European Copper Institute
Copper Alliance

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 forces[1] 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, 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.

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

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 as proposed by ECI and task force commenting documents.

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	-	-	-	-

Solubility

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*

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

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