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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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ABSTRACT:

This study is a first attempt to develop globally applicable and spatially differentiated marine Comparative Toxicity Potentials (CTPs) or ecotoxicity characterization factors for metals in coastal seawater for use in Life Cycle Assessment. The toxicity potentials are based exclusively on marine ecotoxicity data and take account of metal speciation and bioavailability. CTPs were developed for nine cationic metals (Cd, Cr(III), Co, Cu(II), Fe(III), Mn, Ni, Pb and Zn) in 64 Large Marine

Ecosystems (LMEs) covering all coastal waters in the world. The results showed that the CTP of a specific metal varies 3-4 orders of magnitude across LMEs, largely due to different seawater residence time. Therefore the highest toxicity potential for metals was found in the LMEs with the longest seawater residence times. Across metals, the highest CTPs were observed for Cd, Pb and Zn. At the concentration levels occurring in coastal seawaters, Fe acts not as a toxic agent but an essential nutrient and thus has CTPs of zero.

1 Introduction

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

Metals are often ranked at the top of toxicity concerns in Life Cycle Assessment (LCA)³. Large quantities of metals are released from anthropogenic resources to the natural environment (up to 3×10^5 tons/year for selected metals, e.g. Mn)⁴. Waterborne emissions contribute 50-80%, and originate mainly in industrial sectors such as iron or steel production, thermal power stations, mineral oil and gas refineries etc.⁵ Waterborne metal emissions typically reach freshwater first and move towards seawater through fluvial pathways, thus potentially causing ecotoxicity in both freshwater and marine compartments⁶. Hitherto, metal toxicity in the aquatic environment has been modelled in LCIA using models developed to simulate the behaviour of organic chemicals with

poor representation of the speciation behaviour of metals and bioavailability (e.g. USES-LCA 2.0⁷ used in ReCiPe, IMPACT 2002+⁸). Following the principles laid out in the Apeldoorn Declaration⁹ and the Clearwater Consensus¹⁰, Gandhi et al.^{11,12} developed a new method to calculate the toxicity potential of six metals in freshwater ecosystems (expressed as a Comparative Toxicity Potential (CTP), also known as a Characterization Factor in LCIA), including fate, bioavailability and effect of metals. Their CTP was calculated for a number of archetypical freshwater chemistries. Dong et al.¹³ further adapted the method, expanding its scope of metals and calculated freshwater CTP for 14 metals. The results showed that for some metals (e.g. Al, Be, Cr(III), Cu and Fe(III)), freshwater CTP was highly dependent on the speciation of metal in a certain water chemistry, thus varying by 2-6 orders of magnitude in different water archetypes. This reveals the importance of 1) including metal speciation and bioavailability in the modelling and 2) identifying spatially determined and differentiated water chemistries.

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

Not all metal forms are toxic. Only bioavailable forms, often within the truly dissolved forms, can access a sensitive receptor, the biotic-ligand, and become hazardous^{16,17}. In addition to metal availability, also its residence time in the coastal seawater is essential for the exposure and hence its CTP. For most metals, a substantial removal happens after entering coastal zone, where complex binding to Suspended Particulate Matter (SPM) followed by removal through sedimentation is

66 increased⁶. 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 matter¹⁸.

69 Until now metal marine CTP in the previous LCIA models has either not been calculated (e.g.
70 USEtox¹⁹, IMPACT 2002+⁸) or it has been derived neglecting speciation and bioavailability, and
71 using freshwater toxicity data (e.g. USES-LCA⁷), with a questionable representativeness for
72 saltwater organisms²⁰. Moreover, as demonstrated by Gandhi and co-workers, metal freshwater
73 CTP is highly sensitive to water chemistry²¹. 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 database²⁴, 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·m³/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. 1¹¹.

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

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)·m³/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 transfers²⁵. 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.

116 **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 emissions²⁷. 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 km², estuary discharge rate (water flow rate from freshwater to coastal seawater)
131 from 0- 1.3×10^5 m³/s, temperature from -1°C-29°C, pH from 7.75-8.35, DOC from 0.6-6.5 mg/l,
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 Mg²⁺, K⁺, Ca²⁺, SO₄²⁻, 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 salinities²⁹. 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 LMEs³³.

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 USEtox¹⁹ 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 LCA³⁴. 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 K_{pSS} (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 K_{pSS} 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 K_{pSS} and K_{DOC} were recalculated in WHAM VII³⁵ for each metal in each LME
170 respectively, to replace the default values in USEtox. WHAM³⁵ 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 K_{pSS} 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 K_{pSS} 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.

184 **2.3.2 Bioavailability model**

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

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

197 **2.3.3 Ecotoxicity model**

198 Currently there are two main ecotoxicity models to explain how cationic metals cause toxicity in
199 organisms. The Free Ion Activity Model (FIAM) assumes that the toxic compound is free metal ion
200 represented by its activity. The Biotic Ligand Model (BLM) further includes the competition
201 between free metal ion and other cations (e.g. Ca^{2+} , H^+) for binding to biotic ligand – the receptor in
202 the target organism where the metal binds to exert its uptake and/or toxicity. Due to lack of BLMs
203 for metals in seawater, FIAM was chosen in this study. It has been validated to assess metal toxicity
204 to marine organisms in saltwater^{40,41}. As stated in Clearwater Consensus¹⁰, we calculated EF based
205 on truly dissolved metal, assuming that free ion is a fraction of truly dissolved metal and is
206 responsible for the toxicity. In risk assessment, Predicted No Effect Concentration (PNEC) is
207 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 conservative⁴². 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 database²⁴ 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 VII³⁵, 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 $HC_{50-trophic}$ 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 $HC_{50-trophic}$ 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 $0.5/\text{truly dissolved } HC_{50}$ ⁴³.

231 3 Results and Discussion

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

234 3.1 Fate Factors

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

240 Both log K_{DOC} and log K_{pSS} vary linearly with OM concentrations and salinity ($0.31 < R^2 < 0.93$,
241 $p < 0.001$, Table S8) for all metals except Pb and Fe. OM in WHAM is considered as humic
242 molecules, which are “rigid spheres, with proton-dissociating groups at the surface that can bind
243 metal ions.”⁴⁸ Metal ion binding to a humic molecule can be simply expressed by the general
244 reaction in Eq.2, which is described by the intrinsic association constant K_M (Eq.3)⁴⁸.

$$246 \quad K_M = \frac{[RM^{Z+z}]}{[R^Z][M^z]} \quad (\text{Eq.3})$$

247 Here R is the humic molecule, M is metal and z is the net charge. Under similar conditions (e.g.
248 pH value, temperature, etc.), K_M stays within a comparably narrow range. Therefore increasing OM
249 concentration leads to a higher concentration of metal-OM complex, resulting in a higher log K_{DOC}
250 and log K_{pSS} . When salinity increases, the metal ions are in stronger competition with major cations
251 in the seawater for the binding sites on OM, thus decreasing log K_{DOC} and log K_{pSS} ⁴⁹. The exception
252 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 K_{pSS-D} ^a values (L/kg) in this study compared with empirical log K_{pSS-D} ^b values (L/kg)
256 developed in other studies.

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

257 a. Log K_{pSS} (L/kg) in this study represents the calculated partitioning coefficient between metal
258 bound to SPM and truly dissolved metal. Log K_{pSS-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 K_{pSS-D} values from the log K_{pSS} that we determined in
261 this study.

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

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

282

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

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

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 cycling⁵⁵
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 years⁵⁶, 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 years⁵⁷, 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 years⁵⁸, 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 K_{pSS} across LMEs (Figure 1b). For all metals, clear correlations were observed
302 between BF and log K_{DOC} or log K_{pSS} (Figure S6). This implies that BF is largely determined by
303 metal binding to DOC (log K_{DOC}) and SPM (log K_{pSS}). Co has the highest BF in all LMEs across
304 metals, due to its low log K_{DOC} and log K_{pSS} . Similarly, Cr, Cu and Fe have the lowest BF across all
305 LMEs, due to their high log K_{DOC} and log K_{pSS} 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 declaration⁷. 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 sedimentation⁶. Meanwhile, fluvial pathways contribute 75% of Fe inputs to seawater¹⁸, 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 EF⁶⁴. 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 EF⁶⁵. When
331 OM decreases, a fraction of metal may be released into truly dissolved forms, which leads to a
332 higher truly dissolved HC₅₀, thus lower EF.

333 **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.

338 **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.

348 **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

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

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

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

3.4.3 Comparison between freshwater and coastal CTPs

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

377 to log K_{DOC} and log K_{pss} . These two values are negatively correlated with both SPM and salinity in
378 estuaries⁴⁹. 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 K_{pss} , 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/m³ in different freshwater ecosystems at various locations⁶⁷. 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 seawater⁶⁸, 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

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

3.4.5 Sensitivity analysis

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

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

LME-specific land surface areas were applied in USEtox to calculate CTPs for metals in this study. Compared to the CTPs calculated by applying default land surface area in USEtox, the differences are less than 2%, caused by slightly different air deposition (which is also proportional 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 10°C lower or 10°C 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 database⁷⁴. 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, K_{pss} , 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, K_{pss} , 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 K_{pss} and K_{doc} values (e.g., Cr, Cu and Fe), BF
462 can vary up to one order of magnitude and K_{pss} , 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, K_{pss} , 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 K_{pss} , 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 modelling²¹.

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 EC₅₀s 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 exist⁷⁵. 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 Minteq³⁷, CHEAQS Pro⁷⁶ or PHREEQC³⁹)
495 covering other metals and supporting the modelling of precipitation and redox reactions where

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

506

507 ASSOCIATED CONTENT

508 **Supporting Information**

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

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References

- (1) EC-JRC. *International Reference Life Cycle Data System (ILCD) Handbook - General guide for Life Cycle Assessment - Detailed guidance*; first edit.; Publications Office of the European Union: Luxembourg, LU, 2010.
- (2) Hellweg, S.; Milà i Canals, L. Emerging approaches, challenges and opportunities in life cycle assessment. *Science (80-.)*. **2014**, *344*, 1109–1113.
- (3) Huijbregts, M. A. J.; Thissen, U.; Guinée, J. B.; Jager, T.; Kalf, D.; van de Meent, D.; Ragas, A. M. J.; Wegener Sleeswijk, A.; Reijnders, L. Priority assessment of toxic substances in life cycle assessment. Part I: Calculation of toxicity potentials for 181 substances with the nested multi-media fate, exposure and effects model USES–LCA. *Chemosphere* **2000**, *41*, 541–573.
- (4) Pacyna, J. M.; Scholtz, M. T.; (Arthur) Li, Y.-F. Global budget of trace metal sources. *Environ. Rev.* **1995**, *3*, 145–159.
- (5) The European Pollutant Release and Transfer Register. *European industrail annual pollutant release*; European Environment Agency (EEA): Copenhagen, Denmark, 2012.
- (6) Chester, R.; Jickells, T. The transport of material to the oceans: the fluvial pathway. In *Marine Geochemistry*; Blackwell Publishing Ltd., 2012; pp. 11–51.
- (7) Van Zelm, R.; Huijbregts, M. A. J.; van de Meent, D. USES-LCA 2.0—a global nested multi-media fate, exposure, and effects model. *Int. J. Life Cycle Assess.* **2009**, *14*, 282–284.
- (8) Jolliet, O.; Margni, M.; Charles, R.; Humbert, S.; Payet, J.; Rebitzer, G.; Rosenbaum, R. IMPACT 2002+: a new life cycle impact assessment methodology. *Int. J. Life Cycle Assess.* **2003**, *8*, 324–330.
- (9) Aboussouan, L.; Saft, R. J.; Schonnenbeck, M.; Hauschild, M. Z.; Delbeke, K.; Struijs, J.; Russell, A.; de Haes, H. U.; Atherton, J.; van Tilborg, W.; et al. Declaration of Apeldoorn on LCIA of non-ferro metals. Results of a workshop by a group of LCA specialists, held in Apeldoorn, NL. *SETAC Globe* **2004**, *5*, 46–47.
- (10) Diamond, M. L.; Gandhi, N.; Adams, W. J.; Atherton, J.; Bhavsar, S. P.; Bulle, C.; Campbell, P. G. C.; Dubreuil, A.; Fairbrother, A.; Farley, K.; et al. The clearwater consensus: the estimation of metal hazard in fresh water. *Int. J. Life Cycle Assess.* **2010**, *15*, 143–147.
- (11) Gandhi, N.; Diamond, M. L.; van de Meent, D.; Huijbregts, M. A. J.; Peijnenburg, W. J. G. M.; Guinee, J. New method for calculating Comparative Toxicity Potential of cationic

- metals in freshwater: application to copper, nickel, and zinc. *Environ. Sci. Technol.* **2010**, *44*, 5195–5201.
- (12) Gandhi, N.; Diamond, M. L.; Huijbregts, M. A. J.; Guinée, J. B.; Peijnenburg, W. J. G. M.; van de Meent, D. Implications of considering metal bioavailability in estimates of freshwater ecotoxicity: examination of two case studies. *Int. J. Life Cycle Assess.* **2011**, *16*, 774–787.
 - (13) Dong, Y.; Gandhi, N.; Hauschild, M. Z. Development of Comparative Toxicity Potentials of 14 cationic metals in freshwater. *Chemosphere* **2014**, *112*, 26–33.
 - (14) Bruland, K.; Lohan, M. Controls on trace metals in seawater. In *The Oceans and Marine Geochemistry, Volume 6 of Treatise on geochemistry*; Holland, H. D.; Turekian, K. K., Eds.; Elsevier: Amsterdam, 2004; pp. 23–47.
 - (15) Fu, F.; Wang, Q. Removal of heavy metal ions from wastewaters: a review. *J. Environ. Manage.* **2011**, *92*, 407–418.
 - (16) Paquin, P. R.; Gorsuch, J. W.; Apte, S.; Batley, G. E.; Bowles, K. C.; Campbell, P. G. C.; Delos, C. G.; Di Toro, D. M.; Dwyer, R. L.; Galvez, F.; et al. The biotic ligand model: a historical overview. *Comp. Biochem. Physiol. Part C Toxicol. Pharmacol.* **2002**, *133*, 3–35.
 - (17) Sunda, W. Trace metal interactions with marine phytoplankton. *Biol. Oceanogr.* **1989**, *6*, 411–442.
 - (18) Mason, R. P. Trace metal(loid)s in marine waters. In *Trace Metals in Aquatic Systems*; Blackwell Publishing Ltd, 2013; pp. 219–309.
 - (19) Rosenbaum, R. K.; Bachmann, T. M.; Gold, L. S.; Huijbregts, M. A. J.; Jolliet, O.; Juraske, R.; Koehler, A.; Larsen, H. F.; MacLeod, M.; Margni, M.; et al. USEtox-the UNEP-SETAC toxicity model: recommended characterisation factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment. *Int. J. Life Cycle Assess.* **2008**, *13*, 532–546.
 - (20) Leung, K. M. Y.; Morritt, D.; Wheeler, J. R.; Whitehouse, P.; Sorokin, N.; Toy, R.; Holt, M.; Crane, M. Can saltwater toxicity be predicted from freshwater data? *Mar. Pollut. Bull.* **2001**, *42*, 1007–1013.
 - (21) Gandhi, N.; Huijbregts, M. A. J.; van de Meent, D.; Peijnenburg, W. J. G. M.; Guinee, J.; Diamond, M. L. Implications of geographic variability on Comparative Toxicity Potentials of Cu, Ni and Zn in freshwaters of Canadian ecoregions. *Chemosphere* **2011**, *82*, 268–277.
 - (22) Tankere, S. P. C.; Price, N. B.; Statham, P. J. Mass balance of trace metals in the Adriatic Sea. *J. Mar. Syst.* **2000**, *25*, 269–286.

- (23) Brodie, J.; Wolanski, E.; Lewis, S.; Bainbridge, Z. An assessment of residence times of land-sourced contaminants in the Great Barrier Reef lagoon and the implications for management and reef recovery. *Mar. Pollut. Bull.* **2012**, *65*, 267–279.
- (24) USEPA. ECOTOX database; <http://cfpub.epa.gov/ecotox/>.
- (25) Rosenbaum, R. K.; Margni, M.; Jolliet, O. A flexible matrix algebra framework for the multimedia multipathway modeling of emission to impacts. *Environ. Int.* **2007**, *33*, 624–634.
- (26) Cosme, N.; Larsen, H. F.; Hauschild, M. Z. Chapter 3- Spatially-explicit characterisation factors for marine eutrophication. In *Recommended assessment framework, method and characterisation and normalisation factors for ecosystem impacts of eutrophying emissions: phase 3 (report, model and factors)*. LC-IMPACT deliverable report D3.7 (T3.1: Aquatic eutrophication); Azevedo, L. B.; Cosme, N.; Hauschild, M. Z.; Henderson, A. D.; Huijbregts, M. A. J.; Jolliet, O.; Larsen, H. F.; van Zelm, R., Eds.; Kgs. Lyngby, Denmark, 2013; pp. 58–154.
- (27) Chen, C.-T. A.; Liu, K.-K.; Macdonald, R. Continental margin exchanges. In *Ocean Biogeochemistry*; Fasham, M. R., Ed.; Springer Berlin Heidelberg, 2003; pp. 53–97.
- (28) Sherman, K. The Large Marine Ecosystem concept: research and management strategy for living marine resources. *Ecol. Appl.* **1991**, *1*, 349–360.
- (29) Brown, E.; Colling, A.; Park, D.; Phillips, J.; Rothery, D.; Wright, J. *Seawater: its composition, properties and behaviour*; Bearman, G., Ed.; 2nd editio.; The Open University, 1995.
- (30) Coston, J. A.; Fuller, C. C.; Davis, J. A. Pb²⁺ and Zn²⁺ adsorption by a natural aluminum - and iron-bearing surface coating on an aquifer sand. *Geochim. Cosmochim. Acta* **1995**, *59*, 3535–3547.
- (31) Agrawal, A.; Sahu, K. K. Kinetic and isotherm studies of cadmium adsorption on manganese nodule residue. *J. Hazard. Mater.* **2006**, *B137*, 915–924.
- (32) Phuengprasop, T.; Sittiwong, J.; Unob, F. Removal of heavy metal ions by iron oxide coated sewage sludge. *J. Hazard. Mater.* **2011**, *186*, 502–507.
- (33) Slemons, L.; Paul, B.; Resing, J.; Murray, J. W. Particulate iron, aluminum, and manganese in the Pacific equatorial undercurrent and low latitude western boundary current sources. *Mar. Chem.* **2012**, *142-144*, 54–67.
- (34) Hauschild, M. Z.; Huijbregts, M.; Jolliet, O.; MacLeod, M.; Margni, M.; van de Meent, D.; Rosenbaum, R. K.; McKone, T. E. Building a model based on scientific consensus for life cycle impact assessment of chemicals: The search for harmony and parsimony. *Environ. Sci. Technol.* **2008**, *42*, 7032–7037.

- (35) Tipping, E.; Lofts, S.; Sonke, J. E. Humic Ion-Binding Model VII: a revised parameterisation of cation-binding by humic substances. *Environ. Chem.* **2011**, *8*, 225–235.
- (36) Stockdale, A.; Tipping, E.; Hamilton-Taylor, J.; Lofts, S. Trace metals in the open oceans: speciation modelling based on humic-type ligands. *Environ. Chem.* **2011**, *8*, 304–319.
- (37) Gustafsson, J. P. *Visual MINTEQ 3.0 user guide*; KTH, Department of Land and Water Resources Engineering: Stockholm, Sweden, 2011.
- (38) Schecher, W. D.; McAvoy, D. C. *MINEQL+ [4.6]: Environmental Research Software*; Hallwell, ME, USA, 2003.
- (39) Parkhurst, D. L.; Appelo, C. A. J. *Description of input and examples for PHREEQC version 3- A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*; U.S. Department of the Interior and U.S. Geological Survey, 2013.
- (40) Lorenzo, J. I.; Nieto, O.; Beiras, R. Effect of humic acids on speciation and toxicity of copper to *Paracentrotus lividus* larvae in seawater. *Aquat. Toxicol.* **2002**, *58*, 27–41.
- (41) Sunda, W. The relationship between free cupric ion activity and the toxicity of copper to phytoplankton. Ph.D. Dissertation, Massachusetts Institute of Technology and Woods Hole Oceanographic Institution, Cambridge, MA, 1975.
- (42) Payet, J. Assessing toxic impacts on aquatic ecosystems in LCA. Ph.D. Dissertation, Ecole Polytechnique Federale de Lausanne: EPFL, CH-1015 Lausanne, 2004.
- (43) Henderson, A. D.; Hauschild, M. Z.; van de Meent, D.; Huijbregts, M. A. J.; Larsen, H. F.; Margni, M.; McKone, T. E.; Payet, J.; Rosenbaum, R. K.; Jolliet, O. USEtox fate and ecotoxicity factors for comparative assessment of toxic emissions in life cycle analysis: sensitivity to key chemical properties. *Int. J. Life Cycle Assess.* **2011**, *16*, 701–709.
- (44) Larsen, H. F.; Hauschild, M. Evaluation of ecotoxicity effect indicators for use in LCIA. *Int. J. Life Cycle Assess.* **2007**, *12*, 24–33.
- (45) Larsen, H. F.; Hauschild, M. Z. GM-troph: a low data demand ecotoxicity effect indicator for use in LCIA. *Int. J. Life Cycle Assess.* **2007**, *12*, 79–91.
- (46) Jolliet, O.; Rosenbaum, R.; Chapman, P. M.; McKone, T.; Margni, M.; Scheringer, M.; van Straalen, N.; Wania, F. Establishing a framework for life cycle toxicity assessment - findings of the Lausanne review workshop. *Int. J. Life Cycle Assess.* **2006**, *11*, 209–212.
- (47) Yang, R.; van den Berg, C. M. G. Metal complexation by humic substances in seawater. *Environ. Sci. Technol.* **2009**, *43*, 7192–7197.

- (48) Tipping, E. Humic Ion-Binding Model VI: An Improved Description of the Interactions of Protons and Metal Ions with Humic Substances. *Aquat. Geochemistry* **1998**, 4, 3–48.
- (49) Turner, A. Trace-metal partitioning in estuaries: importance of salinity and particle concentration. *Mar. Chem.* **1996**, 54, 27–39.
- (50) Turner, A.; Martino, M.; Le Roux, S. M. Trace metal distribution coefficients in the Mersey Estuary, UK: evidence for salting out of metal complexes. *Environ. Sci. Technol.* **2002**, 36, 4578–4584.
- (51) Li, Y.-H.; Burkhardt, L.; Buchholtz, M.; O'Hara, P.; Santschi, P. H. Partition of radiotracers between suspended particles and seawater. *Geochim. Cosmochim. Acta* **1984**, 48, 2011–2019.
- (52) Benoit, M. D.; Kudela, R. M.; Flegal, A. R. Modeled trace element concentrations and partitioning in the San Francisco estuary, based on suspended solids concentration. *Environ. Sci. Technol.* **2010**, 44, 5956–5963.
- (53) Baeyens, W.; Parmentier, K.; Goeyens, L.; Ducastel, G.; De Gieter, M.; Leermakers, M. The biogeochemical behaviour of Cd, Cu, Pb and Zn in the Scheldt estuary: results of the 1995 surveys. *Hydrobiologia* **1998**, 366, 45–62.
- (54) Benoit, G.; Cantu, S. D. O.-M.; Hood, E. M.; Coleman, C. H.; Corapcioglu, M. O.; Santschi, P. H. Partitioning of Cu, Pb, Ag, Zn, Fe, Al and Mn between filter-retained particles, colloids, and solution in six Texas estuaries. *Mar. Chem.* **1994**, 45, 307–336.
- (55) Deleersnijder, E.; Campin, J.; Delhez, E. J. M. The concept of age in marine modelling I. Theory and preliminary model results. *J. Mar. Syst.* **2001**, 28, 229–267.
- (56) Markus Meier, H. E. Modeling the pathways and ages of inflowing salt- and freshwater in the Baltic Sea. *Estuar. Coast. Shelf Sci.* **2007**, 74, 610–627.
- (57) Ivanov, L. M.; Margolina, T. M.; Danilov, A. I. Application of inverse technique to study radioactive pollution and mixing processes in the Arctic Seas. *J. Mar. Syst.* **2004**, 48, 117–131.
- (58) Orre, S.; Gao, Y.; Drange, H.; Nilsen, J. E. Ø. A reassessment of the dispersion properties of 99Tc in the North Sea and the Norwegian Sea. *J. Mar. Syst.* **2007**, 68, 24–38.
- (59) Morel, F. M. M.; Milligan, A. J.; Saito, M. A. Marine bioinorganic chemistry: the role of trace metals in the oceanic cycles of major nutrients. In *The Oceans and Marine Geochemistry*; Elderfield, H.; Holland, H. D.; Turekian, K. K., Eds.; Elsevier, 2006.
- (60) Rengel, Z. Heavy metal as essential nutrients. In *Heavy Metal Stress in Plants: From Molecules to Ecosystems*; Prasad, M.; Hagemeyer, J., Eds.; Springer-Verlag Berlin Heidelberg: New York, U.S.A., 1999.

- (61) Martin, J. H. Iron as a limiting factor in oceanic productivity. In *Primary Productivity and Biogeochemical Cycles in the Sea*; Falkowski, P. G.; Woodhead, A. D., Eds.; Environmental Science Research; Springer US, 1992; Vol. 43, pp. 123–137.
- (62) Sato, G.; Negassi, S.; Tahiri, A. Z. The only elements required by plants that are deficient in seawater are nitrogen, phosphorous and iron. *Cytotechnology* **2011**, *63*, 201–204.
- (63) Barsanti, L.; Gualtieri, P. *Algae: Anatomy, Biochemicstry, and Biotechnology*; 2nd editio.; CSC Press, 2014.
- (64) Millero, F. J.; Woosley, R.; Ditrolio, B.; Waters, J. Effect of ocean acidification on the speciation of metals in seawater. *Oceanography* **2009**, *22*, 72–85.
- (65) Deruytter, D.; Garrevoet, J.; Vandeghehuchte, M. B.; Vergucht, E.; Samber, B. De; Vekemans, B.; Appel, K.; Falkenberg, G.; Delbeke, K.; Blust, R.; et al. The combined effect of Dissolved Organic Carbon and salinity on the bioaccumulation of Copper in marine mussel larvae. *Environ. Sci. Technol.* **2014**, *48*, 698–705.
- (66) Wheeler, J. R.; Leung, K. M. Y.; Morritt, D.; Sorokin, N.; Rogers, H.; Toy, R.; Holt, M.; Whitehouse, P.; Crane, M. Freshwater to saltwater toxicity extrapolation using species sensitivity distributions. *Environ. Toxicol. Chem.* **2002**, *21*, 2459–2467.
- (67) Azevedo, L. B.; Verones, F.; D, H. A.; van Zelm, R.; Jolliet, O.; Huijbregts, M. A. J. Freshwter eutrophication. In *LC-Impact. A spatially differentiated life cycle impact assessment approach*; Huijbregts, M. A. J.; Azevedo, L. B.; Chaudhary, A.; Cosme, N.; Fantke, P.; Goedkoop, M.; Hauschild, M.; Hellweg, S.; Laurent, A.; Mutel, C. L.; et al., Eds.; 2014.
- (68) Goedkoop, M.; Heijungs, R.; Huijbregts, M.; De Schryver, A.; Struijs, J.; van Zelm, R. *ReCiPe 2008: A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endoint level*; 2013.
- (69) Allison, J. D.; Allison, T. L. *Partition coefficients for metals in surface water, soil, and waste*; U.S. Environmental Protection Agency: Washington, 2005.
- (70) National Oceanographic data center (NODC) in United States Department of Commerce. World Ocean Database; <http://www.nodc.noaa.gov/OC5/SELECT/dbsearch/dbsearch.html>.
- (71) Sea Around us. A global database on marine fisheries and ecosystems; www.seaaroundus.org/lme.
- (72) HANNA instruments. pH meter by accuracy; <http://hannainst.com/usa/subcat.cfm?id=044>.
- (73) Vernier Software & Technology. Salinity sensor; <http://www.vernier.com/products/sensors/sal-bta/>.

- (74) NASA. Moderate Resolution Imaging Spectroradiometer (MODIS); http://aqua.nasa.gov/about/instrument_modis.php.
- (75) Sadiq, M. Chapter 6 Chromium in marine environments. In *Toxic Metal Chemistry in Marine Environments*; CRC Press, 1992.
- (76) Verweij, W. CHEAQS Pro, computer program for calculating CHEmical Equilibria in AQUatic Systems; <http://home.tiscali.nl/cheaqs/>.
- (77) Li, S.-X.; Liu, F.-J.; Zheng, F.-Y.; Zuo, Y.-G.; Huang, X.-G. Effects of nitrate addition and iron speciation on trace element transfer in coastal food webs under phosphate and iron enrichment. *Chemosphere* **2013**, *91*, 1486–1494.
- (78) Wang, W.; Dei, R. Effects of major nutrient additions on metal uptake in phytoplankton. *Environ. Pollut.* **2001**, *111*, 233–240.