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Metal toxicity Characterization Factors for marine ecosystems – considering the importance of the estuary for freshwater emissions

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Abstract:

Purpose The study develops site-dependent Characterization Factors (CFs) for marine ecotoxicity of metals emitted to freshwater, taking their passage of the estuary into account. To serve LCA studies where emission location is often unknown, site-generic marine CFs were developed for metal emissions to freshwater and coastal seawater respectively. The new CFs were applied to calculate endpoint impact scores for the same amount of metal emission to each compartment, to compare the relative ecotoxicity damages in freshwater and marine ecosystems in LCA.

Methods Site-dependent marine CFs for emission to freshwater were calculated for 64 comparatively independent seas (Large Marine Ecosystems, LMEs). The site-dependent CF was calculated as the product of Fate Factor (FF), Bioavailability Factor (BF) and Effect Factor (EF). USEtox modified with site-dependent parameters was extended with an estuary removal process to calculate FF. BF and EF were taken from Dong et al. (2016). Site-generic marine CFs were derived from site-dependent marine CFs. Different averaging principles were tested, and the approach representing estuary discharge rate was identified as the best one. Endpoint marine and freshwater metals CFs were developed to calculate endpoint ecotoxicity impact scores.

Results and discussion Marine ecotoxicity CFs are 1.5 orders of magnitude lower for emission to freshwater than for emission to seawater for Cr, Cu and Pb, due to notable removal fractions both in freshwater and estuary. For the other metals, the difference is less than half an order of magnitude, mainly due to removal in freshwater. The site-dependent

25 CFs generally vary within two orders of magnitude around the site-generic CF. Compared to USES-LCA 2.0 CFs
26 (Egalitarian perspective), the new site-generic marine CFs for emission to seawater are 1-4 orders of magnitude lower
27 except for Pb. The new site-generic marine CFs for emission to freshwater lie within 2 orders of magnitude difference
28 from USES-LCA 2.0 CFs. The comparative contribution share analysis shows a poor agreement of metal toxicity ranking
29 between both methods.

30 **Conclusions** Accounting for estuary removal particularly influences marine ecotoxicity CFs for emission to freshwater
31 of metals that have a strong tendency to complex-bind to particles. It indicates the importance of including estuary in the
32 characterization modelling when dealing with those metals. The resulting endpoint ecotoxicity impact scores are 1-3
33 orders of magnitude lower in seawater than in freshwater for most metals except Pb, illustrating the higher sensitivity of
34 freshwater ecosystems to metal emissions, largely due to the higher species density there.

35 **Keywords (6-8 words): Comparative Toxicity Potential, CTP, estuary, fate model, USEtox, marine ecotoxicity**

36

37 **Acknowledgement**

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41 **1. Introduction**

42 Ecotoxicity impacts of metals often rank high in Life Cycle Assessment (LCA), due to their persistence in the
43 environment and their toxicity to biota (Huijbregts et al. 2000). However, up to now Life Cycle Impact Assessment
44 (LCIA) methods have largely relied on models developed for organics. Unlike organics, metals are non-degradable and
45 can exist in multiple species in water. Within those species not all of the dissolved metals are available for biota uptake
46 thus causing toxicity. Also the fate of the metals can be affected by their speciation. This may lead to an inappropriate
47 estimation of Characterization Factors (CFs) (also known as comparative toxicity potentials, CTPs, for the ecotoxicity
48 impact category) for metals emitted to water. Metal emissions can reach freshwater via different pathways, including
49 airborne emission followed by deposition, waterborne emission, and emission to soil followed by leaching or runoff.
50 Metal emissions can reach coastal seawater directly via releases to the sea, or indirectly, via freshwater inflow or
51 deposition from air.

52 Following the Apeldoorn Declaration (Aboussouan et al. 2004) and the Clearwater Consensus (Diamond et al. 2010)
53 on good practice in characterization modelling for metals, ecotoxicity characterization methods have been further
54 developed to reflect the specific behaviour of metals, and a new framework has been developed to calculate regionalized
55 freshwater ecotoxicity CFs of metals emitted to freshwater (Gandhi et al. 2010, 2011; Dong et al. 2014). Marine
56 ecotoxicity CFs for metals emitted to coastal seawater were developed based on a similar principle (Dong et al. 2016).
57 These studies found that metal CFs are very sensitive to water chemistry and emission location, varying by 3-4 orders of
58 magnitude among coastal ecosystems for most metals (e.g. Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) and 2-6 orders of
59 magnitude in freshwater for some metals (e.g. Al, Be, Cu, Cr, and Fe(III)). These results point to the importance of
60 applying archetype-specific or site-dependent CFs of metals in LCA studies whenever these are relevant contributors to
61 overall ecotoxicity. However, the inventory in LCA studies does not (yet) systematically specify the location of emissions,
62 which means that assessment often has to rely on site-generic CFs that represent impact potentials without consideration
63 of the location. Site-generic freshwater CFs for metals were determined as weighted averages of archetype-specific
64 freshwater CFs using weighting factors based on annual metal emission quantities to the different archetypes (Dong et al.
65 2014). Site-generic marine CFs, however, have not been developed.

66 Another important missing element in the characterization of aquatic ecotoxicity for metals is the modelling of their
67 behaviour in estuaries, the transition zone between freshwater and seawater. In two of the most widely used
68 characterization models for ecotoxicity in LCA, USES-LCA (van Zelm et al. 2009) and USEtox (Rosenbaum et al. 2008),

69 the fate modelling for metals emitted to the freshwater includes removal from the water column by sedimentation to
70 freshwater sediments (including burial and re-suspension). The rest of the metal is assumed to be transported directly to
71 coastal seawater and potentially affect marine ecosystems there. However, several studies show that estuaries function as
72 a filter for metals. They can trap a fraction arriving with the freshwater by adsorption to suspended particulate matter
73 (SPM). The SPM can then sediment directly or be taken up into biota, followed by sedimentation to estuary sediments
74 (USEPA 2006; Chester and Jickells 2012). As a result, only a fraction of the metal leaving the freshwater compartment
75 will reach the coastal seawater, which should be reflected in the CF that represents impacts in coastal seawater for
76 emissions to freshwater. None of the current LCIA models consider this aspect.

77 Therefore, this study aims at 1) modelling metal behaviour in estuaries and applying it for developing site-dependent
78 marine ecotoxicity CFs for metals emitted to freshwater; 2) developing site-generic marine ecotoxicity CFs for metals;
79 and 3) applying newly developed CFs to investigate and compare metal ecotoxicity in marine ecosystems to freshwater
80 ecotoxicity. Following Dong et al. (2016), CFs were calculated for metals emitted to a generic freshwater and received in
81 64 relatively independent coastal seas, Large Marine Ecosystems (LMEs). A LME covers the coastal zone from the coastal
82 line extending to the seaward boundary of the continental shelf (Sherman 1991), and together the 64 LMEs cover all
83 coastal water in the world. The filtering influence of an estuary is taken into account. Different averaging principles were
84 tested to calculate site-generic marine CFs for each metal emitted to freshwater, aiming to identify the best approach.
85 Similarly, we also developed site-generic marine CFs for metal emission directly to seawater based on the site-dependent
86 CFs from Dong et al. (2016). A comparison of the ecotoxicity in freshwater and marine ecosystems was performed for
87 the same amount of metal emitted to either compartment. The new set of site-generic marine metal CFs from this study
88 and the previously developed freshwater CFs (Dong et al. 2014) were applied to calculate the ecotoxicity impact scores
89 in marine and freshwater ecosystems respectively.

90 **2. Methods**

91 **2.1 Site-dependent marine Characterization Factors for metal emission to freshwater**

92 **2.1.1 General framework**

93 To be consistent with metal emission reported in the inventory, metals emitted to the environment are assumed to be
94 in the form of total metal. It includes free metal ions as well as metal associated with SPM, or forming complexes with
95 Dissolved Organic Carbon (DOC), or inorganic ions (figure 1). Among these metal forms, only inorganic complex metal

96 and free metal ions are considered bioavailable (Sunda 1989). Following Gandhi et al. (2010), $CF_{i,j}$ [(PAF)·day·m³/kg] is
97 the Characterization Factor expressing the ecotoxic impact per kg *total* metal in compartment j after emission to
98 compartment i. $CF_{i,j}$ is the product of three factors- a Fate Factor (FF_{ij}), a Bioavailability Factor (BF_j), and an Effect
99 Factor (EF_j) as shown in equation 1.

$$CF_{i,j} = FF_{ij} \cdot BF_j \cdot EF_j \quad (\text{Eq. 1})$$

100 This equation can be applied for different compartments. In this study, compartment i and j represent freshwater and
101 coastal seawater respectively. FF_{ij} is proportional to the residence time of total metal in the receiving coastal seawater
102 compartment including the transfer efficiency of chemical from the freshwater compartment. EF_j represents the
103 ecotoxicity effects caused by the truly dissolved metal in coastal seawater. FF_{ij} (referring to total metal) and EF_j (referring
104 to truly dissolved metal) are linked through BF_j , which represents the fraction of truly dissolved metal within the total
105 metal. Using equation 1, we calculated marine ecotoxicity CFs for each metal for an emission to freshwater with
106 subsequent transfer to coastal seawater.
107

108 The calculation of FF_{ij} is further described in section 2.1.2. BF_j and EF_j are the same as in the calculation of marine
109 CF for emission to seawater (Dong et al. 2016), since speciation and ecotoxic effects in coastal seawater are not affected
110 by the emission compartment. There BF_j were calculated using the chemical speciation model WHAM VII (Tipping et
111 al. 2011) and the Free Ion Activity Model FIAM (Campbell 1995) were used for calculating EF_j .

112 BF_j and EF_j were available in Dong et al. (2016) for the nine metals Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. However,
113 in that study, the marine EF of Fe was set to zero, due to the essentiality of Fe at the low concentrations that occur in the
114 seawater (Martin 1992; Sato et al. 2011; Barsanti and Gualtieri 2014), meaning that toxicity is unlikely to be caused by
115 the increments emitted by product systems. Accordingly, the marine CF for Fe emitted to freshwater is zero and it is
116 excluded from the following sections in this study, limiting the calculation of CF to the metals Cd, Co, Cr, Cu, Mn, Ni,
117 Pb and Zn.

118 2.1.2 Fate model

119 We adapted the multi-media fate model embedded in the scientific consensus model USEtox 1.01 (Rosenbaum et al.,
120 2008) to calculate FF_{ij} . To be consistent with freshwater and marine CFs developed in Dong et al. (2014; 2016), we did
121 not use the recently released USEtox 2.0 (USEtox Team 2016). However, the same adaptations can be applied in USEtox
122 2.0 for future updates. In USEtox, the environment is represented by several interlinked compartments, including
123 freshwater, seawater, soil, and air compartments, both on continental scale and global scale. FF_{ij} is calculated by
124 modelling chemical mass balance at steady state in different environmental compartments, considering removal,

125 immobilisation, and transfer processes between compartments. We calculated the fate of metal emitted to the continental
 126 freshwater compartment, passing through estuary and received in the continental seawater compartment (i.e. coastal
 127 seawater compartment). It is the product of two factors. One factor is the metal residence time in the coastal seawater
 128 compartment, which is the same as the FF calculated in Dong et al. (2016). It is determined by metal inflow to the coastal
 129 seawater compartment from other compartments (e.g. freshwater and air), metal removal in the coastal seawater
 130 compartment and metal outflow from the coastal seawater compartment to other compartments (e.g. ocean and air). The
 131 other factor is the fraction of metal that is transferred from freshwater to the coastal seawater compartment after emission
 132 to freshwater. This fraction is calculated from the metal loss rate constant in freshwater and the metal transfer rate constant
 133 from freshwater to the coastal seawater compartment. The transfer rate constant for chemicals from freshwater to coastal
 134 seawater (TRC_{fw-sw}) is calculated in USEtox as presented in equation 2.

$$135 \quad TRC_{fw-sw} = \frac{WaterF_{fw-sw}}{V_{fw}} \quad (\text{Eq. 2})$$

136 Where: $WaterF_{fw-sw}$ is the water flow rate [m^3/day] from freshwater to seawater compartment.

137 V_{fw} is the volume of the freshwater compartment [m^3].

138 This assumes that all metal contained in the water will be transferred from freshwater to coastal seawater compartment.
 139 It ignores that the estuary, acting as a metal filter between freshwater and coastal seawater, may retain a fraction of the
 140 metal in estuary sediments. We adapted USEtox to include the removal of metal in estuaries by introducing an estuary
 141 removal rate constant after the freshwater compartment, representing the retention of metal in the estuary. The estuary
 142 removal rate constant was calculated as described in equation 3.

$$143 \quad \text{estuary removal rate constant} = \frac{WaterF_{fw-sw} * R_{et}}{V_{fw}} \quad (\text{Eq. 3})$$

144 Where: R_{et} is the metal removal fraction in the estuary, representing the ratio between the amount of metal that
 145 is retained in the estuary and the total metal input to the estuary.

146 Introducing the removal in the estuary, the transfer rate constant for a metal from freshwater to seawater (TRC_{fw-sw})
 147 was correspondingly reduced with the estuary removal rate as expressed in equation 4.

$$148 \quad \text{New } TRC_{fw-sw} = \frac{WaterF_{fw-sw} * (1 - R_{et})}{V_{fw}} \quad (\text{Eq. 4})$$

149 Equation 4 was used in our study to replace equation 2 in the USEtox model. In addition, in the calculation of site-
 150 dependent FF_{ij} (and thus CF_{ij}), following Dong et al.(2016), the following USEtox parameters were adapted to fit the
 151 conditions of each LME: residence time of continental coastal seawater, surface area of continental coastal seawater,
 152 surface area of continental land area, water flow rate from freshwater to seawater, DOC and SPM concentration in

153 continental coastal seawater. K_{pSS} (L/kg) (the ratio of metal concentration between *SPM bound* metal and *truly dissolved*
154 metal) and K_{DOC} (L/kg) (the ratio of metal concentration between *DOC complex bound* metal and *truly dissolved* metal)
155 were recalculated for each metal in each LME, taking its specific water chemistry into account. The LME and metal
156 specific values for K_{pSS} and K_{DOC} were used instead of the original default values for that metal in USEtox. Other
157 parameters in the USEtox fate module were kept unchanged.

158 ***Removal Fraction (R_{et}) of metals in the estuary***

159 The fractions of metals that can be removed in estuaries are not universal. They depend on the removal mechanism and
160 metal speciation that is determined by water chemistry. Metals exist in the estuary either in dissolved form or particle-
161 bound forms. Only the particle-bound metal is trapped in the estuary. The removal of metal from the water column in the
162 estuary can occur through four processes, namely flocculation, adsorption to SPM, precipitation, and biological uptake
163 (Chester and Jickells 2012). Flocculation only has significant effects on “clay mineral suspensions, colloidal species of
164 iron and dissolved organics” and aluminium to a smaller extent (Chester and Jickells 2012). Though other metals can
165 flocculate with these flocculation-agents, the limited presence of flocculation-agents in natural estuary systems means
166 that it is not likely that flocculation will contribute significantly to the removal of other metals than iron and aluminium
167 (Chester and Jickells 2012). Biological uptake does not contribute significantly to the removal of metals from the water
168 column in estuary except in the case of silicon and nitrogen (Chester and Jickells 2012). Visual Minteq 3.1 (KTH 2010)
169 was used to investigate the possibility of metal precipitation in the estuary for all eight metals in this study (Cd, Co, Cr,
170 Cu, Mn, Ni, Pb and Zn) at their background concentration in standard seawater chemistry (salinity 35‰ and pH 8.1), and
171 in several freshwater chemistry archetypes presented by Gandhi et al. (2011). The possible precipitate solids considered
172 in Visual Minteq are presented in table S1 in SI. Modelling results showed that none of the investigated metals precipitate,
173 neither in the investigated freshwater nor in the seawater. This is expected since the applied background concentrations
174 are obtained from empirical data representing total dissolved metals. Therefore, it is assumed that the only important
175 metal removal mechanism in the estuary is adsorption to SPM, followed by particle removal through sedimentation or
176 other mechanisms (e.g. SPM flocculation). This is in accordance with previous studies finding that heterogeneous
177 precipitation in the presence of particle clouds is especially important for the removal of metals from the solution. Chester
178 and Jickells (2012) reviewed several studies describing the removal of particulate matter in different estuaries (including
179 the Scheldt estuary, Mississippi delta, Amazon river mouth and St Lawrence system). They concluded that in general 90%
180 of SPM is retained in the estuary as the water passes through the estuary. This is a result of the high sedimentation rate of
181 SPM in the estuary (Malmgren and Brydsten 1992), and we have confirmed this fraction with other studies (Lykousis and

182 Chronis 1989; Zhang et al. 1990; Karageorgis and Anagnostou 2001). Though some studies reported higher fractions
183 (Malmgren and Brydsten 1992; Kim et al. 2006), or slightly lower fractions of down to 70% retention (Liu et al. 2007), a
184 retention of 90% is judged to be a good assumption for the modelling of metal removal in a generic estuary in our study.

185 Different estuaries may differ widely in terms of e.g. area, water volume, particle concentration, DOC and water
186 residence time. Nevertheless, metal removal mechanisms- partitioning with SPM followed by sedimentation- are similar.
187 Note that the partitioning depends on the water chemistry. Water chemistry is very different in freshwater and seawater.
188 In the transient zone between the two compartments, freshwater enters the estuary gradually mixing with seawater, which
189 results in a continuously changing water chemistry throughout the estuary with salinity changing from ~0 to 35‰, DOC
190 from 5 to 1 mg/l and pH from ~7.0 to 8.1 (Stumm and Morgan 1996). In addition, trace metal background concentrations
191 decrease by up to two orders of magnitude from freshwater to seawater (Salminen 2005; Mason 2013). As described in
192 Dong et al. (2016) the main water chemistry parameters affecting metal partitioning and speciation are salinity and organic
193 matter content. These are gradually changing in all estuaries in a similar way from the freshwater to the seawater. E.g. a
194 linear relationship has been found between salinity and DOC in several estuaries (Cawley et al. 2014; Asmala et al. 2016).
195 Salinity increases linearly with distance from the seashore (Wit et al. 2015). Therefore, a simplification was assumed
196 valid for our purpose, modelling the removal in the estuary for a generic estuary, calculating only one estuary removal
197 fraction for each metal to be used in the calculation of CFs for all LMEs. The generic estuary was divided into eight
198 consecutive sub-cells according to salinity with a gradually changing water chemistry from close to freshwater chemistry
199 in the first sub-cell to close to seawater chemistry in the last sub-cell (table S2 in SI). Metals pass through the sub-cells
200 sequentially. Within each sub-cell, metals are assumed to equilibrate with the water chemistry before the dissolved metal
201 and a fraction of the SPM-bound metal passes on to the next sub-cell. According to previous studies (Li et al. 1984),
202 adsorption and desorption between metals and SPM reaches equilibrium for most metals after half a day. Therefore, with
203 the chosen eight sub-cells, full equilibrium can be reached within each sub-cell for all metals, in an estuary that has a
204 water residence time longer than four days. According to Chester and Jickells (2012), water residence times in different
205 estuaries vary from a few days to a few months. Thus a water residence time longer than four days is a reasonable
206 assumption for the majority of the estuaries and it seems reasonable to assume that equilibrium is reached within each
207 sub-cell. For each sub-cell, the dissolved metal concentration and water chemistry was entered into the speciation model
208 WHAM VII (Tipping et al. 2011) to calculate the concentration of metal bound to SPM. It is assumed that dissolved
209 metals are at their background concentration in the estuary. Since dissolved metals from freshwater are gradually diluted

210 by seawater, which contains much lower concentrations of metals, as described above, we further assume that the metal
 211 background concentrations decrease linearly with the increase in salinity from freshwater to seawater (table S2 in SI).

212 The concentration of SPM is assumed to decrease linearly with salinity from freshwater to seawater (Turner 1996; Cai
 213 et al. 2012; Takata et al. 2012). This gives us equation 5 to calculate SPM concentration at any given salinity between 0
 214 and 35‰.

$$215 \quad SPM_n = a * Sal_n + b \quad (n \in [0, 35\text{‰}]) \quad (\text{Eq. 5})$$

216 Where:

217 SPM_n is the concentration of SPM at salinity value Sal_n ,
 218 b is the initial SPM concentration at the freshwater end,
 219 a is a constant.

220 The increase in salinity from freshwater to seawater is caused solely by the mixing of freshwater and seawater with a
 221 different fraction of seawater and freshwater at each salinity point. The SPM concentration, on the other hand, is also
 222 affected by removal processes as previously described.

223 In the absence of SPM removal processes, the mixing of freshwater and seawater would give SPM a conservative
 224 behaviour (Chester and Jickells 2012), as expressed by equation 6.

$$225 \quad SPM_{n,o} = c * Sal_n + b \quad (n \in [0, 35\text{‰}]) \quad (\text{Eq. 6})$$

226 Here $SPM_{n,o}$ represents the hypothetical SPM concentration at salinity value Sal_n without any removal process involved,
 227 and c is a constant, which differs from constant a . Representing the initial SPM concentration, constant b remains the
 228 same as in equation 5 because at the freshwater end, salinity is close to zero, where the estuarine SPM removal has not
 229 started yet. Combining equations 5 and 6, provides equation 7:

$$230 \quad SPM_{rem,n} = SPM_n - SPM_{n,o} = (a - c) * Sal_n \quad (n \in [0, 35\text{‰}]) \quad (\text{Eq. 7})$$

231 Here $SPM_{rem,n}$ represents the reduction in the concentration of SPM solely caused by the removal process at salinity
 232 value Sal_n . Applying two different salinities, i and j in equation 7, yields:

$$233 \quad \frac{SPM_{rem,i}}{SPM_{rem,j}} = \frac{Sal_i}{Sal_j} \quad (i, j \in [0, 35\text{‰}]) \quad (\text{Eq. 8})$$

234 Since the estuary was divided into eight sub-cells according to salinity, it is reasonable to use the generic water
 235 chemistry in each sub-cell as a proxy to represent its relevant salinity ranges (table S2 in SI). Therefore, equation 8 can
 236 be adapted into equation 9.

$$237 \quad \frac{SPM_{cellrem,k1}}{SPM_{cellrem,k2}} = \frac{Sal_{cellk1}}{Sal_{cellk2}} \quad (k1, k2 \in [1, 2, 3, 4, 5, 6, 7, 8]) \quad (\text{Eq. 9})$$

238 Where $SPM_{cellrem,k}$ and Sal_{cellk} represent the removed SPM concentration and the salinity value in sub-cell k1 and k2
239 respectively.

240 If we allow the fraction of SPM that has not been removed in each sub-cell to be transferred to the next sub-cell, then
241 after eight sub-cells, the remaining amount of SPM should in total account for 10% of initial SPM input to the estuary, in
242 accordance with the assumed 90% SPM removal in the estuary. This results in equation 10.

$$243 \quad \prod_{k=1}^8 \left(1 - \frac{SPM_{cellrem,k}}{SPM_{cellk}}\right) = 10\% \quad (\text{Eq. 10})$$

244 Here SPM_{cellk} is the SPM concentration in sub-cell k. Correspondingly, $SPM_{cellrem,k}/SPM_{cellk}$ presents the removal
245 fraction in sub-cell k. Fitting equation 9 and 10 with SPM and salinity values of each sub-cell, the removal fraction of
246 SPM in each sub-cell can be calculated (result shown in table S2 in SI). These removal fractions also apply to the metals
247 bound to SPM. Summing up over all sub-cells, the total removed SPM-bound metal is found and the resulting removal
248 fractions in the estuary can be calculated for each metal as the ratio between total removed metal and total input of metal
249 from freshwater.

250 2.2 Averaging principles and site-generic characterization factors

251 Although the estuary model does not distinguish between different locations in this study, CFs for each LME and each
252 metal vary due to differences in environmental parameters of the LME (e.g. seawater residence time, temperature and
253 water chemistry). For the purpose of LCA, where emission location is often unspecified for emissions reported in the life
254 cycle inventory, a site-generic CF is needed for marine ecotoxicity, derived by averaging the metal CFs across the
255 individual LMEs. Ideally, the averaging should apply weighting factors that, for a given LME, reflect the probability that
256 this LME receives the metal emission, e.g. based on the geographic distribution of the annual emission quantities for the
257 metal. As this information is currently not available for all LMEs, we instead tested four alternative weighting principles
258 based on the surface area of the LME, the primary productivity of the LME, the estuary discharge rate to the LME, and
259 the inshore fishing area of the LME (resulting in average values CF_{surfa} , CF_{pripro} , CF_{dis} , and CF_{fisha} respectively). For each
260 of the weighting principles and each metal, the site-generic CF is calculated as shown in equation 11 and 12. Weighting
261 factors are available in table S3 in SI.

$$262 \quad \text{weighted site-dependent CF} = \text{site-dependent CF} * \text{corresponding weighting factor} \quad (\text{Eq. 11})$$

$$263 \quad \text{site-generic CF} = \sum \text{weighted site-dependent CF} \quad (\text{Eq. 12})$$

264 CF_{surfa} assumes that each unit surface area of coastal seawater has the same probability of receiving emissions, i.e. the
265 larger the LME, the larger the share of anthropogenic metal emissions that it receives. CF_{dis} presumes that the share of
266 metal emissions reaching an LME is proportional to the freshwater discharge that it receives. CF_{pripro} and CF_{fisha} follow
267 the hypothesis that the effect caused by metal emission can be judged by the relative size of affected primary production
268 or inshore fishing area respectively. In addition, the arithmetic mean over the 64 site-dependent CFs (CF_{ave}) was
269 calculated, inherently assuming an equal possibility of each LME to receive the metal emission. These weighting
270 principles were applied to marine CFs for metals emitted to freshwater and for metals emitted to coastal seawater
271 respectively. A recommendation of site-generic principle was developed and the sensitivity of site-generic CFs to the
272 applied weighting principle were analysed.

273 3. Results and discussion

274 First the site-dependent marine ecotoxicity CF for metals emitted to freshwater are presented. Afterwards, site-generic
275 marine CFs for metals emitted to freshwater and coastal seawater are shown. Then they are applied to an emission
276 inventory with equal quantities of all metals to examine the effects on the freshwater ecotoxicity and marine ecotoxicity
277 impact scores.

278 3.1 Site-dependent marine Characterization Factors for metals emitted to freshwater

279 As previously mentioned in section 2, the fraction of metal which is transferred from freshwater to the coastal seawater
280 compartment is dependent on metal loss in both freshwater and the estuary. In USEtox our proposed methodology allows
281 the marine ecotoxicity CF for emission to freshwater ($CF_{\text{fw-sw}}$) to be calculated in a simple way from the marine
282 ecotoxicity CF for emission to seawater ($CF_{\text{sw-sw}}$), using the removal rate constant in freshwater (R_{fw}) and removal rate
283 constant in the estuary (R_{et}) as shown in equation 13.

$$284 \quad CF_{\text{fw-sw}} = CF_{\text{sw-sw}} * (1-R_{\text{et}}) * (1-R_{\text{fw}}) \quad (\text{Eq. 13})$$

285 A metal-specific estuary removal fraction, R_{et} was calculated for each of the metals, to fit the fate model embedded in
286 USEtox for the modelling of metal fate in coastal seawater compartments after emission to freshwater. Removal fractions
287 in the estuary vary considerably among metals according to the applied model as shown in table 1, where larger fractions
288 are retained for the metals Pb, Cu, and Cr due to their high affinity to SPM as expressed by their K_{pSS} (Dong et al. 2016).
289 The calculated removal fractions show good agreement with ranges and tendencies found in other studies (table 1).
290 Applying the USEtox fate model, close to 90% of Cr, Cu, Pb, and 40%-60% of the other metals emitted to freshwater

291 were removed in the freshwater compartment before ever reaching the estuary (table 1), indicating that the residence time
292 in freshwater is sufficient to allow a large fraction of metals to adsorb to SPM, which is then removed by sedimentation.
293 In the estuary, 19% of Cr, 21% of Cu and 61% of Pb were removed before entering the coastal seawater, while less than
294 2% of the other metals are removed in estuary. The resulting site-dependent marine FF and CF for emission to freshwater
295 are presented in table S4 in SI.

296 Regardless the uncertainties associated with site-dependent marine CFs as discussed in Dong et al. 2016, for the same
297 metal in the same LME, the marine FF for emission to freshwater is always lower than for emission to seawater due to
298 metal removal in freshwater and the estuary. For Cd, Co, Mn, Ni, and Zn, the difference between the two marine FFs is
299 less than half an order of magnitude, mainly caused by the removal process in freshwater. However, for Cr, Cu, and Pb,
300 both estuary and freshwater removal processes contribute noticeably, resulting in a 1.5 orders of magnitude lower marine
301 FF for metal emitted to freshwater than for metal emitted to seawater . This indicates that for metals forming strong
302 complexes with particulate matter such as Cr, Cu and Pb, it is necessary to include estuary removal in the fate modelling.
303 For other metals such as Cd, Co, Mn, Ni, and Zn, the estuary removal can be simplified in the modelling. Since the BF
304 and EF are the same in both cases, this difference in FFs translates directly into the marine ecotoxicity CFs for emissions
305 to freshwater and seawater as illustrated in figure 2.

306 **3.2 Site-generic marine Characterization Factors**

307 The purpose of LCA is to assess the impacts related to products, and an important source of metal emissions from the
308 product's life cycle will often be the manufacturing stage or mining operations, metallurgical operations extracting metal
309 ores and refining the metal. With few exceptions, such facilities are located inland with initial discharge to freshwater or
310 estuaries (EPRTR 2012). A large share of the metal emissions will thus be transported to seawater through estuary
311 discharge. As a consequence, fluvial input is the major source (>50%) of most metals in seawater with Hg and Pb as
312 exceptions for which atmospheric deposition is dominant (Mason 2013). Therefore, the annual estuary discharge seems
313 to be the most relevant weighting principle for deriving a site-generic marine CF to be applied in LCA studies when
314 emission location is unknown, both for emissions to freshwater and seawater. It is therefore recommended as the preferred
315 averaging principle.

316 Site-generic marine CFs may also be calculated by applying other averaging principles if preferred for particular reasons.
317 We have provided four other options as described previously in section 2.2, including three weighting principles and

318 arithmetic mean. The resulting site-generic CFs are presented in table S5 in SI. The four weighting principles (including
319 the recommended one) lead to minor differences in the calculated site-generic CF, which lies within less than a factor of
320 three for all metals. To understand if there is any significant difference between different weighting principles, we looked
321 into the differences between two selected sets of weighted site-dependent CFs that are calculated in equation 11. For each
322 metal, there are five sets of site-dependent CFs including equal weighting. This gives us 10 sets of differences (table S6
323 in SI). Running t-tests on the 10 sets of differences for each of the metals, we observed that most of the p-values are above
324 0.05, meaning there is no significant difference between the weighted site-dependent CFs (table S7 in SI). The only
325 exceptions are Cu and Cr, where significant differences were observed for two and one sets of comparison respectively.
326 This is largely due to their larger variation of CFs across LMEs. This indicates that the site-generic CFs are not very
327 sensitivity to the chosen averaging principle. All investigated averaging principles including arithmetic mean give results
328 located in the upper half of the CF ranges across the 64 LMEs. This indicates that for all averaging principles, LMEs with
329 higher CFs, which tend to be the LMEs with longer seawater residence times, have a relatively strong influence on the
330 generic CF.

331 **3.3 Parameter uncertainty**

332 Sensitivity and uncertainty analyses for the site-dependent marine CF were conducted by Dong et al. (2016), covering
333 most input parameters applied in the model. For some parameters, the inherent uncertainty is judged to be low (i.e. pH
334 values, salinity, freshwater inflow and land surface area), varying less than 3%. For the parameters that are more uncertain,
335 i.e. Fe, Mn, and Al oxide concentrations, DOC, POC, SPM concentrations, seawater residence time (SRT) and
336 temperature, further sensitivity analysis were conducted in Dong et al. (2016) . The results show that CFs are mostly
337 sensitive to DOC, POC and SPM concentration, and seawater residence time (SRT), leading to further analysis of the
338 potential uncertainty of those parameters in this study.

339 Taking LME22 and LME24 as examples, SPM varied from 0.2 to 66 mg/L at different locations between year 1970 and
340 1994 (Radach et al. 1996), with an average of 0.79 and 0.59 mg/L respectively. Assuming a positive correlation between
341 DOC, POC and SPM as shown by Dong et al. (2016), this gives an uncertainty of CFs of about two orders of magnitude
342 for Cu and Cr, but less than a factor of three for all other metals. Note that this is the uncertainty caused by the natural
343 variation of water chemistry in different time and locations within one LME.

344 Marine CFs are strongly driven by SRT. In Dong et al. (2016), some of the LMEs do not have a reported SRT available
345 for calculation. For those LMEs, the SRT are estimated from the coastal seas that have similar conditions. According to
346 Cosme et al. (2017), the SRTs that are estimated to be 0.25 years may vary from 0.03 years to 0.5 years. For a SRT of 2
347 years, variation from 0.2 to 3.8 years occurs. For LMEs with longer SRT such as 25 years and 90 years, literatures reported
348 up to one order of magnitude lower SRT (Cosme et al. 2017). We therefore varied SRT by a factor of 0.1 or 2 of the
349 original value, which reasonably covers the potential range of estimated SRTs. The resulted CFs for different metals vary
350 by a factor of 0.05-0.8 or 1.1-2.6 respectively.

351 All of the above uncertainties are present in the marine CFs for emission to both freshwater and seawater, due to the
352 inherent methodology for the calculation. From the uncertainty analysis, it is reasonable to judge that the parameter
353 uncertainty associated with the site-dependent marine CFs is within two orders of magnitude. It is noteworthy that only
354 the variability of parameters has been considered in this analysis, whereas other sources of uncertainty may also contribute
355 to the overall uncertainty of CFs, but which may not always be quantifiable.

356 We also assessed the uncertainty of site-generic CFs caused by the variation of site-dependent CFs. For most of the
357 metals (i.e. Cd, Co, Cr, Cu, and Pb), the 64 site-dependent CFs follow a lognormal distribution (table S8 in SI). Their
358 geometric standard deviation are presented in table 2, indicating that site-generic CFs are accompanied by a considerable
359 additional parameter uncertainty due to neglected spatial variability.

360 In addition to the parameter uncertainty associated with CFs, the differences between the deterministic site-dependent
361 and site-generic CFs for a specific metal are within one order of magnitude for ~50% of the LMEs and within two orders
362 of magnitude for more than 90% of the LMEs (figure 2). The strongest deviation was up to three orders of magnitude.
363 This emphasizes the importance of providing emission locations in the inventory in order to enable the use of site-
364 dependent CFs.

365 **3.4 Comparison between recommended generic Characterization Factors and USES-LCA Characterization** 366 **Factors**

367 The USES-LCA 2.0 characterization model, applied as part of the ReCiPe LCIA method, provides three sets of CFs for
368 marine ecotoxicity representing different cultural perspectives, considering different modelling choices and time scales
369 (Goedkoop et al. 2012). CF(I) and CF(H) represent the Individualist and Hierarchist perspectives. CF(E) represents an
370 Egalitarian perspective, where a longer time scale is applied and steady state is established (in most cases). In this study,

371 we used USEtox to calculate the FF, which is based on a steady-state mass balance applying an infinite time horizon.
372 Thus, among the three perspectives, the Egalitarian is the scenario which corresponds best to the assumptions in this study.

373 Note that ecotoxicity CFs in USES-LCA 2.0 are expressed in a relative metric as 1,4-DCB equivalents, which differs
374 from the absolute metric applied in this study [(PAF).m³.day/kg]. To compare factors from both models, we converted
375 our CFs to 1,4-DCB equivalents by dividing the metal CFs with marine CFs for 1,4-DCB emitted to freshwater or seawater
376 in corresponds with the metal emission compartments. Here marine CFs for 1,4-DCB are site-generic ones calculated
377 using default USEtox settings. However, marine CF of 1,4-DCB emitted to freshwater is 1.5 orders of magnitude lower
378 than when it is emitted to seawater. This is because 1,4-DCB degrades in freshwater, which results in a much lower
379 transfer fraction from freshwater to seawater (4%) than for most of the metals. This potentially introduces a bias in the
380 conversion of the new metal CFs in this study to 1,4-DCB equivalents, which may result in higher marine CFs for metal
381 emissions to freshwater than to seawater after the conversion. Though this does not affect the ecotoxicity ranking of
382 metals, it highlights a problem in the use of an organic reference substance when expressing ecotoxicity of metals in
383 different compartments (Dreyer et al., 2003). In general, site-generic marine CFs developed in this study are higher than
384 USES-LCA 2.0 CFs with Individualist and Hierarchist perspectives, but lower than or similar to USES-LCA 2.0 CFs with
385 Egalitarian perspective (table S9 in SI).

386 To understand the differences of both methods in relative terms, we conducted a contribution analysis following Dreyer
387 et al. (2003) and Pizzol et al. (2011). We created a hypothetical inventory with emissions of one kg of each metal (Cd,
388 Co, Cr, Cu, Mn, Ni, Pb and Zn). In scenario 1, they are all assumed to be emitted to freshwater. In scenario 2, the emission
389 compartment is coastal seawater. For each of the scenarios, we have calculated the marine ecotoxicity impact scores by
390 using USES-LCA Egalitarian CFs and the recommended site-generic CFs in this study respectively. The contribution of
391 each metal to the total impact score is presented in figure 3. The figure shows poor agreement between both methods in
392 that the same metal contributes very different shares for the two different methods. For emission to freshwater, the marine
393 ecotoxicity mainly comes from Ni, Cu and Co in USES-LCA, contributing to more than 90% in total. In contrast, applying
394 CFs developed in this study, these three metals contribute less than 20% to the total marine ecotoxicity score, which is
395 dominated by Zn, Cd and Pb. A similar observation was made for emission to coastal seawater. This means that the most
396 toxic metals according to USES-LCA become less important in the new methodology.

397 **3.5 Metal ecotoxicity in the aquatic system**

398 The newly developed site-generic marine and freshwater ecotoxicity CFs, allow us to compare the severity of the
399 ecotoxic impacts that are caused by emitting metals to different aquatic compartments. The CFs that we developed in the
400 previous sections are known as midpoint CFs, expressed as the potentially affected fraction of species integrated over
401 volume and time [PAF in m³.day]. For a comparison of impacts in freshwater and marine ecosystems it is important to
402 note that the species density (number of species per volume compartment) is different in freshwater and seawater.
403 Therefore, the midpoint marine CFs cannot be compared directly with the midpoint freshwater CFs from Dong et al.
404 (2014), since the fractions expressed by the potentially affected fraction of species (PAF) relate to different total species
405 numbers. To make the ecotoxicity scores comparable, marine and freshwater endpoint CFs were developed. Endpoint
406 CFs build on midpoint CFs but also consider the severity of the midpoint impacts by modelling the damages on the
407 exposed ecosystem, represented by the resulting potentially *disappeared* number of species. Therefore, PAF in the
408 midpoint score needs to be converted to the potentially disappeared fraction (PDF) to arrive at the endpoint score. Thus,
409 in addition to species density, a PAF to PDF ratio is applied on the midpoint CF to derive the endpoint CF
410 [(species).day/kg], as shown in equation 14.

411
$$\text{Endpoint CF} = \text{midpoint CF} \times \text{species density} \times \text{PAF to PDF ratio} \quad (\text{Eq. 14})$$

412 Equation 12 can be used to calculate endpoint ecotoxicity CFs in any environmental compartment. In this study, we
413 took the PAF to PDF ratio (dimensionless) from IMPACT 2002+ (Jolliet et al. 2003). Marine and freshwater species
414 densities [species/m³] were taken from ReCiPe (Goedkoop et al. 2013). To calculate the site-generic marine ecotoxicity
415 endpoint CF, we used the site-generic marine ecotoxicity midpoint CF [(PAF).m³.day/kg] from this study. Site-generic
416 freshwater ecotoxicity CFs from Dong et al. (2014) were used to calculate freshwater ecotoxicity endpoint CFs. The
417 results are presented in figure S1 in SI.

418 The site-generic endpoint ecotoxicity impact score (EIS, [(species).day]) for emission to freshwater and seawater can
419 be calculated by equation 15 and 16 respectively.

420
$$\text{EIS for emission to freshwater} =$$

421
$$(\text{Freshwater endpoint CF} + \text{Marine endpoint CF for emission to freshwater}) \times \text{emission quantity} \quad (\text{Eq. 15})$$

422
$$\text{EIS for emission to seawater} = \text{Marine endpoint CF for emission to seawater} \times \text{emission quantity} \quad (\text{Eq.16})$$

423 For comparison of metal ecotoxicity impacts on freshwater ecosystems and marine ecosystems, we calculated endpoint
424 impact scores for emissions of one kg metal to either freshwater or seawater. The resulting endpoint impact scores for
425 such emissions are presented for eight metals in figure 4.

426 The result shows that for all metals investigated except Pb, emissions to freshwater result in 1-3 orders of magnitude
427 higher endpoint EIS than emissions to seawater (figure 4). When metals are emitted to freshwater, the major ecotoxicity
428 impact is on freshwater species. Though some metals will pass through the estuary and reach seawater, consequently
429 causing toxicity on marine species, the impacts on marine species (marine ecotoxicity for emission to freshwater) only
430 contribute little (<3.5% for any of the metals except Pb) to the total EIS for emissions to freshwater. The freshwater
431 ecotoxicity CF is either similar or slightly higher than the marine ecotoxicity CF (Dong et al. 2016), but the species density
432 in freshwater is two orders of magnitude higher than in marine water (Goedkoop et al. 2013), which is the main driver
433 behind the higher endpoint EIS for freshwater ecotoxicity. For Pb, the emission to seawater causes one order of magnitude
434 higher marine ecotoxicity endpoint scores than emission to freshwater (figure 4). Here 30% of the EIS for emissions to
435 freshwater is coming from the impacts on marine species. This is largely caused by the much higher CF of Pb in marine
436 water than in freshwater as discussed in Dong et al. (2016).

437 **4. Conclusions and recommendations**

438 Following the methodological recommendations from the Apeldoorn declaration and the Clearwater Consensus, we
439 developed site-dependent marine ecotoxicity CFs for 64 Large Marine Ecosystems for eight metals emitted to freshwater,
440 taking estuary removal into account. By introducing an estuary into the multi-compartment fate model of USEtox, marine
441 CFs for metals with a strong tendency to associate with particles (e.g. Pb, Cu, and Cr) were notably reduced for emission
442 to freshwater. 61% of Pb, 21% of Cu and 19% of Cr that enters the estuary were retained there. In combination with the
443 metals that are retained in freshwater, this results in 1.5 orders of magnitude lower marine ecotoxicity CFs for emission
444 to freshwater compared to emission to seawater for those three metals, clearly indicating the importance of including an
445 estuary in the fate model for those metals. In LCA studies where emission location is unknown, we recommend to use
446 estuary discharge rate weighted CFs. Compared with USES-LCA 2.0's marine ecotoxicity CFs, the new site-generic
447 marine ecotoxicity CF for emission to seawater is ca. 1-4 orders of magnitude lower. The new site-generic marine
448 ecotoxicity CF for emission to freshwater is within two orders of magnitude difference compared with USES-LCA 2.0
449 values. However, the comparative contribution share analysis shows little similarity for the rankings of most toxic metals
450 between USES-LCA and the new method. While Ni, Cu and Co are the major ecotoxicity contributors in USES-LCA,

451 they become less important in the new method. We further developed marine and freshwater ecotoxicity endpoint CFs,
452 to compare damages from metal emissions on freshwater and marine ecosystems respectively. For the same amount of
453 metal, emissions to freshwater result in 1-3 orders of magnitude higher endpoint impact scores than emissions to seawater
454 for all investigated metals except Pb. For metal emissions to freshwater, the ecotoxicity impact on marine species has a
455 minor contribution to the total ecotoxicity damage score, except for Pb. However, this study only covers eight metals for
456 which a marine ecotoxicity CF has been developed. It is recommended to consider more metals when their marine CFs
457 become available, especially those that may behave similarly to Pb (e.g. Sn and Ag). Largely due to higher species density,
458 the damage scores are higher for freshwater ecosystems than for marine ecosystems.

459 This is the first attempt in LCA to include an estuary in the multi-compartment fate model. We took a simplified
460 approach with a generic fate model and developed only one set of removal fractions to simulate metal fate in estuaries. It
461 is recommended to further look into different types of estuaries and investigate the relevance of deriving different sets of
462 removal fractions to better represent the removal process in each type of estuary, which was essentially treated as a filter
463 in this study. We did not develop any CF representing ecotoxicity of the metals to organisms in the estuary, considering
464 the relatively short water residence time there and the lack of ecotoxicity effect data representing the species and the
465 fluctuating conditions in the estuary. However, considering the importance of estuaries for biodiversity and economy in
466 many regions, it is recommended to further look into the relevance of including the impacts of chemicals in the estuary
467 in the characterization modelling of aquatic ecotoxicity.

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- 570

571 **Figures and tables**

572 Table 1 The calculated fraction of metal removed in the estuary and freshwater, and ranges for estuarine removal fraction
 573 in other studies

Metals	Removal in estuary	Removal in freshwater	Removal in estuary in other studies
Cd	0.3%	55.6%	<10% (Audry et al. 2007)
Co	0.2%	42.3%	
Cr	18.8%	92.5%	
Cu	20.6%	91.8%	10%-28% (Audry et al. 2007) ~40% (Paulson et al. 1988)
Mn	0.7%	61.4%	<0% (Audry et al. 2007)*
Ni	1.3%	53.4%	
Pb	60.8%	91.6%	72% (Paulson et al. 1988) 80.5% (Monbet 2006)
Zn	2.0%	61.2%	15%-26% (Jouanneau and Latouche 1982) ~40% (Paulson et al. 1988)

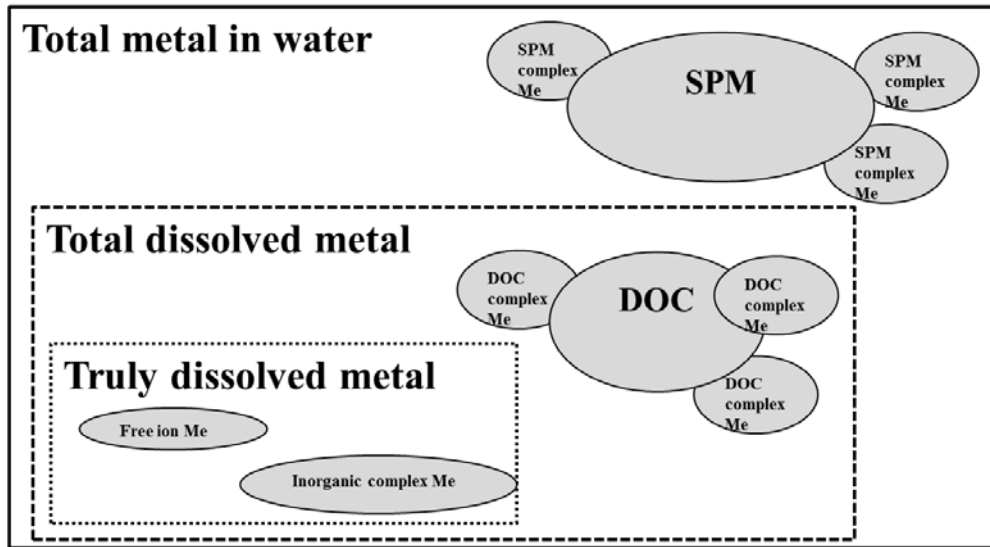
574 *When the value is below 0, it means the exported metal is more than input metal. The enrichment is most likely due to
 575 sediment input in addition to the low fraction of metal removed.

576 Table 2 Recommended site-generic CFs for marine ecotoxicity of metals emissions to freshwater and seawater,
 577 accompanied by the geometric standard deviation representing the spatially determined variation.

Metal	Marine CFs for metal emission to freshwater	Geometric Standard deviation	Marine CFs for metal emission to seawater	Geometric Standard deviation
Cd	6.28E+05	4.96	1.42E+06	4.97
Co	2.66E+05	4.33	4.61E+05	4.33
Cr	1.54E+01	8.90	2.51E+02	8.90
Cu	1.08E+04	8.29	1.65E+05	8.29
Mn	7.20E+04	5.50	1.88E+05	5.51
Ni	1.66E+05	5.79	3.62E+05	5.79
Pb	2.96E+04	6.17	8.96E+05	6.17
Zn	6.02E+05	5.92	1.58E+06	5.92

578

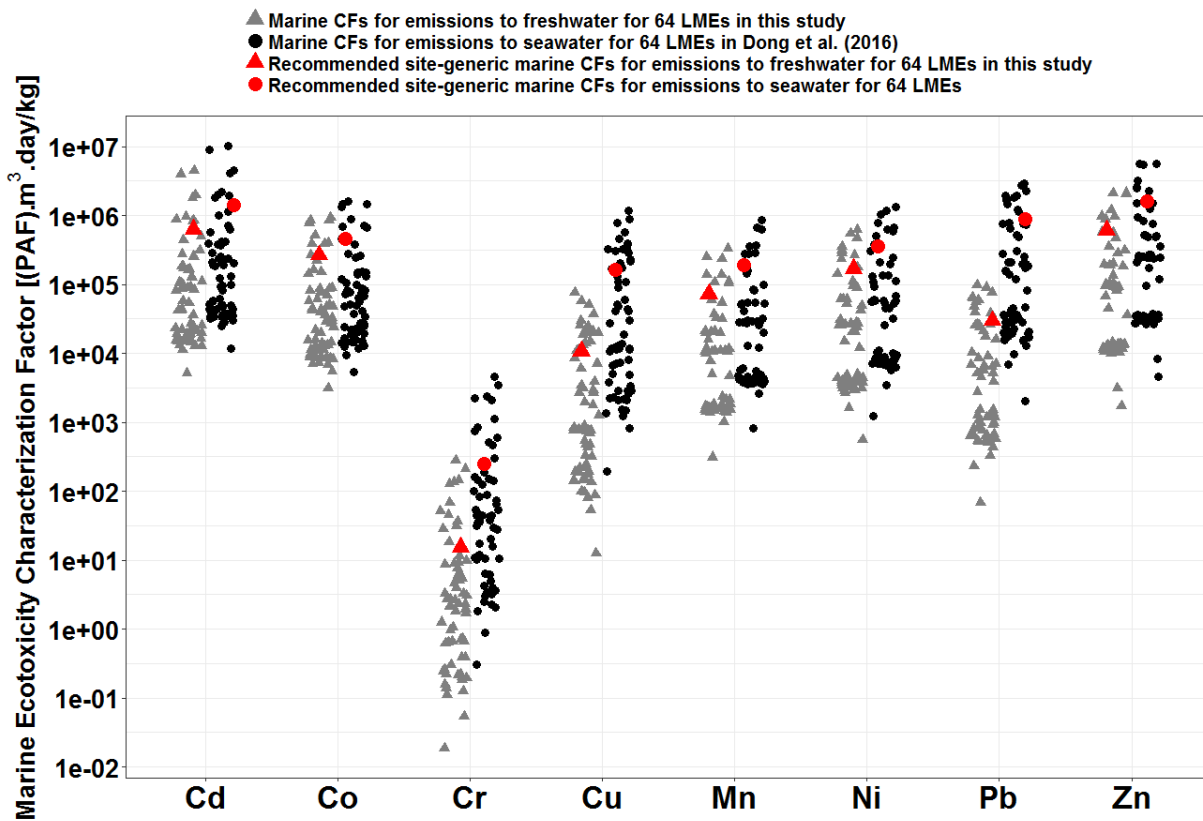
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580

581 **Figure 1.** Metal speciation illustration in water. “Me” represents metal. SPM is suspended particle and DOC is
 582 Dissolved Organic Carbon.

583

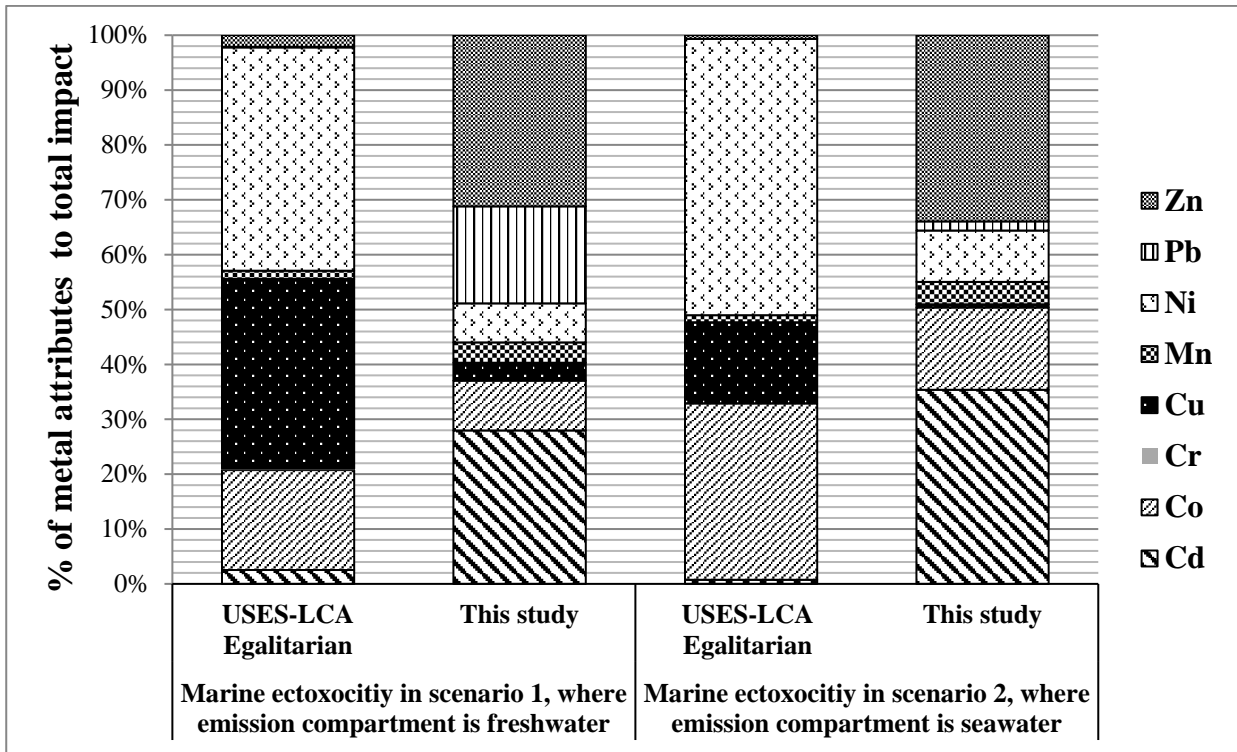


584

585 **Figure 2.** Recommended site-generic marine ecotoxicity Characterization Factors (CFs) and site-dependent marine
 586 ecotoxicity Characterization Factors (CFs) in 64 LMEs for eight metals emitted to freshwater. Marine
 587 ecotoxicity CFs for the same metals emitted to seawater (Dong et al. 2016) also shown for comparison.

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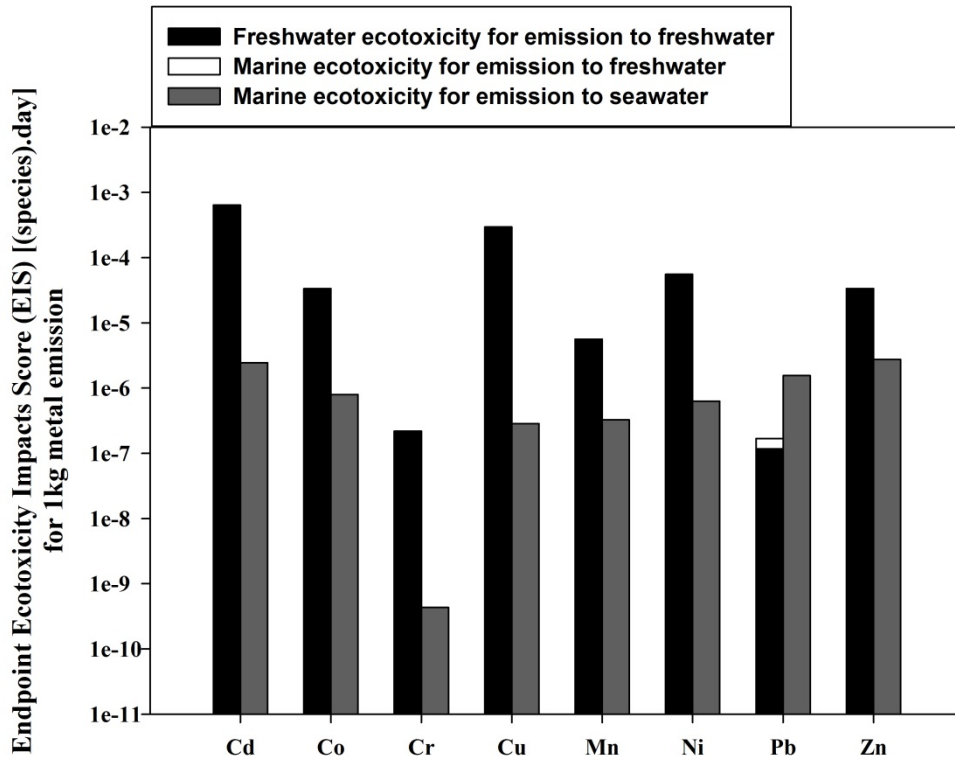
590

591 **Figure 3.** Contribution analysis based on emission inventory with one kg of each metal (Cd, Co, Cr, Cu, Mn, Ni, Pb and

592 Zn) emitted to water. In scenario 1, all metals are emitted to freshwater. In scenario 2, all metals are emitted

593 to coastal seawater. The share (%) of each metal in the total marine ectoxicity impact is shown.

594



595

596 **Figure 4.** Site-generic ecotoxicity endpoint impact scores for emission of one kg metal into freshwater and marine
 597 water respectively