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Assessing the variability of the bioavailable fraction of zinc at the global scale using geochemical modeling and soil archetypes

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Abstract
Purpose Total metal-based toxicity potentials, like the ones used in life cycle assessment (LCA), can sometimes introduce bias and significantly affect the validity of LCA results since toxicity is associated with the bioavailable metal fraction.
Methods Here, the bioavailable fraction of zinc (Zn) for world soil types is obtained using the WHAM 6.0 geochemical speciation model. Prior to this, the usability of the WHAM model for soils using only globally available soil properties (soil texture, pH, cation exchange capacity, carbonate, and organic matter content) was validated with experimental soil data and compared to the use of empirical regressions.
Results and discussion The results confirm that WHAM can predict Zn bioavailable fraction with an uncertainty of less than 2 orders of magnitude—41 % being of the same order of magnitude—for a wide variety of soils relative to field data, yielding estimates that are better than empirical regression results in terms of rank and value. World BFs for Zn span over 6 to 18 orders of magnitude for soluble and true solution Zn, respectively, thus confirming the importance of considering spatial variability. In total, 231 soil archetypes are defined based on the soil properties that influence speciation.
Conclusions When compared to experimental values, soluble Zn obtained with WHAM seems to constitute a more reliable indicator of the bioavailable fraction of Zn than true solution Zn. Estimates obtained with the WHAM 6.0 model for soluble Zn were closer to field data in terms of value and rank as compared to estimates obtained with empirical regressions. Refining is required to obtain true solution Zn in organic soils. Although not exhaustive, the validation process covers a considerable proportion of world soils, therefore indicating that the method is promising to study Zn bioavailability at the global scale.

Keywords Bioavailability · Life cycle impact assessment · Metal speciation · Modeling · Terrestrial ecotoxicity · Zinc

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1 Introduction

The ecotoxicological impacts of metals are difficult to evaluate because their toxicity depends on speciation, which is related to highly variable environmental physicochemical parameters (Fairbrother et al. 2007). Omitting metal bioavailability and the spatial variability of soil properties could overestimate or underestimate the ecotoxicological impacts (Fairbrother et al. 2007). In life cycle assessment (LCA), metals tend to dominate ecotoxicological impacts, mainly because characterization factors (CFs) either do not account for metal speciation (Huijbregts et al. 2000, 2010) or are developed for free metal ion (Humbert et al. 2005) and are applied to other metal species (particulate, aqueous, etc.). For this reason, metals tend to be excluded from LCA conclusions, thus raising a credibility issue (Pizzol et al. 2011).

Including speciation in a global approach, such as LCA, is not straightforward since speciation is linked to parameters with high geographical variability and missing information, such as location and soil type. In the last decade, two workgroups of the United Nations Environmental Program

(UNEP) and Society of Environmental Toxicology and Chemistry (SETAC) life cycle initiative reached a consensus and suggested a framework to include metal speciation in the definition of CFs for freshwater by incorporating a bioavailability factor (BF) that represents the bioavailable fraction obtained with a geochemical speciation model and by taking into account the spatial variability of the physicochemical parameters influencing speciation with the creation of freshwater archetypes of the same properties (Diamond et al. 2010; Jolliet et al. 2005; Ligthart et al. 2004). The use of archetypes is important in LCA when the emission sources are unknown. In fact, using archetypes makes it possible to obtain default values and corresponding variability ranges (minimum and maximum values for each archetype) that are more representative of the variability of the influent parameters on the CFs—in this case, the freshwater properties that affect metal speciation (Diamond et al. 2010). The authors suggest defining BFs as the ratio of true solution metal concentration (free ions and ions pairs) and the total metal concentration in the studied environmental compartment, assuming that the true solution metal concentration represents the metal bioavailable fraction, and using the commonly used WHAM 6.0 model because it takes into account the complexity of organic matter (OM) (Diamond et al. 2010). This is coherent with the fact that plants generally absorb Zn in its free ion form, although $ZnOH^+$ is also important for adsorption and absorption by plants (Bertling et al. 2006; Brennan 2005).

Following these recommendations, new freshwater ecotoxicity CFs that consider speciation were obtained for six metals: nickel (Ni), copper (Cu), zinc (Zn), cobalt (Co), cadmium (Cd), and lead (Pb) for seven freshwater archetypes, with bioavailable metal fraction determined with the WHAM 6.0 chemical speciation model (Gandhi et al. 2010). Archetypes were defined according to the variability of three freshwater properties that influence metal speciation (pH, DOC, and water hardness) and each archetype groups of all freshwaters with the same combination of properties (e.g., archetype 1 grouped all freshwaters with high pH and water hardness and medium DOC values) (Gandhi et al. 2010). New CFs were tested in two study cases: a Zn gutter system and a Cu pipe system. The results indicate that including metal speciation led to significant differences in terms of the contribution of each metal to the total score (sum of CFs × emissions) and values of the total metal freshwater ecotoxicity scores attributable to metal emissions, which were lower by 1 to 4 orders of magnitude (Gandhi et al. 2011a). The approach was extended and standardized to 14 cationic metals (Al(III), Ba, Be, Cd, Co, Cr(III), Cs, Cu(II), Fe(II), Fe(III), Mn(II), Ni, Pb, Sr, and Zn) using the same seven freshwater archetypes (Dong et al. 2014). The authors showed that for metals such as Cd, Mn, Ni, and Zn, which are less pH dependent and have high partition coefficients (with DOC and particles), the spatial differences are not as important since new CFs only vary between 0.7 and 0.9 orders of magnitude, and when compared to current CFs, most newly calculated CFs are similar or higher and fall within the same 2 orders of magnitude (Dong et al. 2014).

Recently, another approach was tested to obtain terrestrial ecotoxicity CFs for Cu and Ni (Owsianiak et al. 2013). Owsianiak et al. calculated CFs for 760 different soils by introducing bioavailability and accessibility factors computed with empirical regressions. A CF spatial variability of 3 and 3.5 orders of magnitude was observed for Cu and Ni, respectively (2 orders of magnitude for a 95 % confidence interval) (Owsianiak et al. 2013).

Although the results for freshwater ecotoxicity are more mitigated, these latter developments (Dong et al. 2014; Gandhi et al. 2010, 2011a, b; Owsianiak et al. 2013) suggest that including speciation and the spatial variability of environmental properties in CF calculation could have an incidence on the results in global approaches such as LCA.

Although quite interesting, the UNEP/SETAC consensus approach (Diamond et al. 2010) adopted for freshwater ecotoxicity (Dong et al. 2014; Gandhi et al. 2010, 2011b) could be difficult to apply to soils because of the use of a geochemical speciation model. While there is a wide array of speciation models and software (e.g., MINEQL+, MINTEQ, GEOCHEM, WATSPEC, WATEQ, PHREEQ, ECOSAT, ORCHESTRA, WASP, WHAM, and NICA-Donnan) (Barona et al. 1995; Cancès et al. 2003; Caruso 2004; Dijkstra et al. 2004; Fairbrother et al. 2007; Fan 2004; Ge 1999, 2002; Van Riemsdijk et al. 2007), only two models enable the simulation of metals and organic ligands: Windermere humic aqueous model (WHAM) and non-ideal competitive adsorption-Donnan model (NICA-Donnan) (Ge 2002). These models are equilibrium models adapted to the heterogeneity of organic matter (Almas et al. 2006; Ge et al. 2005; Koopal et al. 2005; Tipping 2005). WHAM 6.0 also makes it possible to model metal complexation reactions with inorganic ligands. Another problem with the geochemical speciation models is that they do not consider the kinetics of precipitation and dissolution (Ge 1999; Sauvé 2002).Generally, a kinetic approach better represents natural environments since the reactions involving metals in soils do not all occur in a sufficiently short timeline to enable modeling in equilibrium conditions (Al-Fasfous 2005). In fact, the kinetics of certain metal dissolution reactions are so slow that they are practically impossible as compared to other reactions involving metals (Bachmann 2006). Using an equilibrium approach puts all these reactions at the same level by assuming that they all occur instantly. However, the use of kinetics requires data that are not available, especially with regard to kinetics related to reactions with organic matter (Al-Fasfous 2005; Bhavsar et al. 2008; Ge 1999, 2002). In a global approach, such as LCA, integrating a kinetic component would also mean integrating kinetics in emissions and fate, which, along with the complexity of regionalization, would lead to gigantic equation systems and disproportionately complicated data storage and calculations.

Nonetheless, the models are applied to soils, generally using soil solution characteristics as input values (Almas et al. 2006; Bertling et al. 2006; Cloutier-Hurteau et al. 2007; Ge et al. 2005; Meers et al. 2006; Ponizovsky et al. 2008; Shi et al. 2007, 2008; Thakali 2006; Thakali et al. 2006; Weng et al. 2002). However, there is no consensus on which model and parameterization are best suited to soils. In fact, certain studies reveal good model predictions for cation speciation (Ge et al. 2005; Nolan et al. 2003), whereas others resulted in inadequate predictions (Cloutier-Hurteau et al. 2007; Meers et al. 2006). Also, global scale soil solution data are not available, raising the question of whether geochemical speciation models can be used for soils when specific soil solution data are missing. Moreover, since soils are more heterogeneous than water, regionalization and archetype determination—especially the selection of influent soil properties—are more complex.

Alternatively, Owsianiak et al. used empirical regressions instead of speciation models to determine bioavailable fractions through multiple linear regressions performed on field data relating metal speciation (soluble metal concentration or free ion activity) to soil properties (total metal burden, soil pH, and soil organic matter (OM) content) (de Vries and Groenenberg 2009; Groenenberg et al. 2010, 2012; Rodrigues et al. 2010a, b; Römkens et al. 2004). Some authors found that these types of regressions could be applied to a wide range of soil conditions (Groenenberg et al. 2010; Rodrigues et al. 2010a). When comparing the two approaches, Groenenberg et al. concluded that, although empirical regressions can be robust speciation predictors for most cations, they depend on the choice and number of soil properties used and are generally applicable only to the soils that were used to obtain them (Groenenberg et al. 2010, 2012). Groenenberg et al. showed that models yield satisfactory results for a wide range of conditions and are better predictors of extreme conditions, but the results may vary according to model setup and parameterization (Groenenberg et al. 2012). Even so, Groenenberg et al. found that the two methods are equivalent for most soil types and affirmed that further research is required to quantify model uncertainty when the models are used generically (Groenenberg et al. 2012). Also, the use of empirical regressions implies deriving BFs in terms of soluble, free metal ions, or exchangeable metal concentrations, which are not in line with the Clearwater Consensus recommendation to use true solution metal concentration.

The main goal of this project was to determine the bioavailability of Zn in soil at the global scale using a geochemical speciation model with limited soil data (only those available in world soil databases) and soil archetypes in order to facilitate its integration into a global method such as LCA and its generalization to other metals. The first step was to see whether current models can be used since they could represent a quick solution to a significant issue in LCA. The WHAM 6.0 model was selected for this project for several reasons: It is part of the Clearwater recommendations and is commonly used to determine speciation in freshwater and soil solutions (Diamond et al. 2010), it models reactions with OM content and other important metal ligands in soils, and makes it possible to quantitatively input particulate matter, making it simpler to use beyond its standard framework. To test the validity of WHAM 6.0 in this specific case, a literature review was carried out to collect field data on Zn speciation in soils and the corresponding soil properties. BFs were calculated with the collected field data. The speciation of Zn in soils using the same field data was modeled using WHAM 6.0, and a second series of BFs was calculated with these results. These two series of BFs were compared to quantify the differences between field and modeled data in terms of values and ranking. A third series of BFs was obtained with the same field data using empirical regressions in order to compare the use of WHAM 6.0 and empirical regressions. In this regard, the applicability of empirical regressions derived by Groenenberg et al. (2012) to predict soluble concentration for a set of soils that fall in the same range as the one used to obtain the regressions (results are shown in the Electronic Supplementary Material) was tested. Soil archetypes were created to determine the extent of the validation process and applicability of WHAM 6.0 at the global scale by matching field data validation results and the corresponding soil archetype. Archetypes will also be useful to determine generic values when BFs are ultimately integrated into the determination of CFs. The Zn bioavailable fraction was then calculated for each world soil type using a detailed world soil database. Zinc was chosen because it is one of the main contributors to the Canadian ecological footprint for terrestrial ecotoxicity (Lautier et al. 2010). It is therefore crucial to study Zn to determine its true contribution.

2 Methods

2.1 Nomenclature

The following Zn fractions used in this study are illustrated in Fig. 1 and described below.

In this figure, *total Zn* represents total Zn concentration in soil as obtained analytically by using an acid digestion method, except cold or dilute acid extractions (Sauvé et al. 2000). In addition to the elemental form of the metal, it includes at least all the fractions defined here. Part of total Zn, *soluble Zn* stands for total soluble Zn (free ion, ion pairs, and complexes) concentration in soil obtained by extracting soil solution by water or neutral salt extractions, lysimeter, water displacement, centrifugation, or rhizon moisture samplers (Sauvé

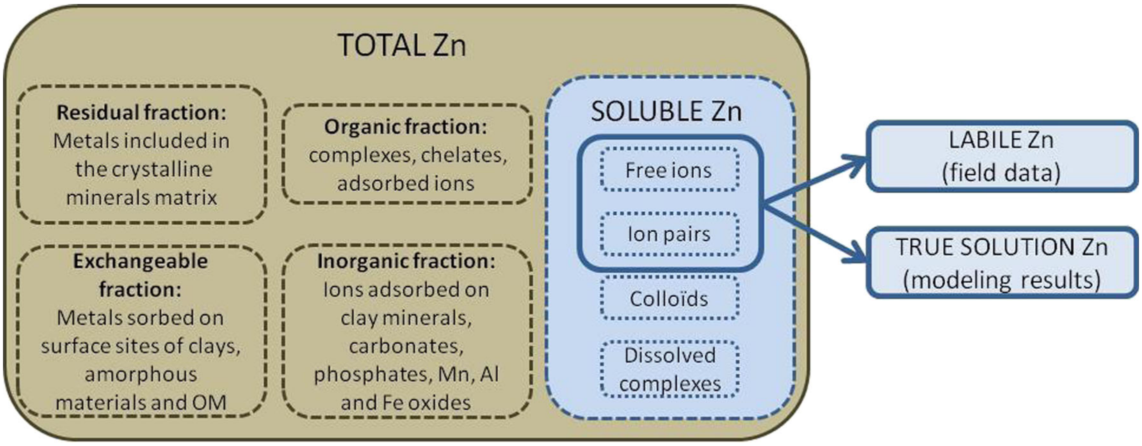


Fig. 1 Description of zinc fractions used in this study

et al. 2000). Part of soluble Zn, *labile Zn* includes free metal and metal ion pairs that can dissociate rapidly in soils. This definition of labile Zn was chosen because it is the experimentally obtained Zn fraction that is the closest to true solution Zn (Nolan et al. 2005). In fact, labile Zn concentrations in soil are obtained by mixing soil samples (1:4 soil/solvent ratio) for 2 h, filtering the supernatant of the soil slurry, adjusting the concentration with KNO_3, and measuring the concentration with square wave anodic stripping voltammetry (Lessard et al. 2013; Stephan et al. 2008). The labile Zn considered here does not include DTPA, EDTA, or acetic acid-extracted Zn since they are much stronger ligands and represent a much higher metal fraction than true solution. The true solution Zn needed to calculate the BF is defined by free Zn ions and ion pairs in soil solution, as modeled by a geochemical model. It is analogous to labile Zn but is obtained in a different way (geochemical modeling vs. field data measurements).

2.2 Use of WHAM 6.0 to obtain Zn bioavailable fraction in soils

2.2.1 BF calculation from literature field data

The first step of this study was to test the use of WHAM when only limited soil data are available. A literature review for Zn soil speciation was therefore conducted in order to compare WHAM 6.0 speciation results and experimental speciation data. In total, 40 soils previously sampled around galvanized Zn structures (Lessard 2013) and 248 additional field samples from 18 published studies were listed (Aldrich et al. 2002; Catlett et al. 2002; Dawson et al. 2006; de Groot et al. 1998; Degryse and Smolders 2006; Ge 1999; Gooddy et al. 1995; Holm et al. 1998; Kim and Owens 2009; Kim et al. 2010; Lorenz et al. 1997; Mallmann et al. 2012; Meers et al. 2006; Muhammad et al. 2012; Nolan et al. 2003; Rheinheimer dos Santos et al. 2013; van Gestel 2008; Wu et al. 2000). The samples provided measurements of soil properties (pH, cation exchange capacity (CEC), texture, OM, and carbonate contents), total Zn and soluble (278), or labile (36) Zn. The soil data that were gathered cover a wide variety of soil properties for the broadest possible validation. A description of the experimental data is available in the Electronic Supplementary Material. For each soil sample, an experimental BF (BF_{exp}) was calculated using total Zn and soluble or labile Zn.

To ensure coherence with work on freshwater ecotoxicity, it was considered that the bioavailability factor (BF) was given by the ratio of bioavailable Zn ($[Zn]_{bioavailable}$) to total Zn ($[Zn]_{total}$) (Eq. 1) (Diamond et al. 2010; Gandhi et al. 2010, 2011b):

$$BF = \frac{[Zn]_{bioavailable}}{[Zn]_{total}} \quad (1)$$

According to available Zn speciation field data, experimental BFs were calculated using soluble and labile Zn to represent the bioavailable fraction of Zn. These BFs are used throughout the study to validate the use of WHAM 6.0 and empirical regressions. Labile Zn was chosen because it is the closest fraction for which field data were available to the bioavailable Zn fraction as defined in the Clearwater Consensus (Diamond et al. 2010). Soluble Zn fraction was chosen because it generally includes most of Zn bioavailable fraction and more field data are available.

In order to obtain dimensionless BFs (mg/L soil)/(mg/L soil), soil density and available water capacity were used to transform concentrations into the proper units (see Electronic Supplementary Material for details).

2.2.2 BF calculation with WHAM 6.0

The WHAM 6.0 model was initially developed to model chemical equilibria in oxic waters (Lofts and Tipping 2001).

It contains sub-models that represent ion binding on humic substances (humic ion-binding model VI) (Tipping 1998) and mineral solids (SCAMP sub-model) (Lofts and Tipping 1998). The latter sub-model contains a surface complexation model to four surface types—silica, iron, manganese, and aluminum oxides—and a cation-exchange model for clays (Lofts and Tipping 1998, 2001). While it does not consider precipitation, WHAM 6.0 was chosen for its coherence with LCA-derived freshwater ecotoxicological CFs (Gandhi et al. 2010, 2011b). The model is also frequently used in soil metal speciation studies and includes data on 19 other common metals, thus facilitating its generalization (Almas et al. 2006; Bertling et al. 2006; Cloutier-Hurteau et al. 2007; Ge et al. 2005; Meers et al. 2006; Ponizovsky et al. 2008; Shi et al. 2007, 2008; Thakali 2006; Thakali et al. 2006; Weng et al. 2002), and makes it possible to quantitatively enter particulate phases as input parameters, thus facilitating its adaptation to soils.

WHAM 6.0 is only applied to field data listing all soil properties (28 for labile Zn and 78 for soluble Zn; see details in the Electronic Supplementary Material) to ensure that divergences are not due to missing data. An exception was made for four peat soils for which texture is not listed to determine whether these extreme soils can also be modeled. However, the results for these samples must be interpreted carefully since their modeling is based on incomplete data.

The objective was to obtain bioavailable Zn fractions at the global scale with limited input data in order to integrate the approach into a global assessment method such as LCA. In this case, global coherence was preferred over precision. For this reason, various assumptions were made to convert soil properties to fit WHAM input parameter requirements. Some may seem quite rough to soil scientists, but the study should be viewed as a first attempt to use a geochemical speciation model for this purpose. This will make it possible to compare and highlight the eventual need to improve the assumptions (or not).

WHAM 6.0 was used with default parameters as if soil was oxic water with a high level of particulate phases (particulate oxides, silica, quartz, clay, and organic matter). Using an oxic model for anoxic conditions could increase the uncertainty since variations in the redox conditions can influence Zn speciation (Bostick et al. 2001). Nonetheless, although soils can be under anoxic conditions, the method was chosen as a first estimate. Also, since LCA models do not consider a very large soil depth (10 cm for USEtox), it seems reasonable to consider oxic conditions.

Particulate silica, quartz, clay, and iron oxide were obtained using soil texture (% sand, silt, and clay); particulate humic and fulvic acids (HA and FA, respectively) were used to account for soil OM content; major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, and Al^{3+}) in solution were obtained with CEC and total Zn; and carbonate content (CO_3), Cl^-, and SO_4^{2-} were entered as solution components. The inclusion of estimated dissolved organic carbon (DOC) as colloidal HA and FA was also tested to determine whether it improves the modeling results. The equations used for WHAM 6.0 modeling data preparation are described in the supporting information.

A second set of BFs was obtained (BF_{WHAM}), and the values and ranking were compared to the values and ranking of BF_{exp}. BF_{WHAM} were first obtained for each experimental sample.

Model predictions were considered valid if a difference of less than 2 orders of magnitude was observed between experimental and modeling results—the acceptable uncertainty in LCA toxic impact assessment (Humbert et al. 2005; Rosenbaum et al. 2008). This uncertainty level is higher than the single order of magnitude uncertainty usually found for speciation models or empirical relations in other studies (Groenenberg et al. 2010; Römkens et al. 2004). However, this work is the first attempt to encompass all soil types, even extreme soils, perhaps creating more bias than in previous, more restricted studies. We are aware that 2 orders of magnitude are the acceptable uncertainty for CF and not BF (i.e., including fate and effect). However, Gandhi et al. and Dong et al. showed that most of the variability of regionalized CFs is attributable to BFs, and the fate and effect factors contribute much less to CF variability (Gandhi et al. 2010, 2011a, b; Dong et al. 2014).We are also aware that this uncertainty of 2 orders of magnitude can be insufficient if the span is of 5 to 8 orders of magnitude. For this reason, the proportions of soils for which BFs fall in the same order of magnitude, in a 1 order of magnitude range, 2, 3, 4, and up orders of magnitude, were also shown. Not all data points must meet this criterion because WHAM used in this context could work for certain soils and not others.

BF ranking was compared using the Spearman rank correlation coefficient. The Spearman coefficient was used by Fenner et al. (2005) to compare the rankings of long-range transport potential estimates of persistent organic chemicals (Fenner et al. 2005). The coefficient was computed with Eq. 2 (Gauthier 2001):

$$\text{rho} = 1 - \frac{6\sum_n d_i^2}{n(n^2-1)} \qquad (2)$$

Equation 2 defines the Spearman rank correlation coefficient (Gauthier 2001).

In Eq. 2, n represents the number of samples, and d_i is the difference between the ranks of the two series (rank_{WHAM}–rank_{exp}). The Spearman rank correlation coefficient is a value between −1 and 1. A value close to 0 indicates no correlation between the ranks of the two series. To determine whether the correlation is significant, a lack of correlation between the two series was assumed. The calculated correlation coefficient was then compared to a critical value representing the correlation coefficient that would be obtained randomly. When two series had more than 30 pairs, as is the case for soluble Zn (with 82 pairs), a t value could be obtained with Eq. 3 and compared to a corresponding critical value in a t table (Gauthier 2001):

$$t = \frac{\mathrm{rho}\sqrt{n-2}}{\sqrt{\left(1-\mathrm{rho}^2\right)}} \qquad (3)$$

In Eq. 3, t value is calculated to evaluate the significance of the Spearman rank correlation coefficients for samples of over 30 pairs (Gauthier 2001). If the absolute value of the correlation coefficient or the corresponding t value for numerous samples is higher than the critical value, the correlation is significant. The root mean square error (RMSE) and the coefficient of determination (R^2) were also determined.

2.3 BF calculation with empirical regressions and comparisons

In order to compare the two approaches, a third series of BFs (BF_{reg}) was calculated with empirical regressions using the same process as the one used by Owsianiak et al. (2013). Dimensionless (mg/L soil/mg/L soil) BF_{reg} was also obtained using the available water capacity, as was done for BF_{exp}. The various empirical regressions and available water capacity values that were used are presented in the supporting information. Comparing BF_{WHAM}, BF_{reg}, and BF_{exp} highlights the advantages of each methodology for the global assessment of Zn bioavailability.

2.4 Defining Zn bioavailable fraction for all soil types

2.4.1 Creating soil archetypes

Soil archetypes were created to determine the extent of the validation and applicability of WHAM 6.0 at the global scale. In fact, they are a way to match field data validation results to analogous world soils, supposing that soils with similar properties will have similar bioavailability factors.

The first step was to determine the most influential properties on Zn speciation. The influence of soil pH is regularly observed in the literature (Brennan 2005; Catlett et al. 2002; Chadi et al. 2008; Kabata-Pendias and Mukherjee 2007; Knight et al. 1998; Nolan et al. 2003). Clay, OM, and oxides are also important ligands for Zn (Aldrich et al. 2002; Brennan 2005; Catlett et al. 2002; Ge 1999; Kabata-Pendias and Mukherjee 2007). For these reasons, the selected properties include pH, OM and carbonate content, CEC, and soil texture (clay and sand fractions). Although oxides are important ligands, they were not considered in the creation of archetypes due to data availability but were nonetheless included in WHAM 6.0 modeling (see Section 2.2.2).

When creating the soil archetypes, the soil properties influencing Zn speciation were used as a basis to establish the different soil archetypes because we believed they would better represent the spatial variability of Zn bioavailable fraction. Of course, soil orders group soils with at least one common feature and certainly affect the definition of soil properties (e.g., proportion of cations and type of organic matter content) (Duchaufour 2001). However, they can also group soils with very different properties. For example, according to FAO90 taxonomy groups in HWSD, eutric regosols can have pH values from 4.4 to 8.8 and total organic carbon from 0.04 to 13.32 %. Knowing that pH and OM content are very influent parameters for metal speciation, these differences are likely to influence Zn speciation. Even so, a table relating soil taxonomy to the archetypes is available in the supporting information.

Data for labile and soluble Zn were treated separately. Multiple linear regressions were performed using XLSTAT software (Addinsoft 2013) with soil samples that contained all soil properties (28 for labile Zn and 78 for soluble Zn). Linear regressions were also performed using the same software for each soil property in order to determine individual influence and include more samples. Soil properties for which $Pr>|t|<0.05$ were considered significantly influent. The results are detailed in the supporting information.

The classification was based on thresholds for each soil property commonly used in literature. Three subgroups for pH (acid, neutral, and alkaline soils), CEC, OM, and carbonate contents were chosen. Clay and sand contents are accounted for in USDA soil texture classes, and the subgroups are presented in the supporting information. Every combination of soil properties using this classification that could be linked to at least one experimental soil was kept as an archetype. The list of archetypes that could be created with experimental soil samples is included in the supporting information.

2.4.2 Defining Zn bioavailable fraction for all soil types—extension of archetypes

The Harmonized World Soil Database (HWSD) version 1.1 (FAO/IIASA/ISRIC/ISS-CAS/JRC 2009) was used. It contains data suited to model some 16,000 soil units and provides information on important soil parameters (FAO/IIASA/ISRIC/ISS-CAS/JRC 2009). Selected properties taken from HWSD are soil pH, CEC, soil texture (% of sand, clay, and silt), carbonate, and OM content. All possible combinations of these soil properties found in HWSD are listed, making it possible to restrict speciation modeling to 5213 samples instead of 16,000 soil units. HWSD statistics are listed in the supporting information.

An estimation of Zn background natural concentration was based on a mean value according to soil texture from (Kabata-Pendias and Mukherjee 2007) (see Electronic Supplementary Material for details on the assumptions). Since current emissions do not occur in pristine soils, a previous emission level of 1 g Zn/l of soil, which represents background anthropogenic emission levels between 510 and 1176 mg/kg (mean 718 mg/kg) according to bulk density of soil, was also considered. These emission levels fall within the range of anthropogenic emission levels according to Kabata-Pendias and Mukherjee (2007). In fact, non-ferric smelters and contaminated sites contain between 443 and 1112 mg/kg of Zn, and the average concentration of Zn in sludge for the EU is around 811 mg/kg. The use of background metal concentration was recommended by the Clearwater Consensus (Diamond et al. 2010), and an average background concentration based on European average metal concentrations in water was applied when developing freshwater BFs (Gandhi et al. 2010).

HWSD statistics are listed in the supporting information. For all properties, only topsoil values were considered, assuming that the topsoil is where most of the terrestrial living organisms are located and most soil emissions occur. Also, the approach is only applicable to the vadose zone of soil, and groundwater was not considered in this study.

BFs were calculated with soluble or true solution Zn obtained using the same assumption for WHAM 6.0 as for experimental soil samples for each of the 5213 soil samples. The soil samples were then grouped into archetypes based on the same classification as the one defined for experimental soil data in order to match experimental data to analogous HWSD soil samples. The model was considered valid for an archetype when WHAM predictions were below 2 orders of magnitude, as compared to experimental data for experimental soil samples comprised in the archetype.

For each archetype, BF minimum, maximum, median, and mean values and an indication of WHAM validation were attributed. A BF variability of 2 orders of magnitude within one archetype was considered acceptable since it corresponds to the acceptable variability between BF_{WHAM} and BF_{exp} and uncertainty in toxic impacts in LCA (Humbert et al. 2005; Rosenbaum et al. 2008). This acceptable uncertainty must be low enough to distinguish between archetypes. Soil maps showing the extent of the validation and BF spread were obtained to target the needs to further extend WHAM parameterization validation and refine the archetype definition, especially in cases in which variability was higher than 2 orders of magnitude.

3 Results

3.1 Zn speciation in soils—field data BFs (BF_{exp})

Figure 2 presents dimensionless (mg/L soil/mg/L soil) labile and soluble Zn BF_{exp}. According to Fig. 2, BF_{exp} span over 5 orders of magnitude (5.77) for labile Zn (2.12E-02 to 3.63E-08) and over eight for soluble Zn (1.44E-08 to 1.68E-01). The span is greater than what was determined for soluble Zn by Gandhi et al. (about 2 orders of magnitude) (Gandhi et al. 2010, 2011b). Since soils are more heterogeneous environments (Sauvé 2002), a larger range for soil BFs, as compared to freshwater BFs, is not surprising. Labile Zn falls in the same range as soluble Zn. It is interesting to note that the span also exceeds the one modeled for Cu and Ni by Owsianiak et al. (2013). This difference could stem from the different speciation patterns between the three metals and the methodological choices made in the two studies.

3.2 BF_{WHAM} calculation with WHAM 6.0

Figure 3 presents soluble and labile Zn BF_{WHAM} calculated with the 84-16 OM assumption and estimated DOC. According to Fig. 3, soluble Zn BF_{WHAM} span over 3 orders of magnitude (1.2E-1 to 2.5E-4) and fall in the range of the BF_{exp} (4.94E-02 to 4.92E-06). Using WHAM tends to overestimate BF values (64 of 82 samples). For most samples (77 of 82), the difference between BF_{WHAM} and BF_{exp} is less than 2 orders of magnitude, the highest being 3.35 orders of magnitude. The soluble Zn Spearman rank correlation coefficient is 0.276, indicating a significant correlation between BF_{WHAM} and BF_{exp} rankings (t value of 2.57 obtained for 80 pairs as compared to a critical t value of 1.99 for a 95 % confidence level) (Gauthier 2001). The labile Zn Spearman rank correlation coefficient is 0.637 (t value of 4.53 as compared to t table critical value of 2 for 32 pairs for a 95 % confidence level), indicating a significant correlation between the BF_{WHAM} and BF_{exp} rankings (Gauthier 2001).

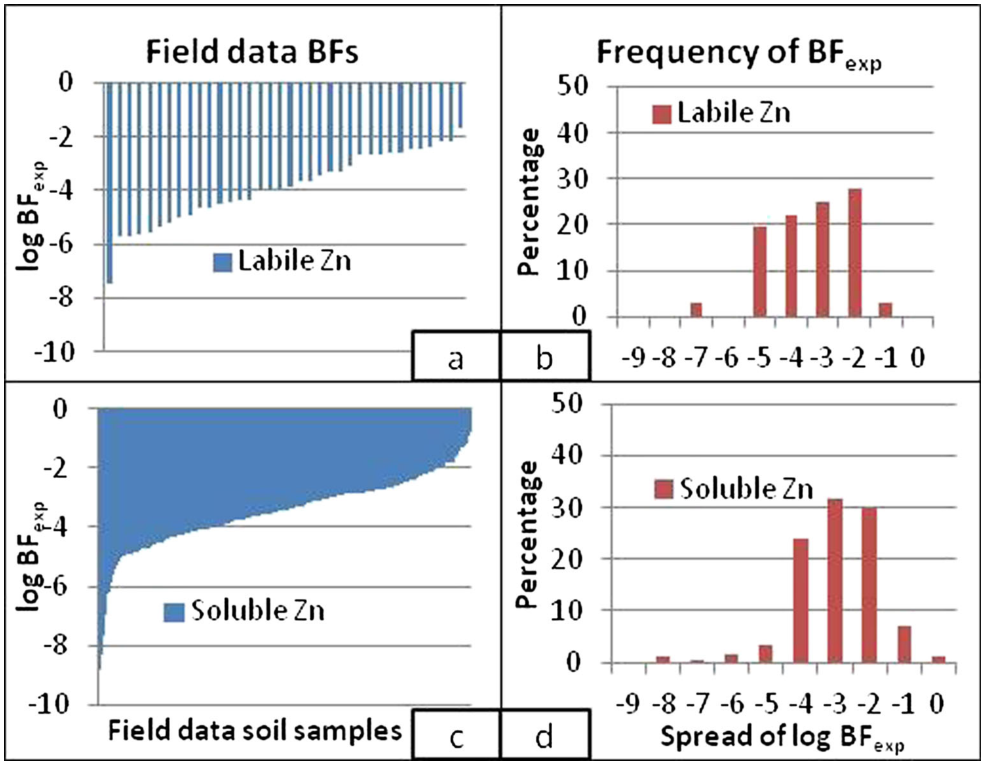
4 Discussion

4.1 BF_{WHAM} calculation with WHAM 6.0

The inclusion of DOC was tested, and the results indicated that the inclusion improves modeling estimates (see results in the Electronic Supplementary Material). Thus, the results are only shown for modeling estimates including DOC.

When looking at soluble Zn, among the 82 samples, BF_{WHAM} fall in the same order of magnitude as BF_{exp} for 34 soil samples (41 %). For 43 samples (52 %), the difference is between 1 and 2 orders of magnitude, and

Fig. 2 BF_{exp} and spread of $\log(BF_{exp})$ for labile (*1a* and *1b*) and soluble Zn (*1c* and *1d*)



for the remaining 5 (7 %), the difference is around 2 orders of magnitude except for two samples for which the differences are 2.79 and 3.35 orders of magnitude. Considering that BF_{exp} for soluble Zn span over 8 orders of magnitude, an uncertainty below 2 orders of magnitude would still make it possible to distinguish the major differences between BFs for soluble Zn. For labile Zn, among the 32 samples, BF_{WHAM} fall in the same order of magnitude as BF_{exp} for 4 soil samples (12.5 %). For 12

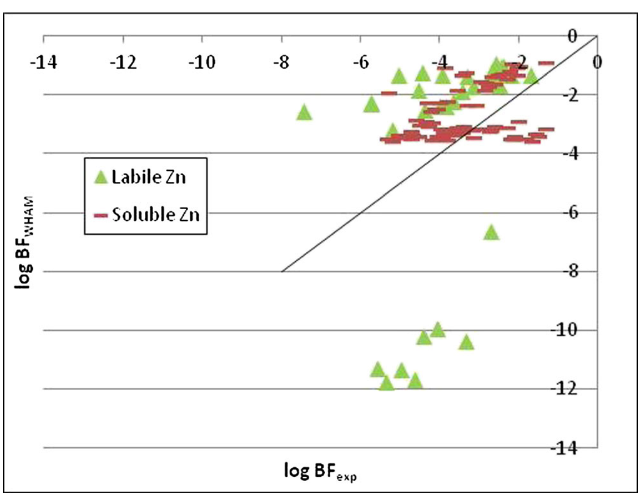


Fig. 3 Comparison of BF_{WHAM} and BF_{exp} for soluble and labile Zn

samples (37.5 %), the difference is between 1 and 2 orders of magnitude; for three samples (9 %), the difference is between 2 and 3 orders of magnitude; and for the remaining 13 (41 %), the difference ranges between 3.18 and 7 orders of magnitude. Considering that BF_{exp} for labile Zn span over 5 orders of magnitude, the uncertainty below 2 orders of magnitude would still make it possible to differentiate between the lowest and highest BFs. This represents some 50 % of soils for labile Zn. For 13 soils, the discrepancies are very high. Among them, nine are soils with a high OM content (between 8 and 70 %) and high CEC (between 29 and 245 cmol/kg), indicating that WHAM 6.0 used in this way may not be appropriate for these types of soils.

The 84-16 OM assumption yielded either the best or an equivalent result for almost all soil archetypes. This assumption and estimated DOC were used to compute worldwide BFs.

Labile Zn measurements are the closest experimental results from true solution Zn modeled by WHAM 6.0. Given the availability of published Zn speciation data, there was generally only one experimental soil sample per archetype, giving a lot of weight to experimental bias. For example, for one soil sample, modifying the pH from 7.2 to 7.6 induced a gap of one order of magnitude in BF_{WHAM}. Moreover, some approximations used in WHAM 6.0 modeling may not be adequate for all soil types. For this reason, we tested various proportions of cations in CEC and oxide types. For some soils, the results varied over several orders of magnitude, indicating that part of the difference could come from inadequate assumptions. In the tested soils, however, the estimates that were initially selected were the closest to the experimental results.

The results confirm that WHAM 6.0 can be used with limited soil data as input parameters to obtain bioavailable Zn fraction, that the results fall in the same order of magnitude for most soil samples (41 %), and that, for the remaining soils, with the exception of two soil samples, the uncertainty is not higher than 2.07 orders of magnitude, still making it possible to broadly distinguish the bioavailable Zn fractions when using soluble Zn as the bioavailable fraction. Also, the soil ranking according to experimental bioavailable fraction and the ranking proposed using the modeled results are significantly correlated. Although the results obtained with labile Zn in soil solution indicate that WHAM 6.0 could also adequately predict true solution Zn (for 50 % of soil samples, the difference was less than 2 orders of magnitude between the 2 BF series and the ranking of BF_{WHAM} was significantly correlated to the ranking of BF_{exp}), further investigation—especially an increased number of validation samples and a different parameterization—is required to confirm the adequacy of using WHAM 6.0 for true solution Zn with limited soil data. Also, it would be interesting to compare the results with the newer version of WHAM. In fact, WHAM 7.0 provides a newer version of the humic ion-binding model (version 7) (Lofts 2012), which could perhaps help solve the problem of soils with high OM content.

4.2 Empirical BFs

Figure 4 shows the soluble Zn BF_{reg} obtained for the soil samples used in WHAM modeling. Since no empirical regression that could allow a comparison with labile and true solution Zn was found for Zn, only soluble Zn obtained by regression was compared.

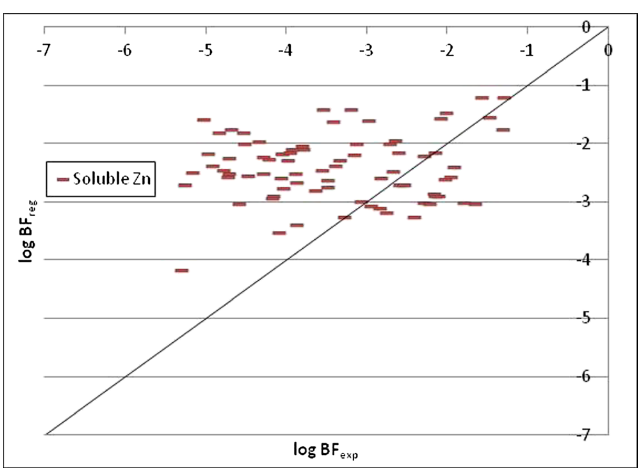


Fig. 4 Comparison between BF_{reg} and BF_{exp} for soluble Zn

According to Fig. 4, soluble Zn BF_{reg} span over 2.98 orders of magnitude (6.37E-02 to 6.74E-5) and falls in the range of BF_{exp} (4.94E-02 to 4.92E-06) obtained for this set of soil samples. As for the use of WHAM 6.0, the use of regressions tends to overestimate BF values (59 of 78 cases). Of the 78 soil samples, 35 (45 %) fall in the same order of magnitude as BF_{exp}. For 27 samples (35 %), the difference is between 1 and 2 orders of magnitude; for 14 samples (18 %), the difference is between 2 and 3 orders of magnitude; and for the remaining 2, the difference is between 3 and 3.44 orders of magnitude (see details in Electronic Supplementary Material). The results are similar to those obtained with WHAM, though the proportion of soils for which results fall within two orders of magnitude as experimental values is lower when using empirical regression (80 % as compared to 93 %). Unlike WHAM, the Spearman rank correlation coefficient is very close to 0 (0.05), indicating that experimental value ranking is not respected when using these regressions.

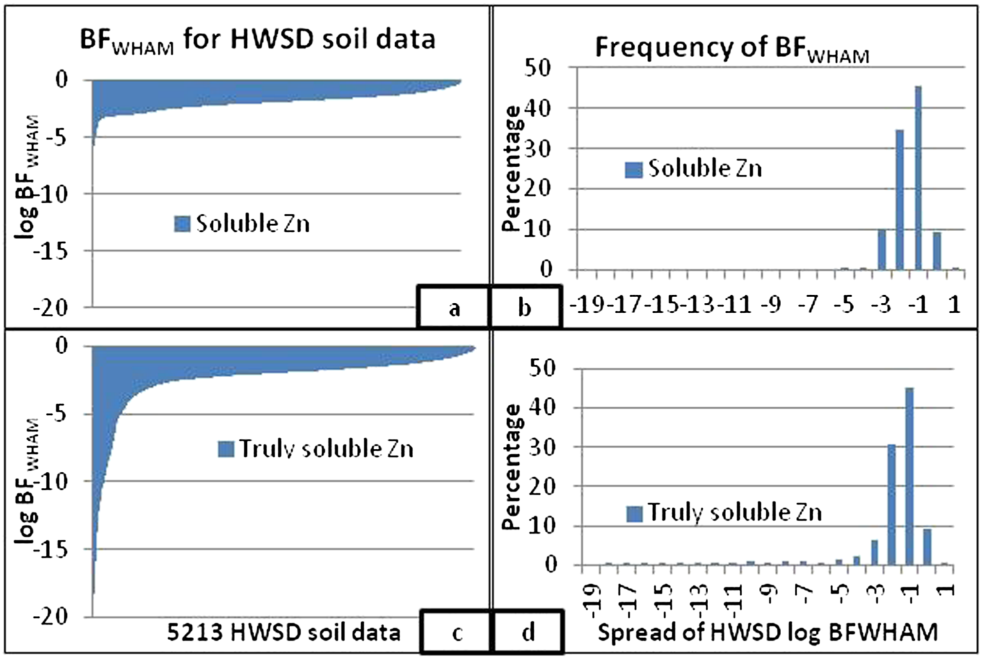
The results confirm that the use of WHAM to represent bioavailable Zn fraction defined as soluble Zn seems to provide better estimates than empirical regressions in terms of rank and value, apparently confirming that empirical regressions are not easily applicable outside the range of soils used to obtain them (Groenenberg et al. 2012) (additional results in the Electronic Supplementary Material).

4.3 Zn bioavailable fraction for worldwide soil types

Figure 5 presents soluble and true solution Zn HWSD BF_{WHAM}. According to Fig. 5, HWSD true solution Zn BF_{WHAM} spread over 18 orders of magnitude (from 4.62E-19 to 8.48E-01), which is much higher than for BF_{exp}. Almost all BFs (98 %) are comprised within the first 10 orders of magnitude, and some 85 % of BFs are in the range, according to Gandhi et al. (2010), between 0 and 0.01. Soluble Zn HWSD BF_{WHAM} are coherent with BF_{exp} (a spread between 1.44E-08 and 1.68E-01).

The next step was to match validation results to HWSD soil types in order to show the coverage of the validation. HWSD soil samples were grouped into 231 soil archetypes (listed in the Electronic Supplementary Material), of which 29 were part of the previous empirical validation. As shown in Fig. 6, these 29 archetypes represent some 25 % of the HWSD soil units. The validation process presented above covers approximately 25 % of HWSD soil units for soluble Zn and only 2.9 % for labile Zn, highlighting the need to further extend the validation process, especially for labile Zn. The soils covered by the validation process (representing one quarter of the earth's soil-covered surface) and for which the WHAM 6.0 predictions that

Fig. 5 HWSD BF_{WHAM} and spread of $\log(BF_{WHAM})$ for true solution (*5a* and *5b*) and soluble Zn (*5c* and *5d*)



fall in the range of less than 2 orders of magnitude are found on all continents and cover some high population density zones, which are assumed likely to receive Zn emissions. This shows that the breadth of the validation process is considerable. For the other 75 %, no experimental data was available to confirm the applicability of WHAM 6.0 for these soils. However, that is not to say that WHAM 6.0 is invalid for the 75 %; it was simply not verified with experimental data. Nonetheless, for at least soluble Zn, BF_{WHAM} fall in the same range as BF_{exp}. It can therefore be assumed that WHAM 6.0 could yield satisfactory results for a greater proportion of soils.

The use of WHAM seems appropriate, and soluble Zn is not necessarily sufficient to define Zn bioavailable fraction. Future studies should therefore consider two options: one that

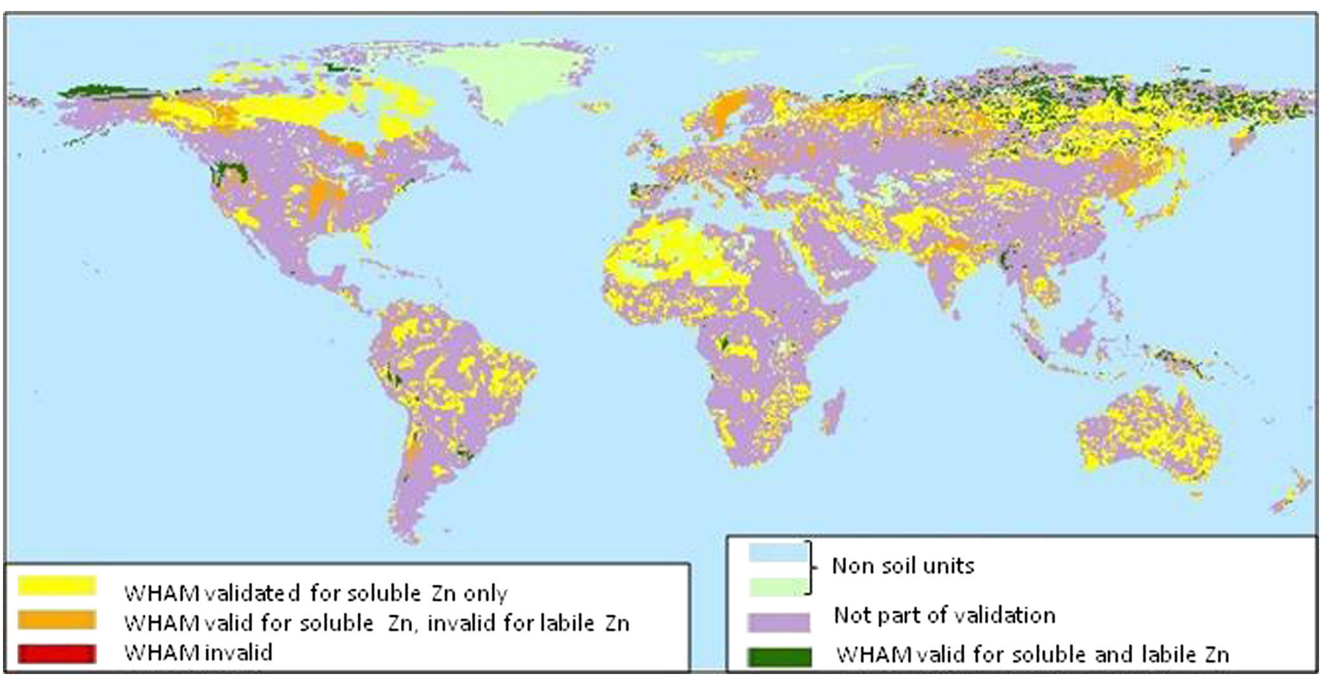


Fig. 6 Extent of WHAM validation for HWSD soil archetypes

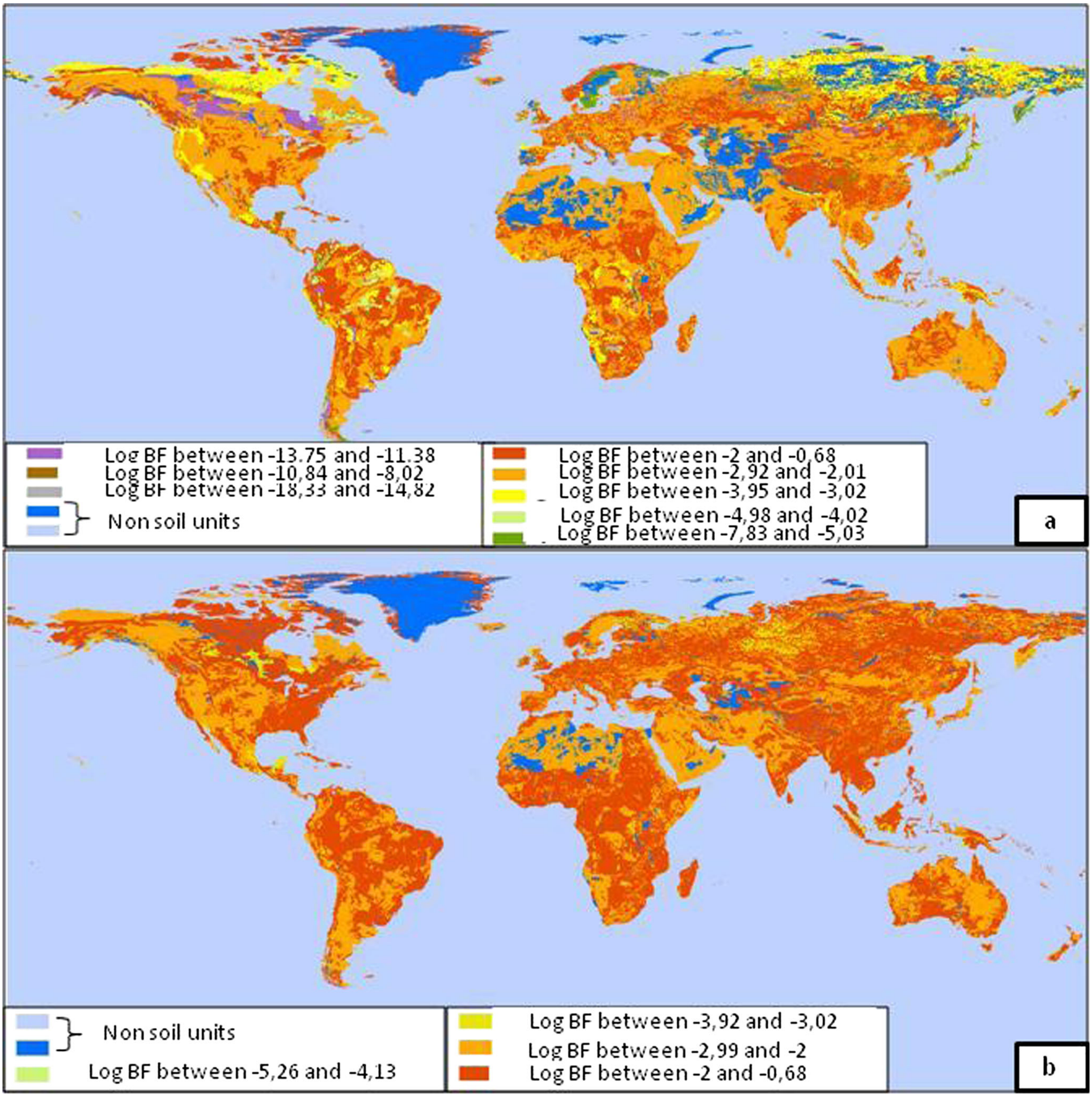


Fig. 7 Mean BF_{WHAM} for HWSD soil data for true solution (*6a*) and soluble (*6b*) Zn

is more representative of the bioavailable fraction of Zn (true solution Zn), but for which the validation coverage is limited, and another validated with more confidence (soluble Zn).

Figure 7 illustrates the mean BF_{WHAM} values allocated for each of the 231 archetypes for true solution and soluble Zn. Looking at the large proportion of mean BF_{WHAM} values between 0 and 10^{-4}, the number of useful archetypes could be reduced. Also, a large proportion of archetypes present variability greater than 2 orders of magnitude (39.9 % for true solution and 27.6 % for soluble Zn). However, although refining is needed, mean values per archetype still represent a broad BF span.

5 Conclusions

The objective of this study was to obtain the bioavailability of Zn in soil at global scale with limited soil data (only those available in world soil databases) to ultimately facilitate its integration into a global method such as LCA and its generalization to other metals. To do so, the method aimed to determine Zn bioavailable fraction with a geochemical speciation model. Since no speciation model has been developed specifically for soils in this context, the usability of WHAM 6 to calculate the Zn bioavailable fraction for world soil types with limited soil input parameters was tested. The results confirm that WHAM can predict Zn bioavailable fractions with an acceptable uncertainty of 2 orders of magnitude for a large proportion of soils (with predictions of the same order of magnitude for 41 % of soils) and that WHAM estimates are better than empirical regression results in terms of rank and value. Soluble Zn seems to constitute a more reliable indicator than true solution Zn when compared to experimental results, except for soils with an OM content lower than 8 %. Zn world BFs span over 6 and 18 orders of magnitude for soluble and true solution Zn, respectively, confirming the importance of considering this variability. The validation work carried out as part of this project is not exhaustive, and there is no certainty that WHAM is a good predictor of true solution Zn if it is a good predictor of soluble Zn. However, it remains an important step in validating the use of WHAM for soils with limited soil data and global scale impact assessments. The use of soil archetypes, created on the basis of the variability of influent soil properties on Zn speciation, was important to gauge the coverage of the validation process. Soil archetypes could also be an interesting avenue to reduce the required number of BF values to a manageable global scale number. This could constitute a promising approach to derive toxicity potentials in LCA. Prior to this redefinition, it must be determined whether validated soils correspond to soils that are more likely to be contaminated by metals in order to target further needs in speciation modeling and validation and focus efforts where they are truly needed. Also, soil archetype definition must be coherent with toxicity potential variability, which may differ since it also accounts for exposure and effect factors.

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