European Copper Institute
Copper Alliance

ECI COMMENTS TO

CLH REPORT: PROPOSAL FOR HARMONIZED CLASSIFICATION AND LABELLING OF COPPER HYDROXIDE (CUH_2O_2)

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 (RAR) and used for the REACH dossiers.

We have some comments on the proposed environmental chronic classification and propose to revise the classification to:

Environmental hazard classification as Chronic 2 - H411[1]

[1] CLH report : Chronic 1, M factor = 1

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 report (RAR) 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

Please find below a more detailed review for hazard endpoints, demonstrating the differences in classification between the CLH and RAR reports for copper hydroxide.

2) HUMAN HEALTH HAZARDS

No comments.

3) ENVIRONMENTAL HAZARDS

We propose the following classification for environmental hazard as follows:

Chronic category 2[2].

The difference in classification (CLH report/this proposal) is related to a difference in data inclusion, interpretation and data aggregation. Please find below the rationale for the classification proposed.

3.1 ECOTOXICITY DATA

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 DAR, based on tests with CuH_2O_2

Only test results expressed as measured dissolved copper concentrations were retained for the CLH report (RAR and DAR data-set) and REACH dossiers (RAR data-set). Considering that the ecotoxicity data from the RAR relies on tests with soluble copper compounds while the ecotoxicity data from the DAR relies also on sparingly soluble copper species, 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 >72-100% of the total fraction and 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, up to 4 times lower L(E)C_{50} or NOEC values expressed as total versus dissolved copper concentrations were recorded. This indicates that some of the less soluble copper compounds (e.g. CuH_2O_2) may have

[2] CLH report : Chronic 1, M factor = 1

precipitated and reproducibility of the dissolved concentrations and dose–response relationship for dissolved copper concentrations therefore needs further elaboration.

- Although considered as soluble for classification purposes, copper hydroxide is a sparingly soluble substance with (as reported in the CLH report) a strong pH-dependent water solubility: solubility at pH 4.1 of 8 g/L; solubility at pH 7 of 0.9 mg/L; solubility at pH 8.9 of 0.0066mg/L (compared to a solubility of 220 g/l for copper sulphate). 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.

- Flow-through acute toxicity tests (e.g. Schaefer's 2002), are carried out at pH around 8. The mesocosm study, retained in the CLH report (Schaefer's, 2002 a), reported pH values ranging between 7.4 and 9.8. It is therefore expected that the solubility of copper hydroxide is low to very low in the aqueous media.

- Because of such strong pH-dependent water solubility of copper hydroxide it is further challenging to maintain the dissolved copper concentrations during testing. Indeed in the mesocosm study, the measured dissolved Cu concentrations were always lower than the measured total copper concentrations during the test. On average the dissolved copper concentrations were a factor 2 lower compared to the dissolved Cu concentrations, but maximum differences up to a factor 4 were noticed.

- The strong pH-dependent water solubility of the sparingly-soluble Cu-hydroxide therefore explains the discrepancy between the measured total and dissolved copper concentrations in the aqueous media

The robustness of the concentration-response relationships and LC50/NOEC, based on dissolved copper concentrations, are therefore considered unreliable.

As proposed in the CLP guidance, ecotoxicity data from tests carried out with fully soluble compounds (cfr. RAR/REACH data-sets) and expressed as soluble copper ions are therefore preferred.

The use of the mesososm study for hazard classification purposes is questioned for the following reasons:

- Mesocosms are multi-species tests not considered in the CLP guidance.

- The report mentions that the substance contains 49.6 % copper while a Molecular weight translations points towards 65% Cu in CuH_2O_2.

- The mesocosm applications were consistent with pesticide applications: 6 applications with 10 days windows and thus have high variations in test concentrations. For the nominal treatment of 24 µg/L, total copper concentrations varied between 4.3 and 22.0 µg/L, while the dissolved Cu concentrations varied between 2.9 and 21.0 µg/L. For the nominal treatment 120 µg/L, total copper concentrations varied between 30 and 108 µg/L, while the dissolved Cu concentrations varied between 28 and 60 µg/L. To derive an L(E)Cx or NOEC based on dissolved concentrations, the dissolved concentrations are time weighted averages. The relevance of such test-set-up for hazard classification is therefore questioned.

- The RAR ERVs, retained in the CLH report, are slightly higher than the ones defined in the REACH dossier because in the RAR geometric mean values were derived, also 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 2).

Table 1 summarises the ERVs retained from the DAR, RAR and REACH, expressed as mg CuH_2O_2/L (after molecular weight translation)

Table 1: Summary of the acute and chronic ERVs for CuH_2O_2

Source	pH range	Acute ERV CuH_2O_2	Chronic ERV CuH_2O_2
DAR	-	0.012	0.008
RAR	5.5-6.5	0.045	0.031
	>6.5-7.5	0.073	0.011
	>7.5-8.5	0.046	0.025
REACH	5.5-6.5	0.038	0.031
	>6.5-7.5	0.054	0.011
	>7.5-8.5	0.046	0.018
	across all pHs	0.053	0.023

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 considered water solubility data and concluded that CuH_2O_2 is fully soluble at pH 7 (solubility of 0.9 mg/L at pH 7; solubility of 0.0066 mg/L at pH 8.9). No transformation/ dissolution data are available. For comparison purposes, the classification versus solubility for copper compounds and copper flake is presented in Attachment 2 for completeness.

Classification is therefore based on straight comparison between ERV values (Table 1) and classification cut-off values.

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**. We therefore agree with this classification proposal

For chronic toxicity, all ERV are <0.1 mg/L and >0.01 mg/L, except for the ERV based on the mesocosm study (0.005 mg/L). As discussed we do not consider the mesocosm as applicable to hazard classification. Therefore, an environmental hazard classification entry as **Chronic 2 - H411, is proposed.**

4) RELEVANT ATTACHMENTS

Attachment 1: Van Sprang and Delbeke, 2010

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

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