

**Committee for Risk Assessment
RAC**

Opinion

proposing harmonised classification and labelling
at EU level of

Copper

**EC Number: 231-159-6
CAS Number: 7440-50-8**

CLH-O-0000007208-73-01/F

Adopted

1 December 2022

OPINION OF THE COMMITTEE FOR RISK ASSESSMENT ON A DOSSIER PROPOSING HARMONISED CLASSIFICATION AND LABELLING AT EU LEVEL

In accordance with Article 37 (4) of Regulation (EC) No 1272/2008, the Classification, Labelling and Packaging (CLP) Regulation, the Committee for Risk Assessment (RAC) has adopted an opinion on the proposal for harmonised classification and labelling (CLH) of:

Chemical name: **Copper**
EC Number: **231-159-6**
CAS Number: **7440-50-8**

The proposal was submitted by **Sweden** and received by RAC on **22 October 2021**.

In this opinion, all classification and labelling elements are given in accordance with the CLP Regulation.

PROCESS FOR ADOPTION OF THE OPINION

Sweden has submitted a CLH dossier containing a proposal together with the justification and background information documented in a CLH report. The CLH report was made publicly available in accordance with the requirements of the CLP Regulation at <http://echa.europa.eu/harmonised-classification-and-labelling-consultation/> on **29 November 2021**. Concerned parties and Member State Competent Authorities (MSCA) were invited to submit comments and contributions by **28 January 2022**.

ADOPTION OF THE OPINION OF RAC

Rapporteur, appointed by RAC: **Irina Karadjova**

The opinion takes into account the comments provided by MSCAs and concerned parties in accordance with Article 37(4) of the CLP Regulation and the comments received are compiled in Annex 2.

The RAC opinion on the proposed harmonised classification and labelling was adopted on **1 December 2022** by **consensus**.

Classification and labelling in accordance with the CLP Regulation (Regulation (EC) 1272/2008)

	Index No	Chemical name	EC No	CAS No	Classification		Labelling			Specific Conc. Limits, M-factors and ATEs	Notes
					Hazard Class and Category Code(s)	Hazard statement Code(s)	Pictogram, Signal Word Code(s)	Hazard statement Code(s)	Suppl. Hazard statement Code(s)		
Current Annex VI entry	No current Annex VI entry										
Dossier submitter's proposal	TDB	copper; [specific surface area > 0.67 mm ² /mg]	231-159-6	7440-50-8	Aquatic Acute 1 Aquatic Chronic 1	H400 H410	GHS09 Wng	H410		M = 10 M = 1	
RAC opinion	TDB	copper; [specific surface area > 0.67 mm ² /mg]	231-159-6	7440-50-8	Aquatic Acute 1 Aquatic Chronic 1	H400 H410	GHS09 Wng	H410		M = 10 M = 1	
Resulting Annex VI entry if agreed by COM*	TDB	copper; [specific surface area > 0.67 mm ² /mg]	231-159-6	7440-50-8	Aquatic Acute 1 Aquatic Chronic 1	H400 H410	GHS09 Wng	H410		M = 10 M = 1	

FOUNDATIONS FOR ADOPTION OF THE OPINION

ENVIRONMENTAL HAZARD EVALUATION

RAC evaluation of aquatic hazards (acute and chronic)

Summary of the Dossier Submitter's proposal

The DS proposed a harmonised aquatic hazard classification for copper metal (EC 231-159-6; CAS 7440-50-8). There are already harmonised aquatic environmental hazard classifications available for copper metal in the form of (i) copper flakes (coated with aliphatic acid), which was introduced to Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation) by Commission Regulation (EU) 2016/1179 of 19 July 2016, and (ii) copper granulate introduced in to Annex VI by the Commission Delegated Regulation (EU) 2020/1182. The aim of the proposal is to classify copper metal as such. In addition, the Dossier Submitter (DS) proposed to replace the previously adopted harmonised aquatic environmental hazard classifications of copper flakes and copper granulates. RAC notes that this is an issue for the European Commission and was not addressed by the Committee.

The DS considered the ECHA Guidance on the Application of the CLP Criteria and the metal classification strategy in Annex IV and that copper metal can be placed on the market in different physical forms, such as copper flakes and granules. However, these forms are chemically the same substance and classification should not depend on the physical form. In order to classify these different physical forms correctly, the DS based the classification of copper on the specific surface area (SSA) of 0.67 mm²/mg (equivalent to the surface area of a copper sphere of 1 mm diameter) as a limit between copper massive and copper powder.

The proposed hazard classification:

copper; [specific surface area ≤ 0.67 mm ² /mg]	231-159-6	7440-50-8	No classification
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copper; [specific surface area > 0.67 mm ² /mg]	231-159-6	7440-50-8	Aquatic Acute 1 Aquatic Chronic 1	H400 H410	GHS09 Wng	H410	M = 10 M = 1
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Data sources used by DS

The information available in the previous CLH reports for copper flakes (coated with aliphatic acid; December 2013) and copper, granulated (February 2017) has been used to compile the information relevant for this aquatic environmental hazard classification proposal for copper. Additionally, the conclusions drawn by RAC in its opinions on copper flakes (December 2014) and copper granulate (June 2018) were also taken into account. Consequently, no new data searches for aquatic toxicity were performed. However, the IUCLID data file has recently been updated with new information considering aquatic environmental hazard classification (ECI, 2021), including new study reports of transformation/dissolution tests and this new information has been included in the current CLH report. New information on copper in massive and powder forms, including information on particles < 1 mm formed during reasonably expected use of massive copper were acquired from the registrant and included in the REACH registration dossier during the development of this dossier and have been taken into account (see Annex I).

Solubility of copper

The DS compiled all available data from transformation/dissolution studies for copper (including new studies in the updated REACH registration) in three separate tables for pH 6, pH 7 and pH 8, since copper ion release is pH dependent. In addition, the DS presented a summary of the applicability of study results in the classification of copper. The DS noted that the dissolution of copper from a given material to the medium depends on the exposed surface area and that is why data for copper release in transformation-dissolution tests is expressed per unit surface area. The data is summarised in the below tables.

Table: Summary of all transformation/dissolution data of copper at pH 6.

Reference	Time (days)	Surface loading used in test (mm ² /L)	Measured release (µg Cu/mm ²)	Remarks incl. dimensions of particles if available
Rodriguez <i>et al.</i> (2012)	7	0.67	1.5	Surface loading equivalent to 1 mg/L mass loading of spheres of 1 mm diameter. Massive metal wire (1.35 mm diameter) embedded in epoxy resin.
	28	0.67	5	
ECTX (X01-203) (2016b)	7	3.21	1.3	Granulated copper (length 0.9-6 mm; diameter 0.5-0.9 mm). Longest pieces used and embedded in epoxy resin.
	28	3.21	5	
Rodriguez <i>et al.</i> (2011)	7	46.69	0.41	Massive metal embedded in epoxy resin.
Rodriguez <i>et al.</i> (2007)	7	1.22-281	1.15	Copper wire with varying diameters (0.16-0.4 mm)
	28	1.22-2.85	4.2	
ECTX (X01-280) (2019)	7	60	1.223	Copper powder D50 11 µm
ECTX (X01-281) (2019)	7	340	0.324	Copper powder with dendritic (branched) shape, D50 26 µm
ECTX (X01-282) (2019)	7	28	1.289	Copper powder D50 30 µm
ECTX (X01-296) (2020)	7	60	1.833	Copper powder D50 11 µm
	28	60	5.817	
Skeaff & Hardy (2005)	7	107	0.77	High variability. Surface area of particles measured by BET (Brunauer-Emmet-Teller analysis). Particle size: 100% <160 µm, 77.3% <50 µm
	7	10700	0.1	
Schäfer (2014)	7	2080-2900*	0.35**	Coated copper flakes, D50: 9-11 µm.
	28	2080-2900*	0.37***	

* - In the study by Schäfer (2014) mass loading of 1 mg/L was used. The surface loading mentioned in this table is calculated based on the mass loading of 1 mg/L in the study and on the information in ECI (2021) where ECI reports the specific surface area of coated copper flakes as extremely high; 2080-2900 mm²/mg.

** - Calculated from data in Schäfer 2014 and surface loading (see *); $721 (\mu\text{g Cu/L})/2080 (\text{mm}^2/\text{L}) = 0.35 \mu\text{g Cu/mm}^2$.

*** - Calculated from data in RAC Opinion (2014) on coated copper flakes where an equilibrium concentration for copper release after 28 days is calculated and surface loading (see *); $773 (\mu\text{g Cu/L})/2080 (\text{mm}^2/\text{L}) = 0.37 \mu\text{g Cu/mm}^2$.

Table: Summary of all transformation/dissolution data of copper at pH 7.

Reference	Time (days)	Surface loading used in test (mm ² /L)	Measured release (µg Cu/mm ²)	Remarks incl. dimensions of particles if available
Rodriguez <i>et al.</i> (2017)	7	0.67	0.6	Surface loading equivalent to 1 mg/L mass loading of spheres of 1 mm diameter. Massive metal wire (1.35 mm diameter) embedded in epoxy resin.
	28	0.67	1.2	
ECTX (X01-203) (2016b)	7	3.21	0.88	Granulated copper (length 0.9-6 mm; diameter 0.5-0.9 mm). Longest pieces used and embedded in epoxy resin.
	28	3.21	3.3	
Rodriguez <i>et al.</i> (2007)	7	1.22-281	0.19	Copper wire with varying diameters (0.16-0.4 mm)
ECTX (X01-296) (2020)	7	60	0.675	Copper powder D50 11 µm
	28	60	2.083	
Schäfer (2014)	7	2080-2900*	0.17**	Coated copper flakes, D50: 9-11 µm.
	28	2080-2900*	0.31***	

** - Calculated from data in Schäfer 2014 and surface loading (see *); $363 \text{ (}\mu\text{g Cu/L)}/2080 \text{ (mm}^2\text{/L)} = 0.17 \text{ }\mu\text{g Cu/mm}^2$.

*** - Calculated from data in RAC Opinion (2014) on coated copper flakes where an equilibrium concentration for copper release after 28 days is calculated and surface loading (see *); $639 \text{ (}\mu\text{g Cu/L)}/2080 \text{ (mm}^2\text{/L)} = 0.31 \text{ }\mu\text{g Cu/mm}^2$.

Table: Summary of all transformation/dissolution data of copper at pH 8.

Reference	Time (days)	Surface loading used in test (mm ² /L)	Measured release (µg Cu/mm ²)	Remarks incl. dimensions of particles if available
Rodriguez <i>et al.</i> (2017)	7	0.67	<0.3	Surface loading equivalent to 1 mg/L mass loading of spheres of 1 mm diameter. Massive metal wire (1.35 mm diameter) embedded in epoxy resin.
	28	0.67	0.9	
ECTX (X01-203) (2016b)	7	3.21	0.45	Granulated copper (length 0.9-6 mm; diameter 0.5-0.9 mm). Longest pieces used and embedded in epoxy resin.
	28	3.21	1.9	
Rodriguez <i>et al.</i> (2007)	7	1.22-281	0.13	Copper wire with varying diameters (0.16-0.4 mm)
ECTX (X01-296) (2020)	7	60	0.623	Copper powder D50 11 µm
	28	60	1.733	

Skeaff & Hardy (2005)

This study was evaluated and used for classification proposals in the CLH report of copper flakes (December 2013). However, during the public consultation of the Copper flake report, a new study (Schäfer 2013, see below) was submitted, which was considered to provide better information than the study by Skeaff & Hardy (2005).

Skeaff & Hardy (2005) performed 7-day transformation-dissolution tests on a fine copper powder sample (particle size: 100% <160 µm, 77.3 % < 50 µm). The SSA was **107 mm²/mg** measured

by BET (Brunauer-Emmet-Teller analysis). Tests were conducted at mass loadings of 1 and 100 mg/L and at pH 6. The measured release of copper was 82 µg/L for the mass loading of 1 mg/L (coefficient of variation 32%), and 1118 µg/L for the mass loading of 100 mg/L (coefficient of variation 34%). The study was performed with few replicates (n=2) and in addition abrasion of the particles was observed, which causes increased copper release to solution, explaining high CV. The surface area was measured by BET. The release per unit surface was 0.77 µg Cu/mm² in the experiment with 1 mg/L mass loading, and 0.10 µg Cu/mm² in the experiment with 100 mg/L mass loading. The results are not directly useful for classification purposes but are shown in order to support the weight of evidence. Additionally, this study indicates the size of the smallest copper particle on the market. According to Guidance on the Application of the CLP Criteria, Annex IV (IV 5.5; version 5.0 – July 2017) the DS proposed this particle size for the classification of copper > 0.67 mm²/mg.

Schäfer (2014)

This study was submitted during public consultation of the CLH report of copper flakes (December 2013), evaluated by RAC and used for classification proposals of copper flakes (RAC Opinion of Copper flakes (coated with aliphatic acid), December 2014).

The study was performed with coated copper flakes (KU 7600 Standard Material; D50: 9-11 µm) according to *OECD Series on testing and assessment. Number 29. Guidance document on transformation/dissolution of metals and metal compounds in aqueous media (2001)* (hereafter OECD TP 29) in test media at pH 6 and pH 7 with a loading of 1 mg/L. The measured copper concentrations after the 7 days T/D test at pH 6 and 7 were 721 and 363 µg/L, respectively. The final equilibrium concentrations in the 28 days test at pH 6 and 7 were 773 and 639 µg/L, respectively. According to ECI (2021), the specific production process and the surface coating of the flakes results in a very high specific surface area (measured as 2080-2900 mm²/mg), resulting in rather low release per square millimetre.

Rodriguez et al. (2007)

This study was conducted using massive copper (pieces of copper wire, 99.9% purity) with varying diameters (0.16-0.4 mm). The tests were carried out with various mass loadings (1-100 mg/L, corresponding to surface loadings 1.22-281 mm²/L), and were conducted at pH 6, 7 and 8 (for duration of 7 days) and at pH 6 (for duration of 28 days). These tests demonstrated that copper release from wires with different diameters is determined by the exposed surface area.

Rodriguez et al. (2007) further found that copper ion releases during the transformation/dissolution tests depend on the stirring rate. At high stirring rates above 50 revolutions per minute (> 50 rpm), copper ion release increased, which was related to particle abrasion, which should be prevented (GHS rev. 8, 2019, Annex 10, A10.2.3.1 and OECD TP 29). The copper release during transformation/dissolution tests was pH dependent. The release was 6 times higher at pH 6 compared to pH 7 and 8. Additionally, copper releases during transformation/dissolution tests increased linearly with the surface loading (mm²/L) during the test.

From tests conducted at surface loadings between 1.2 and 281 mm²/L (corresponding to mass loadings between 1 and 100 mg/L), the average surface-specific copper release (µg dissolved Cu/mm² exposed) were:

- 1.15 µg Cu/mm² after 7 days T/D tests at pH 6
- 0.19 µg Cu/mm² after 7 days T/D tests at pH 7
- 0.13 µg Cu/mm² after 7 days T/D tests at pH 8
- 4.2 µg Cu/mm² after 28 days T/D test at pH 6 (excluding one outlier)

This study has some shortcomings; e.g., the stirring rate is lower than recommended in the OECD TP 29 and abrasion of the massive copper particles occurred.

Rodriguez *et al.* (2011)

The study was conducted using massive copper samples at a surface loading of 43-47 mm²/L, at pH 6 for 7 days. Since the abrasion impacts metal release of massive samples, transformation/dissolution (T/D) was performed using two alternative anti-abrasion devices: a) two polypropylene wheels were added to the ends of copper wire samples to avoid direct contact with the vessel; b) the samples were embedded in epoxy resin leaving one face exposed to the media. As an alternative b, a surface polishing procedure was included to minimize variations related to differences in the starting surface conditions. The results showed that samples embedded in epoxy resin showed a linear correlation between metal releases and incubation time in OECD medium, with less variability between the measurements and higher metal release, 0.41 µg/mm², compared with samples with polypropylene wheels. Therefore, a methodology where the massive copper is embedded in epoxy resin is preferred over polypropylene wheels.

Rodriguez *et al.* (2012)

This study has not been evaluated or used in any previous proposals for harmonised classification.

The study was conducted using copper in massive form at a surface loading of 0.67 mm²/L, equivalent to the surface of spheres of 1 mm diameter at 1 mg/L mass loading. The copper (wire with diameter 1.35 mm) was embedded in epoxy resin and the study was conducted over 28 days at pH 6. The results meet the requirements of the OECD guideline for the within-vessel and between-vessel coefficients of variations (CV), recorded at the end of the test. The OECD guidelines look for a within-vessel CV of less than 10% and between-vessel CV of less than 20%, to metal concentrations higher than 10 times the quantification limit.

The results showed a copper release of 1.5 µg/mm² after 7 days (acute) and 5.0 µg/mm² after 28 days (chronic).

The results of this study can be used to predict the release of copper ions from massive copper at pH 6.

Rodriguez *et al.* (2017)

This study has not been evaluated or used for any previous proposals for harmonised classification.

The study was conducted using copper in massive form (wire with 1.35 mm diameter) at a surface loading of 0.67 mm²/L, equivalent to the surface of spheres of 1 mm diameter at 1 mg/L mass loading. The copper was embedded in epoxy resin and the study was conducted during 28 days in pH 7 and 8.

The metal release levels after 28 days of test for both pHs, showed a variability of the measurements around 20%, as coefficient of variation (CV). The OECD guidelines look for a within-vessel CV of less than 10% and between-vessel CV of less than 20%, to metal concentrations higher than 10 times the quantification limit. The variability in the present study is higher than OECD requirements because the low copper release obtained at both pHs was close to the method detection limit, estimated to be 0.2 µg/L for both, pH 7 and pH 8.

The results at pH 7 showed copper release of 0.6 µg/mm² after 7 days (acute endpoint) and 1.2 µg/mm² after 28 days (chronic endpoint). At pH 8 the copper release was below the method detection limit (0.2 µg/L) after 7 days and 0.9 µg/mm² after 28 days.

The results of this study can be used to predict the release of copper ions from massive copper at pH 7 and pH 8.

ECTX (2016a; study no. X01-204)

This study was evaluated but not used for classification proposals in the CLH report of Copper, Granulated (February 2017). The material was tested as such, without anti-abrasion measures. Only one particle of granulated copper was added to each vessel in order to attain the desired mass loading of 1 mg/L only at pH 6. This experiment showed a copper release of 1.4 µg/L after 7 days at pH 6, and 6.0 µg/L after 28 days at pH 6 (coefficients of variation 23 and 27%). The high variability of these results could be explained by the limited number of particles (only 8) used.

ECTX (2016b; study no. X01-203)

This study was evaluated and used for classification proposals in the CLH report of Copper, Granulated (February 2017). The study was performed, at different pH-values, using granulated copper (length 0.9-6 mm; diameter 0.5-0.9 mm) at loadings of 1 mg/L. A specific surface area defined for the copper particles was **2.56 mm²/mg**. The longest pieces of the granulated copper particles were used in the study and embedded in epoxy resin. This allows setting the exposed surface area more accurately, it avoids abrasion, and the surfaces were polished before exposure. These results had much higher reliability (coefficients of variation only 7–11%) and showed more copper release than the first experiment (ECTX 2016a, see above). This second study was therefore retained for classification purpose of granulated copper. The results from this study are presented below:

- 1.3 µg Cu/mm² after 7 days T/D tests at pH 6
- 0.88 µg Cu/mm² after 7 days T/D tests at pH 7
- 0.45 µg Cu/mm² after 7 days T/D tests at pH 8
- 5 µg Cu/mm² after 28 days T/D test at pH 6
- 3.3 µg Cu/mm² after 28 days T/D tests at pH 7
- 1.9 µg Cu/mm² after 28 days T/D tests at pH 8

ETCX (2019; study no. X01-280, X01-281, X01-282)

These are new studies that have not been evaluated or used in any previous proposals for harmonised classification.

The OECD TP 29 was applied to determine the rate of dissolution of three different copper powders;

- a) copper powder with D50 11 µm and a specific surface area of **60 mm²/mg**,
- b) a special copper powder with dendritic (branched) shape, with D50 26 µm and specific surface area of **340 mm²/mg**, and
- c) copper powder with D50 30 µm and a specific surface area of **28 mm²/mg**.

The powders were tested at 1 mg/L mass loading in standard aqueous solutions at pH 6, for 7 days. The studies were well performed, and validity criteria were fulfilled.

The average surface-specific copper release (µg dissolved Cu/mm² exposed) after 7 days (at pH 6) were:

- Copper powder a) 1.223 µg Cu/mm²
- Copper powder b) 0.324 µg Cu/mm²
- Copper powder c) 1.289 µg Cu/mm²

Another study was performed to further investigate the release of copper ions from copper powder a), see ETCX (2020) described below.

ETCX (2020; study no. X01-296)

This is a new study that has not been evaluated nor used in any previous proposal for harmonised classification.

OECD TP 29 was applied to determine the rate of dissolution of a copper powder with D50 11 µm and a specific surface area of **60 mm²/mg** (same as copper powder a) in ETCX (2019); see above). The powder was tested at 1 mg/L mass loading (equals 60 mm²/L surface loading) in standard aqueous solutions at pH 6, pH 7 and pH 8 during 7 and 28 days. The agitation speed was 100 rpm. The study was well performed, and validity criteria were fulfilled.

The average surface-specific copper release (µg dissolved Cu/mm² exposed) after 7 days were:

- 1.833 µg Cu/mm² at pH 6
- 0.675 µg Cu/mm² at pH 7
- 0.623 µg Cu/mm² at pH 8

And after 28 days:

- 5.817 µg Cu/mm² at pH 6
- 2.083 µg Cu/mm² at pH 7
- 1.733 µg Cu/mm² at pH 8

The results of this study can be used to predict the release of copper ions from copper powder at pH 6, pH 7 and pH 8, at both 7 and 28 days.

Conclusion on solubility of copper and classification approach

Copper is an element with extensive toxicity/dissolution datasets as well as an extensive aquatic toxicity dataset. Both copper dissolution and aquatic toxicity depend on the pH. The DS concluded that transformation/dissolution data at different pHs (pH 6, pH 7, and pH 8) should be compared with aquatic toxicity data at similar a pH.

Following Annex IV 5.5 in the Guidance on the Application of the CLP criteria (2017), the DS presented a discussion on the size of particles used in T/D studies and concluded that the smallest representative copper particle has a specific surface area of 107 mm²/mg.

The REACH registrant in their document on environmental hazard classification considered the particles with a specific surface area of 60 mm²/mg used in ETCX (2019 and 2020) to be the smallest representative particle size sold.

The DS also considered the criteria for accepting a split classification for massive metal and metal powder: the powder has to be a structurally different material than the massive metal and/or it has to be produced by a special process and not generally generated from the massive metal during reasonable expected use.

Arguments presented in the REACH registration dossier ECI (2021) indicate that copper powder is not structurally different from copper massive, but copper powder is produced by specific processes, clearly different from the production of copper massive. Copper powder is not produced or generated as a by-product during the production of copper massive, or during the processing of copper massive into articles. This is corroborated by the observation that none of the copper cathode producers in Europe produce or market any copper powder. Instead, copper powder is produced by different companies, at different sites, and through a special, dedicated process. The production of copper powder and copper massive in Europe occurs at different sites and by different companies. Copper is highly resistant to fracture due to its ductility, elongation, malleability. When exerting mechanical forces on copper, the material is bent and deformed to

yield a different shape. Copper does not break apart during mechanical processes, handling, storage, transport, processing, and use. Considering all these properties, the DS concluded that there is no potential for copper metal to break apart into smaller pieces under mechanical stress and produce particle < 1 mm from the normal handling and use of massive copper. The registrant lists an overview of dominant industrial processes for the production of copper particles from copper massive, including e.g., cutting, sawing, drawing, milling, and finishing and in none of these processes are copper particles < 1 mm generated or produced. From photos of the sizes of the produced chips from some of these processes the DS concludes that it is unlikely that sufficient amounts of copper particles with a specific surface area > 0.67 mm²/mg are produced in these processes.

Consequently, the DS concluded that a split classification is justified since copper powder is produced by a special process and copper particles with a specific surface area > 0.67 mm²/mg are not generally generated from the massive metal during reasonable expected handling and use.

The DS selected a representative transformation/dissolution dataset based on particle size, pH range tested, and reliability. For short-term hazard, data was converted to a copper solubility at a mass loading of 1 mg/L and for long-term aquatic hazard, converted to a copper solubility at a mass loading of 1 mg/L and 0.1 mg/L (when no evidence of rapid environmental transformation is available). The most reliable and relevant data was ECTX (2020) and Rodriguez *et al.* (2012 and 2017).

Table: Transformation/dissolution data used in the current proposal for aquatic environmental hazard classification of copper with a specific surface area > 0.67 mm²/mg. Based on transformation/dissolution data from ECTX (2020).

period (days)	pH	Measured release (µg Cu/mm ²)	Calculated release from particles with SSA of 107 mm ² /mg and at mass loading of 1 mg/L (µg Cu/L)*	Calculated release from particles with SSA of 107 mm ² /mg and at mass loading of 0.1 mg/L (µg Cu/L)**
7	6	1.833	196.1	
	7	0.675	72.2	
	8	0.623	66.7	
28	6	5.817	622.4	62.2
	7	2.083	222.9	22.3
	8	1.733	185.4	18.5

* - Calculated as measured release in µg Cu/mm² x SSA of 107 mm²/mg x mass loading of 1 mg/L. ** - Extrapolated linearly from mass loading of 1 mg/L.

Table: Transformation/dissolution data used in the current proposal for aquatic environmental hazard classification of copper with a specific surface area ≤ 0.67 mm²/mg. Based on transformation/dissolution data from Rodriguez *et al.* (2012 and 2017).

Testing period (days)	pH	Release (µg Cu/mm ²)	Release from particles with SSA of 0.67 mm ² /mg and at mass loading of 1 mg/L (µg Cu/L)*	Calculated release from particles with SSA of 0.67 mm ² /mg and at mass loading of 0.1 mg/L (µg Cu/L)**
7	6	1.5	1.0	
	7	0.6	0.4	
	8	<0.3	<0.2	
28	6	5	3.4	0.3
	7	1.2	0.8	0.08
	8	0.9	0.6	0.06

* - Calculated as measured release in $\mu\text{g Cu}/\text{mm}^2 \times \text{SSA of } 0.67 \text{ mm}^2/\text{mg} \times \text{mass loading of } 1 \text{ mg/L}$, ** - Extrapolated linearly from mass loading of 1 mg/L

As seen in the available T/Dp data, the copper release generally increases linearly with the exposed surface area, for measurements conducted at surface loadings between approximately 0.5 and 100 mm^2/L (see inserted Figure 17 from ECI (2021) CLH). Along the same lines, the copper release expressed per unit surface is remarkably consistent between different forms of copper tested.

- The copper release at pH 6 after a 7-day test range 1.1—1.8 $\mu\text{g Cu}/\text{mm}^2$ with mentioned exception.
- The copper release at pH 6 after a 28-day test range 4.2—5.8 $\mu\text{g Cu}/\text{mm}^2$.

The REACH registrant derived the following equations for pH 6:

- $\text{Log [Copper release after 7 days in } \mu\text{g/L}] = 0.16 + 0.98 * \text{Log [Surface loading in } \text{mm}^2/\text{L}]$ (equation 1)
- $\text{Log [Copper release after 28 days in } \mu\text{g/L}] = 0.70 + 1.03 * \text{Log [Surface loading in } \text{mm}^2/\text{L}]$ (equation 2)

Some data points were not included due to deviation from the regression line. The REACH registrant considered this as a conservative choice since these data points had a lower release than expected based on the overall trend. The REACH registrant argued that the dendritic copper powder tested by ECTX (2019) does not follow the trend exhibited by the other, more typical copper powders and that this is explained by the specific shape of this powder which may change during the test: the thinnest or most exposed parts of these particles may be dissolved during the initial stages of the test, leaving behind the coarser cores of the particles. The REACH registrant noted that the data point at very high loading from Skeaff and Hardy (2005), and the data point from Rodriguez *et al.* (2011), exhibit lower copper release than expected based on the trend suggested by the other data.

The DS found the linear regressions by the REACH registrant relevant and suggested that these could be used to support their conclusions for the aquatic environmental hazard classification of copper.

Environmental fate and other relevant information

The DS conclusions for copper's environmental fate are based on the information reproduced from the CLH report on copper, granulated (February 2017). The concept of rapid removal has been discussed and found inappropriate for hazard assessment as concluded by CARACAL (November 2019, CA/68/2019).

In water, according to CLH dossier, copper cannot be transformed into related metabolites or degradation products and, consequently, hydrolysis and biodegradation processes will have no action on copper in this respect. Copper exists in water as free Cu^{2+} ions, whose concentration depends on the propensity of the metal cation to hydrolysis in water, and pH as kinetically labile inorganic complexes with a range of inorganic ligands (e.g., OH^- , $\text{HCO}_3^-/\text{CO}_3^{2-}$, $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$, Cl^- , SO_4^{2-} and S_2^-) and as complexes with organic ligands (e.g., humic and fulvic acids) associated with dissolved organic matter.

In a water-sediment systems, total copper was re-distributed from the surface water to the sediment, the worst case was a dissipation rate of 30.5 days (considered as a DT_{50} for the water column), calculated using first-order kinetics. The majority of the applied copper in the sediment is bound to solid matter. Therefore, in a complex environment, total or even dissolved copper levels are not appropriate to assess bio-available copper exposure. The DS noted the Guidance

on the Application of the CLP criteria (version 4.1, June 2015), section IV.3: Naturally occurring geochemical processes can partition metal ions from the water column while also other processes may remove metal ions from the water column (e.g., by precipitation and speciation). Data on water column residence time, the processes involved at the water – sediment interface (i.e., deposition and re- mobilisation) are fairly complex, depend on chemical elements properties and external factors. However, environmental transformation of one species of a metal to another species of the same metal does not constitute 'degradation' as applied to organic compounds and may increase or decrease the availability and bioavailability of the toxic species.

Copper is a chemical element and exists in soil in different phases, bound to organic and inorganic solid soil components or as a soluble species in soil solution (mostly inorganic and organic complexes and small inorganic ions). The distribution of these different forms and the fate and bioavailability of copper in soil strongly depend on the factors such as soil pH, texture, and organic matter content.

The DS also considered the updated Copper REACH registration dossier (dated 18/01/2017), presenting newly available evidence that under "environmentally relevant" conditions, more than 70% of dissolved copper is removed within 28 days. Copper is transformed to sulphide complexes (Cu-S) which are stable. Remobilisation of copper to the water-column is not likely to occur. Copper is therefore considered rapidly removed, conceptually equivalent to "rapid degradation" for organic substances.

Further, in the RAC Opinion on Granulated Copper (June 2018) the following is stated; "*Based on the data provided in the CLH dossier and submitted during public consultation, granulated copper is not considered to be rapidly transformed by normal environmental processes. RAC recommends that future CLH dossiers for other copper compounds could take account of all relevant information once an internationally agreed approach to this issue has been reached. This may in turn affect classification decisions drawn for this substance and previous copper compound cases.*"

To conclude, the DS accepted that the fate and behaviour of copper in soil and water compartments and that 'degradation' of copper is a complex process (bioavailability depends on distribution and equilibrium), but copper could not be subject to rapid environmental transformation for the purpose of classification and labelling.

Bioaccumulation

All data presented by the DS are from the CLH report for copper, granulated (February 2017).

Based on a log Pow of 0.44, no concern over any potential for bioaccumulation could be concluded by the DS for copper. Copper is an essential nutrient for all living organisms and homeostatically controlled in all organisms. The control efficiencies increase towards higher levels of the trophic chain. Therefore, BCF/BAF values decrease with increasing exposure concentrations (water and food), vary depending on nutritional needs (seasonal, life stage), are species dependent, or vary pending on "internal detoxification" mechanisms. Copper BMF values are < 1. The DS considered the RAC opinion on Granulated Copper (June 2018), which stated that "*The bioaccumulation behaviour of copper (II) ions is complicated by essentiality and homeostatic mechanisms in organisms but does not need to be considered further because it does not influence the determination of the chronic M-factor (in view of the conclusion about removal).*" and concluded that due to the essentiality of copper, no further consideration of bioaccumulation was required.

Aquatic toxicity data

The complete dataset for aquatic toxicity data is presented in Annex II and Annex III to the CLH report.

The DS considered aquatic ecotoxicity data available from section “5.4 Aquatic Toxicity” and section “7 Annexes” of the CLH report for copper, granulated (February 2017). Since that time, no additional or new data have become available. The same data is also included in the registration dossier. The DS accepted the validity of these data and based on the 2018 RAC opinion on copper, granulated, and accepted them for comparison with the classification criteria.

The DS noted that the ERVs from the RAC opinion on copper granulate (June 2018) are slightly different from those ERVs used in the earlier RAC opinion on copper flakes (December 2014). The acute ERV for copper flakes was 8.1 µg/L based on a single study with *P. promelas* at pH 5.5-6.5. In the RAC opinion on copper granulate, a geometric mean of the LC₅₀ for this species was used instead and resulted in an ERV of 12.1 µg/L for *P. promelas*. The NOEC for copper flakes, based on a geometric mean of data from studies with *C. dubia*, was 7.4 µg/L in the earlier RAC opinion on copper flakes (December 2014). This ERV was based on a geomean of 4 available (non-DOC normalised) NOEC values without distinguishing between mortality and reproductive effects. During the evaluation of copper granulates, RAC concluded that it is only appropriate to use the geometric mean when there are 4 or more data available in a pH band for specific endpoints (e.g., reproduction) for a species. The lowest NOEC becomes 4 µg/L without DOC normalisation, corresponding to 6.2 µg/L with DOC normalisation when this information (mortality and reproductive effects) is split.

In addition, RAC’s ERVs for copper granulate (used in the current proposal) also slightly deviate from those presented by the registrant in ECI (2021). The largest deviation is for the chronic ERV at pH 7, where ECI (2021) reports a NOEC of 12/13 µg/L (non-normalised/normalised) compared to RAC’s NOEC of 4/6.2 µg/L (non-normalised/normalised). This discrepancy does not affect the conclusion for the aquatic hazard classification.

The ERV values proposed by RAC (2018) are presented in the table below.

Table: ERV values for comparison with the CLP criteria as defined in CLH dossier, 2017 (copper granulate)

		pH band		
		5.5-6.5 (acidic)	>6.5-7.5 (neutral)	>7.5-8.5 (alkaline)
Values not normalised for DOC level				
Acute ERV	L(E)C₅₀ (µg/L)	12.1 (<i>Pimephales promelas</i>)	11.7 (<i>Danio rerio</i>)	40 (<i>Ceriodaphnia dubia</i>)
Chronic ERV	EC₁₀/NOEC (µg/L)	13.2 (<i>Daphnia magna</i>)	4 (<i>Ceriodaphnia dubia</i>)	12.6 (<i>Daphnia magna</i>)
Values normalised to a DOC level of 2 mg/L				
Acute ERV	L(E)C₅₀ (µg/L)	11 (<i>Daphnia magna</i>)	24.1 (<i>Ceriodaphnia dubia</i>)	31.4 (<i>Chlamydomonas reinhardtii</i>)
Chronic ERV	EC₁₀/NOEC (µg/L)	10.5 (<i>Daphnia magna</i>)	6.2 (<i>Ceriodaphnia dubia</i>)	11.8 (<i>Ceriodaphnia dubia</i>)

a - if 7-d for *P. promelas* were used, the ERV would be 8.7 µg/L (n=3), or 13.3 µg/L if the OSU (2017) study is taken account.

b -This is the main difference from DS’s proposal. The lowest reported long-term NOEC at neutral pH for *C. Dubia* in the previous CLH reports for copper compounds was 7.4 µg/L, which was a geomean of the 4 available (non-normalised) NOEC values without distinguishing between mortality and reproductive effects. As the CLH dossier now splits this information, the lowest NOEC becomes 4 µg/L without DOC normalisation, corresponding to 6.2 µg/L with DOC normalisation.

The DS discussed the conclusion for acidic pH from the previous RAC opinions, i.e., the concentration that causes 50% mortality in acute tests is effectively the same as that which causes no adverse effects in long-term tests (with the same species in the case of the DOC normalised values). Different explanations were considered such as:

- the acute-to-chronic ratios (ACRs) being generally low and tending to decrease with decreasing pH (approaching unity at around pH 6),
- far more acute than chronic data being present, especially for lower pH, which might produce misleading ACRs (since the result is highly dependent on the representative nature of a very small number of chronic values) or,
- the change in species sensitivity across the pH bands could also be an artefact of the varying amounts of data available as there are still potential information gaps, including for Zebrafish (*D. rerio*) and Brook Trout (*S. fontinalis*) at acidic pH, e.g. an acute LC₅₀ below 10 µg/L (normalised for DOC) cannot be ruled out.

Acute aquatic hazards

Acute (short-term) toxicity to fish

Acute data are reported for five fish species, which becomes three species when the data are normalised for DOC. The large majority of studies have been conducted in the highest (most alkaline) pH band, so data are only available for two fish species in the lower acidic pH band (5.5-6.5) at which toxicity is greatest. At pH 5.5-6.5, the lowest acute LC₅₀ value for fish, when not normalised for DOC, is 12.1 µg/L (geomean for *P. promelas*, n = 5). If DOC normalisation is performed, the lowest fish LC₅₀ value is 14.9 µg/L (for *P. promelas*, n = 3). At pH 6.5-7.5, the lowest fish LC₅₀ is 11.7 µg/L (for *D. rerio*). However, RAC does not think this is an appropriate data point as it was obtained in very soft water outside the range of the OECD TP 29 recommendation. The data point could therefore be considered as conservative. The toxicity at this pH-range is however not decisive for the classification proposal.

Even though the data set is relatively large, RAC concludes that there are still potential information gaps, including for Zebrafish (*D. rerio*) and Brook Trout (*S. fontinalis*) at acidic pH (e.g., an acute LC₅₀ below 10 µg/L (normalised for DOC) cannot be ruled out).

Acute (short-term) toxicity to aquatic invertebrates

Over 300 individual acute data points are available for two aquatic invertebrate species (*Daphnia magna* and *Ceriodaphnia dubia*). There are more than 4 studies available for each pH band, with greatest sensitivity apparent at acidic pH. Geometric mean acute EC₅₀ values at pH 5.5-6.5 are 16.3 µg/L (not normalised, n=29) and 11 µg/L (normalised for a DOC level of 2 mg/L, n=26) for *D. magna* and 12.6 µg/L (not normalised, n=9) and 16 µg/L (normalised for a DOC level of 2 mg/L, n=8) for *C. dubia*.

Acute (short-term) toxicity to algae or other aquatic plants

Over 50 individual acute data points are available for three algal species (*Pseudokirchneriella subcapitata* (n=36), *Chlamydomonas reinhardtii* (n=3) and *Chlorella sp.* (n=16)). Unlike fish and invertebrates, copper appears to become more acutely toxic to algae with increasing pH. When all data are considered, *P. subcapitata* is the most sensitive species, with more than 4 studies available for each pH band: the lowest geometric mean E_rC₅₀ (duration not specified) is 104.9 µg/L (n=12) at pH >7.5-8.5 (alkaline). *P. subcapitata* is still the most sensitive species when data are normalised for a DOC level of 2 mg/L, with a lowest geometric mean E_rC₅₀ (duration not specified) of 31.6 µg/L (n=11) at pH >7.5-8.5 (alkaline), which is effectively the same result as for *C. reinhardtii* (31.4 µg/L, n=1). For comparison, the E_rC₅₀ values at pH 5.5-6.5 (acidic) are above 100 µg/L for all species regardless of DOC normalisation.

Long-term aquatic hazard

Chronic toxicity to fish

Chronic data are available for three species (*O. mykiss*, *P. promelas* and Brook Trout *Salvelinus fontinalis*). Nevertheless, there is a relative scarcity of information for the acidic pH band (a single study for *O. mykiss*, three for *P. promelas* and none for *S. fontinalis*). The lowest NOEC/EC₁₀ value for fish is 5.9 µg/L for *P. promelas* mortality at pH >6.5-7.5 (not normalised for DOC level). If DOC normalisation is taken into account, the lowest NOEC/EC₁₀ value for fish is 10.7 µg/L for *S. fontinalis* reproduction at pH 6.5-7.5.

Chronic toxicity to aquatic invertebrates

About 44 individual chronic data points are available for two aquatic invertebrate species (*D. magna* and *C. dubia*). There are only two data points for the neutral pH band, but more than 4 studies are available for the other two pH bands, with greatest sensitivity apparent at acidic pH. At pH 5.5-6.5, the geometric mean 21-d NOEC_{reproduction} values are 13.2 µg/L (not normalised for DOC) and 10.5 µg/L (normalised for a DOC level of 2 mg/L) (n=7).

During the evaluation of copper granulates, RAC concluded that it is only appropriate to use the geometric mean when there are 4 or more data available in a pH band for specific endpoints (e.g., reproduction) for a species. At pH 6.5-7.5, the lowest NOEC (*C. dubia*) becomes 4 µg/L without DOC normalisation, corresponding to 6.2 µg/L with DOC normalisation when this information (mortality and reproductive effects) is split.

There is only one study reporting effects on growth, in the alkaline pH band, resulting in a 21-d NOEC_{growth} = 12.6 µg/L (*D. magna*), regardless of DOC normalisation.

Chronic toxicity to algae or other aquatic plants

Over 50 individual chronic data points are available for three algal species (*P. subcapitata* (n=34), *C. reinhardtii* (n=4), and *Chlorella vulgaris* (n=16)) and the macrophyte *Lemna minor* (n=1). Due to the limited number of data points for some species and pH ranges RAC considers that it is not possible to draw a clear conclusion about chronic toxicity trends with pH. When data are not normalised for DOC, *C. reinhardtii* is the most sensitive species, with a lowest NOE_rC (duration not specified) of 22 µg/L at pH 5.5-6.5 (n=2). This is similar to the NOE_rC (duration not specified) of 30 µg/L for *L. minor* (n=1) at pH 5.5-6.5. When the data are normalised to a DOC level of 2 mg/L, the lowest geometric mean NOE_rC (duration not specified) is 13.3 µg/L (n=15) for *P. subcapitata* at pH 6.5-7.5.

DS comparison of the data with the CLP criteria

The DS proposed classification for copper metal, which should not depend on the physical form and thus included all copper forms on the market: copper massive, copper powder, copper flakes and copper granulate. They noted that copper flakes and copper granulate have larger specific surface areas than massive copper (specific surface area ≤ 0.67 mm²/mg, see further below) and should both be covered by the proposal for copper powder (specific surface area of > 0.67 mm²/mg).

The classification is based on the comparison of acute and chronic ERVs (derived via testing of the soluble metal species) with the concentration of metal ions in solution after a period of 7 days (short-term test) and 28 days (long-term test), respectively, at different loadings and according to the Transformation/Dissolution protocol, according to the Guidance on the Application of the CLP criteria (2017) the classification strategy for metals.

The DS compiled data from T/D studies with data for ERV values in two tables for copper metal with specific surface area > 0.67 mm²/mg (Table below) and for copper metal with specific surface area ≤ 0.67 mm²/mg (Table below) to conclude on the classification.

As there is no standardised DOC value for hazard assessment and driving such a value would be a matter of policy, RAC clarified in its opinion on copper granulate (June 2018) that it was not in a position to recommend an appropriate DOC value for use under CLP. Consequently, both normalised and non-normalised ERVs were therefore presented in the RAC opinion on copper granulate, and the most stringent classification was derived. In the current aquatic environmental hazard classification proposal for copper, both normalised and non-normalised ERV-data is presented. For both powder and massive copper, the resulting classification proposal is independent of whether ERV data are normalized for DOC or not.

DS conclusion on copper metal classification

Acute aquatic hazard

Copper particles with a specific surface area ≤ 0.67 mm²/mg (massive copper particles); no classification (Table below).

Table: Comparison of acute ERV and release of copper ions from copper massive (particles with specific surface area ≤ 0.67 mm²/mg) after 7 days and proposal for classification based on these data.

pH	Transformation/dissolution at loading rate 1 mg/L (µg Cu/L)	ERV (µg Cu/L)		Classification	Ratio T/D and ERV	M-factor
		Not normalised for DOC	Normalised to DOC of 2 mg/L			
6	1.0	12.1		No		
7	0.4	11.7		No		
8	<0.2	40		No		
6	1.0		11	No		
7	0.4		24.1	No		
8	<0.2		31.4	No		

Copper powder particles with a specific surface area > 0.67 mm²/mg; Aquatic Acute 1 with an M-factor of 10 (Table below).

Table: Comparison of acute ERV and release of copper ions from copper powder (particles with a specific surface area > 0.67 mm²/mg) after 7 days and proposal for classification based on these data.

pH	Transformation/dissolution at loading rate 1 mg/L (µg Cu/L)	ERV (µg Cu/L)		Classification	Ratio T/D and ERV	M-factor
		Not normalised for DOC	Normalised to DOC of 2 mg/L			
6	196.1	12.1		Acute 1	16	10
7	72.2	11.7		Acute 1	6.2	1
8	66.7	40		Acute 1	1.2	1
6	196.1		11	Acute 1	18	10
7	72.2		24.1	Acute 1	3.0	1
8	66.7		31.4	Acute 1	2.1	1

As described in section 11.2, the REACH registrant uses the critical surface area approach as described in the CLP Guidance Annex IV, section IV.5.5 to support the relevance of the data used for classification.

The DS proposes the critical surface area approach, calculating copper release for mass loading of 1 mg/L equal to 107 mm²/L after 7 days using a linear regression derived by REACH registrant (see equation 1). The resulting copper release is 141 µg/L. This value is well above the lowest acute ERV at pH 6 of 11 µg/L, hence supporting the conclusion that copper powder particles should be classified Category Acute 1 with an M-factor of 10.)

The same calculation for copper spherical particles with a diameter of 1 mm (representing massive copper) is 0.67 mm²/L resulted in value 0.98 well below the lowest acute ERV of 11 µg/L, hence supporting the conclusion above that no acute classification is triggered for massive copper.

Long-term aquatic hazard (including bioaccumulation potential and degradation)

Based on the available data, copper is not considered to be rapidly transformed by normal environmental processes. The bioaccumulation behaviour of copper does not influence the determination of the classification of copper and does therefore not need to be considered further.

Adequate chronic ecotoxicity data were available for all three trophic levels. Comparison between T/D values and ERV concentrations is presented below.

Copper particles with a specific surface area ≤ 0.67 mm²/mg or less (massive copper particles); no classification is triggered (table below).

Table: Comparison of chronic ERV and release of copper ions from copper massive (particles with specific surface area ≤ 0.67 mm²/mg) after 28 days and proposal for classification based on these data.

pH	Transformation/dissolution		ERV (µg Cu/L)		Classification	Ratio T/D and ERV	M-factor
	At loading rate 0.1 mg/L (µg Cu/L)	At loading rate 1 mg/L (µg Cu/L)	Not normalised for DOC	Normalised to DOC of 2 mg/L			
6	0.3	3.4	13.2		none	-	-
7	0.08	0.8	4		none	-	-
8	0.06	0.6	12.6		none	-	-
6	0.3	3.4		10.5	none	-	-
7	0.08	0.8		6.2	none	-	-
8	0.06	0.6		11.8	none	-	-

Copper powder particles with a specific surface area > 0.67 mm²/mg; Aquatic Chronic 1 with an M-factor of 1 (table below).

Table: Comparison of chronic ERV and release of copper ions from copper powder (particles with a specific surface area > 0.67 mm²/mg) after 28 days and proposal for classification based on these data.

pH	Transformation/dissolution		ERV (µg Cu/L)		Classification	Ratio T/D and ERV	M-factor
	At loading rate 0.1 mg/L (µg Cu/L)	At loading rate 1 mg/L (µg Cu/L)	Not normalised for DOC	Normalised for DOC 2 mg/L			
6	62.2	622.4	13.2		Chronic 1	4.7	1
7	22.3	222.9	4		Chronic 1	5.6	1
8	18.5	185.4	12.6		Chronic 1	1.5	1
6	62.2	622.4		10.5	Chronic 1	5.9	1
7	22.3	222.9		6.2	Chronic 1	3.6	1
8	18.5	185.4		11.8	Chronic 1	1.6	1

The DS accepts the critical surface area approach, calculating copper release for mass loading at 0.1 mg/L equal to 10.7 mm²/L after 28 days using linear regression derived by the REACH registrant (see equation 2). Resulting copper release is 57.6 µg/L. This value is well above the lowest chronic ERV at pH 6 of 10.5 µg/L, hence supporting the conclusion that copper powder particles should be classified Category Chronic 1 with an M-factor of 1).

The same calculation for copper spherical particles with a diameter of 1 mm (representing massive copper) is 0.67 mm²/L resulted in value 3.3 µg/L well below the lowest acute ERV of 10.5 µg/L, hence supporting the conclusion that no chronic classification is triggered for massive copper.

Comments received during the consultation

Three MSs, one national authority, 17 Industry and Trade association, 20 Company-Manufacturers, 5 Company downstream users and Biocidal Core Copper Subgroup (2 comments) submitted comments on the DS's proposals during the public consultation.

One MS commented on copper flammability and different information presented in Table 2 and Table 9 of CLH. One MS supported the proposed separate classification for copper massive and copper powder. The MS supported the DS's argumentation that SSA is a crucial factor with limit value of 0.67 mm²/mg in this way encompassing the harmonised classifications for copper granulate and copper flakes. Comments on the structure of the CLH report were also presented. One MS questioned why the Annex VI entry for copper coated flakes remains in place, while the entry for granulated copper is proposed to be deleted, if both are covered by the proposal SSA > 0.67 mm²/mg. They also questioned how granulated copper would be covered by the new proposed classification for copper [specific surface area > 0.67 mm²/mg] if the length of particles ranges between 0.9 mm and 6.0 mm, with a mean length at 2.1 mm as an SSA below the limit value would be expected.

One national authority supported the proposed harmonised classification and presented several observations and proposals. To avoid the term "powder" in a new Annex VI entry, they suggested only quoting the specific surface area. The dimensions and SSA for particles of granulated copper should be clarified. The RAC opinion on the long-term aquatic hazard for copper flakes adopted in 2019 to reflect updates to the ERVs should be referenced in the current CLH proposal. The National authority commented on the criteria for separate classifications of metal forms and their application for copper flakes. A discussion at UN GHS level is proposed as far the classification of copper forms affects other metals too.

An extensive list of comments and two study reports (one for *Lymnaea stagnalis* and one for *Ceriodaphnia dubia*) were received from the European Copper Institute (ECI). ECI agreed with the DS to include one entry in Annex VI of CLP, with as Chemical name: *copper*; [specific surface area > 0.67 mm²/mg] and supported the DS's view that the SSA is the crucial parameter and that the entry in Annex VI of CLP should be based on the SSA.

ECI clarified in a comment that additional data were available for copper in the REACH registration dossier – massive copper traded as "copper cathode" and forms of copper powder. They commented that the choice of the DS to consider the copper powder with specific surface area of 48 mm²/mg as calculated by screen analysis, and of 107 mm²/mg as measured by gas adsorption (BET) (Skeaff & Hardy (2005)) as the smallest representative copper particle. The particle size is reported as 77.3% < 50 µm, and further inquiry established that it has D50 = 40 µm. It is produced by water atomization which results in particles with an *irregular* shape, and this could explain the relatively higher specific surface area compared to its particle size. ECI mentioned that water atomization is a less common technique to produce copper powders: most copper powders are produced through air atomization, which results in approximately *spherical* particles. The copper release from the water-atomized copper powder after 7 days at pH 6 and

at a mass loading of 1 mg/L was measured as 101 and 64 µg/L (average 82 µg/L, coefficient of variation 32%) (Skeaff & Hardy, 2005). ECI pointed out that while the variability is high, both measured values are lower than:

- The copper release of 110 µg/L which was measured under the same conditions for copper powder with D50 = 11 µm and specific surface area 60 mm²/mg (BET) (ECTX, 2020).
- The copper release of 196.1 µg/L calculated by the DS using derived by the REACH Registrant regression equation. Explanation for the divergence could be due to the changes of the shape of particles during dissolution or due to the kind of surface passivation.

ECI further suggested that based on the experimental data, copper ions do indeed undergo rapid environmental transformation and subsequent removal from the water column. ECI commented on the ERV values used by the DS and found them reliable. In addition, ECI supported the approach for comparing Transformation/dissolution data to the ERVs at specific pH level, as presented in the report by the DS, which is in line with the CLP guidance.

Eurometaux supported the classification of metal forms proposed by DS, based on specific surface area. They also commented on the environmental fate and evidence and evidence that copper ions undergo rapid environmental transformation and removal was presented.

Most company-manufacturers support proposed no classification for copper massive and accept 0.67 mm²/mg as an SSA limit value as a basis for classification. One company-manufacturer strongly disagreed with harmonized classification of copper granulated (BPR approved biocidal active substance), proposing separate classification between copper massive and copper powder. Disagreement is based on the RAC opinion (2018), copper granulate is not classified for acute toxicity and is classified as Aquatic Chronic 2. Arguments presented include the special process of production, specific particle shape, specific surface area of 2.56 mm²/mg being closer to copper massive (0.67 mm²/mg) and much higher than accepted for harmonized classification copper powder (107 mm²/mg).

One Industry and trade association agreed with the derived ERVs and accept that they are in line with bioavailability concepts. However, they also supported the registrant's selection of particles with specific surface area of 60 mm²/mg instead of the proposal by the DS to use particles with specific surface area of 107 mm²/mg. The argument being that particles with smaller area (approximately spherical particles, produced by air atomization) released higher copper concentration in comparison with particles with higher area (with irregular shape, produced by water atomization) due to the possible surface passivation. Extrapolating the measured release from the air atomized powder to a higher SSA is therefore not justified. They instead supported the REACH registrant's conclusions on rapid environmental transformation of copper ions and removal from the water column.

Two Comments were received from the Biocidal Core Copper Subgroup (BCCSG) which represents companies involved in the manufacture and/or supply of copper-based biocidal active substances. Under the BPR, the reference specification for all BCCSG copper forms and compounds follow the ECHA BPR Guidance on reference specification and this has resulted in a specific specification for each based on:

- The purity/impurity profile of the active substance.
- The size and shape of the active substance.

In addition, BCCSG pointed out that the approval of specific forms of copper under the BPR does not constitute normal circumstances as considered by the CLP Guidance, and on this basis the BCCSG proposes that it is therefore justified to have more than two entries for copper under CLP. See Table 1 (Classification Status of Copper Forms Evaluated Under the BPR) in the RCOM.

Assessment and Comparison with the classification criteria

General comments

For the purposes of hazard assessment, metals can be considered in 3 forms:

- **Powder** – refers to marketed metal deliberately produced by a dedicated production method with a diameter < 1 mm and an SSA greater than that of a spherical particle of 1 mm;
- **Massive form** – refers to marketed metals in any form (> 1 mm) with a surface area equal to or less than the surface area of a 1 mm sphere;
- **Generated particles** – refers to particles > 1 mm and an SSA greater than the surface area of a 1 mm sphere, unintentionally generated from reasonably expected use of the massive form.

The intrinsic hazard of any forms of a metal on the market depends on the metal ions released to the aquatic environment in a given time-window. As far as dissolution of metal forms is governed by chemical surface activity (structure and energy of metal crystal lattice and metal chemical properties), surface area is a crucial parameter for hazard assessment if all marketed metal forms have the same crystal structure. In order to standardise the surface area measurement, it is corrected for mass of the particles as spheres and presented as mm²/mg, i.e., Specific Surface Area (SSA). RAC supports the DS's conclusion that all copper forms on the market (copper massive, copper powder, copper flakes, copper granulate) has to be classified depending only on the SSA as far as they all have same face-centred cubic lattice of copper and same chemical properties. RAC supports the DS following the CLP criteria to base classification of copper metal forms on the SSA of 0.67 mm²/mg as a limit between copper massive and all other copper forms on the market (copper powder, copper flakes and copper granulates). The classification of copper massive would depend on copper particles (< 1 mm) being generated during the normal handling and use and if such particles are relevant for classification of the massive form. If so, the massive form should ideally be classified based on T/Dp testing of such generated small particles or of powder, if representative of the generated particles.

Transformation to non-bioavailable forms

Copper is a natural element that occurs in the earth's crust at low levels. It is generally assumed that the free hydrated copper ion (Cu²⁺) together with copper hydroxy species are the most toxic inorganic species to aquatic organisms (Brown and Markich, 2000). In natural waters, copper is complexed by natural dissolved organic matter (DOM) such as humic, fulvic and tannic acids, or adsorbed to colloidal, humic-coated iron and/or manganese oxide particles. The complexation of copper with DOM increases in freshwaters as the pH and concentration of DOM are increased, and as the concentrations of competing ions are decreased. In freshwaters, particularly acidic soft waters with low complexation capacity, copper may be highly toxic. The vast majority of studies have shown that natural dissolved organic matter (e.g., fulvic and humic acids) reduce the uptake and toxicity of copper in freshwater organisms (Erickson *et al.*, 1996). However, several studies (e.g., Buchwalter *et al.*, 1996) have shown that some of these organic complexing agents may enhance the uptake and toxicity of copper under certain conditions. Sorption onto minerals, clays and biotic surfaces and precipitation play major roles in determining the fate of copper in aquatic systems. In addition, partitioning and bioaccumulation of copper in natural waters is controlled by active biological processes as much as by chemical equilibria. Organisms such as algae and fish release dissolved organic ligands, which bind copper and control its uptake and bioavailability. Exudate production is dependent on the copper concentration, nutrients, and physiological status of the organisms (Zhou *et al.*, 1989). Various speciation codes based on defined equilibrium stability constants have been developed and used for calculation and prediction of aquatic chemistry of copper. These speciation models allowed relatively reliable

calculation of toxic fraction of copper toward aquatic organisms. RAC considered the possibility for transformation of copper to non-bioavailable species in the presence of sulphides and thiol groups and available data shows that at environmentally relevant concentrations of Cu^{2+} , about 1 nM sulphide and median values for DOM, copper precipitation, and transformation to non-bioavailable species is not expected. RAC considered studies presented by the REACH Registrant for copper transformation and removal. In the study of Cervi *et al.* (2021), behaviour of copper ions added to freshwater sediments was studied under suboxic and anoxic conditions. In anoxic sediments sulphur species are reduced to sulphide and most of the copper is precipitated as CuS , an extremely insoluble and stable compound copper compound. However, in suboxic sediments sulphur species are oxidized to sulphate and copper exists mostly in soluble and reducible fractions. Cervi *et al.* (2021) concluded that copper speciation altered from acid soluble to the oxidizable fraction under anoxia. RAC notes that various types of sediments and conditions exists in the aquatic environment which determine the solubility of copper species. It is expectable that reducing conditions and sulphide content would reduce copper toxicity as shown in the study. In the new study for "The Fate of Copper Added to Surface Water: Field, Laboratory, and Modelling Studies" Rader *et al.* (2019) it was observed that 70% removal of Cu^{2+} ions is possible at extremely high concentrations (250-1000 $\mu\text{g/L}$ Cu^{2+}) when precipitation of copper as hydroxides or sulphides might be expected. Overall, results from these studies showed that copper precipitation is possible under specific conditions but do not support the conclusion for copper transformation to non-bioavailable forms under environmentally relevant conditions (low copper and low sulphide content). RAC does not agree with Industry that studies under conditions with high sulphide and copper concentrations (much above typical copper concentrations in the aquatic environment) support copper ion transformation to non-bioavailable forms. In addition, calculations using VisualMinteq, for example, do not show copper precipitation at concentrations in the range 0.5-1.5 $\mu\text{g/L}$ and 1 nM sulphide.

In conclusion, RAC supports the DS's conclusion that copper is not subject to rapid environmental transformation to non-available forms for the purpose of classification and labelling.

Bioaccumulation

A considerable amount of information is available for copper bioaccumulation. Copper BCFs and BAFs have been calculated for aquatic species such as algae, molluscs, arthropods, and fish (McGeer *et al.*, 2003; DeForest *et al.*, 2007). While copper accumulates in the tissues of organisms as a result of exposure, the tissue concentrations are inversely proportional to the exposure concentrations (i.e., lower BCFs and BAFs at higher exposure concentrations; McGeer *et al.*, 2003). This phenomenon is mainly due to essentiality of copper which, in turn, leads to the strong regulation and control of copper in aquatic organisms (DeForest *et al.*, 2007). In addition, copper biouptake depends on aquatic chemistry and organism physiology. Homeostatic control enables aquatic organisms to establish a negative relationship between exposure and accumulation. Therefore, biomagnification of copper does not generally occur in aquatic organisms (McGeer *et al.*, 2003).

RAC supports the conclusion of the DS that the bioaccumulation behaviour of Cu^{2+} is complicated by essentiality and homeostatic mechanisms in organisms. However, in contrast to the DS, RAC considers that there is sufficient information to conclude that copper is not bioaccumulative in the aquatic environment for classification and labelling purposes.

Aquatic chemistry and influence of water chemistry parameters on copper

Copper is an essential micronutrient for aquatic biota. However, both copper deficiency and copper concentrations at levels that are required for biological functioning can produce adverse effects on aquatic biota. At relatively low concentrations, copper can become acutely toxic, especially to aquatic organisms. Chronic effects of copper include inhibition of photosynthesis

and metabolism, inhibition of growth in aquatic plants and algae; reduced feeding, growth, and reproduction, as well as gill damage in aquatic invertebrates; and significant effects on behaviour, growth, migration, changes in metabolism and organ or cellular damage, as well as changes in olfactory responses in freshwater fish species.

Dissolved copper occurs in various chemical forms in the aquatic environment with the relative amounts of those chemical forms varying as a function of water chemistry. Not all chemical species of copper can be taken up by the biochemical receptors (i.e., biotic ligands) of an organism (e.g., gill). Therefore, copper toxicity is not only determined by its concentration in water, but also depends on the chemistry of the aquatic environment. Free ionic copper (Cu^{2+}) is the main toxic form. Some hydroxyl species of copper (e.g., CuOH^+) can be toxic, however, many other species, such as copper carbonates, are less bioavailable and consequently less toxic. Generally, copper complexes with DOC are inert and least bioavailable. Several physicochemical properties can affect copper speciation and the availability of ligands for complexation with copper thereby modify copper toxicity. In addition, some ions (i.e., calcium, magnesium) compete with copper at biological binding sites and decrease its uptake. The effects of some specific water chemistry parameters of relevance for hazard assessment are discussed below.

Dissolved Organic Carbon

Dissolved organic carbon (DOC) binds to the toxic inorganic forms of copper in water (i.e., Cu^{2+} and CuOH^+) forming organic complexes that cannot bind to biotic ligands, such as gill and olfactory tissues. As a result, DOC can ameliorate copper toxicity significantly which has been demonstrated in algae, macrophytes, invertebrates, and fish (Azenha *et al.*, 1995; Erickson *et al.*, 1996). However, the ameliorative effect of DOC is weaker at low pH values because H^+ ions can compete with copper at the binding sites of DOC.

Hardness

Water hardness, defined as the concentration of calcium (Ca) and magnesium (Mg), can ameliorate copper toxicity through the competition between Cu^{2+} and Ca^{2+} for branchial uptake on gill surfaces. While Ca^{2+} is shown to provide a stronger ameliorative effect in fish, Mg^{2+} seems to provide more protection in aquatic invertebrates (Meyer *et al.*, 2007).

The ameliorative influences of hardness on copper toxicity are not consistent. For example, Winner (1985) observed very little protection against copper toxicity in *Daphnia pulex*. Hardness did not influence copper uptake and the lethal effects of short-term copper exposure in rainbow trout (*Oncorhynchus mykiss*) (Laurén and McDonald, 1986; Grosell and Wood, 2002). These inconsistencies may be caused by variations in other water quality parameters, such as alkalinity (Erickson *et al.*, 1996) or the Ca:Mg ratio in the laboratory test water (Naddy *et al.*, 2002). However, it is demonstrated that Ca^{2+} has only minor ameliorative effects in protecting olfactory tissues against copper toxicity (McIntyre *et al.*, 2008; Green *et al.*, 2010; Dew *et al.*, 2012).

Alkalinity

Copper toxicity to fish is reduced in waters of high alkalinity because the anions associated with alkalinity (i.e., CO_3^{2-} and HCO_3^-) bind with free ionic copper to form compounds like $\text{Cu}(\text{CO}_3)_x$, which are less toxic. However, the protective effect of alkalinity is further influenced by other water quality conditions. For example, Miller and Mackay (1980) demonstrated that alkalinity moderated copper toxicity at high hardness but did not have the same ameliorative effect at low hardness. For aquatic plants, it has been suggested that compounds like $\text{Cu}(\text{CO}_3)_x$ and $\text{Cu}(\text{HCO}_3)$ may also be bioavailable (Antunes *et al.*, 2012). Therefore, alkalinity may play less of a role in ameliorating copper toxicity in aquatic plants than it does in aquatic animals.

pH

In de-ionized, low pH water (< 6), the majority of copper is in the toxic ionic form Cu^{2+} . As pH increases, the concentration of Cu^{2+} drops dramatically and other less toxic forms become abundant (e.g., $\text{CuOH}^{\cdot-}$). However, in natural waters the influence of pH is complicated by interactions with other water chemistry factors, such as the presence of other ions and DOC.

The effects of pH on copper toxicity vary among taxonomic groups. Tests on fish and invertebrates have generally shown decreasing copper toxicity with increasing pH. Erickson *et al.* (1996) tested copper toxicity in larval fathead minnows (*Pimephales promelas*) in test waters with pH values 6.5, 7.4, 8.1, and 8.8 demonstrating lower toxicity at higher pH values. Cladocerans also demonstrated lower sensitivity to copper exposure at higher pH values (Hyne *et al.*, 2005; Ryan *et al.*, 2009). In contrast, freshwater algae (*Chlorella sp.*) and duckweed (*Lemna minor*) demonstrated higher sensitivity to copper at higher pH values (Wilde *et al.*, 2006; Antunes *et al.*, 2012, respectively). The inconsistency might be due to different mechanisms of toxicity in algae and plants compared to fish and aquatic invertebrates. RAC noted that these are experimental results and pH influence could be regarded only in combination with other parameters such as DOC content, alkalinity, hardness etc. In conclusion, RAC considers that there is sufficient extensive available data and information on the influence of pH on copper toxicity to justify following Annex IV.2.3(2) of the CLP Guidance. Consequently, RAC supports the DS's proposal to band the available T/Dp and ERV data by pH, applying the most stringent classification outcome.

In general, copper exhibits highest bioavailability in waters with low DOC, low pH, and low hardness. As DOC, pH, and hardness increase, the bioavailability and thus toxicity of copper decreases.

The important conclusion is that for copper, it is not possible to assess the effect of only one water chemistry parameter and only the assessment of the combined effects of all parameters leads to acceptable results; the situation may be quite different for other metals.

The biotic ligand model (BLM)

The toxicity of copper varies depending on water chemistry. However, when metal toxicity is reported as free metal ion concentrations, water chemistry plays less of a role in predicting toxicity. Based on this concept, the BLM was developed to predict metal speciation, the binding capacity of available organic and inorganic compounds with various metal species, and the protective effects of competing cations to model the accumulation of the metal at a biologically sensitive receptor (i.e., biotic ligand). Therefore, the BLM can be used to predict the amount of metal accumulation at the biotic ligand (e.g., gill), which represents the site of action for metal toxicity, for a variety of water chemistry conditions and metal concentrations.

Acute and chronic BLM models have been developed and used from regulatory bodies mostly for risk assessment. Acute BLM-based copper water quality criteria were derived in the USA (US EPA, 2007) using HydroQual (HydroQual, 2007) and Biotic Ligand Model Windows Interface (Windward Environmental, 2017). Chronic BLM-based predicted no effect concentrations (PNECs) were derived using three chronic BLMs described in the European Union Risk Assessment Reports i.e., algae, *Daphnia magna*, and fish appropriate for each taxonomic group (De Schamphelaere *et al.*, 2002; De Schamphelaere and Janssen, 2006; De Schamphelaere and Janssen, 2004) (EU-RAR) (ECHA, 2008). The dependencies of key parameters, such as pH and DOC, on PNECs may vary due to differences in the model structure and biotic ligand constants of the BLM used.

In order to facilitate regulatory application, user friendly BLMs were also developed, using only three parameters (pH, DOC, Ca). Comparison with full BLMs indicates relatively good agreement.

RAC accepts that BLMs predict toxicity of copper under different local conditions and are powerful tools for risk characterization. However, their application for hazard assessment is still not validated for water quality parameters beyond pH. BLMs might be used for normalization of copper concentrations under water quality conditions used in the T/Dp test but these conditions are not always well defined in available studies and use of the parameters in these tests is not agreed for this purpose. RAC agrees with DS's proposal to band results from T/D tests and aquatic toxicity tests for different pH ranges to present ERV values for the same ranges and to use available DOC normalised and non-normalised ERVs. Here, both non-normalized and normalized values would be used, and the most stringent classification will be proposed. RAC notes that experimental results depend on the combined action of water quality parameters such as pH, DOC, Ca, alkalinity etc. As it is not possible to normalize ecotoxicity results for all conditions and for some studies not all conditions are known, RAC agrees with the DS's proposed approach as the most reliable way to achieve robust hazard assessment with the available data.

Aquatic toxicity and ERV derivation

RAC agrees with the DS for aquatic toxicity to use data taken from section "5.4 Aquatic Toxicity" and section "7 Annexes" of the CLH report for copper, granulated (February 2017) due to the absence of additional or new data. RAC accept all conditions used for data: reported adverse effect levels have to be expressed as measured, dissolved copper concentrations (nominal data are not acceptable); the geometric mean can be used if at least 4 data points on the same species and endpoint are available and in order to analyse the impact of the use of geomean or lowest value if less than 4 data points are available, both approaches will be presented.

Acute ERV derivation

Fish

As a rule, toxicity decreases at higher pH. The lowest acute LC₅₀ value for fish in the data set when not normalised for DOC is 12.1 µg/L (geomean for *P. promelas* at pH 5.5-6.5, n = 5). For DOC normalized data the lowest fish LC₅₀ value is 14.9 µg/L (for *P. promelas* at pH 5.5-6.5, n = 3; the geomean is in the same concentration band). For calculated geomeans n ≥ 4 data points for a species in a pH band, the lowest fish LC₅₀ would be 11.7 µg/L (for *D. rerio* at pH >6.5-7.5).

Invertebrates

Over 300 individual acute data points are available for two aquatic invertebrate species (*Daphnia magna* and *Ceriodaphnia dubia*). More than 4 studies are available for each pH band, with greatest sensitivity apparent at acidic pH. For geomen calculated values the lowest EC₅₀ value of 16.3 µg/L is obtained at pH 5.5-6.5 (not normalised, n = 29) and 11 µg/L (normalised for a DOC level of 2 mg/L, n = 26) for *D. magna* and 12.6 µg/L (not normalized, n = 9) and 16 µg/L (normalized for a DOC level of 2 mg/L, n = 8) for *C. dubia*. Invertebrates provide the lowest endpoint value at pH band > 7.5 - 8.5 with a geomean value of 40 µg/L for *C. dubia*.

Algae

Over 50 individual acute data points are available for three algal species (*Pseudokirchneriella subcapitata* (n = 36), *Chlamydomonas reinhardtii* (n = 3) and *Chlorella* sp. (n = 16). Generally, copper appears to become more acutely toxic to algae with increasing pH. The most sensitive species is *P. subcapitata*, the lowest geometric mean ErC₅₀ (duration is 104.9 µg/L (n = 12) at pH > 7.5 - 8.5 *P. subcapitata* for not normalized data and for normalized data with lowest geometric mean ErC₅₀ (duration not specified) of 31.6 µg/L (n = 11) at pH > 7.5 - 8.5 (alkaline).

Chronic ERV derivation

– Fish

Chronic data are available for three species (*O. mykiss*, *P. promelas* and Brook Trout *Salvelinus fontinalis*). The DS has separated mortality, growth, and reproduction endpoints for each species, giving 70 chronic endpoints in total. However, the number of actual studies is lower since more than one endpoint will have been reported for some studies. RAC notes that the most sensitive endpoint should be selected from a study for a particular species, so RAC is uncertain how much double counting of studies has taken place. The data set includes two specifically commissioned studies for *O. mykiss* and *P. promelas* at acidic pH, and some previously accepted data have been re-evaluated by the DS. Nevertheless, there is a relative scarcity of information for the acidic pH band (a single study for *O. mykiss*, three for *P. promelas* and none for *S. fontinalis*). The lowest NOEC/EC₁₀ value for fish is 5.9 µg/L for *P. promelas* mortality at pH > 6.5 - 7.5 (not normalised for DOC level). If DOC normalisation is taken into account, the lowest NOEC/EC₁₀ value for fish is 10.7 µg/L for *S. fontinalis* reproduction at pH > 6.5 - 7.5.

In summary, the lowest NOEC/EC₁₀ value for fish is 5.9 µg/L for *P. promelas* mortality at pH > 6.5 - 7.5 (not normalised for DOC level). If the geomean is used irrespective of the number of available data points, the lowest NOEC/EC₁₀ value for fish is 6.4 µg/L for *S. fontinalis* reproduction at pH > 6.5 - 7.5 (not normalised for DOC level). If DOC normalisation is taken into account, the lowest NOEC/EC₁₀ value for fish is 10.7 µg/L for *S. fontinalis* reproduction at pH > 6.5 - 7.5.

Information was not available about reproduction for any fish species at acidic pH.

– Invertebrates

The general trend indicates decreased toxicity for higher pH ranges. At pH 5.5 - 6.5, the geometric mean 21d NOEC_{reproduction} values are 13.2 µg/L (not normalised for DOC) and 10.5 µg/L (normalised for a DOC level of 2 mg/L) (both *D. magna*) (n=7). At pH > 6.5 - 7.5, the lowest NOEC (*C. dubia*) becomes 4 µg/L without DOC normalisation, corresponding to 6.2 µg/L with DOC normalisation when this information (mortality and reproductive effects) is split. The lowest NOEC/EC₁₀ value for invertebrates was 12.6 µg/L (normalised/non-normalized) recorded for *D. magna* at pH > 7.5 and 8.5 for growth effect (n = 1). If the normalisation with the DOC is taken into account, the lowest NOEC/EC₁₀ value for invertebrates was calculated to be 10.5 µg/L (n = 7, geomean) corresponding to the lowest value recorded for *D. magna* at pH between > 6.5 and 7.5 for reproduction effect and 11.8 µg/L for *C. dubia* at pH > 7.5 - 8.5. RAC agrees with the conclusion of DS that the data submitted for two additional studies for *Lymnaea stagnalis* and *C. dubia* is considered reliable but would not have any impact on the classification as the ERVs are higher than the lowest available for pH ranges 7.5 - 8.5 and 6.5 - 7.5, respectively.

– Algal/macrophyte

Over 50 individual chronic data points are available for three algal species (*P. subcapitata* (n = 34), *C. reinhardtii* (n = 4) and *Chlorella vulgaris* (n = 16)) and the macrophyte *Lemna minor* (n = 1). Generally chronic toxicity tends to increase at higher pH ranges according to both normalised and non-normalised values. The lowest NOE_rC of 22 µg/L was found for *C. reinhardtii* (n = 2) at pH 5.5 - 6.5. This is similar to the NOE_rC (duration not specified) of 30 µg/L for *L. minor* (n = 1) at pH 5.5 - 6.5. Data for higher pH values are not available. When the data are normalised to a DOC level of 2 mg/L, the lowest geometric mean NOE_rC (duration not specified) is 13.3 µg/L (n = 15) for *P. subcapitata* at pH > 6.5 - 7.5.

– Conclusion on ERVs

Overall, RAC agrees with the DS on the choice of ERVs as summarised in the table below.

Table: RACs selected ERV values by pH bands for comparison with the CPL criteria.

		pH band		
		5.5-6.5 (acidic)	>6.5-7.5 (neutral)	>7.5-8.5 (alkaline)
Values not normalised for DOC level				
Acute ERV	L(E)C50 (µg/L)	12.1 (<i>Pimephales promelas</i>)	11.7 (<i>Danio rerio</i>)	40 (<i>Ceriodaphnia dubia</i>)
Chronic ERV	EC10/NOE C (µg/L)	13.2 (<i>Daphnia magna</i>)	4 (<i>Ceriodaphnia dubia</i>)	12.6 (<i>Daphnia magna</i>)
Values normalised to a DOC level of 2 mg/L				
Acute ERV	L(E)C50 (µg/L)	11 (<i>Daphnia magna</i>)	24.1 (<i>Ceriodaphnia dubia</i>)	31.4 (<i>Chlamydomonas reinhardtii</i>)
Chronic ERV	EC10/NOE C (µg/L)	10.5 (<i>Daphnia magna</i>)	6.2 (<i>Ceriodaphnia dubia</i>)	11.8 (<i>Ceriodaphnia dubia</i>)

For consistency, RAC also presents the application of BLMs for PNEC derivation for copper. For the freshwater pelagic compartment, 139 individual NOEC/EC₁₀ values resulting in 27 different species-specific NOEC values, covering different trophic levels (fish, invertebrates, and algae) were used for the PNEC derivation. The large intra-species variabilities in the reported single species NOECs were related to the influence of test media characteristics (e.g., pH, dissolved organic carbon, hardness) on the bioavailability and thus toxicity of copper. Species-specific NOECs were therefore calculated after normalizing the NOECs towards a series of realistic environmental conditions in Europe (typical EU scenario's, with well-defined pH, hardness, and DOC). Such normalization was done by using chronic copper bioavailability models (BLMs), developed, and validated for three taxonomic groups (fish, invertebrates, and algae) and additional demonstration of the applicability of the models to a range of other species. The species specific BLM-normalized NOECs were used for the derivation of log-normal Species Sensitivity Distributions (SSD) and HC₅₋₅₀ values (the median fifth percentile of the SSD), using statistical extrapolation methods. The HC₅₋₅₀ values of the typical EU scenarios ranged between 7.8 to 22.1 µg Cu/L. Additional BLM scenario calculations for a wide range of surface waters across Europe further demonstrated that the HC₅₋₅₀ of 7.8 µg Cu/L, is protective for 90% of the EU surface waters and can thus be considered as a reasonable worst case for Europe in a generic context (Evaluation of active substance (EU-RAR, Regulation (EU) No 528/2012), Assessment Report Copper flakes (coated with aliphatic acid) Product-type 21).

As seen, the proposed ERV values agreed very well with derived PNEC values.

Solubility of copper

The solubility of copper depends on pH and according to OECD TP 29, all experiments were performed in the presence of 2 mg/L total organic carbon. The aquatic toxicity of copper depends on the combination of pH, DOC, and at least Ca as parameters. This is the basis for RAC supporting the DS in splitting the data from T/D studies of copper metal forms for different pH values. Copper dissolution depends on the specific surface area and RAC consequently supports presentation of solubility data as micrograms per specific area (mm²/mg). Results presented in the above tables showed relatively consistent release of copper per unit area as would be expected with release generally increasing in a linear manner with the exposed surface area, for measurements conducted at surface loadings between approximately 0.5 and 100 mm²/L (shown by REACH Registrant). Deviation for some samples might be explained with physical modification of their surface, which influenced copper dissolution.

Forms of copper

According to Annex IV.5.5 in the Guidance on the Application of the CLP criteria (2017), for classification of powders T/D data generated with smallest particle size marketed should be used. The DS proposed classification be based on particles with an SSA measured by BET of 107 mm²/mg (Skeaff and Hardy (2005)). RAC agrees with this choice and accepts arguments presented for copper flakes and special copper powder with dendric (branched) shape and D50 26 µm, both characterized with smaller surface area. A specific production process was used for the production of coated copper flakes yielding fine flakes with very high surface area and organic coating. Calculated surface area if assuming spherical particles with diameters of 5 - 100 µm is much lower than when measured by BET. In addition, coated copper flakes are only a very marginal part of the total amount of copper produced. Particles with a specific surface area of 340 mm²/mg were characterized with an irregular shape that results in a specific dissolution pattern, different from the other particles. The thinnest or most exposed parts of these particles may be dissolved during the initial stages of the test, leaving behind the coarser cores of the particles. The REACH registrant instead considered particles with the specific surface area of 60 mm²/mg used in the test of ECTX (2019 and 2020) for aquatic hazard classification.

RAC considered a significant influence of pH on transformation/dissolution and the preference for 28-day full test to be performed at the pH range of 5.5 - 8.5, in order to take into account possible long term effects on acidic lakes, as indicated in OECD TP 29. RAC notes that this pH is not experimentally validated, most probably due to the low buffer capacity of carbonate buffer at this pH, resulting from very high ratio carbonic acid to carbonate. Consequently, RAC extrapolates data from other pH values and calculates copper released at pH 5.5 – obtained value is 7.6 µg Cu/mm² (extrapolated by power function). This value is used for the calculation of copper released from particles with area 0.67 mm²/mg, 60 mm²/mg, and 107 mm²/mg for 28 days. Results obtained are included in the classification derivation table.

For the final classification of copper metal forms, the DS considered the possibility for the generation of particles with specific area ≤ 0.67 mm²/mg. RAC accepts the DS's conclusion that copper powder is produced by a special process and copper particles with a specific surface area > 0.67 mm²/mg are not generally generated from the massive metal during reasonable handling and use, which justifies separate assessments for massive copper and copper powder. It also appears that dissolution from the powder is much higher than that from particles with a specific area ≤ 0.67 mm²/mg, indicating it is not suitable for classifying massive. In line with the DS, RAC considers the arguments for separate classifications for copper powder and copper massive presented by the registrant (section 2 of The environmental hazard classification of copper; ECI (2021)): copper powder is produced by specific processes, clearly different from the production of copper massive: the production of copper powder and copper massive in Europe occurs at different sites and by different companies, there is no potential for the formation of particles from massive copper due to break apart during mechanical processes, handling, storage, transport, processing and use based on copper metal complex properties such as ductility, elongation, malleability, resistance to fracture, and softness; copper powder is not produced or generated as a by-product during the production of copper massive or during the processing of copper massive into articles (registrant lists an overview of dominant industrial processes for the production of copper particles from copper massive, including e.g. cutting, sawing, drawing, milling and finishing) and in none of these processes are pure copper with a diameter < 1 mm (SSA > 0.67 mm²/mg) generated or produced.

Taking into account the scheme derived from Annex IV.5.5 of the CLP guidance for the classification of massive metals (Figure below), it is concluded that the massive form should be classified based on the T/Dp data for particles with surface area of 0.67 mm²/mg (i.e., 1 mm particles). Consequently, RAC agrees with the DS that massive and powder copper warrant independent assessment for classification and labelling.

Flow chart for aquatic hazard assessment of the massive form > 1 mm of a metal

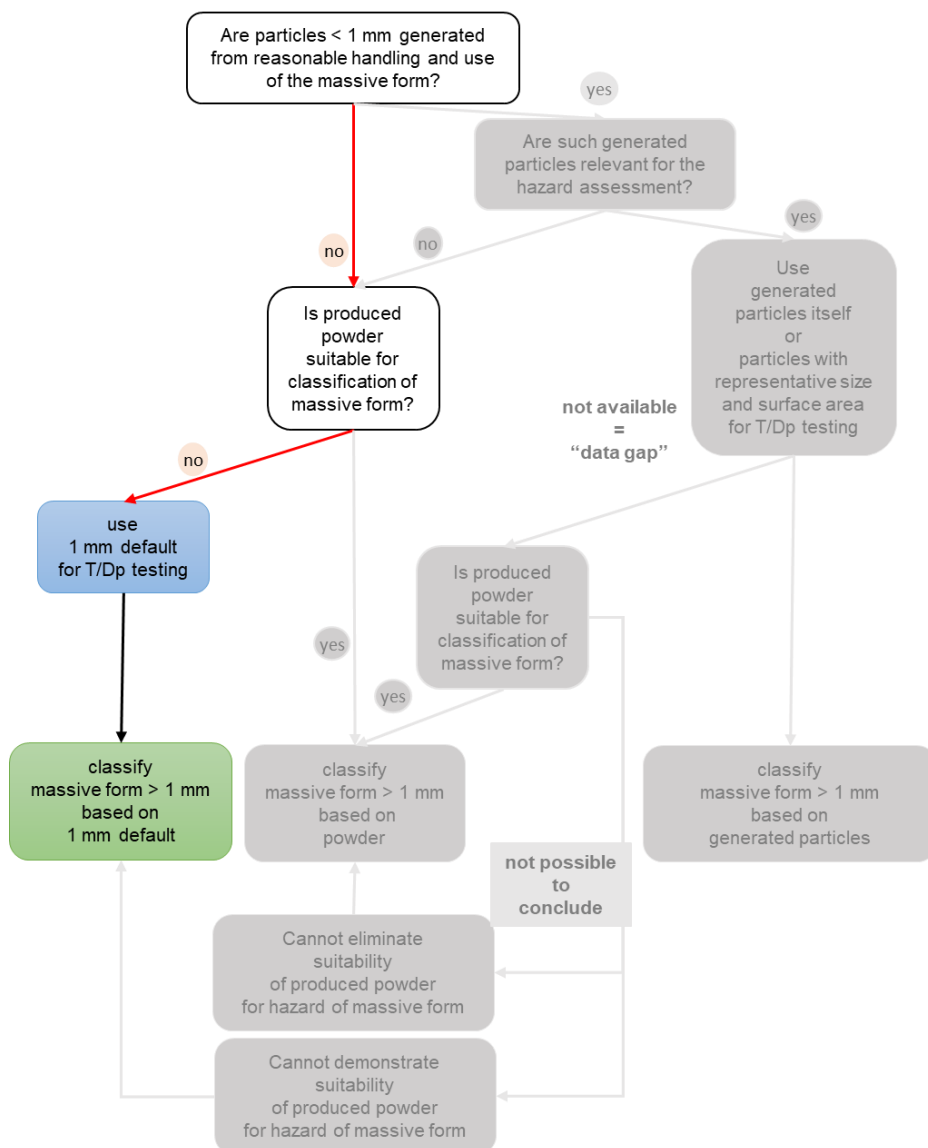


Figure: Flow chart for the aquatic hazard assessment of the massive form > 1 mm of a metal under CLP.

Comparison with the CLP criteria

In comparison with the CLP criteria, RAC supports the DS in using the pH and ERV values both normalised and non-normalised for DOC content. Finally, the most stringent classification should be accepted. The classification would be based on the specific surface area of copper forms: copper massive (specific surface area 0.67 mm²) and all other marketed forms.

All results and conclusions from the transformation/dissolution studies are presented in pH bands, results for derived ERVs are also presented in pH bands and in addition non-normalised/normalised to 2 mg/L. RAC accepts that both parameters most strongly influence copper dissolution and bioavailability. Therefore, in the absence of guidance for the application of BLMs for metal classification, RAC agrees with the DS to use both pH and DOC concentration for reliable classification. Although RAC is unable to recommend a specific DOC value in order to normalise aquatic toxicity data, the available data normalised at 2 mg/L are used as well as the non-normalised data and the most stringent outcome is then used. In addition, RAC supports the DS in banding T/Dp and ERVs by pH. Results summarised for massive copper and log/log regression functions presenting dependence of copper release on the specific surface area derived

by the REACH registrant (equation 1 and equation 2) lead to the conclusions on the harmonized classification of copper forms.

RAC accepts that particles with a specific surface area of 107 mm²/mg are the smallest particles on the market and should be used for classification. However, the REACH registrant did not include them in the derived regression line (equation 1 and 2) due to remarkably low copper release and poor reproducibility of results (above 30%); instead particles with an SSA of 60 mm²/mg were used. RAC considers that if the regression line derived by REACH registrant is used for extrapolation, particles with specific surface area of 60 mm²/mg should be used for classification of copper with SSA > 0.67 mm²/mg. If particles with a specific surface area of 107 mm²/mg would be used, then a new regression line should be constructed taking into account copper released from these particles. Extrapolation should be done with newly derived regression lines.

RAC performed such calculations with data from the Table: Summary of all transformation/dissolution data of copper at pH 6. RAC notes, that such calculations could be performed only for pH 6 and for 7 days, since experimental data for particles with surface area of 107 mm²/mg, for other pH ranges are not available. Data for copper dissolution for 28 days with these particles were also not available.

The derived equation for acute toxicity is Log [Copper release after 7 days in µg/L] = 0.12 + 0.97 * Log [Surface loading in mm²/L] (equation 3) and the calculated concentration is 125 µg/L, which supports the same classification.

RAC recalculated regressions for dissolution over 7 days at pH 6 using all data available and this resulted in a copper dissolution of 125 µg/L as opposed to 196 µg/L and 141 µg/L calculated from the regressions of the DS and REACH registrant, respectively. RAC considers that the approach using all valid data for the regression is the most robust and therefore selected the value of 125 µg/L as the preferred dissolution for acute hazards of copper powder. RAC notes that the classification outcome is not altered.

Acute aquatic toxicity

Copper particles with an SSA ≤ 0.67 mm²/mg (massive copper particles) warrant no classification as the dissolution is lower than the ERVs in all pH bands (Table below).

Table: Comparison of acute ERV and release of copper ions from copper massive (particles with specific surface area ≤ 0.67 mm²/mg) after 7 days and proposal for classification based on these data.

pH Band	pH tested	T/D at 1 mg/L (µg Cu/L)	ERV (µg Cu/L)		Hazard	T/D:ERV	M-factor
			Not DOC normalised	DOC Normalised (2 mg/L)			
5.5 – 6.5	6	1.0	12.1		none	-	-
>6.5 – 7.5	7	0.4	11.7		none	-	-
>7.5 – 8.5	8	<0.2	40		none	-	-
5.5 – 6.5	6	1.0		11	none	-	-
>6.5 – 7.5	7	0.4		24.1	none	-	-
>7.5 – 8.5	8	<0.2		31.4	none	-	-

Copper powder with a specific surface area > 0.67 mm²/mg warrants classification as Aquatic Acute 1 as the dissolution at pH 5.5 – 6.5 is higher than the acute ERV at the same pH. As the

ratio between the dissolution and ERV is 10, an M-factor of 10 is warranted (Table below). Although a classification of Aquatic Acute 1 is derived at all pH bands, the M-factor at pH 5.5 – 6.5 is higher than in other pH bands, so the classification derived at pH 5.5 – 6.5 is used for copper with a specific a surface area > 0.67 mm²/mg.

Table: Comparison of acute ERV and transformation/dissolution (T/D) data for copper ion release from copper powder (particles with a specific surface area > 0.67 mm²/mg) at 1 mg/L loading after 7 days and proposal for classification based on these data. M-factors are shown for respective T/D values.

pH Band	pH tested	T/D at 1 mg/L (µg Cu/L)	ERV (µg Cu/L)		Hazard	T/D:ERV	M-factor
			Not DOC normalised	DOC Normalised (2 mg/L)			
5.5 – 6.5	6	196*/141**/125***	12.1		Acute 1	16.1/11.7/10.3	10/10/10
>6.5 – 7.5	7	72.2 (DS)/40 (exp)	11.7		Acute 1	6.2/3.4	1/1
>7.5 – 8.5	8	66.7 (DS)/37 (exp)	40		Acute 1/NC	1.2	1/1
5.5 – 6.5	6	196*/141**/125***		11	Acute 1	17.8/12.8/11.4	10/10/10
>6.5 – 7.5	7	72.2 (DS)/40 (exp)		24.1	Acute 1	3.0/1.6	1/1
>7.5 – 8.5	8	66.7 (DS)/37 (exp)		31.4	Acute 1	2.1/1.1	1/1

* - calculated by DS for particles with area 107 mm²/mg, based on data from ECTX (X01-296) 2020 for particles with area 60 mm²/mg.

** - calculated by DS using regression line for 60 mm²/mg, derived by Registrant. Excludes data from particles at 107 mm²/mg.

*** - RAC – calculated by RAC using new regression line. Includes data for particles at both 107 and 60 mm²/mg.

DS – Dossier submitter calculated value

EXP – Experimentally derived value

NC – No Classification

Chronic aquatic toxicity

RAC supports the conclusion of DS for the chronic aquatic hazard.

Copper is not considered to be rapidly transformed by normal environmental processes and is considered to be not bioaccumulative in aquatic organisms. As copper dissolution increases with decreasing pH, RAC calculated dissolution values at pH 5.5 over 28 days for particles with sufficient data to address the chronic concern expressed for acid lakes in OECD TP 29. It is noted that while dissolution predictably increases, the classification outcome is not altered.

Copper particles with an SSA ≤ 0.67 mm²/mg (massive copper particles) warrant no classification as the dissolution at 1 mg/L loading is lower than the chronic ERVs in all pH bands (Table below).

Table: Comparison of chronic ERV and release of copper ions from copper massive (particles with specific surface area $\leq 0.67 \text{ mm}^2/\text{mg}$ after 28 days and proposal for classification based on these data.

pH band	pH	Transformation/dissolution ($\mu\text{g Cu/L}$)		ERV ($\mu\text{g Cu/L}$)		Hazard	T/D: ERV	M-factor
		At loading rate 0.1 mg/L ($\mu\text{g Cu/L}$)	At loading rate 1 mg/L ($\mu\text{g Cu/L}$)	Not DOC normalised	DOC normalised (2 mg/L)			
5.5 – 6.5	5.5*	0.5	5.1	13.2		none		
	6	0.3	3.4	13.2		none	-	-
>6.5 – 7.5	7	0.08	0.8	4		none	-	-
>7.5 – 8.5	8	0.06	0.6	12.6		none	-	-
5.5 – 6.5	5.5*	0.5	5.1		10.5	none		
	6	0.3	3.4		10.5	none	-	-
>6.5 – 7.5	7	0.08	0.8		6.2	none	-	-
>7.5 – 8.5	8	0.06	0.6		11.8	none	-	-

* - calculated by RAC for pH 5.5

For copper with an SSA $> 0.67 \text{ mm}^2/\text{mg}$ classification as Aquatic Chronic 1 is warranted as the dissolution at 0.1 mg/L is lower than the ERV in all pH bands except pH $> 7.5 - 8.5$. Furthermore, the dissolution/ERV ratio for all instances where Chronic 1 results is > 1 and < 10 , resulting in an M-factor of 1.

Table: Comparison of acute ERV and transformation/dissolution (T/D) data for copper ion release from copper powder (particles with a specific surface area $> 0.67 \text{ mm}^2/\text{mg}$) after 28 days and proposal for classification based on these data. M-factors are shown for respective T/D values.

pH band	pH	Transformation/dissolution		ERV ($\mu\text{g Cu/L}$)		Hazard	T/D: ERV	M-factor
		At loading rate 0.1 mg/L ($\mu\text{g Cu/L}$)	At loading rate 1 mg/L ($\mu\text{g Cu/L}$)	Not DOC normalised	DOC Normalised (2 mg/L)			
5.5 – 6.5	5.5*	81 [¥] 45 [‡]	810 [¥] 454 [‡]	13.2		Chronic 1	6.1 3.4	1 1
	6	62.2(DS) 57.6***	622.4**	13.2		Chronic 1	4.7 4.4 2.6	1 1 1
>6.5 – 7.5	7	22.3 (DS) 12.4 (exp)	222.9 124	4		Chronic 1	5.6 3.1	1 1
>7.5 – 8.5	8	18.5 (DS) 10.4 (exp)	185.4 104	12.6		Chronic 1 Chronic 2	1.5	1
5.5 – 6.5	5.5*	81 [¥] 45 [‡]	810 [¥] 454 [‡]		10.5	Chronic 1	7.7 4.3	1 1
	6	62.2(DS); 34.9(exp)	622.4** 349***		10.5	Chronic 1	5.9 3.3	1 1
>6.5 – 7.5	7	22.3 (DS) 12.4 (exp)	222.9 124		6.2	Chronic 1	3.6 2	1 1
>7.5 – 8.5	8	18.5 (DS) 10.4 (exp)	185.4 104		11.8	Chronic 1/ Chronic 2	1.6	1

* - calculated by RAC for pH 5.5 for particles with area $107 \text{ mm}^2/\text{mg}$ [¥] and $60 \text{ mm}^2/\text{mg}$ [‡]

** - calculated by DS for particles with area $107 \text{ mm}^2/\text{mg}$, based on data from ECTX (X01-296) 2020 for particles with area $60 \text{ mm}^2/\text{mg}$.

*** - calculated by DS, using regression line, derived by Registrant. No data from particles at $107 \text{ mm}^2/\text{mg}$.

DS - Dossier submitter calculated value

EXP - Experimentally derived value

Classification conclusion

RAC agrees with the DS that copper warrants the following classification:

copper; [specific surface area ≤ 0.67 mm ² /mg]	231-159-6	7440-50-8	No classification					
copper; [specific surface area > 0.67 mm ² /mg]	231-159-6	7440-50-8	Aquatic Acute 1 Aquatic Chronic 1	H400 H410	GHS09 Wng	H410	M=10 M=1	

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ANNEXES:

- Annex 1 The Background Document (BD) gives the detailed scientific grounds for the opinion. The BD is based on the CLH report prepared by the Dossier Submitter; the evaluation performed by RAC is contained in 'RAC boxes'.
- Annex 2 Comments received on the CLH report, response to comments provided by the Dossier Submitter and RAC (excluding confidential information).