



METALS ENVIRONMENTAL RISK ASSESSMENT GUIDANCE

FACT SHEET

MERAG

05

INCORPORATION OF BIOAVAILABILITY FOR WATER,
SOILS AND SEDIMENTS



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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.

1. INTRODUCTION

The degree to which metals are available to aquatic and terrestrial organisms varies depending on the site-specific geochemical conditions controlling metal speciation, and therefore also influence the degree to which organisms may be exposed to metals and experience adverse effects from such exposure. In the environment organisms are not only exposed through water but also via the dietary route. The science on the incorporation of the dietary route is very preliminary and as such for the water compartment this fact sheet focuses mainly on waterborne metals¹.

From the perspective of a risk assessment or in Environmental Quality Standard (EQS) setting, it is therefore critical to understand which geochemical characteristics influence the toxicity of metals and metal compounds. In order to reduce the uncertainty and to increase the ecological relevance of the assessment both effects and/or exposure data should be normalized to the bioavailable metal fraction by incorporation of bioavailability concepts such as Biotic Ligand Model (BLM) and SEM-AVS concept (SEM = Simultaneously Extracted Metals; AVS = Acid Volatile Sulfides) etc. Depending on the compartment under investigation different levels of bioavailability refinement can be distinguished (Figure 1).

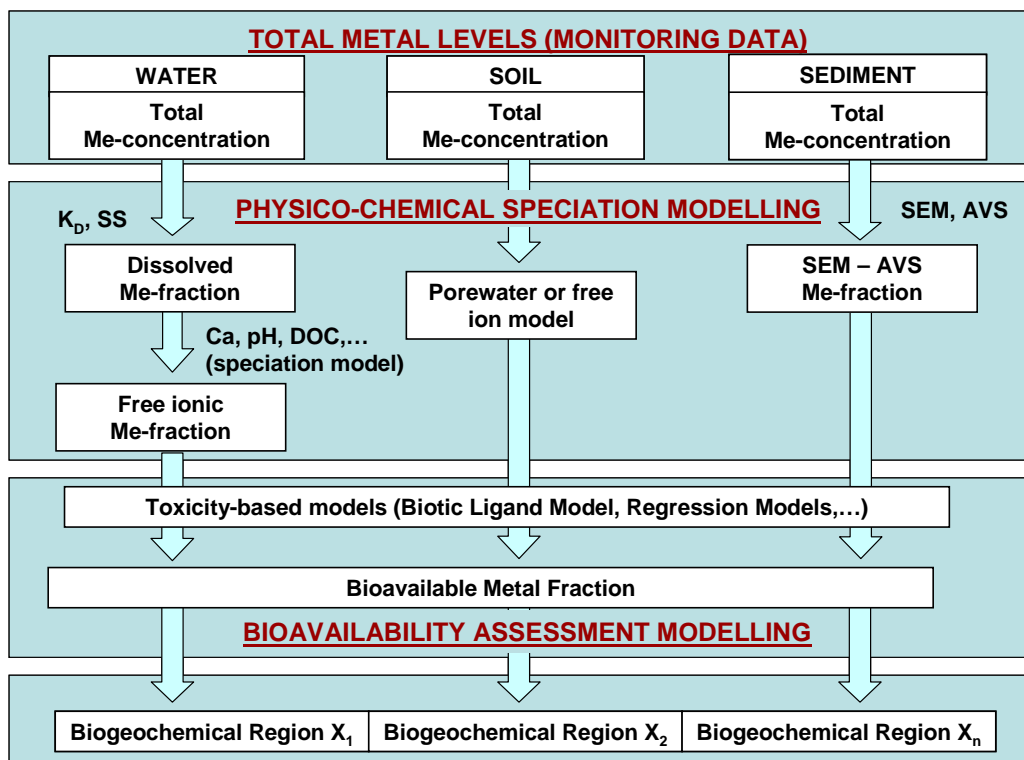


Figure 1: Refinement levels for the incorporation of bioavailability concept for the water, sediment and soil compartment. * = It should be noted that the free ion is not necessarily the best predictor for all metals and other metal species (e.g. AgCl, HgS) may contribute to the observed toxicity (Campbell, 1995), ** = example for sulfide binding metals

Depending on the knowledge level for the metal/metal compound under investigation bioavailability can be introduced at different levels. The most simple form for the aquatic compartment makes use of the information on partitioning (i.e. K_d) and the amount of suspended solids (SS) present in the aquatic compartment to translate the total metal concentration into a dissolved concentration. A further refinement

¹ Although it should, be noted that during the development of a chronic invertebrate BLM the organisms are fed with algae that will absorb metals during the experiment. As such dietary is covered to some extent.

of this approach would be to estimate the true free ionic metal fraction by using metal speciation programs (e.g. WHAM, MINTEQA2 etc.) taking into account the presence of important binding ligands (e.g. DOC, chlorides etc.). For some metals toxicity based models are available or under development that range from simple regression models to the more refined Biotic Ligand Models (BLM) which allows a mechanistic understanding of metal toxicity. For the terrestrial compartment the bioavailable fraction can be assessed through the use of empirical relationships of toxicity as a function of soil physical and chemical properties (e.g. pH, cationic exchange capacity = CEC, organic matter = OM etc.). For metals/metal compounds that exhibit a strong preference to bind with sulfides the SEM-AVS concept could be useful to quantify the amount of metals not bound to the sulfide pool which provides an estimate of potentially bioavailable metals. In analogy with the aquatic and soil compartment toxicity based models for sediments are currently under development (Di Toro, 2005).

Selection of methods and approaches for incorporating bioavailability corrections will depend on the aim and scope of the assessment, e.g. for generic chemical safety programs (e.g. the EU Existing Substance Program) or local environmental impact studies (EQS setting). Furthermore, metal specific considerations should always be taken into account (e.g. affinity of the metal to bind with sulfides differs greatly, and separate BLMs must be developed for each metal).

Different datasets for abiotic factors (and environmental concentrations) should be considered based on the goal of the assessment. Specifically, data sets of abiotic factors and environmental concentrations should be representative of the area under investigation. The breadth of the data sets will usually be proportional to the scope of the assessment. That is broader data sets will be necessary for regional assessments, with national to continental scales, than local assessments which address site-specific operational scales. The choice of abiotic factors is particularly important for when the biogeochemical region approach is applied.

It must also be stressed that the philosophy between both assessments are somewhat different. The local environmental impact studies, typically required for environmental permits, aim at a precise and as exact possible description/quantification of the present impact of an activity/emission to a specific environment. Accuracy of the local parameters (e.g. abiotic factors) determining the potential impact are therefore crucial. In contrast, the methodological approach applied for generic chemical safety programs has used much more default values/assumptions to define the environment and therefore the level of accuracy of parameters such as abiotic factors (or environmental concentrations) were traditionally viewed less important in generic chemical safety programs. However, the use of default values and worst case assumptions needs to be carefully evaluated. This is especially true for metals, where the use of worst case assumptions for parameterizing BLMs may yield PNEC values that are below natural background concentrations.

Following from the analysis of the ecotoxicity data, a $PNEC_{generic}$, i.e. the PNEC not corrected for any bioavailability should be derived. In case bioavailability models can be applied, this generic PNEC can be modified to:

- 1) a specific PNEC normalized to well characterized specific local or regional conditions (i.e. $PNEC_{local, bioavailable}$ or $PNEC_{regional, bioavailable}$). These specific conditions can be defined case-by-case generally using typical value for the bioavailability modifying factors;
- 2) a reference PNEC normalized to realistic worst case conditions, i.e. $PNEC_{reference, bioavailable}$.

In this respect, *reasonable worst case conditions*, at the local and regional scale, are generally defined as the lower (e.g. 10th %) or higher (e.g. 90th %) values of the bioavailability modifying factors depending on the bioavailability models used. On the other hand, *typical conditions* are generally referring to average values of the bioavailability modifying factors,

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 parameters. The plausibility of such combinations should, therefore, carefully be assessed and take co-variance into account when possible to avoid ending up with an unrealistic worst case scenario.

The application of the concepts applicable to the aquatic compartment (overlying water column and sediments) is outlined in more details hereunder. The guidance given applies to both deterministic as probabilistic approaches.

2. IMPLEMENTATION OF BIOAVAILABILITY: WATER

2.1 General concept

A tiered approach for assessing risks has been proposed in fact sheet 1 in which the possibility is put forward for refining the risk assessments by taking into account bioavailability in case a risk scenario has been identified. If no risk is identified at a total metal level the assessment may already stop there (assuming that the effect data were generated under realistic worst case conditions).

The application of the bioavailability concepts to the water compartment consists of the translation of the conventional estimated effect thresholds (i.e. PNEC value, Tox values, water quality criteria) towards the conditions prevailing in a certain region or for a certain continent-wide percentage of surface waters using either transformation to soluble fractions, speciation and bioavailability algorithms (e.g. the free metal ion, BLM) as visualized in Figure 2.

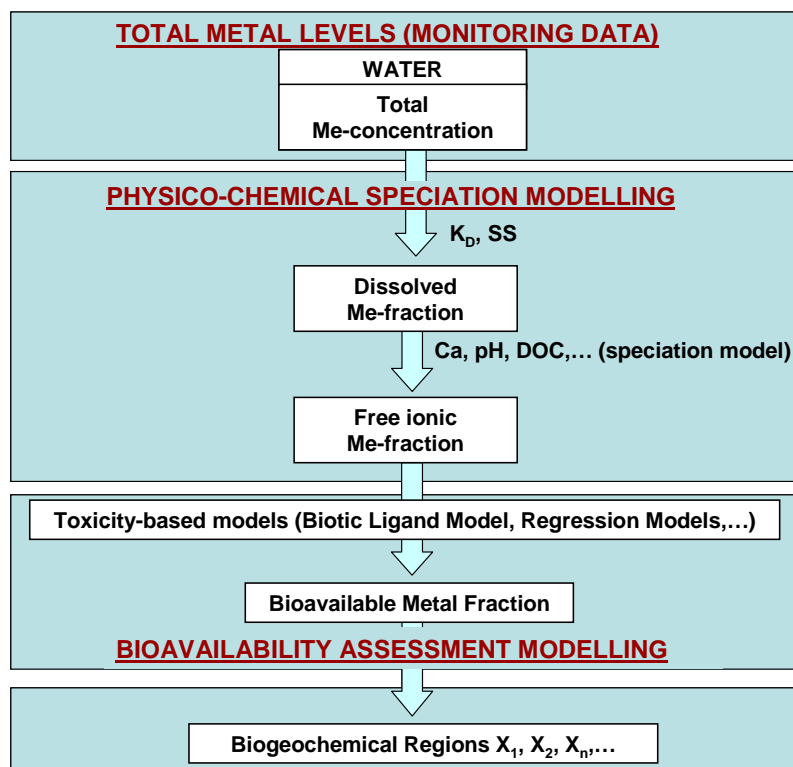


Figure 2: Refinement levels for the incorporation of bioavailability concept for the water, compartment. Note total Me-concentration is only needed if info on the “dissolved” fraction is not available.

In order to perform the bioavailability correction with a speciation or toxicity related model information on the water quality characteristics of the receiving watershed needs to be collected. This type of data can be obtained from existing monitoring databases (regional scenario) or from specific tailored monitoring campaigns (local scenario). Depending on the scenario (low/high) (reference) and average values (typical at local or regional scale) of the modifiers of metal-toxicity should be selected

An EQS corrected for bioavailability assessment should preferably be derived by an HC5 SSD value expressed as a formula based on the parameters known to affect bioavailability for the metal in question.

The reasonable worst case scenario is used as a reference scenario when correcting bioavailability with toxicity related models providing us with a $PNEC_{reference}$ or $Tox_{reference}$ that corresponds to a maximized bioavailability.

When calculating a bioavailability factor (in case no normalization of the whole SSD can be performed) this reference value ($PNEC_{reference}$) is in turn compared to the specific conditions that can be deployed to derive a regional $PNEC_{bioavailable}$ or local $PNEC_{bioavailable}$.

Where possible preference should be given to derive bioavailable PNEC (referring to given conditions) directly by normalizing the complete effects data set. Finally, comparing these bioavailable PNEC values with the outcome of the exposure assessment at the same level of bioavailability (e.g. expressed in the same units i.e. dissolved vs dissolved) 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 surface water) different approaches can be used to ‘translate’ the effects data to bioavailable metal fractions in representative specific surface waters.

2.2 Use of transformation to soluble fraction

In case 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 basis as outlined in Figure 3.

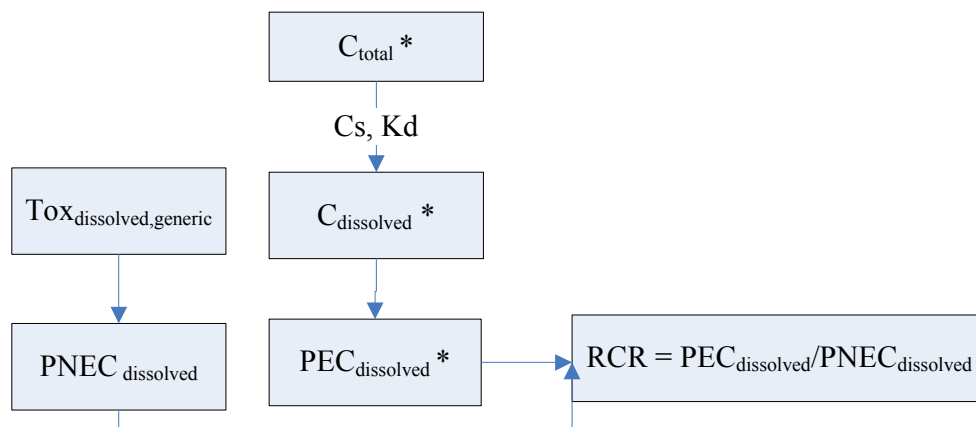


Figure 3: Framework for assessing risks of metals/metal compounds in water on a dissolved basis. (Tox = ecotox value = geometric mean in case of more than one value), C = environmental concentration; *=sequence applies to both the local and regional environment)

The translation of ambient total metal concentrations into the dissolved 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 $C_{dissolved}$ concentrations using Eq-1:

$$C_{dissolved} = \frac{C_{total}}{(1 + K_d \times C_s \times 10^{-6})} \quad (\text{Eq-1})$$

K_d = Partitioning distribution coefficient (L/kg)

C_s = Suspended solids concentration (mg/L)

In selecting an appropriate K_d value it should be acknowledged that K_d values can not be considered as true constants and will vary as a function of the metal loading and as a function of environmental characteristics such as pH (due to proton competition for binding sites) and ionic strength. Ranges spanning different orders of magnitude have been reported in literature.

Since the choice of a K_d value may drive the outcome of the risk assessment, the assessment of the data quality and relevance of all collected measured K_d -values should be done with care. Preference should

always be given too coupled measured data for the surface water in question for which information is available on both sampling and analytical measuring techniques. When sufficient distribution coefficients are collected, it is possible to fit a normal, log-normal or other statistical distribution through the data points. Using goodness-of-fit statistics, the distribution(s) that best fits the input data is selected for further assessment. From these distributions, it is possible to determine the probability that a Kd-value measure will exceed a certain value. If insufficient measured Kd values are available an alternative approach that can be used is based on derived Environmental Concentration Distributions (ECDs) for ambient or background dissolved metal concentrations in surface waters/soil pore water on the one hand and sediment/Suspended Particulate Matter (SPM)/soil metal concentrations on the other hand. Based on the median background or ambient concentrations, respectively, two water-sediment Kd values can be derived. The combination of low end and high end values can be used to estimate a realistic range of variation between Kd-values. The latter approach has the disadvantage that the values are not coupled.

When few distribution coefficients are available, only summary statistics (average, median, minimum and maximum) are calculated. The median Kd-value should be used in the exposure assessment. In case percentiles cannot be calculated, a low end value (e.g. 10th percentile) and a high end value (e.g. 90th percentile), or the minimum and maximum, can be used as lower and upper bound as worst-case scenarios.

Due to the concentration dependency and the uncertainty surrounding a Kd value, introduced by the fact that there are different forms of metal in and on the solid phase and in solution, and the fact that different methodologies are used to measure each phase, it could be worthwhile to favour a modelling approach instead. When using a model (e.g. SCAMP/WHAM VI) for deriving site-specific Kd-values it should be ensured that all relevant factors on which the Kd 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 Kd and these parameters. If a modelled Kd is to be used, care should be taken that these models have been field validated.

2) Calculate the $PEC_{dissolved}$ for a predefined local or regional environment (high end value e.g.. 90th percentile of the environmental concentrations)

3) Calculate the $PNEC_{generic,dissolved}$ from all $Tox_{generic,dissolved}$ values. Note that aquatic toxicity tests tend to maximize toxicity. Hence it is assumed that for all toxicity data no additional conversion to a dissolved fraction has to be applied.

4) The risks for a regional or local environment are subsequently calculated from the comparison between the local/regional $PEC_{dissolved}$ and the $PNEC_{generic,dissolved}$ (Eq-2).

$$RCR = \frac{PEC_{dissolved}}{PNEC_{generic,dissolved}} \quad (\text{Eq-2})$$

2.3 Use of speciation models

In case ambient total 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 concern² in order to reduce uncertainty as outlined in Figure 4. 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 dissolved concentrations into concentrations the metal species of concern is outlined hereunder.

² 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. SeO²⁻, AsO₄²⁻) may contribute to the observed toxicity (Campbell, 1995).

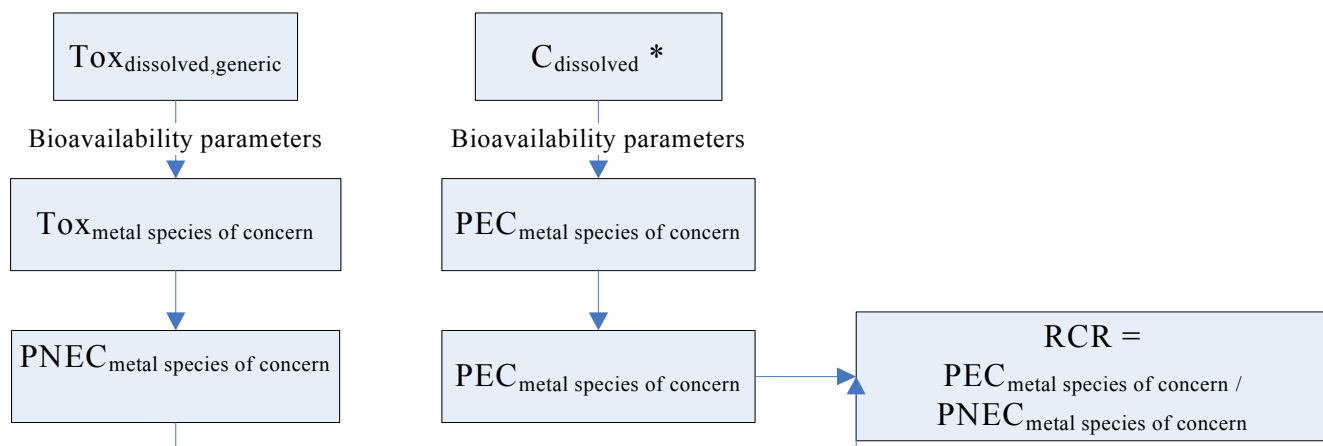


Figure 4: Framework for assessing risks of metals/metal compounds in water on a free metal ion basis (Tox = ecotox value = geometric mean in case of more than one value, C = environmental concentration; *=sequence applies to both the local and regional environment)

- 1) The different generic Tox values that are in the effects assessment are generally generated in test media with varying physico-chemical characteristics known to alter metal bioavailability and toxicity (e.g. pH, hardness, dissolved organic matter) which may influence the speciation and toxicity. Also other like stable sulfide clusters may be important as has been shown for Ag (Bell and Kramer, 1999; Bianchini et al., 2002). Also, polysulfides species are shown to be important. If possible the reported dissolved Tox concentrations ($Tox_{generic,dissolved}$) should be translated into Tox concentrations expressed as the metal species of concern ($Tox_{metal\ species\ of\ concern}$) using the speciation translator (e.g. WHAM, MINTEQA2,...) taking into account the main physico-chemical conditions driving the bioavailability (e.g. pH, DOC,...) of the individual toxicity test. If no specific information on relevant physico-chemical parameters is available then the toxicity data should not be used unless the possibility of using default values instead for some of these parameters can be substantiated. For example for copper Santore et al. (2002) used a default DOC value of 1 mg/L to calibrate the acute copper BLM. It should be noted that depending on which speciation model is used and on which parameter is the most influential, different speciation models can give different answers.
- 2) Calculate the $PNEC_{metal\ species\ of\ concern}$ from all $Tox_{metal\ species\ of\ concern}$ values
- 3) If possible translate the dissolved exposure concentrations ($C_{dissolved}$) 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, MINTEQA2,...). For that purpose, the physico-chemical parameters of the generic environment or site specific watershed driving the bioavailability (e.g. pH, DOC,...) should be gathered or estimated. Reference is given to either realistic worst case or typical conditions.
- 4) Calculate the $PEC_{metal\ species\ of\ concern}$ from all individual $C_{free\ metal}$ values for a predefined environment taking a high end value (e.g. the 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 between the $PEC_{metal\ species\ of\ concern}$ and the $PNEC_{metal\ species\ of\ concern}$ (Eq-3):

$$RCR = \frac{PEC_{metalspeciesofconcern}}{PNEC_{metalspeciesofconcern}} \quad (Eq-3)$$

2.4 Use of toxicity related bioavailability models

2.4.1 General outline

In case ambient dissolved metal concentrations are reported and appropriate bioavailability models (e.g. Biotic Ligand model) have been developed and validated for the metal/metal compounds of concern and relevant input data (i.e. physico-chemical parameters) are available, the risk characterization or the EQS setting should be performed preferentially on a 'bioavailable' basis. A detailed overview of the BLMs, uncertainties and limitations are given in the background document.

The toxicity of metals depends not only on the metal species (or sum of species) to which organisms are exposed, but also on the interaction between metal species and other ions at the site of action in organisms. The presence of the biological component therefore suggests that the bioavailability correction should be applied on the effects side of the equation. Of course, in the comparison of the environmental concentrations and the effect concentrations care should be taken that both are expressed in the same units.

The first step in using a toxicity related bioavailability model consists in the determination of a critical biotic ligand accumulation ($Tox_{critical\ biotic\ ligand, organism\ xi}$) calculated from the experimentally generated organism specific toxicity values ($Tox_{dissolved, organism\ xi}$), expressed as dissolved concentration. Organism-specific bioavailability models should be used as much as possible for that purpose (see section 2.4.2 for further guidance) In the second step of the approach each organism specific critical biotic ligand accumulation ($Tox_{critical\ biotic\ ligand, organism\ xi}$) is translated into a critical bioavailable dissolved concentrations ($Tox_{(critical\ bioavailable\ dissolved)y, organism\ xi}$) for a specific area under investigation characterized by a specific set of water-quality conditions (pHy, Hy, DOCy). Finally, these critical bioavailable dissolved concentrations ($Tox_{(critical\ bioavailable\ dissolved)y, organism\ xi}$) or the $PNEC_{(bioavailable\ dissolved)y}$ are compared with the dissolved environmental concentrations of the metal/metal compounds representative for the area under investigation.

All individual for bioavailability corrected Tox and PNEC values are expressed as dissolved concentrations and are therefore at the same level of bioavailability as the environmental concentrations.

The general outline of this approach is outlined in Figure 5.

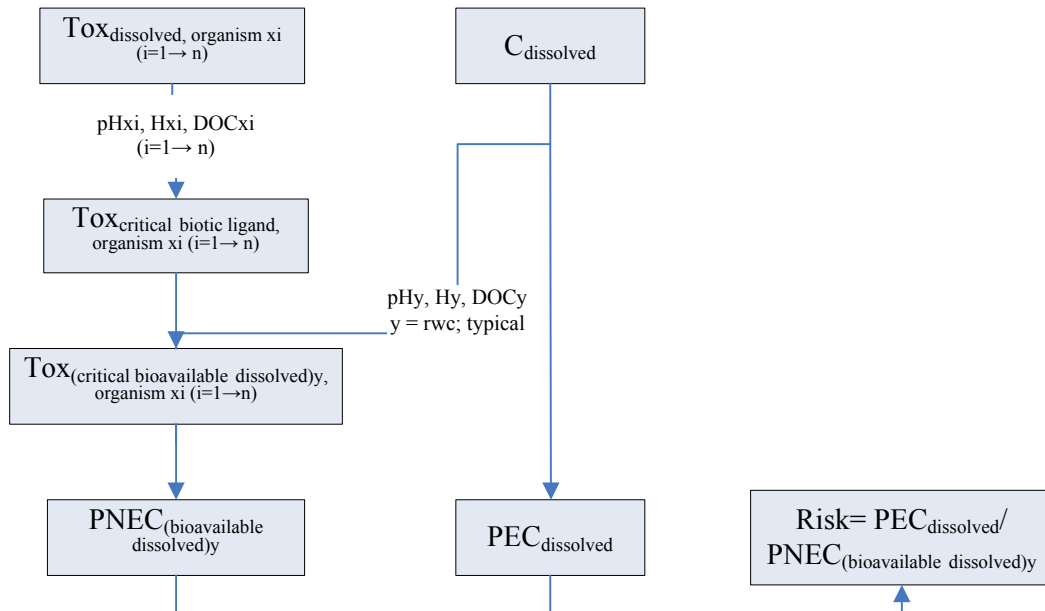


Figure 5: Framework for incorporation of bioavailability models in water

The effects data can be modified to well characterized specific local or regional conditions (i.e. establishing $EQS/PNEC_{local, bioavailable}$ or $EQS/PNEC_{regional, bioavailable}$) using generally typical value for the

bioavailability modifying factors or to a reference PNEC normalized to reasonable worst case conditions, i.e. $PNEC_{reference, bioavailable}$ in the context of a generic risk assessment.

2.4.2 Normalization and read-across

Where bioavailability models (e.g. BLM) 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 pHs, hardness, DOC). 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. BLM) 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 soil compartment, fact sheet 6)

It is proposed to verify read-across of the available bioavailability models (e.g. BLM algae, fish, daphnids) developed and the subsequent PNEC derivation using the scheme as outlined in Figure 6 and explained hereunder.

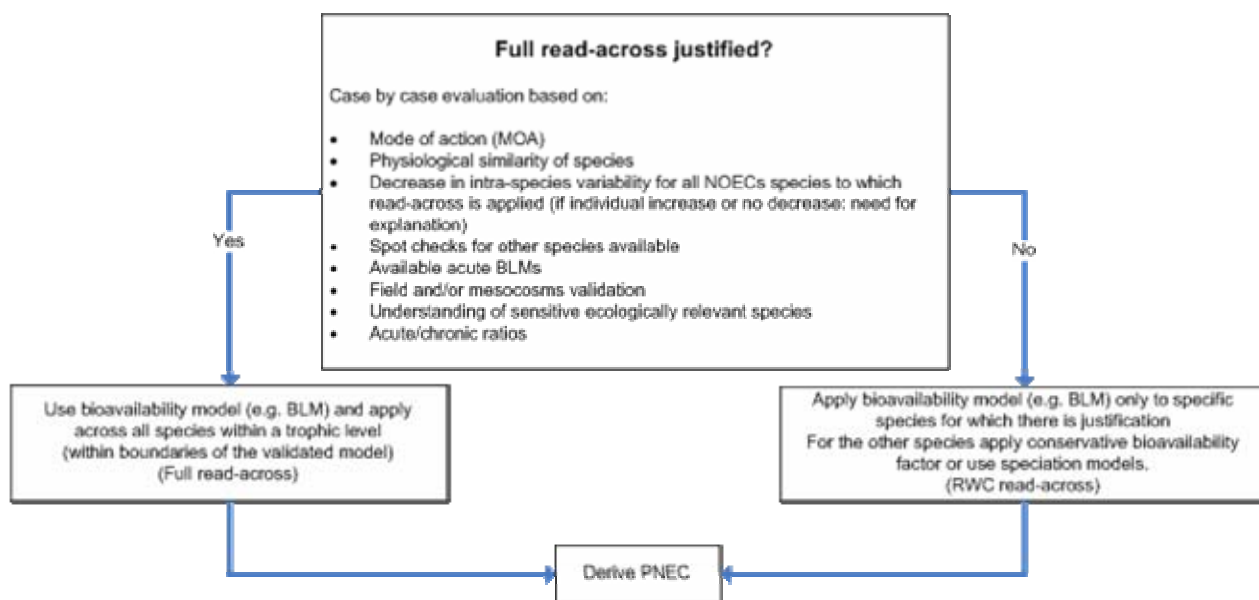


Figure 6: Approach for read-across of bioavailability models.

- 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 variability³ after application of the bioavailability model across species as outlined in figure 1, spot check

³ 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.

validations for specific species (a few ecotoxicity tests, performed under different geochemical conditions for a range of key bioavailability parameters (e.g. pH & DOC)) 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 *Daphnia magna* BLM⁴ for normalization of the toxicity data from other invertebrates like amphipods, insects,...) 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 geometric mean 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 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 care⁵. 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 Normalisation of toxicity data is only allowed within the boundaries of the developed/validated bioavailability model

⁵ Both acute (e.g. Cu, Ni, Pb, Zn, Ag, Co...) and chronic (i.e. Zn, Cu, Ni) BLMs for metals have been developed/validated and proposed for regulatory purposes, both for environmental risk assessment exercises and for the development of site specific water quality criteria. More details can be found in Santore et al, 2001, De Schampelaere et al 2002a, De Schampelaere et al 2002b, Paquin et al 1999, ; Heijerick et al, 2002a, Heijerick et al 2002b, De Schampelaere et al., 2003, De Schampelaere and Janssen, 2004. Comprehensive reviews with regard to the developed BLM models have been written by Paquin et al. (2002) and Niyogi and Wood (2004).

2.4.3 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:

$$RCR = \frac{PEC_{dissolved}}{PNEC_{bioavailable, reference}} \quad (\text{Eq-4})$$

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. BLM) 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-5). The most conservative value (smallest correction for bioavailability, $Bio-F_{reference}$) should then be used⁶

$$Bio - F_{reference} = \frac{Tox_{bioavailable, reference}}{Tox_{dissolved, generic}} \quad (\text{Eq-5})$$

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

$$RCR = \frac{PEC_{dissolved}}{PNEC_{bioavailable, reference}} \quad (\text{Eq-6})$$

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. $PNEC_{local, bioavailable}$, $PNEC_{regional, bioavailable}$).

⁶ 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.

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:

$$RCR = \frac{PEC_{dissolved}}{PNEC_{bioavailable, local / regional}} \quad (\text{Eq-7})$$

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. BLM) 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-8). The most conservative value (smallest correction for bioavailability, $Bio-F_{local/regional}$) should then be used⁷.

$$Bio - F_{local / regional} = \frac{Tox_{bioavailable, local / regional}}{Tox_{bioavailable, reference}} \quad (\text{Eq-8})$$

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

$$RCR = \frac{PEC_{dissolved}}{PNEC_{bioavailable, local / regional}} \quad (\text{Eq-9})$$

1) 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. IMPLEMENTATION OF BIOAVAILABILITY: SEDIMENT

3.1 General considerations

Assessing sediment quality is complex and different approaches have been developed for evaluating the risks of contaminated sediments. The usual approach is to use a weight of evidence approach (Chapman et al. 1999/2000, Borgmann et al. 2001, Borgmann 2003).

For a correct interpretation of observed effects in the field similar to the water compartment there is a need to take metal bioavailability of metals/metal compounds in sediments into account. Metal bioavailability in sediments is governed by different ligands/processes (e.g. organic carbon, sulfides, iron and manganese oxy hydroxide and redox potential) and the relative importance of these binding phases may differ depending on the metals binding capacity and general behavior). It is recommended to make a clear differentiation between for example metal/metal compounds that are susceptible for binding with sulfides and those metals that are not sulfide binders, but where the use of partitioning to Fe-Mn (oxy)hydroxides, speciation calculations (reduced forms under anoxic conditions) and organic carbon normalization as an alternative approach may be more appropriate (Figure 7).

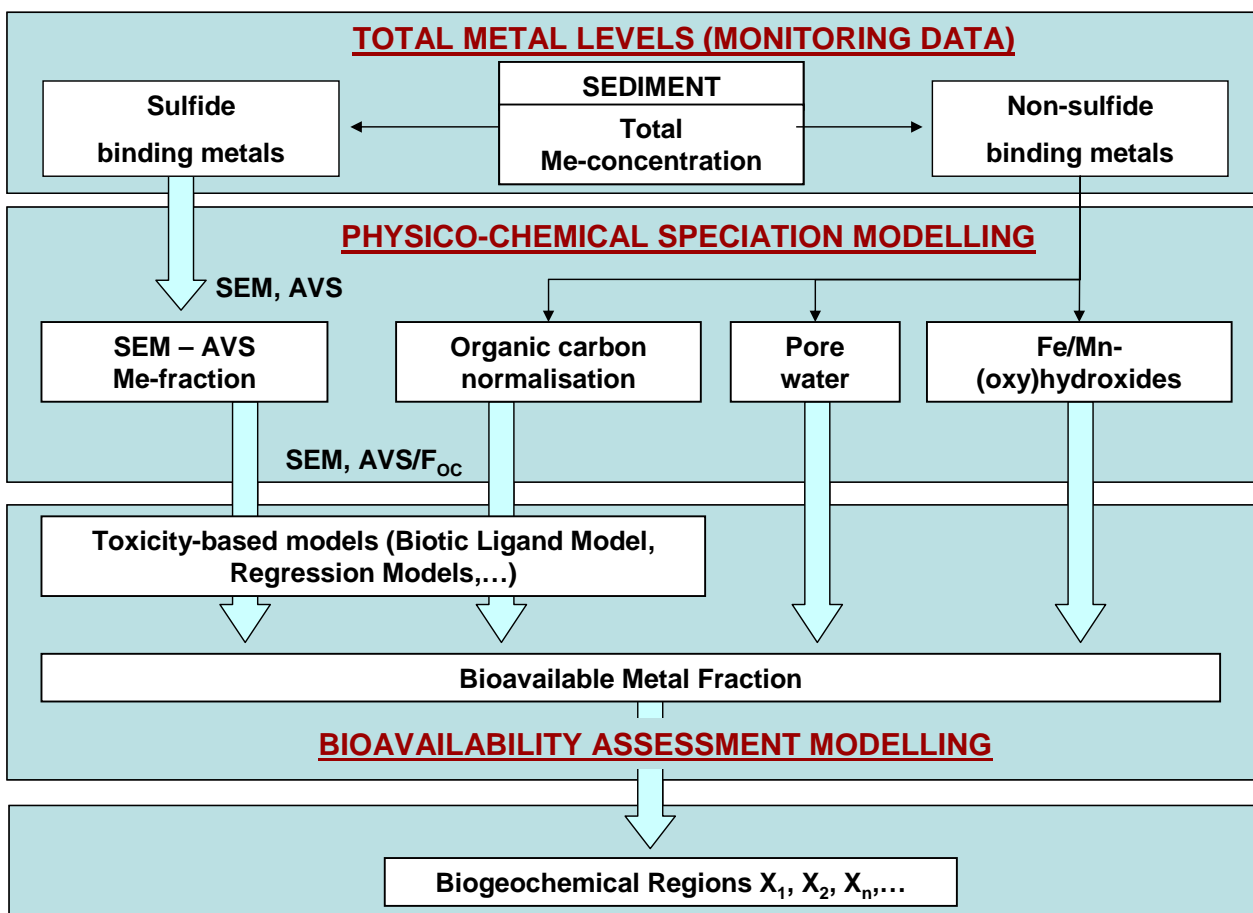


Figure 7: Refinement levels for the incorporation of bioavailability concept for the sediment

It should be noted that strictly spoken the outcome of the use of the SEM-AVS concept and the use of organic carbon and other ligands to normalize the total metal concentrations is a physico-chemical correction and do not represent the true bioavailable fraction. As for the other compartments the effect of competition with biotic ligands should be taken into account. In this regard Di Toro et al (2005) recently did some modelling work as a first step towards the development of a sediment BLM. The *Daphnia magna* BLM was used to compute the LC₅₀ concentration of metal on sediment particulate organic carbon that is in equilibrium with the LC₅₀ in pore water-following the precepts of the Equilibrium Partitioning model-and in equilibrium with the critical concentration at the site of action (the biotic ligand). The results showed that pH of the pore water seem to play an important role.

3.2 Non-sulfide binding metals

3.2.1 Organic carbon normalization

For metals that do not bind with sulfides it may be worthwhile to explore if a relationship can be established between the observed toxicity levels and the presence of organic carbon. If a relationship can be discerned the variability introduced by the presence of toxicity values generated at different organic carbon concentrations can be captured by normalizing each Tox value using the following formula:

$$Tox_{OC, normalized} = \frac{Tox_{total}}{fOC} \quad (\text{Eq-10})$$

Tox_{total} (mg Me/kgdw)

fOC = fraction organic carbon

$Tox_{OC, normalized}$ (mg/g OC)

The PNEC sediment can be translated back to mg/kg dry wt. when a default OC value is assumed for the area/region under investigation. The latter value can be used as a generic EQS value. In the EU, a standard sediment has a default OC value of 5 %. The risks for the local site can subsequently be calculated from the comparison between the PEC_{total} and the $PNEC_{normalized, OC (5\%)}$ taking into account site specific information on the OC content (Eq-11)

$$RCR = \frac{PEC}{PNEC_{normalized, OC_{region}} \times \frac{fOC_{site}}{fOC_{region}}} \quad (\text{Eq-11})$$

3.2.2 Other ligands (e.g. Fe/Mn oxy-hydroxides)

In a similar way the normalization could be performed with other sediment ligands such as Fe/Mn oxy hydroxides when it can be shown that a relationship exists between the observed toxicity and the ligand.

Fe and Mn oxides and organic matter have been identified by different authors as important factors controlling bioavailability of metals. An overview of their influence and the uncertainties and limitations are given in the background document.

The importance of these Fe oxides for assessing metal bioavailability towards benthic organisms has been demonstrated by various authors. Prediction of trace metal levels was improved when the trace metal concentrations extracted from the sediments were normalized with respect to iron (hydrated oxide) (Pb: Luoma and Bryan, 1978; As: Langston, 1980; Cu: Tessier et al., 1983, 1984, Cd: Tessier et al., 1993).

3.2.3 Pore water normalization

Pore water concentrations could be used to account for bioavailability if it can be proven that the pore water is the primary route of exposure. If it can be expected that dietary route will contribute significantly to the exposure than the assessment should not only focus on the pore water but should also take sediment ingestion into account.

To ensure consistency in the approaches to assess the bioavailable concentration in sediment pore water and water additional research is recommended before pore water normalization can be routinely used.

3.3 Sulfide binding metals: SEM-AVS concept

The fraction of metals that may bind to sulfides in the sediment and thus be sequestered in the sediment can be estimated using the SEM-AVS concept. The basic concept behind the SEM-AVS⁸ approach is that the activity of most divalent metals (e.g. Zn, Ni, Cu, Pb, Cd, ...) in sediments is controlled by the amount of acid-volatile sulfide (AVS) present in the sediment matrix. Incorporation of the AVS model is a definite improvement to sediment toxicity assessments but the approach does have some limitations and should be considered more as one of the tools available to be used in a kind of weight approach. A detailed overview of the SEM-AVS concept, the uncertainties and limitations are given in the background document. The way the SEM-AVS concept can be used is outlined below.

The value of the SEM-AVS difference gives the amount of SEM_{Me} that is not bound (excess SEM_{Me}) and consequently potentially bioavailable. Although it is recognized that other important ligands such as organic carbon and Fe/Mn oxides in the sediment or pH, DOC and hardness conditions in the pore water may further reduce bioavailability, the remainder of this section uses the nomenclature of excess SEM_{Me} as "bioavailable" for purposes of estimating the extent to which metal/metal compounds in sediments may cause toxicity (Eq-12).

$$SEM_{Me, bioavailable} = SEM_{Me} - \Delta AVS_{Me} \quad (\text{Eq-12})$$

In order to verify if the SEM-AVS concept is applicable to other metals and which ranking it will have the solubility product of the MeS can be compared with the solubility products summarized in Table 1.

Table 1: Solubility products of metal sulfides

Metal sulfide	Log K ^a	Log K ^b
MnS (s)	-19.15	- 13.50
FeS (amorphous)	-21.80	-
FeS (s)	-22.39	-18.10
NiS (s)	-27.98	-
ZnS (s)	-28.39	-24.70
CdS (s)	-32.85	-27.00
PbS (s)	-33.42	-27.50
CuS (s)	-40.94	-36.10
Ag ₂ S (s)		-50.10
HgS	-57.25	-52.70

^aDi Toro et al, 1990

^bStumm and Morgan, 1981

In applying the SEM-AVS model for a specific metal it has to be taken into consideration that metals are acting in a competitive manner when binding to AVS. Acknowledging the existence of competitive displacement kinetics the SEM-AVS model can be made metal specific. The procedure that is used is to assign the AVS pool to the metals in the sequence of their solubility products. For example ranked from the lowest to the highest solubility product the following sequence is observed for these five metals: SEM_{Cu}, SEM_{Pb}, SEM_{Cd}, SEM_{Zn} and SEM_{Ni} (Table 1). Meaning copper has the highest affinity for AVS, followed by lead, cadmium etc until the AVS is exhausted. The remaining SEM is that amount present in excess of the AVS.

⁸ SEM = Simultaneously Extracted Metals, AVS = Acid Volatile Sulfides

To be specific, let $\Delta \{SEM_i\}$ be the excess SEM for each of the i^{th} metals. The least soluble metal sulfide (of the five metals considered above) is copper sulfide. Thus if the simultaneously extracted copper is less than the AVS ($\{SEM_{Cu}\} < \{AVS\}$), then essentially all of it must be present as copper sulfide with no additional SEM_{Cu} present, such that $\Delta \{SEM_{Cu}\} = 0$. The remaining AVS binding pool is $\Delta \{AVS\} = \{AVS\} - \{SEM_{Cu}\}$. This computation is repeated next for lead and cadmium because these are the next least soluble sulfides. Just suppose as an example that unlike copper and lead the simultaneously extracted cadmium is not less than the remaining AVS = $\Delta \{AVS\} = \{AVS\} - \{SEM_{Cu}\} - \{SEM_{Pb}\}$. Hence, only a portion of the simultaneously extracted cadmium is present as cadmium sulfide and the remainder is present as excess SEM. Because the AVS has been exhausted by the cadmium in this example, the remaining two metals, zinc and nickel, would all be present as excess SEM.

The observation that metals may bind strongly to organic carbon suggests that in some case organic carbon normalization might further reduce the variability observed in toxicity levels.

The incorporation of organic carbon into the existing AVS concept has been suggested by Di Toro to predict not only the lack but also the onset of metal toxicity in spiked and field contaminated sediments (Di Toro et al., 2001). In this context it is assumed that toxicity occurs if the excess SEM goes beyond the binding capacity of the organic carbon present in the sediment. Using this information it was shown that the organic carbon normalized excess SEM can be used to predict toxicity (Eq-13):

$$SEM_{x,oc} = \frac{\Sigma SEM - AVS}{f_{OC}} \quad (\text{Eq-13})$$

where f_{OC} is the organic carbon fraction in the sediment.

The SEM-AVS (SEM-AVS/foc) concept can be applied to both a regional scale as a local scale. Depending on the available information the following approaches can be followed.

Application to a regional scenario

The SEM-AVS concept can be applied to a region if extensive SEM-AVS data representative for that region is available. Knowledge with respect to spatial and seasonal variations of AVS and SEM levels is required for a proper application of the AVS concept. SEM-AVS data should represent the seasonal worst case scenario (i.e lowest AVS levels being measured, spring season). In addition, since AVS levels decrease with increasing depth it is important to focus the analysis on the biological active layer of the sediment (0-20 cm). But even over this distance the AVS profile could differ dramatically and in top layers (0-2cm) a significant lower amount of AVS could be present.

Incorporation of the SEM-AVS (SEM-AVS/foc) concept in the risk characterization should be performed as outlined in Figure 8.

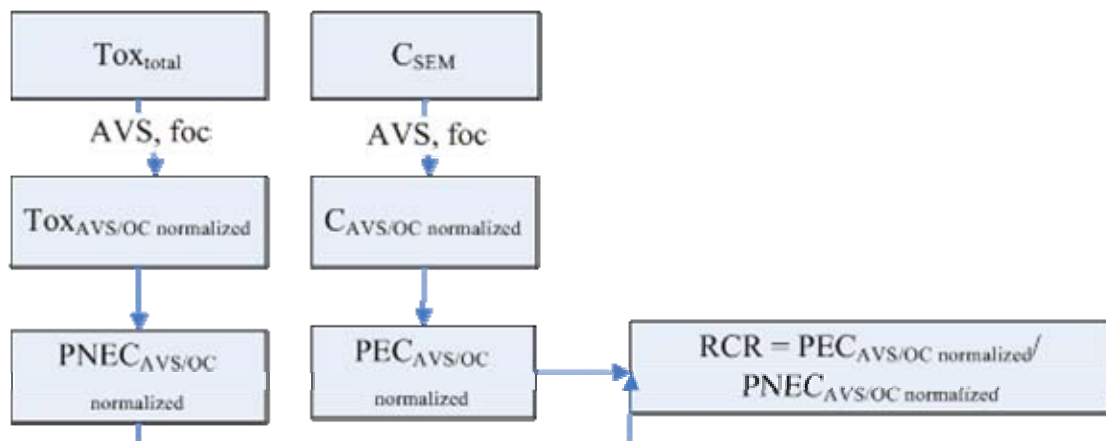


Figure 8: Framework for assessing risks of metals/metal compounds in sediments based on the SEM-AVS concept

- 1) From the compiled SEM and AVS data set the potential bioavailable SEM_{Me} fraction for each individual sampling point is derived by coupling the ΔAVS and SEM_{Me} data⁹ for that specific station. As such a distribution function of all individual (SEM_{Me} - ΔAVS) or (SEM_{Me} - ΔAVS)/fOC values across the region can be established. Note that if this value is negative than 100 % of SEM_{Me} is bound to sulfide. In case this difference is positive (meaning not enough AVS is available for binding with the SEM_{Me}), this fraction corresponds with the amount of SEM_{Me} potentially bioavailable. In this way the information on SEM_{Me} can be transformed into SEM_{Me} bioavailable.
- 2) Calculate the PEC_{AVS normalized}/PEC_{AVS, OC normalized} as the higher value (e.g. 90th percentile) of the measured bioavailable SEM_{Me}
- 3) Calculate the PNEC_{AVS normalized}/ PNEC_{AVS, OC normalized} from the Tox_{bioavailable} values. In case SEM-AVS values has been measured in a sediment toxicity test the Tox values should be expressed as SEM_{Me, bioavailable} and used to calculate the PNEC_{AVS, normalized}. In case no SEM-AVS measurements are available the sediments that should be used for the PNEC derivation should be in the initial phase screened to exclude those samples for which the bioavailability is limited due to the presence of AVS. Only Tox values originating from sediments with expected low AVS levels should be used for deriving the PNEC_{rwc}. The risks for the region can subsequently be calculated from the comparison between the PEC_{AVS normalized}/ PEC_{AVS, OC normalized} and the PNEC_{AVS, normalized} or PNEC_{AVS, OC normalized} (Eq-14a and Eq-14b)

$$RCR = \frac{PEC_{AVS \text{ normalised}}}{PNEC_{AVS \text{ normalised}}} \quad (\text{Eq-14a})$$

$$RCR = \frac{PEC_{AVS, OC \text{ normalized}}}{PNEC_{AVS, OC \text{ normalized}}} \quad (\text{Eq-14b})$$

In case specific information on prevailing SEM/AVS levels is lacking a default correction factor based on the AVS profile of another region that is expected to have similar sediment characteristics could be applied but with caution..

With regard to the derivation of default SEM-AVS values two options are available: a) the use of paired SEM-AVS data to calculate the Δ(AVS)¹⁰ available to bind with a certain metal or b) the use of total AVS data only from which the specific regional background of metals with a higher affinity is subtracted). Both methodologies have their pros and cons, as shown in Table 2.

Table 2: Advantages and disadvantages of using paired SEM-AVS data versus total AVS approach

Starting point : paired SEM-AVS data	Starting point: total AVS data
Advantage: describes realistic field conditions - SEM concentrations are correlated with AVS concentrations.	Disadvantage: does not reflect realistic field conditions - Low AVS-high SEM concentrations are unlikely to be found
Disadvantage: possible over- or underestimation of the amount of ΔAVS available to bind the metal because regional ambient	Advantage: provides the necessary flexibility to take into account region-specific metal concentrations, and hence enables a better

⁹ Considering the observed co-variance between AVS and SEM_{Me} it is recommended to take only measured coupled data into account to maintain the ecological relevance of the analysis. (Vangheluwe et al, 2003).

¹⁰ E.g. Δ(AVS)Cd = (AVStotal) - (SEM_{Hg}) - (SEM_{Cu}) - (SEM_{Pb}).

<p>concentrations of metals with a higher affinity can be higher or lower than the region from which the default ΔAVS has been derived</p>	<p>estimate to be made of the amount of AVS available to bind with the metal of concern in a certain region.</p>
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The use of paired SEM-AVS or total AVS data is a pragmatic choice depending on whether the aim is to incorporate flexibility for those regions where ambient metal concentrations can be expected to differ to a large extent from the data set used to derive the default AVS value. . Paired SEM-AVS data have a higher level of field realism.

Application to a local scenario

Application of the SEM-AVS concept to a local scenario can be conducted in a tiered way (Figure 9):

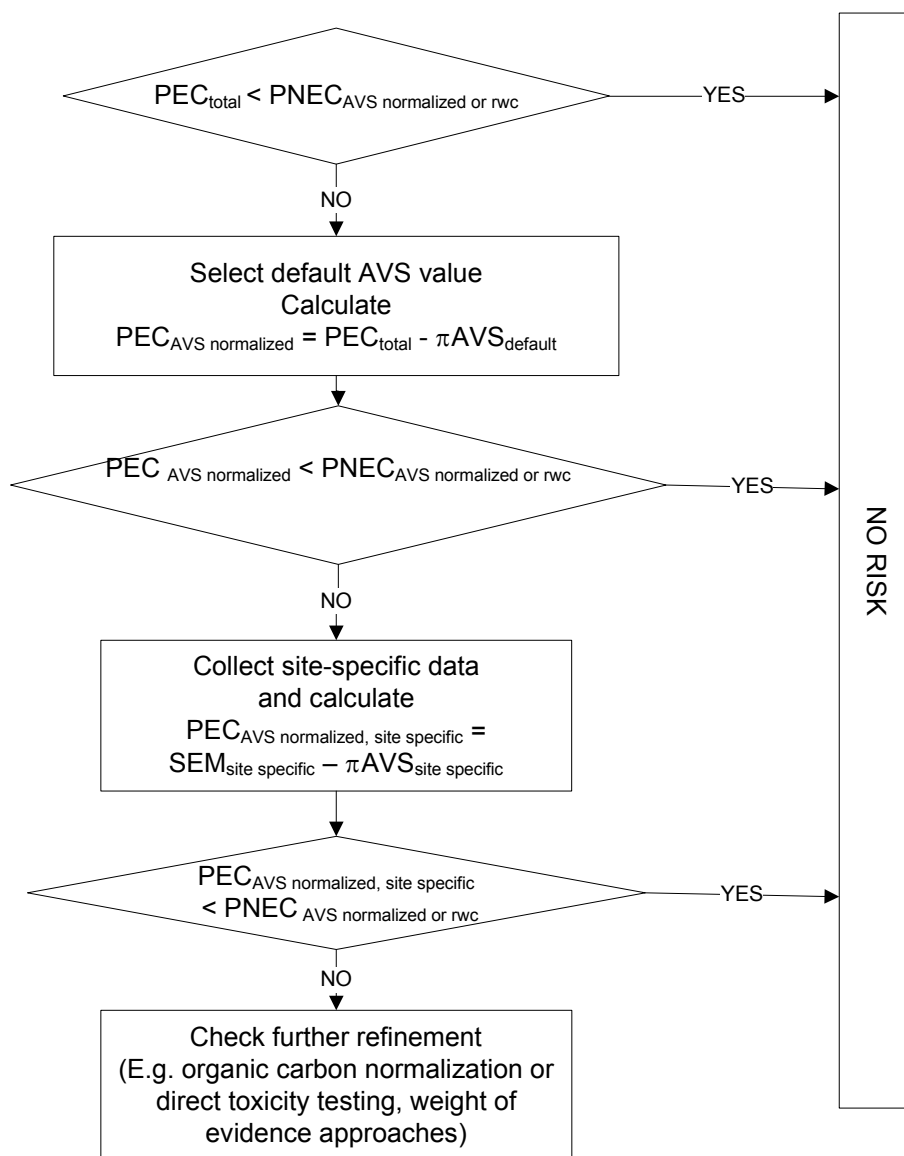


Figure 9: Overview tiered approach for assessing risks of metals/metal compounds in sediments using the SEM-AVS concept for the local scenario

- 1) No risk is identified when the total metal concentration is smaller than the $PNEC_{AVS, normalized}$ or $PNEC_{rwc}$. The latter values represent either the SEM-AVS difference measured in the toxicity tests or reflect those test results which were conducted under reasonable worst case conditions (i.e. AVS levels $< 1 \mu\text{mol/g dry wt}^{11}$)
- 2) If a risk is identified but SEM-AVS data are lacking a default correction can be applied. Depending on the redox potential of the sediment a default AVS concentration can be selected (for example for oxidized sediments it can be assumed that the AVS concentration in the sediment is low i.e. an AVS concentration of $< 1 \mu\text{mol/g dry wt}$. can be used as default scenario for a sediment with low AVS content) and that the total metal concentration can be used as a conservative estimate of SEM_{Me} . $PEC_{AVS, normalized}$ is then calculated using Eq-15.

$$PEC_{AVS, normalized} = PEC_{total} - \Delta AVS_{default} \quad (\text{Eq-15})$$

$PEC_{Me, total}$ expressed as $\mu\text{mol/g dry wt}$.

- 3) If local SEM-AVS data are available then calculate the $PEC_{AVS, normalized}$ using Eq-16

$$PEC_{AVS, normalized} = SEM_{Me, site\ specific} - \Delta AVS_{site\ specific} \quad (\text{Eq-16})$$

- 4) The risks for the local site can subsequently be calculated from the comparison between the $PEC_{bioavailable}$ and the $PNEC_{AVS, normalized\ or\ rwc}$ (Eq-17)

$$RCR = \frac{PEC_{AVS, normalized}}{PNEC_{AVS, normalized}} \quad (\text{Eq-17})$$

In case the organic carbon normalization can be used in combination with AVS correction the scheme as visualized in Figure 10 is applicable.

¹¹ For the regional SEM-AVS data set available for Flanders (Belgium) the 10th percentile of the AVS concentrations is $0.77 \mu\text{mol/g dry wt}$. For the Netherlands the 10th percentile is $2 \mu\text{mol/g dry wt}$ (Vangheluwe et al, 2003)

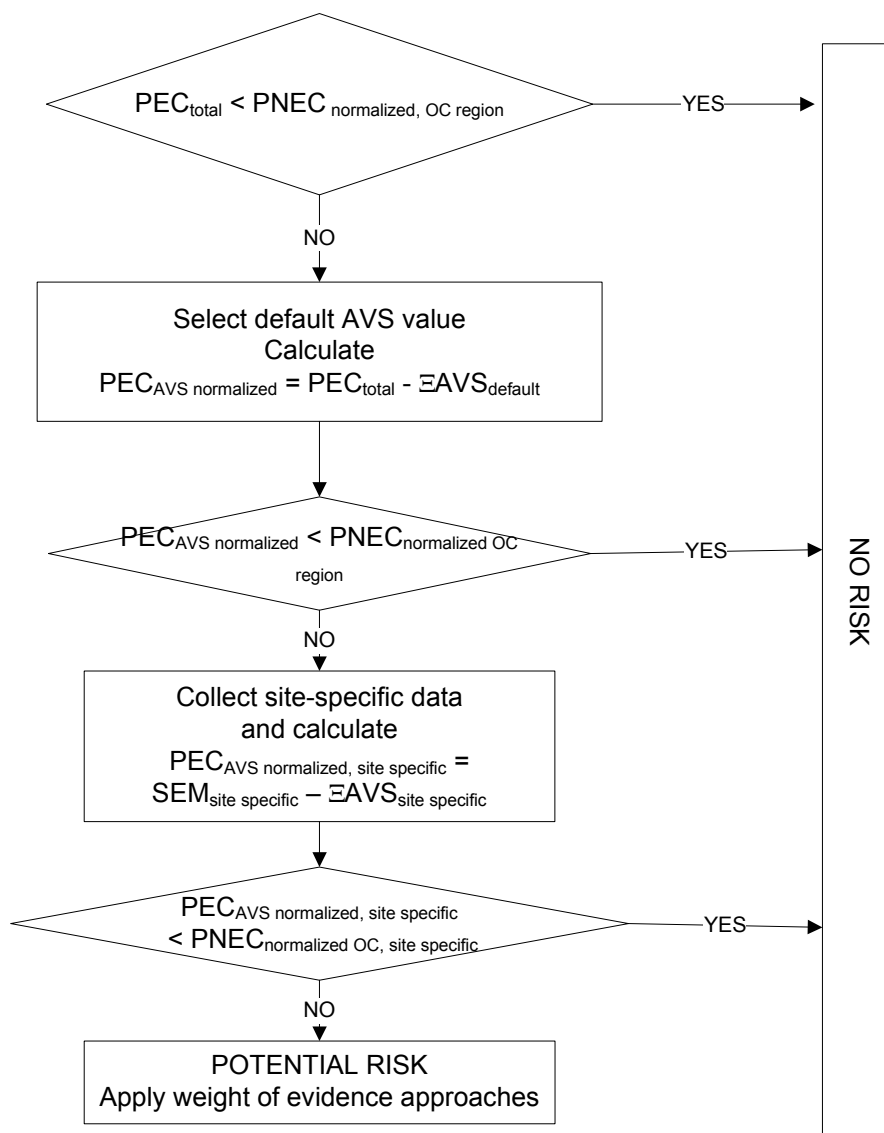


Figure 10: Overview tiered approach for assessing risks of metals/metal compounds in sediments using the SEM-AVS concept in combination with organic carbon normalization for the local scenario

- 1) No risk is identified when the total metal concentration is smaller than the $PNEC_{normalized, OC\ region}$ (in the EU this means normalized to 5 % OC). If a risk is identified but SEM-AVS data are lacking a default correction can be applied. Depending on the redox potential of the sediment a default AVS concentration can be selected (for example for oxidized sediments it can be assumed that the AVS concentration in the sediment is low i.e. an AVS concentration of $< 1\ \mu\text{mol/g}$ dry wt. can be used as default scenario for a sediment with low AVS content) and that the total metal concentration can be used as a conservative estimate of SEM_{Me} . The $PEC_{AVS\ normalized}$ is then calculated using Eq-18.

$$PEC_{AVS\ normalized} = PEC_{total} - AVS_{default} \quad (\text{Eq-18})$$

- 2) If local SEM-AVS data are available then calculate the $PEC_{AVS\ normalized, site\ specific}$ using Eq-19.

$$PEC_{AVS \text{ normalized, site specific}} = SEM_{Me, \text{ site specific}} - AVS_{\text{site specific}} \quad (\text{Eq-19})$$

- 3) The risks for the local site can subsequently be calculated from the comparison between the $PEC_{AVS \text{ normalized}}$ and the $PNEC_{\text{normalized, OC region}}$ (Eq-20) taking into account site specific information on the OC content.

$$RCR = \frac{PEC_{AVS \text{ normalized}}}{PNEC_{\text{normalized, OC region}} \times \frac{fOC_{\text{site}}}{fOC_{\text{region}}}} \quad (\text{Eq-20})$$

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