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Assessment of Metal Toxicity in Marine Ecosystems: Comparative Toxicity Potentials for Nine Cationic Metals in Coastal Seawater

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4 # Assessment of metal toxicity in marine ecosystems -

5 # Comparative Toxicity Potentials for nine cationic

6 # metals in coastal seawater

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13 ABSTRACT:

14 This study is a first attempt to develop globally applicable and spatially differentiated marine

15 Comparative Toxicity Potentials (CTPs) or ecotoxicity characterization factors for metals in coastal

16 seawater for use in Life Cycle Assessment. The toxicity potentials are based exclusively on marine

17 ecotoxicity data and take account of metal speciation and bioavailability. CTPs were developed for

18 nine cationic metals (Cd, Cr(III), Co, Cu(II), Fe(III), Mn, Ni, Pb and Zn) in 64 Large Marine

19 Ecosystems (LMEs) covering all coastal waters in the world. The results showed that the CTP of a

20 specific metal varies 3-4 orders of magnitude across LMEs, largely due to different seawater

21 residence time. Therefore the highest toxicity potential for metals was found in the LMEs with the

22 longest seawater residence times. Across metals, the highest CTPs were observed for Cd, Pb and

23 Zn. At the concentration levels occurring in coastal seawaters, Fe acts not as a toxic agent but an

24 essential nutrient and thus has CTPs of zero.

25 **1   Introduction**

26 Life Cycle Assessment (LCA) "quantifies all relevant emissions and resources consumed"[1]

27 associated with a good or service in a Life Cycle Inventory (LCI) and assesses "the related

28 environment and health impacts and resource depletion issues"[1] by Life Cycle Impact Assessment

29 (LCIA). LCA has been broadly used to support environmentally informed decisions in policy-

30 making, product development and procurement, and consumer choices[2]. It is a valuable screening

31 tool to facilitate identifying environmental hotspots[2]. The uncertainties associated with LCA results

32 can be high due to data and simplified modelling[2]. This can be partially compensated by enhancing

33 regional detailed modelling.

34 Metals are often ranked at the top of toxicity concerns in Life Cycle Assessment (LCA)[3]. Large

35 quantities of metals are released from anthropogenic resources to the natural environment (up to

36 3×10^5 tons/year for selected metals, e.g. Mn)[4]. Waterborne emissions contribute 50-80%, and

37 originate mainly in industrial sectors such as iron or steel production, thermal power stations,

38 mineral oil and gas refineries etc.[5] Waterborne metal emissions typically reach freshwater first and

39 move towards seawater through fluvial pathways, thus potentially causing ecotoxicity in both

40 freshwater and marine compartments[6]. Hitherto, metal toxicity in the aquatic environment has been

41 modelled in LCIA using models developed to simulate the behaviour of organic chemicals with

42 poor representation of the speciation behaviour of metals and bioavailability (e.g. USES-LCA 2.0[7]

43 used in ReCiPe, IMPACT 2002+[8]). Following the principles laid out in the Apeldoorn Declaration[9]

44 and the Clearwater Consensus[10], Gandhi et al.[11,12] developed a new method to calculate the toxicity

45 potential of six metals in freshwater ecosystems (expressed as a Comparative Toxicity Potential

46 (CTP), also known as a Characterization Factor in LCIA), including fate, bioavailability and effect

47 of metals. Their CTP was calculated for a number of archetypical freshwater chemistries. Dong et

48 al.[13] further adapted the method, expanding its scope of metals and calculated freshwater CTP for

49 14 metals. The results showed that for some metals (e.g. Al, Be, Cr(III), Cu and Fe(III)), freshwater

50 CTP was highly dependent on the speciation of metal in a certain water chemistry, thus varying by

51 2-6 orders of magnitude in different water archetypes. This reveals the importance of 1) including

52 metal speciation and bioavailability in the modelling and 2) identifying spatially determined and

53 differentiated water chemistries.

54   In comparison, marine CTP of metals has received less attention. Following the Apeldoorn

55 Declaration[9], "the oceans are deficient in essential metals, and the CTP for essential metals should

56 be set at zero for toxicity in the oceans."[9] In contrast, coastal seawater receives higher

57 anthropogenic metal emissions not just through fluvial pathways[6], but also from airborne emission

58 and metals resuspended from the seabed[14], leading to the observable metal concentrations in the

59 coastal zones, and even reach the mmol/l level close to wastewater discharges[15]. This can lead to

60 exceeding the levels where metal becomes toxic to organisms.

61   Not all metal forms are toxic. Only bioavailable forms, often within the truly dissolved forms, can

62 access a sensitive receptor, the biotic-ligand, and become hazardous[16,17]. In addition to metal

63 availability, also its residence time in the coastal seawater is essential for the exposure and hence its

64 CTP. For most metals, a substantial removal happens after entering coastal zone, where complex

65 binding to Suspended Particulate Matter (SPM) followed by removal through sedimentation is

3

66 increased[6]. The fate of a metal in coastal seawater is thus strongly influenced by its tendency to

67 adsorb to SPM, its solubility in seawater and its complexation affinity with particulate and

68 dissolved organic matter[18].

69   Until now metal marine CTP in the previous LCIA models has either not been calculated (e.g.

70 USEtox[19], IMPACT 2002+[8]) or it has been derived neglecting speciation and bioavailability, and

71 using freshwater toxicity data (e.g. USES-LCA[7]), with a questionable representativeness for

72 saltwater organisms[20]. Moreover, as demonstrated by Gandhi and co-workers, metal freshwater

73 CTP is highly sensitive to water chemistry[21]. While water chemistry parameters such as pH,

74 Dissolved Organic Carbon (DOC), SPM and salinity affect the speciation of metals, different

75 seawater residence times (SRT) in different coastal zones also play a large role when determining

76 the fate of metal in coastal compartment[22,23]. So far, no study has given a coherent treatment of the

77 global spatial variability of metal marine CTP, considering speciation and applying toxicity data for

78 marine organisms. As a consequence, toxic impacts on the marine ecosystem were either not at all

79 considered in LCA studies or they were assessed with methods of limited reliability based on

80 questionable assumptions. These shortcomings and the strives for a coherent consideration of

81 marine biodiversity in LCA studies set the objectives of this study.

82   Aiming for consistency with the methodology developed for characterizing metal toxicity in

83 freshwater[11,13] and applying marine ecotoxicity data availability in ECOTOX database[24], the

84 objective of this paper is to develop new, spatially differentiated and globally applicable marine

85 CTPs for Cadmium (Cd), Cobalt (Co), Chromium(III) (Cr), Copper(II) (Cu), Iron(III) (Fe),

86 Manganese(II) (Mn), Nickel (Ni), Lead (Pb) and Zinc (Zn), taking metal speciation and

87 bioavailability into account, and investigating their variation over 64 Large Marine Ecosystems

88 (LMEs) for emissions received in coastal seawater all over the world.

89 **2   Methods**

90 **2.1   General framework**

91   For metals, CTP_i for ecosystems is expressed as the Potentially Affected Fraction of species

92 integrated over time and space [(PAF)·day·m^3/kg$_{emitted}$], representing the ecotoxicity potential for

93 the *total* metal in compartment i. It is calculated as the product of three factors: Fate Factor (FF),

94 Bioavailability Factor (BF) and Effect Factor (EF) as presented in Eq. 1[11].

95 $$CTP_i = FF_i \cdot BF_i \cdot EF_i \qquad \text{(Eq.1)}$$

96   Where:

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

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

102 EF_i: Effect Factor [(PAF)·m^3/kg], representing the fraction of species potentially affected
103   by the toxicity of the *truly dissolved* metal in compartment *i*.

104   This framework can be used for any single environmental compartment (e.g. freshwater, soil).

105 When considering a multi-compartment system, the terms of eq.1 become matrices, which besides

106 residence times also include inter-compartmental transfers[25]. In this paper we focus on metals

107 received from adjacent environmental compartments or directly emitted into the coastal seawater

108 compartment. Therefore, FF represents the persistence of the metal in coastal seawater, while BF

109 and EF represent bioavailability and metal ecotoxicity effects in coastal seawater respectively. FF is

110 modelled for the total metal rather than dissolved metal, due to the fact that this is the entity which

111 is reported in LCI and that the metal in the water may re-partition between particulate and dissolved

112 forms during transportation. Note that the partitioning pattern can vary over time and with local

113 environmental conditions. This can have an impact on the FF of metals. For the purpose of LCA

114 temporal variations need to be averaged over a year to be compatible to the information in the life

115 cycle inventory.

2.2 Spatial differentiation of environmental conditions and parameters

117 To explore the spatial variability of CTP in coastal seawater, we worked with the LMEs

118 following Cosme et al.[26]. The coastal compartment that is represented by a LME covers the marine

119 area from the coastal line to the seaward boundary of the continental shelf and includes any

120 estuaries. Thus defined, the coastal compartment with its adjacency to the continents receives

121 emissions related to human activity through the influx of continental freshwater or direct discharges

122 to the sea. 80%-90% of marine net primary production occurs in this compartment, which thus

123 comprises the majority of species and biomass that potentially may be affected by metal

124 emissions[27]. The global coastal seawater zone was divided into 64 LMEs according to "distinct

125 bathymetry (seabed topography), hydrography, productivity and trophically dependent

126 populations"[28], where each LME represents a relatively independent coastal zone. Data on SRT,

127 seawater surface area, temperature and water chemistry were collected for each LME from literature

128 (Table S1 in Supporting Information (SI)). The values for these parameters show large variations

129 across the 64 LMEs (Figure S1 in SI). SRT varies from 11 days-90 years, surface area from

130 1.5×10^5-5.7×10^6 km^2, estuary discharge rate (water flow rate from freshwater to coastal seawater)

131 from 0-1.3×10^5 m^3/s, temperature from -1°C-29°C, pH from 7.75-8.35, DOC from 0.6-6.5 mg/l,

132 Particulate Organic Carbon (POC) from 31-802 ug/l, SPM from 0.2-2.9 mg/l and salinity from 6.2-

133 40.3‰. For speciation modelling, salinity was translated into concentrations of the major ions (Na$^+$,

134 Mg^{2+}, K$^+$, Ca^{2+}, SO$_4^{2-}$, and Cl$^-$) by scaling from a standard salinity (35 ‰) and its corresponding

135 major ion concentrations (Table S2 in SI), assuming a fixed relationship between the major ion

136 concentrations at different salinities[29]. For each LME, the relevant environmental parameter and

137 water chemistry values were applied to derive a CTP value for each metal.

138   Note that also within one LME, environmental parameters such as pH, salinity, DOC, POC, and

139 SPM show both spatial and temporal variation. The annual variation ranges are shown for pH,

140 salinity and POC within each LME in Figure S2 in SI. Fe, Mn and Al oxides have been shown to be

141 strong adsorbents for metal ions[30–32], because of their large surface area. Due to lack of spatially

142 differentiated concentration data for these oxides, fixed concentrations of 0.15, 0.02 and 0.4 µg/L

143 for Fe, Mn, and Al oxides respectively had to be assumed across all LMEs[33].

144 **2.3   Model and parameter selection**

145 **2.3.1   Fate model**

146   With the intended use in LCA in mind, the multimedia fate model embedded in USEtox[19] was

147 chosen for this study. USEtox is an LCIA model for assessing ecotoxicity and human toxicity

148 impacts. It has been developed in a scientific consensus process involving LCIA and chemical fate

149 modelling experts. It is the recommended characterization model for toxicity impacts in LCA[34]. In

150 USEtox, the fate is calculated based on a steady-state mass balance. USEtox determines metal FF in

151 the coastal seawater compartment by modelling of metal inflow, metal outflow and metal removal

152 (including sedimentation and sediment burial/re-suspension). Metal inflow and outflow largely

153 depend on the retention time of the coastal seawater. Thus the default SRT of seawater on

154 continental scale in USEtox was replaced by the SRT representative for each LME. To be

155 consistent, also the default surface area of continental seawater and the water flow rate from

156 continental freshwater to continental seawater (estuary discharge rate) were replaced by the

157 corresponding LME-specific data. Water flow from ocean to coastal seawater is then automatically

158 calculated from parameters mentioned above. Details of LME-specific data and calculations are

159 available in Table S1 in SI. Metal removal is simulated by metal sedimentation and diffusion of

160   metal from seawater to sediment. The former process is modelled by metal complexation with

161   SPM, followed by SPM sedimentation. The removal largely depends on the fraction of metal

162   adsorbing to SPM, the concentration of SPM and the SPM sedimentation velocity. Metal diffusion

163   into sediment is determined by the dissolved fraction of metal and the metal's mass transfer

164   coefficient between sediment and water. The metal fraction adsorbed to SPM can be calculated

165   from a spatially differentiated adsorption coefficient Kp_{SS} (L/kg; the ratio of metal concentration

166   between *SPM bound* metal and *truly dissolved* metal). The truly dissolved fraction of metals is

167   calculated using both Kp_{SS} and K_{DOC} (L/kg; the ratio of metal concentration between *DOC complex*

168   *bound* metal and *truly dissolved* metal). All parameters mentioned above vary between different

169   LMEs. Thus Kp_{SS} and K_{DOC} were recalculated in WHAM VII[35] for each metal in each LME

170   respectively, to replace the default values in USEtox. WHAM[35] is a metal speciation modelling

171   software. Based on the input of target metal concentration and relevant water chemistry, it can

172   deliver the concentration of target metal in a specific form. In WHAM's calculation of Kp_{SS} and

173   K_{DOC} values, it is assumed that metals are in equilibrium with the discrete sites of DOC and the

174   organic fraction of SPM. Here target metals have to compete with other cations (e.g. Ca^{2+}, Mg^{2+}, K^+

175   and Na^+) to form complexes with SPM or DOC. The ratio between the concentration of metal that is

176   truly dissolved in water and the concentration of metal forming complexes with SPM or DOC were

177   calculated for each LME and each metal as the specific Kp_{SS} and K_{DOC} value. Default DOC and

178   SPM concentration in USEtox were also replaced by the corresponding specific parameter values

179   for each LME. Other landscape parameters were kept unchanged. All parameters used in FF

180   calculation are listed in Table S3 in SI. There were no substance parameter values for Mn and Fe in

181   default USEtox inorganic database. They thus had to be collected from literatures. The retrieved

182   values are presented together with substance parameter values for the other metals in Table S4 in

183   SI.

2.3.2 Bioavailability model

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

WHAM VII[35] was used to calculate metal speciation in seawater. While originally developed for freshwater, its applicability for prediction of metal free ion activity in seawater has been validated[36]. Furthermore it contains data and has a good reputation for simulating metal binding to DOC, POC, Fe oxide and Mn oxide. These two criteria favoured the choice of WHAM VII over other speciation models (e.g. Visual Minteq[37], MINEQL+[38], PHREEQC[39]).

2.3.3 Ecotoxicity model

Currently there are two main ecotoxicity models to explain how cationic metals cause toxicity in organisms. The Free Ion Activity Model (FIAM) assumes that the toxic compound is free metal ion represented by its activity. The Biotic Ligand Model (BLM) further includes the competition between free metal ion and other cations (e.g. Ca^{2+}, H^+) for binding to biotic ligand – the receptor in the target organism where the metal binds to exert its uptake and/or toxicity. Due to lack of BLMs for metals in seawater, FIAM was chosen in this study. It has been validated to assess metal toxicity to marine organisms in saltwater[40,41]. As stated in Clearwater Consensus[10], we calculated EF based on truly dissolved metal, assuming that free ion is a fraction of truly dissolved metal and is responsible for the toxicity. In risk assessment, Predicted No Effect Concentration (PNEC) is typically used as effect indicator to protect the sensitive species of the ecosystem. Compared to

208   PNEC, the geometric mean HC_{50} calculated from EC_{50}, representing the Potentially Affected

209   Fraction (PAF) of species exposed above chronic EC_{50} values, is more robust but less

210   conservative[42]. The purpose of LCA is to compare alternatives, where robustness is highly required.

211   Therefore HC_{50} values calculated from EC_{50} are normally applied in LCA. It can use all the

212   available toxicity data for a metal and is a measure associated with less uncertainty than the

213   PNEC[43,44]. Detailed descriptions of calculation methods for the PAF method and HC_{50} can be found

214   in Larsen et al.[44,45]. EFs were calculated exclusively from data on chronic marine EC_{50} from

215   literature. The availability of marine ecotoxicity data in the ECOTOX database[24] allowed us to

216   apply our model to nine cationic metals, including Cd, Co, Cr, Cu, Fe(III), Mn, Ni, Pb, and Zn

217   (Table S5 in SI). For metals where chronic marine ecotoxicity data were insufficient, extrapolation

218   from acute marine ecotoxicity data was performed applying an Acute-to-Chronic Ratio (ACR)

219   derived from the available toxicity data as described in Table S6 in SI. Total metal marine EC_{50}

220   reported in literature were translated into free ion EC_{50} using WHAM VII[35], taking into account

221   water chemistry of the test medium in which the reported EC_{50} was determined. This conversion

222   reduced the standard deviation of the EC_{50} of each metal by at least an order of magnitude (Table

223   S5), which also justifies the use of FIAM in EF calculation.

224   The calculation of EF was based on the recommended principles for LCA[43,45,46]. For each metal at

225   each trophic level (i.e. primary producers, primary and secondary consumers), a free ion activity

226    $HC_{50\text{-trophic}}$ was calculated as the geometric mean of the corresponding free ion EC_{50} for all species

227   with available data. The geometric mean of the resulting three $HC_{50\text{-trophic}}$ represents the free ion

228   activity HC_{50} in saltwater for that specific metal. Then, for each combination of metal and LME, a

229   truly dissolved HC_{50} was calculated using WHAM VII, based on the free ion activity HC_{50} and

230   corresponding LME water chemistry. Finally, EF was calculated as 0.5/truly dissolved HC_{50}[43].

3   Results and Discussion

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

3.1   Fate Factors

Cr, Cu and Fe have the highest log K_{DOC} and log Kp_{SS} among all metals, indicating their strong tendency of complexation with Organic Matter (OM, represented by DOC and the organic fraction of SPM (POC)) in seawater (Figure S3 in SI). This is in accordance with previous findings that Cr, Cu and Fe have high affinity for OM[47]. Compared with empirical values, Kp_{SS} in this study were generally within an order of magnitude (Table 1).

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

$$R^Z + M^z = RM^{Z+z} \qquad \text{(Eq. 2)}$$
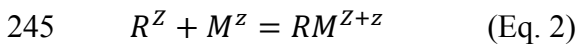
$$K_M = \frac{[RM^{Z+z}]}{[R^Z][M^z]} \qquad \text{(Eq.3)}$$

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

253 influenced by OM concentrations and salinity, but also by other parameters (e.g. temperature and

254 pH values).

255 **Table 1:** Log Kp_{SS-D}[a] values (L/kg) in this study compared with empirical log Kp_{SS-D}[b] values (L/kg)

256 developed in other studies.

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

257   a. Log Kp_{SS} (L/kg) in this study represents the calculated partitioning coefficient between metal

258   bound to SPM and truly dissolved metal. Log Kp_{SS-D} (L/kg) in other studies represents the

259   partitioning coefficient between metal bound to SPM and total dissolved metal. To make the

260   values comparable, we calculated log Kp_{SS-D} values from the log Kp_{SS} that we determined in

261   this study.

262　　b. Log Kp_{SS-D} values in literature were presented as a function of other water chemistry

263　　　　parameters (e.g. salinity and SPM). Here we took approximate values derived from water

264　　　　chemistry similar to this study (e.g. SPM≈1mg/L, Salinity≈30‰-35‰, etc.)

265　　FF is largely influenced by log Kp_{SS} and log K_{DOC}. Metals with high log Kp_{SS} and log K_{DOC} (e.g.

266　　Cr, Cu and Fe) have an efficient removal, due to complex formation with OM followed by

267　　sedimentation. Therefore they have the lowest FF in all LMEs (Figure 1a). In contrast, FFs of Cd

268　　and Co are the highest across all metals, due to their low log Kp_{SS} and log K_{DOC}. For a given metal,

269　　FF increases with SRT across LMEs (Figure S4 in SI). For Cd, Co, Mn, Ni, Pb and Zn, FF and SRT

270　　are linearly correlated with SRT (R^2>0.97, p<0.001, Table S8 in SI). It means that FF variation

271　　mainly depends on SRT and metal removal processes play a minor role. For the metals with high

272　　log Kp_{SS} and log K_{DOC} (e.g. Cr, Cu and Fe), metal removal processes show a stronger influence on

273　　FF. Thus FFs for these three metals are less strongly correlated to SRT, but rather determined by the

274　　variation of SRT, log Kp_{SS}, and log K_{DOC} together. Note that the metals with lower Kp_{SS} and log

275　　K_{DOC} (Cd, Co, Mn, Ni and Zn) can have a FF that is higher than SRT in some LMEs. The reason is

276　　that for these combinations of metal and ecosystem, the removed fraction is insignificant compared

277　　to the total input. A non-negligible fraction of the metal flows out to the ocean, from where some of

278　　it eventually recirculates back to the coastal seawater system after reaching steady state that USEtox

279　　calculates. This results in a longer FF than the water that originally carried them out. The effect is

280　　most pronounced in the LMEs with short SRTs because the inflow from the ocean is more

281　　important compared to the volume and the freshwater input for these LMEs.

282
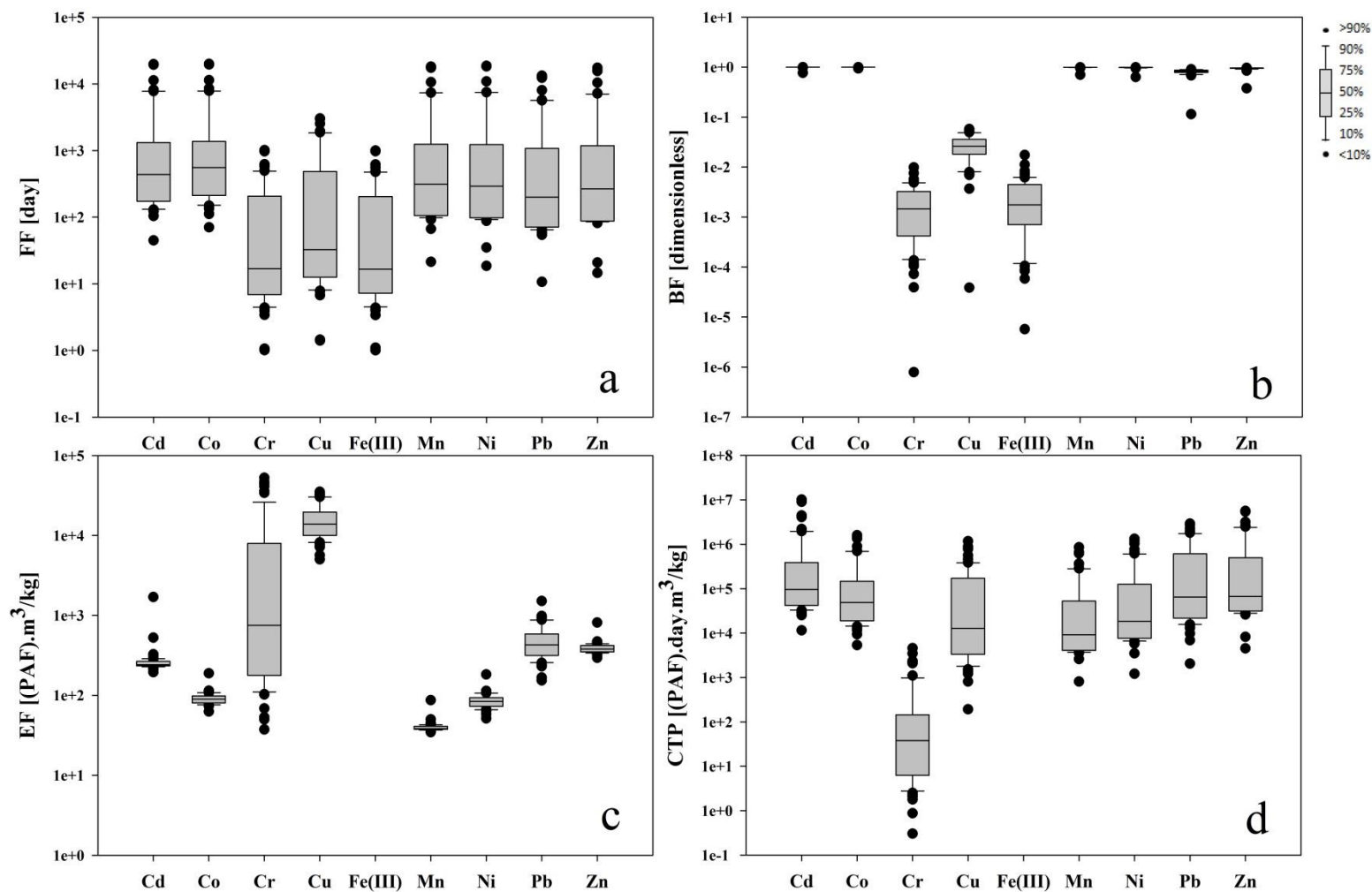
Figure 1. Variation of Fate Factor (FF, 1a), Bioavailability Factor (BF, 1b), Effect Factor (EF, 1c) and Comparative Toxicity Potential

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

14

285   FF varies 2-3 orders of magnitude across LMEs for each metal. Within one LME, FF variation

286   between different metals is within two orders of magnitude (Figure S5a in SI). It indicates that FF is

287   slightly more sensitive to environmental parameters than to properties of metal.

288   We compared our FF with data from other studies. The age of water constituent models the

289   residence time of seawater constituents in particle forms in seawater by simulating particle cycling[55]

290   and is similar to the concept of FF in this study. The constituent age of Baltic Seawater varies

291   between a few days and up to 40 years[56], which is similar to the range of metal FF in the Baltic Sea

292   (LME 23) in this study (3-21years). The constituent age of Kara Seawater is 1-2 years[57], which is

293   within the range of the metal FF in the Kara Sea (LME 58) in this study (1-4 years). The constituent

294   age of Norwegian Seawater and North Seawater combined together is 5-8 years[58], which is slightly

295   larger than the sum of metal FF ranges in the Norwegian Sea (LME 21) and the North Sea (LME

296   22) in this study (1-5 years).

297   **3.2   Bioavailability Factors**

298   Representing the fraction of total metal in coastal water that is truly dissolved, BF of Cd, Co, Mn,

299   Ni, Pb and Zn varies less than a factor of eight across LMEs (Figure 1b). For Cr, Cu and Fe the

300   variations in BF are much larger with 3-4 orders of magnitude, due to their large variations in log

301   K_{DOC} and log Kp_{SS} across LMEs (Figure 1b). For all metals, clear correlations were observed

302   between BF and log K_{DOC} or log Kp_{SS} (Figure S6). This implies that BF is largely determined by

303   metal binding to DOC (log K_{DOC}) and SPM (log Kp_{SS}). Co has the highest BF in all LMEs across

304   metals, due to its low log K_{DOC} and log Kp_{SS}. Similarly, Cr, Cu and Fe have the lowest BF across all

305   LMEs, due to their high log K_{DOC} and log Kp_{SS} values (Figure 1b and Figure S6 in SI).

3.3 Effect Factors

Some nutrient metals are essential for biota growth (e.g. Co, Cu, Fe, Mn, Ni and Zn)[59,60]. However, some of them may not reach the essential concentration to support biota growth under normal conditions in seawater, due to their low concentrations (at nmol level, Table S4 in SI). Under such circumstances, instead of being a toxic pollutant, a metal emission is more likely to facilitate biota growth. It is meaningless to talk about contribution to ecotoxicity under these circumstances. Therefore a true zero value of coastal CTP is given for those metals, in agreement with the recommendation in the Apeldoorn declaration[7]. For the metals covered in this study the essentiality condition appears to be relevant only for Fe, where the essential concentration range lies above its background concentration in coastal waters. This is caused by efficient removal of Fe in the estuary (ca. 90%) via precipitation, flocculation, and sedimentation[6]. Meanwhile, fluvial pathways contribute 75% of Fe inputs to seawater[18], which leads to a low concentration of dissolved Fe in seawater. Morel et al. [59] reviewed the essential concentration of metals in seawater and found that for the metals Co, Cu, Mn, Ni and Zn, the background concentration in seawater is sufficient to support biota growth. This is in accordance with other studies showing that iron is the only limiting nutrient metal for algae growth in seawater[61–63]. Therefore, a true zero was given to the EF of Fe in all LMEs, which were excluded from the discussions in the rest of this section.

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

EF is influenced by temperature, pH, salinity and OM through their impacts on the speciation (the fraction of free ion activity within truly dissolved metal). In general, with increasing pH, the metal may form hydroxide or carbonate complexes, decreasing the metal free ion concentration in solution, which leads to a lower EF[64]. Increases in salinity leads to a higher ionic strength, which

330   results in lower free ion activity for a given free ion concentration, and thus a lower EF[65]. When

331   OM decreases, a fraction of metal may be released into truly dissolved forms, which leads to a

332   higher truly dissolved HC_{50}, thus lower EF.

3.4   Comparative Toxicity Potentials

334   The comparative toxicity potentials are calculated as the product of FF, BF and EF following

335   Eq.1. Results are shown in Figure 1d. Due to its background concentration below essentiality levels

336   in coastal seawater ecosystems, the effect factor of Fe was set to zero and as a consequence its CTP

337   also becomes zero.

3.4.1   Spatial variability of Comparative Toxicity Potentials

339   Cr and Cu show the largest variation in CTP across LMEs with four orders of magnitude (Figure

340   1d). For Cr the variation is mainly driven by the variation in EF (R^2=0.60, p<0.001, Figure S7 in

341   SI), and less influenced by variation of FF and BF (R^2<0.15). For Cu no single individual parameter

342   shows a significant correlation with CTP.

343   CTPs of Cd, Co, Mn, Ni, Pb and Zn vary by three orders of magnitude across LMEs (Figure 1d).

344   These metals have rather stable BF and EF, which vary less than one order of magnitude across

345   LMEs. Thus CTP variations are largely caused by FF. As FF of these metals is linearly correlated

346   with SRT, CTP is overall strongly driven by the variation in SRT (0.64<R^2<0.96, Figure S8b in SI),

347   with higher CTP for longer SRT.

3.4.2   Ranking of Comparative Toxicity Potentials

349   Among all metals, Cd has the highest CTP in 45% of the LMEs (Figure S5d in SI), followed by

350   Zn (31%) and Pb (24%). These three metals have high FF, BF and middle to high EF. They are

351   ranked among the top four CTPs in all LMEs. In contrast, Cr has the lowest CTP in all LMEs (apart

352   from Fe, for which CTP is zero). Although its EF is in the middle range compared to the other

17

353   metals, its BF and FF are constantly low in all LMEs, due to its high log K_{DOC} and log Kp_{SS}. Also

354   Mn and Ni are consistently in the lower ranking of CTP in all LMEs (5th-7th), due to their low EFs.

355   For Cd, Co, Mn, Ni, Pb and Zn, variation in CTP is significantly driven by SRT. Thus, the highest

356   CTPs for these metals are observed in LME 5 (Gulf of Mexico), LME 26 (Mediterranean), and

357   LME 62 (Black Sea), which have the longest residence time across LMEs (90 years). In contrast,

358   the lowest CTP is observed in LME 35 (Golf of Thailand), which has the 2nd shortest SRT among

359   all LMEs (15 days).

360   CTPs ranking for Cr and Cu across LMEs are largely determined by SRT and by temperature

361   through its influence on speciation. The highest CTPs are found in LME 64 (Antarctic), where the

362   2nd lowest temperature (-1.20 ºC) and long SRT (11 years) are observed. In contrast, they have the

363   lowest CTP value in LME 35 (Golf of Thailand), which has the 2nd highest temperature and 2nd

364   shortest SRT.

365   **3.4.3   Comparison between freshwater and coastal CTPs**

366   Cd, Co, Cr, Mn, Ni and Zn marine CTPs show similar ranges to freshwater CTP determined by

367   Dong et al.[13] using a parallel approach (Figure 1d). These similarities hide remarkable differences in

368   fate and effect behaviour in freshwater and coastal waters, which tend to neutralize each other in the

369   calculation of the CTPs. For these metals, EFs are thus up to two orders of magnitude lower in

370   seawater due to higher free ion activity HC_{50} in seawater (Table S9 in SI). This is in accordance

371   with previous research that freshwater species are more sensitive to metals than marine species[66]. In

372   contrast, FFs are up to two orders of magnitude higher in seawater due to longer water residence

373   times in many LMEs (the residence time of freshwater is 143 days at maximum in USEtox[13]). For

374   the metals Cd, Co, Cr, Mn, Ni and Zn, BF in freshwater and seawater are rather similar. Cd, Co,

375   Mn, Ni, and Zn were insensitive to variations in water chemistry in freshwater[13]. Thus it may be

376   reasonable to expect similar BF in freshwater and seawater for these metals. BF of Cr is correlated

377 to log K_{DOC} and log Kp_{SS}. These two values are negatively correlated with both SPM and salinity in

378 estuaries[49]. From the freshwater end to seawater end, salinity increases and SPM decreases, which

379 in combination leads to similar ranges of log K_{DOC} and log Kp_{SS}, and thus similar BF ranges in

380 seawater and freshwater for Cr. In summary, a combination of similar BF in sea- and freshwater,

381 lower EF in seawater, and higher FF in seawater results in a similar range of CTP in seawater and

382 freshwater for Cd, Co, Cr, Mn, Ni, and Zn (Figure S9 in SI).

383 Cu has up to two orders of magnitude higher FF in freshwater. It has a similar BF in freshwater

384 and seawater, for similar reasons as Cr. But its EF is 2-4 orders of magnitude lower in seawater,

385 which results in a slightly lower CTP in seawater (Figure S9 in SI).

386 Pb has a FF up to three orders of magnitude higher and a slightly lower EF in seawater than in

387 freshwater. At the same time its BF is 1-2 orders of magnitude higher in seawater, possibly due to

388 lower SPM and OM concentrations in seawater. This results in 1-4 orders of magnitude higher CTP

389 in coastal seawater than in freshwater (Figure S9 in SI).

390 CTP is expressed in potentially affected fraction of species integrated over time and space.

391 However, the species density varies considerably depending on location - from 7×10^{-12} to 5×10^{-4}

392 species/m^3 in different freshwater ecosystems at various locations[67]. Thus, even if two different

393 archetypes have the same CTP, the number of affected species can in extreme cases differ up to

394 eight orders of magnitude in freshwater. Variation would also be expected for species density in

395 coastal marine ecosystems. Moreover, species density in freshwater is generally about three orders

396 of magnitude higher than in seawater[68], which should be taken into account when comparing CTP

397 values in freshwater and seawater.

398 **3.4.4 Comparison of Fate Factors and Bioavailability Factors from USEtox**

399 The current version of USEtox does not provide marine CTP and only has seawater as a fate

400 compartment supporting FF and the eco-exposure factor (XF) calculation for seven of the metals

401   covered in this study (Cd, Co, Cr, Cu, Ni, Pb and Zn). USEtox operates with a default SRT of one

402   year, which is at the middle range of SRTs applied for the LMEs in this study. The default USEtox

403   FF thus falls within the range of the new FF in this study for all the metals (Figure S9 in SI). BF in

404   this study is similar to the concept of eco-exposure factor (XF) in USEtox. The default XF in

405   USEtox falls within or close to the range of BF found in this study for most metals. The only

406   exceptions are Cr and Cu, for which the USEtox XF is 1-6 orders of magnitude higher (Figure S9 in

407   SI). This is because the default K_{DOC} and Kp_{SS} values in USEtox were taken from literature[69], where

408   it was defined as the ratio between absorbed metal and total dissolved metal. Recall that K_{DOC} and

409   Kp_{SS} calculated in this study represent the ratios between absorbed metal and truly dissolved metal.

410   This results in a lower K_{DOC} and Kp_{SS} in USEtox, which leads to a higher XF.

411   **3.4.5   Sensitivity analysis**

412   Several water chemistry parameters (DOC, POC, SPM, pH, salinity, metal background

413   concentration and concentrations of Fe oxides, Mn oxides and Al oxides) and environmental

414   parameters (SRT, surface area, freshwater inflow and temperature) are involved in the calculation

415   of CTP in this study. In the following section, we will test the sensitivity of CTP to these

416   parameters.

417   Salinity and pH values were extracted from a complete datasets[70]. Surface area and freshwater

418   inflow were measured data taken from a global database[71]. They are well established values and

419   their uncertainty are only caused by measurement error. Thus the uncertainty is hence judged to be

420   low (e.g. uncertainty of pH meter measurement accuracy <0.1[72], salinity probe <3%[73]).

421   LME-specific land surface areas were applied in USEtox to calculate CTPs for metals in this

422   study. Compared to the CTPs calculated by applying default land surface area in USEtox, the

423   differences are less than 2%, caused by slightly different air deposition (which is also proportional

424   to the land area).

425   The importance of the uncertainty accompanying the Fe, Mn and Al oxide concentrations was

426   tested by changing them by a factor of 10. As a result CTPs varied less than 10% for all metals

427   except Pb, for which the variation amounted to 1-35% across all LMEs.

428   DOC, POC and SPM affect metal partitioning in water, and thus the CTP. These three parameters

429   show a significant positive correlation in natural waters (Figure S10 in SI). The parameter values

430   are accompanied by variation among different seawater and locations, along with the transition

431   from fresh to marine waters. We therefore tested the sensitivity of CTP to these three parameters, by

432   varying them all together by a factor of 0.1-10. These variations can cover DOC, POC, and SPM

433   concentrations ranging from conditions in freshwater to the open ocean. For these variations, CTP

434   of Cr and Cu show the highest sensitivity, varying between a factor of 0.004 and 168. The other

435   metals show very modest sensitivity, varying between a factor of 0.2 and 2.2 (Figure S11 in SI).

436   This indicates that CTP is sensitive to DOC, POC and SPM concentrations for Cr and Cu, but less

437   sensitive for the other metals. Note that within each LME, DOC, POC and SPM vary across

438   locations and time. The average value of these parameters in a specific LME was applied in our

439   study to calculate the corresponding CTP in that LME. Considering the large water volume and

440   surface area in each LME, and the comparatively constant pH, salinity and POC values (Figure S2

441   in SI), the average value of DOC, POC and SPM, thus CTPs are not likely to change dramatically

442   within one LME. However, the uncertainty associated with CTPs of Cr and Cu is still comparably

443   larger than the other metals. This needs to be noted when comparing CTPs across metals.

444   SRT has a strong influence on FF for all metals and hence also on the CTP. We varied SRT by

445   two orders of magnitude (0.1X-10X of original values) resulting in a variation in CTP by a factor of

446   0.05-21(Figure S12 in SI). The variations of CTP and SRT show a similar trend, indicating that

447   CTP positively covariates with SRT. Therefore, SRT is an important parameter determining CTP

448 when comparing metal CTP across LMEs, but it is less relevant for comparing CTP across metals

449 within the same LME.

450   Temperature has influence on metal speciation, thus potentially influencing FF, BF, and EF. We

451 calculated CTP by changing temperatures to 10ºC lower or 10ºC higher than the original values.

452 This variation range covers the surface seawater temperature for the whole year, judging from data

453 in the MODIS database[74]. We found that CTP only varies within a factor of 0.4-2.8 (Figure S13 in

454 SI) for all metals. For Cr, BF and EF vary up to one order of magnitude. However, BF and EF have

455 positive and negative correlation respectively with temperature and hence partly compensate each

456 other, which results in a moderate change of CTP. It can be concluded here that CTP is not very

457 sensitive to temperatures.

458   BF, Kp_{SS}, and K_{DOC} were calculated from metal background concentration in generic seawater,

459 which may differ in different locations. Therefore we tested the dependence of BF, $Kp_{SS,}$ and K_{DOC}

460 on metal background concentration, by varying background concentration by a factor of 10 (0.1X-

461 10X of original value). For the metals with higher Kpss and Kdoc values (e.g., Cr, Cu and Fe), BF

462 can vary up to one order of magnitude and $Kp_{SS,}$ and K_{DOC} can vary up to two orders of magnitude.

463 The variation is largely caused by metal binding with OMs. For the other metals, the variations of

464 BF, $Kp_{SS,}$ and K_{DOC} are less than 2X. This result is similar to the observation in Gandhi et al.[21]. It

465 shows that in the systems with higher background concentrations, BFs thus CTPs of metals with

466 higher $Kp_{SS,}$ and K_{DOC} values may be underestimated. However, this might be offset by the

467 adaptation of aquatic biota in those systems, which is not considered in the current effect

468 modelling[21].

469 **3.5   Practical implications**

470   This study is the first attempt to derive marine CTP considering speciation, bioavailability,

471 seawater specific toxicity, and spatial differentiation. The results show that CTP for one metal can

472   vary 3-4 orders of magnitude across LMEs, except for Fe, for which CTP is zero due to its low

473   background concentration and essentiality to marine biota. It was clearly demonstrated that it is of

474   great importance to apply spatially differentiated CTP for metals in coastal seawater, as shown for

475   all metals covered by this study except Fe. This raises the requirement for LCA practitioners to

476   consider the emission location in the inventory. The variation of CTPs is primarily driven by SRT

477   for most metals except Cr and Cu. If there is any updates on SRT in future research, it is strongly

478   recommended to recalculate metal CTPs correspondingly. Due to limited ecotoxicity data for

479   marine species and the metal coverage of the speciation model WHAM VII, it is difficult to derive

480   marine CTP for additional metals at this point. It is recommended to look into methods to estimate

481   marine ecotoxicity data by extrapolation from freshwater ecotoxicity data, or from known metal

482   properties. This can potentially provide ecotoxicity data for more metals and thus allow calculation

483   of additional marine CTPs. Where measured chronic data was missing, acute toxicity data was

484   extrapolated to chronic EC_{50}s for the EF calculation of some metals (e.g. Co, Cr, Mn, Ni, Pb and

485   Zn, Table S5 in SI). It is recommended to revise these data when chronic data is available. The

486   speciation model WHAM VII cannot simulate metal redox reactions and precipitation except Al

487   and Fe hydroxide. Due to the fact that the CTP developed in this study is for metal in coastal

488   seawater where water column depth is modest and presence of oxides are limited, the occurrence of

489   extreme redox conditions will be rare in most LMEs. E.g., When Cr(III) is emitted to coastal

490   seawater, its oxidation to Cr(IV) is limited and slow, unless abundant Mn dioxide and hydroxides

491   exist[75]. However, the lack of precipitation modelling in WHAM can cause some uncertainties,

492   especially for metals which may form insoluble compounds with major anions in seawater.

493   Therefore, it is recommended to explore the possibility of applying other metal speciation models to

494   complement WHAM VII (e.g. MINEQL+[38], Visual Minteq[37], CHEAQS Pro[76] or PHREEQC[39])

495   covering other metals and supporting the modelling of precipitation and redox reactions where

496   needed. Literature reported that eutrophication can increase metal bioavailability up to an order of

497   magnitude[77,78]. However, this may be offset by decreasing EF due to organism adaptation, which is

498   not considered in this study. Comparing to 3-4 orders of magnitude variation in CTPs, the

499   uncertainty introduced by differences in eutrophication across LMEs will not have significant

500   influences on the result. FIAM was used to assess EF in this study. However, unlike BLM it does

501   not include competition between free metal ion and other cations for binding to biotic ligands. Thus

502   it is recommended to estimate EFs with marine BLM when available. This study only developed

503   CTP for metals in the water column of the seawater compartment. Ecotoxicity potentials in

504   sediments were not considered here. In LCIA this is typically considered as a separate compartment

505   (if at all) and would require a separate study.

506

507   ASSOCIATED CONTENT

508   **Supporting Information**

509   9 tables and 13 figures addressing additional data were presented in supporting information. This

510   material is available free of charge via the internet at http://pubs.acs.org.

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