Metal toxicity characterization factors for marine ecosystems: considering the importance of the estuary for freshwater emissions

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1   **Metal toxicity Characterization Factors for marine ecosystems – considering the**

2   **importance of the estuary for freshwater emissions**

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9   **Abstract:**

10   *Purpose* The study develops site-dependent Characterization Factors (CFs) for marine ecotoxicity of metals emitted to

11   freshwater, taking their passage of the estuary into account. To serve LCA studies where emission location is often

12   unknown, site-generic marine CFs were developed for metal emissions to freshwater and coastal seawater respectively.

13   The new CFs were applied to calculate endpoint impact scores for the same amount of metal emission to each

14   compartment, to compare the relative ecotoxicity damages in freshwater and marine ecosystems in LCA.

15   *Methods* Site-dependent marine CFs for emission to freshwater were calculated for 64 comparatively independent seas

16   (Large Marine Ecosystems, LMEs). The site-dependent CF was calculated as the product of Fate Factor (FF),

17   Bioavailability Factor (BF) and Effect Factor (EF). USEtox modified with site-dependent parameters was extended with

18   an estuary removal process to calculate FF. BF and EF were taken from Dong et al. (2016). Site-generic marine CFs were

19   derived from site-dependent marine CFs. Different averaging principles were tested, and the approach representing

20   estuary discharge rate was identified as the best one. Endpoint marine and freshwater metals CFs were developed to

21   calculate endpoint ecotoxicity impact scores.

22   *Results and discussion* Marine ecotoxicity CFs are 1.5 orders of magnitude lower for emission to freshwater than for

23   emission to seawater for Cr, Cu and Pb, due to notable removal fractions both in freshwater and estuary. For the other

24   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

1. Introduction

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

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

Another important missing element in the characterization of aquatic ecotoxicity for metals is the modelling of their behaviour in estuaries, the transition zone between freshwater and seawater. In two of the most widely used 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·m^3/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 Factor

99 (EF_j) as shown in equation 1.

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

101 This equation can be applied for different compartments. In this study, compartment i and j represent freshwater and

102 coastal seawater respectively. FF_{ij} is proportional to the residence time of total metal in the receiving coastal seawater

103 compartment including the transfer efficiency of chemical from the freshwater compartment. EF_j represents the

104 ecotoxicity effects caused by the truly dissolved metal in coastal seawater. FF_{ij} (referring to total metal) and EF_j (referring

105 to truly dissolved metal) are linked through BF_j, which represents the fraction of truly dissolved metal within the total

106 metal. Using equation 1, we calculated marine ecotoxicity CFs for each metal for an emission to freshwater with

107 subsequent transfer to coastal seawater.

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 CF

109 for emission to seawater (Dong et al. 2016), since speciation and ecotoxic effects in coastal seawater are not affected by

110 the emission compartment. There BF_j were calculated using the chemical speciation model WHAM VII (Tipping et al.

111 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 modelling

124 chemical mass balance at steady state in different environmental compartments, considering removal, immobilisation,

125 and transfer processes between compartments. We calculated the fate of metal emitted to the continental freshwater

126 compartment, passing through estuary and received in the continental seawater compartment (i.e. costal seawater

127 compartment). It is the product of two factors. One factor is the metal residence time in the coastal seawater compartment,

128 which is the same as the FF calculated in Dong et al. (2016). It is determined by metal inflow to the coastal seawater

129 compartment from other compartments (e.g. freshwater and air), metal removal in the coastal seawater compartment and

130 metal outflow from the coastal seawater compartment to other compartments (e.g. ocean and air). The other factor is the

131 fraction of metal that is transferred from freshwater to the coastal seawater compartment after emission to freshwater.

132 This fraction is calculated from the metal loss rate constant in freshwater and the metal transfer rate constant from

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

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

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

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. Kp_{SS} (L/kg) (the ratio of metal concentration between *SPM bond* 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 Kp_{SS} 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 Laurence 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

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

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

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

Where:

SPM_n is the concentration of SPM at salinity value Sal_n,

b is the initial SPM concentration at the freshwater end,

a is a constant.

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

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

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

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

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

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

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

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

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

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

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   weighted site-dependent CF = site-dependent CF * corresponding weighting factor   (Eq. 11)

263   site-generic CF=$\sum$ weighted site-dependent CF   (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_{fw-sw}) to be calculated in a simple way from the marine ecotoxicity

282   CF for emission to seawater (CF_{sw-sw}), using the removal rate constant in freshwater (R_{fw}) and removal rate constant in

283   the estuary (R_{et}) as shown in equation 13.

284      $$CF_{fw-sw} = CF_{sw-sw} * (1-R_{et}) * (1-R_{fw})$$ (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 Kp_{SS} (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).m^3.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.

3.5 Metal ecotoxicity in the aquatic system

The newly developed site-generic marine and freshwater ecotoxicity CFs, allow us to compare the severity of the ecotoxic impacts that are caused by emitting metals to different aquatic compartments. The CFs that we developed in the previous sections are known as midpoint CFs, expressed as the potentially affected fraction of species integrated over volume and time [PAF in m^3.day]. For a comparison of impacts in freshwater and marine ecosystems it is important to note that the species density (number of species per volume compartment) is different in freshwater and seawater. Therefore, the midpoint marine CFs cannot be compared directly with the midpoint freshwater CFs from Dong et al. (2014), since the fractions expressed by the potentially affected fraction of species (PAF) relate to different total species numbers. To make the ecotoxicity scores comparable, marine and freshwater endpoint CFs were developed. Endpoint CFs build on midpoint CFs but also consider the severity of the midpoint impacts by modelling the damages on the exposed ecosystem, represented by the resulting potentially *disappeared* number of species. Therefore, PAF in the midpoint score needs to be converted to the potentially disappeared fraction (PDF) to arrive at the endpoint score. Thus, in addition to species density, a PAF to PDF ratio is applied on the midpoint CF to derive the endpoint CF [(species).day/kg], as shown in equation 14.

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

Equation 12 can be used to calculate endpoint ecotoxicity CFs in any environmental compartment. In this study, we took the PAF to PDF ratio (dimensionless) from IMPACT 2002+ (Jolliet et al. 2003). Marine and freshwater species densities [species/m^3] were taken from ReCiPe (Goedkoop et al. 2013). To calculate the site-generic marine ecotoxicity endpoint CF, we used the site-generic marine ecotoxicity midpoint CF [(PAF).m^3.day/kg] from this study. Site-generic freshwater ecotoxicity CFs from Dong et al. (2014) were used to calculate freshwater ecotoxicity endpoint CFs. The results are presented in figure S1 in SI.

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

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

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

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

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.

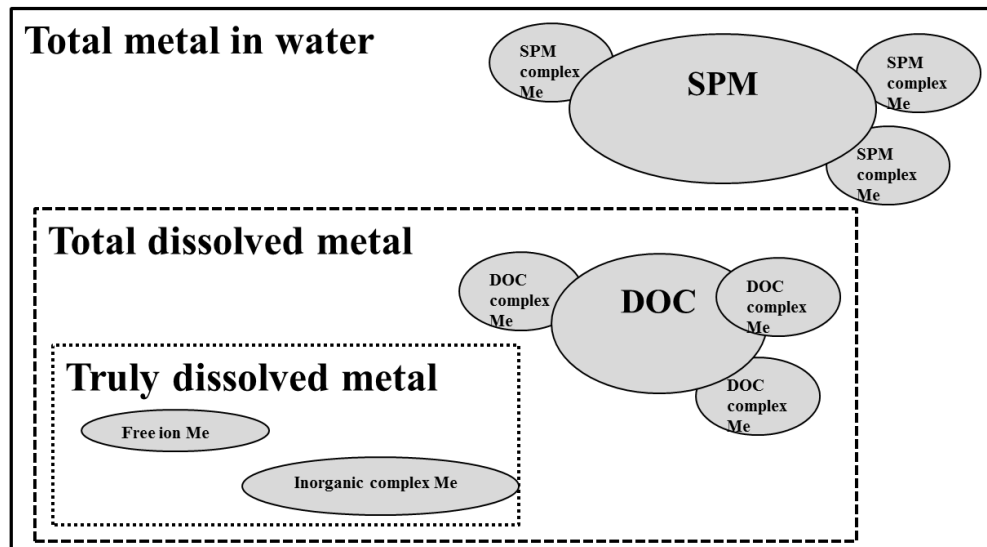| Metal	Marine CFs for metal emission to freshwater	Geometric Standard deviation	Marine CFs for metal emission to seawater	Geometric Standard deviation
Cd	6.28E+05	4.96	1.42E+06	4.97
Co	2.66E+05	4.33	4.61E+05	4.33
Cr	1.54E+01	8.90	2.51E+02	8.90
Cu	1.08E+04	8.29	1.65E+05	8.29
Mn	7.20E+04	5.50	1.88E+05	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

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Figure 1. Metal speciation illustration in water. "Me" represents metal. SPM is suspended particle and DOC is
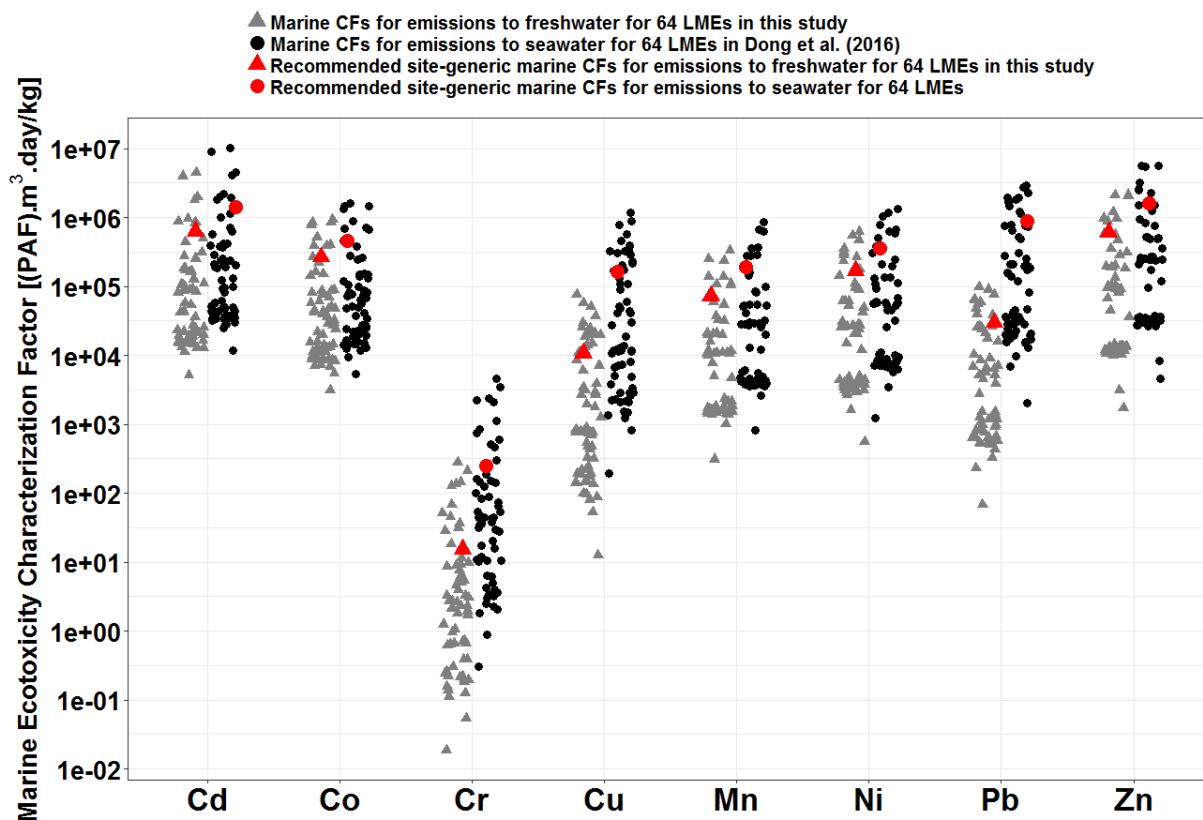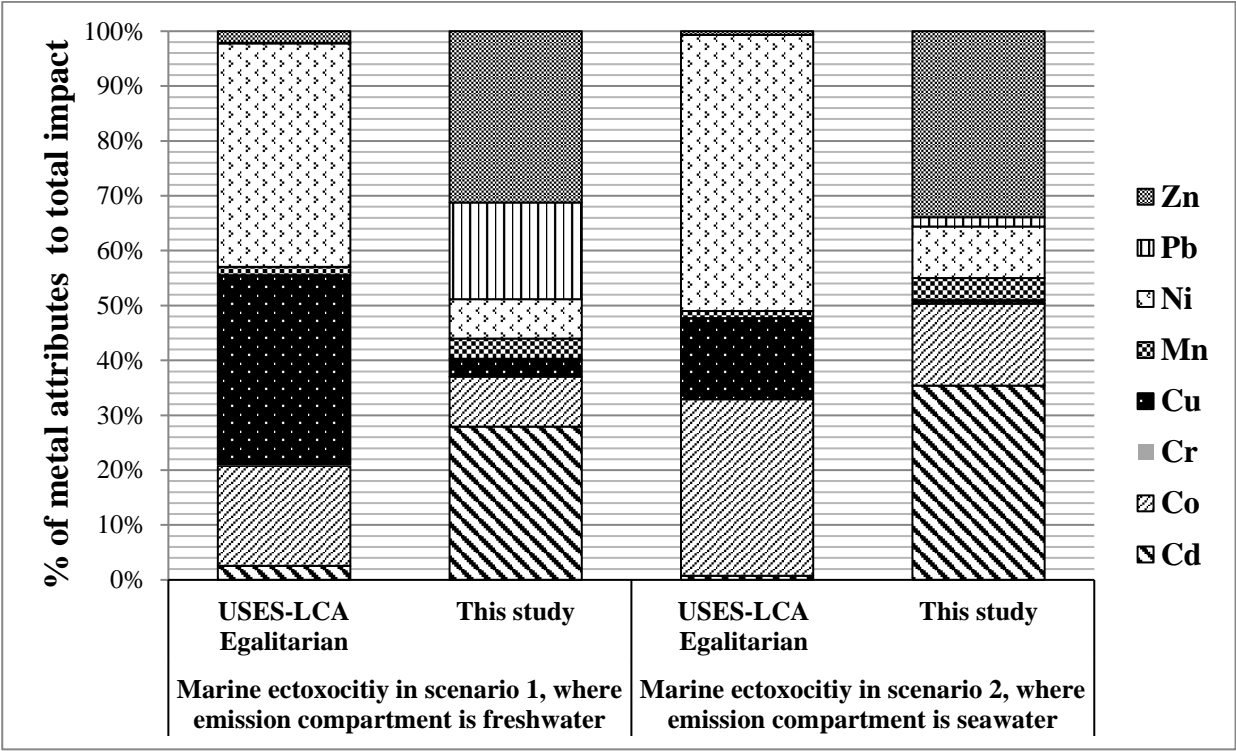Dissolved Organic Carbon.

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Figure 2. Recommended site-generic marine ecotoxicity Characterization Factors (CFs) and site-dependent marine

ecotoxicity Characterization Factors (CFs) in 64 LMEs for eight metals emitted to freshwater. Marine

ecotoxicity CFs for the same metals emitted to seawater (Dong et al. 2016) also shown for comparison.

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

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

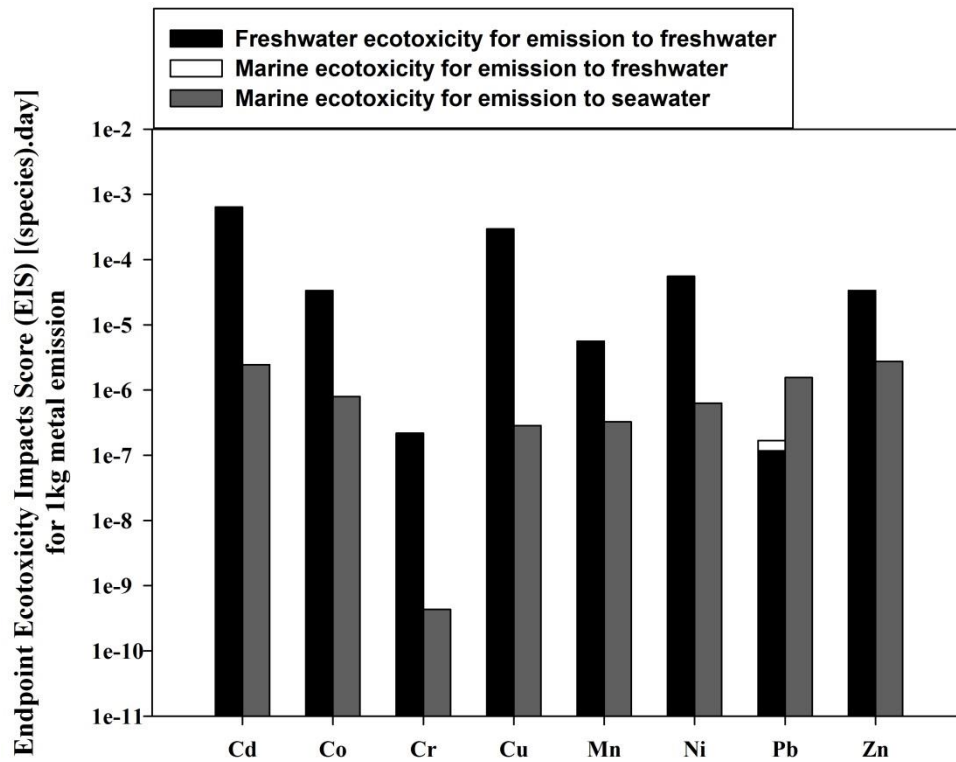to coastal seawater. The share (%) of each metal in the total marine ecotoxicity impact is shown.

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

597   water respectively