+/- 200 at NOEC level	

⁸ Tests performed with readily soluble salts such as metal sulphates and metal chlorides.

⁹ To speciate to non-bioavailable and non-classifiable form(s) for aquatic hazard as to fulfil the requirements for rapid removal means that the potential for the reverse change to occur has been considered, and assessed as negligible.

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2 **Aquatic hazard assessment, conclusions and comments:**

3 Transformation/Dissolution screening outcome:

4 • The substance fail the 24 h screening Transformation Dissolution test given the
5 dissolution at a loading of 100 mg/l :

6 ➤ at pH 6 is 74 µg/l < acute ERV of the soluble ion being 78 µg/l (borderline case)

7 ➤ at pH 8 is 34 µg/l < acute ERV of the soluble ion being 102 µg/l

8 Acute aquatic toxicity: for more details see example A

9 • Adequate data on pH 6 and 8 are available allowing to derive an acute ERV for the
10 (soluble) metal ion :

11 ➤ at the lower pH end (around pH 6) : **78 µg/l**

12 ➤ at the higher pH end (around pH 8) : **102 µg/l**

13 7 days Transformation/Dissolution outcome :

14 • The acute release after 7 d is the highest at pH 6 (50 µg/l) being lower than the acute
15 toxicity level (78 µg/l) at this corresponding pH

16 • The acute release is lower at or around pH 8 (16 µg/l), which is significantly lower than
17 the acute toxicity level (102 µg/l) at this corresponding pH

18 Degradation/Transformation (evidence of rapid removal from the water column):

- 1 • More than 90 % removal from the water column through speciation to an insoluble and
2 non classifiable form for aquatic hazard¹⁰ (so non bioavailable) is demonstrated, thereby
3 fulfilling the conditions for rapid removal from the water column.

4 Chronic aquatic toxicity for a substance rapidly removing from the water column

- 5 • The chronic ERV for the (soluble) metal ion is **8.6 µg/l** around pH 6 and **21.6 µg/l** around
6 pH 8

7
8 28 days transformation/dissolution outcome for a substance rapidly removing from the water
9 column:

- 10 • The release after 28 d at a loading of 0.01 mg/l is the highest at **pH 6** (2 µg/l) being lower
11 than the acute toxicity level 8.6 µg/l at this corresponding pH. The measured release rate
12 at 0.1 mg/l loading (18 µg/l) which is already twice as high as the chronic ERV of the
13 soluble metal ion and the release rate at 1 mg/l loading (182 µg/l) almost 9 times as high.
- 14 • The release after 28 d at a loading of 0.01 mg/l is lower at **pH 8** being <1 µg/l, which is
15 significantly lower than the chronic toxicity level of the soluble metal ion (21.6 µg/l) at
16 this pH level. The measured release rates at 0,1 mg/l loading and at 1 mg/l respectively
17 are 7 and 71 µg/l which would be respectively smaller and larger than the chronic ERC at
18 pH 8 (21.6 µg/l)

19

20 **Aquatic hazard classification and, where applicable, established M-factor(s):**

21 Acute (short-term) aquatic hazard: no acute hazard classification

22 Long-term aquatic hazard: category Chronic 2

23

24 **Reasoning:**

25 The metal compound can be considered as poorly soluble since failing the OECD
26 transformation dissolution screening test at a 100 mg/l loading. The screening test further
27 confirmed pH 6 as the pH of the highest release rate.

28 Acute aquatic hazard

- 29 • The acute ecotoxicity reference value is driven by the Fish data for the high pH and by
30 algae data for the low pH level. For the high pH end (around pH 8) a species mean of 102
31 µg/l for the metal ion is calculated for *Oncorhynchus mykiss* and a single reference of 78
32 µg/l for *Scenedesmus subspicatus* at around pH 6.
- 33 • A poorly soluble substance is evaluated for classification by comparing the dissolved
34 metal ion level resulting from the TDp at 7d, at a loading rate of 1 mg/l with the acute
35 ERV as determined for the (soluble) metal ion. A molecular weight correction for the
36 poorly metal compound is consequently not required given this factor has already been
37 included for the loading rate of the TDp test.

¹⁰ To speciate to non-bioavailable and non-classifiable form(s) for aquatic hazard as to fulfil the requirements for rapid removal means that the potential for the reverse change to occur has been considered, and assessed as negligible.

- 1 • The dissolution level of the poorly soluble metal compound from the 7d TDp at 1 mg
 2 loading is lower than the acute ERVs of the soluble metal ion for both pH levels, thereby
 3 not resulting in an acute classification.

4

5 **Long-term aquatic hazard:**

- 6 • Adequate information on chronic toxicity (all 3 trophic levels) for the higher and lower
 7 pH levels are available allowing direct long-term hazard classification (no use of the
 8 surrogate approach).
- 9 • The speciation of the metal compound in water to form insoluble and non classifiable¹¹
 10 forms for aquatic hazard is high (>90% removal of the soluble species within 28 days).
- 11 • As indicated for the acute assessment level no Molecular Weight Correction is applied to
 12 the poorly soluble metal compound given the classification scheme is based on the
 13 comparison of the dissolved fraction of the poorly metal compound with the chronic ERV
 14 of the soluble metal ion at both pH 6 and pH8.
- 15 • The dissolution level from the 28 d TDp at 0.01mg/l for the poorly soluble metal
 16 compound (2 µg/l at pH 6 and < 1 µg/l at pH 8) is lower than the chronic ERVs of the
 17 soluble metal ion for both pH levels (8.6 µg/l at pH 6 and 21.6 µg/l at pH 8) thereby not
 18 warranting a chronic 1 classification. The measured dissolved concentration at the 0.1
 19 mg/l loading rate at pH 6 (18 µg/l) is > than the chronic ERV at pH 6 (8.6 µg/l)
 20 warranting a chronic 2 classification. The classification is somewhat less at pH 8 given a
 21 less sensitive toxicity response and a lower dissolution rate.
- 22 • No M-factor is required given a classification as Chronic 2.

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24 **Labelling elements based on the classification:**

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Element	Code
GHS Pictogram	GHS09
Signal Word	none
Hazard Statement	H411
Precautionary statement(s)	P273, P391, P501

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¹¹ To speciate to non-bioavailable and non-classifiable form(s) for aquatic hazard as to fulfil the requirements for rapid removal means that the potential for the reverse change to has been considered, and assessed as negligible.

1 **Example C: Poorly soluble metal compound with acute and chronic toxicity data**
 2 **equal to example B, transformation/dissolution data at 7 days (low loading rate) and**
 3 **at 28 days (only low and medium loading rates) and no evidence of rapid removal**
 4 **from the water column**

5

DATA ELEMENTS	Value	Test method ((EC) No. 440/2008) or OECD guideline / remarks
Transformation dissolution protocol evidence	See example B	
<u>Screening test (24 h) at 100 mg/l loading</u>	pH 6: 74 µg/l pH 8: 34 µg/l	Metals TDp, non-GLP
<u>7 d TDp test</u> at 1 mg/l loading	pH 6: 50 µg/l pH 8: 16 µg/l	Metals TDp, non-GLP Metals TDp, non-GLP
<u>28 d TDp test</u> at 0.1 mg/l loading	pH 6: no data available pH 8: no data available	Metals TDp, non-GLP Metals TDp, non-GLP
at 0.01 mg/l loading	pH 6: 9 µg/l pH 8: <1 (DL)	Metals TDp, non-GLP Metals TDp, non-GLP
MWT of the metal ion versus compound	60 / 91	
Acute aquatic toxicity of metal ion¹²	See example B	
Chronic aquatic toxicity¹³	See example B	
Degradation (evidence of rapid degradation)		
<u>Rapid removal</u>	No data available therefore considered as not rapidly removing from the water column	
Bioaccumulation		
Bioconcentration factor in fish	+/- 200 at NOEC level	

¹² Tests performed with readily soluble salts such as metal sulphates and metal chlorides.

¹³ Tests performed with readily soluble salts such as metal sulphates and metal chlorides.

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Aquatic hazard assessment, conclusions and comments:

Transformation Dissolution screening outcome: see example B

- The substance fail the 24 h screening Transformation Dissolution test at both pH levels

Acute aquatic toxicity: see example B

7 days Transformation/Dissolution outcome : see example B

Degradation/Transformation (evidence of rapid removal from the water column):

- No information, so substance considered as failing the Rapid Removal criterion.

Chronic aquatic toxicity for a substance not rapidly removing from the water column :

- The chronic ERV for the (soluble) metal ion is **8.6 µg/l** around pH 6 and **21.6 µg/l** around pH 8 (see example B)

28 days Transformation dissolution outcome for a substance not rapidly removing from the water column:

- The release after 28 d at pH 6 at a loading of 0.1 mg/l isn't available and needs to be extrapolated from the 0.01 loading rate assuming a 10 times higher dissolution level ($10 \times 9 = 90 \mu\text{g/l}$), which is significantly larger than the chronic ERV at pH 6 (8.6 µg/l).
- The release for the 0.1 mg/l loading is also extrapolated in the same way and is much lower at pH 8. The calculated release rate of $< 10 \mu\text{g/l}$ is still lower than the chronic toxicity level 21.6 µg/l at this pH level. The calculated release rates at 1 mg/l loading would be $< 100 \mu\text{g/l}$ which is significantly larger than the chronic ERV at pH 8.

Aquatic hazard classification and, where applicable, established M-factor(s):

Acute (short-term) aquatic hazard: no acute classification

Long-term aquatic hazard: category Chronic 1, M-factor 10

Reasoning:

The metal compound is considered as poorly soluble since it fails the OECD transformation dissolution screening test at a 100 mg/l loading. The test confirmed pH 6 as the pH of the highest release rate.

Acute aquatic hazards: see example B

Long-term aquatic hazard:

- 1 • Adequate information on chronic toxicity (all 3 trophic levels) for the higher and lower
 2 pH levels are available allowing direct long-term hazard classification (no use of the
 3 surrogate approach).
- 4 • No valid info is available on the removal rate so the poorly soluble metal compound is
 5 considered to be not rapidly removing from the water column.
- 6 • No Molecular Weight Correction is applied for the poorly soluble metal compound given
 7 the classification scheme is based on the comparison of the dissolved fraction of the
 8 poorly metal compound with the chronic ERV of the soluble metal ion at both pH 6 and
 9 pH 8.
- 10 • No TDp data are available for the 0.1 mg/l and 1 mg/l loading. The calculated dissolution
 11 level from the 28d TDp at pH 6 at 0.1mg/l loading (+/- 90 µg/l) for the poorly soluble
 12 metal compound is much higher than the chronic ERV's of the soluble metal ion for pH 6
 13 (8.6 µg/l) warranting a chronic 1 classification. The classification is much less sensitive at
 14 pH 8 given a less toxic and a lower dissolution rate.
- 15 • The M-factor associated with the long-term hazard classification is derived by using the
 16 solubility level derived from the 28d TDp test at the 0,1 mg/l loading (90 µg/l at pH 6)
 17 divided by the ERV of the dissolved metal ion (8.6 µg/l at pH 6): $90/8.6=10.45$.
 18 Accordingly to section IV.5.5.2 the substance will get an M-factor 10, given this factor
 19 was between 10 and 100.

20

21 **Labelling elements based on the classification:**

22

Element	Code
GHS Pictogram	GHS09
Signal Word	WARNING
Hazard Statement	H410
Precautionary statement(s)	P273, P391, P501

23

24

1 **Example D: Metal in powder and massive form with acute and chronic toxicity data**
 2 **and Transformation/Dissolution data at 7 days (low, medium and high loading rates)**
 3 **and at 28 days (only the high loading rate) and evidence of rapid removal from the**
 4 **water column.**

5

DATA ELEMENTS	Value	Test method ((EC) No. 440/2008) or OECD guideline / remarks
Transformation dissolution protocol evidence For metal in POWDER form		
<u>Screening test (24 h) at 100 mg/l loading</u>	Not applicable for metals	Metals TDp, non-GLP
<u>7 d TDp test</u> at 1 mg/l loading at 10 mg/l loading at 100 mg/l loading	pH 6 : 1.7 µg/l (.) pH 8 : 3 µg/l pH 6 : 24 µg/l pH 8 : 29 µg/l pH 6 : 340 µg/l pH 8 : 280 µg/l	Metals TDp, non-GLP
<u>28 d TDp test</u> at 1 mg/l loading at 0.1 mg/l loading at 0.01 mg/l loading	pH 6: 2.3 µg/l pH 8: 3.5 µg/l no measured data available no measured data available	Metals TDp, non-GLP
MWT of the metal	59	
Acute aquatic toxicity of metal ion¹⁴		
<u>Fish:</u>	Large data sets available for the 2 pH ends but less sensitive than crustacean at high pH end and Algae at low pH end	C.1. / static, non-GLP C.1. / static, GLP
<u>Crustacea</u> <i>Ceriodaphnia dubia</i>	Most sensitive species at high pH end (pH 8.3-8.7) : Geometric mean for 6 values under comparable test conditions (EC ₅₀ 48h): 68 µg metal ion/l	C.2. / static, non-GLP
<u>Algae/aquatic plants</u> <i>Pseudokirchneriella subcapitata</i>	Data sets available for the 2 pH ends but less sensitive than crustacean at high pH end and most sensitive endpoint at low end. Most sensitive value (96 h EC ₁₀) at the low pH range: 120 µg metal ion/l	C.3. / static, GLP And non-GLP C.26. / static, non GLP

¹⁴ Tests performed with readily soluble salts such as metal sulphates and metal chlorides.

Chronic aquatic toxicity¹⁵		
<u>Fish:</u>	Large data sets available for different pHs but less sensitive than crustacean at high and low pH	
<u>Crustacea:</u> <i>Ceriodaphnia dubia</i>	Most sensitive species at high and low pH end: - At low pH (NOEC 7d): 20 µg/l - At high pH: (EC10 7d): 2.4 µg /l	C.20. / semi-static, non-GLP
<u>Algae/aquatic plants:</u>	Large data sets available for different pH's but less sensitive than crustacean at high and low pH	C.3. / static, GLP C.3. / static, non-GLP
Degradation (evidence of rapid degradation)		
<u>Rapid removal</u>	The speciation of the metal compound in water to form insoluble and non classifiable ¹⁶ forms for aquatic hazard is in this case high (>70% removal of the soluble species within 28 days).	Based on literature data and empirical reaction kinetics.
Bioaccumulation		
Bioconcentration factor in fish	<< 500 at NOEC or EC50 level	

1

¹⁵ Tests performed with readily soluble salts such as metal sulphates and metal chlorides.

¹⁶ To speciate to non-bioavailable and non-classifiable form(s) as to fulfil the requirements for rapid removal means that the potential for the reverse change to occur has been considered, and assessed as negligible.

1 Transformation Dissolution screening outcome: not applicable for metals

2

3 Acute aquatic toxicity:

4 • Adequate data at high and low pH are available allowing deriving an acute ERV for the
5 (soluble) metal ion

6 ➤ at the lower pH end (around pH 6) : **120 µg/l**

7 ➤ at the higher pH end (above pH 8) : **68 µg/l**

8

9 7 days Transformation/Dissolution outcome for the powder form:

10 • The release after 7 d's is the highest at pH 8 while lower at pH 8. The table below
11 compares the TDp results with the acute ERV values at the corresponding pH ranges

12

13

14

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Loading (mg metal ion/l)	pH*	Highest dissolution (mg metal/l)	Reference toxicity value (mg metal/l)	Dissolution > toxicity reference value?
1	low	0.0017	0.12	No
10	low	0.024	0.12	No
100	low	0.35	0.12	Yes
1	high	0.003	0.068	No
10	high	0.029	0.068	No
100	high	0.28	0.068	Yes

16 * pH value at which dissolution testing was conducted and similar to the pH for the acute toxicity reference
17 value

18 • The release from the metal powder¹⁷ at a loading of 100 mg/l is for both pH ranges higher
19 than the acute ERV.

20

21 7 days Transformation/Dissolution outcome for the massive form :

22 The CSA Approach can be used to calculate a Critical Particle Diameter (CPD) for the
23 dissolution rates from the metal powder. The metal in massive form will be classified as
24 hazardous to the aquatic environment if the CPD is above or equal to 1 mm. The measured
25 critical surface area (SA_{crit}) that releases sufficient ions at to reach the acute ERV for the most
26 critical pH (6) is SA_{crit} **0.101 m²/g** corresponding to an equivalent critical spherical particle
27 diameter (CD_{spec}) of 6.67 µm at a 100 mg/l loading rate. This is far less than 1 mm.

28

29

¹⁷ The finest representative metal powder should be used for TDp testing.

1 Degradation/Transformation (evidence of rapid removal from the water column):

- 2 ○ A 70 % removal rate from the water column through speciation to the non bioavailable
3 form is demonstrated within 28 days, thereby fulfilling the conditions of rapid removal
4 from the water column.

5

6 Chronic aquatic toxicity:

- 7 • The chronic ERV for the (soluble) metal ion is **2.4 µg/l** at around pH 8 and **20 µg/l**
8 around pH 6 which is an inverse relationship with pH as for the acute level.

9

10 28 days Transformation/Dissolution outcome for a substance rapidly removing from the
11 water column:

- 12 • The release after 28 d at a loading of 1 mg/l is slightly higher at **pH 8** (3.5 µg/l) than at
13 pH 6 (2.3 µg/l).
- 14 • TDp data for lower loadings are not available and were calculated given that the rate of
15 metal ion release from the metal in the OECD 203 medium at high pH at the 28 days can
16 be predicted by the equation: $\log(C_{Me(aq)}) = -5.144 + 1.0229\log(A_{meas})$, whereby

17 $C_{me(aq)}$ = total dissolved concentration of metal (mg/l)

18 A_{meas} = initial surface area loading (mm²/l) [equals (measured specific surface area,
19 SA, in m²/g) × (substance mass loading in g/l) X 10¹⁸], where SA was
20 measured with the BET nitrogen adsorption-desorption technique.

21 An equal approach can be followed for the lower pH level.

- 22 • Measured and estimated transformation dissolution data for the *metal powder* are listed in
23 the table below

Loading (mg metal ion/l)	Measured or calculated	pH*	Highest dissolution (mg metal/l)	Reference toxicity value (mg metal/l)	Dissolution > toxicity reference value?
1	Measured	low	0.0023	0.020	No
1	Measured	high	0.0035	0.0024	Yes
0.1	Estimated	Low	0.00023	0.020	No
0.1	Estimated	High	0.00035	0.0024	No

24 * pH value at which dissolution testing was conducted and similar to the pH for the acute toxicity reference
25 value

26

- 27 • The release after 28 days at the 1 mg/l loading for the higher pH level slightly exceeds the chronic
28 ERV, while no such effect is noted at pH 6 mainly due to the lower sensitivity of the species.

29

30

¹⁸ To speciate to non-bioavailable and non-classifiable form(s) for aquatic hazard as to fulfil the requirements for rapid removal means that the potential for the reverse change to occur has been considered, and assessed as negligible.

1 **Aquatic hazard classification and, where applicable, established M-factor(s):**

2 Acute (short-term) aquatic hazard:

- 3 - for the powder form: no acute hazard classification
4 - for the massive form: no acute hazard classification

5 Long-term aquatic hazard:

- 6 - for the powder form: category Chronic 3
7 - for the massive form: no long-term hazard classification

8

9 **Reasoning :**

10 The single environmental classification for all *metal powders* (spherical diameter ≤ 1 mm) of the
11 considered metal can be derived by comparing the transformation/dissolution data for the smallest
12 commercially representative metal powder with the acute and chronic toxicity reference values (for
13 the soluble metal compounds).

14 Acute hazard classification:

- 15 • The *dissolution rate for the finest powder* on the market does not reach the concentration
16 corresponding with the ERV, within 7 days at a loading of 1 mg/l. This is only reached at a
17 loading of 100 mg/l. Therefore, **no acute hazard classification is required.**
- 18 • The *dissolution rate for the massive forms* (spherical diameter > 1 mm) is lower than those for
19 powders given the lower available surface area. The Critical surface area approach confirms that
20 above a diameter of 6.7 μm the acute ERV cannot be reached within 7 days at a loading of 1 mg/l.
21 (Not even at a 100 mg/l loading.) Thereby confirming no need for an acute hazard classification.
22 More explanation on the CSA assessment of the powder form for this metal is included in the
23 explanatory note to example D (see below).

24 Long-term hazard classification:

- 25 • The metal fulfils the criterion for rapid removal from the water column given that > 70 % of the
26 substance is transformed through speciation in a non-bioavailable form within 28 days.
- 27 • T/D data are only available for 1 mg/l loading rate. The medium loading rate of 0,1 mg/l required
28 for the long term hazard assessment could be safely extrapolated from existing evidence given
29 clear relationships between concentration and dissolution were established for both pH levels.
- 30 • The comparison of chronic ERV's with the 28 days TDp results concludes that the chronic ERV
31 for the metal ion is only reached at a loading rate of 1 mg/l at pH 8. Given the metal is rapidly
32 removing from the water column, this results in a ***chronic 3 hazard classification for the metal in***
33 ***the powder form***¹⁹.
- 34 • Given the surface of the particle reference *for massive metal* is > 100 larger than for the
35 smallest commercially representative form this corresponds to a Critical Particle Diameter $>$
36 1 mm at the high loading rate. Therefore there is no need to classify the massive form for
37 long-term hazard.

38

39

40

¹⁹ The metal in the powder form would have been classified as chronic 2 in case evidence on rapid removal from the water column would not have been available or negative.

1 **Labelling elements based on the classification for the powder form:**

Element	Code
GHS Pictogram	none
Signal Word	none
Hazard Statement	H412
Precautionary statement(s)	P273, P501

2

3

4 **Labelling elements based on the classification for the massive form: none**

Element	Code
GHS Pictogram	none
Signal Word	none
Hazard Statement	none
Precautionary statement(s)	none

5

1 Explanatory note to Example D - Critical Surface Area (CSA) approach

2 Acute hazard:

3 For the metal powder in this example, the data showed that the concentration of metal released in the OECD 203
4 medium at pH 8 at the 168 hr can be predicted by the equation:

$$5 \log (C_{\text{Me(aq)}}) = -5.122 + 0.9875 \log (A_{\text{meas}})$$

6 $C_{\text{Me(aq)}}$ = total dissolved concentration of Metal ion (mg/l) at 168 hr and pH 8;

7 A_{meas} = initial surface area loading (mm²/l) [equals (measured specific surface area, SA, in m²/g) ×
8 (substance mass loading in g/l) × 10⁶], where SA was measured with the BET nitrogen
9 adsorption-desorption technique.

10 The CSA approach can subsequently determine what surface areas and particle diameters would result in
11 different levels of aquatic toxicity classification using the regression coefficients from the above equation, *a* (-
12 5.122) and *b* (0.9875), and the proposed acute toxicity reference value (0.068 mg Me/l) as the $C_{\text{Me(aq)}}$. The
13 critical surface area (CSA) would be the A_{meas} at which the metal ion is released at the concentration of the acute
14 toxicity reference value. The following equations can be used to derive these values for this case:

$$15 \log L(E)C_{50} = -5.122 + 0.9875 \log CSA$$

16 $L(E)C_{50}$ = acute ecotoxicity reference value for classification (mg/l)

17 CSA = critical surface area (mm²/l) that releases metal ion in the concentration of the acute ecotoxicity
18 reference value to the aquatic medium

19 The CSA can be derived as follows:

$$20 \log CSA = \left(\frac{\log L(E)C_{50} + 5.122}{0.9875} \right)$$

21 For an acute toxicity reference value of 0.068 mg Me/l, the CSA is thus 10,100 mm²/l. This is the surface area
22 loading of metal that will deliver the reference value amount of metal ion to the OECD 203 medium at pH 8 and
23 at a time of 168 hr.

24 The critical specific surface areas, SA_{crit} s for a loading of 1 mg/l will deliver the acute toxicity reference value to
25 the OECD 203 medium at pH 8 and a time of 168 hr can be calculated by:

26 SA_{crit} = critical specific surface area (m²/g) corresponding to the acute ecotoxicity reference value

27 CP = classification cut-off loading of 1 mg/l that yield a classification as acute 1)

28 Thus, for the metal powder under consideration a **CSA of 10.100 mm²/l and the CP of 1 mg/l, the SA_{crit} is 10,1**
29 **m²/g.**

30 The equivalent critical spherical particle diameter (CD_{spec}) associated with the acute ecotoxicity reference value
31 is determined by:

$$32 CD_{\text{spec}} = \left(\frac{6}{SA_{\text{crit}} \times \rho_{\text{Me}}} \right)$$

33 ρ_{Me} = density of the metal (g/cm³)

34 CD_{spec} = critical diameter of the sphere (µm) corresponding to the acute ecotoxicity reference value

35 For the above SA_{crit} of 10,1 m²/g, corresponding to the 1 mg/l loading, the critical diameter would be 0,067 µm.
36 The EU-CLP system defines that the finest representative metal powder should be used for TDp testing and
37 classification of the metal powder form.

38 An acute toxicity classification can therefore be assigned to all metal powders (diameter ≤ 1 mm) by **measuring**
39 **the real surface area** using the BET nitrogen adsorption-desorption technique and comparing it to SA_{crit} . If the
40 surface area of the reference material is greater than the SA_{crit} for the associated acute toxicity classification then
41 the representative metal sample would classify for that acute hazard category **and classify all powder types of**
42 **that metal in the same way.** If the measured surface area is less than the SA_{crit} s of all of the classification
43 categories then all powders of this metal would not classify for aquatic toxicity.

1 The CSA Approach can consequently be used to assign an acute hazard classification to the metal powders
 2 based on measured surface area using the **measured surface area of 0.43 m²/g** for the smallest representative
 3 size powder on the EU market. Since this surface area is greater than 0.1 m²/g but less than 1 m²/g, there is
 4 according to this approach no need for an **acute hazard classification of the metal powders in this example**.

5 The CSA Approach can also be used to calculate a Critical Particle Diameter (CPD) to be used to determine an
 6 accurate classification of the **metal massive** (diameter > 1 mm), where the measured surface area of the tested
 7 granules is 0.086 m²/g. This surface area is far less than all of the SA_{crit} so there is **no need for an acute**
 8 **classification for the metal massive**.

9 Long-term hazard: For this example it has been shown that rate of metal ion release from the metal in the OECD
 10 203 medium at high pH at the 672 hr can be predicted by the equation:

$$\log(C_{Me(aq)}) = -5.144 + 1.0229 \log(A_{meas})$$

12 $C_{me(aq)}$ = total dissolved concentration of metal (mg/l)

13 A_{meas} = initial surface area loading (mm²/l) [equals (measured specific surface area, SA, in m²/g) ×
 14 (substance mass loading in g/l) X 10⁶], where SA was measured with the BET nitrogen
 15 adsorption-desorption technique.

16 The CSA Approach can determine what surface areas and particle diameter would result in chronic (long-term)
 17 hazard classification by using the regression coefficients from the above equation, *a* (-5.144) and *b* (1.0229),
 18 and the proposed chronic toxicity reference value (0.0024 mg Me/l) as the $C_{Me(aq)}$. The critical surface area
 19 (CSA) would be the A_{meas} at which metal ion is released at the concentration of the chronic toxicity reference
 20 value. The following equations can be used to derive these values.

$$\log \text{chronic toxicity} = -5.144 + 1.0229 \log \text{CSA}$$

22 *chronic toxicity* = chronic ecotoxicity reference value for classification (mg/l), using calculated EC₁₀s
 23 or measured NOECs (if the EC₁₀ is less than the NOEC)

24 CSA = critical surface area (mm²/l) that releases metal in the concentration of the chronic toxicity
 25 reference value to the aquatic medium

26 The CSA can be derived as follows:

$$\log \text{CSA} = \left(\frac{\log \text{chronic toxicity} + 5.144}{1.0229} \right)$$

28 For the chronic hazard classification derivation exactly the same approach as for the acute hazard assessment
 29 can be followed to define SA_{crit} and CD_{spec} . For this metal powder example this results in a CSA of 3,420 mm²/l
 30 and the CP of 1 mg/l, the SA_{crit} is 0.342 m²/g.

31 For a SA_{crit} of 0.342 m²/g, corresponding to the 1 mg/l loading, the critical diameter would be 2 μm.

32 Equivalent as for the assessment of the acute hazard the CSA Approach can be used to assign a long-term
 33 hazard classification to all powders based on measured surface area of the reference powder, using the measured
 34 surface area at 100 mg/l loading (0.43 m²/g) for the smallest representative size powder on the EU market. Since
 35 this surface area is greater than 0.342 m²/g, **all metal powders would be classified as Chronic 3**.

36 The CSA Approach can also be used to **classify the massive metal (diameter > 1 mm)**, where the measured
 37 surface area of the massive at 100 mg/l loading) is 0.086 m²/g. This surface area is less than the chronic SA_{crit} so
 38 the massive metal form would **not be classified for long-term environmental hazard**.

39
 40

1 **Example E: Hazard classification of a soluble metal salt: the case of removal through**
2 **speciation in the water column**

3 General approach

4 The example was selected because

5 (i) it illustrates the use of information on the metal oxidation and the removal of metal
6 ions from the water column for classification decisions.

7 (ii) It provides further information related to testing of sparingly soluble metal salts

8 The metal ion selected for this example, Me(II), is unstable when its solutions are exposed to
9 air, and it oxidises to the Me(III), which then forms the familiar insoluble, hydrated,
10 amorphous, gelatinous precipitate, Me(OH)₃ (metal hydroxide). The question then arises as to
11 whether the metal hydroxide precipitate forms rapidly enough to decrease the concentration
12 of Me(II) and Me(III) ions to levels below which there is no cause for concern over the
13 aquatic environment. Consideration of the rates at which Me(II) oxidises to Me(III) is
14 relevant to this question to proof rapid removal from the water column.

15 Additionally, the classification of substances of concern for the aquatic environment requires
16 evaluation of aquatic toxicity. Results for this case were evaluated against standard
17 acceptability criteria for use in this classification assessment.

18 Results

19 *“Metal“ fate and assessment of the removal from the water column:*

20 A review of the scientific literature on the oxidation of metal sulphate reveals the following:
21 *Metal sulphate reacts with oxygen in water to form metal hydroxide (MeOH₂), moderately*
22 *insoluble, $K_{sp} = 1.6 \times 10^{-14}$) this in turn undergoes further oxidation to form metal hydroxide*
23 *(MeOH₃) which is highly insoluble ($K_{sp} = 1 \times 10^{-36}$). Formation of metal hydroxide at pH*
24 *levels above 5.0 limits the presence of metal ions in aqueous systems. In sediments the metal*
25 *hydroxide is expected to result in enriched concentrations of insoluble metal sulphide.*

26 The rates at which dissolved metal sulphate (Me⁺⁺) oxidises to (Me⁺⁺⁺) and forms the metal
27 hydroxide [Me(OH)₃] precipitate:

- 28 – Is highly dependent on pH (100 fold from pH 6 to 8);
29 – decreases with increase in ionic strength of the aqueous medium (pristine waters contain
30 less metal ions);
31 – dependent to some extent on the anions present in solution such as sulphate and chloride;
32 – increases 10-fold for a 15 °C increase in temperature;
33 – exhibits a linear dependence on the partial pressure of oxygen; and
34 – dependent on the initial concentration of metal sulphate and exhibits linear reaction
35 kinetics at Me(II) loadings less than ~50 micromolar (~3 mg/l). At concentrations greater
36 than 50 micromolar, rates of reaction increase with increasing concentration of metal
37 sulfate (about 4× for each order of magnitude).

38 Based on literature data and empirical reaction kinetics, it can be calculated that, at low pH
39 (reasonable worst case scenario) in the OECD 203 medium (diluted by 10 as per the
40 Transformation/Dissolution Protocol), the half-times for the oxidation of Me(II) are 11, 9 and
41 3.6 hr, for 1, 10 and 100 mg/l loadings of MeSO₄, respectively. At high pH, the reaction is
42 estimated to be as short as 8 seconds. The rapid precipitation of metal ions from aqueous

1 systems accounts for low “metal” concentrations found in most natural aquatic systems (all
 2 except natural waters at very low pH values (i.e. < pH 5.5)). Under the reasonable worst case
 3 scenario of low pH and a low initial concentration of 1 mg/l MeSO₄, the 70% removal from
 4 solution is calculated to be achieved in 19hr and 90% removal would be achieved by 36hr.
 5 Since the removal of the metal sulphate are due to reaction with oxygen in water to form
 6 highly insoluble and non classifiable metal hydroxide and the half life for the removal of the
 7 soluble specie are less than 16 days this can be considered as rapid removal from the water
 8 column and the substance considered for classification purposes as rapidly degradable.

9 To support this, evidence of rapid loss of “Metal ions” (and other metals) from the water
 10 column has been reported in mesocosm lake experiments (Perch Lake). The data are
 11 presented as half lives as a function of time, partition coefficient and first stability constant.
 12 Half lives for metal ions in the mesocosms are calculated to be approximately 11 days
 13 under the given conditions. The data support that half lives are short and loss from the
 14 water column can be related to both formation of the metal hydroxide but also to sorption to
 15 suspended particles that are settling.

16 Aquatic Toxicity:

17 Acute ERV values lie in the range of 1-37 mg/l (see Table). Two values for *Daphnia magna*
 18 were less than 10 mg/l. Four *Daphnia magna* studies were performed and the geometric mean
 19 value for this species is 5.77 mg/l. The values for fish were all greater than 10 mg/l. No algal
 20 studies were deemed reliable. All these values are expressed as mg/l Me. If the classification
 21 relates specifically to metal sulphate of which the most common form is the heptahydrate
 22 MeSO₄.7H₂O. The numerical ERV values detailed should be adjusted according to the table
 23 below and the species under consideration to calculate the toxicity on a metal sulfate basis.

Chemical Species	Molecular Weight	Ratio
MeSO ₄ .7H ₂ O	278.0	4.978
MeSO ₄ H ₂ O	169.91	3.043
MeSO ₄	151.90	2.720
Me	55.84	1.0

25 The data cover all the reliable results available for aquatic toxicity of binary “metal” and any observed
 26 toxicity effects could relate to the Me ion which could be in Me(II) or metal Me(III) oxidation states.

27 Conversion of the acute ERV values for the metal ion to those appropriate for MeSO₄.7H₂O implies
 28 an acute toxicity range of 6.4 to 199 mg/l.

30 **Table IV.7.1** Acute toxicity data deemed reliable for “Metal” are presented as mg/l Me.

Test substance	Test organism	Duration	Endpoints	L(E)C ₅₀ (mg Me L ⁻¹)
MeCl ₃ .6H ₂ O	<i>Pimephales promelas</i>	96h	Survival	21.8
	<i>Lepomis macrochirus</i>	96h	Survival	20.3
MeSO ₄ .7H ₂ O	<i>Oncorhynchus mykiss</i>	96h	Survival	16.6
Me ₂ (SO ₄) ₃	<i>Oncorhynchus mykiss</i>	96h	Survival	>27.9
MeSO ₄	<i>Daphnia pulex</i>	24h	Immobility	36.9
MeSO ₄	<i>Daphnia magna</i>	24h	Immobility	17

Test substance	Test organism	Duration	Endpoints	L(E)C ₅₀ (mg Me L ⁻¹)
MeCl ₃ .6H ₂ O	<i>Daphnia pulex</i>	48h	Immobility	12.9
Me ₂ (SO ₄) ₃	<i>Daphnia longispina</i>	48h	Immobility	11.5
MeCl ₃ .6H ₂ O	<i>Daphnia magna</i>	48 h	Immobility	9.6
MeSO ₄	<i>Daphnia magna</i>	24h	Immobility	5.25
MeSO ₄ .7H ₂ O	<i>Daphnia magna</i>	48h	Immobility	1.29

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Table IV.7.2 Chronic toxicity data deemed reliable for “Metal” are presented as mg/l Me.

Test substance	Test organism	Duration	Endpoints	NOEC/LOEC (mg Me L ⁻¹)
Fe(OH) ₃	<i>Salvelinus fontinalis</i>	30 days	Hatching Growth Survival	>10.3
Fe(OH) ₃	<i>Oncorhynchus kisuth</i>	30 days	Hatching Growth Survival	>10.3 2.81/>10.3 >10.3
FeCl ₃ .6H ₂ O	<i>Pimephales promelas</i>	33 days	Survival Length Weight	1.0/1.6 1.61/2.81
FeCl ₃ .6H ₂ O	<i>Daphnia pulex</i>	21 days	Immobility Total offspring Brood size	2.51/5.01 0.63/1.26 1.26/2.51
FeCl ₃ .6H ₂ O	<i>Daphnia magna</i>	21 days	Immobility Reproduction	5.9 EC50 4.4 EC16

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Aquatic hazard classification:

Acute hazard: Not classified.

Long-term hazard: Not classified.

Reasoning:

Acute aquatic toxicity > 1 mg/l.

Chronic aquatic toxicity values are all greater than 1 mg/l. Rapid and permanent removal from the water column. Metal precipitates form large polymers that remain insoluble and become buried in the sediments.

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Labelling elements based on the classification:

Element	Code
GHS Pictogram	none
Signal Word	none
Hazard Statement	none
Precautionary statement(s)	none

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