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LCIA OF IMPACTS ON HUMAN HEALTH AND ECOSYSTEMS

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

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Abstract
Purpose The study develops site-dependent characterization factors (CFs) for marine ecotoxicity of metals emitted to freshwater, taking their passage of the estuary into account. To serve life cycle assessment (LCA) studies where emission location is often unknown, site-generic marine CFs were developed for metal emissions to freshwater and coastal seawater, respectively. The new CFs were applied to calculate endpoint impact scores for the same amount of metal emission to each compartment, to compare the relative ecotoxicity damages in freshwater and marine ecosystems in LCA.
Methods Site-dependent marine CFs for emission to freshwater were calculated for 64 comparatively independent seas (large marine ecosystems, LMEs). The site-dependent CF was calculated as the product of fate factor (FF), bioavailability factor (BF), and effect factor (EF). USEtox modified with site-dependent parameters was extended with an estuary removal process to calculate FF. BF and EF were taken from Dong et al. Environ Sci Technol 50:269–278 (2016). Site-generic marine CFs were derived from site-dependent marine CFs. Different averaging principles were tested, and the approach representing estuary discharge rate was identified as the best one. Endpoint marine and freshwater metals CFs were developed to calculate endpoint ecotoxicity impact scores.
Results and discussion Marine ecotoxicity CFs are 1.5 orders of magnitude lower for emission to freshwater than for emission to seawater for Cr, Cu, and Pb, due to notable removal fractions both in freshwater and estuary. For the other metals, the difference is less than half an order of magnitude, mainly due to removal in freshwater. The site-dependent CFs generally vary within two orders of magnitude around the site-generic CF. Compared to USES-LCA 2.0 CFs (egalitarian perspective), the new site-generic marine CFs for emission to seawater are 1–4 orders of magnitude lower except for Pb. The new site-generic marine CFs for emission to freshwater lie within two orders of magnitude difference from USES-LCA 2.0 CFs. The comparative contribution share analysis shows a poor agreement of metal toxicity ranking between both methods.
Conclusions Accounting for estuary removal particularly influences marine ecotoxicity CFs for emission to freshwater of metals that have a strong tendency to complex-bind to particles. It indicates the importance of including estuary in the characterization modelling when dealing with those metals. The resulting endpoint ecotoxicity impact scores are 1–3 orders of magnitude lower in seawater than in freshwater for most metals except Pb, illustrating the higher sensitivity of freshwater ecosystems to metal emissions, largely due to the higher species density there.

Keywords Comparative toxicity potential (CTP) · Estuary · Fate model · Marine ecotoxicity · USEtox

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1 Introduction

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

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

Another important missing element in the characterization of aquatic ecotoxicity for metals is the modelling of their behaviour in estuaries, the transition zone between freshwater and seawater. In two of the most widely used characterization models for ecotoxicity in LCA, USES-LCA (van Zelm et al. 2009) and USEtox (Rosenbaum et al. 2008), the fate modelling for metals emitted to the freshwater includes removal from the water column by sedimentation to freshwater sediments (including burial and re-suspension). The rest of the metal is assumed to be transported directly to coastal seawater and potentially affect marine ecosystems there. However, several studies show that estuaries function as a filter for metals. They can trap a fraction arriving with the freshwater by adsorption to suspended particulate matter (SPM). The SPM can then sediment directly or be taken up into biota, followed by sedimentation to estuary sediments (USEPA 2006; Chester and Jickells 2012). As a result, only a fraction of the metal leaving the freshwater compartment will reach the coastal seawater, which should be reflected in the CF that represents impacts in coastal seawater for emissions to freshwater. None of the current LCIA models consider this aspect.

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

2 Methods

2.1 Site-dependent marine characterization factors for metal emission to freshwater

2.1.1 General framework

To be consistent with metal emission reported in the inventory, metals emitted to the environment are assumed to be in the form of total metal. It includes free metal ions as well as metal associated with SPM, or forming complexes with dissolved organic carbon (DOC), or inorganic ions (Fig. 1). Among these metal forms, only inorganic complex metal and free metal ions are considered bioavailable (Sunda 1989). Following Gandhi et al. (2010), $CF_{i,j}$ [(PAF)·day·m^3/kg] is the characterization factor expressing the ecotoxic impact per kg *total* metal in compartment j after emission to compartment i. $CF_{i,j}$ is the product of three factors—a Fate Factor (FF_{ij}), a Bioavailability Factor (BF_j), and an Effect Factor (EF_j) as shown in Eq. (1).

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

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

The calculation of FF_{ij} is further described in Section 2.1.2. BF_j and EF_j are the same as in the calculation of marine CF for emission to seawater (Dong et al. 2016), since speciation and ecotoxic effects in coastal seawater are not affected by the emission compartment. There, BF_j was calculated using the chemical speciation model WHAM VII (Tipping et al. 2011) and the free ion activity model FIAM (Campbell 1995) was used for calculating EF_j.

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

2.1.2 Fate model

We adapted the multi-media fate model embedded in the scientific consensus model USEtox 1.01 (Rosenbaum et al. 2008) to calculate FF_{ij}. To be consistent with freshwater and marine CFs developed in Dong et al. (2014, 2016), we did not use the recently released USEtox 2.0 (USEtox Team 2016). However, the same adaptations can be applied in USEtox 2.0 for future updates. In USEtox, the environment is represented by several interlinked compartments, including freshwater, seawater, soil, and air compartments, both on continental scale and global scale. FF_{ij} is calculated by modelling chemical mass balance at steady state in different environmental compartments, considering removal, immobilisation, and transfer processes between compartments. We calculated the fate of metal emitted to the continental freshwater compartment, passing through estuary and received in the continental seawater compartment (i.e. costal seawater compartment). It is the product of two factors. One factor is the metal residence time in the coastal seawater compartment, which is the same as the FF calculated in Dong et al. (2016). It is determined by metal inflow to the coastal seawater compartment from other compartments (e.g. freshwater and air), metal removal in the coastal seawater compartment, and metal outflow from the coastal seawater compartment to other compartments (e.g. ocean and air). The other factor is the fraction of metal that is transferred from freshwater to the coastal seawater compartment after emission to freshwater. This fraction is calculated from the metal loss rate constant in freshwater and the metal transfer rate constant from freshwater to the coastal

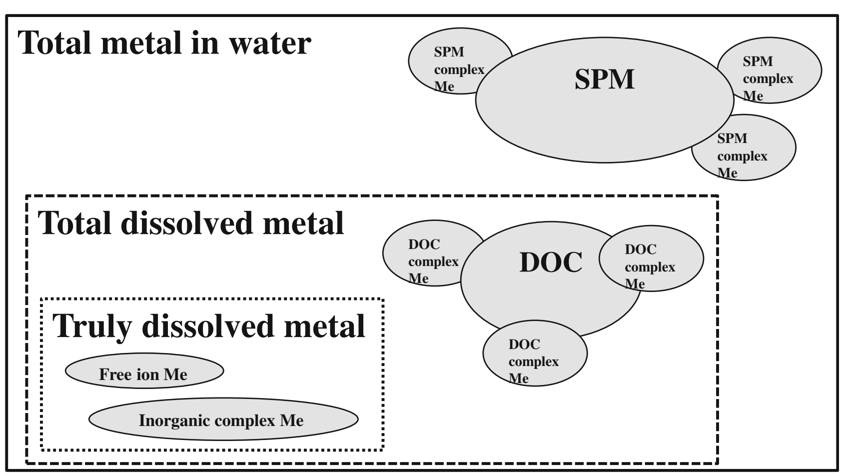

Fig. 1 Metal speciation illustration in water. *Me* represents metal. *SPM* is suspended particle and *DOC* is dissolved organic carbon

seawater compartment. The transfer rate constant for chemicals from freshwater to coastal seawater (TRC_{fw-sw}) is calculated in USEtox as presented in Eq. (2).

$$TRC_{fw-sw} = \frac{WaterF_{fw-sw}}{V_{fw}} \tag{2}$$

where

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

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

$$estuary\ removal\ rate\ constant = \frac{WaterF_{fw-sw}{}^{*}\ R_{et}}{V_{fw}} \tag{3}$$

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

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

$$New\ TRC_{fw-sw} = \frac{WaterF_{fw-sw}{}^{*}\ (1-R_{et})}{V_{fw}} \tag{4}$$

Eq. (4) was used in our study to replace Eq. (2) in the USEtox model. In addition, in the calculation of site-dependent FF_{ij} (and thus CF_{ij}), following Dong et al. (2016), the following USEtox parameters were adapted to fit the conditions of each LME: residence time of continental coastal seawater, surface area of continental coastal seawater, surface area of continental land area, water flow rate from freshwater to seawater, DOC and SPM concentrations in continental coastal seawater. Kp_{SS} (L/kg) (the ratio of metal concentration between *SPM bond* metal and *truly dissolved* metal) and K_{DOC} (L/kg) (the ratio of metal concentration between *DOC complex bound* metal and *truly dissolved* metal) were recalculated for each metal in each LME, taking its specific water chemistry into account. The LME and metal-specific values for Kp_{SS} and K_{DOC} were used instead of the original default values for that metal in USEtox. Other parameters in the USEtox fate module were kept unchanged.

2.1.3 Removal fraction (R_{et}) of metals in the estuary

The fractions of metals that can be removed in estuaries are not universal. They depend on the removal mechanism and metal speciation that is determined by water chemistry. Metals exist in the estuary either in dissolved form or particle-bound forms. Only the particle-bound metal is trapped in the estuary. The removal of metal from the water column in the estuary can occur through four processes, namely flocculation, adsorption to SPM, precipitation, and biological uptake (Chester and Jickells 2012). Flocculation only has significant effects on "clay mineral suspensions, colloidal species of iron and dissolved organics" and aluminium to a smaller extent (Chester and Jickells 2012). Though other metals can flocculate with these flocculation-agents, the limited presence of flocculation-agents in natural estuary systems means that it is not likely that flocculation will contribute significantly to the removal of other metals than iron and aluminium (Chester and Jickells 2012). Biological uptake does not contribute significantly to the removal of metals from the water column in estuary except in the case of silicon and nitrogen (Chester and Jickells 2012). Visual Minteq 3.1 (KTH 2010) was used to investigate the possibility of metal precipitation in the estuary for all eight metals in this study (Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) at their background concentration in standard seawater chemistry (salinity 35 ‰ and pH 8.1), and in several freshwater chemistry archetypes presented by Gandhi et al. (2011). The possible precipitate solids considered in Visual Minteq are presented in Table S1 in the Electronic Supplementary Material. Modelling results showed that none of the investigated metals precipitate, neither in the investigated freshwater nor in the seawater. This is expected since the applied background concentrations are obtained from empirical data representing total dissolved metals. Therefore, it is assumed that the only important metal removal mechanism in the estuary is adsorption to SPM, followed by particle removal through sedimentation or other mechanisms (e.g. SPM flocculation). This is in accordance with previous studies finding that heterogeneous precipitation in the presence of particle clouds is especially important for the removal of metals from the solution. Chester and Jickells (2012) reviewed several studies describing the removal of particulate matter in different estuaries (including the Scheldt estuary, Mississippi delta, Amazon river mouth, and St Laurence system). They concluded that in general, 90% of SPM is retained in the estuary as the water passes through the estuary. This is a result of the high sedimentation rate of SPM in the estuary (Malmgren and Brydsten 1992), and we have confirmed this fraction with other studies (Lykousis and Chronis 1989; Zhang et al. 1990; Karageorgis and Anagnostou 2001). Though some studies reported higher fractions (Malmgren and Brydsten 1992; Kim et al. 2006), or slightly lower fractions of down to 70% retention (Liu et al. 2007), a retention of 90% is judged to be a good assumption for the modelling of metal removal in a generic estuary in our study.

Different estuaries may differ widely in terms of, e.g. area, water volume, particle concentration, DOC, and water residence time. Nevertheless, metal removal mechanisms—partitioning with SPM followed by sedimentation—are similar. Note that the partitioning depends on the water chemistry. Water chemistry is very different in freshwater and seawater. In the transient zone between the two compartments, freshwater enters the estuary gradually mixing with seawater, which results in a continuously changing water chemistry throughout the estuary with salinity changing from ~0 to 35 ‰, DOC from 5 to 1 mg/l and pH from ~7.0 to 8.1 (Stumm and Morgan 1996). In addition, trace metal background concentrations decrease by up to two orders of magnitude from freshwater to seawater (Salminen 2005; Mason 2013). As described in Dong et al. (2016) the main water chemistry parameters affecting metal partitioning and speciation are salinity and organic matter content. These are gradually changing in all estuaries in a similar way from the freshwater to the seawater, e.g. a linear relationship has been found between salinity and DOC in several estuaries (Cawley et al. 2014; Asmala et al. 2016). Salinity increases linearly with distance from the seashore (Wit et al. 2015). Therefore, a simplification was assumed valid for our purpose, modelling the removal in the estuary for a generic estuary, calculating only one estuary removal fraction for each metal to be used in the calculation of CFs for all LMEs. The generic estuary was divided into eight consecutive sub-cells according to salinity with a gradually changing water chemistry from close to freshwater chemistry in the first sub-cell to close to seawater chemistry in the last sub-cell (Table S2 in the Electronic Supplementary Material). Metals pass through the sub-cells sequentially. Within each sub-cell, metals are assumed to equilibrate with the water chemistry before the dissolved metal and a fraction of the SPM-bound metal passes on to the next sub-cell. According to previous studies (Li et al. 1984), adsorption and desorption between metals and SPM reaches equilibrium for most metals after half a day. Therefore, with the chosen eight sub-cells, full equilibrium can be reached within each sub-cell for all metals, in an estuary that has a water residence time longer than 4 days. According to Chester and Jickells (2012), water residence times in different estuaries vary from a few days to a few months. Thus, a water residence time longer than 4 days is a reasonable assumption for the majority of the estuaries and it seems reasonable to assume that equilibrium is reached within each sub-cell. For each sub-cell, the dissolved metal concentration and water chemistry was entered into the speciation model WHAM VII (Tipping et al. 2011) to calculate the concentration of metal bound to SPM. It is assumed that dissolved metals are at their background concentration in the estuary. Since dissolved metals from freshwater are gradually diluted by seawater, which contains much lower concentrations of metals, as described above, we further assume that the metal background concentrations decrease linearly with the increase in salinity from freshwater to seawater (Table S2 in the Electronic Supplementary Material).

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

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

where

SPM$_n$ is the concentration of SPM at salinity value Sal$_n$,
b is the initial SPM concentration at the freshwater end,
a is a constant.

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

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

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

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

$$\begin{aligned} SPM_{rem,\ n} &= SPM_n - SPM_{n,o} \\ &= (a-c)^* Sal_n \qquad n \in [0,\ 35‰] \end{aligned} \tag{7}$$

Here SPM$_{rem,n}$ represents the reduction in the concentration of SPM solely caused by the removal process at salinity value Sal$_n$. Applying two different salinities, i and j in Eq. (7), yields:

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

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

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

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

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

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

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

2.2 Averaging principles and site-generic characterization factors

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

$$\textit{weighted site–dependent}\ \mathrm{CF} = \textit{site–dependent}\ \mathrm{CF}^{*}\ \textit{corresponding weighting factor} \tag{11}$$

$$\textit{site–generic}\ \mathrm{CF} = \sum \textit{weighted site–dependent}\ \mathrm{CF} \tag{12}$$

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

3 Results and discussion

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

3.1 Site-dependent marine characterization factors for metals emitted to freshwater

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

$$\mathrm{CF}_{fw-sw} = \mathrm{CF}_{sw-sw}{}^{*}\ (1-\mathrm{R}_{et})^{*}\ (1-\mathrm{R}_{fw}) \tag{13}$$

A metal-specific estuary removal fraction, R_{et} was calculated for each of the metals, to fit the fate model embedded in USEtox for the modelling of metal fate in coastal seawater compartments after emission to freshwater. Removal fractions in the estuary vary considerably among metals according to the applied model as shown in Table 1, where larger fractions are retained for the metals Pb, Cu, and Cr due to their high affinity to SPM as expressed by their Kp_{SS} (Dong et al. 2016). The calculated removal fractions show good agreement with ranges and tendencies found in other studies (Table 1). Applying the USEtox fate model, close to 90% of Cr, Cu, Pb, and 40%-60% of the other metals emitted to freshwater were removed in the freshwater compartment before ever reaching the estuary (Table 1), indicating that the residence time in freshwater is sufficient to allow a large fraction of metals to adsorb to SPM, which is then removed by sedimentation. In the estuary, 19% of Cr, 21% of Cu, and 61% of Pb were removed before entering the coastal seawater, while less than 2% of the other metals are removed in estuary. The resulting site-dependent marine FF and CF for emission to freshwater are presented in Table S4 in the Electronic Supplementary Material.

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

3.2 Site-generic marine characterization factors

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

Site-generic marine CFs may also be calculated by applying other averaging principles if preferred for particular reasons. We have provided four other options as described previously in Section 2.2, including three weighting principles and arithmetic mean. The resulting site-generic CFs are presented in Table S5 in Electronic Supplementary Material. The four weighting principles (including the recommended one) lead to minor differences in the calculated site-generic CF, which lies within less than a factor of three for all metals. To understand if there is any significant difference between

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

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

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

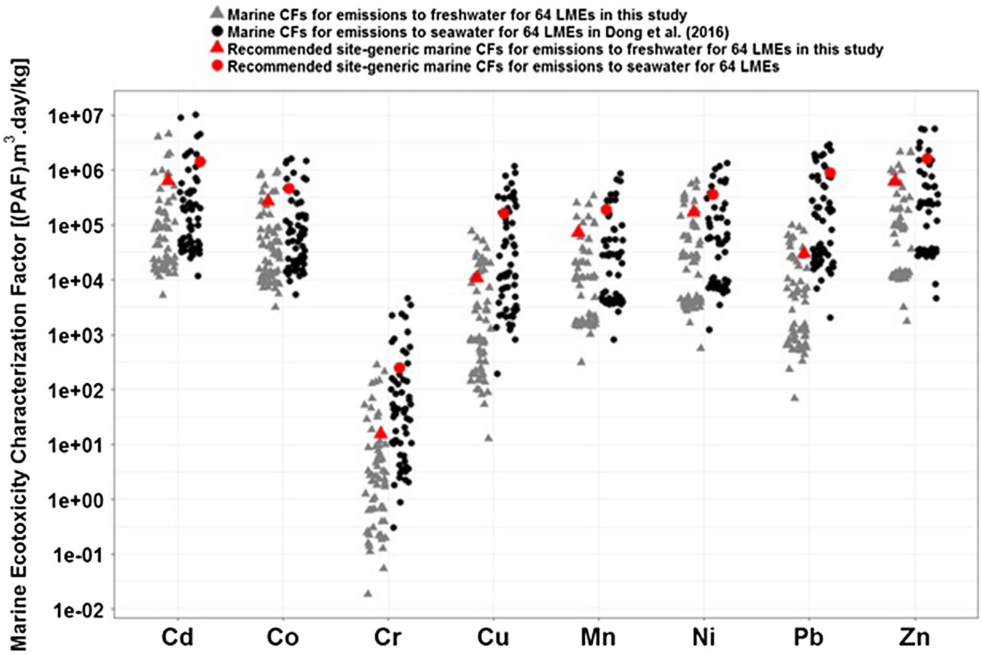

Fig. 2 Recommended site-generic marine ecotoxicity characterization factors (CFs) and site-dependent marine ecotoxicity CFs in 64 LMEs for eight metals emitted to freshwater. Marine ecotoxicity CFs for the same metals emitted to seawater (Dong et al. 2016) also shown for comparison

different weighting principles, we looked into the differences between two selected sets of weighted site-dependent CFs that are calculated in Eq. (11). For each metal, there are five sets of site-dependent CFs including equal weighting. This gives us 10 sets of differences (Table S6 in the Electronic Supplementary Material). Running *t* tests on the 10 sets of differences for each of the metals, we observed that most of the *p* values are above 0.05, meaning there is no significant difference between the weighted site-dependent CFs (Table S7 in the Electronic Supplementary Material). The only exceptions are Cu and Cr, where significant differences were observed for two and one sets of comparison, respectively. This is largely due to their larger variation of CFs across LMEs. This indicates that the site-generic CFs are not very sensitive to the chosen averaging principle. All investigated averaging principles including arithmetic mean give results located in the upper half of the CF ranges across the 64 LMEs. This indicates that for all averaging principles, LMEs with higher CFs, which tend to be the LMEs with longer seawater residence times, have a relatively strong influence on the generic CF.

3.3 Parameter uncertainty

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

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

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

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

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

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

3.4 Comparison between recommended generic characterization factors and USES-LCA characterization factors

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

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

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

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

Note that ecotoxicity CFs in USES-LCA 2.0 are expressed in a relative metric as 1,4-DCB equivalents, which differs from the absolute metric applied in this study [(PAF).m^3.day/kg]. To compare factors from both models, we converted our CFs to 1,4-DCB equivalents by dividing the metal CFs with marine CFs for 1,4-DCB emitted to freshwater or seawater in corresponds with the metal emission compartments. Here marine CFs for 1,4-DCB are site-generic ones calculated using default USEtox settings. However, marine CF of 1,4-DCB emitted to freshwater is 1.5 orders of magnitude lower than when it is emitted to seawater. This is because 1,4-DCB degrades in freshwater, which results in a much lower transfer fraction from freshwater to seawater (4%) than for most of the metals. This potentially introduces a bias in the conversion of the new metal CFs in this study to 1,4-DCB equivalents, which may result in higher marine CFs for metal emissions to freshwater than to seawater after the conversion. Though this does not affect the ecotoxicity ranking of metals, it highlights a problem in the use of an organic reference substance when expressing ecotoxicity of metals in different compartments (Dreyer et al. 2003). In general, site-generic marine CFs developed in this study are higher than USES-LCA 2.0 CFs with Individualist and Hierarchist perspectives, but lower than or similar to USES-LCA 2.0 CFs with Egalitarian perspective (Table S9 in the Electronic Supplementary Material).

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

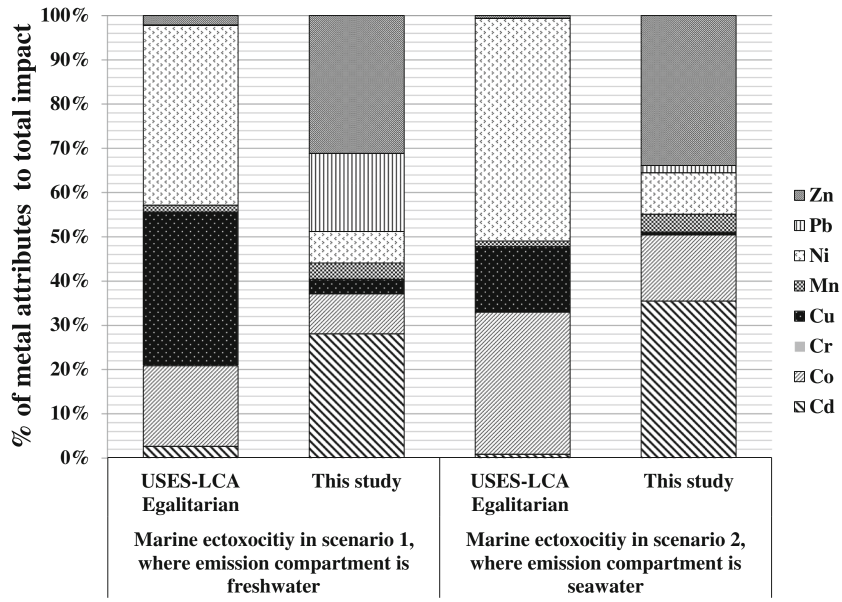

Fig. 3 Contribution analysis based on emission inventory with one kg of each metal (Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) emitted to water. In scenario 1, all metals are emitted to freshwater. In scenario 2, all metals are emitted to coastal seawater. The share (%) of each metal in the total marine ecotoxicity impact is shown

3.5 Metal ecotoxicity in the aquatic system

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

$$\textit{Endpoint}\ \mathrm{CF} = \textit{midpoint}\ \mathrm{CF} \times \textit{species density} \times \mathrm{PAF\ to\ PDF}\ \textit{ratio} \tag{14}$$

Eq. (14) can be used to calculate endpoint ecotoxicity CFs in any environmental compartment. In this study, we took the PAF to PDF ratio (dimensionless) from IMPACT 2002+ (Jolliet et al. 2003). Marine and freshwater species densities [species/m^3] were taken from ReCiPe (Goedkoop et al. 2013). To calculate the site-generic marine ecotoxicity endpoint CF, we used the site-generic marine ecotoxicity midpoint CF [(PAF).m^3.day/kg] from this study. Site-generic freshwater ecotoxicity CFs from Dong et al. (2014) were used to calculate freshwater ecotoxicity endpoint CFs. The results are presented in Fig. S1 in the Electronic Supplementary Material.

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

$$\mathrm{EIS\ for}\ \textit{emission}\ \mathrm{to}\ \textit{freshwater} = (\textit{Freshwater endpoint}\ \mathrm{CF} + \textit{Marine endpoint}\ \mathrm{CF\ for}\ \textit{emission}\ \mathrm{to}\ \textit{freshwater}) \times \textit{emission quantity} \tag{15}$$

$$\mathrm{EIS\ for}\ \textit{emission}\ \mathrm{to}\ \textit{seawater} = \textit{Marine endpoint}\ \mathrm{CF\ for}\ \textit{emission}\ \mathrm{to}\ \textit{seawater} \times \textit{emission quantity} \tag{16}$$

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

The result shows that for all metals investigated except Pb, emissions to freshwater result in 1–3 orders of magnitude higher endpoint EIS than emissions to seawater (Fig. 4). When metals are emitted to freshwater, the major ecotoxicity impact is on freshwater species. Though some metals will pass through the estuary and reach seawater, consequently causing toxicity on marine species, the impacts on marine species (marine ecotoxicity for emission to freshwater) only contribute little

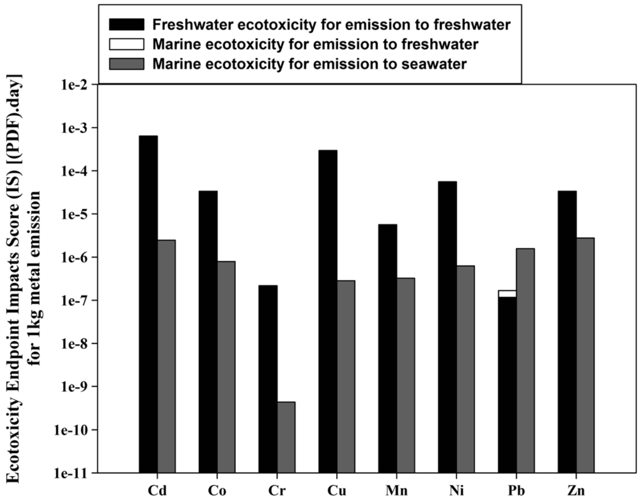

Fig. 4 Site-generic ecotoxicity endpoint impact scores for emission of 1 kg metal into freshwater and marine water, respectively

(<3.5% for any of the metals except Pb) to the total EIS for emissions to freshwater. The freshwater ecotoxicity CF is either similar or slightly higher than the marine ecotoxicity CF (Dong et al. 2016), but the species density in freshwater is two orders of magnitude higher than in marine water (Goedkoop et al. 2013), which is the main driver behind the higher endpoint EIS for freshwater ecotoxicity. For Pb, the emission to seawater causes one order of magnitude higher marine ecotoxicity endpoint scores than emission to freshwater (Fig. 4). Here 30% of the EIS for emissions to freshwater is coming from the impacts on marine species. This is largely caused by the much higher CF of Pb in marine water than in freshwater as discussed in Dong et al. (2016).

4 Conclusions and recommendations

Following the methodological recommendations from the Apeldoorn declaration and the Clearwater Consensus, we developed site-dependent marine ecotoxicity CFs for 64 Large Marine Ecosystems for eight metals emitted to freshwater, taking estuary removal into account. By introducing an estuary into the multi-compartment fate model of USEtox, marine CFs for metals with a strong tendency to associate with particles (e.g. Pb, Cu, and Cr) were notably reduced for emission to freshwater. 61% of Pb, 21% of Cu, and 19% of Cr that enters the estuary were retained there. In combination with the metals that are retained in freshwater, this results in 1.5 orders of magnitude lower marine ecotoxicity CFs for emission to freshwater compared to emission to seawater for those three metals, clearly indicating the importance of including an estuary in the fate model for those metals. In LCA studies where emission location is unknown, we recommend to use estuary discharge rate weighted CFs. Compared with USES-LCA 2.0's marine ecotoxicity CFs, the new site-generic marine ecotoxicity CF for emission to seawater is ca. 1–4 orders of magnitude lower. The new site-generic marine ecotoxicity CF for emission to freshwater is within two orders of magnitude difference compared with USES-LCA 2.0 values. However, the comparative contribution share analysis shows little similarity for the rankings of most toxic metals between USES-LCA and the new method. While Ni, Cu and Co are the major ecotoxicity contributors in USES-LCA, they become less important in the new method. We further developed marine and freshwater ecotoxicity endpoint CFs, to compare damages from metal emissions on freshwater and marine ecosystems respectively. For the same amount of metal, emissions to freshwater result in 1–3 orders of magnitude higher endpoint impact scores than emissions to seawater for all investigated metals except Pb. For metal emissions to freshwater, the ecotoxicity impact on marine species has a minor contribution to the total ecotoxicity damage score, except for Pb. However, this study only covers eight metals for which a marine ecotoxicity CF has been developed. It is recommended to consider more metals when their marine CFs become available, especially those that may behave similarly to Pb (e.g. Sn and Ag). Largely due to higher species density, the damage scores are higher for freshwater ecosystems than for marine ecosystems.

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

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References

Aboussouan L, Saft RJ, Schonnenbeck M et al (2004) 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 5:46–47

Asmala E, Kaartokallio H, Carstensen J, Thomas DN (2016) Variation in riverine inputs affect dissolved organic matter characteristics throughout the estuarine gradient. Front Mar Sci. doi:10.3389/fmars.2015.00125

Audry S, Blanc G, Schäfer J et al (2007) Budgets of Mn, Cd and Cu in the macrotidal Gironde estuary (SW France). Mar Chem 107:433–448

Barsanti L, Gualtieri P (2014) Algae: Anatomy, Biochemicstry, and Biotechnology, 2nd edition. CSC Press, Pisa

Cai Y, Guo L, Wang X et al (2012) The source and distribution of dissolved and particulate organic matter in the Bay of St. Louis, northern Gulf of Mexico. Estuar Coast Shelf Sci 96:96–104

Campbell PGC (1995) Interactions between trace metals and aquatic organisms : a critique of the free-ion activity model. In: Tessier A, Turner DR (eds) Metal speciation and bioavailability in aquatic systems. Wiley, New York

Cawley KM, Yamashita Y, Maie N, Jaffé R (2014) Using optical properties to quantify fringe mangrove inputs to the Dissolved Organic Matter (DOM) pool in a subtropical estuary. Estuar Coasts 37:399–410

Chester R, Jickells T (2012) The transport of material to the oceans: the fluvial pathway. In: Marine Geochemistry, 3rd edition. Blackwell Publishing Ltd., Chichester, pp 11–51

Cosme N, Mayorga E, Hauschild MZ (2017) Spatially explicit fate factors of waterborne nitrogen emissions at the global scale. Int J Life Cycle Assess. doi:10.1007/s11367-017-1349-0

Diamond ML, Gandhi N, Adams WJ et al (2010) The clearwater consensus: the estimation of metal hazard in fresh water. Int J Life Cycle Assess 15:143–147

Dong Y, Gandhi N, Hauschild MZ (2014) Development of comparative toxicity potentials of 14 cationic metals in freshwater. Chemosphere 112:26–33

Dong Y, Rosenbaum RK, Hauschild MZ (2016) Assessment of metal toxicity in marine ecosystems—comparative toxicity potentials for nine cationic metals in coastal seawater. Environ Sci Technol 50: 269–278

Dreyer LC, Niemann AL, Hauschild MZ (2003) Comparison of three different LCIA methods: EDIP97, CML2001 and Eco-indicator 99. Int J Life Cycle Assess 8:191–200

EPRTR (2012) European industrial annual pollutant release. European Environment Agency (EEA), Copenhagen

Gandhi N, Diamond ML, Huijbregts MAJ et al (2011) Implications of considering metal bioavailability in estimates of freshwater ecotoxicity: examination of two case studies. Int J Life Cycle Assess 16:774–787

Gandhi N, Diamond ML, van de Meent D et al (2010) New method for calculating comparative toxicity potential of cationic metals in freshwater: application to copper, nickel, and zinc. Environ Sci Technol 44:5195–5201

Goedkoop M, Heijungs R, Huijbregts M et al (2012) ReCiPe 2008. A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level. First edition (revised) report I: characterisation. Ministry of Housing, Spatial Planning and the Environment, Bilthoven

Goedkoop M, Heijungs R, Huijbregts M et al (2013) ReCiPe 2008: A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endoint level

Huijbregts MAJ, Thissen U, Guinée JB et al (2000) 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 41:541–573

Jolliet O, Margni M, Charles R et al (2003) IMPACT 2002+: a new life cycle impact assessment methodology. Int J Life Cycle Assess 8: 324–330

Jouanneau JM, Latouche C (1982) Estimation of fluxes to the ocean from mega-tidal estuaries under moderate climates and the problems they present. Hydrobiologia 91:23–29

Karageorgis AP, Anagnostou CL (2001) Particulate matter spatial–temporal distribution and associated surface sediment properties: Thermaikos Gulf and Sporades Basin, NW Aegean Sea. Cont Shelf Res 21:2141–2153

Kim TI, Choi BH, Lee SW (2006) Hydrodynamics and sedimentation induced by large-scale coastal developments in the Keum River Estuary, Korea. Estuar Coast Shelf Sci 68:515–528

KTH (2010) Visual MINTEQ ver 3.0. Retrived from: https://vminteq.lwr.kth.se/download/. Accessed 8 April 2014

Li Y-H, Burkhardt L, Buchholtz M et al (1984) Partition of radiotracers between suspended particles and seawater. Geochim Cosmochim Acta 48:2011–2019

Liu JP, Xu KH, Li AC et al (2007) Flux and fate of Yangtze River sediment delivered to the East China Sea. Geomorphology 85:208–224

Lykousis V, Chronis G (1989) Mechanisms of sediment transport and deposition: sediment sequences and accumulation during the Holocene on the Thermaikos plateau, the continental slope, and basin (Sporadhes basin), northwestern Aegean Sea, Greece. Mar Geol 87:15–26

Malmgren L, Brydsten L (1992) Sedimentation of river-transported particles in the Öre estuary, northern Sweden. Hydrobiologia 235–236: 59–69

Martin JH (1992) Iron as a limiting factor in oceanic productivity. In: Falkowski PG, Woodhead AD (eds) Primary Productivity and Biogeochemical Cycles in the Sea. Springer US, pp 123–137

Mason RP (2013) Trace Metals in Aquatic Systems. Wiley-Blackwell Publishing Ltd., Chichester

Monbet P (2006) Mass balance of lead through a small macrotidal estuary: the Morlaix River estuary (Brittany, France). Mar Chem 98:59–80

Paulson AJ, Feely RA, Curl HC Jr et al (1988) The impact of scavenging on trace metal budgets in Puget Sound. Geochim Cosmochim Acta 52:1765–1779

Pizzol M, Christensen P, Schmidt J, Thomsen M (2011) Eco-toxicological impact of "metals" on the aquatic and terrestrial ecosystem: a comparison between eight different methodologies for Life Cycle Impact Assessment (LCIA). J Clean Prod 19:687–698

Radach G, Gekeler J, Becker G et al (1996) The NOWESP research data base. Dtsch Hydrogr Zeitschrift 48:241–259

Rosenbaum RK, Bachmann TM, Gold LS et al (2008) 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 13:532–546

Salminen R (2005) FOREGS Geochemical Atlas of Europe, Part 1: Background Information, Methodology and Maps. Geological Survey of Finland, Espoo

Sato G, Negassi S, Tahiri AZ (2011) The only elements required by plants that are deficient in seawater are nitrogen, phosphorous and iron. Cytotechnology 63:201–204

Sherman K (1991) The large marine ecosystem concept: research and management strategy for living marine resources. Ecol Appl 1:349–360

Stumm W, Morgan JJ (1996) Aquatic chemistry. Wiley, New York

Sunda W (1989) Trace metal interactions with marine phytoplankton. Biol Oceanogr 6:411–442

Takata H, Aono T, Uchida S (2012) Distributions of trace metals Co, Cu and Cd in northern Sagami Bay, Japan and their relationship to estuarine variables. Estuar Coast Shelf Sci 111:84–94

Tipping E, Lofts S, Sonke JE (2011) Humic Ion-Binding Model VII: a revised parameterisation of cation-binding by humic substances. Environ Chem 8:225–235

Turner A (1996) Trace-metal partitioning in estuaries: importance of salinity and particle concentration. Mar Chem 54:27–39

USEPA (2006) Volunteer estuary monitoring: a methods manual, 2nd edition. USEPA, Washington

USEtox Team (2016) USEtox. Retrieved from http://www.usetox.org/. Accessed April 2017 van Zelm R, Huijbregts MAJ, van de Meent D (2009) USES-LCA 2.0—a global nested multi-media fate, exposure, and effects model. Int J Life Cycle Assess 14:282–284

Wit F, Müller D, Baum A et al (2015) The impact of disturbed peatlands on river outgassing in Southeast Asia. Nat Commun 6:10155

Zhang J, Wen Huang W, Chong Shi M (1990) Huanghe (Yellow River) and its estuary: sediment origin, transport and deposition. J Hydrol 120:203–223