

# 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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## Executive summary

To implement the MARPOL convention, the International Maritime Organization (IMO) has established criteria for hazard classification of solid bulk cargoes as “harmful to the marine environment” (HME). This guidance document describes how to apply these criteria to copper concentrates. Copper concentrates are solid mining products transported in bulk. The classification of these materials according to the HME criteria were assessed following the methodologies and procedures described in the 10<sup>th</sup> revised edition of UN GHS and the ICMM guidance on ores and concentrates, revised in 2021. The information of elemental and mineral compositions of 106 copper concentrates, representative of world-wide production, was collected in 2012. Elemental compositions are dominated by copper, iron and sulfur. These elements are incorporated in sulfidic minerals, such as chalcopyrite, bornite, digenite, covellite, and chalcocite. Other major elemental constituents (Al, Ca, Mg, K, Si, Mn) are incorporated in minerals, usually defined as “gangue”, such as calcite, dolomite, hornblende, and quartz. Copper concentrates may also contain small amounts of zinc, lead, arsenic, nickel, cobalt and silver. Depending on the ore body, the composition of copper concentrates may vary widely, and consequently, different copper concentrates may have different hazard profiles. Therefore, the hazards of copper concentrates should be assessed on a case-by-case basis by the producers.

To assess the environmental criteria, the metal release from 12 representative copper concentrates and 8 pure copper minerals was measured in transformation/dissolution tests, in accordance to OECD Guidance Document 29 . The environmental transformation and bioaccumulation of the released metal ions was assessed following the principles and recommendations of the metals UN GHS Annex 9.7. The results demonstrate low metal releases from the copper minerals and copper concentrates to environmental media. The environmental classification was assessed by comparing the metal release from the copper concentrates to the relevant ecotoxicity reference values derived by the relevant metal associations and consortia. To assess the human health criteria, information was gathered on the bioaccessibility of the metal ions, (tested in accordance with ASTM 5517), on their classification for mutagenicity, carcinogenicity, reproductive toxicity and specific target organ toxicity after repeated exposure (STOT-RE), and on their potential for biomagnification, bioaccumulation and rapid environmental transformation.

A read-across approach was developed, allowing producers to assess the environmental and human health HME criteria for individual copper concentrates based on information on the elemental and mineralogical composition of the copper concentrates. This read-across approach was then applied to calculate the classifications of the entire database of 106 copper concentrates. The assessment shows that 87% of copper concentrates are classified as not HME. Only 13% of copper concentrates are classified as Aquatic Acute category 1 and therefore as HME, mainly due to the presence of chalcocite which has high environmental solubility compared to the other tested copper minerals. All copper concentrates with more than 15% chalcocite content will be HME, while some copper concentrates with less than 15% chalcocite may also be classified as HME depending on the other copper minerals and metals in the concentrate. For human health, some copper concentrates are classified as reproductive toxicant category 1 due to the lead content, but this does not lead to HME classification. This approach has been implemented in the metals classification calculation tool MeClas (version 5.12) to help producers derive compliant classifications for copper concentrates.

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## 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) (1), that established 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. Later in 2016, the IMO, adopted resolution MEPC 277(70) (2) that replaces the “2012 guidelines for the implementation of MARPOL Annex V”, where the HME criteria was included in regulation 4 and 6, as Appendix 1.

The criteria encompass six hazard classes/categories relevant to inorganic substances. The hazard classification rules of the GHS are used: The criteria are based on UN GHS. For specific products (e.g., metals and inorganic metal compounds), guidance available in UN GHS (3), annexes 9 and 10, is essential for proper interpretation of the criteria and classification. The 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<sup>i</sup> Category 1A or 1B, combined with not being rapidly degradable and having high bioaccumulation; and/or
4. Mutagenicity<sup>i</sup> Category 1A or 1B, combined with not being rapidly degradable and having high bioaccumulation; and/or
5. Reproductive Toxicity<sup>i</sup> Category 1A or 1B, combined with not being rapidly degradable and having high bioaccumulation; and/or
6. Specific Target Organ Toxicity Repeated Exposure<sup>i</sup> Category 1, combined with not being rapidly degradable and having high bioaccumulation.

<sup>i</sup> 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.

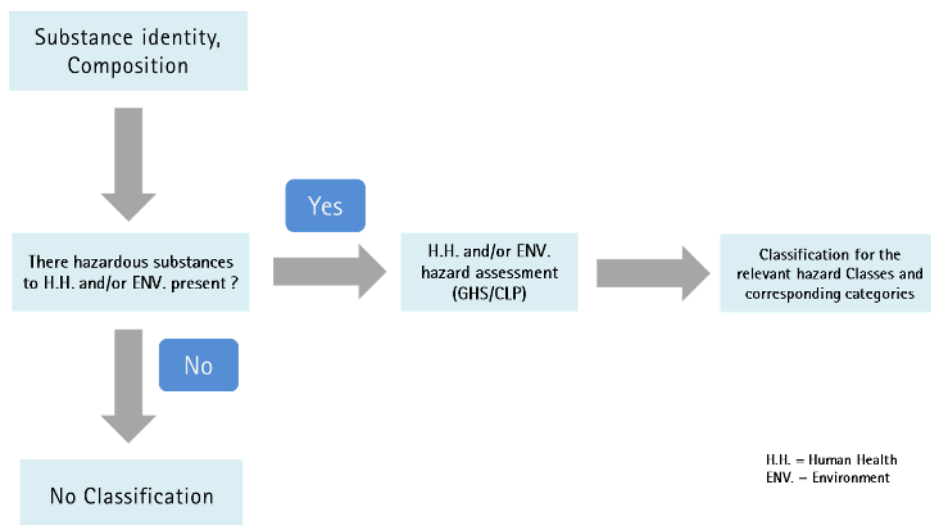
Copper concentrates are solid mining products transported in bulk. It is therefore necessary to determine the classifications for the human health and environmental hazard categories set out in the HME criteria.

## 1.2. The Globally 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 provides the latest progress on implementation (<https://unece.org/ghs-implementation-0>).

## 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 may pose a hazard, must be accounted for, considering the percentages that trigger classification (see Scheme 1). Third, the hazard classification is determined following the GHS criteria and rules. A detailed flowchart of the approach can be found in the ICMM guidance document “Hazard Assessment of Ores and Concentrates for Marine Transport” (4).



**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 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 increased to  $\pm 30\%$  w/w. The unwanted fraction of the ore is discarded as tailings.



**Figure 1.** Distribution of the main copper ore deposits (8).

Copper concentrates are mainly produced by the froth flotation method. The ore is crushed and milled to a particle size of less than  $100\ \mu\text{m}$ . This produces a mix of particles containing pure crystalline phases of primary or secondary copper sulfides. The ore is then 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 (rich in chalcopyrite) contain, on average, 20 to 30% copper, whereas the secondary sulfide concentrates (rich in chalcocite) 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.

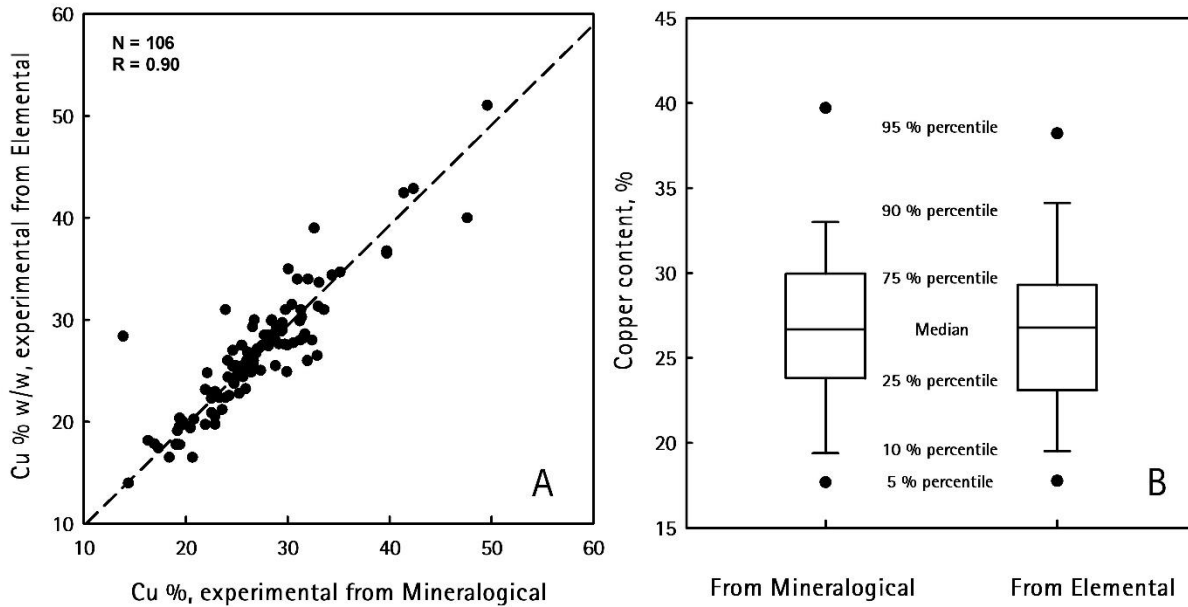
## 2.2. Copper Concentrates - Substance Identity

As can be envisaged from the production process, 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 geology of the location and age of the mine site. Concentrates are therefore considered to be naturally occurring substances of variable composition. Under GHS, they may be considered as complex mixtures or complex substances. Under the European legislation, i.e., the Regulation on Classification, Labelling and Packaging of substances and mixtures (CLP) and the REACH regulation, copper concentrates are considered as UVCB substances: chemical substances of Unknown or Variable composition, Complex reaction products and Biological materials (6, 9, 10).

In 2012, the International Copper Association collected a database of elemental and mineralogical composition of 106 copper concentrates, originating from mines around the world. This dataset represents most of the copper concentrate that is transported globally (See Tables 1-3). Table 4 further demonstrates the importance of chalcopyrite, as the main copper bearing mineral, as well as the possible presence of other copper minerals, especially chalcocite, bornite and covellite, in some copper concentrates. 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 mineralogy was determined by Scanning Electron Microscopy with Energy Dispersive X-Ray Spectrometer (SEM/EDS), by X-ray diffraction (XRD) or by 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 2 and indicates a good general agreement.

**Table 1.** Elemental composition of 106 copper concentrates from around the world

	<b>Cu</b>	<b>Sb</b>	<b>As</b>	<b>Zn</b>	<b>Pb</b>	<b>Ni</b>	<b>Ag</b>	<b>Cd</b>	<b>Co</b>
<b>Min</b>	14.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<b>p50%</b>	26.78	0.01	0.11	0.62	0.15	0.00	0.01	0.00	0.01
<b>p60%</b>	27.59	0.02	0.14	1.95	0.28	0.00	0.01	0.01	0.01
<b>p70%</b>	28.49	0.02	0.18	2.94	0.58	0.01	0.01	0.01	0.01
<b>p80%</b>	30.00	0.04	0.26	3.85	1.52	0.01	0.02	0.02	0.03
<b>p90%</b>	34.00	0.10	0.36	5.77	3.75	0.03	0.07	0.03	0.04
<b>Max</b>	51.05	7.25	7.50	9.28	12.71	0.83	1.91	0.07	0.25



**Figure 2.** Correlation between measured copper content and calculated copper content based on mineralogical analysis

**Table 2.** Mineral species found in copper concentrates in concentrations above 0.01% and relevant for hazard classification

Mineral	Chemical Formula	Mineral	Chemical Formula
Anglesite	PbSO <sub>4</sub>	Digenite	Cu <sub>9</sub> S <sub>5</sub>
Argentotennantite	(Ag, Cu) <sub>10</sub> (Zn, Fe) <sub>2</sub> (As, Sb) <sub>4</sub> S <sub>13</sub>	Enargite	Cu <sub>3</sub> As <sub>4</sub>
Arsenopyrite	FeAsS	Galena	PbS
Bornite	Cu <sub>5</sub> FeS <sub>4</sub>	Malachite	Cu <sub>2</sub> (CO <sub>3</sub> )(OH) <sub>2</sub>
Chalcocite	Cu <sub>2</sub> S	Pentlandite	(Fe, Ni) <sub>9</sub> S <sub>8</sub>
Chalcopyrite	CuFeS <sub>2</sub>	Quartz	SiO <sub>2</sub>
Copper (II) oxide	CuO	Sphalerite	ZnS
Cosalite	Pb <sub>2</sub> Bi <sub>2</sub> S <sub>5</sub>	Tennantite	Cu <sub>12</sub> As <sub>4</sub> S <sub>13</sub>
Covellite	CuS	Tetrahedrite	Cu <sub>12</sub> Sb <sub>4</sub> S <sub>14</sub>
Cubanite	Cu <sub>2</sub> Fe <sub>2</sub> S <sub>3</sub>		



**Table 3.** Mineralogical composition of copper concentrates (n=106). Only minerals relevant to hazard classification are presented.

Mineral	Min	p50%	p60%	p70%	p80%	p90%	Max
Anglesite	0.00	0.00	0.00	0.00	0.00	0.00	6.00
Argentotennantite	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Arsenopyrite	0.00	0.00	0.00	0.00	0.00	0.01	2.50
Bornite	0.00	0.17	1.10	3.66	6.00	14.95	42.10
Chalcocite	0.00	0.00	0.33	1.02	3.11	8.08	44.32
Chalcopyrite	2.12	64.00	67.55	73.50	78.00	82.00	86.50
Copper (II) oxide	0.00	0.00	0.00	0.00	0.00	0.00	0.15
Cosalite	0.00	0.00	0.00	0.00	0.00	0.00	1.00
Covellite	0.00	0.02	0.50	0.90	1.72	3.86	25.00
Cubanite	0.00	0.00	0.00	0.00	0.00	0.00	6.00
Digenite	0.00	0.00	0.00	0.00	0.00	0.00	4.70
Enargite	0.00	0.00	0.00	0.00	0.00	0.06	25.00
Galena	0.00	0.14	0.30	0.70	1.50	3.95	15.00
Malachite	0.00	0.00	0.00	0.00	0.00	0.00	0.15
Pentlandite	0.00	0.00	0.00	0.00	0.00	0.00	5.00
Quartz	0.00	2.65	3.46	4.77	7.00	10.90	30.00
Sphalerite	0.00	0.83	1.58	5.00	6.08	8.12	18.84
Tennantite	0.00	0.00	0.00	0.00	0.15	0.88	5.80
Tetrahedrite	0.00	0.00	0.00	0.00	0.00	0.40	5.50

**Table 4.** Elemental copper distribution within copper minerals present in concentrates.

Cu in Mineral	Min	p50%	p60%	p70%	p80%	p90%	Max
Cu-Bornite (BO)	0.00%	0.40%	2.65%	8.97%	14.25%	29.10%	77.60%
Cu-Chalcocite (CC)	0.00%	0.00%	1.02%	3.18%	8.05%	24.04%	91.67%
Cu-Chalcopyrite (CP)	2.96%	91.36%	94.99%	98.05%	100.00%	100.00%	100.00%
Cu-Copper (II) oxide (CuO)	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.46%
Cu-Covellite (CV)	0.00%	0.05%	1.07%	2.22%	3.88%	8.92%	50.98%
Cu-Cubanite	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	8.62%
Cu-Digenite (DG)	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	16.61%
Cu-Enargite (EN)	0.00%	0.00%	0.00%	0.00%	0.00%	0.13%	61.46%
Cu-Tennantite (TN)	0.00%	0.00%	0.00%	0.00%	0.22%	1.45%	8.01%
Cu-Tetrahedrite (TH)	0.00%	0.00%	0.00%	0.00%	0.00%	0.52%	8.73%

### 3. Environmental hazard assessment of copper concentrates

The environmental hazard assessment of copper concentrates follows the general principles of the 10th revised edition of the UN GHS (3), of the ICMM Guidance on Hazard Assessment of Ores and Concentrates for Marine Transport (4) and of the Metals Environmental Risk Assessment Guidance (29).

In the context of hazards to the aquatic environment, the UN GHS section 4.1.1.2.2 states that *“in general (...) freshwater and marine species toxicity data can be considered as equivalent data”*. Historically, the most comprehensive and robust datasets on metals classification have been developed for freshwater. Marine effects data on metals are scarcer and would result in a less robust hazard assessment. Therefore, the HME assessment focuses on data for the freshwater compartment, which are considered equivalent to the marine compartment.

#### 3.1. Rapid environmental transformation

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, 2019 Table 4.1.1.) (3). This concept has been developed for organic substances, but it can also be applied to metals for the purposes of aquatic hazard classification (GHS, Annex 9, A9.7.3). The information on “rapid environmental transformation”, as equivalent to “degradation of organic substances”, was assessed, following the information in the UN GHS Annex 9, and following the industry guidance published by Eurometaux (28). The UN GHS, section A9.7.3.1, mentions that *“naturally occurring geochemical processes metal ions can partition from the water column”* and that it may be possible to incorporate this approach into the classification for chronic environmental hazard.

In accordance with the principles outlined in the GHS, the potential for “rapid environmental transformation” of metal ions has been evaluated by assessing the removal rates of metal ions through partitioning and their subsequent potential for sediment mineralization/remobilization. The assessments have been done using a weight of evidence approach based on laboratory and mesocosm studies, field data, and fate models. The assessments have focused on typical conditions representing a majority of water bodies, but not aiming to cover all possible environmental conditions and scenarios. The model assessment is based on The Tableau Input Coupled Kinetics Equilibrium Transport Unit World Model for Metals in Lakes (TICKET-UWM, available from <http://unitworldmodel.net> ), developed to assess the complexities and fate of metal speciation and its influence on effects of metals in the environment (11, 12). For Cu, Cd, Co, Ni, Pb, Sb, and Zn, the large weight of evidence obtained from this fate modelling work demonstrates that under most environmentally relevant conditions, these metal ions are rapidly transformed and removed from the water column (13). This has been further confirmed through a review of field and experimental evidence (14, 15).

For copper, the evidence base is extensive because it is also supported by field data. Under most “environmentally relevant” conditions, dissolved copper ions are generally transformed and removed from natural waters within 28 days. Remobilisation of Cu to the water column is not likely to occur under typical conditions. This is based on the extensive weight-of-evidence for metals in general (14) and for copper and copper concentrates specifically (15, 16, 17), together with the data obtained through a

standardized test protocol, the Extended Transformation and Removal Protocol (18). The evidence is summarized in the EU REACH registration dossier for copper (20). Copper is therefore considered to undergo rapid environmental transformation and removal, conceptually equivalent to “rapid degradation” for the purposes of hazard classification of organic substances.

Based on the above modelling, field, and laboratory evidence, it is concluded that Cu, Cd, Co, Ni, Pb, Sb, and Zn ions undergo rapid environmental transformation, equivalent to the “degradability” of organic substances, and consistent with the metal-specific guidance in the UN GHS.

### 3.2. Bioaccumulation Assessment

The Copper Voluntary Risk Assessment Report (19) and REACH Chemical Safety Report (2010) (20) have provided detailed information on the essentiality of copper, the homeostatic control of copper, the mechanisms of action of copper ions, and 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 copper. The RAC committee of the European Chemicals Agency recently confirmed that copper is not bioaccumulative according to the classification criteria under EU CLP (30). Similarly, in the zinc risk assessment and chemical safety report, 2010 (21), it has been concluded that the bioaccumulation criterion does not apply to the essential element zinc.

The bioaccumulation potential of lead and nickel has been assessed in the lead and nickel risk assessments and under the EU Water Framework Directive. These assessments concluded that both lead and nickel are not biomagnified and do not pose a secondary poisoning concern.

This assessment therefore concludes that copper and zinc are not bioaccumulative, and that lead and nickel do not biomagnify.

### 3.3. Aquatic hazard assessment

#### Principles of the assessment

Copper concentrates exhibit a broad range of elemental and mineralogical compositions (Tables 1—3). To assess the classification of such a varied family of materials, without engaging in an extremely extensive and expensive testing campaign, a read across approach, aligned with the GHS metal-specific guidance (Annex 9.7) (3) and with ICMC guidance was developed (4). Copper concentrates are complex, sparingly soluble inorganic materials. The transformation/dissolution (TD) protocol (OECD Guidance Document 29) was developed as a standard operating procedure to assess the rate and extent of metal release from metals and sparingly soluble inorganic metal compounds (5, 22, 23). Among the 106 copper concentrate samples, twelve reference concentrates were selected to be representative of the global copper concentrate production (Table 5). These reference concentrates and 8 pure minerals were subject to 28-day TD testing at 1 mg/L loading and pH 6; the low pH being selected to mimic worst case (highest) metal release. In accordance with the GHS, their environmental classification is determined by comparing the metal release (measured after TD testing) to the corresponding ecotoxicity reference values (ERVs). The

ERVs were provided by the relevant commodity associations or EU REACH consortia (Table 6). MeClas version 5.12, the metals classification calculation tool, was used for this assessment.

### Aquatic hazard assessment of pure minerals

For the main minerals in the copper concentrates, metal release as measured in TD tests on pure minerals are reported in Table 7.

Comparison of the measured copper releases (at 1 mg/L and after 7 days) and the acute copper ERV shows that the copper releases from tennantite, bornite and chalcocite are above the acute copper ERV value, resulting in a classification of Acute category 1 under GHS. The copper release from chalcopyrite, digenite, covellite and enargite (at 1 mg/L and after 7 days) is below the acute copper ERV value, but when the release values are multiplied by 10 to extrapolate to a mass loading of 10 mg/L, they are all above the acute copper ERV, resulting in classification as Acute category 2.

Comparison of the measured copper releases (at 1 mg/L and after 28 days) and the chronic copper ERV shows that chalcopyrite and enargite are not classified for long-term aquatic toxicity. Digenite, covellite, tennantite and bornite are classified as Chronic category 3, as the copper release measured at a mass loading of 1 mg/L is above the chronic copper ERV. For chalcocite, the copper release after 28 days extrapolated to a mass loading of 0.1 mg/L is still above the chronic copper ERV, which indicates a classification as Chronic category 2.

The measured arsenic releases from the three main arsenic bearing minerals are low compared to the acute and chronic arsenic ERVs. Therefore, for enargite and tennantite, the arsenic release does not affect the classification derived above. For arsenopyrite, no classification is concluded.

According to these results, if transported in their pure form, chalcocite, tennantite and bornite would meet the criteria for HME classification. The classification of copper concentrates can be assessed using the summation rules of classified minerals, leading to the classification of copper concentrates as Aquatic Acute category 1 and HME when the sum of chalcocite, tennantite and bornite concentrations is above 25 %. As a result, 11 % (12/106) of the concentrate samples meet the HME criteria. However, this outcome will be further refined in the next sections.

**Table 5.** Properties of the 12 reference copper concentrates assessed during 28-day transformation/dissolution tests. ND = Not Detected.

Metals	% In reference concentrates		Cu Minerals	% In reference concentrates	
	Min.	Max		Min.	Max.
Ag	ND	1.9	Chalcopyrite	2	79.8
As	0.08	0.36	Covellite	ND	9.7
Cd	ND	0.05	Bornite	ND	42.1
Co	ND	0.12	Enargite	ND	0.56
Cu	14.0	34.0	Tennantite	ND	1.5
Ni	0.002	0.02	Chalcocite	ND	28.43
Pb	0.006	12.5			
Zn	0.01	9			

**Table 6.** Ecotoxicity Reference Values (ERV) used for copper concentrate environmental hazard classification.

Metal	Acute ERV, µg/L	Chronic ERV, µg/L
Ag	0.22	0.09
As	1500	234
Cd	18	0.21
Co	52	7.6
Cu	12	13
Ni	285	23
Pb	73.6	17.8
Sb	1770	1130
Zn	413	82

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

Mineral	pH 6, 7 days, 1 mg/L	pH 6, 28 days, 1 mg/L	GHS
	Cu, µg/L	Cu, µg/L	Aquatic hazard classification
Chalcopyrite	2.8	3	Acute 2 No chronic classification
Digenite	5.3	18.7	Acute 2 Chronic 3
Covellite	5.7	14.5	Acute 2 Chronic 3
Enargite	5.9	10	Acute 2 No chronic classification
Tennantite	13.3	22.8	Acute 1 Chronic 3
Bornite	23.9	37.8	Acute 1 Chronic 3
Chalcocite	67.8	143	Acute 1 Chronic 2

Mineral	pH 6, 7 days, 1mg/L	pH 6, 28 days, 1mg/L
	As, µg/L	As, µg/L
Arsenopyrite	49	107
Tennantite	1.8	5.13
Enargite	BDL	1.2

## Metal releases from 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, such as Pb from anglesite and galena, Ag from argentotennantite, Zn from sphalerite

The environmental classification was therefore refined by assessing the releases of metals from the concentrate during TD tests. Results from TD tests (1 mg/L, pH 6), as well as detailed elemental and mineral compositions, are available for the 12 selected reference concentrates (Table 5 and Table 9). While the results from the 28-day TD tests do demonstrate some metal releases, those for copper are much lower for the chalcopyrite dominated concentrates compared to the chalcocite-rich ones. The classifications of individual copper concentrates 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 release of copper from copper concentrates can be predicted based on the release of copper from pure copper minerals. This read-across approach was subsequently validated.

For the other metals (As, Cd, Co, Ni, Pb, Zn and Ag), the release rates could not be related to mineral release rates. They were therefore estimated as the highest reliable release rate observed in the TD tests of the group of 12 representative concentrates. In the absence of validation data, ICA's precautionary approach is to select the highest measured experimental release for each element, from the tested reference concentrates. Data below the limit of quantification, or data with coefficient of variation above 20% were not considered. The measured release for each metal was quantified as the Environmental Solubility (ES) in acute (7 days) and chronic (28 days) conditions. The range of ES are shown in Table 9, and those values that were retained for the read-across approach to classify copper concentrates are shown in Table 10.

**Table 8.** Short-term (7 day) and long-term (28 day) Environmental Solubility (%) for copper as measured in transformation/dissolution tests on copper minerals. The Environmental Solubility is calculated as: ( $\mu\text{g}$  metal released/ $\mu\text{g}$  total metal) \*100%. Values used for the read-across approach to classify copper concentrates are in bold.

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

**Table 9.** Short-term (7 day) and long-term (28 day) Environmental Solubility (%) for Cu, As, Cd, Co, Ni, Pb and Zn, as measured in transformation/dissolution tests on 12 reference copper concentrates. The Environmental Solubility is calculated as: ( $\mu\text{g}$  metal released/ $\mu\text{g}$  total metal) \*100%. Values used for the read-across approach to classify copper concentrates are in bold and underlined.

Number of Samples Experimental conditions	% Environmental Solubility					
	4		12		12	
	7 days		7 days		28 days	
	Loading 100 mg/L		Loading 1 mg/L		Loading 1 mg/L	
	Min.	Max.	Min.	Max.	Min.	Max.
Ag	Not detected	Not detected	Not detected	Not detected	Not detected	Not detected
As	0.5 ± 0.05	1.2 ± 0.07	2.7 ± 0.27	<b><u>5.00 ± 0.50</u></b>	3.2 ± 0.61	<b><u>14.2 ± 0.57</u></b>
Cd	5.9 ± 0.30	<b><u>9.8 ± 0.49</u></b>	Not detected	6.7 ± 0.60	Not detected	<b><u>10.0 ± 1.40</u></b>
Co	4.9 ± 0.10	7.6 ± 0.95	Not detected	<b><u>11.7 ± 0.82</u></b>	Not detected	<b><u>30.0 ± 1.5</u></b>
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	<b><u>7.3 ± 0.95</u></b>	Not detected	Not detected	Not detected	<b><u>29.2<sup>i</sup></u></b>
Pb	7.6 ± 0.30	19.8 ± 1.39	5.7 ± 2.05	61.1 ± 1.22*	11.3 ± 2.20	<b><u>52.6 ± 5.3</u></b>
Zn	2.4 ± 0.17	<b><u>9.1 ± 0.27</u></b>	0.9 ± 0.13	15.3 ± 2.60*	1.0 ± 1.04	15.3 ± 18.83*

<sup>i</sup> Estimated as 4 times the release at 7 days

\*Measured concentration below limit of quantification and/or coefficient of variation >20%. Values were not retained.

**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.

	% Environmental Solubility	
	<u>Acute</u> , from 7 Days TD test	<u>Chronic</u> , from 28 Days TD test
Ag	Not detected <sup>i</sup>	Not detected
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 <sup>ii</sup>	0.8 ± 0.08 - 9.9 ± 0.40	0.9 ± 0.08 – 20.9 ± 0.63
Ni	7.3 ± 0.95	29.2
Pb	50.3 ± 3.02*	52.6±5.3
Zn	9.1 ± 0.27	11.6 ± 1.39*

<sup>i</sup> The release of silver was below detection limit for copper concentrates containing up to 1.9% Ag

<sup>ii</sup> The copper environmental solubility depends on the specific concentration of the copper bearing mineral in the concentrate



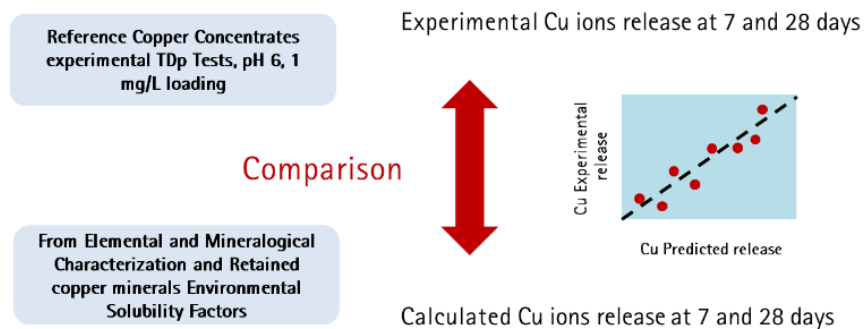
Validation of the read-across approach: predicting the copper releases from concentrates

The read-across procedure for copper was validated (Scheme 2). Using the copper Environmental Solubilities for different pure minerals, and the mineralogical composition of each reference concentrate, the % copper releases from the copper concentrates were calculated (see Equation 1).

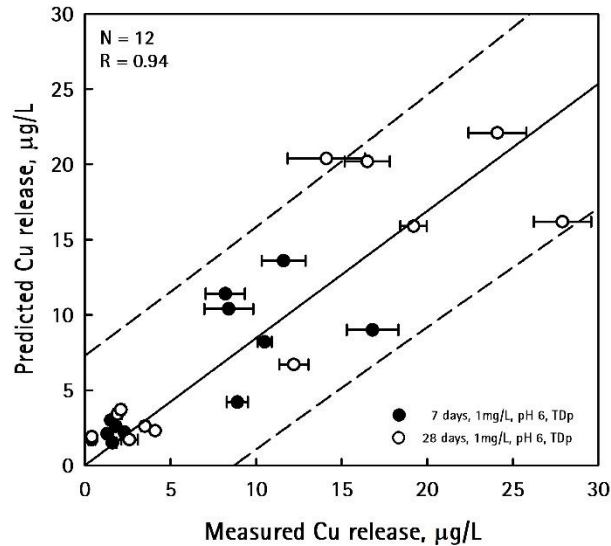
$$\sum_i ES_i \times [Cu_{mineral}]_i = [Cu_{dissolved\ from\ concentrate}]_j \quad \text{Equation 1}$$

Where *ES* = environmental solubility (%) at 7 or 28 days of the pure mineral *i* (from Table 10), [*Cu mineral*] = % of the mineral *i* present in the concentrate and [*Cu dissolved from concentrate*] = calculated copper release from concentrate *j*.

Figure 3 compares the calculated and measured copper release rates, from the 7- and 28-day TD tests (at 1 mg/L loading), for the 12 reference concentrates. The overall correlation coefficient (R) was 0.94. In general, there is a good agreement between measured and calculated values. For most observations, predicted values were within a factor of 2 of measured values.



**Scheme 2.** Validation procedure

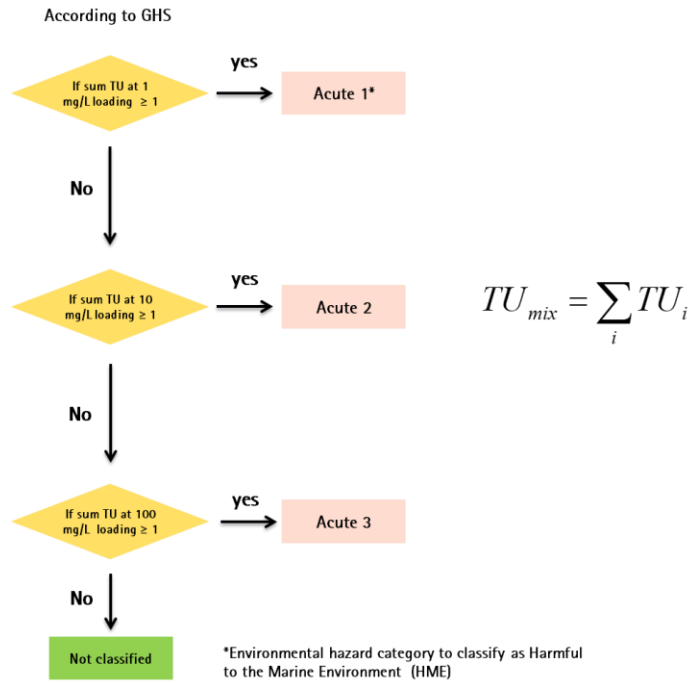


**Figure 3.** Experimental validation of read across from copper bearing minerals to copper concentrates. The full line is the regression line, dashed lines indicate the 95% prediction interval, and error bars represent the standard deviation in the experimental measurements.

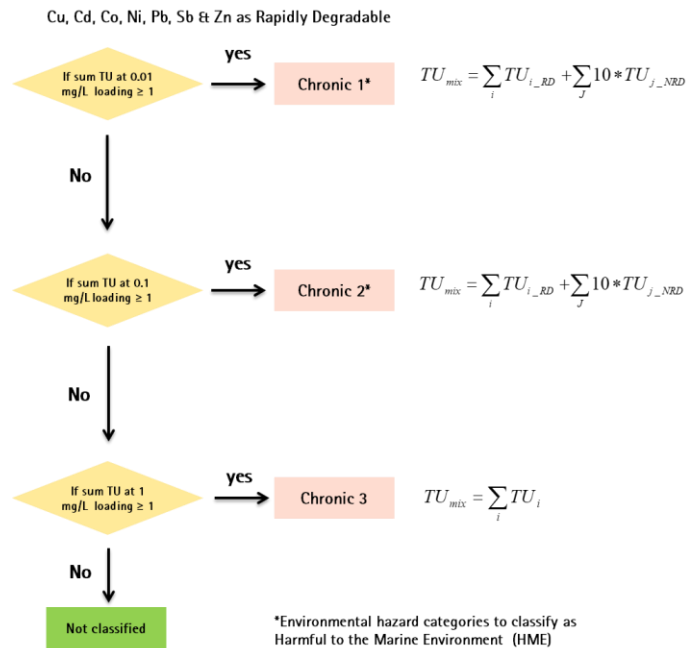
### Aquatic hazard classification of copper concentrates

The released metal concentrations, measured or calculated from the read across procedure, were compared to the corresponding 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). In line with the additivity rules described in the GHS (section 4.1.3.5.2), the sum of Toxic Units is used to determine if a substance or mixture is classified in any given acute or chronic category. 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 and at mass loadings of 1, 10, 100 mg/L) and the acute ERV for each metal. If the sum of toxic units is equal to or greater than 1, the substance is classified in the corresponding category (Scheme 3). The same general rationale is applied to chronic classification, where the measured or calculated metal releases after a 28-day TD test (at pH 6 and at mass loadings of 0.01, 0.1 and 1 mg/L) and the corresponding chronic ERVs are used (see Scheme 4). The releases at loadings other than 1 mg/L were calculated from the available data obtained at a loading of 1 mg/L, by assuming a linear relationship between mass loading and metal release.

For chronic classification, due consideration must be given to the environmental transformation of each constituent, equivalent to the degradability of organic substances. Among the metals present in copper concentrates, only Cu, Cd, Co, Ni, Pb, Sb and Zn are considered rapidly degradable (see section 3.1). 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. This approach is implemented in the online metals classification calculation tool MeClas version 5.12 (24).



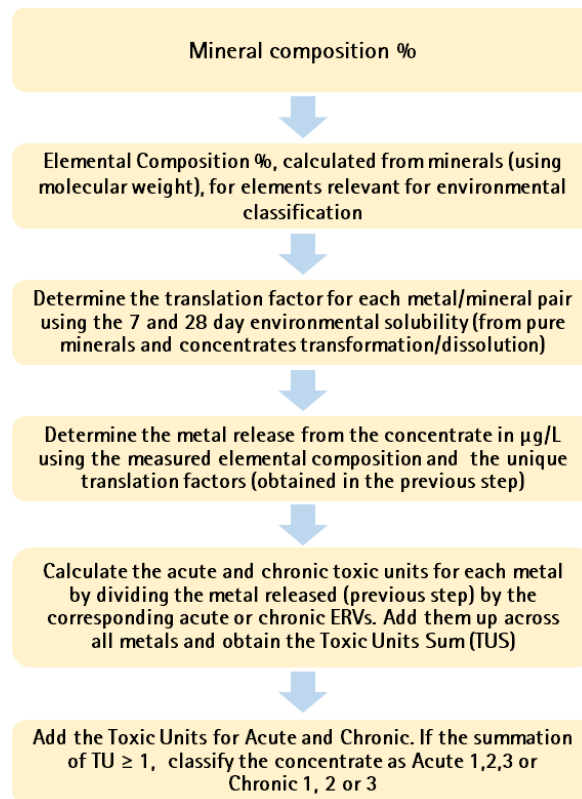
**Scheme 3.** Decision tree for acute environmental classification of copper concentrates



**Scheme 4.** Decision tree for chronic environmental classification of copper concentrates, where RD corresponds to the readily degradable constituents, and NRD to the non-degradable constituents.

Transformation dissolution data are available for 12 reference concentrates. The classification assessment shows that 1 concentrate is classified as HME, due to an Aquatic Acute category 1 classification. Eleven concentrates are classified as Aquatic Acute category 2, and six are classified as Aquatic Chronic category 3, but these do not lead to HME classification.

The classification of each of the 106 copper concentrates was assessed using the read across approach (scheme 5), based on their elemental and mineral compositions, and based on the information in Table 8 and Table 10. Only 14 out of 106 copper concentrates (13%) are identified as Harmful to the Marine Environment (HME) under MARPOL Annex V, due to a classification as Aquatic Acute category 1. These are mainly attributed to high releases of copper, predicted for chalcocite and/or bornite-rich concentrates. This assessment shows that all copper concentrates with chalcocite content above 15% will be classified as Aquatic Acute category 1 and HME. Some copper concentrates with chalcocite below 15% may also be classified as Aquatic Acute category 1 and HME, depending on the contribution to the aquatic toxicity from other copper minerals and other metals in the concentrate. The assessment confirms that the majority of copper concentrates (87%) do not meet the environmental HME criteria. Regarding the release of other elements than copper from copper concentrates, the assessment 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. The contribution of all other elements to the sum of toxic units is minor (<1%). The classification assessment of an individual copper concentrate, based on the read-across approach, can always be further refined by generating TD data.



**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.

## 4. Human health hazard assessment

### Principles of the assessment

The human health criteria, to classify as HME under MARPOL Annex V, are: carcinogenicity category 1, mutagenicity category 1, reproductive toxicity category 1 and repeated dose Specific Target Organ Toxicity (STOT-RE) category 1, following dermal and oral exposures. The GHS concentration limits 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.

Therefore, the toxicity profiles of the copper concentrates were further assessed, considering the hazard profiles of the relevant constituents and their compounds, the potential release of the relevant metals in body fluids, and the GHS mixtures rules. This assessment was done based on the methodology described by ICMM (4), Eurometaux (2020) (25), and Verougstraete (26), using the metals classification tool MeClas version 5.12 (24), for 106 concentrates with known elemental and mineral composition.

Considering the elemental and 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, Ni, As, Cd and Co may be relevant to MARPOL Annex V human health hazards.

**Table 11.** Metals naturally present in copper concentrates with compounds classified as CMR or STOT-RE in category 1 (A or B). Information obtained from the relevant commodity associations (2021).

Metal and Metal compound	Mutagen	Carcinogen	Reproductive toxicant	STOT-RE
As (metal, salts, oxides)		Cat 1	Cat 1	
Cd (salts)	Cat 1	Cat 1	Cat 1	Cat 1
Co (metal, salts)		Cat 1 <sup>i</sup>	Cat 1	
Ni (salts)		Cat 1 <sup>i</sup>	Cat 1	Cat 1 <sup>i</sup>
Pb (metal, salts, oxides)			Cat 1	Cat 1

<sup>i</sup> Inhalation route only. Not relevant to HME criteria.

### Oral bioaccessibility of metals in copper concentrates

The metal release from the reference concentrates was determined through in vitro bio-elution tests in gastric fluids (pH 1.5), following the international ASTM D 5517-07 (7) protocol with refinements by Eurometaux. This test method has been validated by the EU Commission (27) and is presently under discussion by the OECD. Comparison of the gastric bioaccessibility shows consistently limited bioaccessibility of the metals contained in the minerals and reference concentrates, compared to soluble compounds.

Table 12 summarizes the metal releases for those elements identified as relevant to the assessment. The gastric bioaccessibility was calculated for each of the reference concentrates as ( $\mu\text{g}$  metal released in gastric fluid) / ( $\mu\text{g}$  total metal in sample) and expressed as percentage (%). The worst-case bioaccessibility for each of the metals was determined from the maximal reliably measured release among the tested reference concentrates (Table 13).

In line with the approach by Eurometaux (25), to classify complex materials for human health hazards, the bioaccessibility must be determined relative to a selected reference substance. The speciation of copper concentrates is variable and depends on the ore body. A suitable reference substance can be selected by considering that the toxic effects are preceded by dissolution and uptake of the metal ion. Based on this, soluble compounds are selected as reference substance, as they fully dissolve in body fluids to release metal ions. Such fully soluble substances (salts) have a well-established toxicological profile, since key toxicological studies used to establish the hazard profile of metals are typically conducted with e.g., a chloride, nitrate, or sulphate. The choice for considering the soluble compound as reference substance includes a level of conservatism: such soluble compounds are usually classified more stringently than other less soluble compounds, such as oxides, sulphides, or metallic forms. For consistency, the chloride forms are selected here as reference substance, and arsenic acid is selected as reference substance for As. The relative bioaccessibility is shown in Table 13. To classify a copper concentrate for any of the hazards listed in Table 11, the relative bioaccessibility of metal must be multiplied with the total metal content in the concentrate to yield the relative bioaccessible concentration, which is then compared to the relevant concentration limits in the GHS to determine if a classification is triggered.

For the 11 reference concentrates, the relative bioaccessible concentrations of As, Cd, Co, and Ni are in all cases below the relevant concentration limits in the GHS. The relative bioaccessible concentration of lead is in some cases above the concentration limit for reproductive toxicity (0.3%).

To assess the classification of all 106 copper concentrates, the maximum (worst-case) relative bioaccessibility measured among the 11 tested reference concentrates was assumed. The relative bioaccessible concentrations of Cd, Co and Ni are, in all cases, below the relevant GHS concentration limits. The relative bioaccessible concentration of As is above the concentration limit for carcinogenicity and mutagenicity in two out of 106 copper concentrates. The relative bioaccessible concentration of Pb is above the concentration limit for reproductive toxicity (0.3%) in 37 of 106 copper concentrates (35%). This corresponds to a total lead content above 0.39%. Lead is therefore the key driver for human health classification of some copper concentrates as a category 1 reproductive toxicant under GHS. The classification assessment of an individual copper concentrate, based on the read-across approach using a worst-case bioaccessibility, can always be further refined by generating bioelution data.

According to the MARPOL Annex V human health criteria, in order to classify a substance as HME, reproductive toxicity needs to be combined with not being rapidly degradable and with high bioaccumulation. However, as described in section 3, Pb is subject to rapid environmental transformation which is equivalent to rapid degradation for organic substances. Furthermore, lead is not biomagnified. Lead is a Substance of Very High Concern under the EU REACH regulation, but not a priority hazardous substance under the EU Water Framework Directive, confirming that lead is not to be considered as a Persistent, Bioaccumulative and Toxic (PBT) substance.

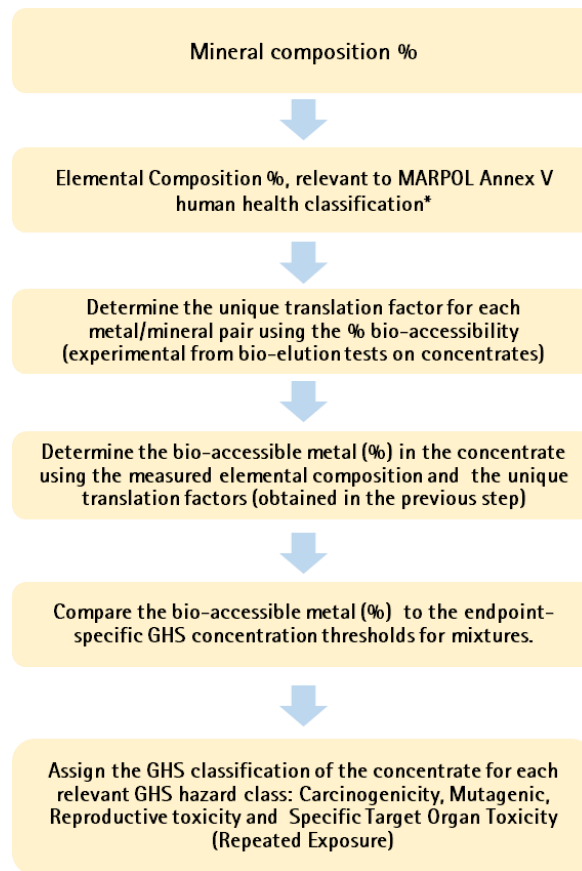
In summary, it can be concluded that copper concentrates do not meet the MARPOL Annex V human health criteria.

**Table 12.** Minimum and maximum gastric bioaccessibility of As, Cd, Co, Ni, and Pb measured among 11 reference copper concentrates, at pH 1.5 after 2 hours of bioelution testing at a mass loading of 200 mg/L. The maximum values were determined based on all measurements above the quantification limit and with coefficient of variation <20%.

	Gastric bioaccessibility (%)	
	pH 1.5, 2 h, loading 200 mg/L	
	Min.	Max.
As	Not detected	1.81 ± 0.25
Cd	Not detected	14.1 ± 0.28
Co	Not detected	4.00 ± 0.12
Ni	3.80 ± 0.72	11.00 ± 5.72
Pb	4.15 ± 0.176	56.8 ± 0.00

**Table 13.** Gastric bioaccessibility and relative bioaccessibility for the metals of toxicological concern present in copper concentrates. Values used for the read-across approach to classify copper concentrates are in bold.

	Max. gastric bioaccessibility (%)	Reference substance	Max. relative bioaccessibility (%)
As	1.81 ± 0.25	as H <sub>3</sub> AsO <sub>4</sub>	<b>3.4 ± 0.5</b>
Cd	14.1 ± 0.28	as CdCl <sub>2</sub>	<b>23.0 ± 0.5</b>
Co	4.00 ± 0.12	as CoCl <sub>2</sub>	<b>8.8 ± 0.3</b>
Ni	11.00 ± 5.72	as NiCl <sub>2</sub>	<b>24.3 ± 12.6</b>
Pb	56.8 ± 0.00	as PbCl <sub>2</sub>	<b>76.2 ± 0.00</b>



**Scheme 6.** Step by step human health hazard classification procedure for copper concentrates.



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