

# Terrestrial ecotoxicity and effect factors of metals in life cycle assessment (LCA)

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Received 25 August 2006; received in revised form 5 March 2007; accepted 12 March 2007

Available online 27 April 2007

## Abstract

Life cycle impact assessment aims to translate the amounts of substance emitted during the life cycle of a product into a potential impact on the environment, which includes terrestrial ecosystems. This work suggests some possible improvements in assessing the toxicity of metals on soil ecosystems in life cycle assessment (LCA). The current available data on soil ecotoxicity allow one to calculate the chronic terrestrial  $HC50_{EC50}$  (hazardous concentration affecting 50% of the species at their EC50 level, i.e. the level where 50% of the individuals of the species are affected) of nine metals and metalloids (As(III) or (V), Be(II), Cr(III) or (VI), Sb(III) or (V), Pb(II), Cu(II), Zn(II) and Ni(II)). Contrarily to what is generally advised in LCIA, the terrestrial HC50 of metals shall not be extrapolated from the aquatic HC50, using the Equilibrium Partitioning method since the partition coefficient ( $K_d$ ) of metals is highly variable. The experimental ecotoxicology generally uses metallic salts to contaminate artificial soils but the comparison of the EC50 or NOEC obtained for the same metal with different salts reveals that the kind of salt used insignificantly influences these values. In contrast, depending on the metallic fraction of concern, the EC50 may vary, as for cadmium: the EC50 of *Folsomia candida*, expressed as free Cd in pore water is almost 2.5 orders of magnitude lower than that expressed as total metal. A similar result is obtained with *Eisenia fetida*, confirming the importance of metals speciation in assessing their impact on soils. By ranking the metals according to the difference between their terrestrial and aquatic HC50 values, two groups are distinguished, which match the hard soft acids and bases (HSAB) concept. This allows to estimate their affinity for soil components and potential toxicity according to their chemical characteristics.

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**Keywords:** Life cycle impact assessment; Metals; Terrestrial; Ecosystems; Risk assessment

**Abbreviations:** AF, assessment factor; AMI, assessment of mean impact; CEC, cationic exchange capacity; CF, characterization factor; CML, centrum voor milieuwetenschappen leiden (Institute of Environmental Sciences, Leiden University); EC, European commission;  $EC_x$ , effect concentration, x% of individuals affected; EcoRA, ecological risk assessment; EDIP, environmental design of product; EF, effect factor; EPA, environmental protection agency (US); EqP, equilibrium partitioning; FF, fate factor; FIAM, free ion activity model; HCX, hazardous concentration, x % of species affected; HSAB, hard soft acids and bases;  $K_d$ , partition coefficient; LCA, life cycle assessment; LCIA, life cycle impact assessment;  $LC_x$ , lethal concentration on x% of individuals; LOEC, lowest observed effect concentration; NOEC, no observed effect concentration; PAF, potentially affected fraction; PNEC, predicted no effect concentration.

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## 1. Introduction

One of the purposes of life cycle assessment (LCA) is to convert the amounts of substances emitted during a product (or service) life cycle into potential impacts on the ecosystems. Metals emitted during the life cycle of different products and substances may particularly generate damages on the ecosystems, especially the soil. However, their specific behavior and impacts on soil organisms have not been adequately considered within the LCA process so far.

In LCIA (life cycle impact assessment), the impact of a substance (on health or ecosystems) emitted in an environmental compartment (air, water, soil) is estimated by

multiplying the mass of substance emitted by a characterization factor (CF). This characterization factor is itself obtained by multiplying a fate factor (FF; describing the fraction of substance transferred from the compartment of emission to the compartment of reception, and its residence time in it) and an effect factor (EF) expressing the effect of the substance on organisms per concentration of exposure.

Because experimental data on soil ecotoxicology are scarce, the soil EF of metals within LCIA is usually estimated by extrapolating the EF on aquatic ecosystems of the same substance, using the equilibrium partitioning method, based on the specific  $K_d$  value of the substance (coefficient of partition between soil and pore water, expressed in  $l\ kg^{-1}$ ).

As recommended in the Lausanne review workshop (Jolliet et al., 2004), the calculation of the EF of a substance shall rather be based on the HC50, i.e. the Hazardous Concentration leading to an effect on 50% of the species, calculated as the geometric mean of all the EC50 available regarding a single substance. For LCIA aims to exhaustively estimate the ecotoxicity of substances, the experimental toxicity data such as the EC50 have to come from tests performed over organisms from a representative portion of the phyla that compose the ecosystems. Hence the EC50 values have to cover at least three phyla ensuring an acceptable representation of the biological variability.

Nevertheless, some LCIA methods such as the EDIP (environmental design of industrial products) (Wenzel et al., 1997; Stranddorf et al., 2003) recommend the use of the predicted no effect concentration (PNEC) as basis for the calculation of effect factors. The PNEC method was initially developed to ensure the protection of ecosystems against pollutants. Such protection levels are estimated using extrapolation factors introducing a bias to ensure a sufficient level of protection. Therefore, the applicability of the PNEC method in a comparative assessment is disputable. Nevertheless, it has been sometime used following Eq. (1).

$$EF = \frac{1}{PNEC_{soil}} \quad (1)$$

where EF is the effect factor and  $PNEC_{soil}$  is the predicted no effect concentration for the soil organisms.

Whenever soil toxicity data are missing, the soil PNECs are extrapolated from aquatic PNECs, by using the partition coefficient of the substance between soil and water through the equilibrium partitioning (EqP) method.

The USES-LCA method (Huijbregts, 1999), recommended by the CML (Guinee et al., 2001) guideline, describes three distinct ways to calculate a PNEC, which is then compared to the predicted environmental concentration (PEC, based on the emitted substances and their predicted fate through the environmental compartments). In the first one, the  $PNEC_{soil}$  is defined as the 50% confidence limit of the concentration that protects 95% of the terrestrial species ( $HC5_{NOEC}$ ), whenever single-specie NOECs are available for four or more taxonomic groups

(Aldenberg and Slob, 1993). In the second, an assessment factors (AF) is applied to the most toxic value, if at least one toxicity value is available without covering four phyla, in accordance to EC technical guidance (European Commission, 2003). In the third one, an extrapolation from the corresponding aquatic PNEC is made by using the EqP method, when no data on terrestrial ecotoxicity are available. The sorption coefficient solid–water ( $K_d$ ) and the bulk density of soil are required.

The current methods of LCIA do not make any distinction between the different kinds of substances and the same method of calculation of EF is indistinctively used for metals and organic substances, for instance the Equilibrium Partitioning. On the other hand the factors controlling the fate and effects of metals in the environment differ from those for synthetic organic compounds (Campbell et al., 2006). For example, metals are infinitely persistent, they are not subject of degradation, but of different (generally reversible) transformations that determine metal speciation. Furthermore, metal bioavailability is affected strongly by their speciation, which is affected by the physicochemical conditions in the medium in much larger extent than most of the organic pollutants. This point is even more relevant for media characterized by an important heterogeneity, such as terrestrial ecosystems.

So far, the relevancy of using the EqP method within LCIA has not been discussed. The major issue regarding the use of EqP in the extrapolation of metals toxicity upon soil organisms is the variability of their  $K_d$  value (Sauvé et al., 2000; Impellitteri et al., 2003) depending on the pH and the organic matter content in the medium.

Therefore, several questions about the calculation of soil effect factors for metals in LCIA remain open, namely: (i) does data availability allow to calculate enough terrestrial effect factors to cover a significant number of the metals quantified through life cycle inventory? (ii) what are the limitations to the applicability of equilibrium partitioning regarding soil  $HC50_{EC50}$  for metals? (iii) what would be the possible improvement of the existing LCIA methods?

## 2. Materials and method

### 2.1. Calculation of the effect factors

As per the state-of-the-art described in introduction, several LCIA methods recommend the use of the PNEC for the calculation of the effect factors. Nevertheless, the use of PNEC in LCIA suffers from several drawbacks, especially the lack of stability. The EF calculated from a PNEC based on the most sensitive specie relies on the choice of the species, and can vary largely whether a very sensitive species is tested or not. Furthermore, the PNEC is based on the underlying assumption of a level of No Effect in the ecosystem, before each emission of a toxic substance, meaning that below this level, all species in the ecosystem are expected to be protected. This assumption is not compatible with the effects model in LCA for the following

reasons: (i) LCA usually considers small amounts of substances, as a consequence of the functional unit chosen. This amount comes in addition to the existing concentration in the environment; (ii) the impact of this very small amount is estimated using a linear model of effect, which is based on the assumption that each emission, even small, of substance in an ecosystem will produce an effect; (iii) the very small amount of substances emitted is generally averaged over a whole continent leading to extremely small changes in concentration. These variations are not likely to lead to an impact, as per EcoRA principles and the use of PNEC; (iv) in LCIA, this change in concentration is integrated over time under a steady state assumption in order to assess potential impact over an infinite time period. This model is irrelevant for EcoRA benchmarks, such as the PNEC, which is compared to the concentration at a precise moment in time.

To avoid using a PNEC based on the most sensitive species, the effect factor can be based on the hazardous concentration (HC<sub>x</sub>), calculated from the species sensitivity distribution. Indeed, the HC<sub>x</sub> value depends less on the variability of the species responses (Van Straalen and Denneman, 1989) than the PNEC.

In the Ecoindicator 99 method (Goedkoop and Sprinensma, 2000), the potentially affected fraction (PAF) per concentration unit in the soil is calculated as a function of the average available NOECs (which can be expressed as the HC50<sub>NOEC</sub>) and the standard deviation of the function. Among all, the chronic HC50<sub>EC50</sub> (see the definition in introduction) is currently considered as the most relevant toxicity parameter to calculate effect factors in LCIA (Jolliet et al., 2004; Ligthart et al., 2004; Pennington et al., 2004). In this way, Payet and Jolliet (2005) developed the assessment of mean impact (AMI), which, unlike the methods based on the most-sensitive-species, aims to establish the mean toxicity level of a given substance. The HC50<sub>EC50</sub> is calculated as the geometric mean of single species chronic EC50 (the concentration leading to an effect on 50% of the individuals), hence the term “Mean Impact”. The EC50 is preferentially used for the calculation, as the NOEC has proven less stable as a toxicity endpoint (Hoekstra and Van Ewijk, 1993; Laskowski, 1995).

The HC50<sub>EC50</sub> is used in the Impact 2002 + LCIA method (Jolliet et al., 2003) to assess the ecotoxicity of substances, whenever the available EC50 values cover at least three phyla. The HC50 are calculated as the geometric mean of at least three terrestrial chronic EC50 and the confidence interval using the Student distribution.

The effect factor is defined as the change in PAF following an increase in a substance concentration (e.g. if emitted during life cycle) according to Eq. (2):

$$EF = \frac{\Delta PAF}{\Delta C} = \frac{0.5}{HC50} (PAF \text{ m}^3 \text{ kg}^{-1}) \quad (2)$$

(from Pennington et al., 2004) where EF is the Effect Factor and  $\Delta PAF$  the change in potentially affected fraction due to an increase in concentration ( $\Delta c$ ).

## 2.2. Equilibrium partitioning

The equilibrium partitioning (EqP) is generally used to predict the partition of a substance between two compartments of a given medium, mainly sediment solid phase and pore water (Hansen et al., 2005). The EDIP method (Wenzel et al., 1997; Stranddorf et al., 2003) recommends the use of EqP to extrapolate soil PNEC from aquatic PNEC, by using the substance partition coefficient ( $K_d$ ) between soil and water (Wenzel et al., 1997).

$$PNEC_{\text{soil}} = PNEC_{\text{aq}} * (K_d + 0.27) \quad (3)$$

where  $K_d$  is the adsorption coefficient and 0.27, the mean fraction of water contained in soil.

This method is also used in the Impact 2002 + method (Jolliet et al., 2003), using the aquatic HC50 and soil bulk density. So far, the relevancy of EqP to predict toxicity in soil has only been discussed by Van Beelen et al. (2003), who compared terrestrial EC50, NOEC and HC5 calculated from aquatic values using EqP with the same values based on experimental data. Regarding the metals, the  $K_d$  value is selected among a wide range, what makes the extrapolation of terrestrial toxicity values uncertain. Wenzel et al. (1997) also advised that the EqP method is not appropriate for extrapolating the terrestrial effect factors of metals. Nonetheless, the EqP is generally recommended in LCIA methods without any distinction between the different types of substances.

In order to improve the calculation of terrestrial EF in LCIA, terrestrial ecotoxicity values of metals in soil were extracted from the main available databases (mainly EPA’s “ecotox”). The HC50 calculated with these values were compared with the HC50 obtained by using the EqP method. The extrapolation is based on the chronic aquatic HC50 values available in the AMI database (Payet, 2004).<sup>1</sup>

## 2.3. Soilwater partition coefficient

The  $K_d$ , defined as the partition coefficient of a substance between the solid phase of soil and pore water (expressed as the ratio of concentration in soil ( $\text{mg kg}^{-1}$ ) to concentration in pore water ( $\text{mg l}^{-1}$ ) in  $\text{l kg}^{-1}$ ) is a key parameter to assess the behavior and toxicity of substances (Leo, 2000).

As mentioned in the introduction, the range of  $K_d$  values may nevertheless be wide for a metal and the EqP method inapplicable in this case. In order to verify this point, the EqP was tried to be implemented for metals. However, since a single  $K_d$  value per substance needs to be used, the EPA’s  $K_d$  values (Ambrose, 1999), based on the median of calculated  $K_d$  values for each metal in various media, were used to transpose aquatic HC50 of nine metals into terrestrial HC50.

<sup>1</sup> The AMI aquatic Effect Factors database is available on request to [jerome.payet@epfl.ch](mailto:jerome.payet@epfl.ch).

#### 2.4. Databases and choice of data for LCIA

Whereas aquatic toxicity values are really numerous, the data concerning terrestrial toxicity of substances are relatively limited. Four databases were used in this work as sources of EC50 data to calculate the HC50. The US EPA database (<http://www.epa.gov/ecotox/>) gathers terrestrial toxicity data from 1915 to 2006. The most frequently found endpoints are the EC50 (6246 data), the LOEC (1578 data) and the NOEC (1268 data). By selecting the endpoints of interests (EC50 and NOEC), the number of usable values decreases hugely (2545 values only, representing ~1% of the database).

In order to improve the reliability of the HC50, the number of EC50 and NOEC values was increased by using ecotoxicity data from the German ECT institute.<sup>2</sup> As per the AMI requirements, the number of EC50 values in this database was sufficient to calculate the chronic terrestrial HC50 of Cr, Pb, Cd, Cu, Ni and Zn. Because all the values found in the ECT database have not yet been published, the EPA data were used to calculate HC50 in preference to the ECT value whenever the HC50 can be calculated using either the EPA or the ECT database.

Two other additional sources of ecotoxicity data can be used: The French National Institute of Industrial Environment and Risk (INERIS) provides chronic ecotoxicity data (EC50 and NOEC) regarding zinc, lead and copper ([www.ineris.fr](http://www.ineris.fr)). Finally, some data from Fountain and Hopkin (2005) were also included.

The relevant values for the calculation of terrestrial HC50 were extracted from the above mentioned databases through specific parameters that had to be constant: the endpoint, the concentration unit, the phyla and the test duration. The EC50 can describe many types of effects, but the values describing infraspecific or supraspecific type of effects, such as cellular modifications (in isolation), changes in community or microbiological processes in soil were not included in the calculation. The types of effect selected for this work are the lethality, effect on reproduction and reduction of growing/seedling (plants).

#### 2.5. Exposure pathway and unit

In order to simulate soil conditions, data from tests with contaminated soil or multi-exposure tests only were selected, whereas dermal spray or contaminated food do not bring the same type of information. Moreover, in order to calculate a metal Characterization Factor, the toxic concentration included in the effect factor has to be expressed in  $\text{mg kg}^{-1}$  or  $\text{kg m}^{-3}$  (or  $\text{mg l}^{-1}$ , what describes the concentration of the substance used to contaminate the soil. This value is converted using the average mass fraction of water in soil: 0.27, as described in Wenzel et al., 1997),

what is not the case in tests with contaminated food or dermal spray for instance.

#### 2.6. Toxicity of metal applied as various salts

In ecotoxicity tests, the metals are applied as metallic salts (chloride, nitrate, sulfate, ...) or oxides but the toxic endpoint (EC50 or NOEC for instance) is calculated as the toxic concentration of pure metal by using an appropriate conversion factor. For the same metal, several EC50 corresponding to different tested salts might be found for the same organism. As the salt used does not influence the EC50 value for pure metal (see after), the geometric mean of the values was calculated and used as the EC50 value for the metal in question.

#### 2.7. Organisms of interest

As the potential effect of metals on terrestrial ecosystems in LCIA is assessed through their concentration in soil, the EC50 and NOEC of soil dwelling organisms only have been selected. The three main organisms found in the mentioned databases and used in this work are *Folsomia candida* (arthropod), *Eisenia fetida* (annelid) and *Lactuca sativa* (plant). This work is however based on EC50 values from a total of 72 species. The  $\text{HC50}_{\text{EC50}}$  of a metal must be calculated with EC50 values (or NOEC) from three phyla at least.

#### 2.8. Representation of phyla and organisms

The EC50 concerning at least three different phyla (including plant in almost all the cases) are used in the calculation of the HC50, what ensures a good representation of a natural ecosystem. However, toxicity data are sometimes numerous for a specific phylum (e.g. metal toxicity on plants), what influences the HC50 toward this phylum specific sensitivity. If a phylum is under-represented within all the EC50 values used to calculate the HC50, the EC50 value of the species from this phylum are likely to be out of the confidence interval of the HC50. In this situation, the HC50 may not be representative of the ecosystem, what can be compensated by removing some EC50 values of the over represented phylum from the calculation. For instance, one single value can be kept for all the species from the same genus or order (e.g. monocotyledons), either by selecting the most robust or liable, or by calculating the average value for this group.

#### 2.9. Test duration

The last selection criterion is the exposure time: the toxicity of substances should be assessed through long-term data rather than short term data. Attempting this, the main issue is to establish the limits of chronic exposure. Basing ourselves on standardized tests, we select tests with an exposure length of 14 days and more.

<sup>2</sup> Courtesy of Dr. J. Römbke. This source is not of public domain but the majority of data it contains are taken in reviewed or published articles.



### 3. Results and discussion

#### 3.1. Calculation of terrestrial chronic $HC50_{EC50}$

Table 1 shows the terrestrial  $HC50$  and effect factors of nine metals calculated on the basis of chronic terrestrial  $EC50$ . A special attention is given to chromium, which is found under two major oxidation states (III and VI). Cr(III) is usually found in anoxic conditions and has a low toxicity on organisms and Cr(VI) in oxic conditions with high toxicity (Gauglhofer and Bianchi, 1991). The results of tests found in databases are usually made with one form or the other; thus, a specific effect factor can be calculated for each form. Because sufficient data on Cr(VI) effects on three phyla could not be found, an exception was made regarding the three-phyla requirement in this case and the EF was calculated with  $EC50$  values from two phyla only. In conformity with literature data, the toxicity of Cr(III) is lower than Cr(VI). Consequently, the application of the EF for Cr has to be adapted to the proportion of each form in the medium of concern. The interval of confidence for Cr (either III or VI) is relatively narrow, what seems to prove that Chromium equally affects several types of organisms from various phyla. Contrarily, the confidence interval around the  $HC50$  of nickel, antimony or arsenic appears wider, what can be a trend of contrasts in the response of the organisms to these metals.

Logically, the metals with the lowest  $HC50_{EC50}$  have the highest effect factors, what in LCIA is visible as a high potentially affected fraction of the species in the ecosystem per concentration unit in soil. These are Cr(VI), As(III or V) and Cd(II), whereas Pb(II) and Cr(III) would prove lower contribution to the terrestrial toxicity in LCIA, as per the effect factors.

#### 3.2. Influence of metal salt nature in the assessment of metal toxicity

In the ecotoxicity tests performed with metals, different salts are used for soil contamination (chloride, nitrate, and sulfate) and the toxic concentration of metallic salts are

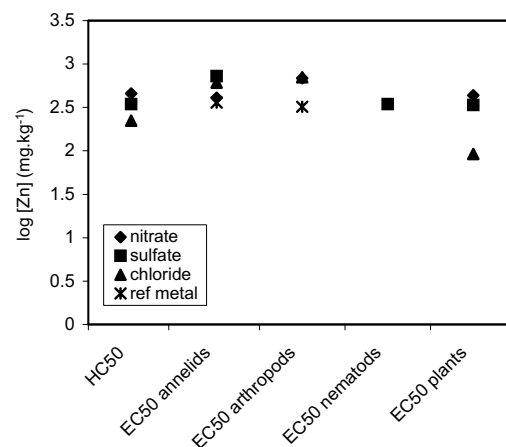


Fig. 1. Comparison of zinc  $HC50/EC50$  estimated with nitrate, sulfate and chloride (in EPA terretox, an  $EC50$  for metal is also given, here as “ref metal”).

then converted in the equivalent toxic concentration of metal. Therefore, Fig. 1 shows the comparison of the  $EC50$  values for annelids, arthropods, nematods and plants experimentally obtained with zinc under several salt compounds, as found in the databases mentioned earlier. Each zinc salt  $EC50$  is converted into a pure zinc  $EC50$ , hence the possibility to compare the different values. For most of the observations, the  $EC50$  varies insignificantly between the tested salts.

#### 3.3. Comparison between metal fractions and $EC50$ 404 values

Fig. 2 indicates that  $EC50$  of Cd on *Folsomia candida* and *Eisenia fetida* varies depending on whether the total metal concentration or a specific fraction of metal is considered. In this test (Vonk et al., 1996), the  $EC50$  has been based on the total concentration of Cd in soil ( $Cd_{soil}$ ), Cd in the pore water ( $Cd_{pw}$ ), and Cd in the pore water as free cation ( $Cd^{2+}$ ), assuming the existence of an equilibrium among the different fractions. Thus the  $EC50$  expressed as free Cd in the pore water was 2.5 orders of magnitude

Table 1  
Terrestrial  $HC50$  and effect factors of nine metals

CAS	Element	Log terr. $HC50_{EC50}$ (mg kg <sup>-1</sup> soil)	Nb of $EC50$ available (single species)	Confidence interval 95%	Effect factors (PAF m <sup>3</sup> /kg)
7439921	Lead (II)	3.13	8	[2.83–3.43]	$3.723 \times 10^{-4}$
7440020	Nickel (II)	2.04	6	[0.70–3.39]	$4.517 \times 10^{-3}$
7440360	Antimony (III) or (V)	2.09	4	[1.04–3.14]	$4.029 \times 10^{-3}$
7440417	Beryllium (II)	1.63	4	[1.36–1.90]	$1.181 \times 10^{-2}$
7440439	Cadmium (II)	2.23	16	[2.05–2.42]	$2.926 \times 10^{-3}$
7440473	Chromium (III)	2.76	4	[2.50–3.02]	$8.703 \times 10^{-4}$
7440473	Chromium (VI)	1.45	14	[1.17–1.73]	$1.766 \times 10^{-2}$
7440508	Copper (II)	2.54	35	[2.34–2.75]	$1.427 \times 10^{-3}$
7440666	Zinc (II)	2.58	37	[2.46–2.69]	$1.328 \times 10^{-3}$
7440382	Arsenic (III) or (V)	1.40	4	[0.73–2.08]	$1.971 \times 10^{-2}$

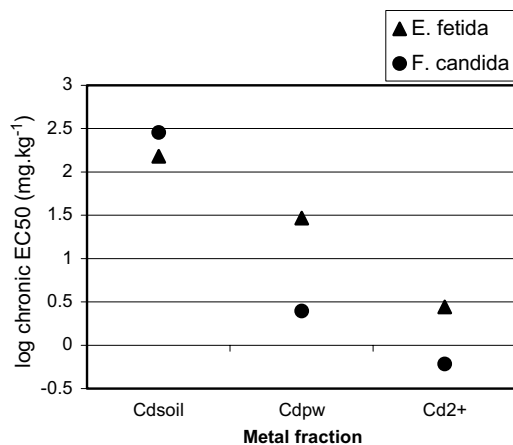


Fig. 2. Variation in Cd chronic EC50 on *Folsomia candida* (after Vonk et al., 1996) (●) and *Eisenia fetida* (after Vonk et al., 1996) (▲).

lower than that expressed as the total metal. A similar observation had been made by Lanno et al. (2004) who indicates that the toxic value for the extractible fraction is lower than the total metal LC50 for *E. fetida*, as well as Parker et al. (2001) regarding the toxicity of Cu and Zn on plants. These observations may be extended to the other metals forming free cations such as Cu(II), Zn(II), Ni(II), Cr(III), Pb(II).

These results confirm the importance of the metals speciation and free metal ion concentration (Free Ion Activity Model, FIAM; Anderson et al., 1978), in the assessment of the ecotoxicological effects of metals on the organisms. Given that the distribution of the metals, e.g. Cd among the different fractions including free metal, depends on soil physico-chemical conditions, in particular pH, organic matter, cationic exchange capacity (CEC), redox potential and content in clay (Crommentuijn et al., 1997), the further implementation of the FIAM in LCIA will allow to take implicitly the role of the medium physicochemistry on ecotoxicity and improve further the existing LCIA methodology.

### 3.4. Evaluation and improvement of equilibrium partitioning model (EqP) applicability for metals in soils

In order to verify their validity, the HC50 calculated by using EqP extrapolation of aquatic HC50 (also named hereafter EqP HC50) and the calculated HC50 (on the basis of chronic terrestrial EC50) were compared. The regression analysis reveals an insignificant correlation ( $r^2 = 0.005$ ,  $P$  value  $> 0.05$ ) between those values, confirming that calculating the HC50 by using the EqP method is irrelevant for metals.

In addition, while EqP HC50 values range over 3 orders of magnitude, the HC50 calculated from terrestrial EC50 range over an interval of magnitude of 1.5. The above results suggest that EqP HC50 values are either over- or underestimated, in line with the findings from Van Beelen et al. (2003).

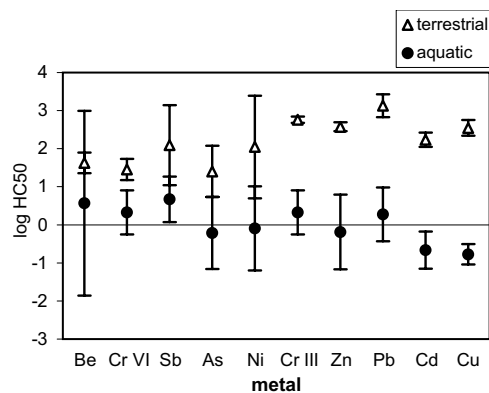


Fig. 3. Aquatic and terrestrial HC50 of nine metals ranking according to the gap between aquatic and terrestrial HC50, respectively in  $\text{mg l}^{-1}$  and  $\text{mg kg}^{-1}$ .

In order to explore a possible correlation between aquatic and terrestrial toxicity of metals, the chronic aquatic HC50 of each of the nine metals were compared with the chronic terrestrial HC50 that have been based on experimental EC50, as shown in Fig. 3. The metals are ranked according to the increasing difference between terrestrial HC50 and aquatic HC50 values.

As per Fig. 3, two groups of metals can be distinguished in line with “hard and soft acids and bases”, HSAB concept (Pearson, 1973). Accordingly, the cations are considered to be Lewis acids and the ligands to be Lewis bases that act as electron donor and acceptor to form complexes. This concept is applied to explain the strength of metal complexation and toxicity. Most toxic in soils (low HC50 value), Cr(VI), Sb(III) or (V) and As(III) or (V) are assigned to the group of “hard bases”, they have a preference to bind to the “hard acids” such as Fe(III); Al(III) etc. largely present in the mineral fraction of soils. The second groups includes Pearson “acids”: Cr(III), Ni(II), Zn(II), Pb(II), Cu(II) and Cd(II) that seem to be less toxic in soils (high HC50). Among them the soft acid Cd(II) and borderlines Ni(II), Zn(II), Pb(II) and Cu(II) have high affinity to the soft bases such as  $-\text{SH}$ ,  $-\text{NH}_2$  found as a binding ligands on the external or internal surfaces of organisms. The observation of Fig. 3 suggests the following interpretation: in soils with pH close to 7, hard acids are likely to form hydroxyl compounds in soil water, reducing their ability to bind with organic matter, thus remaining largely bioavailable, compared to Pearson acids, which link easily with soil organic matter thus show a reduced bioavailability in soil.

Interestingly the chronic aquatic HC50 are about 2 orders of magnitude lower than terrestrial HC50 for the same metal in the case of Ni(II), Cd(II), Cu(II), Cr(III), Zn(II) and Pb(II), while it is about 1 order of magnitude for Cr(VI), Sb(III) and As(III). This difference is in line with the postulate above: considering that soil media is characterized with a higher fraction of organic matter than aquatic test media, the toxicity of Ni(II), Cd(II), Cu(II), Cr(III), Zn(II) and Pb(II), decrease strongly (reduction of

the bioavailable fraction), while Cr(VI), Sb(III) and As(III) remain toxic since they do not bind so easily to organic matter in soil. Be(II) is the only one that does not fit with this assumption; nevertheless, compared to the others, its HC50 is based on a small number of data and that is revealed by its very large confidence interval. This uncertainty in the calculation of the aquatic HC50 suggests beryllium should be considered as an outlier in Fig. 3.

### 3.5. Calculation of terrestrial effect factors within life cycle impact assessment

The effect factors of nine metals and metalloids (As, Be(II), Cd(II), Cr(III), Cr(VI), Cu(II), Ni(II), Pb(II), Sb and Zn(II)) in soils are calculated using the chronic HC50 (Table 1).

In LCA, the calculation of the impact on ecosystems is performed by multiplying the change in concentration of a substance in the environmental compartment considered (water or soil) by the corresponding effect factor. As mentioned above, the metals showing the highest PAF per concentration unit are chromium(VI), arsenic(III or V) and cadmium(II), whereas lead(II) and chromium(III) prove the lowest impact on soil per concentration unit.

## 4. Conclusions

As per the requirements to provide reliable damage factors on terrestrial ecotoxicity, the Effect Factors of 9 metals obtained during this work can be used within LCIA. Based on experimental EC50 and HC50, which prove robust parametric toxicity endpoints, these EF are thus more relevant and reliable than EF extrapolated from aquatic HC50. For the equilibrium partitioning method appears irrelevant to extrapolate the terrestrial chronic HC50 of metals from aquatic chronic HC50, because it is based on  $K_d$ , which is highly variable for metals in soil. Indeed, the  $K_d$  value of metals varies depending on the soil pH, organic matter content or CEC, hence the impossibility to use one single  $K_d$  value to extrapolate the terrestrial HC50 of a substance. Through this work, almost all the metals found in life cycle inventory are covered and their EF factors can be implemented, though constant updates would help refining these values. This work points out the necessity to improve the consideration about the terrestrial ecotoxicity of metals in LCIA, especially concerning the equilibrium partitioning and  $K_d$ , which shall not be used for metals in any case.

The comparison of several EC50 found with different salts associated to the same metal present little differences between the values. Thus, the distinction between the different salts of a single metal might not be relevant regarding terrestrial ecotoxicity in LCIA. Whenever some metallic salts are emitted during life cycle, the concentration of pure metal in the different media shall be calculated in order to assess the effect on terrestrial ecosystems.

A recurring aspect of this work remains the importance of physico-chemical conditions in the medium in the assessment of metal toxicity; as described earlier, the elementary structure influences the ability of metals to bind either to mineral components or organic matter, what will strongly influence their bioavailability and toxicity toward organisms.

The assessment of the global impact on terrestrial ecosystems within LCIA is currently limited to the impact on soil organisms only. Terrestrial vertebrates could be of interest but require a complex modeling that is not currently feasible due to the lack of available data on toxicity upon terrestrial vertebrates and the multiple exposure pathway that should be considered.

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