Committee for Risk Assessment
RAC

Annex 1
Background document
to the 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

The background document is a compilation of information considered relevant by the dossier submitter or by RAC for the proposed classification. It includes the proposal of the dossier submitter and the conclusion of RAC. It is based on the official CLH report submitted to consultation. RAC has not changed the text of this CLH report but inserted text which is specifically marked as 'RAC evaluation'. Only the RAC text reflects the view of RAC.

Adopted

1 December 2022

CLH report

Proposal for Harmonised Classification and Labelling

Based on Regulation (EC) No 1272/2008 (CLP Regulation),
Annex VI, Part 2

Chemical name: Copper

EC Number: 231-159-6

CAS Number: 7440-50-8

Index Number: -

Contact details for dossier submitter: **Swedish Chemicals Agency**

Box 2

172 13 Sundbyberg

kemi@kemi.se

Version number: 2 **Date: October 2021**

CONTENTS

1 IDENTITY OF THE SUBSTANCE

1.1 Name and other identifiers of the substance

Table 1: Substance identity and information related to molecular and structural formula of the substance

Name(s) in the IUPAC nomenclature or other international chemical name(s)	Copper
Other names (usual name, trade name, abbreviation)	-
ISO common name (if available and appropriate)	-
EC number (if available and appropriate)	231-159-6
EC name (if available and appropriate)	Copper
CAS number (if available)	7440-50-8
Other identity code (if available)	-
Molecular formula	Cu
Structural formula	Cu
SMILES notation (if available)	[Cu]
Molecular weight or molecular weight range	63.55 g/mol
Information on optical activity and typical ratio of (stereo) isomers (if applicable and appropriate)	-
Description of the manufacturing process and identity of the source (for UVCB substances only)	-
Degree of purity (%) (if relevant for the entry in Annex VI)	According to ECI (2021): Copper massiv >99.9% Cu° Copper powder: typical purity 99.7% Cu; max 3% Cu_2O (depending on the particle size) Coated copper flakes: composition 96% Cu°; up to 3% Cu_2O; up to 3% stearic acid According to CLH report for copper flakes (coated with aliphatic acid; December, 2013): Degree of purity of copper flakes: ≥95.3% (w/w) as total copper According to CLH report for copper, granulated (February, 2017): Degree of purity of copper granulate: min 99.0% (w/w).

1.2 Composition of the substance

Table 2: Constituents (non-confidential information)

Constituent (Name and numerical identifier)	Concentration range (% w/w minimum and maximum in multi-constituent substances)	Current CLH in Annex VI Table 3 (CLP)	Current self-classification and labelling (CLP)
Copper (CAS 7440-50-8)	Copper massiv >99.9% Cu° Copper powder: typical purity 99.7% Cu; max 3% Cu_2O (depending on the particle size) Coated copper flakes: composition 96% Cu°; up to 3% Cu_2O; up to 3% stearic acid	Copper:- Copper granulate: see Table 7 Coated copper flakes, see Table 6.	Copper: Flam. Sol. 1; H228 Flam. Sol. 2; H228 Acute Tox. 2; H300 Acute Tox. 2; 330 Acute Tox. 3; H331 Acute Tox. 4; H302 Acute Tox. 4; H332 Skin Sense. 1; H317 Skin Irrit. 2; H315 Eye Irrit. 2; H319 STOT SE 2; H371 STOT SE 3; H335 STOT RE 1; H372 STOT RE 2; H373 Aquatic Acute 1; H400 (M=1, 10 or 100) Aquatic Chronic 1; H410 (M=1, 10 or 100) Aquatic Chronic 2; H411 Aquatic Chronic 3; H412 Aquatic Chronic 4; H413

Table 3: Impurities (non-confidential information) if relevant for the classification of the substance

Impurity (Name and numerical identifier)	Concentration range (% w/w minimum and maximum)	Current CLH in Annex VI Table 3 (CLP)	Current self-classification and labelling (CLP)	The impurity contributes to the classification and labelling
Not applicable				

Table 4: Additives (non-confidential information) if relevant for the classification of the substance

Additive (Name and numerical identifier)	Function	Concentration range (% w/w minimum and maximum)	Current CLH in Annex VI Table 3 (CLP)	Current self-classification and labelling (CLP)	The additive contributes to the classification and labelling
Not applicable					

2 PROPOSED HARMONISED CLASSIFICATION AND LABELLING

2.1 Proposed harmonised classification and labelling according to the CLP criteria

This is a proposal for a harmonised aquatic environmental hazard classification for copper. No other hazard classes, than “Hazardous to the aquatic environment” are considered in this proposal.

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 in the 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 the Annex VI by the Commission Delegated Regulation (EU) 2020/1182.

Copper metal can be placed on the market in different physical forms, where flakes and granules can serve as some examples. However, their aquatic environmental hazard classification should not depend on their physical form since they are still chemically the same substance. In order to classify these different physical forms correctly, the ECHA Guidance on the Application of the CLP Criteria in general and the metal classification strategy in Annex IV in particular should be followed. This current aquatic environmental hazard classification proposal aimes at classifying copper metal (EC 231-159-6; CAS 7440-50-8) and as result of this classification, correcting the already adopted harmonised aquatic environmental hazard classifications of copper flakes and copper granulates. Both copper flakes and copper granulates have specific surface areas larger than massive copper (that is larger than 0.67 mm^2/mg). Consequently, copper flakes and copper granulates should both be covered by our proposal for copper with a specific surface area of > 0.67 mm^2/mg.

Below, tables are presented, representing a proposal for aquatic environmental hazard classification of copper (Table 5) and the new aquatic environmental hazard classification proposal of copper flakes (the aquatic environmental hazard classification has been amended, whereas the human health hazard classifications are out of the scope of this proposal and are therefore retained unchanged, Table 6). As a consequence it is also proposed to delete the current Annex VI entry for copper granulate (Table 7). This since copper granulate would be fully covered by the entry proposed in Table 5.

Table 5: Classification proposal for copper, with no current entry in Annex VI of CLP.

	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*	029-XXX-X-X	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 (acute) M=1 (chronic)	

* The terms "powder" and "massive" is used in the guidance to draw a line between two theoretical entries. However, specific surface area is in this regard the crucial parameter, i.e. surface area per weight. While these terms (powder and massive) have remained in the guidance, in practice not only spherical copper powder exists on the market. There are different shapes of particles such as powders, flakes, sticks, granulates etc which are all still the same chemical substance. We suggest therefore, to base the proposal on surface area per weight (mm^2/mg).

Table 6: Classification proposal for copper flakes with an existing entry in Annex VI of CLP.

	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	029-019-01-X	copper flakes (coated with aliphatic acid)	-	-	Acute Tox. 4 Eye Irrit. 2 Acute Tox. 3 Aquatic Acute 1 Aquatic Chronic 1	H302 H319 H331 H400 H410	GHS06 GHS09 Dgr	H302 H319 H331 H410		M=10	
Dossier submitters proposal	029-019-01-X	copper flakes (coated with aliphatic acid)	-	-	**Retain** Aquatic Acute 1 Aquatic Chronic 1	**Retain** H400 H410	**Retain** GHS09 Dgr	**Retain** H410		**Modify** M=10 (acute) M=1 (chronic)	
Resulting Annex VI entry if agreed by RAC and COM	029-019-01-X	copper flakes (coated with aliphatic acid)	-	-	Acute Tox. 4 Eye Irrit. 2 Acute Tox. 3 Aquatic Acute 1 Aquatic Chronic 1	H302 H319 H331 H400 H410	GHS06 GHS09 Dgr	H302 H319 H331 H410		M=10 (acute) M=1 (chronic)	

Table 7: Classification proposal for granulated copper, with an existing entry in Annex VI of CLP.

	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 To be deleted.*	~~029-024-00-X~~	~~granulated copper;~~ ~~[particle length: from 0,9 mm to 6,0 mm; particle width: from 0,494 to 0,949 mm]~~	~~231-159-6~~	~~7440-50-8~~	~~Aquatic Chronic 2~~	~~H411~~	~~GHS09~~	~~H411~~		-	

* It is proposed to delete the current Annex VI entry for copper granulate, since copper granulate would be fully covered by the entry proposed in Table 5.

Table 8: Reason for not proposing harmonised classification and status under public consultation

Hazard class	Reason for no classification	Within the scope of public consultation
Explosives	Hazard class not assessed in this dossier	No
Flammable gases (including chemically unstable gases)	Hazard class not assessed in this dossier	No
Oxidising gases	Hazard class not assessed in this dossier	No
Gases under pressure	Hazard class not assessed in this dossier	No
Flammable liquids	Hazard class not assessed in this dossier	No
Flammable solids	Hazard class not assessed in this dossier	No
Self-reactive substances	Hazard class not assessed in this dossier	No
Pyrophoric liquids	Hazard class not assessed in this dossier	No
Pyrophoric solids	Hazard class not assessed in this dossier	No
Self-heating substances	Hazard class not assessed in this dossier	No
Substances which in contact with water emit flammable gases	Hazard class not assessed in this dossier	No
Oxidising liquids	Hazard class not assessed in this dossier	No
Oxidising solids	Hazard class not assessed in this dossier	No
Organic peroxides	Hazard class not assessed in this dossier	No
Corrosive to metals	Hazard class not assessed in this dossier	No
Acute toxicity via oral route	Hazard class not assessed in this dossier	No
Acute toxicity via dermal route	Hazard class not assessed in this dossier	No
Acute toxicity via inhalation route	Hazard class not assessed in this dossier	No
Skin corrosion/irritation	Hazard class not assessed in this dossier	No
Serious eye damage/eye irritation	Hazard class not assessed in this dossier	No
Respiratory sensitisation	Hazard class not assessed in this dossier	No
Skin sensitisation	Hazard class not assessed in this dossier	No
Germ cell mutagenicity	Hazard class not assessed in this dossier	No
Carcinogenicity	Hazard class not assessed in this dossier	No
Reproductive toxicity	Hazard class not assessed in this dossier	No
Specific target organ toxicity-single exposure	Hazard class not assessed in this dossier	No
Specific target organ toxicity-repeated exposure	Hazard class not assessed in this dossier	No
Aspiration hazard	Hazard class not assessed in this dossier	No
Hazardous to the aquatic environment	Harmonised classification proposed	Yes
Hazardous to the ozone layer	Hazard class not assessed in this dossier	No

3 HISTORY OF THE PREVIOUS CLASSIFICATION AND LABELLING

There is no harmonised aquatic environmental hazard classification for copper metal.

There are, however, two different harmonised classifications of two specific physical forms of copper metal in CLP Annex VI, i.e. copper flakes and copper granulate. Harmonised classification of copper flakes (coated with aliphatic acid) was introduced in the Annex VI of Regulation (EC) No 1272/2008 (CLP Regulation) of 19 July 2016 adapting to technical progress for the 9th time, while classification of copper granulate was introduced in the Annex VI by the Commission Delegated Regulation (EU) 2020/1182.

4 JUSTIFICATION THAT ACTION IS NEEDED AT COMMUNITY LEVEL

[B.] Justification that action is needed at Community level is required.

Reason for a need for action at Community level:

Change in existing entry due to new interpretation/evaluation of existing data.

Further detail on need of action at Community level

According to 1.2.3.3 in the Guidance on the Application of the CLP criteria (2017), when it comes to the aquatic environmental hazard classification, physical forms do not represent intrinsic properties of a substance nor warrant their own specific classifications. The current harmonised classifications of copper flakes and copper granulated (two specific forms of the same chemical substance) are therefore not in line with the CLP principles where one classification applies to one substance. This dossier was therefore developed to propose a classification of copper metal (including all forms of copper) in accordance with the CLP and its Guidance on the Application of the CLP criteria and to correct the current classifications of this metal already present on the Annex VI.

Both copper granulate and copper flakes (coated with aliphatic acid) are different forms of copper metal and should be treated as the same chemical substance under the CLP-regulation. Copper granulate has the same CAS- and EC-number as copper in general and a degree of purity of minimum 99.0% (CLH Report, 2017). Copper flakes (coated with aliphatic acid) is a surface treated metallic copper material in the form of flakes and are characterised by a surface coating. According to Echa guidance on substance identification[1]:

"*The surface treatment of a substance is a "two dimensional" modification of macroscopic particles. A "two dimensional" modification means a chemical reaction between the functional groups only on the surface of a macroscopic particle with a substance which is called a surface treating substance. By this definition it becomes clear that this kind of modification means a reaction of only a minor part (surface) of a macroscopic particle with the surface treating substance, i.e. most of the macroscopic particle is unmodified.*"

Consequently, copper flakes (coated with aliphatic acid) should be regarded as mostly unmodified copper particles and treated as copper metal. The registrant, however, regards copper flakes, under REACH, not as a separate form of copper but as downstream use of copper powder (ECI, 2021).

Any specific evaluation of copper in nanoform has not been included in this report. Neither has the classification proposal been based on the particle size of nanoforms. Nanoforms were not considered when the current Guidance on the Application of the CLP criteria (2017) was developed, therefore

---

[1] Q&As - ECHA (europa.eu)

nanoforms are not necessarily covered by the CLP-strategy for metals described in this guidance. Consequently, a specific dossier and hazard evaluation may be necessary for nanoforms of this substance. However, in the absence of any specific aquatic environmental hazard classification for nanoforms of copper, these forms of copper are included in the present proposal, since the specific surface area of nanocopper is > 0.67 mm^2/mg.

5 IDENTIFIED USES

Copper has a large variety of uses. It is used by consumers, in articles, by professional workers (widespread uses), in formulation or re-packing, at industrial sites and in manufacturing. Much of the copper is used in building constructions, for example in wiring, plumbing and weatherproofing. Also the transport sector is dependent on copper, for example as component in motors, wiring, radiators, connectors, brakes and bearings. Another important use of copper is in the manufacturing of electronic products.

Consumer uses of copper consist of, for example, uses of the following products: metals, metal working fluids, welding and soldering products, cosmetics and personal care products, modelling clay, and metal surface treatment products.

Copper is also used as an active substance in biocidal products as reported, for example, in the previous CLH report for copper flakes (coated with aliphatic acid; December, 2013):

"*Coated copper flake was notified under BPD Directive (98/8/EC) as anti-fouling product (product type 21). Coated copper flake is intended for use in the protection against fouling of both mobile (including but not limited to marine and freshwater vessels) and stationary (including but not limited to buoys, aquaculture nets, immersed structures) objects*."

6 DATA SOURCES

The information already available in the 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 the RAC in the RAC opinions on copper flakes (adopted in December 2014) and copper granulate (adopted in June 2018) were also taken into account. Consequently, no new data searches were performed. However, the IUCLID data file has reacently 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 this CLH report. Also, new information on copper in massive and powder forms, including information on particles formed during the reasonable expected use of copper metal achieved from the registrant and included in the REACH registration dossier during the development of this dossier has been used (see Annex I).

7 PHYSICOCHEMICAL PROPERTIES

Most information in the table below is copied (or slightly modified) from the CLH report for Copper, granulated (February 2017). New information in the table is added for "Water solubility", "Partition coefficient n-octanol/water" and "Granulometry".

Table 9: Summary of physicochemical properties

Property	Value	Reference	Comment (e.g. measured or estimated)
Physical state at 20°C and 101,3 kPa	Course, granular solid Red brown Slight, metallic odour	Hughes 2013; Particulate Copper Metal Analysis; Technical Summary Report TSR 13 01	
Melting/freezing point	1059-1069°C	Liipo, J. et al (2010); Characterisation of copper powder, Outotec Research Oy report number 10113-ORC-T	Measured, method EC A.1
Boiling point	Not necessary as boiling point will occur at temperatures greater than 360°C based on the melting point of granulated copper	-	-
Relative density	8.78	Liipo, J. et al (2010); Characterisation of copper powder, Outotec Research Oy report number 10113-ORC-T	Measured, method EC A.3
Vapour pressure	It is not required to test vapour pressure as the melting point is above 300ºC	-	-
Surface tension	Not required for substances with a water solubility of < 1 mg l^{-1}	-	-
Water solubility	Metals (M_0) in their elemental state are not soluble in water but may transform to yield the available form. This means that a metal in the elemental state may react with water or a dilute aqueous electrolyte to form soluble cationic or anionic products, and in the process the metal will oxidise, or transform. Transformation/dissolution tests are therefore necessary and further described in section 11.2	Annex IV of the Guidance on the Application of the CLP criteria (2017).	
Partition coefficient n-octanol/water	Not relevant for metals because metals, in contrast	Annex IV.4 of the Guidance on the	-

Property	Value	Reference	Comment (e.g. measured or estimated)
	to organic substances, are not lipophilic and are not passively transported through cellular membranes.The bioaccumulation of copper has not been considered further, since it does not influence the aquatic environmental hazard classification, see section 11.4.	Application of the CLP criteria (2017).	
Flash point	Not required because the substance is a solid	-	-
Flammability	Not highly flammable based on chemical composition and experience in use. Granulated copper is thermally stable up to 1000°C.	- Liipo, J. et al (2010); Characterisation of copper powder, Outotec Research Oy report number 10113-ORC-T	-
Explosive properties	Based on the chemical composition and experience in use, it is considered that the test according to EC method A.14 would give a negative result for granulated copper.	-	-
Self-ignition temperature	No data	-	-
Oxidising properties	No oxidising properties based on chemical composition and experience in use.	-	-
Granulometry Copper particles are available in different physical forms and particle size distributions. Here are some examples listed.	Copper granulate (from CLH report for Copper, granulated (February 2017)): The length ranges between 0.9 mm and 6.0 mm, with a mean length (on the 150 measured granules) at 2.1mm. 90% of the particles are below 3mm and 50% of the particles are below 2 mm. The width ranges between 0.494 mm and 0.949 mm. There are two maxima at 0.65 mm and at 0.87 mm	Gordon Fern (2015) Particle size distribution by optical and Scanning Electron Microscopy: Copper granules from Arch Timber Report SNP-079	Measured (optical and Scanning Electron Microscopy) The length of the granules has been determined by measuringthe length of 50 granules, this has been repeated three times with different samples of 50 granules. The cross section of the diameter which is equivalent to the width of the granule (viewed top-down) has been determined by a SEM analysis. The three previous samples have been used. Granule width

Property	**Value**	**Reference**	**Comment (e.g. measured or estimated)**
	with an average particle width (on the 150 measured granules) at 0.706 mm. 90% of the particles are below 0.9 mm and 50% of the particles are below 0.65 mm.		was measured at 3 points along the length.
	Copper flakes (from CLH reports for copper flakes (coated with aliphatic acid; December, 2013): No data	-	-
	Copper powder 1 (QMineral): d_{10}: 4.083 µm d_{50}: 10.84 µm d_{90}: 16.25 µm	ECTX (2020) Study number X01-296	Measured using laser diffraction after wet dispersion.
Stability in organic solvents and identity of relevant degradation products	Not required. The substance as manufactured does not include any organic solvents.	-	-
Dissociation constant	Not relevant, metallic copper cannot dissociate in water, due to its structure. Granulated copper is slightly soluble in water and the solubilisation results of oxido- reduction reaction of the copper metal into ionic copper. Any addition of acid would result in reaction with the copper	-	-
Viscosity	Not required because the substance is a solid	-	-

8 EVALUATION OF PHYSICAL HAZARDS

This part was not evaluated in this CLH report and no classifications for physical hazards are proposed.

9 TOXICOKINETICS (ABSORPTION, METABOLISM, DISTRIBUTION AND ELIMINATION)

This part was not evaluated in this CLH report.

10 EVALUATION OF HEALTH HAZARDS

This part was not evaluated in this CLH report and no classifications for health hazards are proposed.

11 EVALUATION OF ENVIRONMENTAL HAZARDS

The aquatic environmental hazard assessment of copper is based on the information provided and evaluated in the CLH report for copper flakes (coated with aliphatic acid; December, 2013) and in the CLH report for copper, granulated (February, 2017). Additionally, the conclusions drawn by the RAC in the RAC opinions on copper flakes (adopted in December 2014) and copper granulate (adopted in June 2018) were also taken into account. No new ecotoxicity data is available. However, additional transformation/dissolution data, presented in the updated REACH registration dossier of copper, February 2021, has been included in the dossier. Additionally, new information on copper in massive and powder forms achieved from the registrant during the development of this dossier has been used (see Annex I).

The aim of this environmental hazard assessment of copper is not to re-evaluate the data, but rather to interpret all available information according to the CLP principles and Guidance on the Application of the CLP criteria to arrive at a harmonised classification for copper, i.e. irrespective of its particle size and form, see also section “4. Justification that action is needed at community level”.

11.1 Rapid degradability of organic substances

Not applicable since copper is an inorganic substance.

11.2 Environmental transformation of metals or inorganic metals compounds

Based on the Guidance on the Application of the CLP criteria (2017) the classification strategy for metals is based on a comparison of acute and chronic Ecotoxicity Reference Values, 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 (OECD 2001, as included in UN GHS, 2019, Annex 10).

Several Transformation/Dissolution studies at different pH have been performed, using copper particles of varying sizes and shapes. All transformation-dissolution studies are attached to the IUCLID file section 5.6 “Additional information on environmental fate and behaviour”. Some of these studies have been evaluated earlier in the CLH report of Copper, Granulated (February, 2017), in the CLH report of Copper flakes (December, 2013) or in the RAC Opinion of Copper flakes (December 2014), whereas others have not been included in any CLH report earlier. All available studies, including new studies, included in the updated REACH registration, are summarised below. Since copper ion release is pH dependent the data have been compiled for pH 6, pH 7 and pH 8 in the first three tables below. Thereafter short summaries of all studies are presented in a chronological order. In addition, the study summaries discuss shortly the applicability of their results in the classification of copper. The overall conclusion on how these studies are used in the current proposal is presented after the list of short study summaries (in the section “Selection of transformation-dissolution data for environmental hazard classification of copper”).

The transformation/dissolution tests were performed using a specific surface-based concept. This implies that the release of copper from a given material to the media depends on the exposed surface area. The copper release in transformation-dissolution tests is therefore expressed per unit surface area.

Table 10: 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 et al. 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 et al. 2011	7	46.69	0.41	Massive metal embedded in epoxy resin.
Rodriguez et al. 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 D_{50} 11 µm
ECTX (X01-281) 2019	7	340	0.324	Copper powder with dendritic (branched) shape, D_{50} 26 µm
ECTX (X01-282) 2019	7	28	1.289	Copper powder D_{50} 30 µm
ECTX (X01-296) 2020	7	60	1.833	Copper powder D_{50} 11 µm
	28	60	5.817	
Skeaff & Hardy 2005	7	107	0.77	High variability. Surface area of particles measured by BET. Particle size: 100% <160 µm, 77.3 % <50 µm
	7	10700	0.1	
Schäfer 2014	7	2080-2900*	0.35**	Coated copper flakes, D_{50}: 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 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 mm^2/mg.

** Calculated from data in Schäfer 2014 and surface loading (see *); 721 (µg Cu/L)/2080 (mm^2/L) = 0.35 µg 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 (µg Cu/L)/2080 (mm^2/L) = 0.37 µg Cu/mm^2.

Table 11: 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 et al. 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 et al. 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 D_{50} 11 µm
	28	60	2.083	
Schäfer 2014	7	2080-2900*	0.17**	Coated copper flakes, D_{50}: 9-11 µm.
	28	2080-2900*	0.31***	

* 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 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 mm^2/mg.
** Calculated from data in Schäfer 2014 and surface loading (see *); 363 (µg Cu/L)/2080 (mm^2/L) = 0.17 µg 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 (µg Cu/L)/2080 (mm^2/L) = 0.31 µg Cu/mm^2.

Table 12: 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 et al. 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 et al. 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 D_{50} 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 override 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 specific surface area (SSA) was **107 mm^2/mg** measured by BET. 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%). Skeaff & Hardy noted that the high variability may have been related to abrasion of the particles, which causes increased copper release to solution and should be avoided according to the transformation/dissolution protocol (GHS). Additionally, the study was performed with few replicates (n=2) which probably contributed to the high variation.

Based on a SSA of 107 mm^2/mg, the release per unit surface was 0.77 µg Cu/mm^2 in the experiment with 1 mg/L mass loading, and 0.10 µg Cu/mm^2 in the experiment with 100 mg/L mass loading. Despite the high uncertainty, it can be observed that the release per unit surface area is somewhat lower at high surface loadings. This is in line with the findings by Rodriguez et al. (2011, 2012). Given the variability (high coefficients of variation), these 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); "*Normally, the classification data generated would have used the smallest particle size marketed to determine the extent of transformation*". In Skeaff & Hardy (2005) the specific surface area of the particles was measured with two different methods. The specific surface area was 107 mm^2/mg measured by BET, which is the method recommended for specific surface area analysis in OECD (2001) and in Annex 10 of GHS (2019). Consequently, the particles used in the study by Skeaff & Hardy (2005) are considered to be the smallest representative particles available on the market, see further information about the selection of the smallest representative particle size in section "Selection of transformation-dissolution data for environmental hazard classification of copper" below.

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 guidance document 29 (2001). The test was conducted 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. Similarly, 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 mm^2/mg), resulting in rather low release per square millimeter.

Rodriguez et al. (2007)

This study has not been evaluated nor used in any proposal for harmonised classification earlier.

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 mm^2/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. For this reason, the authors suggest to adopted the specific surface area approach for the aquatic environmental hazard classification of copper, meaning that the release of copper in transformation-dissolution tests is expressed per unit exposed surface area.

Rodriguez et al. (2007) furthermore 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 2001).

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 (mm^2/L) during the test. From tests conducted at surface loadings between 1.2 and 281 mm^2/L (corresponding to mass loadings between 1 and 100 mg/L), the average surface–specific copper release (µg dissolved Cu /mm^2 exposed) were:

- 1.15 µg Cu/mm^2 after 7 days T/D tests at pH 6
- 0.19 µg Cu/mm^2 after 7 days T/D tests at pH 7
- 0.13 µg Cu/mm^2 after 7 days T/D tests at pH 8
- 4.2 µg Cu/mm^2 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 Guidance document (OECD 2001) and abrasion of the massiv copper particles were not excluded.

Rodriguez et al. (2011)

This study has not been evaluated nor used in any proposal for harmonised classification earlier.

The study was conducted using massive copper samples at a surface loadings of 43-47 mm^2/L, at pH 6 and during 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 (pp) 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. For 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/mm^2, compared with samples with pp wheels. A methodology to embed the massiv copper in epoxy resin is therefore to prefer compared to a methodology using pp wheels.

Rodriguez et al. (2012)

This study has not been evaluated nor used in any proposal for harmonised classification earlier.

The study was conducted using copper in massive form at a surface loading of 0.67 mm^2/L, equivalent to the surface of spheres of 1mm 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 during 28 days in 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/mm^2 after 7 days of test (acute endpoint) and 5.0 µg/mm^2 after 28 days of test (chronic endpoint).

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 nor used in any proposal for harmonised classification earlier.

The study was conducted using copper in massive form (wire with 1.35 mm diameter) at a surface loading of 0.67 mm^2/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 of the low copper release obtained at both pHs close to the method detection limit, estimated to be 0.2 µg/L for both, pH 7 and pH 8.

The results from pH 7 showed copper release of 0.6 µg/mm^2 after 7 days of test (acute endpoint) and 1.2 µg/mm^2 after 28 days of test (chronic endpoint). At pH 8 the copper release was below the method detection limit (0.2 µg/L) after 7 days of test and 0.9 µg/mm^2 after 28 days of test.

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 in this study.

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 mm^2/mg**. The longest pieces of the granulated copper particles were used is 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 Cu release than the first experiment (ECTX 2016a, see above). This second study was therefore retained for classification purpose of granulated copper. The results of this study is presented below:

- 1.3 µg Cu/mm^2 after 7 days T/D tests at pH 6
- 0.88 µg Cu/mm^2 after 7 days T/D tests at pH 7
- 0.45 µg Cu/mm^2 after 7 days T/D tests at pH 8
- 5 µg Cu/mm^2 after 28 days T/D test at pH 6
- 3.3 µg Cu/mm^2 after 28 days T/D tests at pH 7
- 1.9 µg Cu/mm^2 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 nor used in any proposal for harmonised classification earlier.

The OECD Test Guidance No. 29 (2001) was applied to determine the rate of dissolution of three different copper powders;

a) copper powder with D_{50} 11 µm and a specific surface area of **60 mm^2/mg**,

b) a special copper powder with dendritic (branched) shape, with D_{50} 26 µm and specific surface area of **340 mm^2/mg**, and

c) copper powder with D_{50} 30 µm and a specific surface area of **28 mm^2/mg**.

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

The average surface–specific copper release (µg dissolved Cu /mm^{2}exposed) after 7 days (at pH 6) were:

- Copper powder a) 1.223 µg Cu/mm^2
- Copper powder b) 0.324 µg Cu/mm^2
- Copper powder c) 1.289 µg Cu/mm^2

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

ETCX (2020; study no. X01-296)

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

The OECD (2001) Test Guidance No.29 was applied to determine the rate of dissolution of a copper powder with D_{50} 11 µm and a specific surface area of **60 mm^2/mg** (same as copper powder a) in ETCX (2019); see above). The powder was tested at 1 mg/L mass loading (equals 60 mm^2/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 /mm^{2}exposed) after 7 days were:

- 1.833 µg Cu/mm^2 at pH 6
- 0.675 µg Cu/mm^2 at pH 7
- 0.623 µg Cu/mm^2 at pH 8

And after 28 days:

- 5.817 µg Cu/mm^2 at pH 6
- 2.083 µg Cu/mm^2 at pH 7
- 1.733 µg Cu/mm^2 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 7 and 28 days.

Selection of transformation-dissolution data for aquatic environmental hazard classification of copper

For aquatic environmental hazard classification, a reliable transformation/dissolution dataset should be selected. The overall conclusion on how the available studies are used to derive relevant transformation/dissolution data to be used in the current proposal for aquatic environmental hazard classification of copper is presented below.

- **pH**

In accordance with Annex IV. 2.3 in the Guidance on the Application of the CLP criteria (2017) when more extensive toxicity/dissolution datasets are available, the transformation/dissolution data can be split into pH-categories, which could be compared with ecotox data at similar pH. The ecotoxicity dataset for copper is extensive (and the same as for earlier evaluations of copper). Further, the ecotoxicity seems to be affected by pH (see section 11.5.1-11.6.3). Additionally, the transformation/dissolution dataset is more extensive than earlier evaluations of copper (see Table 10, Table 11 and Table 12). Based on this, it is appropriate to split the transformation/dissolution data into three pH-categories; pH 6, pH 7 and pH 8, and to compare these data with ecotox data at similar pH. This approach is also in accordance with previous copper evaluations (CLH report of Copper flakes, December, 2013 and CLH report of Copper, Granulated, February, 2017) and the RAC Opinions of the earlier copper evaluations (RAC Opinion (2014) and RAC Opinion (2018)). This is also consistent with the conclusion in the registration dossier, see ECI (2021).

According to the Annex IV. 2.2.3 in the Guidance on the Application of the CLP criteria (2017), the Full Transformation Dissolution test should be carried out at the pH that maximises the concentration of dissolved metal ions in solution and that expresses the highest toxicity. It should be noted that the transformation/dissolution protocol (OECD 2001, as included in UN GHS, 2019, Annex 10) specifies a pH range of 6-8.5 for the 7 days test and 5.5 to 8.5 for the 28 days test. In contrast to this guidance, the available transformation/dissolution tests are performed at a pH of 6 as the lowest. Since the copper solubility is higher in lower pH it could be expected that the dissolution of copper should have been even higher if the available 28 days tests had been performed at pH 5.5 (compared to as now, pH 6).

Conclusion: Transformation/dissolution data at different pH (pH 6, pH 7 and pH 8) should be compared with ecotox data at similar pH.

- **Particle size and specific surface area**

Copper metal can be placed on the market in different physical forms. Physical forms do not represent intrinsic properties of a substance. Consequently, the aquatic environmental hazard classification should not depend on the physical form. Both copper granulate and copper flakes (coated with aliphatic acid) are examples of different forms of copper metal and should therefore be treated as the same chemical substance as other physical forms of copper under the CLP-regulation, as earlier described in section 2.1 and 4.

According to Annex IV 5.5 in the Guidance on the Application of the CLP criteria (2017); "*Normally, the classification data generated would have used the smallest particle size marketed to determine the extent of transformation.*"

In the T/D-studies compiled above several different particle sizes with different specific surface areas have been tested. The smallest particles available on the market are the coated copper flakes. According to ECI (2021), coated copper flakes have particle diameters of 5 - 100 μm. If assuming spherical particles, the specific surface area would be 135 - 6.7 mm^2/mg. However, the surface coating of the flakes results in the formation of extremely high specific surface areas (2080 -2900 mm^2/mg), much higher than the specific surface area predicted from the smallest particle size and assuming spherical particles (135 mm^2/mg). This is the result of the specific "coated copper flakes" production process, which yields fine flakes, characterized by a high specific surface area and organic coating. Additionally, coated copper flakes are only a very marginal part of the total amount of copper produced (personal com. Stijn Baken, The Copper Alliance, e-mail 2020-04-21 and ECI 2021).

Due to the specific production method required to yield particles with such a high specific surface area and due to the limited production of these particles compared to other copper particles, the coated copper flakes are not considered here to be the smallest representative copper particle to base aquatic environmental hazard classification upon.

Another small particle tested with a high specific surface area of 340 mm^2/mg was a special copper powder with dendric (branched) shape, with D_{50} 26 µm (ECTX, 2019). Neither this particle size is considered here as the smallest representative, mainly due to its peculiar shape that results in a specific dissolution pattern, different from the other particles. The specific shape of this powder 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.

Instead, the smallest representative copper particle is reported from the study by Skeaff and Hardy (2005). In this study the specific surface area of the particles was measured with two different methods. The specific surface area was 107 mm^2/mg measured by BET, which is the method recommended for specific surface area analysis in OECD (2001) and in Annex 10 of GHS (2019). If assuming spherical particles, this specific surface area represent particles with a diameter of approximately 6 µm (calculated based on copper density of 8926 kg/m^3 and a SSA of 107 mm^2/mg) thus representing “the smallest representative copper particle available on the market”. Consequently, this particle size and its specific surface area is regarded here as the smallest representative particle which should be used in the aquatic environmental hazard classification of copper.

This conclusion is not consistent with the information in the registration dossier. The registrant in its document on environmental hazard classification does not include the particle of 107 mm^2/mg in its discussion on the smallest particle size sold although the study by Skeaff and Hardy (2005) is a part of the data set. Instead, the registrant considers the particle with the specific surface area of 60 mm^2/mg used in the test of ECTX (2019 and 2020) as the smallest representative particle size sold. Since there is no information available that would disregard the relevance of the particle tested by Skeaff and Hardy (2005), e.g. by showing that it is not longer available on the market, this current classification proposal considers the particle with a specific surface area of 107 mm^2/mg as the smallest representative particle size sold.

Conclusion: The smallest representative copper particle has a specific surface area of 107 mm^2/mg.

- **Separate classifications for massive copper and copper powder**

According to Annex IV 5.5 in the Guidance on the Application of the CLP criteria (2017);
“*There may be cases where data generated for a particular metal powder are not considered as suitable for classification of the massive forms. For example, where it can be shown that the tested powder is structurally a different material (e.g. different crystallographic structure) and/or it has been produced by a special process and is not generally generated from the massive metal, classification of the massive can be based on testing of a more representative particle size or surface area, if such data are available. The powder may be classified separately based on the data generated on the powder. However, in normal circumstances it is not anticipated that more than two classification proposals would be made for the same metal.”*

Additionally, according to section 1.2.2. in the Guidance on the Application of the CLP criteria (2017) the term “reasonable expected use” in relation to hazard classification is described as;

- *“Any process, including production, handling, maintenance, storage, transport or disposal.*
- *All technical operations/manufacturing activities like e.g. spraying, filing, and sawing.*
- *Any putative consumer contact through e.g. do-it-yourself or household chemicals.*
- *All professional and non-professional uses including reasonably foreseeable accidental exposure, but not abuse such as criminal or suicidal uses.*

Reasonably expected use is also related to any consumer disposal or any work in which a substance or mixture is used, or intended to be used irrespective of its present limited use or use pattern. Thus, use should not be mixed up with usage category."

Consequently, to consider the criteria for accepting a split classification for massive metal and metal powder to be fulfilled, 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.

Massive copper and copper powder is not structurally different from each other, but other arguments for separate classifications for copper powder and copper massive have been added by the registrant into the registration dossier for copper (see section 2 of The environmental hazard classification of Copper; ECI (2021)), also included as Annex I in this document. In summary, the registrant argues that;
"…it is concluded that 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. This is the only way in which copper powder is produced"

Further the registrant argues:
"The characterization of mechanical properties of metals is complex. When considered in in isolation, none of the above measurements may be sufficient to fully characterize the potential for generating powder from a massive metal. However, when considered together, the ductility, elongation, malleability, resistance to fracture, and softness of copper illustrate a consistent picture: there is no potential for forming powder from massive copper. These properties all confirm that copper metal does not break apart into smaller pieces under mechanical stress. Rather, when exerting mechanical forces on copper, the material is bent and deformed to yield a different shape. As a consequence of these properties, copper does not break apart during mechanical processes, handling, storage, transport, processing and use. 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 (see section 2.2)."

The registrant concludes:
"Therefore, the conditions are fulfilled for deriving separate environmental classifications for copper in powder and massive forms."

The information presented in section 2 of ECI (2021) and included as Annex I, is considered relevant and conclusive to accept split classifications for massive copper (with a specific surface area of 0.67 mm^2/mg or less, representing particles with a diameter of 1 mm or more) and copper powder (with a specific surface area of more than 0.67 mm^2/mg). This is based on information that copper powder is produced by a special process (atomization), where massive metal is melted and thereafter atomized during exposure to air-, inert gas-, or water jets. The production of copper powder requires these specific steps in the process. Furthermore, the registrant has informed that copper is a mallable and ductile metal that does not break apart during handling, storage, transport, processing and use. 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 copper powder is generated or produced. From photos of the sizes of the produced chips from some of these processes we conclude that it is unlikely that sufficient amounts of copper particles with a specific surface area of more than 0.67 mm^2/mg are produced in these processes. However, it could strengthen the argument further if we also had specific measurements of the surface area per weight for these particles. Additionally, the registrant only refers to industrial processes for the absence of generation of small copper particles (specific surface area >0.67 mm^2/mg) from massive metal. No information is available considering generation of small copper particles from a broader range of use (e.g. consumer use). However, we consider that the battery of industrial processes described by the registrant, also generally cover a broader range of use described by the term “reasonable expected use”, since several of these processes (e.g. cutting and finishing) also could be expected to be applied by non-professional users. Consequently, we conclude that small copper particles (specific surface area >0.67 mm^2/mg) is not generally generated from the massive metal.

Conclusion: A split classification is justified since copper powder is produced by a special process and copper particles with an specific surface area > 0.67 mm^2/mg are not generally generated from the massive metal during reasonable expected use.

- **Selection of relevant studies and summary of transformation/dissolution data used for aquatic environmental hazard classification of copper massive and copper powder**

Based on the conclusions above, we conclude that transformation/dissolution data from different pH (pH 6, pH 7 and pH 8) should be compared with ecotox data at similar pH. Further, separate classifications can be used for massive copper and copper powder. For the evaluation of copper powder, the copper particle with a specific surface area of 107 mm^2/mg should be used to represent the smallest representative copper particle on the market.

For aquatic environmental hazard classification, a representative transformation/dissolution dataset should be selected and for acute aquatic hazard, 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) (as required by the GHS transformation-dissolution protocol and in CLP classification schemes).

For powder, the study by ECTX (2020) is regarded as the most reliable dataset to derive the classification of copper powder. This is a full 28-day transformation/dissolution test at each pH that fulfills the validity criteria and has a low variability. Additionally, the transformation/dissolution in this study is high but still rather similar to e.g. ECTX (2016b), which is another reliable study. Also the specific surface area of the particles in ECTX (2020), 60 mm^2/mg, is rather close to the specific surface area of the smallest representativ particle, 107 mm^2/mg. The study by ECTX (2020) was also used in the registration dossier (ECI 2021) to derive the classification of copper powder. However, in the registration dossier, the transformation/dissolution data from ECTX (2020) was used as such for classification of powder and was not recalculated to indicate transformation/dissolution from particles with a higher specific surface area. See Table 13 for relevant transformation/dissolution data used in the current proposal for aquatic environmental hazard classification of copper powder.

Massive copper particles are defined as particles with a diameter of 1 mm or more and, assuming spherical particles, the specific surface area is 0.67 mm^2/mg or less. As transformation/dissolution data should be derived at a mass loading of 1 mg/L and 0.1 mg/L this corresponds to a surface loading of 0.67 mm^2/L and 0.067 mm^2/L, respectively. The transformation/dissolution dataset by Rodriguez et al. (2012 and 2017) were obtained for copper massive at the surface loading of 0.67 mm^2/L. These are therefore the most reliable datasets to derive the aquatic environmental hazard classification of copper massive. This is in agreement with the proposal by the registrant in the registration dossier (ECI, 2021). See Table 14 for relevant transformation/dissolution data used in the current proposal for aquatic environmental hazard classification of copper massive.

Table 13: Transformation/dissolution data used in the current proposal for aquatic environmental hazard classification of copper powder. Based on transformation/dissolution data from ECTX (2020).

Testing 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/mm^2 x SSA of 107 mm^2/mg x mass loading of 1 mg/L
** Extrapolated linearly from mass loading of 1 mg/L

Table 14: Transformation/dissolution data used in the current proposal for aquatic environmental hazard classification of copper massive. 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 µg Cu/mm^2 x SSA of 0.67 mm^2/mg x mass loading of 1 mg/L
** Extrapolated linearly from mass loading of 1 mg/L

In addition, the 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 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) below). 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 µg Cu/mm^2. This is with the exception of the data points mentioned below.
- The copper release at pH 6 after a 28-day test range 4.2—5.8 µg Cu/mm^2.

A linear regression on the log-transformed data allowed the registrant to derive the following equations for pH 6:

- Log [Copper release after 7 days in µg/L] = 0.16 + 0.98 * Log [Surface loading in mm^2/L]
- Log [Copper release after 28 days in µg/L] = 0.70 + 1.03 * Log [Surface loading in mm^2/L]

Some data points deviate somewhat from the observed trend and were not included by the registrant in the above regressions. This is considered by the registrant as a conservative choice, since these data points had lower release than expected based on the overall trend. The registrant argues that the dendritic copper powder tested by ECTX (2019) does not follow the trend exhibited by the other, more typical copper powders. This is likely a consequence of 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. In addition, 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.

We find the linear regressions by the registrant relevant and suggest that these could be used to support the conclusions for the aquatic environmental hazard classification of copper. Below is the linear regression diagrams from ECI (2021) inserted:

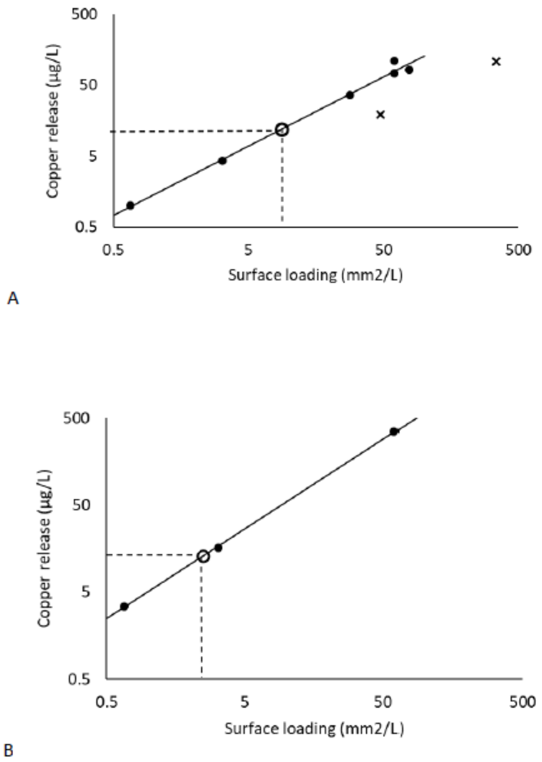


Figure 17: Copper release in 7-day (A, top) and 28 day (B, bottom) transformation-dissolution tests at pH 6, plotted against the surface loading. Full lines are linear regressions on the log-transformed data, where data points indicated by an X were not considered. Open circles and dashed lines indicate the acute (A, top) and chronic (B, bottom) critical surface area. Data from Table 7.

11.2.1 Summary of data/information on environmental transformation

The summary of the transformation/dissolution data used in the current proposal for aquatic environmental hazard classification of copper powder and copper massive is presented in Table 13 and Table 14.

11.3 Environmental fate and other relevant information

The main part of the text in this section consists of information reproduced from the CLH report on Copper, granulated (February, 2017). No new relevant information on environmental fate is available. After the publication of the CLH report on Copper, granulated (February, 2017) the concept of rapid removal has been discussed and conluded not appropriate to be used for hazard assessments, both by RAC (RAC opinion on Granulated Copper, June, 2018) and Caracal (November 2019, CA/68/2019).

The following information was included in the CLH report of Copper, granulated (February, 2017):

In soil

Metals are natural elements and are therefore, by definition, not degradable. It is therefore not possible and not relevant to define a route and a rate of degradation in soils as usually made for organic compounds.

However, copper can be present under different forms, most of which are strongly bound to inorganic and organic ligands contained within soil and sediments; while a marginal fraction of copper is present as various species in the soil solution. The fate and behaviour of copper, as its bio availability, strongly depend on the distribution of these different forms.

The distribution and equilibrium between the different forms of copper in soil depend on many factors, such as soil pH, texture and organic matter content. If the mobile, active and toxicologically significant substance is mainly the free copper ions Cu^{2+} present in the soil solution, it is not possible to predict how much this form will represent from the total applied amount of copper. The activity of the free copper ion will steadily increase with decreasing pH for instance, while the contribution of complex species will decrease. The binding affinities of Cu^{2+} with organic or inorganic matter are also dependent on the presence of competing metal ions and inorganic anions.

In water

In water, copper cannot be transformed into related metabolites or degradation products and consequently hydrolysis and biodegradation processes in water will have no action on copper in this respect. Although unable to degrade, copper is subject to chemical transformation processes with a wide array of materials so that the vast majority of copper in aquatic systems is rapidly bound to mineral particles, precipitated as insoluble inorganic salts, or bound to organic matter. In pure water very low levels of the free Cu^{2+} ion are present in solution, with amounts governed by the propensity of the metal cation to hydrolysis in water, as shown in the following equation:

$$Cu(H_2O)_6^{2+} + H2O \leftrightarrow CuOH(H_2O)_5^{+} + H_3O^{+}$$

The reaction is pH dependent with a distribution constant equal to 6.8. Therefore, below pH 5.8 the predominant form will be $Cu(H_2O)_6^{2+}$, whilst above pH 7.8, the predominant form will be $CuOH(H_2O)_5^{+}$. This latter form of copper is an inorganic complex for which a wide range of other possible types could be formed in natural water, with either cupric or cuprous ions and a range of inorganic ligands (e.g. OH^-, HCO^{3-}/CO_3^{2-}, $H_2PO_4^-/HPO_4^{2-}$, Cl^-, SO_4^{2-} and S^{2-}) and organic ligands (e.g. humic and fulvic acids) associated with dissolved organic matter. In natural water, the solubility of copper is regulated primarily by the formation of malachite ($Cu_2(OH)_2CO_3$) at pH < 7 and by tenorite (CuO) at pH > 7. The concentration of Cu^{2+} ions in solution will be higher at low pH, however, the exact concentration will depend considerably on the type and concentration of ligands present in water.

Copper entering a water body is rapidly bound to material in the water phase resulting in very low levels of free Cu^{2+} ion in solution. In a water-sediment system, total copper was re-distributed from the surface water to the sediment, at a worst case dissipation rate of 30.5 days (considered as a DT50 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. Within the soluble water phase, complexation process reduces the actual amount of copper, available for uptake by biological organisms.

In the Guidance on the Application of the CLP criteria (version 4.1, June 2015), section IV.3, it is stated that:

"*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. In addition 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 extensive for metals. Using the principles and assumptions discussed above in Section IV.1 of this document, it may be possible to incorporate this approach into classification. Such assessments are difficult to give guidance for and will normally be addressed on a case-by- case approach. However, the following may be taken into account:*

a. Changes in speciation if they are to non-available forms, however, the potential for the reverse change to occur must also be considered;
b. Changes to a metal compound which is considerably less soluble than that of the metal compound being considered."

In the sediment compartment, copper binds to the sediment organic carbon (particulate and dissolved) and to anaerobic sulphides, resulting in the formation of CuS. CuS has a very low stability constant/solubility limit (LogK=-41 (Di Toro *et al.,* 1990) – see section 5.2.1 *Adsorption/Desorption* of this report) and therefore the 'insoluble' CuS keeps copper in the anaerobic sediment layers, limiting the potential for remobilisation of Cu-ions into the water column Simpson et al (1998) and Sundelin and Erikson (2001).

In order to demonstrate removal from the water column to assess the "persistence" or lack of degradation of metal ions, responsible for the toxicity of metals and metal compounds (> 70% removal within 28 days), the registrants provided the study of Rader *et al*., 2013. The summary of this study is not detailed in this dossier considering the conclusion of the RAC opinion:

"RAC considers that the TICKET-Unit World Model (UWM) [which describes partitioning to dissolved organic carbon, particulates, etc., deposition and transformation to sulfides in sediment] *provides a useful insight into key fate pathways for metal ions including copper in a model shallow lake system. This generic approach allows systematic comparisons to be made between metals. However, the choice of model defaults is open to question, especially as some properties are likely to vary spatially and temporally. For example, comparison with monitoring data in the CLH dossier suggests that the model may overestimate the extent to which copper binds to particles, and may use a settling velocity that is higher than observed in reality. In*

addition, post-loading simulations for one field study that was claimed to be "more representative of a worst case scenario" (on the basis of settling velocity, distribution coefficient and a relatively low suspended solids concentration compared to model defaults) did not predict 70% removal from the water column after 28 days. As this was a natural lake, RAC does not agree that it should be dismissed as a "worst case". Since the concept of rapid degradation for organic substances is conservative and does not include sequestration by particulate matter (or other fate pathways such as volatility), it seems inconsistent to apply such approaches to metals.

The proposal also relies heavily on the premise that copper (II) ions will partition rapidly to sediment, where they will be transformed at the surface to insoluble minerals (especially copper (II) sulfide) over a relatively short timescale so that binding to sediment is effectively irreversible. RAC notes that the proposal does not describe the behaviour of copper (II) ions in aquatic systems with little or no sediment (e.g. rivers or lakes with sand or gravel substrates), high turbulence or sediment at depths substantially in excess of 3 metres. Even where sediment is present, the oxidation state of surface layers may not always favour sulfide formation, and the situation may also be complicated if there is a high level of existing metal contamination. RAC therefore does not consider that a convincing case has been made that copper (II) ions will always rapidly speciate to non-available forms, or that this process has been demonstrated to be irreversible under all relevant circumstances.

In conclusion, RAC considers that copper (II) ions are not subject to rapid environmental transformation for the purposes of classification and labelling."

This conclusion could also be applied to granulated copper.

In their updated Copper REACH registration dossier (dated 18/01/2017), the applicants consider that newly available evidence, part of which has not been considered by RAC in the previous discussion of copper and copper compounds, demonstrates that under "environmentally relevant" conditions, more than 70 % of dissolved copper is removed within 28 days. Copper is transformed to sulfide complexes (Cu-S) which are stable. Remobilisation of Cu to the water-column is not likely to occur. Copper is therefore considered rapidly removed, conceptually equivalent to "rapid degradation" for organic substances.

As there is no new guidance available about the "rapid removal concept" for metal compounds, these new considerations were not further considered in this dossier.

Summary and discussion of degradation

Considering the fate and behavior of copper in soil and water compartments, 'degradation' of copper is a complex processes (bioavailability depending on distribution and equilibrium). The granulated copper could not be subject to rapid environmental transformation for the purpose of classification and labelling.

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, considering the fate and behavior of copper in soil and water compartments, 'degradation' of copper is a complex processes (bioavailability depending on distribution and equilibrium). Copper could therefore not be subject to rapid environmental transformation for the purpose of classification and labelling.

11.4 Bioaccumulation

No new evaluation considering bioaccumulation is presented in this CLH report. The following was reported in CLH report for Copper, granulated (February 2017);

> Based on its log Pow of 0.44, no concern over any potential for bioaccumulation could be concluded for copper compounds. No study is therefore available to determine bioconcentration factors in fish.
>
> Because of homeostasis of metals in vertebrates, BCF values are not indicative of potential bioaccumulation.
>
> The EU RAR (2008) provided detailed information on (1) the essentiality of copper; (2) the homeostatic control of copper; (3) the mechanisms of action of copper-ions; (4) the comparison between copper toxicity from dietary versus waterborne exposures. These data demonstrate that:
>
> - Copper is an essential nutrient for all living organisms
> - Copper ions are homeostatically controlled in all organisms and the control efficiencies increase with trophic chain.
>
> As a consequence:
>
> - copper BCF/BAF values
>   - decrease with increasing exposure concentrations (water and food)
>   - vary depending on nutritional needs (seasonal, life stage, species dependent)
>   - vary pending on “internal detoxification” mechanisms
> - Copper BMFs values are < 1
>
> Water-borne exposure (not diet borne exposure) is the exposure route critical to copper toxicity.
>
> In the RAC opinions on copper flakes and nine copper compounds adopted in December 2014, it is stated that “*The bioaccumulation behavior of copper (II) ions is complicated by essentiality and homeostatic mechanisms in organism. […]. However, in view of the degradability conclusion, this end-point does not influence the determination of the chronic M-factor and so is not considered further*.”

Further, in the RAC opinion on Granulated Copper (June 2018) it is 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*).

11.5 Acute aquatic hazard

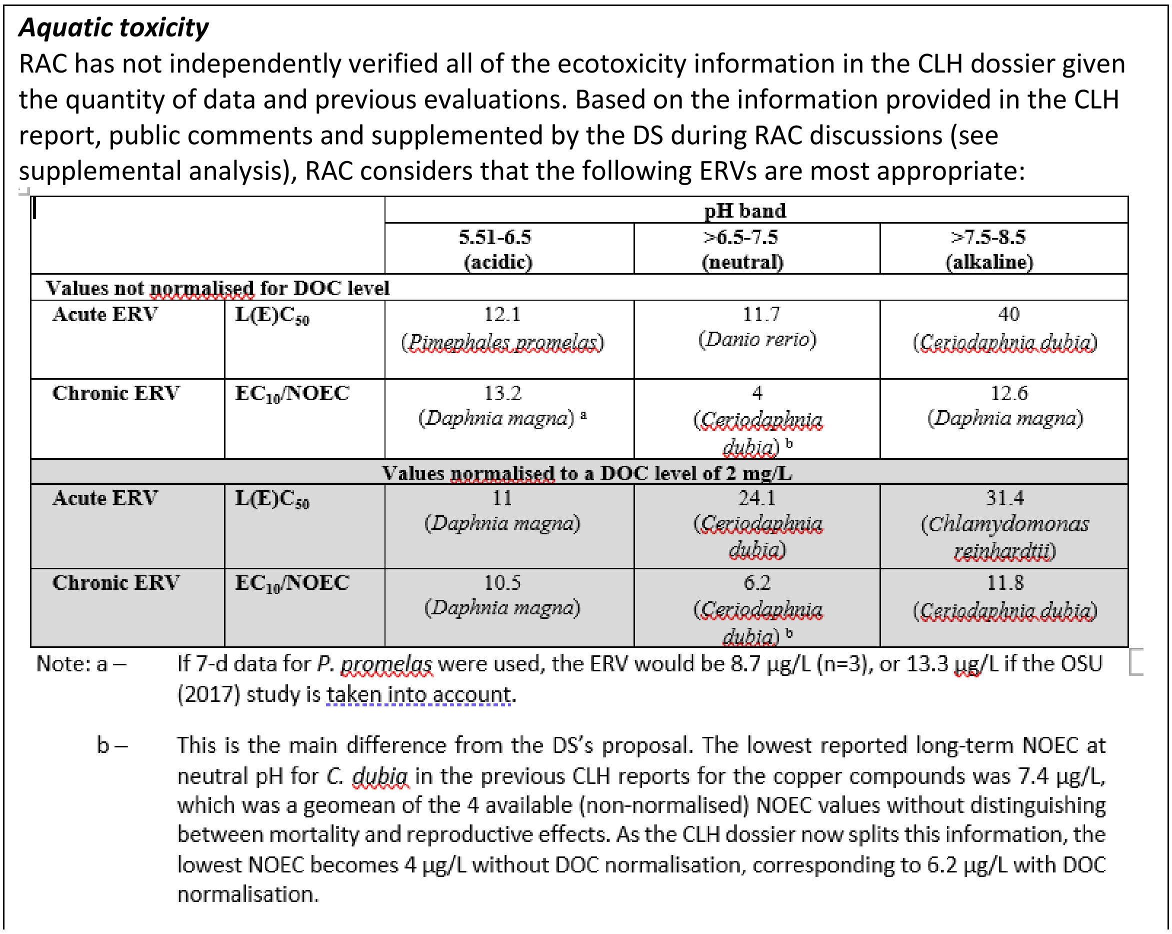
The aquatic ecotoxicity data is taken from section “5.4 Aquatic Toxicity” and section “7 Annexes” of the CLH report for copper, granulated (February, 2017). Since that time, no additional nor new data have become available. The same data is also included in the registration dossier. For the case of transparency, section “5.4 Aquatic Toxicity” and section “7 Annexes” in the CLH report for copper, granulated (February, 2017) is included in Annex II and Annex III, respectively, of the current CLH report.

No new evaluation of the data was performed in the current dossier. Instead, the assessment of the data and the conclusions on aquatic toxicity data regarding ERVs drawn by the RAC in its opinion on copper granulate (adopted in June 2018) are used in the current classification proposal. The data is considered valid and complete for comparison with the classification criteria.

The ERVs from RAC opinion on copper granulate (adopted in June 2018) are slightly different from those ERVs used in the earlier RAC opinion on copper flakes (adopted in 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 RAC opinion on copper granulate a geomean of the LC_{50} for this species was used instead and resulted in a 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 (adopted in December 2014). This ERV was based on a geomean of 4 available (non-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.

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 environmental hazard classification.

Below the conclusions on aquatic toxicity from RAC opinion on copper granulate (adopted in June 2018) are inserted:



Aquatic toxicity

RAC has not independently verified all of the ecotoxicity information in the CLH dossier given the quantity of data and previous evaluations. Based on the information provided in the CLH report, public comments and supplemented by the DS during RAC discussions (see supplemental analysis), RAC considers that the following ERVs are most appropriate:

		pH band		
		5.51-6.5 (acidic)	**>6.5-7.5 (neutral)**	**>7.5-8.5 (alkaline)**
Values not normalised for DOC level				
Acute ERV	**$L(E)C_{50}$**	12.1 (*Pimephales promelas*)	11.7 (*Danio rerio*)	40 (*Ceriodaphnia dubia*)
Chronic ERV	**EC_{10}/NOEC**	13.2 (*Daphnia magna*) [a]	4 (*Ceriodaphnia dubia*) [b]	12.6 (*Daphnia magna*)
Values normalised to a DOC level of 2 mg/L				
Acute ERV	**$L(E)C_{50}$**	11 (*Daphnia magna*)	24.1 (*Ceriodaphnia dubia*)	31.4 (*Chlamydomonas reinhardtii*)
Chronic ERV	**EC_{10}/NOEC**	10.5 (*Daphnia magna*)	6.2 (*Ceriodaphnia dubia*) [b]	11.8 (*Ceriodaphnia dubia*)

Note: a – If 7-d data 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 into account.

b – This is the main difference from the DS’s proposal. The lowest reported long-term NOEC at neutral pH for *C. dubia* in the previous CLH reports for the 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 data aggregation exercise results in an unusual conclusion for acidic pH, *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 DOCnormalised values). In a reply to a question from the RAC rapporteur, the DS considers that the acute-to-chronic ratios (ACRs) are generally low, and tend to decrease with decreasing pH (approaching unity at around pH 6). RAC has some concerns about this general conclusion, because although there may be reasons for similar acute and chronic sensitivities (*e.g.* acclimation, provision of food that could affect bioavailability, etc.), there is far more acute than chronic data especially at lower pH, which might produce misleading ACRs (since the result is highly dependent on the representive nature of a very small number of chronic values). As an example, an ACR below 1 is obtained for *O. mykiss* mortality at acidic pH, implying that the organisms are less sensitive over long-term exposure and/or at sensitive life stages. As a possible “worst case”, applying the apparent ACR for *C. dubia* from the DOC-normalised ERVs at neutral pH (3.9) to the acute ERV for *D. magna* at acidic pH would result in a theoretical DOC-normalised chronic ERV for *D. magna* of 2.8 µg/L at acidic pH.

The change in species sensitivity across the pH bands could also be an artefact of the varying amounts of data available. RAC concludes that the amalgamation of such a diverse data set is not ideal for classification purposes, and that it might have been better to focus more on standard studies that have been specifically designed to investigate pH variation under specific DOC and hardness conditions in a single laboratory. In the absence of such an analysis, the derived ERVs have to be used.

As pointed out in the discussion above, even though the data set is relatively large, 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). RAC considers that if such data became available, the acute and chronic ERVs at acidic pH could be lower than 10 µg/L.

11.5.1 Acute (short-term) toxicity to fish

See 11.5 above and Annex II and Annex III for a complete dataset.

For transparency, a short description is also inserted here: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 acidic pH band (5.5-6.5) at which toxicity is greatest. At pH 5.5-6.5, the lowest acute LC_{50} 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 LC_{50} value is 14.9 µg/L (for *P. promelas*, n = 3). At pH 6.5-7.5, the lowest fish LC_{50} 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 TG 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 LC_{50} below 10 µg/L (normalised for DOC) cannot be ruled out).

11.5.2 Acute (short-term) toxicity to aquatic invertebrates

See 11.5 above and Annex II and Annex III for a complete dataset.

For transparency, a short description is also inserted here:

Over 300 individual acute data points are available for two "standard" 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 EC_{50} 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*.

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

See 11.5 above and Annex II and Annex III for a complete dataset.

For transparency, a short description is also inserted here:

Over 50 individual acute data points are available for three "standard" 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_rC_{50} (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_rC_{50} (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_rC_{50} values at pH 5.5-6.5 (acidic) are above 100 µg/L for all species regardless of DOC normalisation.

11.5.4 Acute (short-term) toxicity to other aquatic organisms

According to RAC opinion on copper granulate (adopted in June 2018), although data for many species are available, only "standard" species and endpoints from standardised methods have been selected. Consequently, toxicity to other species than those considered as standard species is not presented.

11.6 Long-term aquatic hazard

See 11.5 above

11.6.1 Chronic toxicity to fish

See 11.5 above and Annex II and Annex III for a complete dataset.

For transparency, a short description is also inserted here:

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/EC_{10} 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/EC_{10} value for fish is 10.7 µg/L for *S. fontinalis* reproduction at pH 6.5-7.5.

11.6.2 Chronic toxicity to aquatic invertebrates

See 11.5 above and Annex II and Annex III for a complete dataset.

For transparency, a short description is also inserted here:

44 individual chronic data points are available for two "standard" 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.

11.6.3 Chronic toxicity to algae or other aquatic plants

See 11.5 above and Annex II and Annex III for a complete dataset.

For transparency, a short description is also inserted here:

Over 50 individual chronic data points are available for three “standard” 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.

11.6.4 Chronic toxicity to other aquatic organisms

According to RAC opinion on copper granulate (adopted in June 2018), although data for many species are available, only “standard” species and endpoints from standardised methods have been selected. Consequently, toxicity to other species than those considered as standard species is not presented.

11.7 Comparison with the CLP criteria

This is a proposal for aquatic environmental hazard classification of copper. Copper metal can be placed on the market in different physical forms. Physical forms do not represent intrinsic properties of a substance. Consequently, the aquatic environmental hazard classification should not depend on the physical form. Therefore, this proposal also includes copper flakes and copper granulate, as earlier described in section 2.1 and section 4. Both copper flakes and copper granulates have specific surface areas larger than massive copper (that is larger than 0.67 mm^2/mg). Consequently, copper flakes and copper granulates should both be covered by our proposal for copper powder (specific surface area of >0.67 mm^2/mg).

Based on the Guidance on the Application of the CLP criteria (2017) the classification strategy for metals is based on a 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. All results and conclusions from the transformation/dissolution studies are presented in section 11.2 together with justifications for the selection of relevant data for comparison with ERV. All results and conclusions of ERVs are presented in section 11.5 including information that the conclusions on aquatic toxicity data drawn by the RAC in its opinion on copper granulate (adopted in June 2018) also are used in the current classification proposal. For the case of transparency the conclusions from transformation/dissolution studies and ecotoxicity studies are also repeated below in Table 15, Table 16 and Table 17.

Table 15: Transformation/dissolution data used in the current proposal for aquatic environmental hazard classification of copper powder. Based on transformation/dissolution data from ECTX (2020).

Testing period (days)	**pH**	**Release from particles with SSA of 107 mm^2/mg and at mass loading of 1 mg/L (µg Cu/L)**	**Release from particles with SSA of 107 mm^2/mg and at mass loading of 0.1 mg/L (µg Cu/L)**
7	6	196.1	
	7	72.2	
	8	66.7	
28	6	622.4	62.2
	7	222.9	22.3
	8	185.4	18.5

Table 16: Transformation/dissolution data used in the current proposal for aquatic environmental hazard classification of copper massive. Based on transformation/dissolution data from Rodriguez et al. (2012 and 2017).

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

Table 17: Ecotoxicity reference values used in the current classification proposal. Based on information and conclusions from CLH report for copper, granulated (February, 2017) and the conclusions drawn by the RAC in the RAC opinion on copper granulate (adopted in June 2018).

		pH band		
		5.51-6.5 (acidic)	**>6.5-7.5 (neutral)**	**>7.5-8.5 (alkaline)**
Values not normalised for DOC level				
Acute ERV	**L(E)C$_{50}$ (µg/L)**	12.1 (*Pimephales promelas*)	11.7 (*Danio rerio*)	40 (*Ceriodaphnia dubia*)
Chronic ERV	**EC$_{10}$/NOEC (µg/L)**	13.2 (*Daphnia magna*)	4 (*Ceriodaphnia dubia*)	12.6 (*Daphnia magna*)
Values normalised to a DOC level of 2 mg/L				
Acute ERV	**L(E)C$_{50}$ (µg/L)**	11 (*Daphnia magna*)	24.1 (*Ceriodaphnia dubia*)	31.4 (*Chlamydomonas reinhardtii*)
Chronic ERV	**EC$_{10}$/NOEC (µg/L)**	10.5 (*Daphnia magna*)	6.2 (*Ceriodaphnia dubia*)	11.8 (*Ceriodaphnia dubia*)

11.7.1 Acute aquatic hazard

According to the classification strategy for metals in the Guidance on the Application of the CLP criteria (2017) the metal should be classified as Category Acute 1 if the dissolved metal ion concentration after a period of 7 days at a loading rate of 1 mg/l exceeds that of the acute ERV.

The M-factor is estimated from the ratio of the soluble metal ions concentration obtained from transformation/dissolution studies and the ERV. If the ratio is below 10 then an M-factor of 1 should be applied. If the ratio is between 10 and 100 then an M-factor of 10 should be applied.

Further, according to the Guidance on the Application of the CLP criteria (2017), the worst case classification entry across pHs should be used based on comparing transformation/dissolution data with relevant ecotox data across the pH range.

Adequat acute ecotoxicity data were available for all three trophic levels, see section 11.5.1 to 11.5.3.

The comparisons of acute ERV and release of copper ions from copper powder and copper massive are presented in Table 18 and Table 19, respectively.

Table 18: Comparison of acute ERV and release of copper ions from copper powder (particles with a specific surface area of more than 0.67 mm^2/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		Category Acute 1	16	10
7	72.2	11.7		Category Acute 1	6.2	1
8	66.7	40		Category Acute 1	1.2	1
6	196.1		11	Category Acute 1	18	10
7	72.2		24.1	Category Acute 1	3.0	1
8	66.7		31.4	Category Acute 1	2.1	1

Table 19: Comparison of acute ERV and release of copper ions from copper massive (particles with specific surface area of 0.67 mm^2/mg or less) 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		none	-	-
7	0.4	11.7		none	-	-
8	<0.2	40		none	-	-
6	1.0		11	none	-	-
7	0.4		24.1	none	-	-
8	<0.2		31.4	none	-	-

RAC clarified in its opinion on copper granulate (adopted in June 2018) that RAC was not in a position to recommend an appropriate DOC value for the ERV. 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.

Conclusion acute aquatic hazard:

Copper powder particles with a specific surface area of more than 0.67 mm^2/mg; Classification Category Acute 1 with an M-factor of 10.

Copper particles with a specific surface area of 0.67 mm^2/mg or less (massive copper particles); no classification is triggered.

As described in section 11.2 the 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. A linear regression on the log-transformed transformation/dissolution data allowed the registrant to derive the following equation for copper release after 7 days for pH 6:

Log [Copper release after 7 days in µg/L] = 0.16 + 0.98 * Log [Surface loading in mm^2/L]

Powder:
The surface loading at transformation/dissolution studies with mass loading rate of 1 mg/L of particles representing the smallest representative copper particle on the market is 107 mm^2/L. Hence:

Log [Copper release after 7 days in µg/L] = 0.16 + 0.98 * Log [107]
Copper release after 7 days in µg/L = 141 µg/L

A copper release of 141 µg/L is well above the lowest acute ERV of 11 µg/L, hence supporting the conclusion above that copper powder particles should be classified Category Acute 1 with an M-factor of 10

Massive:
The surface loading at transformation/dissolution studies with mass loading rate of 1 mg/L of spherical particles with a diameter of 1 mm (representing massive copper) is 0.67 mm^2/L. Hence:

Log [Copper release after 7 days in µg/L] = 0.16 + 0.98 * Log [0.67]

Copper release after 7 days in µg/L = 0.98 µg/L

A copper release of 0.98 µg/L is well below the lowest acute ERV of 11 µg/L, hence supporting the conclusion above that no acute classification is triggered for massiv copper.

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

According to the Guidance on the Application of the CLP criteria (2017), metals with no evidence of rapid environmental transformation, should be classified as Category Chronic 1 if the dissolved metal ion concentration after a period of 28 days at a loading rate of 0.1 mg/l exceeds or is equal to that of the chronic ERV. The metal should be classified as Category Chronic 2 if the dissolved metal ion concentration after a period of 28 days at a loading rate of 1 mg/l exceeds or is equal to that of the chronic ERV.

The M-factor is estimated from the ratio of the soluble metal ions concentration obtained from transformation/dissolution studies and the ERV. If the ratio is below 10 then an M-factor of 1 should be applied. If the ratio is between 10 and 100 then an M-factor of 10 should be applied.

Further, according to the Guidance on the Application of the CLP criteria (2017), the worst case classification entry across pHs should be used based on comparing transformation/dissolution data with relevant ecotox data across the pH range.

Based on the available data, copper is not considered to be rapidly transformed by normal environmental processes. This is described in section 11.3. Additionally, as described in section 11.4, the bioaccumulation behaviour of copper does not influence the determination of the classification of copper and does therefore not need to be considered further.

Adequat chronic ecotoxicity data were available for all three trophic levels, see section 11.6.1 to 11.6.3.

The comparisons of chronic ERV and release of copper ions from copper powder and copper massive are presented in Table 20 and Table 21, respectively.

Table 20: Comparison of chronic ERV and release of copper ions from copper powder (particles with a specific surface area of more than 0.67 mm^2/mg) after 28 days and proposal for classification based on these data.

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

Table 21: Comparison of chronic ERV and release of copper ions from copper massive (particles with specific surface area of 0.67 mm^2/mg or less) after 28 days and proposal for classification based on these data.

pH	**Transformation/dissolution (µg Cu/L)**		**ERV (µg Cu/L)**		**Classification**	**Ratio T/D and ERV**	**M-factor**
	At loading rate 0.1 mg/L	**At loading rate 1 mg/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	-	-

RAC clarified in its opinion on copper granulate (adopted in June 2018) that RAC was not in a position to recommend an appropriate DOC value for the ERV. 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.

Conclusion long-term aquatic hazard:

Copper powder particles with a specific surface area of more than 0.67 mm^2/mg; Classification Category Chronic 1 with an M-factor of 1.

Copper particles with a specific surface area of 0.67 mm^2/mg or less (massive copper particles); no classification is triggered.

As described in section 11.2 the 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. A linear regression on the log-transformed transformation/dissolution data allowed the registrant to derive the following equation for copper release after 28 days for pH 6:

Log [Copper release after 28 days in µg/L] = 0.70 + 1.03 * Log [Surface loading in mm^2/L]

Powder:
The surface loading at transformation/dissolution studies with mass loading rate of 0.1 mg/L of particles representing the smallest representative copper particle on the market is 10.7 mm^2/L. Hence:

Log [Copper release after 28 days in µg/L] = 0.70 + 1.03 * Log [10.7]
Copper release after 28 days in µg/L = 57.6 µg/L

A copper release of 57.6 µg/L is well above the lowest chronic ERV at pH 6 of 10.5 µg/L, hence supporting the conclusion above that copper powder particles should be classified Category Chronic 1 with an M-factor of 1.

Massive:
The surface loading at transformation/dissolution studies with mass loading rate of 1 mg/L of spherical particles with a diameter of 1 mm (representing massive copper) is 0.67 mm^2/L. Hence:

Log [Copper release after 28 days in µg/L] = 0.70 + 1.03 * Log [0.67]
Copper release after 28 days in µg/L = 3.3 µg/L

A copper release of 3.3 µg/L is below the lowest chronic ERV at pH 6 of 10.5 µg/L, hence supporting the conclusion above that no chronic classification is triggered for massiv copper.

11.8 CONCLUSION ON CLASSIFICATION AND LABELLING FOR ENVIRONMENTAL HAZARDS

Conclusion acute aquatic hazard *:

Copper with a specific surface area of more than 0.67 mm^2/mg; Classification Category Acute 1 with an M-factor of 10.

(For copper with a specific surface area equal to or less than 0.67 mm^2/mg (massive copper) no classification is triggered.)

Conclusion long-term aquatic hazard *:

Copper with a specific surface area of more than 0.67 mm^2/mg; Classification Category Chronic 1 with an M-factor of 1.

(For copper with a specific surface area equal to or less than 0.67 mm^2/mg (massive copper) no classification is triggered.)

* The terms “powder” and “massive” is used in the guidance to draw a line between two theoretical entries. However, specific surface area is in this regard the crucial parameter, i.e. surface area per weight. While these terms (powder and massive) have remained in the guidance, in practice not only spherical copper powder exists on the market. There are different shapes of particles such as powders, flakes, sticks, granulates etc which are all still the same chemical substance. We suggest therefore, to base the proposal on surface area per weight (mm^2/mg).

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 in 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 and as a result to subsequently replace the previously adopted harmonised aquatic environmental hazard classifications of copper flakes and copper granulates (this issue is not for RAC but will be addressed later by COM). 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 mm^2/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

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

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 the RAC 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 acquired from the registrant and included in the REACH registration dossier during the development of this dossier has 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 *et al.* (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 *et al.* (2011)	7	46.69	0.41	Massive metal embedded in epoxy resin.
Rodriguez *et al.* (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 mm^2/mg.

** - Calculated from data in Schäfer 2014 and surface loading (see *); 721 (µg Cu/L)/2080 (mm^2/L) = 0.35 µg 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 (µg Cu/L)/2080 (mm^2/L) = 0.37 µg Cu/mm^2.

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

Reference	**Time (days)**	**Surface loading used in test (mm²/L)**	**Measured release (µg Cu/mm²)**	**Remarks incl. dimensions of particles if available**
Rodriguez *et al.* (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 *et al.* (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 (µg Cu/L)/2080 (mm²/L) = 0.17 µg Cu/mm².

*** - 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 (µg Cu/L)/2080 (mm²/L) = 0.31 µg Cu/mm².

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

Reference	**Time (days)**	**Surface loading used in test (mm²/L)**	**Measured release (µg Cu/mm²)**	**Remarks incl. dimensions of particles if available**
Rodriguez *et al.* (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 *et al.* (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 override 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/mm^2 after 7 days T/D tests at pH 6
- 0.19 µg Cu/mm^2 after 7 days T/D tests at pH 7
- 0.13 µg Cu/mm^2 after 7 days T/D tests at pH 8
- 4.2 µg Cu/mm^2 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 loadings of 43-47 mm^2/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 (pp) 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/mm^2, compared with samples with pp wheels. Therefore, a methodology where the massive copper is embedded in epoxy resin is preferred over pp 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 mm^2/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/mm^2 after 7 days (acute endpoint) and 5.0 µg/mm^2 after 28 days (chronic endpoint).

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 mm^2/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/mm^2 after 7 days (acute endpoint) and 1.2 µg/mm^2 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/mm^2 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 mm^2/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/mm^2 after 7 days T/D tests at pH 6
- 0.88 µg Cu/mm^2 after 7 days T/D tests at pH 7
- 0.45 µg Cu/mm^2 after 7 days T/D tests at pH 8
- 5 µg Cu/mm^2 after 28 days T/D test at pH 6
- 3.3 µg Cu/mm^2 after 28 days T/D tests at pH 7
- 1.9 µg Cu/mm^2 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 nor 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 mm^2/mg**,

b) a special copper powder with dendritic (branched) shape, with D50 26 µm and specific surface area of **340 mm^2/mg**, and

c) copper powder with D50 30 µm and a specific surface area of **28 mm^2/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/mm^2 exposed) after 7 days (at pH 6) were:

- Copper powder a) 1.223 µg Cu/mm^2
- Copper powder b) 0.324 µg Cu/mm^2
- Copper powder c) 1.289 µg Cu/mm^2

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

<u>ETCX (2020; study no. X01-296)</u>

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 mm^2/mg** (same as copper powder a) in ETCX (2019); see above). The powder was tested at 1 mg/L mass loading (equals 60 mm^2/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/mm^2 exposed) after 7 days were:

- 1.833 µg Cu/mm^2 at pH 6
- 0.675 µg Cu/mm^2 at pH 7
- 0.623 µg Cu/mm^2 at pH 8

And after 28 days:

- 5.817 µg Cu/mm^2 at pH 6
- 2.083 µg Cu/mm^2 at pH 7
- 1.733 µg Cu/mm^2 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 systematic 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 mm^2/mg.

The REACH registrant in its document on environmental hazard classification considered the particle with the specific surface area of 60 mm^2/mg used in ECTX (2019 and 2020) as 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 of copper, 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 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 mm^2/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 mm^2/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 mm^2/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/mm^2 x SSA of 107 mm^2/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 mm^2/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 μg Cu/mm^2 x SSA of 0.67 mm^2/mg x mass loading of 1 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 μg Cu/mm^2 with mentioned exception.
- The copper release at pH 6 after a 28-day test range 4.2—5.8 μg Cu/mm^2.

The REACH registrant derived the following equations for pH 6:

- Log [Copper release after 7 days in μg/L] = 0.16 + 0.98 * Log [Surface loading in mm^2/L] (equation 1)

- Log [Copper release after 28 days in µg/L] = 0.70 + 1.03 * Log [Surface loading in mm^2/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 lower release than expected based on the overall trend. The REACH registrant argues that the dendritic copper powder tested by ECTX (2019) does not follow the trend exhibited by the other, more typical copper powders explained with 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). 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. 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^-, HCO_3^- /CO_3^{2-}, $H_2PO_4^-$/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 system, 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.

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 geomean of the

LC_{50} for this species was used instead and resulted in a 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)C_{50} (µg/L)**	12.1 (*Pimephales promelas*)	11.7 (*Danio rerio*)	40 (*Ceriodaphnia dubia*)
Chronic ERV	**EC_{10}/NOEC (µg/L)**	13.2 (*Daphnia magna*)	4 (*Ceriodaphnia dubia*)	12.6 (*Daphnia magna*)
Values normalised to a DOC level of 2 mg/L				
Acute ERV	**L(E)C_{50} (µg/L)**	11 (*Daphnia magna*)	24.1 (*Ceriodaphnia dubia*)	31.4 (*Chlamydomonas reinhardtii*)
Chronic ERV	**EC_{10}/NOEC (µg/L)**	10.5 (*Daphnia magna*)	6.2 (*Ceriodaphnia dubia*)	11.8 (*Ceriodaphnia dubia*)

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 presented discussion on 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 such as the acute-to-chronic ratios (ACRs) being generally low and tend to decrease with decreasing pH (approaching unity at around pH 6), far more acute than chronic data especially at lower pH, 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 LC_{50} below 10 µg/L (normalised for DOC) cannot be ruled out) have been discussed.

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 acidic pH band (5.5-6.5) at which toxicity is greatest. At pH 5.5-6.5, the lowest acute LC_{50} 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 LC_{50} value is 14.9 µg/L (for *P. promelas*, n = 3). At pH 6.5-7.5, the lowest fish LC_{50} 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 LC_{50} 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 EC_{50} 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_rC_{50} (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_rC_{50} (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_rC_{50} 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/EC_{10} 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/EC_{10} 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 views in comparing with the CLP criteria

The DS proposed classification for copper metal, which should not depend on the physical form and included all copper forms on the market: copper massive, copper powder, copper flakes and copper granulate. The DS noted that copper flakes and copper granulate have specific surface areas larger than massive copper (> 0.67 mm^2/mg) and should both be covered by the proposal for copper powder (specific surface area of > 0.67 mm^2/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 mm^2/mg (Table below) and for copper metal with specific surface area ≤ 0.67 mm^2/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 mm^2/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 mm^2/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 mm^2/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 mm^2/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 mm^2/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 mm^2/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 mm^2/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 mm^2/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 mm^2/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 mm^2/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 mm^2/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 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 mm^2/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 cooper is proposed to be deleted, if both are covered by the proposal SSA > 0.67 mm^2/mg. They also questioned how granulated copper would be covered by the new proposed classification for copper [specific surface area > 0.67 mm^2/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 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* mm^2*/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. In addition, ECI comment that for increased clarity the descriptor “powder” or “fine forms” to the entry might be added resulting in *Copper powder [specific surface area > 0.67* mm^2*/mg]* or *Copper, fine forms [specific surface area > 0.67* mm^2*/mg]*. 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. ECI commented that the choice of the DS to consider the copper powder with specific surface area of 48 mm^2/mg as calculated by screen analysis, and of 107 mm^2/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 mm^2/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 support the proposed by DS classification of metal forms, 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 companies-manufacturers support proposed no classification for copper massive and accept 0.67 mm^2/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 mm^2/mg being closer to copper massive (0.67 mm^2/mg) and much higher than accepted for harmonized classification copper powder (107 mm^2/mg).

Industry and trade associations generally support separate assessments for copper massive and agree with a limit value of 0.67 mm^2/mg. The proposed no classification for copper massive is positively commented from the viewpoint of the useful properties of copper, its essential applications in modern technologies, and importance of the proposed classification from a business perspective. Industry and trade associations referred to the scientific and technical comments made by ECI and believe that the assessment is based on robust data and agreed scientific principles in line with the CLP Regulation and the CLP Guidance. 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. Please see Table 1 (Classification Status of Copper Forms Evaluated Under the BPR) in the public attachment.

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 in 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 mm^2/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 mm^2/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 (Cu^{2+}) 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 dissolve 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 µg/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 µg/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 concludes 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 required for biological function 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 $Cu(CO_3)_x$, 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 $Cu(CO_3)_x$ and $Cu(HCO_3)$ 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., $CuOH^-$). 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 it is not possible to assess the effect of only one parameter and only assessment of combined effect of all parameters of aquatic chemistry is reliable**.**

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 predicts 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 LC_{50} 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 LC_{50} 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 LC_{50} 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 EC_{50} 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 E_rC_{50} (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 E_rC_{50} (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/EC_{10} 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/EC_{10} value for fish is 10.7 µg/L for *S. fontinalis* reproduction at pH > 6.5 - 7.5.

In summary, the lowest NOEC/EC_{10} 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/EC_{10} 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/EC_{10} 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/EC_{10} 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/EC_{10} 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)C_{50} (µg/L)**	12.1 (*Pimephales promelas*)	11.7 (*Danio rerio*)	40 (*Ceriodaphnia dubia*)
Chronic ERV	**EC_{10}/NOEC (µg/L)**	13.2 (*Daphnia magna*)	4 (*Ceriodaphnia dubia*)	12.6 (*Daphnia magna*)
Values normalised to a DOC level of 2 mg/L				
Acute ERV	**L(E)C_{50} (µg/L)**	11 (*Daphnia magna*)	24.1 (*Ceriodaphnia dubia*)	31.4 (*Chlamydomonas reinhardtii*)
Chronic ERV	**EC_{10}/NOEC (µg/L)**	10.5 (*Daphnia magna*)	6.2 (*Ceriodaphnia dubia*)	11.8 (*Ceriodaphnia dubia*)

For consistency, RAC also presents the application of BLMs for PNEC derivation for copper. For the freshwater pelagic compartment, 139 individual NOEC/EC_{10} 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 $HC_{5\text{-}50}$ values (the median fifth percentile of the SSD), using statistical extrapolation methods. The $HC_{5\text{-}50}$ 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 $HC_{5\text{-}50}$ 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 (mm^2/mg). Results presented in the above tables showed relatively consistent release of copper per unit are 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 mm^2/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 mm^2/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 mm^2/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 mm^2/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/mm^2 (extrapolated by power function). This value is used for the calculation of copper released from particles with area 0.67 mm^2/mg, 60 mm^2/mg, and 107 mm^2/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 mm^2/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 mm^2/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 mm^2/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 mm^2/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 mm^2/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

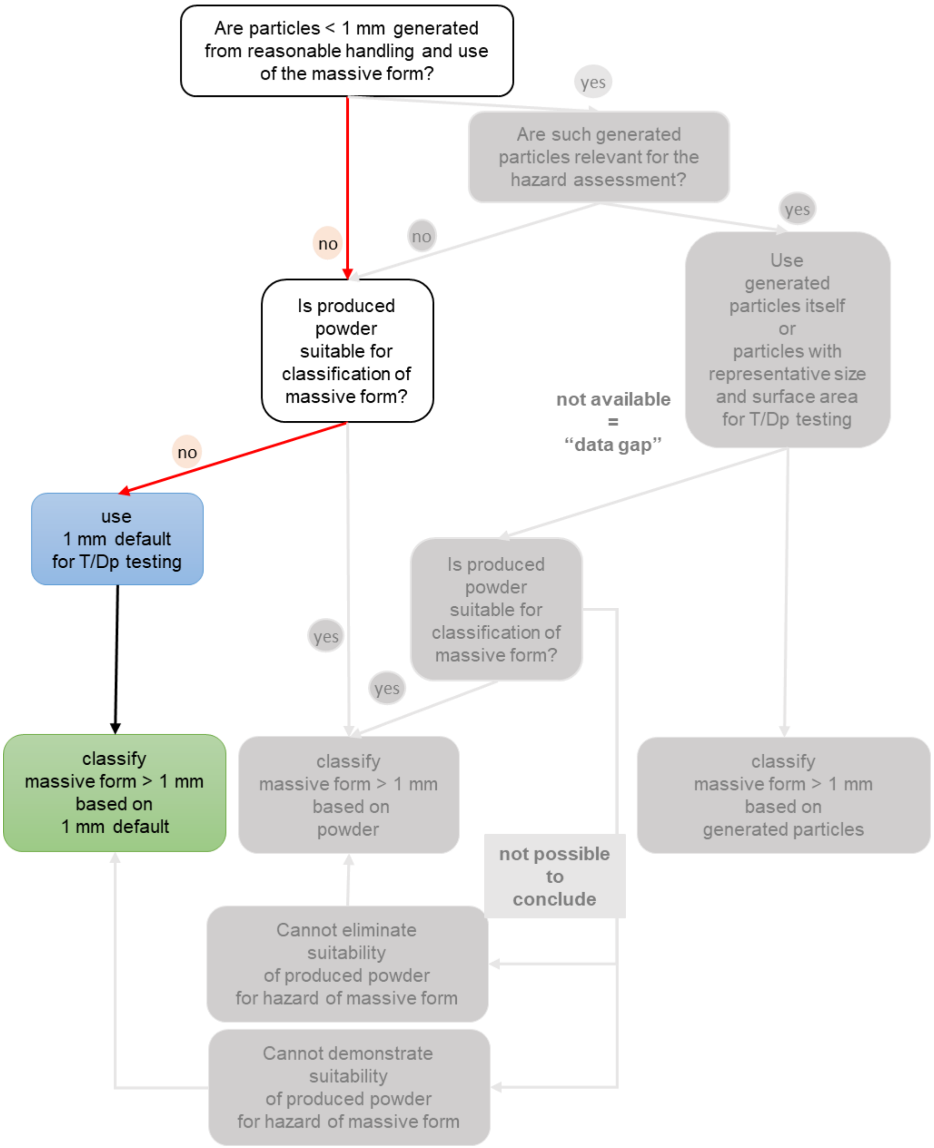


Figure: Flow chart for the aquatic hazard assessment of the massive form > 1 mm of a metal under CLP.

Comparison with the CLP criteria

RAC supports the DS in presenting comparisons with the CLP criteria depending on the pH and using ERV values both non-normalised/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 mm^2) 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 will be 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 specific surface area of 107 mm^2/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 bad reproducibility of results (above 30%), instead particles with an SSA of 60 mm^2/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 mm^2/mg should be used for classification of copper with SSA > 0.67 mm^2/mg. If particles with specific surface area of 107 mm^2/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 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 mm^2/mg, for other pH ranges are not available. Data for copper dissolution for 28 days with these particles were also not available.

Derived equitation for acute toxicity: Log [Copper release after 7 days in μg/L] = 0.12 + 0.97 * Log [Surface loading in mm^2/L] (equation 3) and calculated concentration is 125 μg/L, which support the same classification.

RAC recalculated regression for dissolution over 7 days at pH 6 using all data available and this resulted in 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 approach and will use the value of 125 μg/L from its own regression 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 mm^2/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 mm^2/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) Not DOC normalised	ERV (µg Cu/L) DOC Normalised (2 mg/L)	Hazard	T/D:ERV	M-factor
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 mm^2/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 mm^2/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 mm^2/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) Not DOC normalised	ERV (µg Cu/L) DOC Normalised (2 mg/L)	Hazard	T/D:ERV	M-factor
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 mm^2/mg, based on data from ECTX (X01-296) 2020 for particles with area 60 mm^2/mg.
** - calculated by DS using regression line for 60 mm^2/mg, derived by Registrant. Excludes data from particles at 107 mm^2/mg.
*** - RAC – calculated by RAC using new regression line. Includes data for particles at both 107 and 60 mm^2/mg.
DS – Dossier submitter calculated value
EXP – Experimentally derived value
NC – No Classification

Chronic aquatic toxicity

RAC supports the conclusion of DS for 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 mm^2/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 ≤ 0.67 mm^2/mg after 28 days and proposal for classification based on these data.*

pH band	**pH**	**Transformation/dissolution (µg Cu/L)**		**ERV (µg Cu/L)**		**Hazard**	**T/D: ERV**	**M-factor**
		At loading rate 0.1 mg/L (µg Cu/L)	At loading rate 1 mg/L (µg 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 mm^2/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 mm^2/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 (µg Cu/L)		Hazard	T/D:ERV	M-factor
		At loading rate 0.1 mg/L (µg Cu/L)	At loading rate 1 mg/L (µg Cu/L)	Not DOC normalised	DOC Normalised (2 mg/L)			
5.5 – 6.5	5.5*	$81^{¥}$ $45^{\ddagger}$	$810^{¥}$ $454^{\ddagger}$	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*	$81^{¥}$ $45^{\ddagger}$	$810^{¥}$ $454^{\ddagger}$		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 mm^2/mg$^{¥}$ and 60 mm^2/mg‡
** – calculated by DS for particles with area 107 mm^2/mg, based on data from ECTX (X01-296) 2020 for particles with area 60 mm^2/mg.
*** – calculated by DS, using regression line, derived by Registrant. No data from particles at 107 mm^2/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

12 EVALUATION OF ADDITIONAL HAZARDS

This part was not evaluated in this CLH report and no classifications for additional hazards are proposed.

13 ADDITIONAL LABELLING

Not relevant.

14 REFERENCES

GHS (2019) Globally harmonized system of classification and labelling of chemicals (GHS), eighth revised edition.

CLH Report (2017), Proposal for harmonised classification and labelling, Substance name: Copper, granulated, February, 2017.

CLH Report (2013), Proposal for harmonised classification and labelling, Substance name: Copper flakes (coated with aliphatic acid), December, 2013.

ECI (2021) European Copper Institute report "The environmental hazard classification of copper", version 2.2, attachment to the copper Chemical Safety Report (CSR).

Guidance on the Application of the CLP criteria (2017), Guidance to Regulation (EC) No 1272/2008 on classification, labelling and packaging (CLP) of substances and mixtures, Version 5.0, July 2017.

OECD (2001) OECD Series on Testing and Assessment, Number 29, Guidance document on transformation/dissolution of metals and metal compounds in aqueous media, ENV/JM/MONO(2001)9.

RAC Opinion (2014), Committee for risk assessment RAC Opinion proposing harmonised classification and labelling at EU level of Copper flakes (coated with aliphatic acid), December, 2014.

RAC Opinion (2018), Committee for risk assessment RAC Opinion proposing harmonised classification and labelling at EU level of Granulated copper, June, 2018.

Additional references

Azenha, Vasconcelos, and Cabral (1995) Organic ligands reduce copper toxicity in *Pseudomonas syringae*, Environmental toxicology and chemistry, Volume14, Issue 3, 369-373, https://doi.org/10.1002/etc.5620140303

Brown and Markich (2000) Evaluation of the free ion activity model of metal-organism interaction: extension of the conceptual model, Aquatic Toxicology, 51(2), 177-194

Buchwalter, Linder, and Curtis (1996) Modulation of cupric ion activity by pH and fulvic acid as determinants of toxicity in *Xenopus Laevis* embryos and larvae. Environ Toxicol Chem;15:568-573.

Cervi, Clark, Gustafsso, Baken, and Burton Jr. (2021) Copper transformation, speciation, and detoxification in anoxic and suboxic freshwater sediments, Chemosphere, Volume 282, November, 131063, https://doi.org/10.1016/j.chemosphere.2021.131063

DeForest, Brix, and Adams (2007) Assessing metal bioaccumulation in aquatic environments: The inverse relationship between bioaccumulation factors, trophic transfer factors and exposure concentration. Aquatic toxicology (Amsterdam, Netherlands). 84. 236-46. 10.1016/j.aquatox.2007.02.022.

Erickson, Benoit, Mattson, Nelson, and Leonard, E.N (1996) The effects of water chemistry on the toxicity of copper to fathead minnows. Environ. Toxicol. Chem. 15, 181–193.

Mcgeer, Brix, Skeaff, DeForest, Brigham, Adams, Green (2003) Inverse Relationship Between Bioconcentration Factor and Exposure Concentration for Metals: Implications for Hazard Assessment of Metals in the Aquatic Environment. Environmental toxicology and chemistry / SETAC. 22. 1017-37. 10.1002/etc.5620220509.

Meyer, Clearwater, and Doser (2007) Effects of Water Chemistry on the Bioavailability and Toxicity of Waterborne Cadmium, Copper, Nickel, Lead, and Zinc to Freshwater Organisms, SETAC Press, Pensacola, FL, USA

Rader, Carbonaro, van Hullebusch, Baken, and Delbeke (2019). The fate of copper added to surface water: field, laboratory, and modelling studies. Environmental Toxicology and Chemistry 38, 1386-1399, https://doi.org/10.1002/etc.4440

Zhou, Slauenwhite, Pett, and Wangersky (1989) Production of copper complexing organic ligands during a diatom bloom: tower tank and batch culture experiments. *Marine Chemistry* 27, 19–30

15 ANNEXES

15.1 Annex I: ”Section 2, Information on copper in massive and powder forms" of ECI (2021) European Copper Institute Report “The Environmental Hazard Classification of Copper”, Version 2.2.

15.2 Annex II: “Section 5.4, Aquatic Toxicity" of CLH Report (2017), Proposal for harmonised classification and labelling, Substance name: Copper, granulated, February, 2017.

15.3 Annex III: “Section 7, Annexes" of CLH Report (2017), Proposal for harmonised classification and labelling, Substance name: Copper, granulated, February, 2017.