

New Method for Calculating Comparative Toxicity Potential of Cationic Metals in Freshwater: Application to Copper, Nickel, and Zinc

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Current practice in chemical hazard ranking and toxic impact assessments is to estimate fate and toxicity assuming the chemical exists in dissolved and particulate phases and, for metals, that all dissolved species are equally bioavailable. This introduces significant error since metal effects are related to the truly dissolved phase and free metal ion within it, not the total dissolved phase. We introduce a Bioavailability Factor (BF) to the calculation of hazard or Comparative Toxicity Potentials (CTPs) (also known as Characterization Factors; CFs) for use in Life Cycle Impact Assessment (LCIA). The method uses for calculation (1) USEtox for environmental fate, (2) WHAM 6.0 for metal partitioning and speciation in aquatic systems, and (3) Biotic Ligand Model (BLM) for average toxicity. For 12 EU water-types, we calculated medians (range) of CTPs of 1.5×10^4 (1.5×10^2 to 1.2×10^5), 5.6×10^4 (9.4×10^3 to 4.1×10^5), and 2.1×10^4 (7×10^3 to 5.8×10^4) day·m³/kg for Cu, Ni, and Zn, respectively, which are up to ~1000 times lower than previous values. The greatest contributor to variability in CTPs was the BF, followed by toxicity Effect Factor (EF). The importance of the choice of water-type is shown by changes in the relative ranking of CTPs, which are equally influenced by water chemistry and inherent metal-specific differences.

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Introduction

Screening level hazard identification and risk classification procedures for commercial substances currently conducted in most jurisdictions are based upon three criteria: persistence (P), potential for bioaccumulation (B), and toxicity (T) (1–3). In the Life Cycle Impact Assessment (LCIA) of products, ecotoxicity is dealt with using Comparative Toxicity Potentials (CTPs) (also known as Characterization Factors; CFs), which are quantitative estimates of the ecotoxicological impacts of substances per unit emission via pathways of exposure to defined environmental recipients (4, 5). The methods for adjudicating ecotoxicological impacts rely on translating emissions into potential adverse effects of substances while accounting for environmental fate. These methods are based on those developed for nonpolar organic substances (6, 7). This approach ranks metals among the most ecotoxic both in terms of their effect levels and time-integrated potential toxicity (5, 8).

Several criticisms have been raised regarding the current methods used to evaluate metal impacts (9–11). First, metals are naturally occurring and can occur in very high concentrations. Second, unlike organic chemicals, metals do not degrade in the environment and therefore the traditional measures of persistence used for organic substances do not apply to metals (6). Third, metal exposure is a function of the emission rate plus background levels which can vary geographically and in different environmental media (e.g., soil, sediment, water) by orders-of-magnitude (9). Fourth, metal uptake and toxicity can be highly sensitive to speciation/complexation and species interconversion that vary according to ambient chemistry. For these reasons, an alternative method is necessary to capture the potential effects of metals in hazard ranking and impact assessments (10). Further, the method needs to be scientifically rigorous and yet sufficiently simple to make it tractable such that these competing needs are similarly balanced for organics and metals.

Strandesen et al. (12) developed a fate and exposure model to characterize aquatic ecotoxicological impacts caused by a metal and its multiple species in LCIA. Their model estimated equilibrium partitioning of metal species between solid and dissolved phases (i.e., partition coefficient K_d (L/kg)) based on metal-specific and pH-dependent empirical relationships regardless of the environmental compartment (e.g., water, soil, sediment). Their method can be improved by accounting for the dependence of metal partitioning and speciation within the dissolved phase on additional factors such as presence/concentrations of major cations, anions, and types of suspended matter (minerals vs organic material). The method should also consider differences in the sorption of metals in (suspended) sediment versus soil, in large part because of fundamental differences in binding sites. Bhavsar et al. (13, 14) developed a coupled metal speciation and fate/transport (TRANSPEC) model for fate assessment that incorporated metal species-specific partitioning and distribution as a function of ambient chemistry. Harvey et al. (15), in their Unit World Model (UWM) for hazard assessment of chemicals, used K_d values from the literature which avoided decisions on parameterizing ambient chemistry. They recommended adjusting the compartment volumes to compensate for the nondegradability of metals, adjusting which compartments receive emissions, and performing shorter versus longer term dynamic simulations for metals. The latter two models lack the toxicity calculations for metals that require normalizing toxicity test data for ambient chemistry.

In this paper, we propose a general modeling framework for metals in freshwaters that is illustrated for LCIA; the framework can be used for hazard ranking and risk assessment as well. The framework is based on: (1) fate estimated using a multimedia mass balance model for metals (e.g., 13, 14), (2) aquatic metal chemistry estimated by means of a geochemical speciation model (e.g., 16, 17), and (3) aquatic ecotoxicological effects estimated by means of the Biotic Ligand Model (BLM; 18). The modeling framework incorporates metal-specific geochemical behavior into the fate and toxicity assessments. Note that the issues of analyzing ecotoxicity potentials for metals in Life Cycle Assessment (LCA) not only come from LCIA but also from the Life Cycle Inventory (LCI) stage (19, 20). We limit the scope of this paper to address issues related to LCIA. We present revised CTPs for Cu, Ni, and Zn that express the relative hazard associated with their release into an evaluative freshwater environment for which we have specified 12 water chemistries.

Methods

We adopt definitions and assumptions proposed in the Clearwater Consensus (21) for the estimation of metal hazard in freshwaters. The bioavailable fraction of chemical is defined as "...the fraction of the total amount of a chemical present in a specific environmental compartment that, within a given time span, is either available or can be made available for uptake by (micro)organisms from either the direct surrounding of the organism..." (22). The amount of total chemical is the sum of its amount in *total dissolved* (or *soluble*) and *particulate* phases. The total dissolved phase is further divided into *colloidal*, which is mainly associated with Dissolved Organic Carbon (DOC), and *truly dissolved* fractions.

Current Practice. CTP incorporates the assessment of fate, exposure, and toxicity (effect) of a substance. The fate component is expressed as Fate Factor (FF, day), representing the residence time of the chemical in a specific compartment, and is calculated using an environmental multimedia fate model (5). A substance's ecotoxicological impact is represented by its Effect Factor (EF, m³/kg), indicating the average toxicity of a chemical expressed as a Potentially Affected Fraction (PAF) of organisms (23). Below we present equations for freshwater aquatic ecotoxicity, however, the method can be extended to other environmental compartments (e.g., soil or sediment). The CTP_{i,s} (day·m³/kg) of substance *s* emitted to compartment *i* is

$$CTP_{i,s} = FF_{i,s} \cdot EF_s \quad (1)$$

where *i* can be any compartment including freshwater. The compartment-specific FF is defined as the change in steady-state *total dissolved* amount of a substance in an environmental compartment due to the incremental change in its emission (5). The FF_{i,s} for the freshwater compartment is:

$$FF_{i,s} = \frac{\Delta C_{d,s} \cdot V}{\Delta m_{i,s}} \quad (2)$$

which accounts for the transport efficiency of substances from compartment *i* to freshwater and its persistence in the freshwater compartment, $\Delta C_{d,s}$ is the incremental change in the steady-state concentration of the total dissolved substance *s* (kg/m³), *V* is the volume of freshwater compartment (m³), $\Delta m_{i,s}$ is the incremental change in the emission of total substance *s* (total dissolved and particulate phases) to compartment *i* (kg/day), and *d* refers to the total dissolved fraction of that substance.

The EF_s is calculated as (23, 24)

$$EF_s = \frac{\Delta PAF}{\Delta C_{d,s}} = \frac{\Delta PAF}{\Delta TU} \cdot \frac{\Delta TU}{\Delta C_{d,s}} \approx \frac{0.5}{10^{4s}} \quad (3)$$

where ΔPAF is the incremental change in the potentially affected fraction of biological species in a freshwater community due to exposure to the *total dissolved* fraction *d* of substance *s*, ΔTU is the change in toxic unit (TU), e.g., acute or chronic EC₅₀, of substance *s*, and 10^{4s} is the geometric mean of substance's toxicity across aquatic species (kg/m³). In eq 3, $\Delta PAF/\Delta TU$ can be calculated either (1) as a function of the slope of a Species Sensitivity Distribution (SSD) developed for a specific water chemistry in addition to the choice of the underlying statistical distribution (log-normal, log-logistic) in the case of a nonlinear dose-response function (25), or (2) by simply assuming a constant value (e.g., 0.5) for a linear dose-response function (24).

Proposed Framework. Most fate and effect models (e.g., USES-LCA (5); IMPACT2002+ (26)) do not distinguish between total dissolved and truly dissolved (or free metal ion) fractions of a substance. These models assume that the total dissolved fraction *d* of metal in an environmental compartment represents the fraction of bioavailable species *k*. Our current understanding is that toxicologically relevant species is the metal free ion for cationic metals (11, 27). Further, the toxic impact of a metal is described best by its concentration at the biotic ligand site, and the degree of complexation of metals by these biotic ligands depends on water chemistry. Therefore, the above assumption results in an incorrect estimation of the potential toxic impact of a metal.

To remedy this overestimation of bioavailability by accounting for metal species-specific fate and effects, we propose the use of a Bioavailability Factor (BF) to translate between total concentration of a substance and the bioavailable fraction. The BF of a substance is

$$BF_s = \frac{\Delta C_{k,s}}{\Delta C_{t,s}} \quad (4)$$

where BF_s is the bioavailable fraction of substance *s* in freshwater (dimensionless), $\Delta C_{k,s}$ is the incremental change in the bioavailable fraction *k* of the total substance *s* (kg/m³), and $\Delta C_{t,s}$ is the incremental change in concentration of the total substance *t* (total dissolved and particulate). We assume that the bioavailable fraction is within the truly dissolved fraction. The free metal ion, which is assumed to be toxicologically active (27), is within the truly dissolved fraction. Thus, at low environmental metal concentrations and for constant ambient chemistry, BF is simply the fraction of truly dissolved metal within total metal at equilibrium. The definition of BF can be applied consistently to organics and metals: fate and effect models for organic substances assume that the total dissolved fraction of the substance is bioavailable whereas models that quantify the toxicity of metals (e.g., BLM, FIAM) express the result in terms of truly dissolved or free metal ion fractions.

To accommodate BF in the calculation of CTP, FF and EF are redefined as:

$$FF_{i,s} = \frac{\Delta C_{t,s} \cdot V}{\Delta m_{i,s}} \quad (5)$$

$$EF_s = \frac{\Delta PAF}{\Delta C_{k,s}} = \frac{\Delta PAF}{\Delta TU} \cdot \frac{\Delta TU}{\Delta C_{k,s}} \approx \frac{0.5}{10^{4s}} \quad (6)$$

where $\Delta C_{t,s}$ and $\Delta C_{k,s}$ are the incremental changes in the steady-state concentrations of the *total* (total dissolved and particulate) and bioavailable fractions *k* of substance *s* (kg/m³), respectively. Thus, CTP of substance *s* can be calculated as:

$$CTP_{i,s} = FF_{i,s} \cdot BF_s \cdot EF_s \quad (7)$$

The use of BF to calculate CTP departs from the current practice in two ways. First, it defines FF in terms of *total* rather than the *total dissolved* fraction of a substance entering a system, which allows a direct link with the life cycle inventory data. Second, the BF explicitly acknowledges that the *total dissolved* fraction of a substance is not necessarily the bioavailable fraction. The BF allows equivalent treatment of metals and organics using the same method. Explicitly including the BF also allows practitioners to update the translation between the total substance and its bioavailable fraction as science progresses.

Model Selection and Parameterization

We selected popular and widely available models to calculate metal speciation/complexation and aquatic ecotoxicity, and to couple with the fate model currently used in LCIA practice.

Fate Model. Recently, as a result of collective efforts of LCIA experts, a consensus LCIA model USEtox has been developed through rigorous parameterization and considering important fate and exposure processes from the fate and effects models listed above (24). We adopted USEtox to calculate FFs and then CTPs for metals (see Supporting Information (SI)). USEtox considers particulate and total dissolved phases of metals that are defined according to a specified partition coefficient, K_d (L/kg). Although the total dissolved phase equals the truly dissolved plus colloidal phases, current practice ignores the colloidal phase of chemicals and hence the total dissolved and truly dissolved phases are assumed to be equal (5, 15, 24).

The fate expressions in the consensus model USEtox were used with the following exceptions. As done with TRANSPEC (13, 14), the modified version of USEtox considers multiple, interconverting species within particulate, truly dissolved, and colloidal phases where interconversion is implicitly calculated based on specified values of K_d and metal species fractions (28). This approach differs from that of Toose and Mackay (29) who assumed constant species concentration ratios that do not vary with ambient chemistry. The model considers all metals in air to be in the particulate phase that is subject to wet and dry deposition. Air–water diffusive exchange is neglected although this could be included for volatile metal species such as mono- and dimethylmercury as done in ref 30. Aside from the physical removal processes of burial and outflow, chemical removal processes such as metal precipitation and coprecipitation in soil, sediment, and groundwater compartments should be included. For application to freshwater-types in this paper, we did not include metal precipitation. The values of K_d and species fractions vary according to compartment-specific chemistry data, and can be calculated using geochemical models such as MINEQL+ (16) or WHAM (17) for aquatic systems.

Geochemical Speciation-Bioavailability Model. BF for metals is operationally defined by geochemical speciation models. According to these models, metal bound to particles and organic matter, even in their labile phases, is not considered bioavailable. To calculate K_d (L/kg) among total dissolved and particulate phases, and speciation/complexation including the BF, we used the Windermere Humic-Aqueous Model (WHAM 6.0; 17). WHAM 6.0 is an *equilibrium* based metal speciation/complexation model comprised of the Humic Ion-Binding Model VI and an inorganic speciation code for aqueous solutions. An important advantage of WHAM is its sophisticated treatment of metal binding to humic and fulvic acids in both particulate and total dissolved phases. In addition, WHAM can also estimate metal adsorption to oxides of Fe and Mn. However, the use of WHAM is limited for metal precipitation and redox related reactions

due to its inability to track changes in the thermodynamic distribution of precipitated/redox coupled species.

The values of K_d and aqueous species fractions, including the fraction of free metal ion, for freshwater chemistries were calculated “off line” using WHAM and then the results were coupled with the fate model. Note that the model does not consider nonreactive, insoluble native metal products such as copper ingots or insoluble minerals. Evaluation of insoluble metal compounds requires the application of an additional model or procedure in which the dissolution rates of these compounds into dissolved metal species can be estimated (31).

Aquatic Ecotoxicity Model. We use the BLM approach, in which the toxic effects of metals are assumed to be directly related to the concentration of metals bound to the biotic ligand, which depends on water chemistry parameters such as pH and presence of competing cations (18). The BLM combines chemical equilibrium modeling for metal speciation with a toxicity model that relates metal accumulation at a biotic ligand to a toxic effect. Di Toro et al. (18) describe the structure of BLM in detail.

Currently, acute and chronic BLMs are available for Cu, Ni, and Zn, for three aquatic organism classes (algae, daphnids, and fish). Consistent with the practice for calculating EF in USEtox (24), we used values of chronic EC_{50} (concentration of substance that causes an adverse effect in 50% of the exposed population) to calculate values of μ for each metal and each aquatic organism. BLM parameters of each metal were extrapolated across-biotic species within an organism class (e.g., fish) (32). Details of extrapolating across-biotic species are provided in SI.

We used WHAM 6.0 to estimate metal speciation for toxicity test waters and selected water-type (w). Each value of EC_{50} for each metal and each biotic species was normalized using the chemistry of water-type w, giving a value of EC_{50-w} (32). All values of EC_{50-w} were then used to construct a water-type specific SSD assuming a log-normal distribution to calculate μ . Details of calculating EFs are explained in SI.

Overall Model Structure and Parameterization. The modified metal fate and toxicity (BLM) models, that incorporated metal speciation calculations, were then assembled into the USEtox framework such that metal assessments were conducted on the fully (loosely) coupled sequence of metal speciation, fate, and toxicity models. The overall structure and connections among the models ensured that consistent descriptions of environmental chemistry and characteristics were used throughout.

We applied the full model to estimate the BF, FF, EF, and CTP of the cationic metals Cu, Ni, and Zn for their emission to freshwater systems. We chose these metals because of abundance of toxicity data and availability of BLMs. We assumed that metal emissions enter the freshwater compartment with specified water chemistry in the form of total metal that is then distributed among particulate and total dissolved phases at equilibrium. To explore the effect of variability in freshwater chemistry, we assembled 12 sets of water-types based on measured environmental chemistries in European Union (EU) surface waters (33, 34). These water chemistries encompass different combinations of pH (5.5–8.3), DOC (1.6–18.2 mg/L), and water hardness (8–225 mgCaCO₃/L) categorized at low, medium, and high scales as shown in Table 1 (see details of selecting water-types in SI). We believe these sets represent most freshwater chemistries in EU. For each water-type, we assumed a background total dissolved metal concentration of 1 μ g/L for Cu and Ni and 10 μ g/L for Zn based on measured background concentrations in the European surface waters. Details of WHAM parametrization are provided in SI. The fate model used default landscape data and transport parameters in USEtox (Table S1 in SI), except the values of K_d for 12 water-types

TABLE 1. Freshwater Chemistry Data Used in the Geochemical Model, WHAM 6.0, to Estimate Bioavailability Factors (BFs) for Cu, Ni, and Zn in 12 EU Water-Types (Background Metal Concentrations of 1 $\mu\text{g/L}$ for Cu and Ni and 10 $\mu\text{g/L}$ for Zn Were Used for All Water-Types)

water-types	category			example ecosystem	reference	pH	DOC mg/L	hardness mgCaCO ₃ /L	Ca mg/L	Mg mg/L	Na mg/L	K mg/L	SO ₄ mg/L	Cl mg/L
	pH	DOC	hardness											
EU water-type 1	high	high	high	streams and brooks	33	7.4	18.2	224	75.8	8.5	58.4	0.1	67	102
EU water-type 2	high	med	high	canals and lakes	33	8.1	8.4	221	56.6	19.5	65.8	0.1	67	120
EU water-type 3	high	med	med	mole, United Kingdom	34	7.6	6.1	132	42.48	6.22	26.67	3.52	48.03	32.97
EU water-type 4	high	low	high	River Rhine, Germany	34	8.1	2.0	190	60.52	9.48	25.06	3.25	38.43	41.48
EU water-type 5	high	low	med	Segrino, Italy	34	8.2	1.7	169	58.51	5.59	2.60	0.78	9.61	20.92
EU water-type 6	high	low	low	Lake Monate, Italy	34	8.2	2.5	48	13.59	3.50	2.30	0.74	13.83	24.82
EU water-type 7	med	high	med	Ankeweene, Netherlands	34	7.3	17.8	165	52.10	8.58	11.79	0.82	109.51	20.21
EU water-type 8	med	low	med	small springs	33	6.7	2.2	78	20.3	6.7	17	0.1	67	31
EU water-type 9	med	low	low	Somerain, Belgium	34	6.4	1.6	28	6.69	2.65	7.20	2.82	85.50	5.99
EU water-type 10	low	high	low	Skarsjon, Sweden	34	5.5	10.3	8	2.40	0.49	7.89	6.22	2.79	2.41
EU water-type 11	low	med	low	Bihain, Belgium	34	5.9	8.9	10	2.48	0.95	6.39	1.80	2.88	8.37
EU water-type 12	low	low	low	Clywydog, United Kingdom	34	6.3	2.72	10	2.20	1.12	4.09	0.51	4.80	6.98

that were calculated using WHAM. K_d values for sediment and soil compartments were set to default values of USEtox.

For the toxicity effects assessment, we assembled literature values of EC_{50} for chronic (e.g., data for ≥ 72 h) exposures reported along with the test water conditions (e.g., pH, DOC, etc.). Our metal toxicity database included laboratory tests data for a minimum of three biotic species classes (algae, daphnids, and fish). Depending on the mechanism of toxicity, the BLM for each metal and aquatic organism can be different and requires distinct parameterization of conditional binding constants ($\text{Log}K_{BL}$) with the biotic ligand (as reviewed by ref 35). The values of $\text{Log}K_{BL}$ used in this application were taken from chronic BLM studies and are listed in Table S2.

Results and Discussion

Below we present results for each constituent model within the framework for a unit emission of Cu, Ni, and Zn to the 12 EU freshwater-types. We then compare CTPs obtained using the proposed approach with those calculated using the current USEtox method.

K_d Values. For the 12 EU water-types, the average values of $\text{Log}K_d$ (L/kg) for Cu, Ni, and Zn were 4.1 (4.0–4.3), 3.9 (3.6–4.2), and 4.9 (4.4–5.4), respectively (Figure 1a). The average values were similar to, but the ranges narrower than, those listed in U.S. EPA database of metal K_d values for suspended sediment for Cu, Ni, and Zn of 4.7 (3.1–6.1, $n = 70$), 4.6 (3.5–5.7, $n = 30$), and 5.1 (3.5–6.9, $n = 75$), respectively (http://www.epa.gov/athens/publications/reports/Ambrose_600_R_05_074_Partition_Coefficients.pdf). Huijbregts et al. (5) used $\text{Log}K_d$ values of 4.7, 3.9, and 5.0 L/kg for Cu, Ni, and Zn, respectively, to derive CTPs for these metals. Harvey et al. (15) used the values of 4.72, 4.80, and 5.26 L/kg for Cu, Ni, and Zn, respectively, in a critical load analysis of metals in UWM. There is a broad range in some of the values of $\text{Log}K_d$ and the relative ranking of the metals differs among these sources.

Despite the importance of pH for metal distribution, DOC ($p < 0.05$) and total suspended solids (TSS; $p < 0.05$) but not pH were significantly correlated with values of K_d for Cu and Zn. Neither DOC nor TSS were significantly correlated with values of K_d for Ni ($p = 0.395$ for DOC; $p = 0.395$ for TSS) for the 12 water-types. Multiple linear regression models were unable to provide relationships of K_d with pH, TSS, and DOC (r^2 : 0.029–0.380; $p > 0.05$) for these metals. In comparison, Bhavsar et al. (36) showed that DOC affected Cu speciation most whereas TSS largely controlled values of K_d for Ni and Zn modeled using WHAM for three freshwater systems of varying trophic status.

Fate Factors. The FFs of each metal for the “evaluative freshwater environment” set up in the USEtox fell within a factor of 4 despite the two order-of-magnitude range in values of K_d generated by the 12 water-types (Figure 1b). The results suggest that FFs are not very sensitive to water chemistry. Regardless of the metal, the FFs varied systematically with $\text{Log}K_d$ (Figure 2). This is not surprising because only two processes, export through outflow and sedimentation, control the fate of metals in the water and K_d controls the fraction of chemical subject to one or the other process (37). This is not true for organic chemicals which are subject to these two processes plus volatilization and degradation. In USEtox, water compartments are modeled such that transport by outflow is a more important route of removal than sedimentation. Due to the relative simplicity of processes governing the fate of metals, we suggest that an empirical relationship based on K_d can be developed to obtain FFs. This empirical relationship can be used to explain differences in FF among metals and among geographic sites.

A troubling issue is the role of TSS in this analysis. Through K_d , TSS influences the fraction of metal lost via export through outflow versus sedimentative pathways. Consequently, speciation/complexation and fate calculations require a consistent value of TSS. USEtox uses a value of TSS of 15 mg/L for the freshwater compartment which is linked to a corresponding net sedimentation rate. The use of this default value of TSS (and the net sedimentation rate) in USEtox “decouples” the parameter values used in the fate calculation (FF) from those used in the speciation/complexation calculation (to calculate K_d , BF, and EF).

Bioavailability Factors. BFs varied across ~ 4 , 2, and 2 orders-of-magnitude for Cu, Ni, and Zn, respectively (Figure 1c), mainly due to variations in DOC, TSS, and pH among the 12 water-types. The model estimated that 77–87% of total Cu was bound to DOC and thus not bioavailable, whereas ~ 7 –66% of total Ni was estimated to be bioavailable, despite the similarity of the ranges of K_d of these two metals (Figure S1). The fractions of free metal ions within the truly dissolved phase varied ~ 3 –98%, ~ 20 –99%, and ~ 63 –99% for Cu, Ni, and Zn, respectively (results not shown). The range in estimates of the free metal ion within the total dissolved phase for Cu was larger than that of Ni and Zn, mainly because of the influence of DOC for Cu speciation. For previously reported metal CTPs (5), the fractions of total dissolved metal under current practice were set at 57, 90, and 38% for Cu, Ni, and Zn, respectively. These default values, on average, reflect high and low bioavailability for Ni and Zn, respectively, when compared with BFs calculated for the 12 water-types

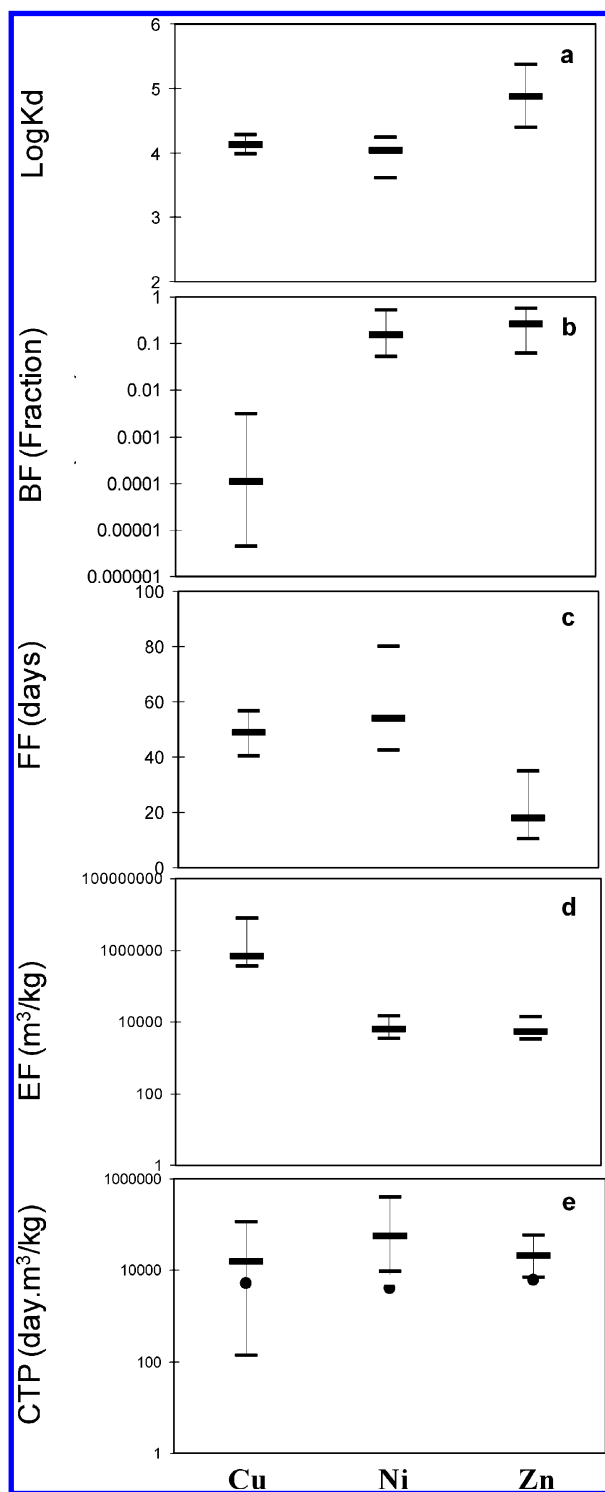


FIGURE 1. Model results for Cu, Ni, and Zn using the chemistry of 12 EU water-types described in Table 1. (a) WHAM estimated metal partition coefficients, $\text{Log}K_d$ (L/kg), used in fate model, (b) WHAM estimated BFs (Bioavailability Factors; dimensionless; calculated as a fraction of total metal in the bioavailable form), (c) freshwater FFs (Fate Factors, days) for emissions in freshwater compartment calculated using the default parameter values of USEtox model and WHAM estimated values of K_d for each water-type, (d) BLM estimated metal EFs (Effect Factors; m^3/kg) corrected for chemistry of each water-type, and (e) comparison of metal CTPs (Comparative Toxicity Potentials; $\text{day}\cdot\text{m}^3/\text{kg}$) for water-types and those calculated using the default parameters for metal assessment in USEtox (\bullet). Note FFs are for total metal and represent the residence time of metals in freshwater due to a unit emission.

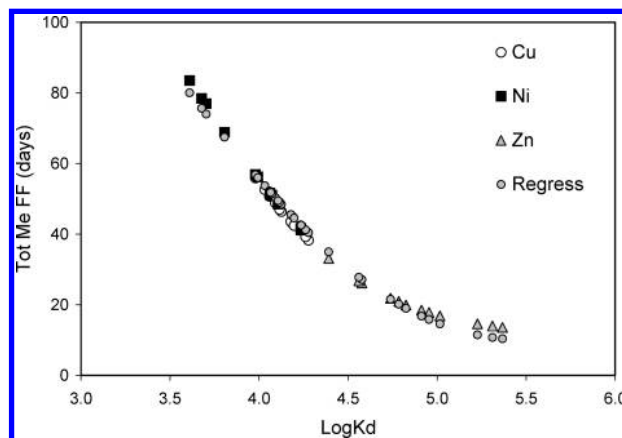


FIGURE 2. Estimated freshwater Fate Factors (FFs, days) of Cu, Ni, and Zn for their unit emissions into the freshwater compartment using the default setting of USEtox model and WHAM estimated values of K_d for the 12 EU water-types (see Table 1). Here FFs represent residence times for total metals in freshwater after emission.

in EU. The corresponding default values of total dissolved fraction recently revised in USEtox are 33, 61, and 73% for Cu, Ni, and Zn, respectively.

Effect Factors. EFs expressed in terms of truly dissolved metal for Cu, Ni, and Zn, that were obtained using the BLMs, varied by ~ 2 , ~ 1 , and ~ 1 order(s) of magnitude, respectively, for the 12 water-types (Figure 1d). The corresponding average toxicity (10^6) values for all water-types were 2.2 (0.6–6.3), 180 (35–445), and 110 (50–150) $\mu\text{g}/\text{L}$ for Cu, Ni, and Zn, respectively. This range reflects the fact that average toxicity depends not only on the intrinsic sensitivity of a biotic species to the metal but also on the bioavailable fraction and competition for biotic ligands, which is a function of water chemistry. Since BLM is semimechanistic, and stronger in treating the chemistry than physiological aspects of ecotoxicity, it does not tease apart the biological impacts of metal exposure. Default values of HC_{50} ($\approx 10^6$) in USEtox are 133.5, 880, and 1050 $\mu\text{g}/\text{L}$ for Cu, Ni, and Zn, respectively. In contrast, Harvey et al. (15) used critical concentrations (equivalent to 10^6) of 9, 52, and 120 $\mu\text{g}/\text{L}$ for Cu, Ni, and Zn, respectively, in their critical load analysis. Thus, considering metal speciation reduces average toxicity by 5–50 times, depending on the metal and selected water chemistry.

Comparative Toxicity Potentials. CTPs of metals varied over three orders-of-magnitude among the 12 water-types which predominantly reflects variability in their BFs and EFs (Figure 1e). The medians (range) of CTPs were 1.5×10^4 (1.5×10^2 to 1.2×10^5), 5.6×10^4 (9.4×10^3 to 4.1×10^5), and 2.1×10^4 (7×10^3 to 5.8×10^4) $\text{day}\cdot\text{m}^3/\text{kg}$ for Cu, Ni, and Zn, respectively. In comparison, CFs of Huijbregts et al. (5) were 1200, 3200, and 92 eq 1–4DCB or when converted to the same units 1–3 orders of magnitude higher than those calculated here for all metals in the EU water-types. However, CTPs calculated using the most recent version of USEtox (released online January, 2010) that considers chemical binding to DOC were 5.5×10^4 , 1.5×10^4 , and 3.9×10^4 $\text{day}\cdot\text{m}^3/\text{kg}$, or within a factor of 2 of CTPs calculated here.

Extreme low CTPs of Cu, Ni, and Zn came from EU water-types 1 and 2 (medium/high DOC, high pH and hardness), while high CTPs were calculated for EU water-type 9 (medium pH and low DOC and hardness). Further, the relative ranking of CTPs for three metals differed for several of the EU water-types (Figure S3).

For the same range of variations in K_d values, FFs were within a factor of 2 but were up to 2 orders of magnitude different for EFs, indicating that toxicity was much more sensitive to water chemistry than fate. Above all, the range

in BF was the greatest for all metals and water-types. The values of coefficient of variance (CV) between the water-types and metals ranged 0.1–0.4 for FFs, 0.7–1.5 for BFs, 0.5–1.3 for EFs, and 0.7–1.3 for CTPs (Table S3). There is a negative covariance (–0.67) between BF and EF of Copper. Further, values of CV ranged 0.5–1.1 among three metals. These results imply that (1) BF and EF indeed have the largest influence on CTP, (2) that the consistent use of water chemistry values for FF, BF, and EF is particularly important for Cu, and (3) that the variability in CTPs between the water-types is as large as the variability between metals investigated.

Practical Implications. Current LCIA practice has been to use generic environmental data to typify a single “evaluative environment”, i.e., one water-type for freshwater. However, we see that CTPs, and the relative ranking among metals, are a product of that water-type. Thus, one’s choice of a freshwater chemistry has an equally important influence on the CTPs compared to the inherent differences in chemical properties, e.g., K_d -values, average toxicity in case of metals. The dependence of metal CTP on both extrinsic freshwater chemistry and intrinsic chemical properties differs from that of organic chemicals for which only intrinsic chemical properties control CTP. This independence on extrinsic properties has not been tackled in the spatially generic LCA studies to date.

The consequences of these results raise yet more questions and issues. First, are these results applicable to other metals and freshwater environments? Second, for geographically generic LCA and chemical hazard assessment, which water chemistry and corresponding values of K_d , BF, and EF should be selected as a default? Third, the variability in results demands developing new methods of coupling LCI information of metal emissions with the up-to-date CTPs of metals in spatially explicit contexts. Finally, LCI must report the species and particle sizes of metals released into the environment. Since most particulate forms of metals emitted undergo a slow dissolution process, the time horizon considered for the dissolution process and the influence of metal mineralization on long-term bioavailability are topics of further research.

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Supporting Information Available

Model descriptions and parameterization details, fate parameter values used in USEtox (Table S1), $\text{Log}K_{BL}$ for BLMs (Table S2), estimated BF, FF, EF, and CTPs for Cu, Ni, and Zn and their coefficients of variance among the 12 EU water-types and metals (Table S3), metal BF as a function of $\text{Log}K_d$ (Figure S1), schematic diagram for the calculation of bioavailability corrected EFs (Figure S2), and the relative ranking of Cu, Ni, and Zn according to their CTPs for 12 EU water-types (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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