European Copper Institute
Copper Alliance

ECI COMMENTS TO

CLH REPORT: PROPOSAL FOR HARMONIZED CLASSIFICATION AND LABELLING OF DICOPPER OXIDE (CU_20)

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 10[1].

Environmental hazard chronic category 2[2].

[1] CLH report proposal: Acute 1, M factor 100
[2] CLH report proposal: Chronic 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 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 Cu_2O. Only test results expressed as measured dissolved copper concentrations were retained for the CLH report (RAR and DAR data-set) and REACH dossier (RAR data-set alone).

The CLP guidance, mentions '*<u>ecotoxicity data of soluble inorganic compounds</u> 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 (Cu_2O 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)C_{50} 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. Cu_2O) 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 Cu_2O 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 LC_{50} values reported for total versus dissolved Cu-concentrations from the acute rainbow trout Cu_2O 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 Cu_2O, 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 Cu_2O 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).

Table 1 summarises the ERVs retained from the DAR, RAR and REACH (after molecular weight translation), expressed as mg Cu_2O/L.

Table 1: Summary of the acute and chronic ERVs for dicopper oxide, expressed as mg Cu_2O/L

Source	pH range	Acute ERV Cu_2O	Chronic ERV Cu_2O
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 Cu_2O as fully soluble for classification purposes;

- The CLH report concluded, from solubility data of the RAR that Cu_2O 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 Cu_2O (1 mg/L) at pH 6 (used for the preceding classification discussions at EU level for Cu_2O) demonstrated that dissolved copper concentrations after 24 hours transformation/dissolution was <10% but exceeded the acute ERV. The REACH dossiers therefore also considered Cu_2O to be fully soluble, for environmental classification purposes.

The CLH and REACH dossiers consider Cu_2O 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 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 Cu_2O appears to be an outlier (all copper compounds are classified as Chronic 2 or less - see Attachment 2). In considering the classification outcome for Cu_2O (Chronic 1 or 2) as borderline, it seems useful to account for the Cu_2O 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 Cu_2O 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

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[3] CLH report : Acute 1, M factor 100 instead