



**Committee for Risk Assessment
RAC**

Annex 2
Response to comments document (RCOM)
to the Opinion proposing harmonised classification and
labelling at EU level of
**dicopper oxide;
copper (I) oxide (Cu₂O)**

**EC number: 215-270-7
CAS number: 1317-39-1**

CLH-O-0000001412-86-31/F

**Adopted
04 December 2014**

ANNEX 2 - COMMENTS AND RESPONSE TO COMMENTS ON CLH PROPOSAL ON DICOPPER OXIDE; COPPER (I) OXIDE

COMMENTS AND RESPONSE TO COMMENTS ON CLH: PROPOSAL AND JUSTIFICATION

Comments provided during public consultation are made available in the table below as submitted through the web form. Any attachments received are referred to in this table and listed underneath, or have been copied directly into the table.

All attachments including confidential documents received during the public consultation have been provided in full to the dossier submitter, to RAC members and to the Commission (after adoption of the RAC opinion). Non-confidential attachments that have not been copied into the table directly are published after the public consultation and are also published together with the opinion (after adoption) on ECHA's website.

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Substance name: Dicopper oxide; copper (I) oxide

CAS number: 1317-39-1

EC number: 215-270-7

Dossier submitter: France

GENERAL COMMENTS

Date	Country	Organisation	Type of Organisation	Comment number
30.01.2014	Spain		MemberState	1
Comment received				
The Spanish CA supports the proposal of the French CA for harmonized classification and labelling of copper (I) oxide.				
Dossier Submitter's Response				
Ok thank you				
RAC's response				
Noted.				

Date	Country	Organisation	Type of Organisation	Comment number
31.01.2014	United Kingdom	Regulatory Compliance Limited	BehalfOfAnOrganisation	2
Comment received				
We acknowledge and appreciate the alignment with the copper risk assessment dossier as well as the incorporation of some post risk assessment data.				
For most endpoints, the data used and interpretation of the data reflect the hazard profiles agreed in the copper Risk Assessment Report and used for the REACH dossiers.				
For a few endpoints, we noted some differences in data-interpretation between the dicopper oxide CLH report and the REACH dossier. We have therefore focused the review on these endpoints and propose to revise the classification to:				
Environmental hazard acute category 1. M factor 10.				
Environmental hazard chronic category 2.				
See non-confidential attachment.				
Dossier Submitter's Response				

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Human health hazard: noted
Environmental hazard: see response to detailed comment no 6 below.
RAC's response
See response to comment no. 6 below.

Date	Country	Organisation	Type of Organisation	Comment number
03.02.2014	Germany		MemberState	3

Comment received

The DE CA supports the FR CA's proposal for addition of Acute Tox 4 – H332 and Eye Irrit 2 – H319. The DE CA has general problems with some methodologies referring to the environmental classification used in the CLH-proposal. The DE CA supports the proposed acute classification as H400 with M-factor of 100 but suggests using lowest acute data from the DAR. In addition, the DE CA suggests considering classification as Aquatic Chronic 1, H410 with M-factor of 10.

Dossier Submitter's Response

Human health hazard: ok thank you
Environmental hazard: see response to detailed comment below.

RAC's response

Human Health Hazard: RAC agrees with the addition of Acute Tox. 4 – H332 but considers that classification as Eye Dam. 1 - -318 is appropriate as corneal opacity effects persisted until the end of the study at 21 days in one animal.
Environmental Hazard: See RAC's response to comment no. 8.

MUTAGENICITY

Date	Country	Organisation	Type of Organisation	Comment number
30.01.2014	Spain		MemberState	4

Comment received

The Spanish CA regards the available genotoxicity data insufficient to evaluate the genotoxic potential of copper compounds. Therefore, it is not possible to reach a final conclusion on this hazard for copper (I) oxide.

Dossier Submitter's Response

Human health hazard: As concluded in the CLH report, data indicates that copper compounds do not meet the criteria for classification as a genotoxic however there was insufficient evidence to exclude a local genotoxic potential of copper as some studies by IP route were positive (but with a low reliability). Moreover, during the EFSA peer review of copper substances, the experts have discussed in detail the results of the genotoxicity studies, their relevance in the case of inhalation exposure as concerns operators and bystanders, and the inconclusive epidemiological data on lung tumours. The expert meeting conclusion was that Genotoxicity is not of concern upon oral administration, but there is insufficient evidence to exclude genotoxic potential of copper after non-oral administration and raised a critical area of concern on the genotoxic potential of copper (I) and (II) variants by inhalation (EFSA 2008).

RAC's response

Noted. RAC however in line with the dossier submitter concluded that, although there is insufficient evidence to exclude a (local) genotoxic potential upon non-oral administration, overall the available data do not support the classification of copper compounds for germ cell mutagenicity.

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OTHER HAZARDS AND ENDPOINTS – Eye Hazard

Date	Country	Organisation	Type of Organisation	Comment number
30.01.2014	Spain		MemberState	5
Comment received				
The Spanish CA regards that the reference to Driscoll study in Table 22 (p.46) should be amended. In the summary of this study (p. 51-52) the results of conjunctival redness calculated as the mean scores following grading at 24, 48 and 72 hours for each animal were ≥ 2 in two rabbits. Therefore, according to these results, copper (I) oxide is an eye irritant. This should be also written in Table 22 because copper (I) oxide seems not irritant from the results inferred in this table (Driscoll study).				
Dossier Submitter's Response				
Human health hazard: ok thank you. Indeed, two animals have a score of 2 for conjunctival redness. In this context, according to CLP regulation, a classification as an eye irritant of category 2 is proposed. Therefore in the table 22 page 46, the following sentence should be presented: "eye irritant under CLP regulation".				
RAC's response				
Noted.				

OTHER HAZARDS AND ENDPOINTS – Hazardous to the Aquatic Environment

Date	Country	Organisation	Type of Organisation	Comment number
31.01.2014	United Kingdom	Regulatory Compliance Limited	BehalfOfAnOrganisation	6
Comment received				
In the REACH dossier, the following classification for environmental hazard was derived: Acute category 1. M factor = 10. Chronic category 2. The difference in classification (CLH report/REACH dossier) is related to a difference in data interpretation and data aggregation. Please see the non-confidential attachment for the rationale for the classification proposed under REACH. <i>ECHA's note: The information below was provided in CLH dossier comments Cu2O ECI Jan 2014.doc [attachment no.1]</i>				
ECI COMMENTS TO				
CLH REPORT: PROPOSAL FOR HARMONIZED CLASSIFICATION AND LABELLING OF DICOPPER OXIDE (CU₂O)				
These comments also reflect the considerations of the following task forces and consortium; European Antifouling Copper Task Force Wood Preservative Copper Task Force The European Union Copper Task Force (Plant Protection Products Regulation [PPPR])				

Copper Compound Consortium

ABSTRACT

We acknowledge and appreciate the alignment with the copper risk assessment dossier as well as the incorporation of some post risk assessment data.

For most endpoints, the data used and interpretation of the data reflect the hazard profiles agreed in the copper Risk Assessment Report and used for the REACH dossiers.

For a few endpoints, we noted some differences in data-interpretation between the dicopper oxide CLH report and the REACH dossier. We have therefore focussed the review on these endpoints and propose to revise the classification to:

Environmental hazard acute category 1. M factor 10¹.

Environmental hazard chronic category 2².

1) INTRODUCTION

We appreciate the opportunity to review the CLH report but do regret the significant overlap between the public consultation period and the year-end holidays.

We acknowledge and appreciate the alignment between the CLH report and the copper risk assessment dossier as well as the incorporation of some post risk assessment data. For most endpoints, the data used and interpretation of the data reflect the hazard profiles agreed in the copper risk assessment report (RAR) and used for the dicopper oxide REACH dossier.

Please find below a more detailed review for hazard endpoints, demonstrating differences in classification between the dicopper oxide CLH report and REACH dossier.

2) HUMAN HEALTH HAZARDS

No comments.

3) ENVIRONMENTAL HAZARDS

In the REACH dossier, the following classification for environmental hazard was derived:

Acute category 1. M factor = 10.

Chronic category 2.

The difference in classification (CLH report/REACH dossier) is related to a difference in data interpretation and data aggregation. Please find below the rationale for the classification proposed under REACH.

3.1 ECOTOXICITY DATABASE

In the CLH report, two data-sets are used independently for the classification: the ecotoxicity data from the RAR, based on tests with soluble copper compounds, and the ecotoxicity data from the Plant Protection Products Regulations (PPPR) DAR, based on tests with Cu₂O. Only test results expressed as measured dissolved copper concentrations were retained for the CLH report (RAR and DAR data-set) and REACH

¹ CLH report proposal: Acute 1, M factor 100

² CLH report proposal: Chronic 1

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dossier (RAR data-set alone).

The CLP guidance, mentions '*ecotoxicity data of soluble inorganic compounds are used and combined to define the toxicity of the metal ion under consideration*'.

The ecotoxicity data from the RAR therefore relies on tests with soluble copper compounds. The ecotoxicity data from the DAR is however based on tests with the sparingly soluble copper species (Cu₂O solubility <1 mg/L at pH >6 - CLH report), a comparison between total and dissolved concentrations is therefore relevant to the data-interpretation.

- In the RAR total and dissolved concentrations were compared for the chronic toxicity tests, carried out with soluble copper species. The data showed dissolved fractions as >72-100% of the total fraction and the assessment concluded that almost all copper was present in the dissolved form in the toxicity tests (more details - see RAR, aquatic effects – *Extract section 3.2.2.27*).

- When evaluating the ecotoxicity data from the DAR (Table, section 5.5 of the CLH report), the L(E)C₅₀ values were up to 6 times lower, when expressed as dissolved versus total copper concentrations as both were recorded. These data suggest that some of the less soluble copper compounds (e.g. Cu₂O) may have precipitated and reproducibility and dose-response relationship for dissolved copper concentrations therefore needs further elaboration.

- Although considered as soluble for classification purposes, dicopper oxide is a sparingly soluble substance with, as reported in the CLH report, a strong pH-dependent water solubility:

- solubility at pH 4 of >25 g/L;
- solubility at pH 6.6 of 0.639 mg/L;
- solubility at pH 9.8 of 0.539 mg/L.

Non-soluble Cu-species (e.g. colloidal or precipitated forms) are expected to dominate in aqueous media with pH values between 7.0 and 9.0, especially when tests are carried out in a flow-through test design.

- The flow-through acute toxicity test, retained in the CLH report (e.g. Schaefer's, 2002) was carried out at pH of around 8. Due to the relatively low water solubility of Cu₂O at the pH of the test waters, it is thus challenging to maintain the dissolved copper concentrations during testing. Indeed in the acute toxicity tests (Schaefer's, 2002), a mean total concentration between 50 and 60% of the nominal concentration was measured but total dissolved concentrations ranged between 5% and 35% of the total measured concentration.

- The low water solubility of the sparingly-soluble Cu-oxide explains the discrepancy between the measured total and dissolved copper concentrations in the aqueous media and therefore also explains the factor 6 difference in LC₅₀ values reported for total versus dissolved Cu-concentrations from the acute rainbow trout Cu₂O tests in the CLH report (2013). **The robustness of the concentration-response relationships and LC50 values, expressed as dissolved copper concentrations obtained, from the tests with Cu₂O, are therefore considered unreliable.**

- As proposed in the CLP guidance, ecotoxicity data from tests carried out with fully soluble compounds (cf. RAR/REACH data-sets) are therefore retained and the ecotoxicity data on Cu₂O rejected for use in classification.

- The RAR ERVs, retained in the CLH report, are slightly higher than the ones defined in the REACH dossier. This is because in the RAR geometric mean values were derived, even when only 2 and 3 data-points per species were available. In the REACH report, the geometric mean was only applied if 4 or more data-points are available. This refinement slightly lowered some species-specific reference values (more information from Van Sprang and Delbeke, 2010 - Attachment 1).

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Table 1 summarises the ERVs retained from the DAR, RAR and REACH (after molecular weight translation), expressed as mg Cu₂O/L.

Table 1: Summary of the acute and chronic ERVs for dicopper oxide, expressed as mg Cu₂O/L

Source	pH range	Acute ERV Cu ₂ O	Chronic ERV Cu ₂ O
DAR	-	0.012	-
RAR	5.5-6.5	0.033	0.023
	>6.5-7.5	0.053	0.008
	>7.5-8.5	0.034	0.018
REACH	5.5-6.5	0.028	0.023
	>6.5-7.5	0.039	0.008
	>7.5-8.5	0.034	0.013
	across all pHs	0.039	0.017

Note: In the RAR and the REACH dossier, the ecotoxicity data from *P. promelas* at pH 6 (Erickson *et al.*, 1996) were rejected and it may be clarifying to also mention this in the CLH report.

The test was performed with larvae (< 24 h old) in a flow-through with a very short retention time (± 45 min.), using a diluted reconstituted medium (prepared from Lake Superior water through reverse osmosis) with a low hardness (22 mg/l CaCO₃) and DOC concentration (reverse osmosis). This test performed represent worst case conditions explaining therefore this low LC50 value. Moreover the observed pH dependency observed for *P. promelas* at (sensitivity at pH 6 versus pH 7) is unexpected and may be related to insufficient adaptation to low pH conditions (from Van Sprang and Delbeke, 2010 -Attachment 1).

3.2 CLASSIFICATION

The CLH and REACH dossiers consider Cu₂O as fully soluble for classification purposes;

- The CLH report concluded, from solubility data of the RAR that Cu₂O is fully soluble (0.639 mg/L at pH 6.6 and 0.539 mg/L at pH 9.8).
- The results from transformation dissolution tests on Cu₂O (1 mg/L) at pH 6 (used for the preceding classification discussions at EU level for Cu₂O) demonstrated that dissolved copper concentrations after 24 hours transformation/dissolution was <10% but exceeded the acute ERV. The REACH dossiers therefore also considered Cu₂O to be fully soluble, for environmental classification purposes.

The CLH and REACH dossiers consider Cu₂O as rapidly degradable (with evidence for rapid removal of copper from the water column presented).

Classification, in both dossiers (CLH and REACH), is therefore based on the comparison between ERV values (Table 1) and classification cut-off values.

The difference in classification outcome between the CLH and REACH reports is related to the choice of ERV values and interpretation of the data.

- Table 1 consistently indicated Acute ERV values between 0.1 mg/L and 0.01 mg/L. The assessment therefore leads to an environmental hazard **Acute 1 - H400. M factor =10**^(footnote 3).
- For chronic classification, the ERVs are < 0.1 mg/L and >0.01 mg/L except for a lower value at pH 7 (0.008 mg/L). Using all of the available ERV data, the classification would be Chronic 2 at pHs 6, 8

³ CLH report : Acute 1, M factor 100 instead

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and across pHs, but Chronic 1 at pH 7. When comparing the classification outcome alongside solubility for the various copper compounds under review, the classification of Cu₂O appears to be an outlier (all copper compounds are classified as Chronic 2 or less - see Attachment 2). In considering the classification outcome for Cu₂O (Chronic 1 or 2) as borderline, it seems useful to account for the Cu₂O being a sparingly soluble substance (although considered as fully soluble for the classification purposes). Taking the next lowest species-specific ERV, which was 0.017 mg/L ('across the pH range'), an environmental hazard classification entry of **Chronic 2** could be applied.

This result would also be consistent with a reduced solubility of Cu₂O compared to soluble copper compounds (see Attachment 2).

4) RELEVANT ATTACHMENTS

Attachment 1: Van Sprang and Delbeke, 2010

Attachment 2: Classification versus solubility for copper compounds and copper flake

CONTACTS

For more information, please contact:

Katrien Delbeke, *Director Health Environment and Sustainable Development*. European Copper Institute, Tervurenlaan 168 b-10. B-1150 Brussels: Tel: +32 2 777 7083, katrien.delbeke@copperalliance.eu

Carol Mackie *Secretariat of the Copper Compound Consortium*, Regulatory Compliance Ltd, 6 Dryden Road, Bilston Glen, Loanhead, Midlothian, EH20 9LZ. Tel: +44(0)131 448 1086, cmackie@regcs.co.uk

ECHA note: The information below was provided in Classification versus pH and solubility.doc [attachment no.2]

ECI ATTACHMENT (2)

FOR INFORMATION - CLASSIFICATION VERSUS SOLUBILITY FOR COPPER COMPOUNDS AND COPPER FLAKE

This paper also reflects the considerations of the following task forces and consortium;
European Antifouling Copper Task Force
Wood Preservative Copper Task Force
The European Union Copper Task Force (Plant Protection Products Regulation [PPPR])
Copper Compound Consortium

1) INTRODUCTION

Following the review of the ANSES CLH documents for copper compounds and copper flakes, ECI in collaboration with the various copper task forces⁴ would like to raise the following discussion as applicable to all the available compounds under consideration.

The ecotoxicity reference values (ERVs) for copper/copper compounds are based on the reliable/relevant ecotoxicity tests carried out with soluble copper compounds (e.g. CuSO₄,

⁴ European Antifouling Copper Task Force; Wood Preservative Copper Task Force; The European Union Copper Task Force (Plant Protection Products Regulation [PPPR]); Copper Compound Consortium

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CuCl) and retained in the copper risk assessment. The test results (e.g. LC50) from various compounds are combined and expressed as soluble copper ions (RAR and Van Sprang and Delbeke, 2010). For classification purposes, the ERV values are obtained after data-aggregation and translation to the respective copper compounds using a molecular weight translation (soluble compounds) or using the results of the transformation/dissolutions (sparingly soluble copper compounds, copper powders and copper massives). Therefore, consistency in classification across copper/copper compounds can be assessed based in information of molecular weight and solubility (see Table 1). From Table 1, the highest classification of CuSO4 is thus expected. In addition, the available data in the CLH reports and transformation dissolution (TD) data also show that the solubility of all the other compounds including copper flakes currently under consideration is dependent on pH.

Table 1: Solubility of copper compound/flakes across the pH range tested

a) Standard OECD solubility testing

Compound	pH range				Source
	5.5-6.5	>6.5-7.5	>7.5-8.5	>8.5-10	
	Solubility (mg/L)				
CuSO4.5H2O	220000				1
BCC	-	4.68	-	0.01	1
Bordeaux Mixture	-	2.2	-	1.1	1
Cu4(OH)6(SO4)	3.42	-	-	0.255	1
CuSCN	-	2.3	-	0.12	1
CuOCl	1.19	-	-	0.525	1
CuOH	-	0.9318	-	0.0066	1
Cu2O	-	0.639	-	0.539	1
Copper flakes*	-	0.27**	-	0.13	2
CuO	0.394	-	-	0.01	1

b) Transformation/dissolution testing

Compound	pH range				Source
	5.5-6.5	>6.5-7.5	>7.5-8.5	>8.5-10	
	Solubility (mg/L)				
Cu2O	0.236	0.098	<1	-	3
Copper flakes	0.721	0.363	-	-	4
CuO	0.049	0.005	0.00	-	5

Key

* Data at pH 4 was reported as 192 mg/L but not presented in table as this was more likely to reflect the oxido-reduction reaction of the copper metal into ionic copper [Cu(0) → Cu(I) → Cu (II)] which is promoted at low pH.

** Carried out at 20°C at 30°C 0.32 mg/L was reported

1 - Endpoints taken from standard OECD solubility studies see Section 5.6 of CLH report from ANSES

2 - Endpoints taken from standard OECD solubility studies see Section 1.3; Table 9 of CLH report from ANSES

3 - Results from T/D study reported for ISO 6341. Data presented to the 2001 'Meeting on environmental effects' part of the Commission Working Group on the Classification and Labelling of Dangerous Substances ref: ECBI/61/95 Add. 135.

4 - Schaefers and Klawonn (2013) data provided by ECI within commenting document to CLH

5 - Rodriguez et al., 2000 - data presented in REACH 2013 updates and available in Report available from the copper RAR (2008) (Annex K3)

The overall impact of solubility on the classification proposals by the CLH report across all the compounds and copper flakes can be seen in see Table 2 in addition the classifications

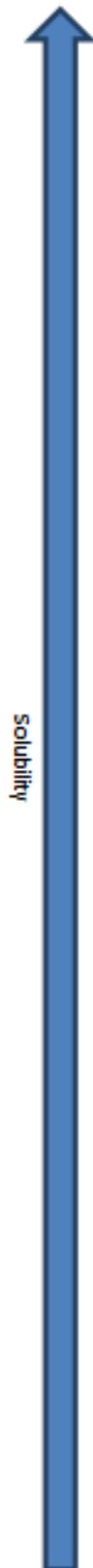
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as proposed by ECI and task force commenting documents.

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Table 2: ECI Proposed Classification of copper compounds and copper flake across pH

Compound	Classification	Proposed CLH	Proposed by ECI at pH range			Proposed ECI
			5.5-6.5	>6.5-7.5	>7.5-8.5	
CuSO4	Acute	1	1	1	1	1
	M-Factor	10	10	10*	10	10
	Chronic	2	2	2	2	2
	M-Factor	-	-	-	-	-
BCC	Acute	1	1	1	1	1
	M-Factor	10	10	10	10	10
	Chronic	2	2	2	2	2
	M-Factor	-	-	-	-	-
Bordeaux Mixture	Acute	1	1	1	1	1
	M-Factor	10	10	10	10	10
	Chronic	2	2	2	2	2
	M-Factor	-	-	-	-	-
Cu4(OH)6(SO4)	Acute	1	1	1	1	1
	M-Factor	10	10	10	10	10
	Chronic	2	2	2	2	2
	M-Factor	-	-	-	-	-
CuSCN	Acute	1	1	1	1	1
	M-Factor	10	10	10	10	10
	Chronic	2	2	2	2	2
	M-Factor	-	-	-	-	-
CuOCl	Acute	1	1	1	1	1
	M-Factor	10	10	10	10	10
	Chronic	2	2	2	2	2
	M-Factor	-	-	-	-	-
CuOH	Acute	1	1	1	1	1
	M-Factor	10	10	10	10	10
	Chronic	1	2	2	2	2
	M-Factor	1	-	-	-	-
Cu2O	Acute	1	1	1	1	1
	M-Factor	100**	10	10	10	10
	Chronic	1	2	2***	2	2
	M-Factor	1	-	-	-	-
Copper flake	Acute	1	1	1	1	1
	M-Factor	10	10	10	10	10
	Chronic	1	2	2	n/c	2
	M-Factor	1	-	-	-	-
CuO	Acute	1	1	1	1	1
	M-Factor	10	1	1	1	1
	Chronic****	1	2	3	n/c	2
	M-Factor	1	-	-	-	-



n/c – Not Classified

**M=1 for RAR data with ERV of 0.119 mg/l*

*** considered to be an error introduced to CLH document by ANSES (see individual commenting document)*

**** judgment made since compound is of relative low solubility and ERV of 0.008 mg/l is borderline, Chronic 1 is considered an over prediction when comparing toxicity with soluble data of CuSO4*

***** Calculated from 28 d TD study by dividing 1 mg/l result by factor of 10*

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2) Overall conclusion

The ERV values for copper and copper compounds for both acute and chronic environmental endpoints have historically been derived using high quality ecotoxicity studies using soluble copper compounds. This ensures that consistent ERV values are derived across compounds. This consistent ERV allows to compare classification based on potential bioavailability, according to the results of solubility studies (derived using OECD guidelines or by transformation/dissolution). Using this proposal, the most soluble copper compounds would carry the most stringent environmental classification (see Table 2).

CONTACTS

For more information, please contact:

Katrien Delbeke, *Director Health Environment and Sustainable Development*. European Copper Institute, Tervurenlaan 168 b-10. B-1150 Brussels: Tel: +32 2 777 7083, katrien.delbeke@copperalliance.eu

Carol Mackie *Secretariat of the Copper Compound Consortium*, Regulatory Compliance Ltd, 6 Dryden Road, Bilston Glen, Loanhead, Midlothian, EH20 9LZ. Tell: +44(0)131 448 1086, cmackie@regcs.co.uk

Dossier Submitter's Response

In the current published version of the CLP guidance (Guidance on the Application of the CLP Criteria Version 4.0 – November 2013) the parts concerning "rapid removal from water column" have indeed been deleted. Moreover, as no consensus was found during the ECHA workshop on the concept of rapid removal on February 8th, 2012, and taking into account comments from several MS (Finland, Germany, Denmark, United Kingdom, Belgium) this concept might be not considered in the current assessment. The long-term classification and M factors would therefore need to be updated accordingly (see final proposal for Chronic classification and M factor at the end of this document).

RAC's response

We agree with the DS response about the rapid removal concept, which affects the chronic classification. Our reasons are given in the opinion.

We note that the DS has not responded to any of the other comments that were made. These point out differences in data aggregation between the REACH registration dossiers and the CLH report which result in different ERV values for some substances. We have considered this in the opinion and shown how the ERVs are calculated for each substance.

The comments also highlight some concerns about the ecotoxicity data for *P. promelas* at pH 6 (Erickson et al., 1996), which are used in the CLH report but rejected in the REACH registration dossiers. This study is important as it appears to be the most sensitive for fish, and we have discussed some of the issues in the opinion.

The comments also refer to transformation/dissolution (T/D) data and relative solubility of the different substances, and state that the most soluble copper compounds would carry the most stringent environmental classification. We note that only some substances have T/D data. We have considered solubility for each substance in the opinions (except for copper flakes, for which T/D data were used) – in our view, all of the substances can be considered to be readily soluble metal compounds in accordance with the CLP Guidance. The stringency of the classification depends not only on solubility but also molecular weight and the number of copper atoms per substance. This is clarified in each opinion.

Date	Country	Organisation	Type of Organisation	Comment number
03.02.2014	Finland		MemberState	7

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Comment received
<p>Comments by the Finnish Competent Authority:</p> <p>The CLH proposal includes an assumption that copper undergoes rapid removal from the water column, which is proposed to correspond to rapid environmental transformation as defined in the classification criteria. The Finnish CA considers that the provided justification for rapid environmental transformation based on the rapid removal of copper (i.e. more than 70% removal of copper from the water column within 28 days, as indicated by the TICKET-UWM model simulations), is not acceptable.</p> <p>In the CLH report, it is mentioned that "the processes considered by the model include complexation by aqueous inorganic and organic ligands such as dissolved organic carbon (DOC), adsorption to particulate phases such as particulate organic carbon (POC) and iron/manganese oxides, binding to biological receptors (biotic ligands), dissolution kinetics of metals powders, and cycling of organic matter and sulfide production in lakes"</p> <p>It is noted that the above-mentioned processes are dependent on site-specific factors and may vary spatially and temporally. Therefore, these factors cannot be used for hazard assessment which should be based on intrinsic properties of the substance and should not be dependent on local conditions.</p> <p>It is also noted that in the current published version of the CLP guidance (Guidance on the Application of the CLP Criteria Version 4.0 – November 2013) the parts concerning "rapid removal from water column" have been deleted for the time being as explained in the comment by ECHA (p.606 of the guidance).</p> <p>In the CLH proposal the aquatic acute classification is based on the ERV-Cu₂O value of 0.01 mg/l which leads to the classification Category Acute 1, H400 with an M-factor of 100. This ERV-Cu₂O value of 0.01 mg/l is extracted from the pesticide monograph. However, in the CLH report the lowest recorded geometric mean LC₅₀ value for pH 5.5-6.5 was mentioned to be 0.0081 mg Cu/l for fish <i>Pimephales promelas</i> (source EU Voluntary risk assessment of Copper compounds). This value has not been used in the proposal as in the table p. 197 the lowest reference value LC₅₀ (mg/l) for pH 5.5-6.6 was claimed to be 0.0292 mg/l. It is unclear where this value 0.0292 mg/l comes from.</p> <p>The classification for acute hazard should be based on the lowest reference value of 0.0081 mg/l (acute ERV- Cu₂O 0.009 mg/l) which, however, would not change the classification in this case.</p> <p>Considering the proposal for chronic hazard, as there is no reliable evidence of rapid environmental transformation and taking into account the lowest chronic ERV- Cu₂O value of 0.008 mg/l (<0.01), the classification for chronic hazard should be Category Chronic 1, H410, with an M-factor of 10.</p>
Dossier Submitter's Response
<p>In the current published version of the CLP guidance (Guidance on the Application of the CLP Criteria Version 4.0 – November 2013) the parts concerning "rapid removal from water column" have indeed been deleted. Moreover, as no consensus was found during the ECHA workshop on the concept of rapid removal on February 8th, 2012, and taking into account comments from several MS (Finland, Germany, Denmark, United Kingdom, Belgium) this concept might be not considered in the current assessment. The long-term classification and M factors would therefore need to be updated accordingly (see final proposal for Chronic classification and M factor at the end of this document).</p>
RAC's response

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We agree with the comments made about the rapid removal concept, and note that the DS does too. This affects the chronic classification.

We note that the DS has not responded to any of the other comments that were made. These include a question about the ERV_{Cu2O} value of 0.01 mg/L. We have addressed this in the opinion.

The comment also points out inconsistencies in acute data presentation for fish, and we have clarified the choice of data in the opinion.

Date	Country	Organisation	Type of Organisation	Comment number
03.02.2014	Germany		MemberState	8

Comment received

The DE CA has general problems with some methodologies referring to the environmental classification used in the CLH-proposal:

i) Methodology for chronic classification

Regarding the chronic environmental classification and labeling, the proposal is based on the concept of "rapid removal" for assessment of environmental transformation. However, the interpretation of this concept is not yet finally agreed upon (cf. comment by the ECHA on page 503 of the Guidance Document for the application of CLP criteria).

In the view of the German Federal Environment Agency the concept of "rapid degradation" as foreseen by the CLP Regulation for organic substances cannot be compared to the risk based concept of "rapid removal/transformation" of inorganic substances (metals are not degraded but simply relocated from the water column to e.g. the sediment). Hence, the concept of "rapid removal" seems not adequate for the hazard based classification according to CLP. For this reason we cannot support the chronic classification proposed by FR.

As long as the concept of "rapid removal" for inorganic compounds is not finally agreed upon, the aquatic chronic classification should be based on the criteria for not rapidly degradable substances as it was done for all substances including metals before.

ii) Use of geometric mean for classification and labeling

According to the CLP Regulation (section 4.1.2.3) "the lowest of the available toxicity values shall normally be used to define the appropriate hazard category(ies)." In the Guidance Document on the application of the CLP criteria the following is stated: "Where more than one acceptable test is available for the same taxonomic group, the most sensitive (the one with the lowest L(E)C50 or NOEC/EC10) is generally used for classification. [...] When larger data sets (four or more values) are available for the same species, the geometric mean of toxicity values may be used as the representative toxicity value for that species."

Accordingly, the geometric mean may be used for the derivation of the lowest acute and chronic endpoint for data rich substances, if four or more endpoints are available for one species. Please note that this is not always the case for the data used for classification in the CLH reports. We therefore suggest using the lowest effects value as it was proposed and agreed for example within the Competent Authority Assessment Reports (e.g. DAR for pesticides, CAR for biocides).

iii) Data basis for classification

Most of the data available on copper compounds has been submitted under the EU Voluntary risk assessment (VRA) under the Existing Substances Regulation. The adequacy of the data presented in the VRA is questionable with regard to classification and labeling as it has not been discussed by any technical group competent for classification as stated by FR in the CLH Report. Therefore we suggest taking into account the data which has recently

ANNEX 2 - COMMENTS AND RESPONSE TO COMMENTS ON CLH PROPOSAL ON DICOPPER OXIDE; COPPER (I) OXIDE

been fully evaluated by competent authorities and which has been taken for a classification and labeling proposal (e.g. DAR for pesticides, CAR for biocides, see specific comments on environmental classification).

For these three indicated points, we propose to revise the CLH-Dossier accordingly.

Further points:

pp. 190ff: In general, we would appreciate more background information in section 5.4 on why data are presented and how they are being used in the course of environmental classification.

p. 190: "As long as copper compounds dissociate in water, all acute tests were conducted with the salt of concern, when the chronic studies were conducted with other salts but considered relevant. All endpoints are expressed as copper."

It is not quite clear what is meant with this statement. If all acute tests were conducted with the salt of concern this would mean that for the assessment of the acute toxicity only those tox-data were taken into account which were actually conducted with the copper salt of concern i.e the classification and labeling dossiers should contain different effect values for acute toxicity. However mainly all dossiers all contain the same data.

p. 192: Please add a NOEC = 0.0017 mg Cu/L dissolved (measured) as relevant result of copper hydroxide WP from ELS-study with *Oncorhynchus mykiss* (Schäfers 2000).

p. 195: Please mention the name of the performed standardtestmethods in Ch. 5.5

p. 196: Please clarify whether the given toxicity data refer to the copper ion only or a copper compound. Some tables also contain the test substance other don't.

p. 197 conclusion on environmental classification and labelling:

The ERV used for environmental classification should be the one calculated with the toxicity data from the pesticide monograph (DAR). These studies have been peer reviewed and found to be acceptable (see general comment).

We support using lowest acute data from the DAR (LC50 *Oncorhynchus mykiss* = 0.0106 mg Cu/L) and the acute ERV -Copper(I)oxide of 0.01 mg Copper(I)oxide /L and the proposed acute classification as H400 with M-factor of 100.

For chronic environmental classification we suggest using lowest chronic data from the DAR the NOEC for *Oncorhynchus mykiss* obtained in the ELS- study by Schäfers (2000) with copper hydroxide WP because no chronic data for Copper(I)oxide is available. The NOEC = 0.0017 mg Cu/L results in a chronic ERV - Copper(I)oxide = 0.0019 mg Copper(I)oxide /L. Since the interpretation of "rapid removal" for assessment of environmental transformation is not finally agreed yet, we suggest considering "no rapid transformation"; hence classification as chronic category 1, H410 with M-factor of 10.

Biocide Regulation: The lowest NOEC reported under the BPD for copper (e.g. in the Assessment Report for the biocidal active substance copper carbonate / Product type 8, RMS France, September 2011) is 2.2 µg Cu/L (growth of *Oncorhynchus mykiss*). This value is given in the CLH Report in the table on page 192, section 5.4.1.2 for the test organism *O. mykiss* in the column "all pHs". The respective Chronic ERV for copper (I) oxide would be 4.95 µg Cu₂O/ L. However, this endpoint has not been considered for the environmental classification in the CLH report (cf. Conclusion of environmental classification according to Regulation EC 1272/2008 on page 197). Please take this endpoint for the aquatic chronic classification of copper (I) oxide into account.

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Dossier Submitter's Response

- i) In the current published version of the CLP guidance (Guidance on the Application of the CLP Criteria Version 4.0 – November 2013) the parts concerning "rapid removal from water column" have indeed been deleted. Moreover, as no consensus was found during the ECHA workshop on the concept of rapid removal on February 8th, 2012, and taking into account comments from several MS

ANNEX 2 - COMMENTS AND RESPONSE TO COMMENTS ON CLH PROPOSAL ON DICOPPER OXIDE; COPPER (I) OXIDE

	(Finland, Germany, Denmark, United Kingdom, Belgium) this concept might be not considered in the current assessment. The long-term classification and M factors would therefore need to be updated accordingly (see final proposal for Chronic classification and M factor at the end of this document).
ii)	We agree, however in this case there is no impact on classification
iii)	The biocide CAR is based on data submitted in the RAR. All data available in the pesticide DAR are also included in this dossier.

RAC's response

i)	We agree with the comments made about the rapid removal concept, and note that the DS does too. This affects the chronic classification.
ii)	We agree with the comments about the use of the geometric mean, provided that the data are all reliable. Contrary to the response of the DS, the way that this is applied to some of the data could have implications for the environmental classification of some of the copper compounds (because of the way that molecular weight and number of copper atoms affects ERVs for individual substances based on the same ecotoxicity data point).
iii)	We are disappointed that the CLH dossier did not in fact include all relevant data available in the REACH CSRs (and voluntary risk assessment report, vRAR), such as for invertebrates. These data have been assessed to be reliable for use in REACH registrations, so we believe they should be used for classification purposes too, even if they have not been independently validated by a regulatory authority (we note that there was some oversight of the data assessment process provided by the Italian Competent Authority and the Technical Committee for New and Existing Substances (TC NES) under the former Existing Substances Regulation, and more recently agreement of the data set at the OECD CoCAM; the overall level of scrutiny provided is unclear – in particular the TC NES did not “agree” any of the data). The opinion therefore considers the impact of the additional data on the classification.

The DS has not responded to the additional points that were made, which raise valid concerns about the transparency of the dossier. The opinion discusses the molecular weight of the hydrated and anhydrous forms where appropriate, the number of copper ions per substance and the use of the copper (II) hydroxide data for *Oncorhynchus mykiss*.

Date	Country	Organisation	Type of Organisation	Comment number
30.01.2014	Denmark		MemberState	9

Comment received

We do not agree that copper (I) oxide can be regarded as rapidly “degrading”, and therefore the M-factor to be applied in the chronic classification should be 10 and not 1 as suggested in the dossier

ECHA note: The information below was provided in Rapid-degradation-copper (I) oxide.doc [attachment 4]

Danish comments on the environmental classification of copper (I) oxide

We do not agree that copper (I) oxide can be regarded as rapidly “degrading”, and therefore the M-factor to be applied in the chronic classification should be 10 and not 1 as suggested in the dossier.

In the section on classification for environmental hazards the concept of “rapid removal” has been applied as an analogy to rapid degradation.

However, the “rapid removal” concept is not generally accepted as an applicable tool in classification of metals in neither the CLP nor in the GHS.

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Thus in the CLP guidance the paragraphs on “rapid removal” that were introduced in a draft were removed because of “lack of scientific consensus” (Guidance on the Application of the CLP Criteria, Version 4.0, November 2013, Appendix IV, IV.3).

Likewise, EUROMETEAUX and ICMM proposed to introduce the concept of “rapid removal” in the GHS guidance document, Annex A9.7, but the GHS correspondence group in December 2013 decided to leave it out for the same reasons as above in the CLP guidance.

The “rapid removal” concept is risk based, and not adequate for hazard classification purposes.

The outlined procedures and models in the “rapid removal” concept assume completely still-standing water, a situation you will hardly find anywhere in natural waters; certainly that would be rather special localities, and the concept is absolutely inapplicable to running waters. Thus, the suggested procedure not only represents risk assessment, it is not even generic risk assessment, but very, very local risk assessment.

Binding to particles in the water column with a following sedimentation and binding in the sediment has not been accepted for organic substances. The reason for this is that such processes will depend highly on local conditions. Also, the rate of such processes will vary with the depth of the water column, and this was the main argument for not taking volatility into account in the hazard assessment. For the same reasons these processes cannot be applied in the hazard assessment and classification of metals.

The Ticket-Unit-World model has been developed for lakes, so far without currents and turbulence. And the model will not be applicable to running waters. The model also employs binding to organic particles and precipitation of these to the sediment, which, as said above, cannot be accepted in the framework of hazard assessment and classification.

The binding in the sediment (e.g. to sulphides) is not really an irreversible process. It requires undisturbed sediment that doesn’t get oxygenized, while in natural waters you will normally see a number of processes that can stir the sediment at different times, such as e.g. storms and burrowing animals. And again, it won’t apply to running waters.

Thus the “rapid removal” concept is purely a risk assessment tool and not applicable to hazard identification and classification, and has not been accepted for hazard identification under the CLP and GHS.

Further, it is in the dossier suggested that 70% removal of the soluble form of a metal would be analogous to 70% degradation (mineralization) of an organic substance.

However, recall that the 70 % (or 60% depending on test-method) mineralization of organic substances really represents close to 100% degradation, as a substantial part of the last 30 % is built into microbial biomass. A 70% removal of a metal is therefore not at all equivalent with the 70 % mineralization of organics.

Also, looking at the transformation/dissolution protocol results given in the voluntary risk assessment (VRAR) Appendix K1, it is evident that there is a marked *increase* in soluble Cu from day 7 to day 28 (about a factor of 4). If there was a rapid transformation of soluble forms to insoluble forms this would be seen as a marked *decrease* of soluble forms in the T/D protocol tests. The table below is from VRAR:

Table 8: Summary of the transformation/dissolution data obtained for CuO, at different loadings and different pHs.

CuO loading rate (mg/l)	Time (days)	Measured Cu concentration (µg/l)		
		pH6	pH7	pH8
1	7	49	5	0
10	7	221	22	3
100	7	980	64	10
1	28	210	9	1

The implication of this is that the substance cannot be regarded as rapidly “degrading”, and therefore the M-factor for Chronic 1 is 10.

Danish Environmental Protection Agency,

Strandgade 29, DK-1401 Copenhagen K, Denmark

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Dossier Submitter's Response
In the current published version of the CLP guidance (Guidance on the Application of the CLP Criteria Version 4.0 – November 2013) the parts concerning "rapid removal from water column" have indeed been deleted. Moreover, as no consensus was found during the ECHA workshop on the concept of rapid removal on February 8 th , 2012, and taking into account comments from several MS (Finland, Germany, Denmark, UK) this concept might be not considered in the current assessment. The long-term classification and M factors would therefore need to be updated accordingly (see final proposal for Chronic classification and M factor at the end of this document).
RAC's response
We agree with the comments made about the rapid removal concept, and note that the DS does too. This affects the chronic classification.

Date	Country	Organisation	Type of Organisation	Comment number
30.01.2014	France	Solvay	BehalfOfAnOrganisation	10

Comment received
Our comment is relative to section 5.5 pages 196-197 of the CLH report. In this section, acute and chronic Ecotoxicological Reference Values (ERV) are reported for both the Cu element and the Cu compound Cu ₂ O. If the calculations performed to obtain the ERVcompound from the ERVelement are well explained, it is less easy for us to understand how the ERVelement were derived from the ecotoxicological data. We thought that the acute and chronic ERV were the lowest L/EC50 and EC10/NOEC obtained during acute and chronic ecotoxicological studies, respectively. However, applying this reasoning, the ERV do not seem consistent with the aquatic toxicity data available in section 5.4 (pages 190 to 195 of the CLH report). As the copper database is a very extensive one, do you perform a statistical calculation to obtain the ERV (e.g. determination of the HC5 = Hazard Concentration 5th percentile, showing no effects to 95% of species)? Please could you clarify the methodology of derivation of the ERVelement in the CLH report?

Dossier Submitter's Response
The methodology applied for ERV calculation is explained in the Guidance Document on the Application of the CLP criteria.
RAC's response
Noted. The opinion clarifies the approach the RAC uses in classification. The comment concerning HC5, see RAC's response to comment no. 11.

Date	Country	Organisation	Type of Organisation	Comment number
03.02.2014	United Kingdom		MemberState	11

Comment received
It is important to note that our comments reflect the general classification approach used for the range of copper compounds and are not specific to individual substances.
Many of the copper compound CLH Reports refer extensively to biocide CARs or pesticide DARs. Whilst we appreciate the time since the reports were initially prepared, we note that a more recent EFSA opinion and agreed endpoints for pesticidal uses of copper (dated 2013) than the one referred to (2008) is available. The authors may wish to consider the final agreed key endpoints and data gaps identified by EFSA (along with more recent biocide reviews) to see if there are any significant changes or new data.

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For all the copper compounds, it would help to be clear throughout the reports whether they are referring to the whole technical substance in question, the pure substance, total copper, or dissociated ionic copper (Cu²⁺). This is important when it comes to how the exposure and (eco)toxicity units are presented. Wherever units are quoted (e.g. µg/L), it should say in what form that copper is expressed.

It is useful to have noted that nano-forms of Cu exist - and we agree with the suggestion that these are considered separately pending further information on representivity/read-across of the existing bulk Cu data. This would be a useful principle to note for all future substances where nano-forms also exist and we feel this distinction should also appear in the final

Environmental fate assessment

Much of the env.fate section attempts to equate removal of dissolved ionic copper from the water phase with the rapid degradation criterion for organic substances of >70% degradation in 28 days. It is noted in the reports that transformation of one metal 'species' to another does not equate with degradation of an organic substance and that (bio)availability of the different forms of copper is a key consideration. The current ECHA CLP Guidance for metals (Annex IV) focuses mainly on exposure to metals and metal compounds dissolved in the water phase and on transformation processes that occur only within the water column. The focus in the guidance is on determining 'rapid environmental transformation'. However, it does suggest that it may be possible to incorporate other processes such as water-column residence times, deposition and subsequent re-mobilisation. Whilst the copper CLH reports clearly attempt to do this, there is currently no standard means of incorporating removal, e.g. to dissolved organic carbon (DOC) or sediment, within the hazard classification system for organic or inorganic substances.

The approach used in the reports to indicate rapid environmental transformation or removal relies on a number of assumptions which are not well supported; for example:

- It assumes that there is sediment present to act as a 'sink' for copper, which may not always be the case.
- It is not always clear what form the initial loading comprised in each case - was it already as dissolved Cu²⁺ and if so, can the model (and fate studies) account for different loading rates and the different forms of copper discussed here (which presumably initially dissociate at different rates)?
- The main scenario discussed is a generalized 3 m deep lake situation. Lakes are usually large, static, permanent and have sediment of some description, however this may not reflect many other EU surface water bodies such as ponds, rivers and streams - where increased water movement, turbidity, less sediment, different depths, etc.. could affect the amount of copper remaining in solution or suspension. We therefore wonder whether a 'realistic worst case' situation has indeed been modelled?
- With various adjustments, e.g. to settling velocity, suspended solids, the TICKET-UWM model appears able to reflect the fate of copper in some (not all) of the available field/semi-field tests. However, it is not then used to extrapolate to other water body types with very different characteristics. We think this should be the main point of the modelling, to add value to the existing field data set, rather than to simply interpret it.
- Where there was continuous 'post-loading' in the MELIMEX experiment, this was more difficult to model and indicated that the rapid removal benchmark was not met. In the 'real-world' there may be continuous or repeated exposures, particularly of larger water bodies, from multiple sources. The chronic criteria (+ M-factor) are meant to address hazards over a longer time period than just a few days - so, for hazard classification purposes we would expect rapid transformation/removal to be able to cover the majority of

situations, not just one-off exposures.

- The reports considers that most copper reaches the sediment, where much of this is then locked up in different forms (especially with sulphides) and is no longer available. This relies upon the assumption that most sediment, if present, is anaerobic and this process is fairly instantaneous. In reality, the top layers of sediment might well be aerobic - and the transit and mixing time with more anaerobic layers will vary according to the water body and sediment type, as well as temporally and spatially. Is this variability covered? Are the levels of sulphide assumed in the model (based on the Flanders data set) representative of other EU water bodies? Also, what happens if the sediment is already contaminated with metals, is there always enough 'spare' AVS left or will there be cases where it is already saturated so not available for new metal?

Because of these difficulties in describing and modelling all (or even one) relevant/realistic 'worst case' scenario for removal to sediment or to DOC/POC - such mitigating factors are rarely used to refine the hazard classification for organic substances. Most tests for organic substances in fact try to minimise such removal mechanisms to make them as bioavailable as possible, therefore taking account of this for metals would be inconsistent with usual practice. Ready biodegradability tests are difficult to pass, so metal transformation/removal should also face a similarly stringent test. Because of this, we cannot currently support the claim of rapid removal of copper based on the evidence in the dossiers.

On bioaccumulation; we agree this is probably not an issue, provided internal homeostatic excretion, transformation and detoxification mechanisms can always regulate levels within organisms under realistic worst case exposure conditions. Could the bioaccumulation potential of copper be related to the standard CLP triggers in a similar way as attempted for rapid degradation?

Ecotoxicity assessment

It isn't always clear why some ecotoxicological endpoints (e.g. from the DAR) are quoted for some forms of copper but not others. They're not just the worst case values and its not always clear between the various reports why they've been selected and how they're treated. Whilst there may be limitations to what was measured and reported in the studies and DAR, some endpoints appear as both total and dissolved Cu, as nominal or measured. Could these all be adjusted and expressed in the same consistent way? The form in which data from the EU Voluntary Risk Assessment Report (VRAR) are expressed is also unclear in the tables (dissolved copper?).

The separation of the VRAR endpoints into the different pH ranges is potentially useful, although there is no explanation why the particular bands have been chosen and only the lowest values are selected anyway, which makes it unclear why the separation was performed in the first place. There is also no discussion of the impact of other water quality parameters (e.g. hardness) on toxicity. Ultimately, at least for some of the substances, the DAR endpoints are preferred anyway - so it is not always clear what role the VRAR data have. As mentioned, these data have never been considered by a 'technical group competent for classification' and there is uncertainty over transformation/dissolution of some of the substances. It might therefore be useful to present more information on data from the VRAR in an Appendix - if their basis and validity were described in more detail, then greater reliance and use might be made of them. All of the DAR and VRAR endpoints might then be considered together instead of separately?

The use of geometric means may be accepted if they cover the same effect end points for the same species, tested under similar enough conditions (the dossiers do not provide any

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rationale for the derivation of geometric means for individual species). The CLP guidance also indicates that at least four endpoints are preferred for each geomean. This may be important for key values such as the short-term *Pimephales promelas* data at pH 5.5-6.5, where only two studies are available. In this case, might it be better to select the lowest value of 0.0044 mg/L for this pH range? Ideally 'sensitive' species in acute tests should also be reflected in the chronic data set. As there is no long-term test for *P. promelas* at this pH range, might this require use of the surrogate approach and affect the acute and chronic reference values that have been selected? For long-term toxicity to fish, it also appears that an *Oncorhynchus mykiss* ELS NOEC of 0.0017 mg dissolved Cu/L (from DAR data) is missing from the study on 'Copper Hydroxide WP' - this would be equivalent to (and lower than) the dissolved Cu values apparently from the VRAR.

Given the amount of ecotoxicological data on copper, could more use be made of species sensitivity distributions (SSD) and HC5 values (if presented separately for each trophic group and for short and long-term). It appears that there are more ecotox data on copper than those given here, particularly for invertebrates where only *Daphnia/Ceriodaphnia* are presented in the reports. Data on various other invertebrates are reported in the VRAR but its not clear why these are omitted.

Additional SSDs are presented in the VRAR, are any of these appropriate? Discussion with colleagues working on the Water Framework Directive highlight that they have derived Environmental Quality Standards (EQS) for copper using the whole available data set, including data in the VRAR. These EQS were, in part, determined using SSDs and Biotic Ligand Model (BLM) calculations and a fairly high degree of confidence was expressed in their derivation. Since there are analogies with at least the chronic classification endpoint for copper, we wonder whether use could also be made of this EQS work? The use of SSDs and HC5s for copper would set new precedents for hazard classification however, so it might be questioned whether we should always default to the lowest value when we have such a data-rich substances.

One HC5 is mentioned in the CLH Reports for sediment dwellers. Given the suggested removal to and persistence in sediment, there is relatively little discussion of the exposure and hazard to sediment dwellers - even though it is said that uncertainty here is high. The SSD behind this HC5 is not presented and there is also little information on the chironomid study from the tribasic copper sulphate DAR (included under algal endpoints at 5.5). Presumably this is based on a water spiking study whereas the VRAR HC5 (in mg/kg) is from sediment spiked studies? With further information from the studies, might it be possible to recalculate the endpoints according to sediment pore water concentrations? How the aquatic hazard classification should be determined in the presence of sediment is still unclear however.

Further reference to the studies reported in the copper DARs for algae may allow presentation of their NOEC values for inclusion in the long-term hazard assessment.

The final 2013 EFSA Conclusion on pesticidal use of copper compounds reports a microcosm 'NOEC' of 0.0048 mg dissolved Cu/L (rather than 0.00312 mg/L at 5.4.4 and 5.5), although it is unclear how this would be used for hazard classification.

In the table at Section 5.5 a 21-day endpoint for *O. mykiss* is reported, but it is not clear how relevant this is for comparison with the classification criteria.

Ideally it would help to have briefly explained the Ecotoxicity Reference Value (ERV) concept, as it is not initially clear why endpoints expressed as either the substance in

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question, or total Cu, or ionic Cu²⁺ (whichever is considered the most appropriate form) cannot be used at face value. We haven't checked all of the ERV calculations, however, whilst the chronic ERVs from the VRAR can be back-calculated to identifiable endpoints, we could not find the endpoint used to derive the acute VRAR ERV at pH 5.5-6.5 of 0.045 mg/L. Overall, the selection of appropriate short and long-term endpoints for each trophic group and the workings for these ERV calculations, could be presented more clearly for each substance.

Overall, and depending on the response to our comments, we do not currently agree that the substances can be considered rapidly removed, therefore we feel that all of the substances should be classified H400/410 with relevant M factors.

Dossier Submitter's Response

In the current published version of the CLP guidance (Guidance on the Application of the CLP Criteria Version 4.0 – November 2013) the parts concerning "rapid removal from water column" have indeed been deleted. Moreover, as no consensus was found during the ECHA workshop on the concept of rapid removal on February 8th, 2012, and taking into account comments from several MS (Finland, Germany, Denmark, UK) this concept might be not considered in the current assessment. The long-term classification and M factors would therefore need to be updated accordingly (see final proposal for Chronic classification and M factor at the end of this document).

For bioaccumulation, the question would need further clarification before answering.

All endpoints are expressed in all available forms in the tables for better transparency. For the VRA, as mentioned in the introduction of section 5.4, all endpoints are expressed in dissolved copper.

Concerning VRAR endpoints, a link to the appendix related to classification could be added in the document. For the question on whether or not data from the DAR and VRAR should be considered together, we considered that they shouldn't as data from the VRAR are not specific for Dicopper oxide; copper (I) oxide, when data from the DAR are.

Considering the use of geo mean values, we agree, however in this case there is no impact on classification.

For long term data on fish issued from the DAR, data on specific salts were related to each compound.

Concerning SSD, it is our knowledge that HC5 are not used for classification purposes. Concerning the remark on microcosm study, it is our understanding that these values are neither used for classification purposes.

In the table at Section 5.5 a 21-day endpoint for *O. mykiss* is reported for information.

For ERV calculations, all endpoints used were expressed in dissolved copper before transformation.

RAC's response

We note that the DS did not respond to the suggestion to check the most recent EFSA opinion for pesticidal uses of copper (dated 2013), which includes microcosm data (a NOEC of 0.0048 mg dissolved Cu/L). Given the amount of data already available, we do not think that significant changes are likely.

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In terms of how the test results were reported (i.e. technical substance, pure substance, total copper or dissociated ionic copper), we note the comments of the DS so have assumed that the results are expressed in terms of dissolved copper ions unless otherwise indicated.

We agree with the comments made about the rapid removal concept, and note that the DS does too. This affects the chronic classification. The comment about bioaccumulation potential was not addressed by the DS, but it does not affect the classification given the decision on rapid removal.

The comments suggest that more information should be provided about the data from the vRAR. The DS said that an appendix could be added, but that the data should not be combined with those for the substance because they are not substance-specific (unlike the DAR). We do not think this is correct – classification has to take account of all reliable relevant data on copper ecotoxicity. This has been done in the opinion.

The DS agrees with the comment that the use of geometric means may not be appropriate for the short-term *P. promelas* data at pH 5.5-6.5 (implying that the surrogate approach should be considered), but states that there is no impact on the classification. We think there is an impact, and this is considered in the opinion. The DS prefers data from the DAR for each substance, but as noted above, all relevant data should be considered, including the missing *O. mykiss* ELS NOEC. This is also considered in the opinion.

The DS does not consider that species sensitivity distributions (SSD) or microcosm data are relevant for classification. We think that these could be used with an adequate justification, especially for data rich substances such as copper, provided that they do not mask differences in sensitivity under different abiotic conditions. The DS does not respond to the comment that copper data have been considered for EQS setting by some Member States, but as no references were provided, this cannot be followed up by RAC.

We do not think that toxicity to sediment dwellers is relevant for the proposal.

The DS does not respond to the comment that it is unclear which end points were used to derive the ERVs. We have therefore clarified this in the opinion and shown how the ERVs are calculated for each substance.

Date	Country	Organisation	Type of Organisation	Comment number
03.02.2014	Belgium		MemberState	12
Comment received				
see attachement				
<i>ECHA note: The information below was provided in Copper (I) oxide.docx [attachment no.5]</i>				
General remark for all copper dossiers. Why was the acute ERV for copper not based on the acute aquatic toxicity results on <i>Pimephalus promelas</i> which are considered of high quality?				
We support the proposed classification of Cu ₂ O as aquatic acute 1, H400 with M=100 and chronic cat 1, H410 with M=1.				
The measured water solubility of Copper(I)-oxide (pH6.6 : 0.639 mg/l, pH9.8 : 0.539 mg/l) is greater than the acute ERV of the dissolved metal ion and therefore the metal compound can be considered readily				

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soluble.

In water copper is rapidly bound to material resulting in very low levels of free Cu²⁺ ion in solution. More than 70% of copper is removed from the water column within 28 days.

Copper remobilization from the sediment is considered limited (the pseudo-steady state total and dissolved copper conc. were lower than the conc. corresponding to 70% removal, which is supported by sediment sensitivity analyses). Copper binds to the sediment organic carbon and the anaerobic sulphides with formation of Copper sulfide. The latter has a very low stability constant and thus the remobilization of the anaerobic sediment layer is considered limited.

There is still lack of scientific consensus on the interpretation of rapid removal for classification purposes.

pH range	Ecotoxicity Reference Value (ERV) for Cu ₂ O	
	Acute ERV (mg/l)	Chronic ERV (mg/l)
DAR	0.01	
EU RAR pH 5.5-6.5	0.005	0.0225
EU RAR pH >6.5-7.5	0.0532	0.0083
EU RAR pH >7.5-8.5	0.0337	0.0180

We agree with the proposed acute classification and acute M-factor of 100 (0.001mg/l < acute ERV ≤ 0.01mg/l) for Copper(I)oxide but we think that following rationale is more appropriate The lowest Acute ERV, adjusted for molecular weight of the metal compound, is lower than 1 mg/l and therefore copper(I) oxide should be classified as Aquatic acute 1, H400. However, the lowest Acute ERV of copper (I) oxide should be based on the results of the metal for Pimephales promelas at pH 5.5-6.5., the ERV is lower than 1 mg/l and therefore copper (I) oxide should be classified as Aquatic acute 1, H400. If the number of datapoints < 4, the lowest value should be taken. The lowest data point (n=2) for Pimephalus promelas = 0.0044mg/l, adjusted for molecular weight, results in a M-factor of 100 (0.001mg/l < acute ERV ≤ 0.01mg/l).

Based on the mean result of the aquatic chronic toxicity test on the most sensitive species (invertebrate Ceriodaphnia dubia, at pH >6.5-7.5), the lowest Chronic ERV for the metal compound is 0.0083 mg/l. If the chronic ERV_{compound} ≤ 0.01 mg/l and there is evidence of rapid environmental transformation, than the compound should be classified as chronic category 1-H410. A chronic M-factor of 1 should be applied (0.001mg/l < Chronic ERV ≤ 0.01mg/l).

Dossier Submitter's Response

In the current published version of the CLP guidance (Guidance on the Application of the CLP Criteria Version 4.0 – November 2013) the parts concerning "rapid removal from water column" have indeed been deleted. Moreover, as no consensus was found during the ECHA workshop on the concept of rapid removal on February 8th, 2012, and taking into account comments from several MS (Finland, Germany, Denmark, United Kingdom, Belgium) this concept might be not considered in the current assessment. The long-term classification and M factors would therefore need to be updated accordingly (see final proposal for Chronic classification and M factor at the end of this document).

For the acute aquatic toxicity for fish, we agree, however in this case there is no impact on classification.

RAC's response

We note that the comment appears to support the approach to rapid removal proposed

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originally by the DS, but that this is no longer the position of the DS (or several other Member State stakeholders). As explained in the opinion, we do not believe that sufficient evidence has been provided to support the rapid removal concept for copper.

The DS does not respond to the comment that the lowest datapoint (n=2) for *Pimephales promelas* (0.0044 mg/l) has an impact on the proposed M-factor for some substances. This is addressed in the opinion.

Dossier Submitter's New Chronic Classification proposal without rapid removal concept

chronic 1

M = 10

ATTACHMENTS RECEIVED:

- 1. ECI comments to CLH report: proposal for harmonized classification and labelling of dicopper oxide (Cu₂O)** (file name: CLH dossier comments Cu₂O ECI Jan 2014.doc) submitted by Regulatory Compliance Limited on 31 January 2014 [The content was copied to comment no. 6]
- 2. ECI attachment (2) for information - classification versus solubility for copper compounds and copper flake** (file name: Classification versus pH and solubility.doc) submitted by Regulatory Compliance Limited on 31 January 2014 [The content was copied to comment no.6]
- 3. Acute & chronic ecotoxicity of soluble copper species in view of hazard classification of copper and copper compounds** (file name: Van Sprang and Delbeke_2010.pdf) submitted by Regulatory Compliance Limited on 31 January 2014 [please refer to comment no.6]
- 4. Danish comments on the environmental classification of copper (I) oxide** (file name: Rapid-degradation-copper (I) oxide.doc) submitted by Denmark on 30 January 2014 [The content was copied to comment no.9]
- 5. General remark for all copper dossiers** (file name: Copper (I) oxide.docx) submitted by Belgium on 3 February 2014 [The content was copied to comment no. 12]