



METALS ENVIRONMENTAL RISK ASSESSMENT GUIDANCE

FACT SHEET

MERAG

06

INCORPORATION OF BIOAVAILABILITY FOR SOILS



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This fact sheet describes the implementation of bioavailability in soil. It therefore builds further on the general concepts developed within fact sheet 5: Incorporation of bioavailability for water, soils and sediments version (September 2006).

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The content of the MERAG fact sheets reflect the experiences and recent progress made with environmental risk assessment methods, concepts and methodologies used in Chemicals Management programs and Environmental Quality Standard setting (soil, water, sediments...) for metals. Since science keeps evolving these fact sheets will be update on a regular basis to take into account new developments. To be sure you have the most recent fact sheet on the current subject check our website: www.metalsriskassessment.org.

4. IMPLEMENTATION OF BIOAVAILABILITY: SOIL

4.1 General concept

The bioavailability of metals and metal compounds in soils is governed by pH, Eh, organic matter, clay content, iron and manganese oxide content and mineralogy of the parent material (including relative abundance of competing cations and anions). This determines the amount and type of metal species available for uptake by plants, invertebrates, and soil microorganisms, and the resulting toxic response or bioaccumulation of metal. In addition to the immediate, short term effects of soil characteristics on metal bioavailability, it has also been shown that time of contact between soil and metal is a critical factor in determining bioavailability for most metals (ICMM, 2001). Long term changes in bioavailability are due to phenomena such as the progressive leaching of more soluble cations and anions reducing the ionic strength of the soil solution, inclusion of natural elements into the crystal lattices of soil minerals, the formation of insoluble precipitates, diffusion of metals into micro pores, etc. These processes significantly influence the bioavailable fraction of metals, thereby changing the soil toxicity profile over longer periods of time. Both the short term and the long term processes, ultimately determine the real bioavailable fraction. As currently the real bioavailable fraction can not be estimated, both a soil dependent- and lab-to-field depended correction factor are needed to translate results obtained from laboratory experiments to the field. In that perspective, the application of bioavailability concepts to the soil compartment consists of two parts, as visualized in Figure 11. First, the conventional estimated effect thresholds (i.e. PNEC value, NOEC values, soil quality criteria) are adjusted to take into account the soil conditions prevailing in a certain region or for a certain continent-wide percentage of soils, using either transformation to soluble fractions or speciation and bioavailability algorithms (e.g. the free metal ion, regressions). Once the immediate effects of different soil types are taken into consideration, a soil lab-to-field factor is applied in the second step yielding the final bioavailable fraction. It must be stressed that the latter correction is not needed at all, if one would have toxicity data from field contaminated soils.

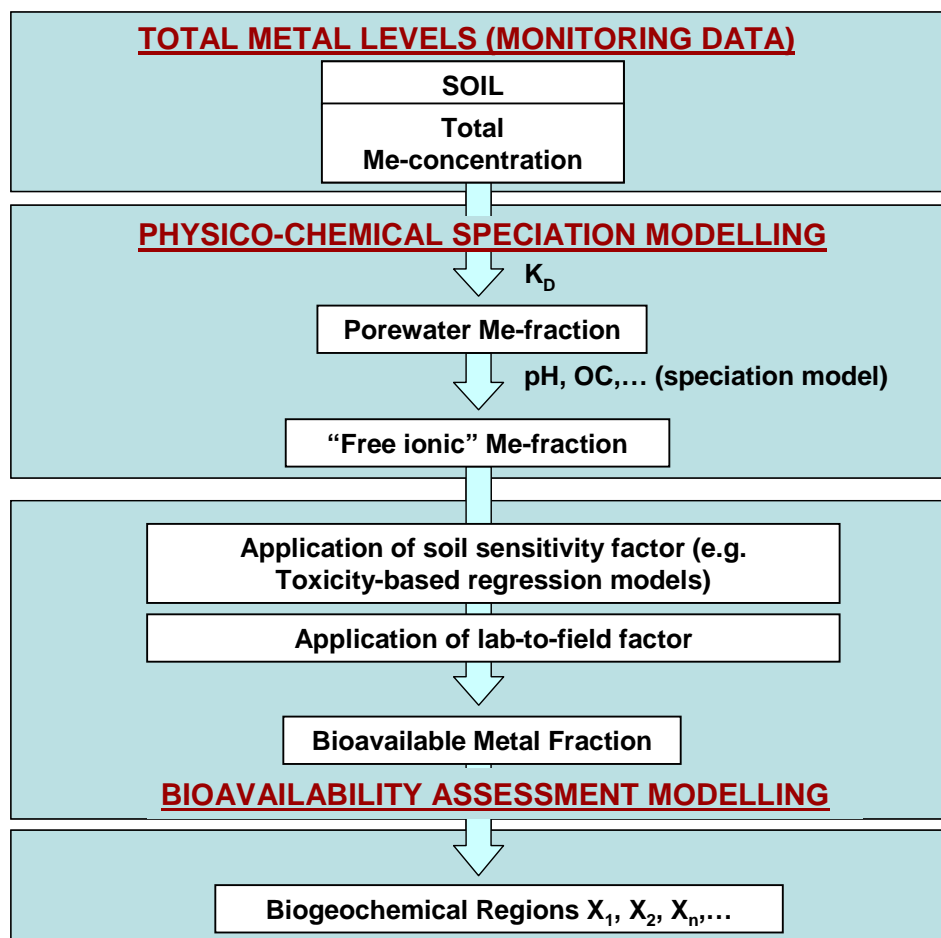


Figure 11: Refinement levels for the incorporation of bioavailability concept for the soil, compartment.

Information on the main abiotic factors controlling metal bioavailability needs to be collected in order to apply the speciation or toxicity models. These types of data can be obtained from existing monitoring databases (regional scenario) or from specifically tailored monitoring campaigns (local scenario). Depending on the scenario and purpose of the assessment low/high (reference) or typical values (typical at local or regional scale) of the modifiers of soil metal toxicity and/or bioavailability should be selected and incorporated in the appropriate model. The realistic worst case scenario is used as a reference scenario when correcting bioavailability with toxicity models, providing a $PNEC_{bioavailable\ reference}$ or $Species\ Sensitivity_{bioavailable\ reference}$ ($Tox_{bioavailable\ reference}$) corresponding to a maximum bioavailability. A simple combination of low/high values may not result in a realistic scenario when influencing parameters co-vary. Therefore, where different parameters influence the bioavailable fraction of the metal, the reference scenario should as far as possible be a realistic combination of the relevant soil parameters. The plausibility of such combinations should, therefore, carefully be assessed and take covariance into account when possible.

When deriving a bioavailability factor for a specific location or region, site or region specific conditions are used when correcting bioavailability with toxicity models, providing $PNEC_{bioavailable\ reference}$ or $Species\ Sensitivity_{bioavailable\ reference}$ ($Tox_{bioavailable\ reference}$)

Where possible, the complete effects data set should be normalized. This assumes that reported effects data contain information on the soil bioavailability parameters that were present in the test system. When bioavailability information is not provided such data can not be normalized and used to derive a $PNEC_{bioavailable}$.

Finally, comparing these $PNEC_{bioavailable}$ values with the outcome of the exposure assessment reported at the same level of bioavailability (i.e. expressed in the same units e.g., total vs total) provides

information on the potential risks associated with that specific metal in that particular regional or local scenario. Depending on the knowledge and availability of bioavailability translators (i.e. the established relationships (models) between toxicity and the physico-chemistry of the soils) different approaches can be used to 'translate' the effects data to bioavailable metal fractions in representative specific soils. These different approaches are discussed in the subsequent sections.

4.2 Use of transformation to pore water fraction

In cases where ambient total metal concentrations are reported and no appropriate bioavailability models and/or relevant input data (i.e. physico-chemical parameters) are available, the risk characterization could be performed on a dissolved pore water basis using the solid-solution partitioning of the metal of interest as outlined in Figure 12. The use of this approach is only recommended in case of clear quantitative evidence that the pore water normalization better approximates the toxic fraction than does the total concentration of metal. Evidence that pore water normalization approximates the toxic fraction better than the total concentration is provided in case a clear reduction in intra-species variability of toxicity data is achieved after incorporation of the concept.

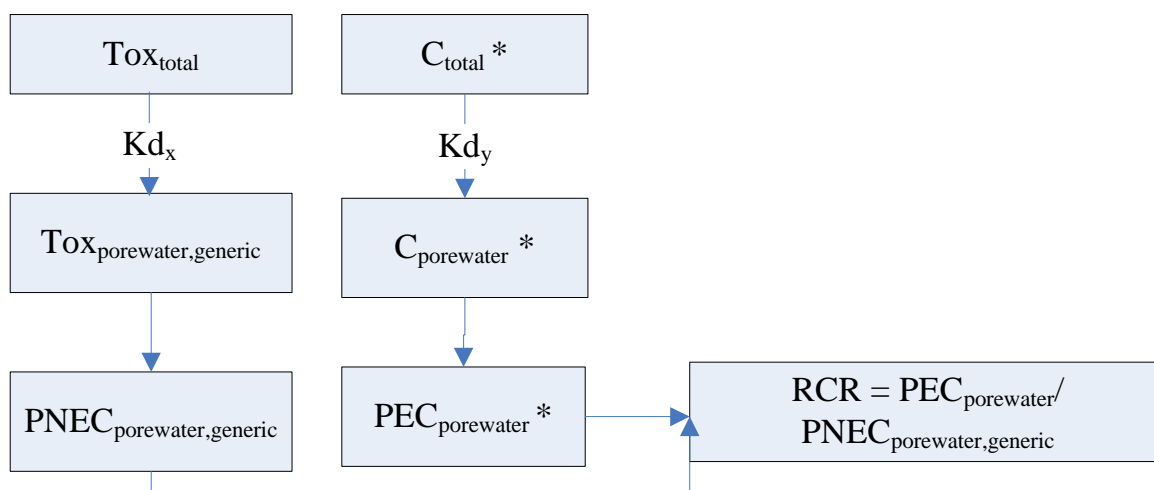


Figure 12: Framework for assessing risks of metals/metal compounds in soil on a dissolved porewater basis. (Tox = ecotox value = $Tox_{porewater, generic}$ = geometric mean in case of more than one value, C = environmental concentration; * = sequence applies to both the local and regional environment, x = soil specific laboratory derived K_d , y = field derived K_d)

Ideally, preference should be given to use measured $Tox_{porewater}$ because the transformation of Tox_{total} to $Tox_{porewater}$ introduces uncertainty. However, currently there are not likely to be many $Tox_{porewater}$ values available in the literature and therefore in absence the translation of ambient total metal concentrations into the dissolved pore water metal form and the derivation of the P(N)EC and risk ratio is done in the following sequence:

- 1) If possible, translate individual C_{total} concentrations into $C_{porewater}$ concentrations using Eq-21:

$$C_{porewater} = \frac{C_{total}}{K_{d(y)}} \quad (\text{Eq-21})$$

$K_{d(y)}$ = Partitioning coefficient (L/kg)

The $K_{d(y)}$ value represents a typical value of the solid-solution partitioning of the metal of interest for the soil under investigation and is dependent on many physico-chemical characteristics of both the soil's solid and solution phases (e.g. pH, organic matter content, total metal content) and can be derived from laboratory batch experiments. However, since the source and age of contamination influence the K_d value, $K_{d(y)}$ should preferably be derived from field data. K_d values from pore water data are hence

preferred over K_d values of batch experiments. A careful evaluation of the available K_d data should be made to select the appropriate value. A comprehensive overview of the determination, use and prediction of the distribution coefficient, K_d , of metals in soil is given by Degryse et al, 2006 and is summarized below.

The indigenous soil solution is the preferred solution phase for K_d determinations, but its isolation is laborious, and deionized-water or dilute-salt extracts are often used instead. Metal concentrations in aqueous extracts are often lower than in soil solutions, but such differences with Cd and Zn, for example, can be minimized using $\text{Ca}(\text{NO}_3)_2$ or CaCl_2 at an ionic strength similar to that of the soil solution. Concentrations of Cu and Pb in such extracts are often much smaller than in soil solution because of lower dissolved organic matter concentrations in the former, and extracts should be avoided whenever possible for obtaining K_d values for these metals.

Total metal concentrations for the solid phase are most often used in K_d expressions, but only a fraction of the total metal is actually reactive. Various methods have been developed to quantify the reactive phase, and K_d values based on this 'labile' pool often correlate better with soil properties and are likely to be more relevant for transport calculations. The difference between 'total' or 'reactive' solid phase-based K_d values is generally marginal for Cd and Cu but is significant for Ni.

The K_d values can be further refined by consideration of just the free metal-ion in the solution phase. These K_d^{free} values invariably show that soil pH is the most important soil property determining the retention of the free metal ion, while K_d values based on total solution concentrations may show little pH dependence if the metal has strong affinity for dissolved organic matter (e.g., Cu). Since uptake of metal by an organism is related to the free-ion concentration of the metal in the surrounding solution, the partitioning coefficient between reactive solid-phase metal and free metal in solution is thought to be the most appropriate to the evaluation of metal bioavailability in soils.

Where no reliable and relevant measured K_d values are available, K_d values can be derived using a modelling approach. When using a model for deriving site-specific K_d -values it should be ensured that all relevant factors on which the K_d of a specific metal depends, are considered (e.g., pH, particulate and dissolved organic and inorganic compounds, etc..) and that the model properly describes the relationship between the K_d and these parameters. If a modelled K_d is to be used, care should be taken that these models have been field validated

Both semi-empirical K_d models (e.g. Sauvé et al., 2000, Lofts and Tipping, 1998, 2001) based on surface complexation algorithms or mechanistic speciation models (e.g. WHAM VI (Tipping, 1998), NICA-Donnan (Kinniburgh et al., 1999), CD-MUSIC (Hiemstra & van Riemsdijk, 1996, 1999) could be used to describe both the sorption onto organic ligands and solid soil components. If these models are field validated they can be an useful tool in evaluating the potential variability of a K_d for a specific situation when the temporal variation of key parameters that determine the K_d -value are available. If validated, emerging alternative models (e.g. distributed ligand models) can also be used for predicting K_d -values. Overall multi-surface models are conceptually more attractive, but require a larger number of input parameters, are less well validated, and are less user-friendly than the strictly empirical models.

The K_d values should, as far as possible, be representative for the environment of interest taking into account the major environmental characteristics influencing the K_d . For soils, the K_d can be derived per soil type of interest taking into account the soil usage (for instance, cultivated versus non-cultivated soils).

2) Calculate the $\text{PEC}_{\text{porewater}}$ for a predefined local or regional environment (e.g high end value such as 90th percentile of the environmental concentrations)

3) If possible translate individual $\text{Tox}_{\text{total}}$ concentrations into $\text{Tox}_{\text{porewater};\text{generic}}$ concentrations using Eq-22:

$$\text{Tox}_{\text{porewater}} = \frac{\text{Tox}_{\text{total}}}{K_{d(x)}} \quad (\text{Eq-22})$$

$K_{d(x)}$ = Partitioning coefficient (L/kg)

4) Calculate the $\text{PNEC}_{\text{generic,dissolved}}$ from all $\text{Tox}_{\text{porewater, generic}}$ values.

5) The risks for a regional or local environment are subsequently calculated from the comparison between the local/regional $PEC_{\text{porewater}}$ and the $PNEC_{\text{porewater, generic}}$ (Eq-23).

$$RCR = \frac{PEC_{\text{porewater}}}{PNEC_{\text{porewater, generic}}} \quad (\text{Eq-23})$$

4.3 Use of speciation models

In cases where ambient total or dissolved pore water metal concentrations are reported and appropriate speciation models and relevant input data (i.e. physico-chemical parameters) are available, the risk characterization should be performed on basis of the metal species of concern¹ as outlined in Figure 13. The use of this approach is only recommended in cases of clear quantitative evidence that normalization to the metal species of concern approximates better the toxic fraction than does the total concentration of metal. (i.e. clear reduction in intraspecies variability). If there is a concern that the investigated metal binds strongly on colloids this should be considered in calculating the speciation of dissolved metal because colloids can pass through filters and if ignored may have an impact on the outcome of the speciation exercise. However, at the moment our understanding on colloids is limited and further research is needed in this field.

The approach suggested for the translation of the total or dissolved pore water concentrations (where this has been measured) into concentrations of the metal species of concern is outlined hereunder.

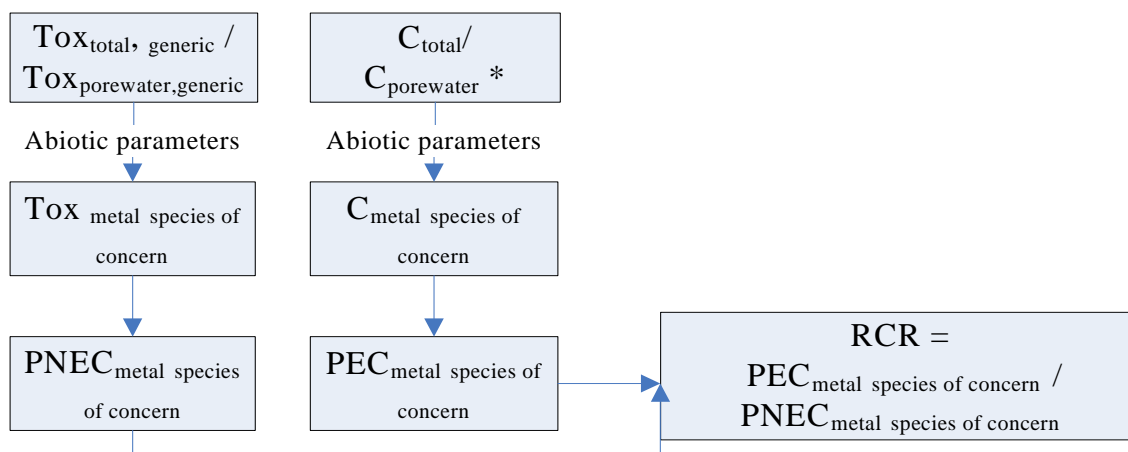


Figure 13: Framework for assessing risks of metals/metal compounds in soil on a free metal ion basis (Tox = ecotox value = geometric mean in case of more than one value; * = sequence applies to both the local and regional environment)

- 1) Translate, the reported total soil or dissolved pore water Tox concentrations ($Tox_{\text{total/porewater, generic}}$) are translated into Tox concentrations expressed as the metal species of concern ($Tox_{\text{metal species of concern}}$) using specific models e.g. linear regressions (Sauve et al, 1998) or a speciation translator (e.g. WHAM VI (Tipping, 1998), NICA-Donnan (Kinniburgh et al., 1999), CD-MUSIC (Hiemstra & van Riemsdijk, 1996, 1999)² taking into account the main physico-chemical conditions driving the bioavailability (e.g. pH/hardness of the pore water, OC/clay content/CEC of the soil,...) of the toxicity test. It should be noted that depending on which

¹ Most often this is the free metal ion but it should be noted that the free ion is not necessarily the best predictor for all metals and other metal species such as neutral species (e.g. AgCl, HgS) and anionic species (e.g. SeO_4^{2-} , AsO_4^{3-}) may contribute to the observed toxicity (Campbell, 1995).

² Please note that depending on the speciation codes used metal speciation may differ significantly

speciation model is used and on which parameter is the most influential, different speciation models can give different answers.

- 2) When several data are available for the same species or function, derive the species or function geometric mean value Calculate the $PNEC_{\text{metal species of concern}}$ from all $Tox_{\text{metal species of concern}}$ values.
- 3) Translate the total soil or dissolved pore water exposure concentrations ($C_{\text{pore water}}$) at the same level of bioavailability (expressed in the same units) as the effects assessment, i.e. into metal species of concern exposure concentrations using the same speciation translator (e.g. WHAM VI, NICA-Donnan, CD-MUSIC, ...). For this purpose, the physico-chemical parameters of the generic environment or site specific soil driving the bioavailability (e.g. pH, OC, clay content, CEC...) should be gathered or estimated. Reference is made to a representative combination of either realistic worst case or typical parameters mitigating the bioavailability of the metal.
- 4) Calculate the $PEC_{\text{metal species of concern}}$ from all individual $C_{\text{free metal}}$ values for a predefined environment taking the high end value (e.g. 90th percentile) of the concentrations of the metal species of concern.
- 5) The risks for a local or regional environment are subsequently calculated from the comparison the $PEC_{\text{metal species of concern}}$ and the $PNEC_{\text{metal species of concern}}$ (Eq-24):

$$RCR = \frac{PEC_{\text{metalspeciesofconcern}}}{PNEC_{\text{metalspeciesofconcern}}} \quad (\text{Eq-24})$$

4.4 Use of toxicity related bioavailability models

4.4.1 General outline

For considering the bioavailability of metals in soils, as described in 4.1, two phenomena on the ecotoxicity of metals to soil organisms should be considered:

1. the toxicity response is dependent on the soil physico-chemistry³ (e.g. pH, CEC, OC, clay content, bulk density or water content and
2. the toxicity response is dependent on the contact time: e.g. metal toxicity under field conditions is hardly detectable for some historically contaminated soils, or only observed at much higher doses than under laboratory conditions.

Therefore, the soil specific $PNEC/Tox$ values corrected for bioavailability should be calculated by applying a bioavailability correction that accounts for (i) differences in metal toxicity among soils to which the metal is freshly added in a soluble form and (ii) differences in metal toxicity between freshly spiked soils and field contaminated soil. Both availability corrections should be integrated to calculate the Tox normalized to specific soil conditions. The following steps can be distinguished.

Step 1: Normalization of NOEC values per soil type: derivation of a soil sensitivity factor

Normalization to soil specific characteristics requires understanding the relationship between soil physico-chemistry and metal toxicity on microbial function, plants and invertebrates. In order to perform this normalization, speciation or bioavailability models, mechanistically based bioavailability models (e.g. T-BLM) or empirically based regression models predicting the metal toxicity in spiked soils based on soil properties (e.g. CEC, pH, background metal,...) should be available or developed. These

³ preference should always be given to linked measured data

models/observed relationships allow the prediction of soil specific metal toxicity in laboratory spiking.. Strong preference should be given to validated models.

Regression models for accounting for bioavailability in soils have recently been developed for zinc, nickel and copper in the framework of the EU risk assessment process (Zn RAR, 2004, Ni-RAR 2006, Cu-RAR 2006

This normalization procedure uses the following steps:

- Link the NOEC/EC_x values of the chronic ecotoxicity database (as total metal concentrations) with the soil properties (CEC, pH and OM) of the soils in which the test was performed
- When the regression approach is used, the NOEC/EC_x should be normalized using the corresponding organism specific slopes (from the regression analysis) to 'reference' soil properties or to specific local /regional conditions, i.e. to the driving abiotic factors of the soil for which the bioavailability corrections can be performed. The normalization equation (Eq-25) is:

$$\frac{EC_{x,x}}{EC_{x,y}} = \left[\frac{abioticfactor_x}{abioticfactor_y} \right]^{slope} \quad (Eq-25)$$

x = scenario with typical local or regional conditions for which the Tox_x is derived

y = the realistic worst case scenario: is used as a reference scenario when correcting bioavailability with toxicity related models providing us with a Tox_{reference} corresponding to a maximized bioavailability.

In case of less reliable models, an uncertainty assessment should be made. See also Uncertainty Fact Sheet

- In cases where the bioavailability model (e.g.T-BLM) approach is used, the NOEC/EC_x should be normalized using the corresponding organism specific T-BLM. After normalization of all individual/limited number of chronic toxicity data, species/process geometric mean values should be calculated and used for a normalized PNEC derivation.

Step 2: Incorporating long term effects on metal bioavailability: derivation of a soil lab-to-field factor

McLaughlin et al (2005) indicated that metal toxicity in the laboratory spiked soil is overestimated compared to field-contaminated soils, because effects due to the added anion, metal-induced acidification and higher ionic strength of the soil solution all having large effects on metal chemistry in soil that are seldom representative of metal contamination occurring in the field. In addition longer equilibration period in field contaminated soils ('aged' metal) and different sources of the metal (different speciation and bioavailability) in the environment may mitigate metal toxicity in the field. Further research is needed to understand the underlying mechanism of these processes.

Where the adverse effect of an elevated metal concentration is generally more pronounced in spiked soils than in historically contaminated field soils at the same total metal level, an additional lab-to-field translator⁴ should be incorporated. This factor relates the differences in metal dose required between lab spiked and field contaminated soil to produce a same toxicity effect in a specific soil. It must be stressed that the latter correction does not need to be applied on ecotoxicity data collected in field contaminated soils.

These lab-to-field factors should be calculated as a ratio between toxicity data, generated from field/laboratory aged soils and freshly spiked soils. As natural metal background concentrations are

⁴ Lab to field factor: This factor addresses the difference in toxicity between tests on soils spiked in the lab and tests on field contaminated soils using single species or micro-organisms functional tests due to differences in ionic strength, ageing of metals in soil (inclusion of natural elements into the crystal lattices of soil minerals, the formation of insoluble precipitates, diffusion of metals into micro pores, etc.). This factor does not address differences in effects between single species lab test and multi-species tests (species interactions). The influence of the latter is addressed by comparing micro/mesocosm or field studies with the PNEC based on single species/functional lab tests.

already “aged”, the derivation of the lab-to-field factors should be based on added concentrations. Again lab-to-field factors could be based on either EC₅₀ or EC₁₀/NOEC values.. In case of an appropriate test design robust EC₁₀ (or EC₂₀) values can be estimated with low variability and these values should be used by preference.

The selection of the most appropriate lab-to-field factor is not straightforward. Preference is given to derive soil specific lab-to-field factors if a relationship can be established between soil properties and the value of the lab-to-field factor. Similarly, where organism specific factors can be derived, preference is given to such values. However, if this is not possible the selection of the lab-to-field factor should be done in a pragmatic and conservative but realistic way for example by selecting one generic value situated at the lower end of the spectrum.

The derivation and incorporation of the lab-to-field factor (L/F-F) can be done as follows:

- Derive added laboratory NOEC/EC_x values and added field contaminated NOEC/EC_x values by subtracting the metal concentration in the control soil from the total NOEC/EC_x value.
- Derive individual lab-to-field ratios between added laboratory NOEC/EC_x values and added field contaminated NOEC/EC_x values (Eq-4.28).

$$\frac{EC_x / NOEC_{Field, add}}{EC_x / NOEC_{Lab, add}} = \text{lab - to - field factor} \quad (\text{Eq-26})$$

- A. When no relationship can be found between soil properties and the lab-to-field factors, and between organism and lab-to-field factor aggregate all individual lab-to-field ratios into a frequency distribution and derive a generic lab-to-field factor.
- Apply the generic lab-to-field factor on all individual non-aged added NOEC/EC_x values.
- B. When no relationship can be found between soil properties and the lab-to-field factors, but a clear difference can be found between lab-to-field factors of different organisms or trophic levels derive organism or trophic level specific lab-to-field factor.
- Apply the organism/trophic level specific lab-to-field factors to the respective individual organism/trophic level non-aged added NOEC/EC_x values.
- C. When a relationship can be found between soil properties and the lab-to-field factors derive the lab-to-field factor relevant for the scenario (site or region specific or reasonable worst case conditions). Apply this factor to the individual normalized added NOEC/EC_x values.

Step 3: Calculation of bioavailable Tox values

As indicated in the previous steps (i) differences in metal toxicity among soils to which the metal is freshly added in a soluble form and (ii) differences in metal toxicity between freshly spiked soils and field contaminated soil can be respectively captured in the “soil sensitivity factor” and “soil lab-to-field factor”.

The correction for bioavailability through the incorporation of both the lab-to-field factor (L/F-F) and soil sensitivity factor (SS-F) can be done as follows (Figure 14).

- Correct each individual generic added NOEC/EC_x (Tox_{generic, added}) with the derived (organisms/soil specific) lab-to-field factor (L/F-F). This generates lab-to-field corrected added NOEC/EC_x (L/F-F x Tox_{generic, added}) values,
- Add the individual background concentrations from the soil test media (C_b) to the corresponding lab-to-field corrected added NOEC/EC_x values (C_b + L/F-F x Tox_{generic, added}). This step generates the lab-to-field corrected total NOEC/EC_x
- Normalize the generated total lab-to-field corrected NOEC EC_x values to soil specific lab-to-field corrected NOEC/EC_x values (SS-F x (C_b + (L/F-F x Tox_{generic, added}))) using the total slopes from the organism specific regression models or using relevant speciation/bioavailability models.. The generated NOEC/ EC_x values represent the bioavailable Tox value.

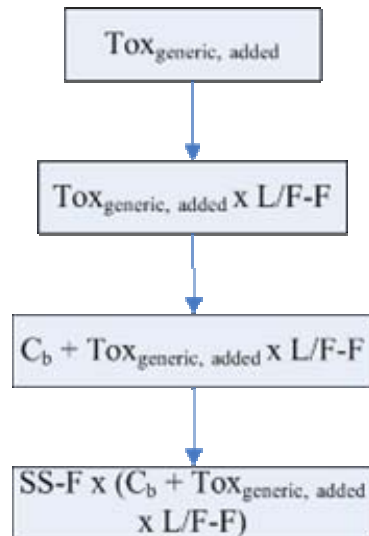


Figure 14: Framework for calculation of a bioavailable Tox value

For the final application of toxicity related bioavailability models in a risk assessment context, a two-tiered approach for the incorporation of bioavailability in risk assessment procedures is proposed hereunder. First, a generic scenario is developed (Tier 1), the outcome of which is subsequently used for a site specific approach (Tier 2).

4.4.2 Normalization and read-across

Where bioavailability models (e.g. T-BLM or regression models) are available, they exist mostly for a limited number of species representing different trophic levels. Toxicity data generated for these species under different abiotic conditions can be normalized to a common set of abiotic conditions (e.g. ecoregion) as long as these abiotic parameters fall within the geochemical boundaries of the bioavailability model (e.g. range of CEC, TOC, pH). For those species for which no specific bioavailability model has been developed it should be verified on a case by case basis whether the bioavailability model of another species within the same trophic level (i.e read-across) can be applied.

Normalization using bioavailability models (e.g. T-BLM or regression models) and read-across to other species for which no bioavailability model is available applies to any compartment where a bioavailability model is available (e.g. it is also applicable to the aquatic compartment, fact sheet 5)

It is proposed to verify read-across of the available bioavailability models (e.g. T-BLM or regression models) developed and the subsequent PNEC derivation using the scheme as outlined in Figure 15 and explained hereunder.

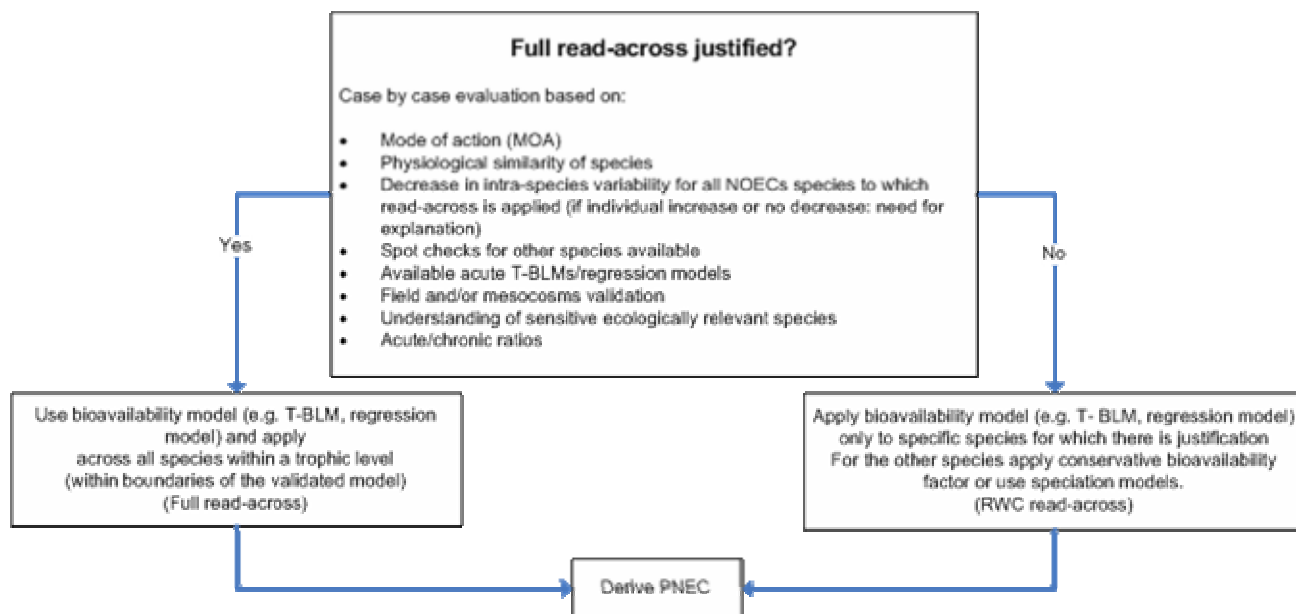


Figure 15: Approach for read-across of bioavailability models.

- 1) The first step consists in evaluating if full read-across to all species (full read-across) within a trophic level is justified. The application of a bioavailability model across species assumes similar mechanism of actions (e.g. similar stability constants between the cations (Ca, Mg, H) and the biotic ligands, similar site of action) and therefore the applicability across species needs to be investigated. Information on the applicability of the bioavailability model across species can be obtained from information on the mechanism of action (MOA) of the metal under consideration, physiological similarities between the species, observed changes in intra-species variability⁵ after application of the bioavailability model across species as outlined in figure 1, spot check validations for specific species (a few ecotoxicity tests, performed under different geochemical conditions for a range of key bioavailability parameters (e.g. CEC & pH)) and/or field/mesocosm data. Considering that sensitive species are driving the PNEC value, it should further be demonstrated that the developed/validated bioavailability models could be applied to the most sensitive species/taxonomic groups of the database.
- 2) If full read-across is justified the next step consists of applying the bioavailability model across species of similar trophic levels (e.g. applying the *Folsomia candida* bioavailability model⁶ for normalization of the toxicity data from other soil invertebrates ...) towards a specific set of geochemical conditions (e.g. a defined eco-region). The bioavailability model normalizes the no-effects threshold concentration of the metal for each species' endpoint and the model therefore retains the intrinsic metal sensitivities of the different species and endpoints. The species-specific normalized geomean NOEC's for the most sensitive endpoints are then used to derive the PNEC using the assessment factor approach (AF) (data poor metals) or by constructing an SSD (data rich metals) from which the HC₅, as outlined in the TGD, can be derived.
- 3) In case read-across is only justified for some species and not for others (e.g. unexplained significant increase in variability after normalization or different mode of action) an alternative approach (reasonable read-across) should be developed. In this RWC approach the

⁵ Induced reductions in intra-species variability can be assessed by e.g. comparing the predicted vs. observed toxicity for the different species or by means of the max./min. ratio between toxicity thresholds.

⁶ Normalisation of toxicity data is only allowed within the boundaries of the developed/validated model

bioavailability models are only applied to those species within the trophic level for which the application can be justified. For those species for which application of the bioavailability model related to their trophic level can not be justified a bioavailability factor based on the most conservative available bioavailability model should be applied. In worst case if there is even no justification to apply the most conservative bioavailability model a correction based on speciation modeling only could be an alternative to account at least for differences in abiotic factors.

Since it is expected that the mechanism of toxicity between short and long term exposures may differ, the use of acute bioavailability models to normalize chronic data should be considered with great care. Such normalization is only allowed in case the predictive capacity of these acute models for estimating chronic toxicity data is sufficient. In case of poor predictive power of the acute models towards chronic toxicity data, the acute model could only be used to normalize the acute toxicity data. The derivation of chronic effects levels could then be derived from the normalized acute toxicity data using an acute to chronic ratio.

4.4.3 Normalization procedure

Depending on the outcome of the verification normalization of the Tox values can be performed in the following manner:

Tier 1: application to a reference scenario

Full read-across

- 1) Predict Tox values for all test organisms under reasonable worst case conditions (rwc), i.e. $Tox_{bioavailable, reference}$ using the bioavailability model of the trophic level (or the justified model)
- 2) When more data are available for the same species, calculate the species geometric mean value.
- 3) Construct a normalized species sensitivity distribution from all normalized $Tox_{bioavailable, reference}$ values and derive the $PNEC_{bioavailable, reference}$
- 4) Finally, the risk characterization ratio can be calculated using the relevant environmental concentrations as follows:

$$RCR = \frac{PEC_{dissolved}}{PNEC_{bioavailable, reference}} \quad (Eq-27)$$

RWC read-across

- 1) Predict Tox values at reasonable worst case conditions (rwc), i.e. using the bioavailability model of the trophic level (or the justified model) for the test organisms for which the bioavailability models were originally developed and for those species for which application of the trophic level specific bioavailability model (e.g. T-BLM, regression model) could be justified
- 2) For those species for which the trophic level specific bioavailability model could not be justified, a bioavailability factor (Bio-F) should be applied to derive the $Tox_{bioavailable, reference}$. This Bio-F can be calculated by comparison of the $Tox_{bioavailable, reference}$ with the $Tox_{dissolved, generic}$ of those species for which the BLM was originally developed (Eq-28). The most conservative value (smallest correction for bioavailability, $Bio-F_{reference}$) should then be used⁷

⁷ In worst case if there is even no justification to apply the most conservative bioavailability model a correction based on speciation modeling only could be an alternative to at least account for differences in abiotic factors.

$$Bio - F_{reference} = \frac{Tox_{bioavailable,reference}}{Tox_{dissolved,generic}} \quad (Eq-28)$$

- 3) Finally, the risk characterization ratio can be calculated using the relevant environmental concentrations as follows:

$$RCR = \frac{PEC_{dissolved}}{PNEC_{bioavailable,reference}} \quad (Eq-29)$$

Tier 2: Application to specific local or regional scenario

If a detailed local or regional investigation is needed, the approach could also be applied for the normalization of the different Tox values to typical local or regional abiotic conditions. This normalization results in a local or regional specific PNEC (i.e. $PNEC_{local, bioavailable}$, $PNEC_{regional, bioavailable}$).

Full read-across

- 1) Predict Tox values for all test organisms at typical local or regional specific conditions, i.e. $Tox_{local, bioavailable} / Tox_{regional, bioavailable}$ using the bioavailability model of the trophic level (or the justified model)
- 2) When more data are available for the same species, calculate the species geometric mean value.
- 3) Construct a normalized species sensitivity distribution from all normalized $Tox_{local, bioavailable} / Tox_{regional, bioavailable}$ values and derive the $PNEC_{local, bioavailable}$ or $PNEC_{regional, bioavailable}$
- 4) Finally, the risk characterization ratio can be calculated using the relevant local or regional environmental concentrations as follows:

$$RCR = \frac{PEC_{dissolved}}{PNEC_{bioavailable, local / regional}} \quad (Eq-30)$$

RWC read-across

- 1) Predict Tox values at typical local or regional specific conditions, i.e. using the bioavailability model of the trophic level (or the justified model) for the test organisms for which the bioavailability models were originally developed and for those species for which application of the trophic level specific bioavailability model (e.g. T-BLM, regression model) could be justified i.e. $Tox_{local, bioavailable} / Tox_{regional, bioavailable}$.
- 2) For those species for which the trophic level specific bioavailability model could not be justified, a bioavailability factor (Bio-F) should be applied to derive the $Tox_{local, bioavailable} / Tox_{regional, bioavailable}$. This Bio-F can be calculated by comparison of the $Tox_{local, bioavailable} / Tox_{regional, bioavailable}$ with the $Tox_{bioavailable, reference}$ of those species for which the bioavailability model (e.g. BLM) was originally developed (Eq-31). The most conservative value (smallest correction for bioavailability, $Bio-F_{local/regional}$) should then be used⁸.

$$Bio - F_{local / regional} = \frac{Tox_{bioavailable, local / regional}}{Tox_{bioavailable, reference}} \quad (Eq-31)$$

⁸ In worst case if there is even no justification to apply the most conservative bioavailability model a correction based on speciation modeling only could be an alternative to account for differences in abiotic factors.

- 3) Finally, the risk characterization ratio can be calculated using the relevant local or regional environmental concentrations as follows:

$$RCR = \frac{PEC_{dissolved}}{PNEC_{bioavailable, local / regional}} \quad (\text{Eq-32})$$

REFERENCES

- Degryse F., E. Smolders and D. Parker, 2006. White paper: The solid–liquid distribution coefficient (K_d) of metals in soils. Final report to the ETAP sponsors
- Hiemstra, T. & W.H. van Riemsdijk, 1996. A surface structural approach to ion adsorption: The charge distribution (CD) model. *Journal of Colloid and Interface Science* 179 (2), 488-508.
- Hiemstra, T. & W.H. van Riemsdijk, 1999. Surface structural ion adsorption modelling of competitive binding of oxyanions by metal (hydr)oxides. *Journal of Colloid and Interface Science* 210, 182-193.
- Lofts S, Tipping E, 1998. An assemblage model for cation binding by natural particulate matter. *Geochim Cosmochim Acta* 62(15):2609–2625.
- Kinniburgh, D.G., W.H. van Riemsdijk, L.K. Koopal, M. Borkovec, M.F. Benedetti & M.J. Avena, 1999. Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 151 (1-2), 147-166.
- Sauve, S., W. Hendershot & H.E. Allen, 2000. Solid-solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter. *Environmental Science and Technology* 34 (7), 1125-1131.
- Tipping, E., 1998. Humic ion-binding model VI: An improved description of the interactions of protons and metal ions with humic substances. *Aquatic Geochemistry* 4, 3-48.