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1 Assessment of metal toxicity in marine ecosystems -
2 Comparative Toxicity Potentials for nine cationic
3 metals in coastal seawater

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10 ABSTRACT:

11 This study is a first attempt to develop globally applicable and spatially differentiated marine
12 Comparative Toxicity Potentials (CTPs) or ecotoxicity characterization factors for metals in coastal
13 seawater for use in Life Cycle Assessment. The toxicity potentials are based exclusively on marine
14 ecotoxicity data and take account of metal speciation and bioavailability. CTPs were developed for
15 nine cationic metals (Cd, Cr(III), Co, Cu(II), Fe(III), Mn, Ni, Pb and Zn) in 64 Large Marine
16 Ecosystems (LMEs) covering all coastal waters in the world. The results showed that the CTP of a
17 specific metal varies 3-4 orders of magnitude across LMEs, largely due to different seawater
18 residence time. Therefore the highest toxicity potential for metals was found in the LMEs with the

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19 longest seawater residence times. Across metals, the highest CTPs were observed for Cd, Pb and
20 Zn. At the concentration levels occurring in coastal seawaters, Fe acts not as a toxic agent but an
21 essential nutrient and thus has CTPs of zero.

22 **1 Introduction**

23 Life Cycle Assessment (LCA) “quantifies all relevant emissions and resources consumed”¹
24 associated with a good or service in a Life Cycle Inventory (LCI) and assesses “the related
25 environment and health impacts and resource depletion issues”¹ by Life Cycle Impact Assessment
26 (LCIA). LCA has been broadly used to support environmentally informed decisions in policy-
27 making, product development and procurement, and consumer choices². It is a valuable screening
28 tool to facilitate identifying environmental hotspots². The uncertainties associated with LCA results
29 can be high due to data and simplified modelling². This can be partially compensated by enhancing
30 regional detailed modelling.

31 Metals are often ranked at the top of toxicity concerns in Life Cycle Assessment (LCA)³. Large
32 quantities of metals are released from anthropogenic resources to the natural environment (up to
33 3×10^5 tons/year for selected metals, e.g. Mn)⁴. Waterborne emissions contribute 50-80%, and
34 originate mainly in industrial sectors such as iron or steel production, thermal power stations,
35 mineral oil and gas refineries etc.⁵ Waterborne metal emissions typically reach freshwater first and
36 move towards seawater through fluvial pathways, thus potentially causing ecotoxicity in both
37 freshwater and marine compartments⁶. Hitherto, metal toxicity in the aquatic environment has been
38 modelled in LCIA using models developed to simulate the behaviour of organic chemicals with
39 poor representation of the speciation behaviour of metals and bioavailability (e.g. USES-LCA 2.0⁷
40 used in ReCiPe, IMPACT 2002+⁸). Following the principles laid out in the Apeldoorn Declaration⁹
41 and the Clearwater Consensus¹⁰, Gandhi et al.^{11,12} developed a new method to calculate the toxicity

42 potential of six metals in freshwater ecosystems (expressed as a Comparative Toxicity Potential
43 (CTP), also known as a Characterization Factor in LCIA), including fate, bioavailability and effect
44 of metals. Their CTP was calculated for a number of archetypical freshwater chemistries. Dong et
45 al.¹³ further adapted the method, expanding its scope of metals and calculated freshwater CTP for
46 14 metals. The results showed that for some metals (e.g. Al, Be, Cr(III), Cu and Fe(III)), freshwater
47 CTP was highly dependent on the speciation of metal in a certain water chemistry, thus varying by
48 2-6 orders of magnitude in different water archetypes. This reveals the importance of 1) including
49 metal speciation and bioavailability in the modelling and 2) identifying spatially determined and
50 differentiated water chemistries.

51 In comparison, marine CTP of metals has received less attention. Following the Apeldoorn
52 Declaration⁹, “the oceans are deficient in essential metals, and the CTP for essential metals should
53 be set at zero for toxicity in the oceans.”⁹ In contrast, coastal seawater receives higher
54 anthropogenic metal emissions not just through fluvial pathways⁶, but also from airborne emission
55 and metals resuspended from the seabed¹⁴, leading to the observable metal concentrations in the
56 coastal zones, and even reach the mmol/l level close to wastewater discharges¹⁵. This can lead to
57 exceeding the levels where metal becomes toxic to organisms.

58 Not all metal forms are toxic. Only bioavailable forms, often within the truly dissolved forms, can
59 access a sensitive receptor, the biotic-ligand, and become hazardous^{16,17}. In addition to metal
60 availability, also its residence time in the coastal seawater is essential for the exposure and hence its
61 CTP. For most metals, a substantial removal happens after entering coastal zone, where complex
62 binding to Suspended Particulate Matter (SPM) followed by removal through sedimentation is
63 increased⁶. The fate of a metal in coastal seawater is thus strongly influenced by its tendency to
64 adsorb to SPM, its solubility in seawater and its complexation affinity with particulate and
65 dissolved organic matter¹⁸.

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66 Until now metal marine CTP in the previous LCIA models has either not been calculated (e.g.
67 USEtox¹⁹, IMPACT 2002+⁸) or it has been derived neglecting speciation and bioavailability, and
68 using freshwater toxicity data (e.g. USES-LCA⁷), with a questionable representativeness for
69 saltwater organisms²⁰. Moreover, as demonstrated by Gandhi and co-workers, metal freshwater
70 CTP is highly sensitive to water chemistry²¹. While water chemistry parameters such as pH,
71 Dissolved Organic Carbon (DOC), SPM and salinity affect the speciation of metals, different
72 seawater residence times (SRT) in different coastal zones also play a large role when determining
73 the fate of metal in coastal compartment^{22,23}. So far, no study has given a coherent treatment of the
74 global spatial variability of metal marine CTP, considering speciation and applying toxicity data for
75 marine organisms. As a consequence, toxic impacts on the marine ecosystem were either not at all
76 considered in LCA studies or they were assessed with methods of limited reliability based on
77 questionable assumptions. These shortcomings and the strives for a coherent consideration of
78 marine biodiversity in LCA studies set the objectives of this study.

79 Aiming for consistency with the methodology developed for characterizing metal toxicity in
80 freshwater^{11,13} and applying marine ecotoxicity data availability in ECOTOX database²⁴, the
81 objective of this paper is to develop new, spatially differentiated and globally applicable marine
82 CTPs for Cadmium (Cd), Cobalt (Co), Chromium(III) (Cr), Copper(II) (Cu), Iron(III) (Fe),
83 Manganese(II) (Mn), Nickel (Ni), Lead (Pb) and Zinc (Zn), taking metal speciation and
84 bioavailability into account, and investigating their variation over 64 Large Marine Ecosystems
85 (LMEs) for emissions received in coastal seawater all over the world.

86 2 Methods

87 2.1 General framework

88 For metals, CTP_i for ecosystems is expressed as the Potentially Affected Fraction of species
89 integrated over time and space $[(PAF) \cdot \text{day} \cdot \text{m}^3/\text{kg}_{\text{emitted}}]$, representing the ecotoxicity potential for
90 the *total* metal in compartment i . It is calculated as the product of three factors: Fate Factor (FF),
91 Bioavailability Factor (BF) and Effect Factor (EF) as presented in Eq. 1¹¹.

$$92 \quad CTP_i = FF_i \cdot BF_i \cdot EF_i \quad (\text{Eq.1})$$

93 Where:

94 FF_i : Fate Factor [day], representing the residence time of *total* metal in compartment i ,

95 BF_i : Bioavailability Factor [dimensionless], representing the ratio between *truly dissolved*
96 and *total* metal. Here truly dissolved metal contains metal free ion and inorganic metal
97 complexes. Total metal includes truly dissolved metal, DOC complexed metal and
98 SPM complexed metal.

99 EF_i : Effect Factor $[(PAF) \cdot \text{m}^3/\text{kg}]$, representing the fraction of species potentially affected
100 by the toxicity of the *truly dissolved* metal in compartment i .

101 This framework can be used for any single environmental compartment (e.g. freshwater, soil).
102 When considering a multi-compartment system, the terms of eq.1 become matrices, which besides
103 residence times also include inter-compartmental transfers²⁵. In this paper we focus on metals
104 received from adjacent environmental compartments or directly emitted into the coastal seawater
105 compartment. Therefore, FF represents the persistence of the metal in coastal seawater, while BF
106 and EF represent bioavailability and metal ecotoxicity effects in coastal seawater respectively. FF is
107 modelled for the total metal rather than dissolved metal, due to the fact that this is the entity which
108 is reported in LCI and that the metal in the water may re-partition between particulate and dissolved
109 forms during transportation. Note that the partitioning pattern can vary over time and with local

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110 environmental conditions. This can have an impact on the FF of metals. For the purpose of LCA
111 temporal variations need to be averaged over a year to be compatible to the information in the life
112 cycle inventory.

113 2.2 Spatial differentiation of environmental conditions and parameters

114 To explore the spatial variability of CTP in coastal seawater, we worked with the LMEs
115 following Cosme et al.²⁶. The coastal compartment that is represented by a LME covers the marine
116 area from the coastal line to the seaward boundary of the continental shelf and includes any
117 estuaries. Thus defined, the coastal compartment with its adjacency to the continents receives
118 emissions related to human activity through the influx of continental freshwater or direct discharges
119 to the sea. 80%-90% of marine net primary production occurs in this compartment, which thus
120 comprises the majority of species and biomass that potentially may be affected by metal
121 emissions²⁷. The global coastal seawater zone was divided into 64 LMEs according to “distinct
122 bathymetry (seabed topography), hydrography, productivity and tropically dependent
123 populations”²⁸, where each LME represents a relatively independent coastal zone. Data on SRT,
124 seawater surface area, temperature and water chemistry were collected for each LME from literature
125 (Table S1 in Supporting Information (SI)). The values for these parameters show large variations
126 across the 64 LMEs (Figure S1 in SI). SRT varies from 11 days-90 years, surface area from
127 1.5×10^5 - 5.7×10^6 km², estuary discharge rate (water flow rate from freshwater to coastal seawater)
128 from 0- 1.3×10^5 m³/s, temperature from -1°C-29°C, pH from 7.75-8.35, DOC from 0.6-6.5 mg/l,
129 Particulate Organic Carbon (POC) from 31-802 ug/l, SPM from 0.2-2.9 mg/l and salinity from 6.2-
130 40.3‰. For speciation modelling, salinity was translated into concentrations of the major ions (Na⁺,
131 Mg²⁺, K⁺, Ca²⁺, SO₄²⁻, and Cl⁻) by scaling from a standard salinity (35 ‰) and its corresponding
132 major ion concentrations (Table S2 in SI), assuming a fixed relationship between the major ion

133 concentrations at different salinities²⁹. For each LME, the relevant environmental parameter and
134 water chemistry values were applied to derive a CTP value for each metal.

135 Note that also within one LME, environmental parameters such as pH, salinity, DOC, POC, and
136 SPM show both spatial and temporal variation. The annual variation ranges are shown for pH,
137 salinity and POC within each LME in Figure S2 in SI. Fe, Mn and Al oxides have been shown to be
138 strong adsorbents for metal ions³⁰⁻³², because of their large surface area. Due to lack of spatially
139 differentiated concentration data for these oxides, fixed concentrations of 0.15, 0.02 and 0.4 µg/L
140 for Fe, Mn, and Al oxides respectively had to be assumed across all LMEs³³.

141 **2.3 Model and parameter selection**

142 **2.3.1 Fate model**

143 With the intended use in LCA in mind, the multimedia fate model embedded in USEtox¹⁹ was
144 chosen for this study. USEtox is an LCIA model for assessing ecotoxicity and human toxicity
145 impacts. It has been developed in a scientific consensus process involving LCIA and chemical fate
146 modelling experts. It is the recommended characterization model for toxicity impacts in LCA³⁴. In
147 USEtox, the fate is calculated based on a steady-state mass balance. USEtox determines metal FF in
148 the coastal seawater compartment by modelling of metal inflow, metal outflow and metal removal
149 (including sedimentation and sediment burial/re-suspension). Metal inflow and outflow largely
150 depend on the retention time of the coastal seawater. Thus the default SRT of seawater on
151 continental scale in USEtox was replaced by the SRT representative for each LME. To be
152 consistent, also the default surface area of continental seawater and the water flow rate from
153 continental freshwater to continental seawater (estuary discharge rate) were replaced by the
154 corresponding LME-specific data. Water flow from ocean to coastal seawater is then automatically
155 calculated from parameters mentioned above. Details of LME-specific data and calculations are
156 available in Table S1 in SI. Metal removal is simulated by metal sedimentation and diffusion of

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157 metal from seawater to sediment. The former process is modelled by metal complexation with SPM,
158 followed by SPM sedimentation. The removal largely depends on the fraction of metal adsorbing to
159 SPM, the concentration of SPM and the SPM sedimentation velocity. Metal diffusion into sediment
160 is determined by the dissolved fraction of metal and the metal's mass transfer coefficient between
161 sediment and water. The metal fraction adsorbed to SPM can be calculated from a spatially
162 differentiated adsorption coefficient K_{pSS} (L/kg; the ratio of metal concentration between *SPM*
163 *bound* metal and *truly dissolved* metal). The truly dissolved fraction of metals is calculated using
164 both K_{pSS} and K_{DOC} (L/kg; the ratio of metal concentration between *DOC complex bound* metal and
165 *truly dissolved* metal). All parameters mentioned above vary between different LMEs. Thus K_{pSS}
166 and K_{DOC} were recalculated in WHAM VII³⁵ for each metal in each LME respectively, to replace
167 the default values in USEtox. WHAM³⁵ is a metal speciation modelling software. Based on the
168 input of target metal concentration and relevant water chemistry, it can deliver the concentration of
169 target metal in a specific form. In WHAM's calculation of K_{pSS} and K_{DOC} values, it is assumed that
170 metals are in equilibrium with the discrete sites of DOC and the organic fraction of SPM. Here
171 target metals have to compete with other cations (e.g. Ca^{2+} , Mg^{2+} , K^+ and Na^+) to form complexes
172 with SPM or DOC. The ratio between the concentration of metal that is truly dissolved in water and
173 the concentration of metal forming complexes with SPM or DOC were calculated for each LME
174 and each metal as the specific K_{pSS} and K_{DOC} value. Default DOC and SPM concentration in
175 USEtox were also replaced by the corresponding specific parameter values for each LME. Other
176 landscape parameters were kept unchanged. All parameters used in FF calculation are listed in
177 Table S3 in SI. There were no substance parameter values for Mn and Fe in default USEtox
178 inorganic database. They thus had to be collected from literatures. The retrieved values are
179 presented together with substance parameter values for the other metals in Table S4 in SI.

180 **2.3.2 Bioavailability model**

181 BF, K_{pSS} , and K_{DOC} all represent ratios between different metal species in coastal seawaters. They
182 are thus dependent on the metal speciation in each LME. In the modelling of this speciation
183 behaviour, we assumed that metals remained at their background concentration (Table S4 in SI) in
184 coastal seawater before the emission. BF, K_{pSS} , and K_{DOC} were then calculated for each LME with
185 its specific water chemistry. This assumption is based on the fact that LCA assesses impacts caused
186 by marginal changes. Nevertheless, a sensitivity analysis of the dependence of BF, K_{pSS} , and K_{DOC}
187 on background concentration change is performed in section 3.4.5.

188 WHAM VII³⁵ was used to calculate metal speciation in seawater. While originally developed for
189 freshwater, its applicability for prediction of metal free ion activity in seawater has been validated³⁶.
190 Furthermore it contains data and has a good reputation for simulating metal binding to DOC, POC,
191 Fe oxide and Mn oxide. These two criteria favoured the choice of WHAM VII over other speciation
192 models (e.g. Visual Minteq³⁷, MINEQL+³⁸, PHREEQC³⁹).

193 **2.3.3 Ecotoxicity model**

194 Currently there are two main ecotoxicity models to explain how cationic metals cause toxicity in
195 organisms. The Free Ion Activity Model (FIAM) assumes that the toxic compound is free metal ion
196 represented by its activity. The Biotic Ligand Model (BLM) further includes the competition
197 between free metal ion and other cations (e.g. Ca^{2+} , H^+) for binding to biotic ligand – the receptor in
198 the target organism where the metal binds to exert its uptake and/or toxicity. Due to lack of BLMs
199 for metals in seawater, FIAM was chosen in this study. It has been validated to assess metal toxicity
200 to marine organisms in saltwater^{40,41}. As stated in Clearwater Consensus¹⁰, we calculated EF based
201 on truly dissolved metal, assuming that free ion is a fraction of truly dissolved metal and is
202 responsible for the toxicity. In risk assessment, Predicted No Effect Concentration (PNEC) is
203 typically used as effect indicator to protect the sensitive species of the ecosystem. Compared to

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204 PNEC, the geometric mean HC_{50} calculated from EC_{50} , representing the Potentially Affected
205 Fraction (PAF) of species exposed above chronic EC_{50} values, is more robust but less
206 conservative⁴². The purpose of LCA is to compare alternatives, where robustness is highly required.
207 Therefore HC_{50} values calculated from EC_{50} are normally applied in LCA. It can use all the
208 available toxicity data for a metal and is a measure associated with less uncertainty than the
209 PNEC^{43,44}. Detailed descriptions of calculation methods for the PAF method and HC_{50} can be found
210 in Larsen et al.^{44,45}. EFs were calculated exclusively from data on chronic marine EC_{50} from
211 literature. The availability of marine ecotoxicity data in the ECOTOX database²⁴ allowed us to
212 apply our model to nine cationic metals, including Cd, Co, Cr, Cu, Fe(III), Mn, Ni, Pb, and Zn
213 (Table S5 in SI). For metals where chronic marine ecotoxicity data were insufficient, extrapolation
214 from acute marine ecotoxicity data was performed applying an Acute-to-Chronic Ratio (ACR)
215 derived from the available toxicity data as described in Table S6 in SI. Total metal marine EC_{50}
216 reported in literature were translated into free ion EC_{50} using WHAM VII³⁵, taking into account
217 water chemistry of the test medium in which the reported EC_{50} was determined. This conversion
218 reduced the standard deviation of the EC_{50} of each metal by at least an order of magnitude (Table
219 S5), which also justifies the use of FIAM in EF calculation.

220 The calculation of EF was based on the recommended principles for LCA^{43,45,46}. For each metal at
221 each trophic level (i.e. primary producers, primary and secondary consumers), a free ion activity
222 $HC_{50-trophic}$ was calculated as the geometric mean of the corresponding free ion EC_{50} for all species
223 with available data. The geometric mean of the resulting three $HC_{50-trophic}$ represents the free ion
224 activity HC_{50} in saltwater for that specific metal. Then, for each combination of metal and LME, a
225 truly dissolved HC_{50} was calculated using WHAM VII, based on the free ion activity HC_{50} and
226 corresponding LME water chemistry. Finally, EF was calculated as $0.5/\text{truly dissolved } HC_{50}$ ⁴³.

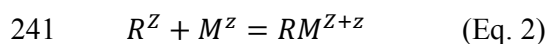
227 3 Results and Discussion

228 In this section the results for the spatially differentiated FF, BF, EF and CTP are discussed. The
229 results are shown for all combinations of metals and LMEs in Table S7 in SI.

230 3.1 Fate Factors

231 Cr, Cu and Fe have the highest log K_{DOC} and log K_{pSS} among all metals, indicating their strong
232 tendency of complexation with Organic Matter (OM, represented by DOC and the organic fraction
233 of SPM (POC)) in seawater (Figure S3 in SI). This is in accordance with previous findings that Cr,
234 Cu and Fe have high affinity for OM⁴⁷. Compared with empirical values, K_{pSS} in this study were
235 generally within an order of magnitude (Table 1).

236 Both log K_{DOC} and log K_{pSS} vary linearly with OM concentrations and salinity ($0.31 < R^2 < 0.93$,
237 $p < 0.001$, Table S8) for all metals except Pb and Fe. OM in WHAM is considered as humic
238 molecules, which are “rigid spheres, with proton-dissociating groups at the surface that can bind
239 metal ions.”⁴⁸ Metal ion binding to a humic molecule can be simply expressed by the general
240 reaction in Eq.2, which is described by the intrinsic association constant K_M (Eq.3)⁴⁸.



$$242 \quad K_M = \frac{[RM^{Z+z}]}{[R^Z][M^z]} \quad (\text{Eq.3})$$

243 Here R is the humic molecule, M is metal and z is the net charge. Under similar conditions (e.g.
244 pH value, temperature, etc.), K_M stays within a comparably narrow range. Therefore increasing OM
245 concentration leads to a higher concentration of metal-OM complex, resulting in a higher log K_{DOC}
246 and log K_{pSS} . When salinity increases, the metal ions are in stronger competition with major cations
247 in the seawater for the binding sites on OM, thus decreasing log K_{DOC} and log K_{pSS} ⁴⁹. The exception
248 for Pb and Fe is due to the fact that the binding of Pb and Fe to DOC and particles is not only

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249 influenced by OM concentrations and salinity, but also by other parameters (e.g. temperature and
 250 pH values).

251 **Table 1:** Log K_{pSS-D} ^a values (L/kg) in this study compared with empirical log K_{pSS-D} ^b values (L/kg)
 252 developed in other studies.

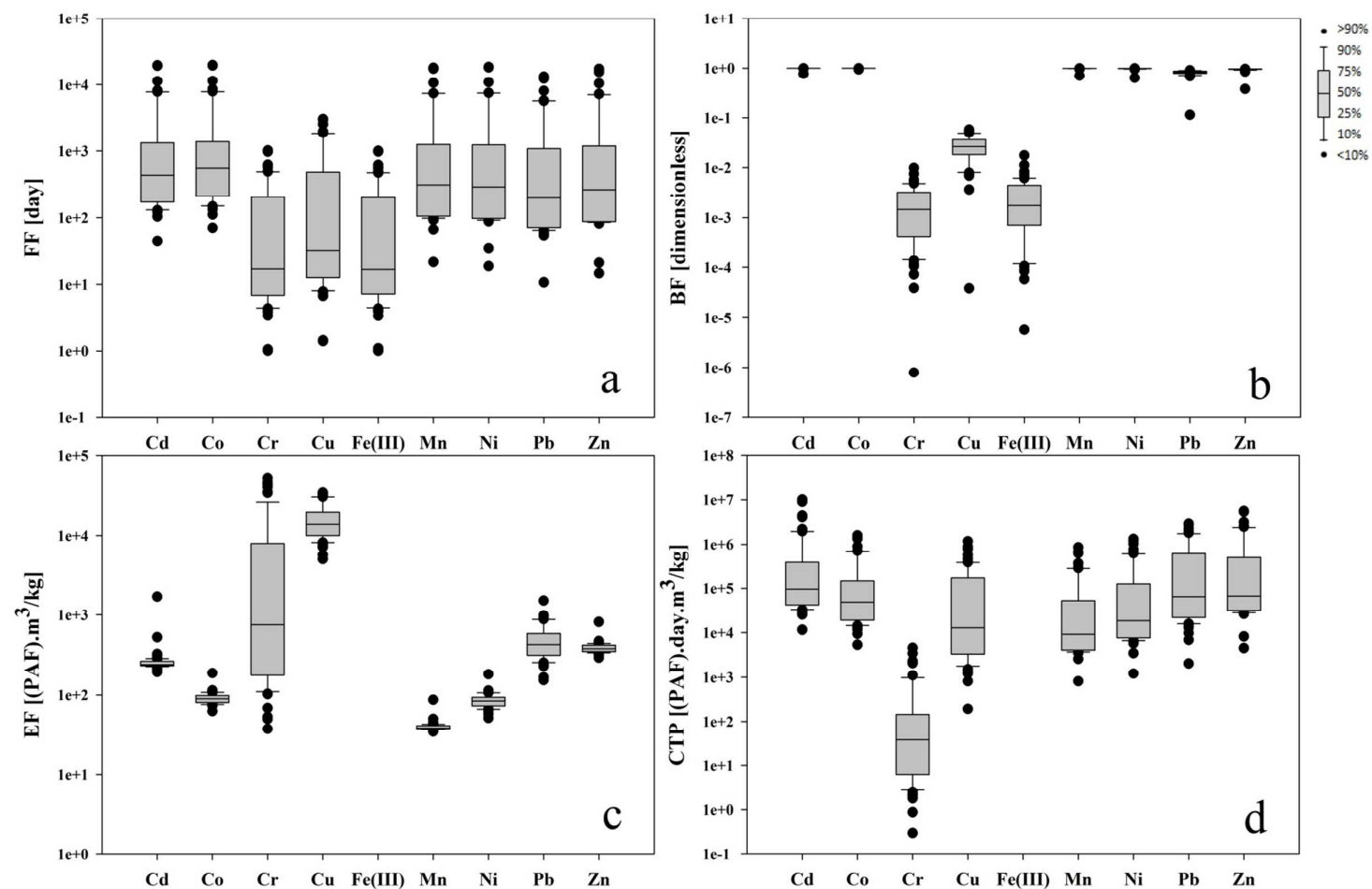
Metals	log K_{pSS-D} in this study (mean±standard deviation)	log K_{pSS-D} in other studies
Cd	2.9±0.3	4.0 ⁵⁰ ; 4.3 ⁵¹ ; 3.5-5.5 ⁵²
Co	2.7±0.2	4.6 ⁵¹ ; 4.5-6.0 ⁵²
Cr	5.5±0.2	5.5 ⁵⁰ ; 5.0-7.0 ⁵²
Cu	5.5±0.2	4.3 ⁵³ ; 4.9 ⁵⁰ ; 5.0 ⁵⁴ ; 3.5-5.5 ⁵²
Fe	5.5±0.2	5.0-7.5 ⁵²
Mn	3.5±0.2	3.5 ⁵¹ ; 3.0-6.0 ⁵²
Ni	3.8±0.2	4.4 ⁵⁰ ; 2.5-5.0 ⁵²
Pb	4.8±0.2	5.5 ⁵⁰ ; 6.0 ⁵³ ; 6.0 ⁵⁴ ; 4.0-6.5 ⁵²
Zn	4.2±0.2	3.0 ⁵¹ ; 4.5 ⁵⁰ ; 5.2 ⁵³ ; 5.5 ⁵⁴ ; 4.0-6.0 ⁵²

253 a. Log K_{pSS} (L/kg) in this study represents the calculated partitioning coefficient between metal
 254 bound to SPM and truly dissolved metal. Log K_{pSS-D} (L/kg) in other studies represents the
 255 partitioning coefficient between metal bound to SPM and total dissolved metal. To make the
 256 values comparable, we calculated log K_{pSS-D} values from the log K_{pSS} that we determined in
 257 this study.

258 b. Log K_{pSS-D} values in literature were presented as a function of other water chemistry
259 parameters (e.g. salinity and SPM). Here we took approximate values derived from water
260 chemistry similar to this study (e.g. $SPM \approx 1 \text{ mg/L}$, $Salinity \approx 30\text{‰}-35\text{‰}$, etc.)

261 FF is largely influenced by log K_{pSS} and log K_{DOC} . Metals with high log K_{pSS} and log K_{DOC} (e.g.
262 Cr, Cu and Fe) have an efficient removal, due to complex formation with OM followed by
263 sedimentation. Therefore they have the lowest FF in all LMEs (Figure 1a). In contrast, FFs of Cd
264 and Co are the highest across all metals, due to their low log K_{pSS} and log K_{DOC} . For a given metal,
265 FF increases with SRT across LMEs (Figure S4 in SI). For Cd, Co, Mn, Ni, Pb and Zn, FF and SRT
266 are linearly correlated with SRT ($R^2 > 0.97$, $p < 0.001$, Table S8 in SI). It means that FF variation
267 mainly depends on SRT and metal removal processes play a minor role. For the metals with high
268 log K_{pSS} and log K_{DOC} (e.g. Cr, Cu and Fe), metal removal processes show a stronger influence on
269 FF. Thus FFs for these three metals are less strongly correlated to SRT, but rather determined by the
270 variation of SRT, log K_{pSS} , and log K_{DOC} together. Note that the metals with lower K_{pSS} and log
271 K_{DOC} (Cd, Co, Mn, Ni and Zn) can have a FF that is higher than SRT in some LMEs. The reason is
272 that for these combinations of metal and ecosystem, the removed fraction is insignificant compared
273 to the total input. A non-negligible fraction of the metal flows out to the ocean, from where some of
274 it eventually recirculates back to the coastal seawater system after reaching steady state that USEtox
275 calculates. This results in a longer FF than the water that originally carried them out. The effect is
276 most pronounced in the LMEs with short SRTs because the inflow from the ocean is more
277 important compared to the volume and the freshwater input for these LMEs.

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278

279 **Figure 1.** Variation of Fate Factor (FF, 1a), Bioavailability Factor (BF, 1b), Effect Factor (EF, 1c) and Comparative Toxicity Potential

280 (CTP, 1d) for nine metals determined across the 64 LMEs in this study.

281 FF varies 2-3 orders of magnitude across LMEs for each metal. Within one LME, FF variation
282 between different metals is within two orders of magnitude (Figure S5a in SI). It indicates that FF is
283 slightly more sensitive to environmental parameters than to properties of metal.

284 We compared our FF with data from other studies. The age of water constituent models the
285 residence time of seawater constituents in particle forms in seawater by simulating particle cycling⁵⁵
286 and is similar to the concept of FF in this study. The constituent age of Baltic Seawater varies
287 between a few days and up to 40 years⁵⁶, which is similar to the range of metal FF in the Baltic Sea
288 (LME 23) in this study (3-21years). The constituent age of Kara Seawater is 1-2 years⁵⁷, which is
289 within the range of the metal FF in the Kara Sea (LME 58) in this study (1-4 years). The constituent
290 age of Norwegian Seawater and North Seawater combined together is 5-8 years⁵⁸, which is slightly
291 larger than the sum of metal FF ranges in the Norwegian Sea (LME 21) and the North Sea (LME
292 22) in this study (1-5 years).

293 **3.2 Bioavailability Factors**

294 Representing the fraction of total metal in coastal water that is truly dissolved, BF of Cd, Co, Mn,
295 Ni, Pb and Zn varies less than a factor of eight across LMEs (Figure 1b). For Cr, Cu and Fe the
296 variations in BF are much larger with 3-4 orders of magnitude, due to their large variations in log
297 K_{DOC} and log K_{pSS} across LMEs (Figure 1b). For all metals, clear correlations were observed
298 between BF and log K_{DOC} or log K_{pSS} (Figure S6). This implies that BF is largely determined by
299 metal binding to DOC (log K_{DOC}) and SPM (log K_{pSS}). Co has the highest BF in all LMEs across
300 metals, due to its low log K_{DOC} and log K_{pSS} . Similarly, Cr, Cu and Fe have the lowest BF across all
301 LMEs, due to their high log K_{DOC} and log K_{pSS} values (Figure 1b and Figure S6 in SI).

302 3.3 Effect Factors

303 Some nutrient metals are essential for biota growth (e.g. Co, Cu, Fe, Mn, Ni and Zn)^{59,60}.
304 However, some of them may not reach the essential concentration to support biota growth under
305 normal conditions in seawater, due to their low concentrations (at nmol level, Table S4 in SI).
306 Under such circumstances, instead of being a toxic pollutant, a metal emission is more likely to
307 facilitate biota growth. It is meaningless to talk about contribution to ecotoxicity under these
308 circumstances. Therefore a true zero value of coastal CTP is given for those metals, in agreement
309 with the recommendation in the Apeldoorn declaration⁷. For the metals covered in this study the
310 essentiality condition appears to be relevant only for Fe, where the essential concentration range lies
311 above its background concentration in coastal waters. This is caused by efficient removal of Fe in
312 the estuary (ca. 90%) via precipitation, flocculation, and sedimentation⁶. Meanwhile, fluvial
313 pathways contribute 75% of Fe inputs to seawater¹⁸, which leads to a low concentration of dissolved
314 Fe in seawater. Morel et al.⁵⁹ reviewed the essential concentration of metals in seawater and found
315 that for the metals Co, Cu, Mn, Ni and Zn, the background concentration in seawater is sufficient to
316 support biota growth. This is in accordance with other studies showing that iron is the only limiting
317 nutrient metal for algae growth in seawater⁶¹⁻⁶³. Therefore, a true zero was given to the EF of Fe in
318 all LMEs, which were excluded from the discussions in the rest of this section.

319 EFs show a modest variation, staying within one order of magnitude difference across all LMEs
320 except for Cr, which shows a larger variation of three orders of magnitude (Figure 1c). Cu has the
321 highest EFs in 90% of the LMEs, while Mn has the lowest EFs in all LMEs.

322 EF is influenced by temperature, pH, salinity and OM through their impacts on the speciation (the
323 fraction of free ion activity within truly dissolved metal). In general, with increasing pH, the metal
324 may form hydroxide or carbonate complexes, decreasing the metal free ion concentration in
325 solution, which leads to a lower EF⁶⁴. Increases in salinity leads to a higher ionic strength, which

326 results in lower free ion activity for a given free ion concentration, and thus a lower EF^{65} . When
327 OM decreases, a fraction of metal may be released into truly dissolved forms, which leads to a
328 higher truly dissolved HC_{50} , thus lower EF.

329 **3.4 Comparative Toxicity Potentials**

330 The comparative toxicity potentials are calculated as the product of FF, BF and EF following
331 Eq.1. Results are shown in Figure 1d. Due to its background concentration below essentiality levels
332 in coastal seawater ecosystems, the effect factor of Fe was set to zero and as a consequence its CTP
333 also becomes zero.

334 **3.4.1 Spatial variability of Comparative Toxicity Potentials**

335 Cr and Cu show the largest variation in CTP across LMEs with four orders of magnitude (Figure
336 1d). For Cr the variation is mainly driven by the variation in EF ($R^2=0.60$, $p<0.001$, Figure S7 in
337 SI), and less influenced by variation of FF and BF ($R^2<0.15$). For Cu no single individual parameter
338 shows a significant correlation with CTP.

339 CTPs of Cd, Co, Mn, Ni, Pb and Zn vary by three orders of magnitude across LMEs (Figure 1d).
340 These metals have rather stable BF and EF, which vary less than one order of magnitude across
341 LMEs. Thus CTP variations are largely caused by FF. As FF of these metals is linearly correlated
342 with SRT, CTP is overall strongly driven by the variation in SRT ($0.64<R^2<0.96$, Figure S8b in SI),
343 with higher CTP for longer SRT.

344 **3.4.2 Ranking of Comparative Toxicity Potentials**

345 Among all metals, Cd has the highest CTP in 45% of the LMEs (Figure S5d in SI), followed by
346 Zn (31%) and Pb (24%). These three metals have high FF, BF and middle to high EF. They are
347 ranked among the top four CTPs in all LMEs. In contrast, Cr has the lowest CTP in all LMEs (apart
348 from Fe, for which CTP is zero). Although its EF is in the middle range compared to the other

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349 metals, its BF and FF are constantly low in all LMEs, due to its high log K_{DOC} and log K_{pss} . Also
350 Mn and Ni are consistently in the lower ranking of CTP in all LMEs (5th-7th), due to their low EFs.

351 For Cd, Co, Mn, Ni, Pb and Zn, variation in CTP is significantly driven by SRT. Thus, the highest
352 CTPs for these metals are observed in LME 5 (Gulf of Mexico), LME 26 (Mediterranean), and
353 LME 62 (Black Sea), which have the longest residence time across LMEs (90 years). In contrast,
354 the lowest CTP is observed in LME 35 (Gulf of Thailand), which has the 2nd shortest SRT among
355 all LMEs (15 days).

356 CTPs ranking for Cr and Cu across LMEs are largely determined by SRT and by temperature
357 through its influence on speciation. The highest CTPs are found in LME 64 (Antarctic), where the
358 2nd lowest temperature (-1.20 °C) and long SRT (11 years) are observed. In contrast, they have the
359 lowest CTP value in LME 35 (Gulf of Thailand), which has the 2nd highest temperature and 2nd
360 shortest SRT.

361 3.4.3 Comparison between freshwater and coastal CTPs

362 Cd, Co, Cr, Mn, Ni and Zn marine CTPs show similar ranges to freshwater CTP determined by
363 Dong et al.¹³ using a parallel approach (Figure 1d). These similarities hide remarkable differences in
364 fate and effect behaviour in freshwater and coastal waters, which tend to neutralize each other in the
365 calculation of the CTPs. For these metals, EFs are thus up to two orders of magnitude lower in
366 seawater due to higher free ion activity HC_{50} in seawater (Table S9 in SI). This is in accordance
367 with previous research that freshwater species are more sensitive to metals than marine species⁶⁶. In
368 contrast, FFs are up to two orders of magnitude higher in seawater due to longer water residence
369 times in many LMEs (the residence time of freshwater is 143 days at maximum in USEtox¹³). For
370 the metals Cd, Co, Cr, Mn, Ni and Zn, BF in freshwater and seawater are rather similar. Cd, Co,
371 Mn, Ni, and Zn were insensitive to variations in water chemistry in freshwater¹³. Thus it may be
372 reasonable to expect similar BF in freshwater and seawater for these metals. BF of Cr is correlated

373 to log K_{DOC} and log K_{pSS} . These two values are negatively correlated with both SPM and salinity in
374 estuaries⁴⁹. From the freshwater end to seawater end, salinity increases and SPM decreases, which
375 in combination leads to similar ranges of log K_{DOC} and log K_{pSS} , and thus similar BF ranges in
376 seawater and freshwater for Cr. In summary, a combination of similar BF in sea- and freshwater,
377 lower EF in seawater, and higher FF in seawater results in a similar range of CTP in seawater and
378 freshwater for Cd, Co, Cr, Mn, Ni, and Zn (Figure S9 in SI).

379 Cu has up to two orders of magnitude higher FF in freshwater. It has a similar BF in freshwater
380 and seawater, for similar reasons as Cr. But its EF is 2-4 orders of magnitude lower in seawater,
381 which results in a slightly lower CTP in seawater (Figure S9 in SI).

382 Pb has a FF up to three orders of magnitude higher and a slightly lower EF in seawater than in
383 freshwater. At the same time its BF is 1-2 orders of magnitude higher in seawater, possibly due to
384 lower SPM and OM concentrations in seawater. This results in 1-4 orders of magnitude higher CTP
385 in coastal seawater than in freshwater (Figure S9 in SI).

386 CTP is expressed in potentially affected fraction of species integrated over time and space.
387 However, the species density varies considerably depending on location - from 7×10^{-12} to 5×10^{-4}
388 species/ m^3 in different freshwater ecosystems at various locations⁶⁷. Thus, even if two different
389 archetypes have the same CTP, the number of affected species can in extreme cases differ up to
390 eight orders of magnitude in freshwater. Variation would also be expected for species density in
391 coastal marine ecosystems. Moreover, species density in freshwater is generally about three orders
392 of magnitude higher than in seawater⁶⁸, which should be taken into account when comparing CTP
393 values in freshwater and seawater.

394 **3.4.4 Comparison of Fate Factors and Bioavailability Factors from USEtox**

395 The current version of USEtox does not provide marine CTP and only has seawater as a fate
396 compartment supporting FF and the eco-exposure factor (XF) calculation for seven of the metals

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397 covered in this study (Cd, Co, Cr, Cu, Ni, Pb and Zn). USEtox operates with a default SRT of one
398 year, which is at the middle range of SRTs applied for the LMEs in this study. The default USEtox
399 FF thus falls within the range of the new FF in this study for all the metals (Figure S9 in SI). BF in
400 this study is similar to the concept of eco-exposure factor (XF) in USEtox. The default XF in
401 USEtox falls within or close to the range of BF found in this study for most metals. The only
402 exceptions are Cr and Cu, for which the USEtox XF is 1-6 orders of magnitude higher (Figure S9 in
403 SI). This is because the default K_{DOC} and K_{pSS} values in USEtox were taken from literature⁶⁹, where
404 it was defined as the ratio between absorbed metal and total dissolved metal. Recall that K_{DOC} and
405 K_{pSS} calculated in this study represent the ratios between absorbed metal and truly dissolved metal.
406 This results in a lower K_{DOC} and K_{pSS} in USEtox, which leads to a higher XF.

407 **3.4.5 Sensitivity analysis**

408 Several water chemistry parameters (DOC, POC, SPM, pH, salinity, metal background
409 concentration and concentrations of Fe oxides, Mn oxides and Al oxides) and environmental
410 parameters (SRT, surface area, freshwater inflow and temperature) are involved in the calculation
411 of CTP in this study. In the following section, we will test the sensitivity of CTP to these
412 parameters.

413 Salinity and pH values were extracted from a complete datasets⁷⁰. Surface area and freshwater
414 inflow were measured data taken from a global database⁷¹. They are well established values and
415 their uncertainty are only caused by measurement error. Thus the uncertainty is hence judged to be
416 low (e.g. uncertainty of pH meter measurement accuracy <0.1 ⁷², salinity probe $<3\%$ ⁷³).

417 LME-specific land surface areas were applied in USEtox to calculate CTPs for metals in this
418 study. Compared to the CTPs calculated by applying default land surface area in USEtox, the
419 differences are less than 2%, caused by slightly different air deposition (which is also proportional
420 to the land area).

421 The importance of the uncertainty accompanying the Fe, Mn and Al oxide concentrations was
422 tested by changing them by a factor of 10. As a result CTPs varied less than 10% for all metals
423 except Pb, for which the variation amounted to 1-35% across all LMEs.

424 DOC, POC and SPM affect metal partitioning in water, and thus the CTP. These three parameters
425 show a significant positive correlation in natural waters (Figure S10 in SI). The parameter values
426 are accompanied by variation among different seawater and locations, along with the transition
427 from fresh to marine waters. We therefore tested the sensitivity of CTP to these three parameters, by
428 varying them all together by a factor of 0.1-10. These variations can cover DOC, POC, and SPM
429 concentrations ranging from conditions in freshwater to the open ocean. For these variations, CTP
430 of Cr and Cu show the highest sensitivity, varying between a factor of 0.004 and 168. The other
431 metals show very modest sensitivity, varying between a factor of 0.2 and 2.2 (Figure S11 in SI).
432 This indicates that CTP is sensitive to DOC, POC and SPM concentrations for Cr and Cu, but less
433 sensitive for the other metals. Note that within each LME, DOC, POC and SPM vary across
434 locations and time. The average value of these parameters in a specific LME was applied in our
435 study to calculate the corresponding CTP in that LME. Considering the large water volume and
436 surface area in each LME, and the comparatively constant pH, salinity and POC values (Figure S2
437 in SI), the average value of DOC, POC and SPM, thus CTPs are not likely to change dramatically
438 within one LME. However, the uncertainty associated with CTPs of Cr and Cu is still comparably
439 larger than the other metals. This needs to be noted when comparing CTPs across metals.

440 SRT has a strong influence on FF for all metals and hence also on the CTP. We varied SRT by
441 two orders of magnitude (0.1X-10X of original values) resulting in a variation in CTP by a factor of
442 0.05-21(Figure S12 in SI). The variations of CTP and SRT show a similar trend, indicating that
443 CTP positively covariates with SRT. Therefore, SRT is an important parameter determining CTP

444 when comparing metal CTP across LMEs, but it is less relevant for comparing CTP across metals
445 within the same LME.

446 Temperature has influence on metal speciation, thus potentially influencing FF, BF, and EF. We
447 calculated CTP by changing temperatures to 10°C lower or 10°C higher than the original values.
448 This variation range covers the surface seawater temperature for the whole year, judging from data
449 in the MODIS database⁷⁴. We found that CTP only varies within a factor of 0.4-2.8 (Figure S13 in
450 SI) for all metals. For Cr, BF and EF vary up to one order of magnitude. However, BF and EF have
451 positive and negative correlation respectively with temperature and hence partly compensate each
452 other, which results in a moderate change of CTP. It can be concluded here that CTP is not very
453 sensitive to temperatures.

454 BF, K_{pSS} , and K_{DOC} were calculated from metal background concentration in generic seawater,
455 which may differ in different locations. Therefore we tested the dependence of BF, K_{pSS} , and K_{DOC}
456 on metal background concentration, by varying background concentration by a factor of 10 (0.1X-
457 10X of original value). For the metals with higher K_{pSS} and K_{DOC} values (e.g., Cr, Cu and Fe), BF
458 can vary up to one order of magnitude and K_{pSS} , and K_{DOC} can vary up to two orders of magnitude.
459 The variation is largely caused by metal binding with OMs. For the other metals, the variations of
460 BF, K_{pSS} , and K_{DOC} are less than 2X. This result is similar to the observation in Gandhi et al.²¹. It
461 shows that in the systems with higher background concentrations, BFs thus CTPs of metals with
462 higher K_{pSS} , and K_{DOC} values may be underestimated. However, this might be offset by the
463 adaptation of aquatic biota in those systems, which is not considered in the current effect
464 modelling²¹.

465 3.5 Practical implications

466 This study is the first attempt to derive marine CTP considering speciation, bioavailability,
467 seawater specific toxicity, and spatial differentiation. The results show that CTP for one metal can

468 vary 3-4 orders of magnitude across LMEs, except for Fe, for which CTP is zero due to its low
469 background concentration and essentiality to marine biota. It was clearly demonstrated that it is of
470 great importance to apply spatially differentiated CTP for metals in coastal seawater, as shown for
471 all metals covered by this study except Fe. This raises the requirement for LCA practitioners to
472 consider the emission location in the inventory. The variation of CTPs is primarily driven by SRT
473 for most metals except Cr and Cu. If there is any updates on SRT in future research, it is strongly
474 recommended to recalculate metal CTPs correspondingly. Due to limited ecotoxicity data for
475 marine species and the metal coverage of the speciation model WHAM VII, it is difficult to derive
476 marine CTP for additional metals at this point. It is recommended to look into methods to estimate
477 marine ecotoxicity data by extrapolation from freshwater ecotoxicity data, or from known metal
478 properties. This can potentially provide ecotoxicity data for more metals and thus allow calculation
479 of additional marine CTPs. Where measured chronic data was missing, acute toxicity data was
480 extrapolated to chronic EC_{50s} for the EF calculation of some metals (e.g. Co, Cr, Mn, Ni, Pb and
481 Zn, Table S5 in SI). It is recommended to revise these data when chronic data is available. The
482 speciation model WHAM VII cannot simulate metal redox reactions and precipitation except Al
483 and Fe hydroxide. Due to the fact that the CTP developed in this study is for metal in coastal
484 seawater where water column depth is modest and presence of oxides are limited, the occurrence of
485 extreme redox conditions will be rare in most LMEs. E.g., When Cr(III) is emitted to coastal
486 seawater, its oxidation to Cr(IV) is limited and slow, unless abundant Mn dioxide and hydroxides
487 exist⁷⁵. However, the lack of precipitation modelling in WHAM can cause some uncertainties,
488 especially for metals which may form insoluble compounds with major anions in seawater.
489 Therefore, it is recommended to explore the possibility of applying other metal speciation models to
490 complement WHAM VII (e.g. MINEQL³⁸, Visual Minteq³⁷, CHEAQS Pro⁷⁶ or PHREEQC³⁹)
491 covering other metals and supporting the modelling of precipitation and redox reactions where

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492 needed. Literature reported that eutrophication can increase metal bioavailability up to an order of
493 magnitude^{77,78}. However, this may be offset by decreasing EF due to organism adaptation, which is
494 not considered in this study. Comparing to 3-4 orders of magnitude variation in CTPs, the
495 uncertainty introduced by differences in eutrophication across LMEs will not have significant
496 influences on the result. FIAM was used to assess EF in this study. However, unlike BLM it does
497 not include competition between free metal ion and other cations for binding to biotic ligands. Thus
498 it is recommended to estimate EFs with marine BLM when available. This study only developed
499 CTP for metals in the water column of the seawater compartment. Ecotoxicity potentials in
500 sediments were not considered here. In LCIA this is typically considered as a separate compartment
501 (if at all) and would require a separate study.

502

503 ASSOCIATED CONTENT

504 **Supporting Information**

505 9 tables and 13 figures addressing additional data were presented in supporting information. This
506 material is available free of charge via the internet at <http://pubs.acs.org>.

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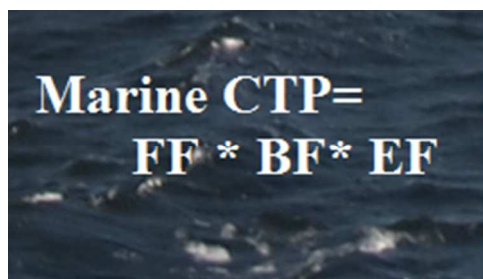
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