Copper Concentrates

Environmental and Human Health hazard classification.

Application to the assessment of substances "Harmful to the Marine Environment" (HME) as set out under the 2012 Annex V MARPOL Convention amendments.

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CONTENT

Abstract

In 2012, the International Maritime Organization (IMO), adopted resolution MEPC 219(63). This establishes the hazard classification criteria for solid substances, transported as bulk cargo, to be considered as "harmful to the marine environment" (HME) for the purposes of restricting the disposal of solid bulk cargo residues under the amended Annex V of the MARPOL Convention.

Copper concentrates are solid mining products transported in bulk. The need for classifications of these materials, for the human health and environmental hazard categories set out in the HME criteria, was assessed following the UN-GHS 4th revision and the ICMM guidance (2013)[1] on HME assessment of ores and concentrates.

The results are summarized as follows:

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[1] ICMM 2013. Assessment of HME criteria of mineral ores and concentrates: the international mining and metals industry approach

- The elemental and mineral compositions of 119 copper concentrates, considered as representative of world-wide production, were collected. Elemental compositions are dominated by copper, iron and sulfur. These elements are incorporated in sulfidic minerals, such as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), diginite (Cu_9S_5), covellite (CuS) and chalcocite (Cu_2S). Other major elemental constituents (Al, Ca, Mg, K, Si, Mn) are incorporated in minerals, usually defined as 'gange', such as calcite, dolomite, hornblende, quartz, chlinochlore, feldspar, kaolinite and biotite. Copper concentrates may also contain small amounts of zinc, lead, arsenic, nickel, cobalt and silver. These metals are incorporated in distinct minerals.

- To assess the environmental criteria, short and long term transformation/dissolution tests (7 and 28 days, pH 6, loading of 1 mg/L in the standard aqueous medium), in accordance to a standard protocol (UN GHS annex 9 and 10), were carried out on 13 copper concentrates, as well as on important pure copper minerals (chalcopyrite, chalcocite, digenite, bornite, covellite, enargite and tennantite). The environmental degradability of the released metal ions were assessed following the principles and recommendations of the metals GHS guidance and the EU's European Chemicals Agency workshop.
    o The results demonstrate low metal releases from the minerals. Comparison between the metal releases from the copper minerals and ecotoxicity reference values, obtained from CLP and REACH dossiers[2], demonstrates that among the copper minerals, chalcocite merits classification as HME. The other copper minerals (chalcopyrite, bornite , diginite, covellite, enargite and tennantite) do not meet the environmental HME criteria.
    o Comparison between the metal releases from the copper concentrates and ecotoxicity reference values, obtained from CLP and REACH[2] dossiers, indicates that only concentrates with high chalcocite content merit HME classification. Such copper concentrates are rare - only 3 to 4% of the copper concentrates assessed trigger an HME classification entry.

- To assess the human health criteria, information on the bio-accessibility of the metal-ions, tested in accordance to a standard protocol (ASTM 5517 test)[3], their classification for mutagenicity, carcinogenicity, reproductive toxicity and STOT-RE, as well as their potential for bio-magnification, bio-accumulation and "rapid degradability", were combined. The assessment demonstrates that the human health criteria do not lead to HME classification of copper concentrates.

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[2] Compiled from the multi-metal Meclas database - http://www.meclas.eu/

[3] ASM D5517-07: Standard Test Method for Determining Extractability of Metals from Art Materials, Philadelphia, PA: American Society for Testing and Materials, 2007

1. Introduction to MARPOL Annex V

1.1 Amendments to the Annex V of the MARPOL 73/78 Convention

In 2012, the International Maritime Organization (IMO), adopted resolution MEPC 219(63). This establishes the hazard classification criteria for solid substances, transported as bulk cargo, to be considered as "harmful to the marine environment" (HME) for the purposes of restricting the disposal of solid bulk cargo residues under the amended Annex V of the MARPOL Convention.

The criteria[4][5] encompass six hazard classes/categories relevant to inorganic substances. The hazard classification rules of the GHS, 4th revision, 2011[6] are used:

Criteria to classify as Harmful to the Marine Environment are:
1. Acute Aquatic Toxicity Category 1; and/or
2. Chronic Aquatic Toxicity Category 1 or 2; and/or
3. Carcinogenicity Category 1A or 1B, combined with not being rapidly degradable and having high bioaccumulation; and/or
4. Mutagenicity Category 1A or 1B, combined with not being rapidly degradable and having high bioaccumulation; and/or
5. Reproductive Toxicity Category 1A or 1B, combined with not being rapidly degradable and having high bioaccumulation; and/or
6. Specific Target Organ Toxicity Repeated Exposure Category 1, combined with not being rapidly degradable and having high bioaccumulation.

Copper concentrates are solid mining products transported in bulk. It is therefore necessary to determine the classifications for the human health and environmental hazard categories set out in the HME criteria.

1.2 The Global Harmonized System of Classification and Labeling (GHS)

The GHS is a methodology for standardizing and harmonizing the classification and labeling of chemicals. It defines a set of physical, health and environmental hazard classes and provides criteria for hazard classification, as well as a consistent method for communicating hazard information, including protective measures on labels and Safety Data Sheets (SDS).

The purpose of the GHS is to serve as a worldwide reference system, on matters of chemical management, which should be implemented in different regulatory jurisdictions and as the basis for worldwide regulatory frameworks (international legal instruments, recommendations, codes and guidelines). The GHS section of the UNECE web site[7] provides the latest progress on implementation.

### 1.3 Overview of Hazard Classification

The steps involved in hazard classification can be summarized as follows. First, it is necessary to determine, as accurately as possible, the identity of the substance (its composition at both the compound and elemental level). Second, all the compounds and elements, which pose a hazard, must be accounted for, considering the percentages that trigger classification. Third, the hazard classification is determined following the GHS criteria and rules. A detailed flowchart of the approach can be found in "Assessment of HME criteria of mineral ores and concentrates: the international mining and metals industry approach" (ICMM, 2013).

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[4] The criteria are based on UN GHS, fourth revised edition (2011). For specific products (e.g. metals and inorganic metal compounds), guidance available in UN GHS, annexes 9 and 10, are essential for proper interpretation of the criteria and classification and should be followed

[5] Products that are classified for Carcinogenicity, Mutagenicity, Reproductive toxicity or Specific Target Organ Toxicity Repeated Exposure for oral and dermal hazards or without specification of the exposure route in the hazard statement

[6] http://www.unece.org/trans/danger/publi/ghs/ghs_rev04/04files_e.html

[7] http://www.unece.org/trans/danger/publi/ghs/implementation_e.html#c25755
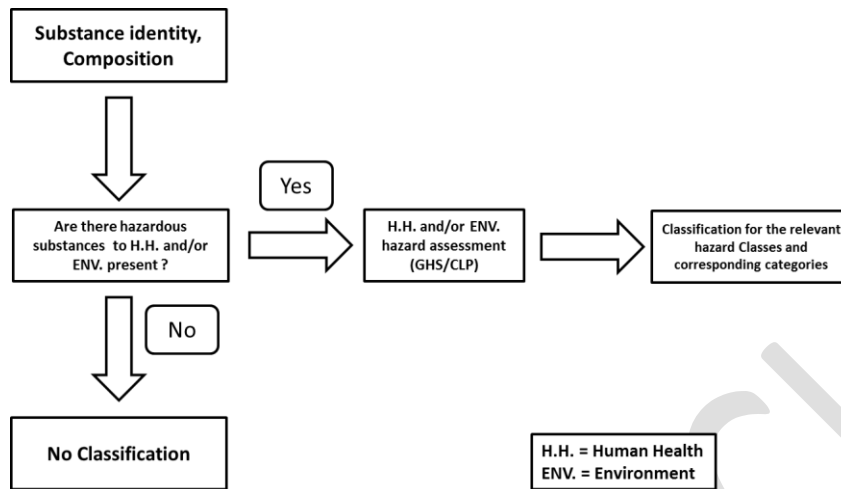
Scheme 1 - General classification scheme

2. Introduction to copper concentrates

2.1 Production process

The typical copper content of copper sulfide ore bodies is 0.6%. The copper is naturally present in a broad variety of copper bearing sulfide minerals, mainly primary sulfides (i.e. Chalcopyrite and Bornite) and secondary sulfides (i.e. Chalcocite and Covellite). Figure 1 shows the main copper ore bodies world-wide.

The first part of the copper production process involves the production of an ore concentrate in which the copper content is boosted to +/- 30%. The unwanted fraction of the ore is discarded as tailings.
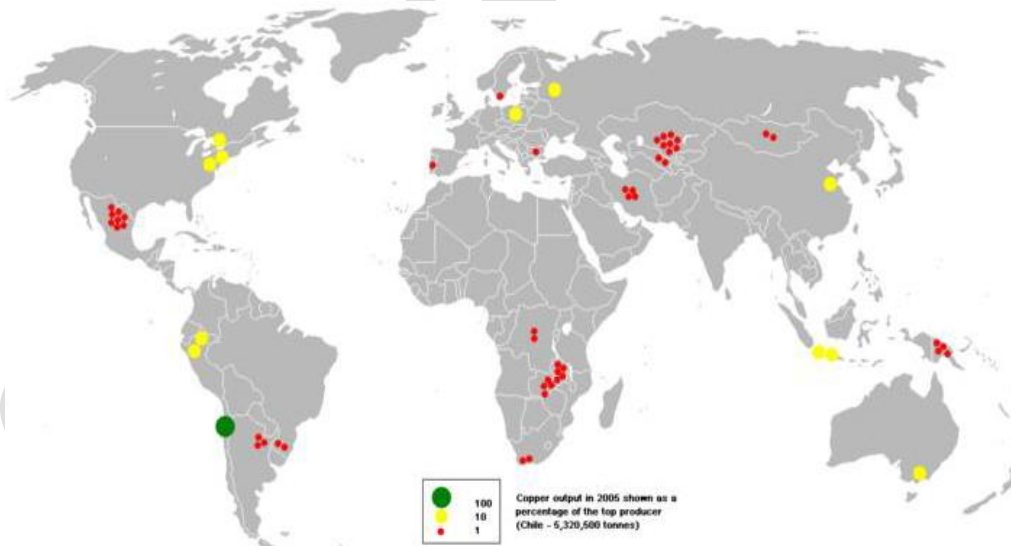
Figure 1 : Distribution of the main copper ore bodies currently exploited

Copper concentrates are mainly produced by flotation. The ore is crushed and milled to a particle size of less than 100 µm. This produces a mix of particles containing pure phases of primary or secondary copper sulfides. The ground ore is mixed with water and reagents, to form a slurry, where the copper sulfide mineral particles bind to the reagent, rendering a hydrophobic complex. Submitted to aeration, this complex binds preferentially to the air bubbles and floats to the surface producing a highly enriched, copper sulfide froth that can be skimmed off the top. This then passes through a cleaning process to remove unwanted impurities. In some cases, the concentrate is submitted to an additional processing step to

extract a by-product (e.g. molybdenum sulfide). Finally, the copper concentrate is dried ready for transportation to the next step (smelting).

The concentrates from primary sulfides (Chalcopyrite rich) contain, on average, 20 to 30% copper, whereas the secondary sulfide concentrates (Chalcocite rich) can reach copper concentrations of up to 40%.

It is important to note that the copper concentrate production process does not involve any chemical modification of the original ore body.

2.2 Copper Concentrates - Substance Identity

As can be envisaged from the production process, outlined above, copper concentrates are made up of primary and/or secondary copper sulfide minerals, containing small amounts of impurities. The variability of the mineral content and composition depends mainly on the geographical location and age of the mine site. Concentrates are therefore considered to be naturally occurring substances of variable composition.

Within the current GHS, these are considered as complex mixtures or complex substances. In its European version, the Regulation on Classification, Labelling and Packaging of substances and mixtures (EC 1272/2008 (CLP)), copper concentrates are considered as UVCB[8] substances.

The European Copper Institute has collected a database of 119 copper concentrates, containing elemental/mineralogical compositions, which represents most of the product that is transported globally (See Table 1 – 3). Table 4 further demonstrates the primary importance of chalcopyrite, as a copper containing mineral, as well as the possible presence of other copper minerals, especially chalcocite, bornite and covellite, in some copper concentrates.

Additionally, a detailed characterization was carried out on representative samples (hereafter called reference materials/reference concentrates) by an independent, specialized laboratory.

The elemental composition was analyzed using several techniques and methodologies including, inductively coupled plasma atomic emission spectroscopy (ICP-AES), or inductively coupled plasma mass spectrometry (ICP-MS) after total dissolution. The amount of silicon oxide, SiO_2, was analyzed colorimetrically. Sulfur and carbon contents were determined in automatic analyzers (i.e. ELTRA CS2000) and the amount of sulfate, SO_4, by ion exchange chromatography.

The mineralogy was determined using methodologies of Scanning Electron Microscopy with Energy Dispersive X-Ray Spectrometer (SEM/EDS) and X-ray diffraction (XRD), also using integrated methodologies like QEMSCAN (Quantitative Evaluation of Minerals by SCANning electron microscopy).

The correlation between elemental copper content measured experimentally and that calculated from mineralogy is shown in Figure 2A and indicates a very good agreement. The statistics are shown in the box plot in Figure 2B.

N=119	Cu	Sb	As	Zn	Pb	Ni	Ag	Cd	Co
Min	14.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
p50%	26.670	0.010	0.110	0.620	0.140	0.002	0.006	0.004	0.005
p60%	27.570	0.015	0.139	1.307	0.266	0.004	0.008	0.006	0.009
p70%	28.452	0.022	0.180	2.872	0.562	0.008	0.011	0.010	0.013
p80%	29.958	0.042	0.272	3.652	1.478	0.010	0.017	0.014	0.024
p90%&	34.000	0.102	0.410	5.632	2.910	0.024	0.068	0.026	0.040
Max	51.050	7.250	7.500	9.280	12.710	1.030	1.907	0.072	0.250

Table 1: Elemental composition of world-wide copper concentrates

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[8] UVCB = Substance of Unknown or Variable composition, Complex reaction products or Biological materials (EU REACH definition)

Figure 2 : Correlation between copper content experimentally measured and that calculated from copper mineral species
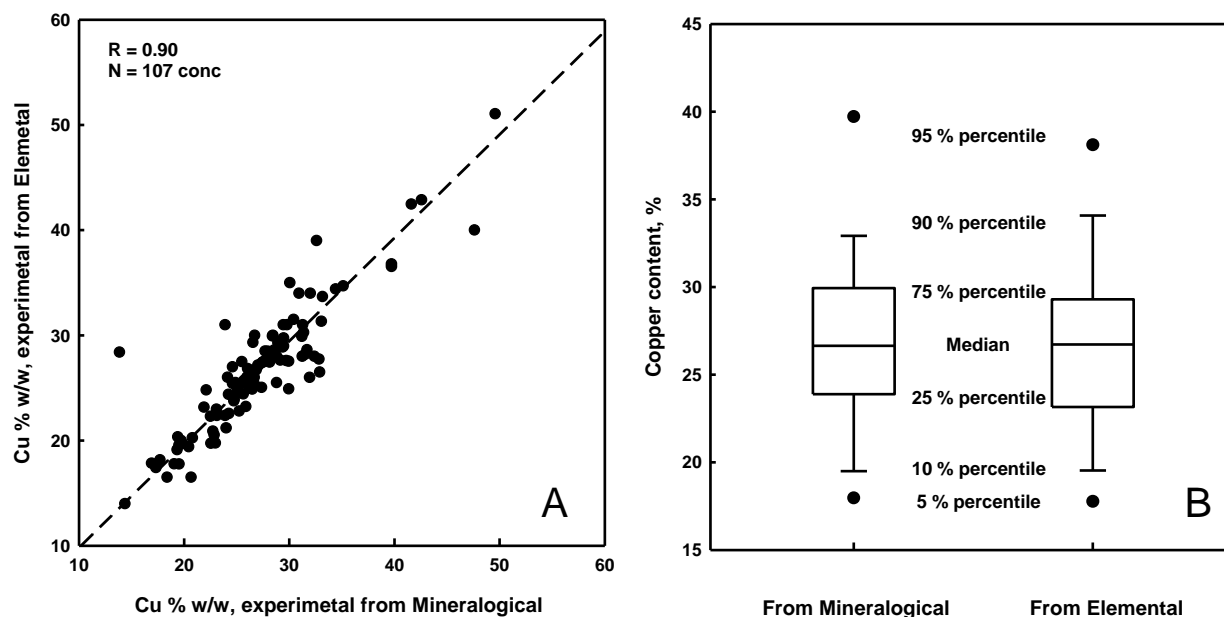
Mineral	Chemical Formula
Anglesite	$PbSO_4$
Argentotennantite	$(Ag,Cu)10(Zn,Fe)2(As,Sb)_4S_{13}$
Arsenopyrite	$FeAsS$
Bornite	Cu_5FeS_4
Chalcocite	Cu_2S
Chalcopyrite	$CuFeS_2$
Copper (II) oxide	CuO
Cosalite	$Pb_2Bi_2S_5$
Covellite	CuS
Cubanite	$Cu_2Fe_2S_3$
Digenite	Cu_9S_5
Enargite	Cu_3AsS_4
Galena	PbS
Malachite	$Cu_2(CO_3)(OH)_2$
Pentlandite	$(Fe.Ni)_9S_8$
Quartz	SiO_2
Sphalerite	ZnS
Tennantite	$Cu_{12}As_4S_{13}$
Tetrahedrite	$Cu_{12}Sb_4S_{14}$

Table 2 : Mineral species found in copper concentrates in concentrations greater than 0.01%

Mineral	Min	p50%	p60%	p70%	p80%	p90%	Max
Tennantite	0.000	0.000	0.000	0.000	0.144	0.944	5.800
Tetrahedrite	0.000	0.000	0.000	0.000	0.000	0.480	5.500
Copper (II) oxide	0.000	0.000	0.000	0.000	0.000	0.000	0.150
Enargite	0.000	0.000	0.000	0.000	0.000	0.084	25.000
Arsenopyrite	0.000	0.000	0.000	0.000	0.000	0.019	2.500
Galena	0.000	0.085	0.300	0.640	1.500	3.810	15.000
Quartz	0.000	2.235	3.030	4.504	7.000	10.000	30.000
Chalcocite	0.000	0.000	0.100	1.000	2.800	7.532	44.322
Sphalerite	0.000	0.725	1.102	4.200	5.980	8.000	18.838
Bornite	0.000	0.115	1.000	3.321	5.907	14.990	42.100
Digenite	0.000	0.000	0.000	0.000	0.000	0.000	4.700
Chalcopyrite	0.000	63.500	67.530	73.700	77.900	81.920	86.500
Covellite	0.000	0.000	0.400	0.800	1.679	3.656	25.000
Anglesite	0.000	0.000	0.000	0.000	0.000	0.000	6.000
Pyrite	0.000	11.000	15.000	18.533	20.026	29.196	55.300

Table 3 : Mineralogical composition of copper concentrates (N=112). Only minerals present in more than 5 samples are reported.

Cu in Mineral	Min.	percentile 50%	percentile 60%	percentile 70%	percentile 80%	percentile 90%	Max.
Cu-Bornite (BO)	0.0%	0.3%	2.6%	8.9%	14.5%	29.9%	77.5%
Cu-Chalcocite (CC)	0.0%	0.0%	0.6%	3.1%	8.0%	24.0%	91.7%
Cu-Chalcopyrite (CP)	3.0%	91.7%	95.4%	97.9%	100.0%	100.0%	100.0%
Cu-Copper (II) oxide (CuO)	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.5%
Cu-Covellite (CV)	0.0%	0.0%	1.0%	1.8%	3.8%	8.6%	51.0%
Cu-Cubanite	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	15.9%
Cu-Digenite (DG)	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	16.6%
Cu-Enargite (EN)	0.0%	0.0%	0.0%	0.0%	0.0%	0.2%	61.5%
Cu-Tennantite (TN)	0.0%	0.0%	0.0%	0.0%	0.2%	1.5%	8.6%
Cu-Tetrahedrite (TH)	0.0%	0.0%	0.0%	0.0%	0.0%	0.5%	11.2%

Table 4 : Elemental copper distribution within copper minerals present in concentrates

3. Hazard identification of Copper Concentrates

3.1 Environmental degradability assessment

Toxic substances that persist in the environment are considered more hazardous than substances that are readily degradable. Therefore, more severe chronic hazard classes are assigned to non-degradable substances (GHS, 2011 Table 4.1.1.).

While it has been recognized that "rapid degradability", as defined for organic substances, does not apply to metals (GHS, Annex 9, A9.7.3.1, 2011), the concept is critical to the environmental classification of metals and metal compounds.

Through multi-metal co-operation, in accordance with the principles outlined in the GHS and EU CLP guidance (ECHA, 2011), the potential for 'rapid loss from the environment' of metal ions (e.g. Cu, Zn, Pb, Ni, As, Cd) has been evaluated by assessing the removal rates of metal ions through partitioning and their subsequent potential for sediment mineralization/remobilization[9, 10 and 11]. The assessments have been done using a weight of evidence approach based on laboratory/mesocosm studies, field data and/or metal fate model.

The model assessment is based on The Tableau Input Coupled Kinetics Equilibrium Transport Unit World Model for Metals in Lakes (hereafter referred to as TICKET-UWM and available from http://blog.unitworldmodel.net), developed to assess the complexities and fate of metal speciation and its influence on effects of metals in the environment.

The principles and methodologies were discussed at the European Chemicals Agency (ECHA) in a workshop carried out on February 8th, 2012. The following conclusions were drawn:

- Metals that methylate, such as Hg, are not rapidly degraded;
- Metals that quickly hydrolyze and form different species that precipitate in the water column (Fe, Al, Sb, Sn, Mo, Cr...) are considered rapidly degraded;
- For the third group of metals (Cu, Zn, Ni, Pb), where the partitioning as well as the binding to Acid Volatile Sulfides are important factors for determining the rate of substance removal from the aquatic compartment, a consensus was not reached. Different views were expressed as to what extent the intrinsic properties of metals drive partitioning and binding to the sediment and what are the parameters (type of information) required to determine irreversibility under different environmental conditions. Further discussions are needed.

ECI, Eurometaux, ICMM and consultants have since provided additional evidence to the ECHA working group. Copper-specific reports are available (Rader 2012 and 2013). A multi-metal report, assessing the third group, is available (Rader et al., 2013)[11].

From this assessment, Cd, Cu, Ni, Pb, Sb and Zn are considered as rapidly degraded. This is integrated in this assessment.

3.2 Bioaccumulation Assessment

The copper Risk Assessment Report (2008)[12] and REACH Chemical Safety Report (2010) have 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. From this information, it has been concluded that the bio-accumulation criterion does not apply to the essential element

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[9] Rader, K et al., 2013. ASSESSMENT OF TIME-VARIABLE SOLUTIONS FOR COPPER IN THE UNIT WORLD MODEL FOR METALS IN LAKES – Report 001, available at ECI, submitted to the European Chemicals Agency (ECHA)

[10] Rader, K et al., 2012. Assessing Copper Concentrates in TICKET-UWM. Report, available at ECI

[11] Rader, K et al., 2013. Metal Classification using a Unit World Model. Eurometaux report, available at ECI, submitted to the European Chemicals Agency (ECHA)

[12] http://echa.europa.eu/copper-voluntary-risk-assessment-reports

copper. Similarly, in the zinc risk assessment and chemical safety report (2010)[13], it has been concluded that the bio-accumulation criterion does not apply to the essential element zinc.

The bio-accumulation potential of lead and nickel has been assessed in the lead and nickel risk assessments and under the EU Water Framework Directive[14]. These assessments concluded that both lead and nickel are not bio-magnified and do not pose a secondary poisoning concern.

> This assessment therefore concludes that copper and zinc are not bio-accumulative and that lead and nickel do not bio-magnify.

3.3. Aquatic Hazard Identification

Principles for the assessment

Copper concentrates exhibit a broad range of elemental and mineralogical compositions (Table 1 - 4). In order to assess the hazards and classifications for such a varied family of materials, without engaging in an extremely extensive and expensive testing campaign, a read across approach, aligned with the GHS and CLP metal-specific guidance and ICMM's hazard assessment guidance on ores and concentrates, was developed. This is briefly described below.

Copper concentrates are complex, sparingly soluble inorganic materials. In accordance with the GHS, their environmental classification is done by comparing the environmental soluble metal ions, measured after Transformation/Dissolution (TD), with their ecotoxicity reference values. The Transformation/Dissolution protocol (TDp) is the outcome of an international effort, under the OECD, to develop a standard operating procedure to assess the rate and extent of metal-ion releases from metals and sparingly soluble inorganic metal compounds (Skeaff et al., 2006)[15].

To assess the environmental solubility of metal ions from copper concentrates, 12 well characterized (elemental and mineral analysis) and representative samples of copper concentrates (Table 5), as well as relevant pure minerals (Chalcopyrite, Arsenopyrite, Chalcocite, Digenite, Bornite, Covellite, Enargite and Tennantite) (Table 8), were submitted to transformation/dissolution testing following the procedures described in the GHS[16], Annex 10 .

Table **5** shows that the reference concentrates selected for transformation/dissolution tests are globally representative.

Metals	% in reference concentrates	
	Min.	Max
Ag	BDL	1.9
As	0.08	0.36
Cd	BDL	0.05
Co	BDL	0.12
Cu	14.0	34.0
Ni	0.002	0.02
Pb	0.006	12.5
Zn	0.01	9

Cu Minerals	% in reference concentrates	
	Min.	Max.
Chalcopyrite (CP)	2	80
Covellite (CV)	BDL	9.7
Bornite (BN)	BDL	42.1
Enargite (EN)	BDL	0.56
Tennantite (Tn)	BDL	1.5
Chalcocite (CC)	BDL	28.43

Table 5: 12 reference copper concentrates assessed during 28 day transformation/dissolution tests

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[13] http://publications.jrc.ec.europa.eu/repository/handle/111111111/15064

[14] http://echa.europa.eu/web/guest/voluntary-risk-assessment-reports-lead-and-lead-compounds

[15] Skeaff JM, Ruymen V, Hardy DJ, Brouwers T, Vreys C, Rodriguez PH, Farina M. 2006. The standard operating procedure for the transformation/dissolution of metals and sparingly soluble metal compounds—revised, June 2006. Natural Resources Canada. CANMET-MMSL Division Report MMSL 06-085 (TR). 555 Booth St., Ottawa, Canada, K1A 0G1

[16] http://www.unece.org/fileadmin/DAM/trans/danger/publi/ghs/ghs_rev04/English/14e_annex10.pdf

The measured soluble metal ion concentrations (tested at 1mg/L loading and pH 6 to mimic worst case solubility) are compared to their corresponding metal ion ecotoxicity reference values, as obtained from the EU CLP and REACH dossiers (table 6).

Metal Ion	Acute ERV, µg/L	Chronic ERV, µg/L
Ag	0.22	0.09
As	430	40
Cd	18	0.21
Co	90.10	4.9
Cu	25	20
Ni	68	2.4
Pb	73.6	17.80
Sb	6900	1130
Zn	413	82

Table 6 : Ecotoxicity Reference Values (ERV) used for copper concentrates environmental hazard classification[17]

Aquatic hazards of the mineral constituents

For the main minerals in the copper concentrates, metal ion concentrations generated from transformation/dissolution tests on pure samples of chalcopyrite, arsenopyrite, chalcocite, digenite, bornite, covellite, enargite and tennantite are provided in Table 7. A comparison of the metal releases (at 1 mg/L), with the acute and chronic ERV values, shows that the metal releases from chalcopyrite, digenite, covellite and enargite are below the acute and chronic ERV values. Therefore, these minerals do not meet the criteria for environmental classification. Tennantite, bornite, chalcocite and arsenopyrite are classified as chronic aquatic toxicity category 3. Chalcocite is the only mineral that merits HME classification, due to an acute aquatic toxicity category 1 classification entry.

Mineral	pH6, 7 days, 1mg/L Cu-ions, µg/L	pH6, 28 days, 1mg/L Cu-ions, µg/L	Aquatic hazard classification
Chalcopyrite	2.8	3	Not classified
Digenite	5.3	18.7	Not classified
Covellite	5.7	14.5	Not classified
Enargite	5.9	10	Not classified
Tennantite	13.3	22.8	Chronic 3 - with rapid removal;
Bornite	23.9	37.8	Chronic 3 - with rapid removal;
Chalcocite	67.8	143	Acute 1 Chronic 3 - with rapid removal

Mineral	pH6, 7 days, 1mg/L As-ions, µg/L	pH6, 28days, 1mg/L As-ions, µg/L	GHS outcome
Arsenopyrite	49	107	Chronic 3
Tennantite	1.8	5.13	Not classified
Enargite	BDL	1.2	Not classified

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[17] Compiled in the multi-metal Meclas database - http://www.meclas.eu/

Table 7 : Results from the transformation/dissolution tests (1 mg pure mineral, ground to <50 μm, tested at pH 6), and corresponding aquatic hazard classification for major minerals present in copper concentrates

Chalcocite is the only <u>major</u> mineral that merits HME classification, due to an acute aquatic toxicity category 1 classification entry. Assessing the classification of copper concentrates, using the summation rules of classified minerals, leads to the classification of concentrates as acute aquatic toxicity category 1 and HME under MARPOL Annex V when chalcocite concentrations are ≥25 %. **As a result, 4 % (4/112 of the concentrate samples (Table 3), meet the HME criteria.**

Metal releases from copper concentrates: transformation/dissolution tests of copper concentrates

The classification of copper concentrates, using the summation rules as outlined above, does not consider:

- Simultaneous releases of copper from non-classified and classified copper minerals
- Simultaneous metal releases from major and minor minerals (e.g. Pb-ions from anglesite and galena, Ag-ions from argentotennantite, Zn-ions in sphalerite)

The environmental classification was therefore also assessed by considering the concentrate as a substance and assessing the releases of metals during transformation/dissolution tests. Results from transformation/dissolution tests (1 mg/L, pH 6), as well as detailed elemental and mineral compositions, are available for 12 representative copper concentrates (

Table **5** and Table 9).

While the results from the 28 day transformation/dissolution tests do demonstrate some metal releases, those for copper are much lower for the chalcopyrite dominated concentrates compared to the chalcocite-rich ones. The individual concentrates classifications therefore need to recognize the different dissolution behaviors of the various copper containing minerals (Table 8). A read-across approach was developed, hypothesizing that the dissolution behavior of copper, from the mineral compounds in concentrates, will be the same as from these minerals in their pure forms. Such a read-across has been validated (see below).

	% Environmental Solubility		
Mineral	**Loading 100 mg/L** **7days TD test**	**Loading 1 mg/L** **7 days TD test**	**Loading 1 mg/L** **28 days TD test**
Chalcopyrite	0.3 ± 0.006	**0.8 ± 0.080**	**0.9 ± 0.081**
Digenite	0.6 ± 0.036	**0.8 ± 0.072**	**2.7 ± 0.243**
Enargite	2.3 ± 0.207	**1.3 ± 0.195**	**2.2 ± 0.198**
Covellite	3.4 ± 0.068	**0.9 ± 0.045**	**2.2 ± 0.264**
Tennantite	2.3 ± 0.069	**3.4 ± 0.170**	**5.8 ± 0.522**
Bornite	2.6 ± 0.104	**4.4 ± 0.176**	**7.0 ± 0.350**
Chalcocite	5.3 ± 0.371	**9.9 ± 0.396**	**20.9 ± 0.627**

Table 8 : Environmental Solubility (%) of copper from copper minerals during short term (7 days) and long term (28 days) Transformation/Dissolution tests (TD test) are expressed as: (μg metal ions released/μg total metal)*100. Retained % Environmental Solubility values are indicated in bold.

For the other metals (As, Cd, Co, Ni, Pb, Zn and Ag), the release rates could not be explained by mineral release rates. They were therefore estimated as the highest reliable release rates observed in the TD tests of the group of 12 representative concentrates. In the absence of validation data, ECI's conservative approach is to select the highest experimental releases, from the tested reference concentrates, covering the range of elemental and mineral compositions.

As a read-across parameter, the % Environmental Solubility (ES) for each metal was derived[18], in acute (7 days) and chronic (28 days) conditions. These are shown in Table 9. The ESs used in the classification procedure are shown in Table 10.

	% Environmental Solubility 7 days				% Environmental Solubility 28 days	
Number of Samples	**4**		**12**		**12**	
	Loading 100 mg/L		**Loading 1 mg/L**		**Loading 1 mg/L**	
Metal	*Min.*	*Max.*	*Min.*	*Max.*	*Min.*	*Max.*
As	0.5 ± 0.05	1.2 ± 0.07	2.7 ± 0.27	**5.00 ± 0.50**	3.2 ± 0.61	**14.2 ± 0.57**
Cd	5.9 ± 0.30	**9.8 ± 0.49**	Not detected	6.7 ± 0.60	Not detected	**10.0 ± 1.40**
Co	4.9 ± 0.10	7.6 ± 0.95	Not detected	**11.7 ± 0.82**	Not detected	**30.0 ± 1.5**
Cu	0.3 ± 0.01	4.0 ± 0.16	0.50 ± 0.04	7.5 ± 0.30	0.74 ± 0.07	13.7 ± 0.55
Ni	4.0 ± 0.12	**7.3 ± 0.95**	Not detected	Not detected	Not detected	**29.2[19]**
Pb	7.6 ± 0.30	19.8 ± 1.39	5.7 ± 2.05	61.1 ± 1.22*	11.3 ± 2.20	**53.3 ± 5.1**
Zn	2.4 ± 0.17	**9.1 ± 0.27**	0.9 ± 0.13	15.3 ± 2.60*	1.0 ± 1.04	15.3 ± 18.83*
Ag	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected

Table 9 : Acute and chronic Environmental Solubility (%) for Cu, As, Cd, Co, Ni, Pb and Zn. Metal releases from the 12 reference copper concentrates during short term (7 days) and long term (28 days) Transformation/Dissolution tests (TD test) are expressed as: (µg metal ions released/µg total metal)*100. Retained values are indicated in bold.
*Measured concentration below limit of quantification and/or coefficient of variation >20%. Those values were therefore not retained.

	% Environmental Solubility	
Metal	**<u>Acute</u>, from 7 Days TD test**	**<u>Chronic</u>, from 28 Days TD test**
Ag	Not detected[20]	Not detected[16]
As	5.00 ± 0.50	14.2 ± 0.57
Cd	9.8 ± 0.49	10.0 ± 1.40
Co	11.7 ± 0.82	30.0 ± 1.50
Cu[21]	0.8 ± 0.08 - 9.9 ± 0.40	0.9 ± 0.08 – 20.9 ± 0.63
Ni	7.3 ± 0.95	29.2[15]
Pb	50.3 ± 3.02*	53.3 ± 5.1
Zn	9.1 ± 0.27	11.6 ± 1.39*

Table 10 : Summary of retained Environmental Solubility (%) for metals of ecotoxicological concern present in copper concentrates. * The highest reliable value (measurement above quantification limit and coefficient of variation <20%) was retained.

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[18] For Cu Environmental Solubility (%)= (µg metal ions released/µg total metal)*100 in the pure mineral, as obtained in 7 days and 28 days TD tests of the pure minerals. For other metals (As, Cd, Co, Ni, Pb and Zn), the Environmental Solubilities were obtained from the 12 reference concentrates. Only results above the reported quantification limits and with coefficient of variation <20% were retained for Environmental Solubility determinations.

[19] Estimated as 4 times the release at 7 days

[20] The release of silver was below detection limit up to 1.9% Ag in the concentrate

[21] The Copper environmental solubility depends on the specific concentration of the copper bearing mineral in the concentrate

Validation of read-across: predicting the copper releases from concentrates

The read–across procedure for copper was validated as follows (see scheme 2). Using the copper Environmental Solubilities - ES (%) for different pure minerals, and the % of each mineral in each reference concentrate, the % copper releases from the copper concentrates were estimated (see Equation 1).

$$\sum_i ES_i * [Cu - Mineral]_i = [Cu - dissolved - Concentrate]_j$$

Equation 1

Where ES = environmental solubility (%) at 7 or 28 days of the pure mineral i (from Table 8), $[Cu\text{-}Mineral]$ = % of the mineral i present in the concentrate and $[Cu\text{-}dissolved\ Concentrate]$ = % copper release from the concentrate j.
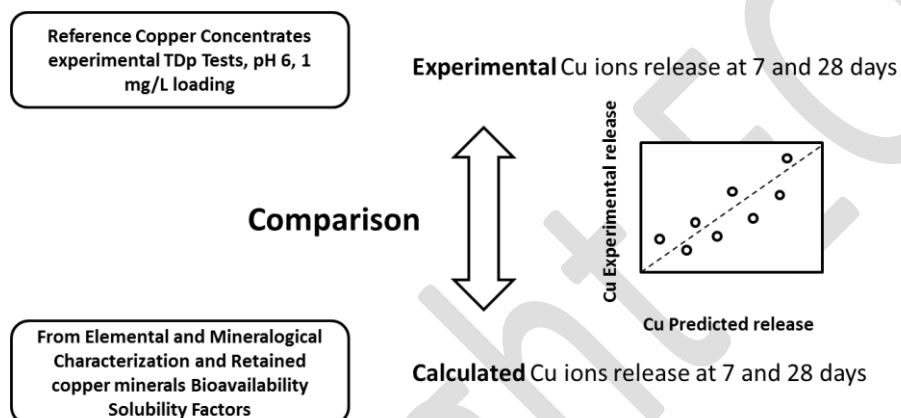
Scheme 2 - Validation procedure

Figure 3 shows the predicted vs. estimated copper release rates, from the 7 and 28 day TD tests (at 1 mg/L loading), for the 12 reference concentrates. The correlation coefficient (R) was 0.75. While only two points deviate significantly from the regression line, only one of them would lead to an underestimate of the release rate.
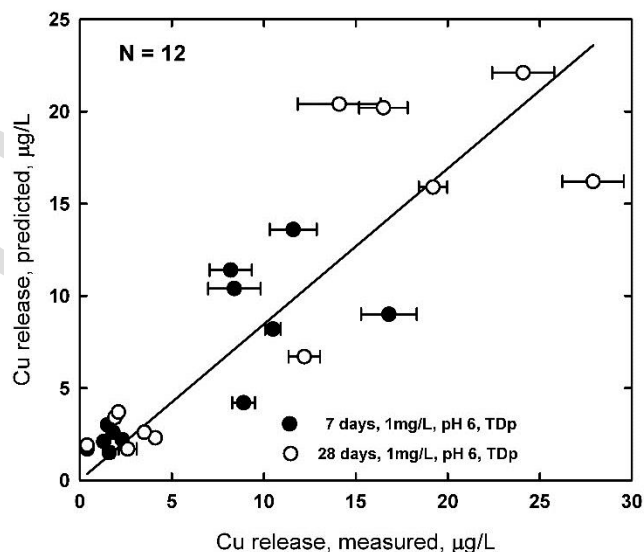
Figure 3: Experimental validation of read across from copper bearing minerals to copper concentrates

Aquatic hazard classification of copper concentrates

The soluble metal ion concentrations, measured or calculated from the read across procedure, were compared to the metal-ion specific acute and chronic ecotoxicity reference values (ERVs). The GHS additivity approach was subsequently used for the derivation of the acute and chronic classification categories (Schemes 3 and 4). The acute and chronic reference values (ERVs) are obtained from Table 6.

The benchmark quantity, to determine if a substance or mixture is classified in any given acute or chronic category, is the sum of Toxic Units for each component. Toxic units in acute classification are defined as the ratio between the concentration of the metal released in the 7 day TD test (at pH 6 at 1, 10, 100 mg/L) and the acute ecotoxicity reference value for each metal ion present. If the toxic units are equal or greater than 1 the substance is classified in the corresponding category (Scheme 3). The same general rationale is applied for chronic classification, where the metal ion releases are measured/calculated (at pH 6, 28 days at loadings of 0.01, 0.1 and 1 mg/L) and the corresponding chronic ERVs are used (see Scheme 4).

However, in the case of chronic classification, due consideration must be given to the environmental degradability of each component of the substance. Among the metals present in copper concentrates, only Cu, Cd, Ni, Pb, Sb and Zn are considered rapidly degradable (see section 5.2.1). Accordingly, a factor of 10 is applied to the non-rapidly degradable components (Scheme 4). The stepwise approach used for the classification is summarized in Scheme 5.

According to GHS, 2011

$$TU_{mix} = \sum_i TU_i$$
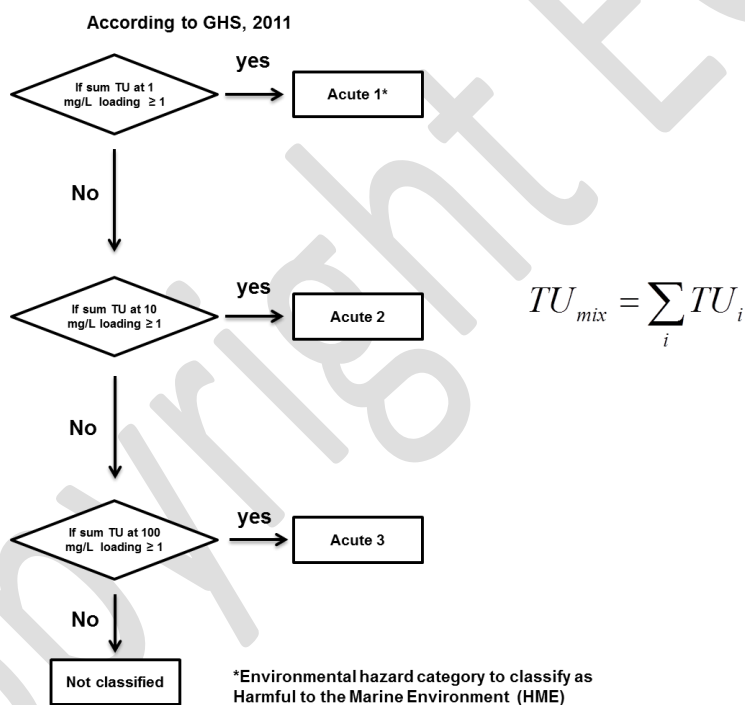
Scheme 3 - Decision tree for acute environmental classification of copper concentrates

Cu, Cd, Ni, Pb, Sb & Zn as Rapidly Degradable

$$TU_{mix} = \sum_i TU_{i\_RD} + \sum_j 10 * TU_{j\_NRD}$$

$$TU_{mix} = \sum_i TU_{i\_RD} + \sum_j 10 * TU_{j\_NRD}$$

$$TU_{mix} = \sum_i TU_i$$

*Environmental hazard categories to classify as Harmful to the Marine Environment (HME)
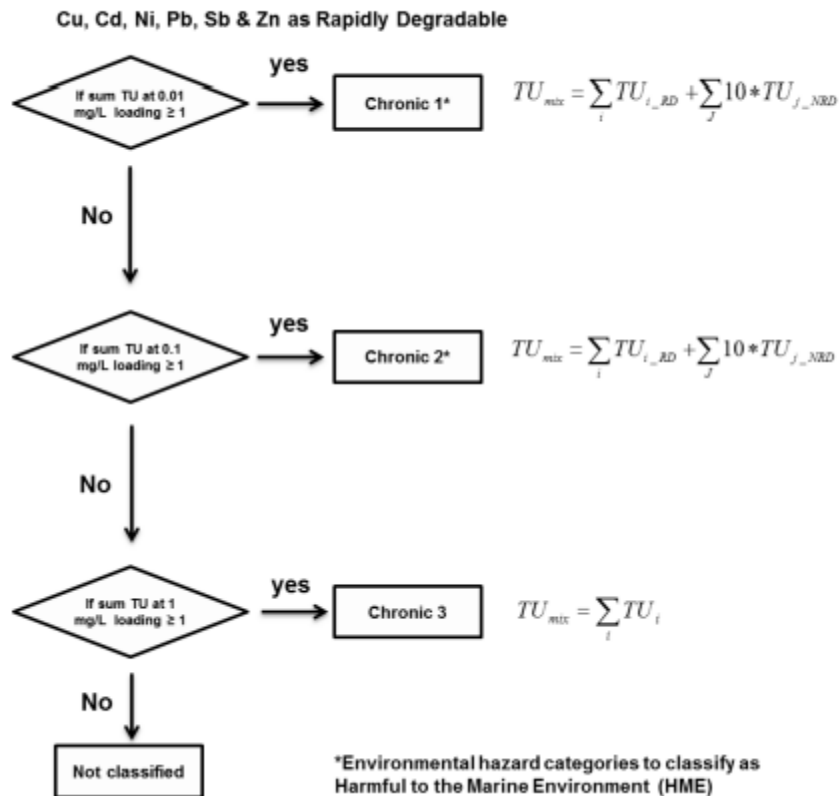
Scheme 4 - Decision tree for chronic environmental classification of copper concentrates, where TU_{i_RD} corresponds to the toxic units of the readily degradable and TU_{i_NRD} to the non-degradable components.

Transformation dissolution data are available for 13 concentrates (12 reference concentrates + 1 without detailed mineral composition). The classification, assessed for each of these, indicates that 1 concentrate merits to be classified as HME, due to an aquatic acute category 1 classification. The releases of metal ions from the other concentrates merit aquatic acute category 2 and, in some cases (6/13), chronic category 3 classifications. However, these do not lead to a need for HME classification.

The classification of each of the 119 copper concentrates was assessed using the read across approach (scheme 5), the elemental and mineral compositions and the % environmental solubility.

The assessment confirms that the vast majority of copper concentrates do not meet the environmental HME criteria.

Out of the 119 concentrates assessed, only 3-4% are identified as Harmful to the Marine Environment under MARPOL Annex V, due to aquatic acute category 1 hazard. The observed acute 1 hazard profiles are attributed to high releases of copper, predicted for concentrates with high concentrations of chalcocite (> 28%) and/or a combination of high concentrations of chalcocite (>20%) and high concentrations of bornite (>30%).

The statistical assessment further demonstrates that, at the 90th percentile of the elemental composition and worst case environmental solubility, only 20% of the acute hazard profile may be attributed to lead, while the contribution of the other elements remains minor (<1%).

To fully account for all minor elements in all copper concentrates, the following formula can be used as criteria to assign a worst case acute 1 classification hazard:

SUM(%As*0.0012+%Zn*0.0022+%Pb*0.068+%Ni*0.011+%Cd*0.054+%Co*0.013+%Chalcocite*0.032+%Bornite*0.011+% chalcopyrite*0.0011+% tennantite*0.0065+ % sum other minerals *0.0025) $\geq$1. [22]

Note: Several concentrates are classified under GHS as acute 2 and aquatic chronic 3, but these categories are not relevant to HME.

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┌─────────────────────────────────────────────────────────────┐
│                    Mineral composition %                     │
└─────────────────────────────────────────────────────────────┘
                              │
┌─────────────────────────────────────────────────────────────┐
│  Elemental Composition %, calculated from minerals (using    │
│  molecular weight), for elements relevant for environmental  │
│  classification                                              │
└─────────────────────────────────────────────────────────────┘
                              │
┌─────────────────────────────────────────────────────────────┐
│  Determine the translation factor for each metal/mineral     │
│  pair using the 7 and 28 day environmental solubility (from  │
│  pure minerals and concentrates transformation/dissolution)  │
└─────────────────────────────────────────────────────────────┘
                              │
┌─────────────────────────────────────────────────────────────┐
│  Determine the metal release from the concentrate in ug/L    │
│  using the measured elemental composition and the unique     │
│  translation factors (obtained in the previous step)         │
└─────────────────────────────────────────────────────────────┘
                              │
┌─────────────────────────────────────────────────────────────┐
│  Calculate the acute and chronic toxic units for each metal  │
│  by dividing the metal released (previous step) by the       │
│  corresponding acute or chronic ERVs. Add them up across     │
│  all metals and obtain the Toxic Units Sum (TU$_S$)*         │
└─────────────────────────────────────────────────────────────┘
                              │
┌─────────────────────────────────────────────────────────────┐
│  Add the Toxic Units for Acute and Chronic. If the           │
│  summation of TU ≥ 1, classify the concentrate as Acute      │
│  1,2,3 or Chronic 1, 2 or 3                                  │
└─────────────────────────────────────────────────────────────┘
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Scheme 5 - Step by step environmental hazard classification procedure for copper concentrates. Concentrates classified as Acute 1, Chronic 1 and /or Chronic 2 also need to be classified as "Harmful to the Marine Environment" under MARPOL Annex V.

3. 4. Human health hazard identification

Principles for the assessment

The human health criteria, to classify as HME under MARPOL Annex V, are: Carcinogenicity – Cat1, Mutagenicity-Cat 1, Reproductive toxicity Cat 1 and Repeated dose Specific Target Organ Toxicity (STOT-RE – Cat 1), following dermal and oral exposures. The GHS cut-off values for mixtures are: Mutagenicity (0.1%); Carcinogenicity (0.1%); Reproductive toxicant (0.3%); STOT-RE (1%). For classification as "harmful to the marine environment", these categories need to be combined with not being rapidly degradable and having high bioaccumulation.

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[22] To be only used if % copper measured from elemental and mineralogical analysis are comparable. Refined assessment with ECI excel tool.

Considering the elemental/mineral composition of the copper concentrates, the hazard profiles of various metal ions are considered as relevant if the bio-accessibilities of these ions are above the classification trigger values. Oral bio-availability of the inorganic metal ions exceeds dermal bio-availability and therefore the assessment focuses on the oral exposure route.

Table 11 shows that when considering oral exposure, releases of Pb, As, Cd and Co may be relevant to MARPOL Annex V human health hazards.

CLP entries	Mutagen REACH	Carcinogen REACH	Reproductive toxicant REACH	STOT-RE REACH
Pb compounds			Cat1	Cat1
Ni in e.g. NiS, NiSO$_4$		*Cat1 **	*Cat1***	*Cat1 **
Cd in e.g. CdCl$_2$	Cat1	Cat1	Cat1	Cat1
Co in e.g. CoCl$_2$	Cat1	*Cat1 **	Cat1	
As compounds		Cat 1***		
* by inhalation only (not relevant to MARPOL Annex V) *** only for soluble nickel compounds* ****only for soluble compounds (arsenic acids and its salts, AsO$_3$ and AsO$_5$)*				

Table 11 : Metal ions whose compounds are classified as CMR or STOT-RE

Bio- elution tests on copper concentrates - oral

The releases of metal-ions from the representative reference concentrates (

Table 5 and Table 12) and the major pure copper minerals (chalcopyrite, chalcocite, digenite, bornite, covellite, enargite and tennantite) were determined through in vitro bio-elution tests in gastric fluids (pH 1.5), following the international ASTM D 5517-07[23],[24] protocol and the refinements considered in the Eurometaux SOP**[25].** Comparison of the % gastric bio-accessibility shows consistently limited bio-accessibility, of the metals contained in the minerals and reference concentrates, compared to soluble compounds.

The release of copper-ions into the gastric fluid ranged, for the various copper concentrates and copper minerals, between 0.3 and 6.5%. Table 12 summarizes the metal releases for Pb, Cd, Co and As (critical elements identified in Table 11). From the results of these bio-elution tests, metal-specific % gastric bio-accessibilities ((µg metal ions released/µg metal in reference concentrate or mineral)*100) were calculated for each of the concentrates. To determine the % gastric bio-accessible metal in each, reliable worst case % bio-accessibilities for each of the metals were determined from the measured releases observed from the tested reference concentrates[26].

To compare the metal releases from the bio-elution tests to the toxicity endpoints of the target classified soluble metal compounds, a molecular weight translation is applied for cadmium as shown in Table 13.

	Bio-elution Test, Gastric media
Number of Samples	11

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[23] ASM D5517-07: Standard Test Method for Determining Extractability of Metals from Art Materials, Philadelphia, PA: American Society for Testing and Materials, 2007

[24] EN71-3: Safety of Toys – Part 3: Migration of certain elements, CEN, Ref No EN 71-3: 1994 E, December 1994

[25] Standard Operating Procedure (SOP) for the Bio-accessibility Testing Programme, November 10, 2010, directed by Eurometaux

	pH 1.5, 2 h, loading 200 mg/L	
	% gastric bio-accessibility	
Metal	*Min.*	*Max.*
As	Not detected	1.81 ± 0.25
Cd	Not detected	14.1 ± 0.28
Co	Not detected	4.00 ± 0.12
Pb	4.40 ± 0.176	56.8 ± 0.00

Table 12 : % gastric bio-accessibility for As, Cd, Co, Pb. Releases found in reference copper concentrates at pH 1.5 after 2 hours of bio-elution testing at loading of 200 mg/L. The maximum values were determined using the reliable measured releases from the 11 concentrates (measurements above the quantification limit and coefficient of variation <20%)

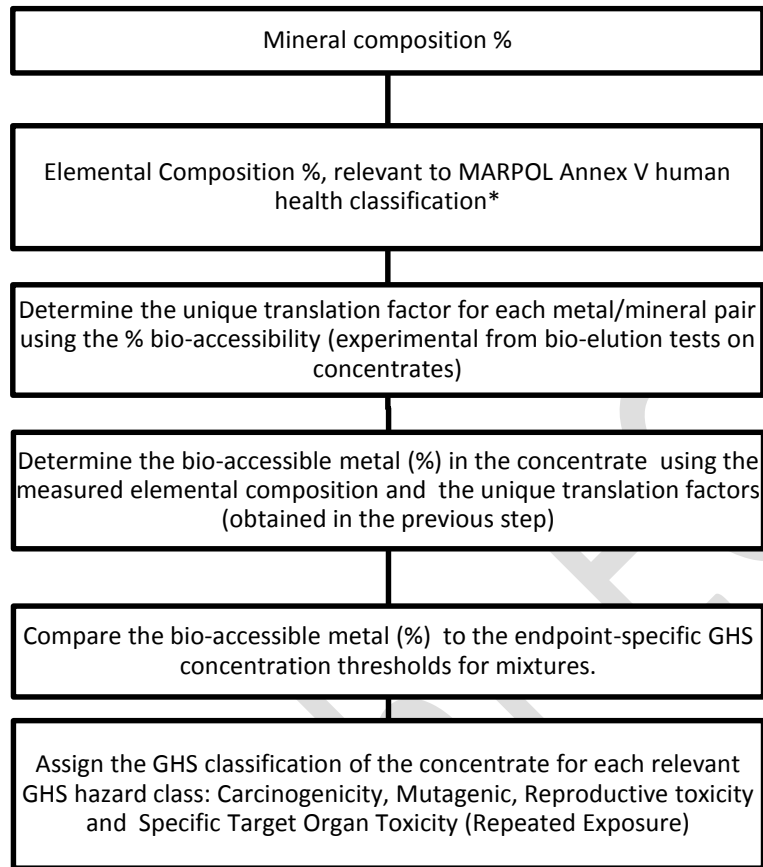| Metal	% gastric bio-solubility	Translated to hazardous compound as listed in annex VI, CLP, as %	
As	1.81 ± 0.25	as As in arsenic acid and its salts [27]	1.81 ± 0.48
Cd	14.1 ± 0.28	as $CdCl_2$	23.03 ± 0.46
Co	4.00 ± 0.12	as Co	4.00 ± 0.12
Pb	56.8 ± 0.00	as Pb compound	56.8 ± 0.00

Table 13 : Selected gastric % bio-accessibility for the metals of toxicological concern present in copper concentrates

The % bio-accessible components calculated for the 11 reference copper concentrates shows that the bio-accessibility of $CdCl_2$, Co and As is, in all cases, below the GHS threshold concentration. Bio-accessible lead concentrations are in some cases above the trigger value for reproductive toxicity (0.3%).

The % bio-accessible components calculated for all copper concentrates, shows that the bio-accessibility of $CdCl_2$, and Co is below the GHS threshold concentration (0.1% for carcinogenicity/mutagenicity). For arsenic, application of the worst case metal-specific bio-solubility factors (Table 13) results in 1/119 cases exceeding the bio-accessible arsenic cut-off value of 0.1% for carcinogenicity (measured bio-accessible Arsenic 0.13 %).

For lead, application of the worst case % metal-specific bio-accessibility (Table 7) results in bio-accessible lead concentrations exceeding the reproductive cut-off value of 0.3% (corresponding to total Pb content >0.53%) in around 30% of the copper concentrates. Lead is therefore the key driver for the human health classification as cat 1 CMR/ STOR-RE. However, lead is rapidly removed from the water column and not bio-magnified. Lead is a priority substance under REACH due to its reprotoxicity classification, but not a priority hazardous substance under the EU Water Framework Directive, confirming that lead is not to be considered as a Persistent, Bio-accumulative and Toxic substance. Therefore, it can be concluded that the copper concentrates do not meet the MARPOL AnnexV human health criteria.

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[27] This is a conservative assessment because the toxicity of As acids and is salts are used

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┌─────────────────────────────────────────────────────────────┐
│                   Mineral composition %                      │
└─────────────────────────────────────────────────────────────┘
                              │
┌─────────────────────────────────────────────────────────────┐
│   Elemental Composition %, relevant to MARPOL Annex V human  │
│                     health classification*                   │
└─────────────────────────────────────────────────────────────┘
                              │
┌─────────────────────────────────────────────────────────────┐
│  Determine the unique translation factor for each metal/mineral pair │
│  using the % bio-accessibility (experimental from bio-elution tests on │
│                         concentrates)                        │
└─────────────────────────────────────────────────────────────┘
                              │
┌─────────────────────────────────────────────────────────────┐
│  Determine the bio-accessible metal (%) in the concentrate using the │
│  measured elemental composition and the unique translation factors │
│                  (obtained in the previous step)             │
└─────────────────────────────────────────────────────────────┘
                              │
┌─────────────────────────────────────────────────────────────┐
│  Compare the bio-accessible metal (%) to the endpoint-specific GHS │
│             concentration thresholds for mixtures.           │
└─────────────────────────────────────────────────────────────┘
                              │
┌─────────────────────────────────────────────────────────────┐
│  Assign the GHS classification of the concentrate for each relevant │
│  GHS hazard class: Carcinogenicity, Mutagenic, Reproductive toxicity │
│    and Specific Target Organ Toxicity (Repeated Exposure)    │
└─────────────────────────────────────────────────────────────┘
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Scheme 6 : Step by step Human Health hazard classification procedure for copper concentrates. Concentrates classified as CMR and/or STOT-RE class 1 <u>and</u> characterized as Bio-accumulative and Not Rapidly degraded need to be classified as "Harmful to the Marine Environment" under MARPOL Annex V.

4. Conclusion

The procedures for environmental and health hazard assessments, described in this report, have been used to test samples of 119 copper concentrates from around the world. The results indicate that only 3-4% of copper concentrates merit classification as HME under the MARPOL Annex V convention. Such an HME classification is driven by high levels of chalcocite/bornite.

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