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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 choices\(^2\). It is a valuable screening tool to facilitate identifying environmental hotspots\(^2\). The uncertainties associated with LCA results can be high due to data and simplified modelling\(^2\). 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 \(3 \times 10^5\) 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 compartments\(^6\). 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 2.0\textsuperscript{7} used in ReCiPe, IMPACT 2002\textsuperscript{+8}). Following the principles laid out in the Apeldoorn Declaration\textsuperscript{9} and the Clearwater Consensus\textsuperscript{10}, Gandhi et al.\textsuperscript{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.\textsuperscript{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 Declaration\textsuperscript{9}, “the oceans are deficient in essential metals, and the CTP for essential metals should be set at zero for toxicity in the oceans.”\textsuperscript{9} In contrast, coastal seawater receives higher anthropogenic metal emissions not just through fluvial pathways\textsuperscript{6}, but also from airborne emission and metals resuspended from the seabed\textsuperscript{14}, leading to the observable metal concentrations in the coastal zones, and even reach the mmol/l level close to wastewater discharges\textsuperscript{15}. 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\textsuperscript{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
increased\textsuperscript{6}. The fate of a metal in coastal seawater is thus strongly influenced by its tendency to adsorb to SPM, its solubility in seawater and its complexation affinity with particulate and dissolved organic matter\textsuperscript{18}.

Until now metal marine CTP in the previous LCIA models has either not been calculated (e.g. USEtox\textsuperscript{19}, IMPACT 2002\textsuperscript{+8}) or it has been derived neglecting speciation and bioavailability, and using freshwater toxicity data (e.g. USES-LCA\textsuperscript{7}), with a questionable representativeness for saltwater organisms\textsuperscript{20}. Moreover, as demonstrated by Gandhi and co-workers, metal freshwater CTP is highly sensitive to water chemistry\textsuperscript{21}. While water chemistry parameters such as pH, Dissolved Organic Carbon (DOC), SPM and salinity affect the speciation of metals, different seawater residence times (SRT) in different coastal zones also play a large role when determining the fate of metal in coastal compartment\textsuperscript{22,23}. So far, no study has given a coherent treatment of the global spatial variability of metal marine CTP, considering speciation and applying toxicity data for marine organisms. As a consequence, toxic impacts on the marine ecosystem were either not at all considered in LCA studies or they were assessed with methods of limited reliability based on questionable assumptions. These shortcomings and the strives for a coherent consideration of marine biodiversity in LCA studies set the objectives of this study.

Aiming for consistency with the methodology developed for characterizing metal toxicity in freshwater\textsuperscript{11,13} and applying marine ecotoxicity data availability in ECOTOX database\textsuperscript{24}, the objective of this paper is to develop new, spatially differentiated and globally applicable marine CTPs for Cadmium (Cd), Cobalt (Co), Chromium(III) (Cr), Copper(II) (Cu), Iron(III) (Fe), Manganese(II) (Mn), Nickel (Ni), Lead (Pb) and Zinc (Zn), taking metal speciation and bioavailability into account, and investigating their variation over 64 Large Marine Ecosystems (LMEs) for emissions received in coastal seawater all over the world.
2 Methods

2.1 General framework

For metals, $CTP_i$ for ecosystems is expressed as the Potentially Affected Fraction of species integrated over time and space $[(PAF)\cdot \text{day} \cdot \text{m}^3/\text{kg}_{\text{emitted}}]$, representing the ecotoxicity potential for the total metal in compartment $i$. It is calculated as the product of three factors: Fate Factor (FF), Bioavailability Factor (BF) and Effect Factor (EF) as presented in Eq. 1\textsuperscript{11}.

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

Where:

- $FF_i$: Fate Factor [day], representing the residence time of total metal in compartment $i$,
- $BF_i$: Bioavailability Factor [dimensionless], representing the ratio between truly dissolved and total metal. Here truly dissolved metal contains metal free ion and inorganic metal complexes. Total metal includes truly dissolved metal, DOC complexed metal and SPM complexed metal.
- $EF_i$: Effect Factor $[(PAF) \cdot \text{m}^3/\text{kg}]$, representing the fraction of species potentially affected by the toxicity of the truly dissolved metal in compartment $i$.

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

When considering a multi-compartment system, the terms of eq.1 become matrices, which besides residence times also include inter-compartmental transfers\textsuperscript{25}. In this paper we focus on metals received from adjacent environmental compartments or directly emitted into the coastal seawater compartment. Therefore, FF represents the persistence of the metal in coastal seawater, while BF and EF represent bioavailability and metal ecotoxicity effects in coastal seawater respectively. FF is modelled for the total metal rather than dissolved metal, due to the fact that this is the entity which is reported in LCI and that the metal in the water may re-partition between particulate and dissolved forms during transportation. Note that the partitioning pattern can vary over time and with local
environmental conditions. This can have an impact on the FF of metals. For the purpose of LCA temporal variations need to be averaged over a year to be compatible to the information in the life cycle inventory.

2.2 Spatial differentiation of environmental conditions and parameters

To explore the spatial variability of CTP in coastal seawater, we worked with the LMEs following Cosme et al.\textsuperscript{26}. The coastal compartment that is represented by a LME covers the marine area from the coastal line to the seaward boundary of the continental shelf and includes any estuaries. Thus defined, the coastal compartment with its adjacency to the continents receives emissions related to human activity through the influx of continental freshwater or direct discharges to the sea. 80%-90% of marine net primary production occurs in this compartment, which thus comprises the majority of species and biomass that potentially may be affected by metal emissions\textsuperscript{27}. The global coastal seawater zone was divided into 64 LMEs according to “distinct bathymetry (seabed topography), hydrography, productivity and trophically dependent populations”\textsuperscript{28}, where each LME represents a relatively independent coastal zone. Data on SRT, seawater surface area, temperature and water chemistry were collected for each LME from literature (Table S1 in Supporting Information (SI)). The values for these parameters show large variations across the 64 LMEs (Figure S1 in SI). SRT varies from 11 days-90 years, surface area from $1.5 \times 10^5$-$5.7 \times 10^6$ km$^2$, estuary discharge rate (water flow rate from freshwater to coastal seawater) from 0-$1.3 \times 10^5$m$^3$/s, temperature from -1°C-29°C, pH from 7.75-8.35, DOC from 0.6-6.5 mg/l, Particulate Organic Carbon (POC) from 31-802 ug/l, SPM from 0.2-2.9 mg/l and salinity from 6.2-40.3‰. For speciation modelling, salinity was translated into concentrations of the major ions (Na$^+$, Mg$^{2+}$, K$^+$, Ca$^{2+}$, SO$_4^{2-}$, and Cl$^-$) by scaling from a standard salinity (35 ‰) and its corresponding major ion concentrations (Table S2 in SI), assuming a fixed relationship between the major ion
concentrations at different salinities. For each LME, the relevant environmental parameter and water chemistry values were applied to derive a CTP value for each metal.

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

2.3 Model and parameter selection

2.3.1 Fate model

With the intended use in LCA in mind, the multimedia fate model embedded in USEtox was chosen for this study. USEtox is an LCIA model for assessing ecotoxicity and human toxicity impacts. It has been developed in a scientific consensus process involving LCIA and chemical fate modelling experts. It is the recommended characterization model for toxicity impacts in LCA. In USEtox, the fate is calculated based on a steady-state mass balance. USEtox determines metal FF in the coastal seawater compartment by modelling of metal inflow, metal outflow and metal removal (including sedimentation and sediment burial/re-suspension). Metal inflow and outflow largely depend on the retention time of the coastal seawater. Thus the default SRT of seawater on continental scale in USEtox was replaced by the SRT representative for each LME. To be consistent, also the default surface area of continental seawater and the water flow rate from continental freshwater to continental seawater (estuary discharge rate) were replaced by the corresponding LME-specific data. Water flow from ocean to coastal seawater is then automatically calculated from parameters mentioned above. Details of LME-specific data and calculations are available in Table S1 in SI. Metal removal is simulated by metal sedimentation and diffusion of
metal from seawater to sediment. The former process is modelled by metal complexation with SPM, followed by SPM sedimentation. The removal largely depends on the fraction of metal adsorbing to SPM, the concentration of SPM and the SPM sedimentation velocity. Metal diffusion into sediment is determined by the dissolved fraction of metal and the metal’s mass transfer coefficient between sediment and water. The metal fraction adsorbed to SPM can be calculated from a spatially differentiated adsorption coefficient \( K_{pss} \) (L/kg; the ratio of metal concentration between SPM bound metal and truly dissolved metal). The truly dissolved fraction of metals is calculated using both \( K_{pss} \) and \( K_{doc} \) (L/kg; the ratio of metal concentration between DOC complex bound metal and truly dissolved metal). All parameters mentioned above vary between different LMEs. Thus \( K_{pss} \) and \( K_{doc} \) were recalculated in WHAM VII\(^{35} \) for each metal in each LME respectively, to replace the default values in USEtox. WHAM\(^{35} \) is a metal speciation modelling software. Based on the input of target metal concentration and relevant water chemistry, it can deliver the concentration of target metal in a specific form. In WHAM’s calculation of \( K_{pss} \) and \( K_{doc} \) values, it is assumed that metals are in equilibrium with the discrete sites of DOC and the organic fraction of SPM. Here target metals have to compete with other cations (e.g. Ca\(^{2+} \), Mg\(^{2+} \), K\(^+ \) and Na\(^+ \)) to form complexes with SPM or DOC. The ratio between the concentration of metal that is truly dissolved in water and the concentration of metal forming complexes with SPM or DOC were calculated for each LME and each metal as the specific \( K_{pss} \) and \( K_{doc} \) value. Default DOC and SPM concentration in USEtox were also replaced by the corresponding specific parameter values for each LME. Other landscape parameters were kept unchanged. All parameters used in FF calculation are listed in Table S3 in SI. There were no substance parameter values for Mn and Fe in default USEtox inorganic database. They thus had to be collected from literatures. The retrieved values are presented together with substance parameter values for the other metals in Table S4 in SI.
2.3.2 Bioavailability model

BF, KpSS, and KDOC 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, KpSS, and KDOC 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, KpSS, and KDOC on background concentration change is performed in section 3.4.5.

WHAM VII\textsuperscript{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\textsuperscript{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\textsuperscript{37}, MINEQL+\textsuperscript{38}, PHREEQC\textsuperscript{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\textsuperscript{2+}, H\textsuperscript{+}) 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\textsuperscript{40,41}. As stated in Clearwater Consensus\textsuperscript{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
PNEC, the geometric mean $HC_{50}$ calculated from $EC_{50}$, representing the Potentially Affected Fraction (PAF) of species exposed above chronic $EC_{50}$ values, is more robust but less conservative\cite{42}. The purpose of LCA is to compare alternatives, where robustness is highly required. Therefore $HC_{50}$ values calculated from $EC_{50}$ are normally applied in LCA. It can use all the available toxicity data for a metal and is a measure associated with less uncertainty than the PNEC\cite{43,44}. Detailed descriptions of calculation methods for the PAF method and $HC_{50}$ can be found in Larsen et al.\cite{44,45}. EFs were calculated exclusively from data on chronic marine $EC_{50}$ from literature. The availability of marine ecotoxicity data in the ECOTOX database\cite{24} allowed us to apply our model to nine cationic metals, including Cd, Co, Cr, Cu, Fe(III), Mn, Ni, Pb, and Zn (Table S5 in SI). For metals where chronic marine ecotoxicity data were insufficient, extrapolation from acute marine ecotoxicity data was performed applying an Acute-to-Chronic Ratio (ACR) derived from the available toxicity data as described in Table S6 in SI. Total metal marine $EC_{50}$ reported in literature were translated into free ion $EC_{50}$ using WHAM VII\cite{35}, taking into account water chemistry of the test medium in which the reported $EC_{50}$ was determined. This conversion reduced the standard deviation of the $EC_{50}$ of each metal by at least an order of magnitude (Table S5), which also justifies the use of FIAM in EF calculation.

The calculation of EF was based on the recommended principles for LCA\cite{43,45,46}. For each metal at each trophic level (i.e. primary producers, primary and secondary consumers), a free ion activity $HC_{50}$-trophic was calculated as the geometric mean of the corresponding free ion $EC_{50}$ for all species with available data. The geometric mean of the resulting three $HC_{50}$-trophic represents the free ion activity $HC_{50}$ in saltwater for that specific metal. Then, for each combination of metal and LME, a truly dissolved $HC_{50}$ was calculated using WHAM VII, based on the free ion activity $HC_{50}$ and corresponding LME water chemistry. Finally, EF was calculated as $0.5/\text{truly dissolved } HC_{50}$\cite{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 \( K_{\text{DOC}} \) and log \( K_{\text{PSS}} \) 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, \( K_{\text{PSS}} \) in this study were generally within an order of magnitude (Table 1).

Both log \( K_{\text{DOC}} \) and log \( K_{\text{PSS}} \) 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) \(^48\).

\[
R^Z + M^z = RM^{Z+z} \quad \text{(Eq. 2)}
\]

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

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 \( K_{\text{DOC}} \) and log \( K_{\text{PSS}} \). 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 \( K_{\text{DOC}} \) and log \( K_{\text{PSS}} \)\(^49\). 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...
influenced by OM concentrations and salinity, but also by other parameters (e.g. temperature and pH values).

Table 1: Log $K_{p_{SS-D}}$ values (L/kg) in this study compared with empirical log $K_{p_{SS-D}}$ values (L/kg) developed in other studies.

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

a. Log $K_{p_{SS}}$ (L/kg) in this study represents the calculated partitioning coefficient between metal bound to SPM and truly dissolved metal. Log $K_{p_{SS-D}}$ (L/kg) in other studies represents the partitioning coefficient between metal bound to SPM and total dissolved metal. To make the values comparable, we calculated log $K_{p_{SS-D}}$ values from the log $K_{p_{SS}}$ that we determined in 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≈1mg/L, Salinity≈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.
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.
FF varies 2-3 orders of magnitude across LMEs for each metal. Within one LME, FF variation between different metals is within two orders of magnitude (Figure S5a in SI). It indicates that FF is slightly more sensitive to environmental parameters than to properties of metal.

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

3.2 Bioavailability Factors

Representing the fraction of total metal in coastal water that is truly dissolved, BF of Cd, Co, Mn, Ni, Pb and Zn varies less than a factor of eight across LMEs (Figure 1b). For Cr, Cu and Fe the variations in BF are much larger with 3-4 orders of magnitude, due to their large variations in log $K_{DOC}$ and log $K_{pSS}$ across LMEs (Figure 1b). For all metals, clear correlations were observed between BF and log $K_{DOC}$ or log $K_{pSS}$ (Figure S6). This implies that BF is largely determined by metal binding to DOC (log $K_{DOC}$) and SPM (log $K_{pSS}$). Co has the highest BF in all LMEs across metals, due to its low log $K_{DOC}$ and log $K_{pSS}$. Similarly, Cr, Cu and Fe have the lowest BF across all 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)\textsuperscript{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\textsuperscript{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\textsuperscript{6}. Meanwhile, fluvial pathways contribute 75\% of Fe inputs to seawater\textsuperscript{18}, which leads to a low concentration of dissolved Fe in seawater. Morel et al.\textsuperscript{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\textsuperscript{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\textsuperscript{64}. Increases in salinity leads to a higher ionic strength, which
results in lower free ion activity for a given free ion concentration, and thus a lower EF\textsuperscript{65}. When OM decreases, a fraction of metal may be released into truly dissolved forms, which leads to a higher truly dissolved HC\textsubscript{50}, thus lower EF.

### 3.4 Comparative Toxicity Potentials

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

#### 3.4.1 Spatial variability of Comparative Toxicity Potentials

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

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

#### 3.4.2 Ranking of Comparative Toxicity Potentials

Among all metals, Cd has the highest CTP in 45\% of the LMEs (Figure S5d in SI), followed by Zn (31\%) and Pb (24\%). These three metals have high FF, BF and middle to high EF. They are ranked among the top four CTPs in all LMEs. In contrast, Cr has the lowest CTP in all LMEs (apart 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 ($5^{th}$-$7^{th}$), 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 (Golf of Thailand), which has the $2^{nd}$ 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 $2^{nd}$ lowest temperature ($-1.20 \, ^\circ\mathrm{C}$) and long SRT (11 years) are observed. In contrast, they have the lowest CTP value in LME 35 (Golf of Thailand), which has the $2^{nd}$ highest temperature and $2^{nd}$ 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.\textsuperscript{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 species\textsuperscript{66}. 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 USEtox\textsuperscript{13}). 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 freshwater\textsuperscript{13}. Thus it may be reasonable to expect similar BF in freshwater and seawater for these metals. BF of Cr is correlated
to log $K_{\text{DOC}}$ and log $K_{\text{pSS}}$. These two values are negatively correlated with both SPM and salinity in estuaries\textsuperscript{49}. From the freshwater end to seawater end, salinity increases and SPM decreases, which in combination leads to similar ranges of log $K_{\text{DOC}}$ and log $K_{\text{pSS}}$, and thus similar BF ranges in seawater and freshwater for Cr. In summary, a combination of similar BF in sea- and freshwater, lower EF in seawater, and higher FF in seawater results in a similar range of CTP in seawater and freshwater for Cd, Co, Cr, Mn, Ni, and Zn (Figure S9 in SI).

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

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

CTP is expressed in potentially affected fraction of species integrated over time and space. However, the species density varies considerably depending on location - from $7 \times 10^{-12}$ to $5 \times 10^{-4}$ species/m$^3$ in different freshwater ecosystems at various locations\textsuperscript{67}. Thus, even if two different archetypes have the same CTP, the number of affected species can in extreme cases differ up to eight orders of magnitude in freshwater. Variation would also be expected for species density in coastal marine ecosystems. Moreover, species density in freshwater is generally about three orders of magnitude higher than in seawater\textsuperscript{68}, which should be taken into account when comparing CTP values in freshwater and seawater.

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

The current version of USEtox does not provide marine CTP and only has seawater as a fate 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 $K_{SS}$ values in USEtox were taken from literature$^{69}$, where it was defined as the ratio between absorbed metal and total dissolved metal. Recall that $K_{DOC}$ and $K_{SS}$ calculated in this study represent the ratios between absorbed metal and truly dissolved metal. This results in a lower $K_{DOC}$ and $K_{SS}$ 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 datasets$^{70}$. Surface area and freshwater inflow were measured data taken from a global database$^{71}$. 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).
The importance of the uncertainty accompanying the Fe, Mn and Al oxide concentrations was tested by changing them by a factor of 10. As a result CTPs varied less than 10% for all metals except Pb, for which the variation amounted to 1-35% across all LMEs.

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

SRT has a strong influence on FF for all metals and hence also on the CTP. We varied SRT by two orders of magnitude (0.1X-10X of original values) resulting in a variation in CTP by a factor of 0.05-21(Figure S12 in SI). The variations of CTP and SRT show a similar trend, indicating that CTP positively covariates with SRT. Therefore, SRT is an important parameter determining CTP.
when comparing metal CTP across LMEs, but it is less relevant for comparing CTP across metals within the same LME.

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

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

3.5 Practical implications

This study is the first attempt to derive marine CTP considering speciation, bioavailability, seawater specific toxicity, and spatial differentiation. The results show that CTP for one metal can
vary 3-4 orders of magnitude across LMEs, except for Fe, for which CTP is zero due to its low background concentration and essentiality to marine biota. It was clearly demonstrated that it is of great importance to apply spatially differentiated CTP for metals in coastal seawater, as shown for all metals covered by this study except Fe. This raises the requirement for LCA practitioners to consider the emission location in the inventory. The variation of CTPs is primarily driven by SRT for most metals except Cr and Cu. If there is any updates on SRT in future research, it is strongly recommended to recalculate metal CTPs correspondingly. Due to limited ecotoxicity data for marine species and the metal coverage of the speciation model WHAM VII, it is difficult to derive marine CTP for additional metals at this point. It is recommended to look into methods to estimate marine ecotoxicity data by extrapolation from freshwater ecotoxicity data, or from known metal properties. This can potentially provide ecotoxicity data for more metals and thus allow calculation of additional marine CTPs. Where measured chronic data was missing, acute toxicity data was extrapolated to chronic EC$_{50}$s for the EF calculation of some metals (e.g. Co, Cr, Mn, Ni, Pb and Zn, Table S5 in SI). It is recommended to revise these data when chronic data is available. The speciation model WHAM VII cannot simulate metal redox reactions and precipitation except Al and Fe hydroxide. Due to the fact that the CTP developed in this study is for metal in coastal seawater where water column depth is modest and presence of oxides are limited, the occurrence of extreme redox conditions will be rare in most LMEs. E.g., When Cr(III) is emitted to coastal seawater, its oxidation to Cr(IV) is limited and slow, unless abundant Mn dioxide and hydroxides exist$^{75}$. However, the lack of precipitation modelling in WHAM can cause some uncertainties, especially for metals which may form insoluble compounds with major anions in seawater. Therefore, it is recommended to explore the possibility of applying other metal speciation models to complement WHAM VII (e.g. MINEQL$^{+}\text{38}$, Visual Minteq$^{37}$, CHEAQS Pro$^{76}$ or PHREEQC$^{39}$) 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. 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.

ASSOCIATED CONTENT

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


(24) USEPA. ECOTOX database; http://cfpub.epa.gov/ecotox/.


(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.


(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.

(74) NASA. Moderate Resolution Imaging Spectroradiometer (MODIS); http://aqua.nasa.gov/about/instrument_modis.php.


(76) Verweij, W. CHEAQS Pro, computer program for calculating CHemical Equilibria in AQuatic Systems; http://home.tiscali.nl/cheaqs/.
