METALS ENVIRONMENTAL RISK ASSESSMENT GUIDANCE

FACT SHEET

MERAG 02

EXPOSURE ASSESSMENT

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1. INTRODUCTION

The main objective of the exposure assessment is the derivation and evaluation of metal concentrations for each environmental compartment (water, air, soil, sediment) that is potentially affected by human activities. Metal concentrations in the environment are the result of the natural background, historical contamination and the emissions associated with the use pattern and the complete life cycle of the metal (i.e., from mining to waste disposal). Due to the inherent variation of metal concentration in the natural environment (e.g., different natural background concentrations) and the variations of anthropogenic input, large differences in observed metal levels can be observed among different locations.

The exposure assessment can be performed using modelled data and/or measured data. Disadvantages and advantages of both approaches are given in Table 1.

Table 1: Advantages and disadvantages of exposure assessment using modelled or measured data

MODELLING	MEASURED DATA
Advantage: possibility of unintentionally • missing unidentified sources, • missing metal compounds or • excluding sources due to regulatory issues (e.g., biocides, mining, medical use, …)	Advantage: reality-check, realistic reflection of environmental exposure, contains all possible sources, contributions and metal compounds
Disadvantage: is typically used in a conservative way by using reasonable worst-case assumptions and default values. However, in some cases, this limitation can be overcome by choosing average values.	Advantage: describes realistic field conditions
Advantage/disadvantage: Depending on the metal, there is a low or high resource allocation compared to collecting measured data.	Advantage: low resource allocation if measured data are available Disadvantage: resource intensive if data are not already available
Advantage: can estimate the contribution of each source (within or out of the regulatory context) or metal compound to overall PECs (this is particularly useful for risk management)	Disadvantage: in general very difficult to differentiate between sources (within or out of the regulatory context) or metal compounds
Advantage: can estimate the anthropogenic contribution	Disadvantage: difficult to differentiate between natural and anthropogenic (including historical) contributions
Advantage: can be used for projection and to test management scenarios	

The preference for using modelled or measured metal concentrations depends on the data availability of the metal under consideration (data poor vs data rich) (Figure 1).

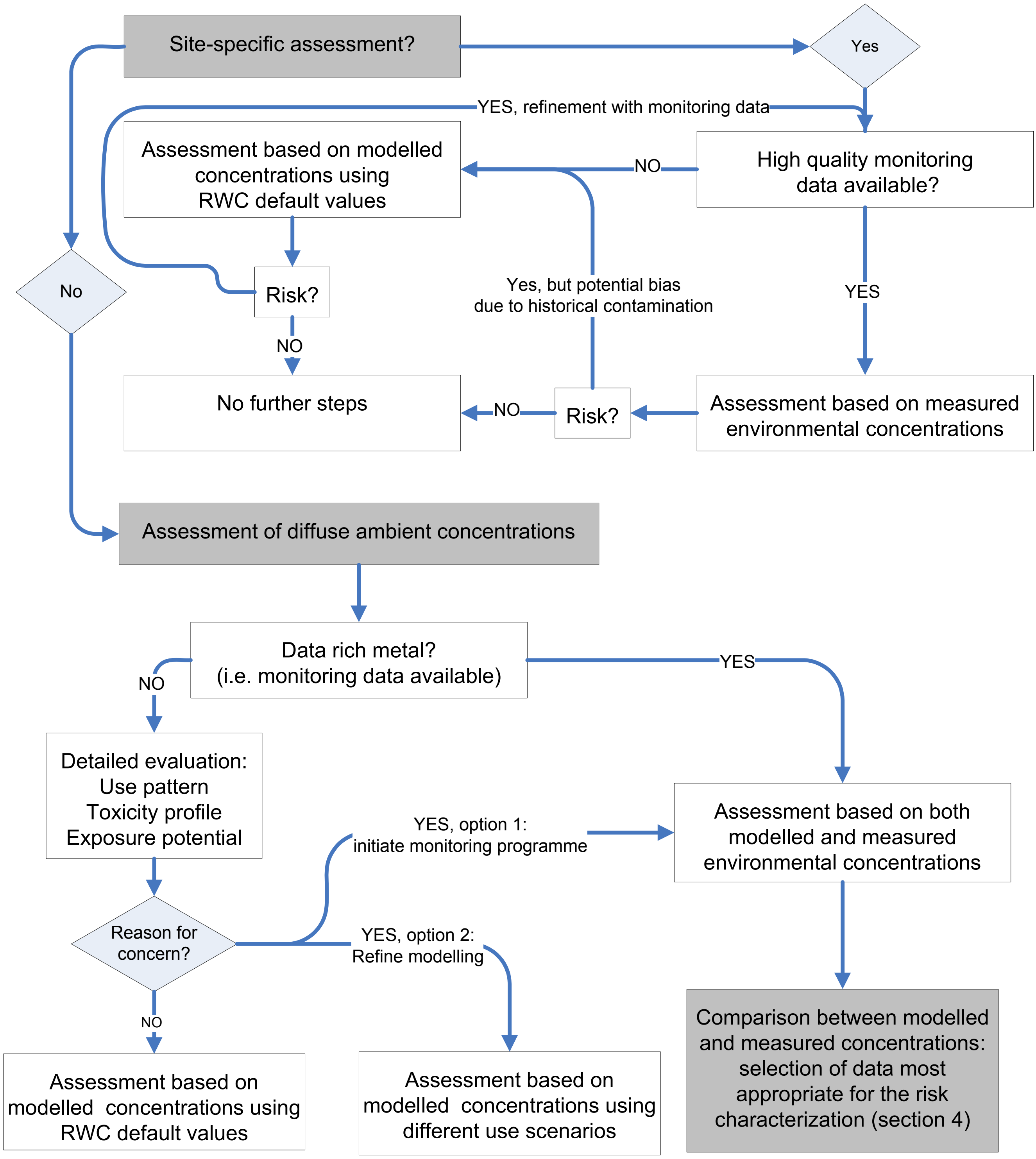

Figure 1: Decision tree for using modelled vs. measured environmental metal concentrations

For a site specific evaluation the assessment should preferentially use measured high quality data if available. If a potential risk is identified based on measured data it should be checked if this is due to historical contamination. If there is a potential bias from historical contamination it could be worthwhile to perform a modelling exercise to evaluate the actual impact of current practices in place on the site.

In the case no reliable measured data are available there is no need for collection of monitoring data if no risk is identified under a conservative modelling approach using reasonable worst case (RWC) default values. If the modelling identifies a potential risk starting a monitoring program on the site may refine the analysis.

At a broader scale (i.e., the assessment of diffuse ambient concentrations) the use of both measured data and modelled data is recommended if these data are available (data rich metals) Measured data provide a quantification of the contribution of all possible metal compounds, processes and sources to the environment. Although using modelled data has the possibility of missing unintentional uses/sources (e.g., impurities in inorganic fertilisers) or excluding sources due to regulatory issues (e.g. biocides, mining medical use) their use in parallel with measured data can be of added value. The outcome of the modelling can be integrated in a weight of evidence approach or can be used to differentiate between both the natural background and the concentration added by past and recent anthropogenic activities which are both integrated in ambient measured monitoring data. At the end a comparison between modelled and measured data has to be performed in order to select the most appropriate exposure estimate to take forward in the risk characterization.

For data poor metals monitoring data will most often be lacking and in those cases a choice has to be made whether to initiate a monitoring program or use only modelling as a way forward for carrying out the exposure assessment. The decision to embark on a monitoring program or not, should be based on a detailed evaluation of the use pattern of the metal (dispersive use versus contained use), the intrinsic toxicity and more importantly the potential for release and likelihood of exposure to these emissions of human and ecological receptors. In this regard it should be noted that the potential for release and exposure is independent of the volume in which the product is being produced. In case there is concern (e.g. the metal is known to have a high intrinsic toxicity and has a wide dispersive use) it could be warranted to initiate a monitoring program to collect measured data for the compartment most likely to be impacted. If monitoring would be too cumbersome an extended model exercise in which different use/dispersion scenarios are performed could be conducted.

It should be noted that also in the type of measured data used a tiered approach can be used. As a first tier quite often total metal concentrations can be used. If risks are observed, it could be warranted to refine the assessment by incorporating for example bioavailability.

2. EXPOSURE ASSESSMENT USING MODELLED DATA

2.1 Introduction

With regard to the modelled exposure analysis for risk assessment purposes, a distinction can be made between different spatial scales. The 'site-specific' scale considers the protection goals in the vicinity of a point source. The assessment of the risks due to all releases from point and diffuse sources[1] in a larger area (country, state, region) is performed on a so-called regional scale. A third spatial scale – the continental scale – is the sum of all regional scales within a continent, and is for example used as background for the regional system in exposure models such as EUSES. An overview of the different interactions between the different spatial scales is presented in Figure 2.

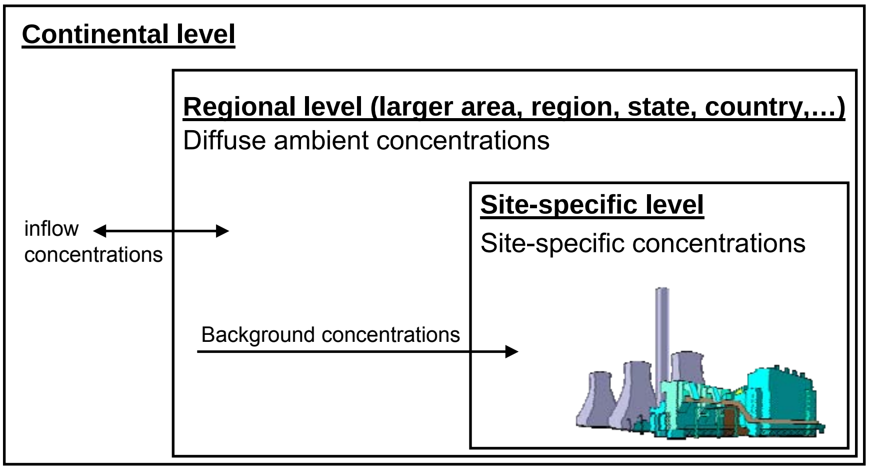

Figure 2: The relationships between the exposure assessments at the different spatial scales

The site-specific scale receives a background concentration from the regional scale, whereas the regional scale receives the inflowing air and water from the continental scale

2.2 Diffuse source emission inventory

2.2.1 General

Most often only a limited number of major emissions or uses predominate for each metal and these must initially be identified. Therefore, an inventory of all relevant emission sources must first be prepared and specific industry and use categories should be identified for the assessment of both the site specific and regional impact. For these industries and use categories specific emission quantification methods need to be developed. In certain frameworks general methods are already well described (e.g. TGD, 2003; EEA, 2003; US EPA, 1996). However, some metals may require specific or targeted assessments (e.g., road border scenario). It is recommended that all sources be included, including those who may be part of other legislative frameworks. The predicted emissions are subsequently used as input parameters into an exposure model that calculates the environmental concentrations in the different environmental compartments.

In general the methodology used for a diffuse source emission inventory is comprised of the following steps:

- Critical evaluation of available data on point and diffuse sources of metals for different countries and the selection of a representative area/region.
- Quantification of regional and continental metal emissions (in the EU the scope of the assessment is limited to current emissions)

[1] Diffuse sources cover essentially all sources that are not point sources and include the many smaller or scattered sources from which pollutants may be released. Diffuse sources are difficult to locate, without a single point of origin or not introduced into a receiving stream from a specific outlet and are in general quantified for an area as a whole (e.g. residential heating, wastewater discharge, agriculture, traffic, ...). In the exposure assessment, diffuse sources include all sources, not included in the local RAR.

Ideally, biogeochemical regions (metallo-regions) that take the ecological dimensions into account should be used in instead of regions based solely on social, demographic, economical and geographical factors (e.g., countries, states). Different background concentrations and bio-availability corrections can then be used in correspondence with different biogeochemical regions. In practise, this may not always be feasible. As an alternative, a well-defined area (region, state, country) that is representative for the global area under consideration (i.e., the continent) could be used for the modelling of diffuse ambient concentrations. A hypothetical standard area should only be used in case no country-specific data or descriptors are available.

It is recommended to start the emission investigation on a country (or a state) level and to include all the sources in the assessment (i.e., also those governed by other legislations).

2.2.2 Critical evaluation of available data

Different sources of information can be consulted to gather the most recent available metal emissions data. Next to national emission inventories available for those countries/states within the area of interest, additional emission data may be available from international organizations (Box 1). Quite often, different methodologies have been used among these various groups to derive the emission estimated and therefore these data should be thoroughly scrutinized to assess the completeness of the available data and the quality of the methodologies applied to quantify the emissions.

Box 1: Sources for emission data covering the European Union

Within the European Union, there are several Registers and Organizations from which relevant emission data can be obtained. The most important are the European Pollutant Emission Register (EPER-database), the European Commission (Directive 76/464/EEC, Water Framework Directive,…), North Sea Conferences, OSPAR (Convention for the Protection of the Marine Environment of the North-East Atlantic of the Oslo and Paris Commissions), HELCOM (Helsinki Commission, Baltic Marine Environment Protection Commission), ICPR (International Conference for the Protection of the Rhine), EMEP (Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air pollutants in Europe), etc.

2.2.2.1 Completeness of data

The main aim of an emission inventory exercise is to obtain a representation as complete as possible of all emission sources for the metal/metal compound under consideration. Therefore the final selected state/country-individual emission inventory should be completed with metal emission sources mentioned by other countries or as described in the international literature. As a result, a complete quantitative list of metal emission sources is created that should include direct emissions to air, direct emissions to the surface water and direct and fugitive emissions to soil.

To facilitate the comparison between regional predicted and measured environmental concentrations, it is also recommended to include to the extent possible also those products that are excluded from the regulatory framework (such as biocides, pesticides, medical product applications) in the emission inventory and subsequent regional PEC derivation. In case not enough information is available on the emissions of these sources or since the use of these products is very specific and therefore the used exposure models may not be suited to assess their distribution in the environment correctly, it is at least recommended to try to distinguish these sources and/or to assess their contribution in a semi-qualitative way. It is also recommended to group the metal of concern and its compounds to reduce the risks that anthropogenic sources are overlooked. In this regard, a detailed market analysis about where the product may end up in the environment could also be useful to ensure that all intended uses would be covered.

A relevancy check of the emission inventory could identify if there is a need to account for non-additive emissions. For example, sewage sludge, fertiliser, other sources of organic matter and minerals, or a combination of these is used on agricultural soil in a certain country. It would be inaccurate to assume that both sewage sludge and fertiliser are used at their full application rate across the entire area of interest. If quantitative information is lacking on non- additive emissions, it is recommended that the following scenarios be run assuming 100% application of one of the inputs (and 0% of the others), then 100% of another, etc. until all possible inputs have been assessed. For example, one assessment can be done assuming 100% sewage sludge application (and 0% fertilisers) and another done assuming 100% fertiliser application (and 0% sludge application). The scenario that deposits the most into a certain medium (soil, water, sediment, air) is then taken forward into the risk characterization. If any risks are identified under this scenario than it can be further investigated if more realistic use patterns apply in the region of interest.

2.2.2.2 Quality assessment of quantification methods

In order to select the most appropriate data the quantification methods should be evaluated with regard to:
- The relative importance of the source;
- The actual quality of the data (uncertainty of data).

To assess the importance of the individual sources, the emission data are ranked in decreasing magnitude. The actual quality of the data underpinning the most important emission estimates should then be carefully evaluated. Special attention should be given to these three variables:

- The quality of the emission factor used: i.e., specific value of an emission, mostly given in physical terms, related to the respective sectoral or process activity rate (e.g., for energy related emissions (Mg/GJ) (EMEP/Corinair, 1999). Most often, average emission factors are used in this perspective.
- The means of expressing/describing activity data: i.e., quantitative representation of the variable that “explains” the emissions in a source category, preferably in physical dimensions (e.g., produced mass of cement [Mg/year] or otherwise in monetary dimensions (e.g., value of glass production [ECU/year]), either in emission inventories or in emission projections (EMEP/Corinair, 1999).
- The choice of the distribution factor: i.e., the partitioning of total emissions to the environmental compartments.

Criteria for evaluating the quality of the emission data have been proposed by EPA (1995) and EMEP/Corinair (EEA, 1999). The assessment of data quality involves a review of individual data elements with respect to how the emission estimate was derived. The following quality codes (from high to low) can be used to assess the quality of the three variables mentioned earlier.

- A = an estimate based on measured emissions;
- B = an estimate based on measured emissions and possibly on an engineering calculation derived from relevant facts;
- C = an estimate based on an engineering calculation derived from relevant facts and some assumptions;
- D = an estimate based on engineering calculation assumptions only; or when no information on the quantification methodology was available but evidence of a scientific study was provided;
- E = an estimate based on non-specified background information.

The overall quality of the emission inventory is determined by the lowest quality score for any of the emissions. A low quality score increases the uncertainty with regard to the outcome of the modelled exposure assessment and, subsequently, the risk characterization based here upon. Based on the quality assessment of the emission inventory, sources and quantification methodologies, which have to be studied in-depth because of their importance and/or low quality quantification method, can further be identified. It is recommended that the quantification method with the highest quality score be selected for each source, depending on the availability of data. For the major sources, estimates with quality scores D and E should not be used.

2.2.3 Calculation of emissions on a regional and continental scale

"Regional" emissions are needed as an input for the regional exposure modelling. To calculate the background for the regional exposure assessment in the generic model (e.g., EUSES), continental emissions also have to be assessed. Emission estimates on the continental scale are based on a continental wide production volume of the substance.

Due to lack of detailed and homogeneous emission data from all involved countries it is nearly impossible to calculate the total emissions by summarizing the country-specific emission data for each emission source. As an alternative, a methodology based on the use of source-specific extrapolation factors to extrapolate regional emissions to total emissions is proposed. In that case, country specific emissions are expressed on the basis of a descriptor or unit (e.g., mileage driven for wearing of tyres) and used as translator to extrapolate the emissions to a continental scale. This methodology can be summarized by the following equation (Eq-1). Due to the structure of the exposure model ("nested multimedia model"), the continental concentration serves as a background for the regional scale. Therefore, double counting would occur if the regional emission would not be subtracted in Eq-1, which would lead to a significant overestimation of the regional PEC.

$$Emission_{continental} = \left(Extrapolation\ factor \times Emissions_{regional}\right)_{sourcespecific} - Emission_{regional} \quad \text{(Eq-1)}$$

Consequently, for each identified source, a source-specific extrapolation factor has to be determined. If the region is not representative for the overall situation, country-specific parameters or more average parameters, representative for the overall continental picture, will have to be selected.

Finally, the continental release can then be estimated based on the summation of the country figures or the source descriptors. In cases no such data are available; assumptions can be made on the allocation to a region. For example in the EU (TGD, 2003) it is assumed that 10 % of the production and use of a substance takes place within a hypothetical standard region[1]. The regional emission then equals 10 % of the total emission and the continental emission 90 %. It should be noted that this is not the most conservative approach since quite often the country specific extrapolation factors are larger.

2.3 Local Emission Inventory

2.3.1 General

In analogy with the diffuse source emission inventory, emission data have to be collected for companies on a site specific (local) scale that mine, produce, refine or use the metal/metal compounds in their industrial processes (i.e., downstream users). Special attention points here are the representativeness of the sector, the amount of the total tonnage consumed/produced that is covered, the covered fraction of the total numbers of sites involved per sector and the coverage of the different production processes per industrial sector.

[1] E.g., according to the TGD (1996), a general standard region is represented by a typical densely populated area with an area of 200 x 200 km^2 and 20 million inhabitants, located in the margin of Western Europe.

2.3.2 Data gathering and evaluation

The first step in the local exposure assessment should be the collection of site specific data (local environment) for all environmental compartments (i.e., air, water, sediment, soil) under study. This collection phase can be performed by distributing detailed questionnaires to the different companies involved in the assessment. An example of such a questionnaire and the level of detail requested is given in Annex 1. The most critical information includes at least the following:

- Production/use data: tonnage, number of production days;
- Environmental exposure data;
- emissions to all environmental compartments (kg/y), emission factors (g/t);
- flow rate of the receiving water (or better dilution factor[1]) for all water discharges (m^3/s);
- is sludge used on agricultural land, put into a landfill, or other route of disposal (tonnes/y/use);
- effluent concentration (µg/L, on daily basis).

2.3.3 Selection emission factor and representativeness sector coverage

The second step is to critically review the collected data from the different companies in the environmental exposure questionnaires, and to identify and summarize data gaps. This data gap analysis should give insight on what additional local exposure data needs to be additionally compiled by industry (Figure 3).

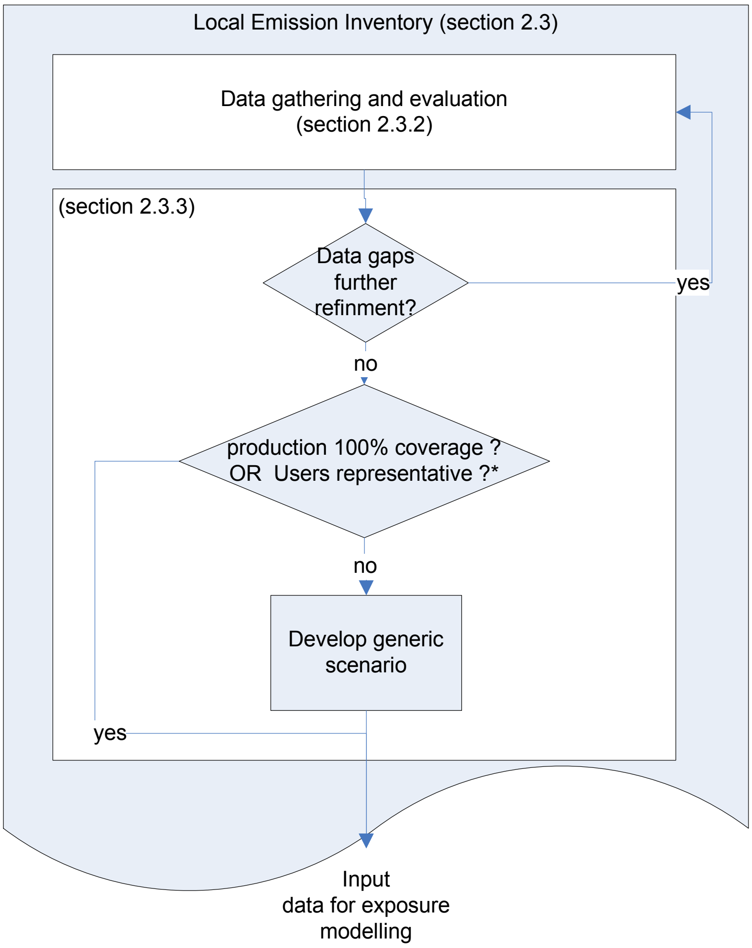

Figure 3: Overview of local emission inventory
* *for one representative country in case of many downstream users*

[1] For example a dispersion model such as CHEMSIM can be useful

Selection of emission factor
Reliable and representative emission factors can be extracted from the collected site-specific information[1] (Figure 4).

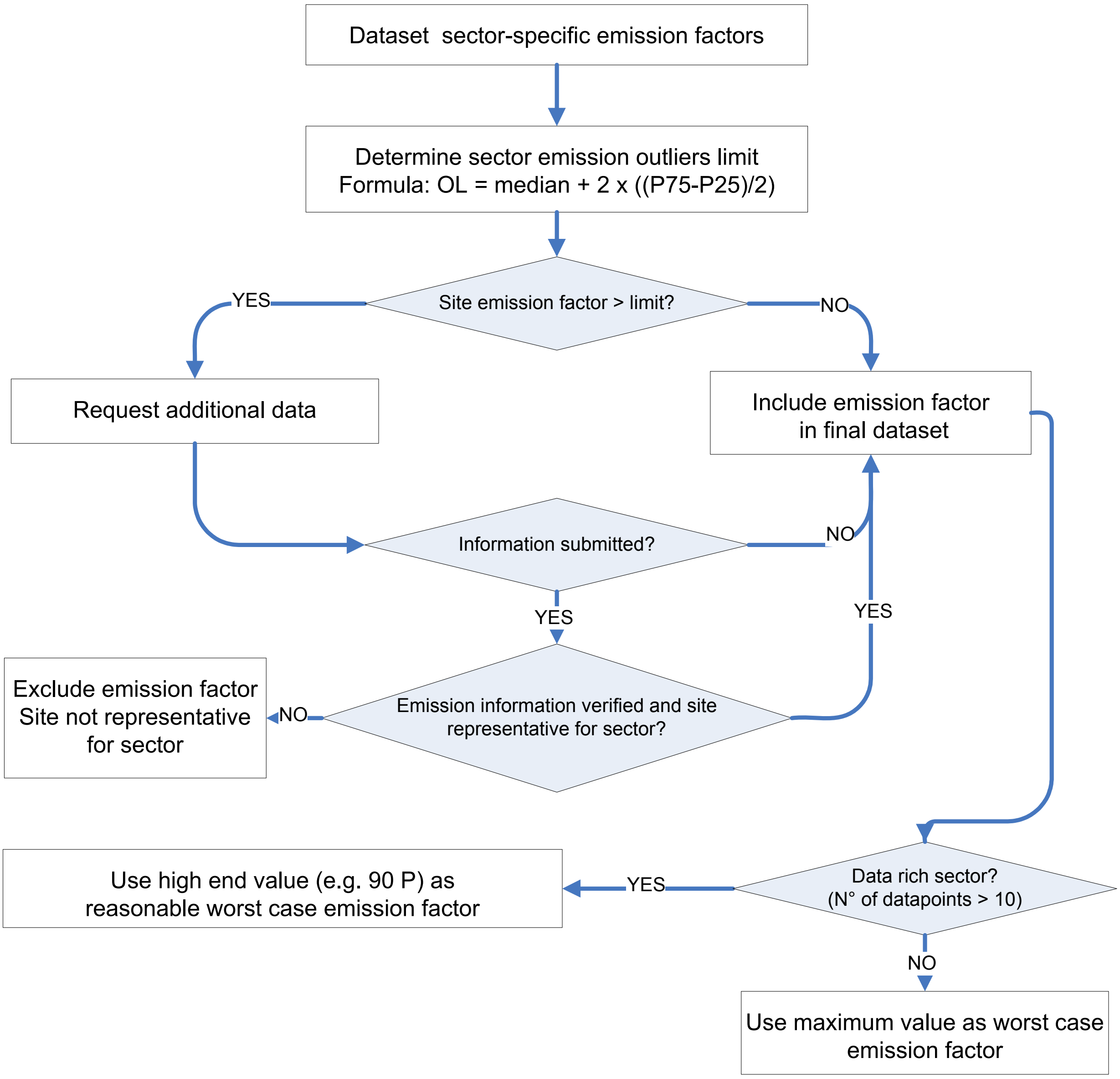

Figure 4: Overview of procedure followed for the selection of reliable, representative sector emission factors

In a first step, the sector emission outlier limit value is derived on the basis of the complete dataset. For each site emission factor it should be verified whether the specific emission factor exceeds the outlier limit value. If this is the case, a request for additional specific emission/exposure data (i.e. production tonnage, emissions, detailed process activities, emission reduction measures) should be directed to the

[1] Next to sector-specific information made available by industry, regulatory sector documents -e.g. IPPC (Integrated Pollution Prevention and Control) Reference Documents for different industry sectors i.e. BREFs- can also be used in order to assess emission factors. Besides, these documents provide process information and information on typical emission reduction measures for the sector that can serve as a basis for the estimation of the potential for releases to air and water. Please note that the information reported in IPPC documents relates mainly to IPPC compliant companies; meaning, companies that follow BAT (Best Available Techniques) requirements. For non-compliant companies, industry information should be provided in order to estimate emission factors.

site. In the other case –emission factor below limit- the emission factor should be included in the final dataset.

If relevant information is obtained from the site, the emission information should be verified and it should be determined if the site is representative for the sector (site emissions only related to main sector activities, no other activities on site). If the site is not considered to be representative for the sector, the emission factor should be excluded from the dataset. In all other cases –emission information verified/site representative for sector as well as no submission of information; the emission factor is included in the final dataset

From the 'reliable and representative emission factor dataset' -established in the first data collection and evaluation step- a reasonable worst case emission factor is finally selected for each industry sector. The use of a maximum *versus* high end emission factor depends on the data availability (see flow-chart below). If the number of data points (emission factors) available is sufficiently large (>10); a high end value (e.g. 90th percentile) of the dataset is proposed as a reasonable worst case emission factor for the sector. In the other case –number of data points <10- the maximum emission factor is used.

Representativeness/sector coverage

The representativeness/sector coverage (covered fraction of total tonnage consumed/produced; covered fraction of total number of sites per sector) and regional distribution of activities (spread in the region of interest) should also be evaluated. For the sectors where coverage is not sufficient, it is recommended to investigate if the industrial processes for which emissions are reported are indeed representative for the commonly used production processes of the sector.

In cases of many downstream users, it is not necessary to collect information of all user companies for all countries as long as the considered downstream user sites are representative for the non-covered fraction in each sector. Representativeness should include the different technologies used, geographic representation and representation in environmental management level (including connection to STP, characteristics of the receiving water…). It should also be taken into account in the exposure assessment that different treatment technologies may result in different removal rates. For the industrial sectors with insufficient coverage (< 100% for producers and considered sites not representative for downstream users), generic scenarios should be applied to the non-covered fraction of the sector using reasonable worst case representative emission factors. Default values (worst case estimates) for other parameters are also applied (e.g., minimum dilution factor of 10 is used in the framework of EU risk assessments).

It should be noted, however, that the applied generic scenarios are worst case scenarios and as a consequence will yield worst case exposure concentrations for the different industry sectors. It must be stressed that the results from this type of exercise should be interpreted with caution and should merely be used as additional -worst case- information (for non-covered sites) next to site specific exposure results (used by preference). Refinement of the exposure estimates are recommended if risks are shown from the worst-case scenario.

For each sector with a non-sufficient coverage and for which production/use data are available, two different generic scenarios could be applied as a kind of uncertainty analysis (see fact sheet 6). In the first scenario, the 'average non-covered tonnage' metal used/produced per site is calculated from the total non-covered tonnage used in the region of interest and the number of non-covered companies in that sector. Emissions to air and water are estimated applying maximum representative emission factors for the sector. In the second scenario, a 'reasonable worst case non-covered tonnage' metal used/produced per site is calculated on the basis of the average non-covered tonnage per site and the variance of the covered sites (assuming normal distribution). Air and water emissions are again calculated applying maximum representative emission factors for the sector. It should be noted that these non-covered tonnage scenarios can only be performed for those sectors for which the total tonnage and number of sites is available. Both scenarios will be used for risk characterization.

In summary the daily emissions to air and surface water in each scenario can then be estimated as follows (one could start with the first generic scenario and proceed to the typical scenario only if risk quotients exceed the value of 1):

Generic scenario 1 (typical):

- Non-covered tonnage metal used/produced in a specific sector (calculated as total tonnage – covered tonnage by sites)
- Non-covered number of sites in a specific sector (calculated as total number of sites in the region (e.g., EU) – number of covered sites)
- Calculation of 'average site tonnage' by dividing the non-covered tonnage by the non-covered number of companies in the sector
- Application of representative reasonable worst-case emission factors (air, water) for the sector
- Application of default number of emission days (e.g., B-tables, TGD)
- Calculation of daily emissions to air, water
- Calculation of environmental concentrations for a defined environment (e.g., discharge rate STP: 2000 m^3/d, dilution factor surface water: 10,…)

Generic scenario 2 (reasonable worst case):

- Average site tonnage for non-covered sector (see scenario 1)
- Derivation of variance of the known sites (assuming normal distribution; 1.29* stdev (individual production tonnage specific sites))
- Calculation of 'reasonable worst case tonnage' (90P) by adding the average site tonnage and the variation of the covered sites
- Application of representative reasonable worst-case emission factors (air, water) for the sector
- Application of default number of emission days (e.g., B-tables, TGD)
- Calculation of daily emissions to air, water
- Calculation of environmental concentrations for a defined environment (e.g. discharge rate STP: 2,000 m^3/d, dilution factor surface water: 10,…)

2.4 Derivation of the Predicted Environmental Concentration using exposure models

Environmental concentrations of metals and metal compounds on a regional/local scale can be calculated using multimedia fate models (e.g., EUSES, Unit World Model, TRIM.FaTE[1] etc). Although it is recognized that metal concentrations in the environment are subject to variation due to topographical and climatological regional and local differences, the modelled PEC calculations are often the results of emissions into a hypothetical environment with predefined, agreed environmental characteristics, the so-called "standard environment". These environmental conditions are in general typical average values for the different environmental compartments. Used default parameters should, to the extent possible, be replaced by more site-specific values (river flow rate, suspended solid concentration, organic carbon concentration) or region-specific information (e.g., density and composition of the different phases, area fractions for different soil types, suspended solid concentration) to obtain more realistic estimates of the site-specific or region-specific metal concentrations.

Most of the current guidance on the use of multimedia models for the purpose of risk assessment has been developed mainly from the experience gained on individual organic substances. This implies that the used methodology/assumptions cannot always be applied directly to metals without modification. For a more refined analysis processes that affect fate and potential exposure of organisms (bioavailability), such as inter-compartment transfer, complexation, adsorption and precipitation reactions, should preferentially be included. Such a refined fate and transport model for metals, the "Unit World" model, is currently under development in the US and Canada and has the added capability of evaluating metal speciation and the persistence (residence time) and toxicity of the bioavailable form by incorporating recently developed approaches for assessing metal bioavailability and their toxicity in water (e.g., the Biotic Ligand Model) and sediment (e.g., Acid Volatile Sulfides and Simultaneously Extractable Metal).

Specific guidance and background on how to run the different models in order to derive the modelled PEC concentrations can be found in the original documents dealing with the subject (TGD, 2003, EUSES, 1996). The main metal specific attention points that should be taken into account when conducting the modelling exercise are addressed below:

2.4.1 Adsorption/desorption processes

The commonly used mathematical relationships used for organic chemicals are based on octanol-water partition coefficients (K_{OW}). K_{OW}s usually can not be used to describe the partitioning of anorganic metal compounds and organic metallo compounds in the different environmental compartments. Instead, the transport of metals between the aqueous phase and soil/sediment/suspended matter should be described on the basis of measured soil/water, sediment/water and suspended matter/water equilibrium distribution coefficients (Kd; also called partition coefficient, Kp). It should, however, be acknowledged that Kd 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.

Therefore, the Kd values should, as far as possible, be representative for the environment of interest taking into account the major environmental characteristics influencing the Kd. For soils, the Kd can be derived per soil type of interest taking into account the soil usage (for instance, cultivated versus non-cultivated soils). For the aquatic compartment, Kd values should be derived under similar water quality parameters (pH, ionic strength, concentration of adsorbing phase) as prevailing in the region of interest. At the moment, most Kd values are expressed in terms of total concentrations present in both the aqueous and the solid phase (Eq-2).

$$Kd = \frac{\text{Total concentration in the solid phase}}{\text{Dissolved concentration in the aqueous phase}} \qquad \text{(Eq-2)}$$

However, it should be noted that the availability of metals for uptake by biota can differ from site to site and may change over time due to many processes, including weathering and (de)sorption processes. It should also be noted that Kd's are accurate only during an equilibrium state, which generally doesn't

[1] multimedia air deposition models http://www.epa.gov/ttn/fera/trim_fate.html

exist for metals in the environment. As a consequence, part of the metal present in the solid phase may be encapsulated in the mineral fraction and is therefore not available.

Since the partitioning coefficient is such an important parameter that can drive the outcome of the exposure assessment, the assessment of the data quality and relevance of all collected measured Kd-values should be done with care. Preference should always be given to coupled measured data for which information is available on both sampling and analytical measuring techniques. A comprehensive overview of the determination, use and prediction of the distribution coefficient, Kd, of metals in soil is given by Degryse et al, 2006).

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. 10^{th} percentile) and a high end value (e.g. 90^{th} 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 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 (see background document).

For aquatic systems, metal partitioning between the solid and solution phases is best predicted on the basis of surface complexation models (WHAM/SCAMP), and semi-empirical models also have been developed for soil (e.g., Sauvé et al., 2000; Lofts and Tipping, 1998, 2001). Such validated surface complexation models can become a useful tool in evaluating the potential variability of a Kd for a specific situation when the temporal variation of key parameters that determine the Kd-value are available. If validated, emerging alternative models (e.g. distributed ligand models) can also be used for predicting Kd-values.

2.4.2 Water solubility

It is important to know whether the metal is soluble in water, or can be transformed into a soluble form. If it is, the prediction of the environmental concentration, PEC_{local}, should be based on the relevant soluble metal ion or species that is bioavailable. Speciation models may be used to determine the soluble fraction. The partitioning behaviour of the substance to sludge/sediment/soil can then be based on the appropriate Kd values for the soluble ion. In some cases, the metal compound will be only poorly soluble and sufficiently stable to not rapidly transform to a water soluble form. In these circumstances, the substance itself should be assessed taking into account its specific partitioning characteristics. For the aquatic environment, it can be assumed as a first estimate that the substance will dissolve up to its water solubility limit, and that this fraction will be the bioavailable form. Refinement of the assessment may take into account kinetics of the dissolution.

2.4.3 Volatilization

For few metals and metal compounds (e.g., mercury-compounds, AsH_3 and stibine) volatilization has to be considered under normal environmental conditions. Also in the case of metallo-organic compounds volatilization can be important, but their assessment is out of the scope of the current metal risk assessment guidance. Most metals, however, are not volatile at ambient temperatures and this low volatilization potential is incorporated in exposure models by setting the Henry-coefficient to a very low value. In such cases, most of the metal present in the atmosphere is predominantly bound to form aerosols, which means that rates of dry and wet deposition (in combination with the scavenging ratio) of atmospheric aerosols will quantify transport from the atmosphere (exceptions: Hg and Se). Therefore, an extremely low value for the vapour pressure should be used e.g., $10E^{-20}$ Pa. If a valid measured value is available, this value can be used.

2.4.4 Degradability

Biotic and abiotic degradation rates should be set to zero for metals. The behaviour of the substance in a wastewater treatment plant can be modelled using for example the SimpleTreat module of EUSES. Irrespective of the model used to assess the partitioning between the sludge phase and water compartment, measured Kd values should be used to explain the removal of the metal from the water column. These values are, however, difficult to find for metals and quite often it is more obvious to obtain removal efficiency rates (expressed in percent) than sludge-water partition coefficients.

2.4.5. Steady state assumption

In many multimedia models PEC values for every compartment on a regional/continental scale is calculated as a steady-state concentration (e.g. EUSES). However for metals, steady-state is typically only reached after several decades or even thousands of years (see example in Figure 5). Steady-state concentrations are uncertain at such time scales and the time scale may no longer be relevant for risk assessments focussed on the present or near future. On the other hand, the observation that metals may be slowly accumulating in the future should not be ignored either. It is therefore recommended to calculate both the PEC values after a surveyable time period and the PEC at steady-state. The time period at which PEC equals PNEC is also a useful calculation for risk management purposes.

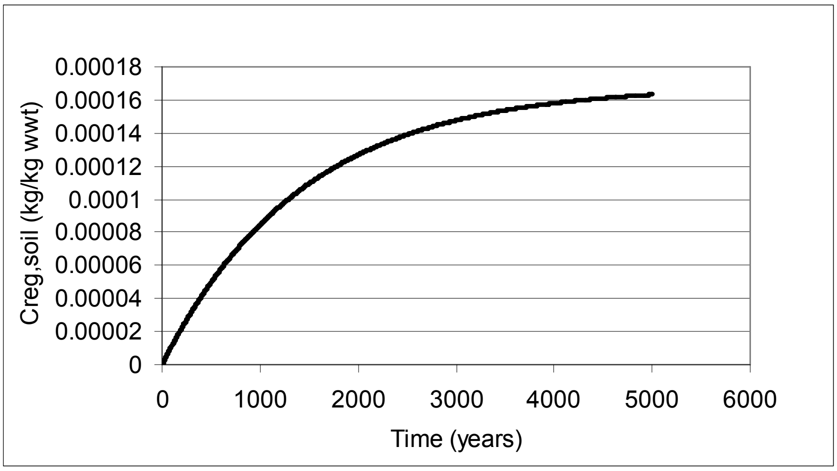

Figure 5: Regional steady-state metal concentrations are typically reached after an unsurveyable time period

On a site specific (local) scale, the time standards that are set in the EUSES model for a surveyable time period are 10 years for soil (after application of sludge, deposition). No time fraction, however, is considered for the air, water and sediment compartment. Here, only the emission ('emission after one year') and dilution factor are taken into account.

If possible, crop uptake can additionally be considered as an additional sink term in the multi-media model. However, it is sometimes difficult to unambiguously identify the contribution of the metal from the soil to the metal concentration of the plant or crop.

2.4.6 Incorporation of bioavailability

Since bioavailability is influenced by various physico-chemical characteristics of the environment, it is also important to define a 'standard environment', especially for a regional assessment with regard to the abiotic factors that influence bioavailability. The values and concentrations of the physicochemical parameters that modify metal bioavailability need to be representative for the environment under consideration. In general, a regional assessment is carried out under conditions that optimize the bioavailability with respect to ranges for pH, major cation concentrations, organic matter concentrations, etc (bioavailability modifiers). Therefore, environmental concentration distributions that are representative for environment under consideration are constructed for each relevant modifier (see section 3.2 and 3.3). Depending on the type of modifier, a low (e.g. 10^{th} P) or high (e.g. 90^{th} P) value of the ECD is taken as a relevant concentration for a ‘worst case standard medium). The number and type of modifiers will probably differ for each metal assessed but they often include pH, water hardness, and dissolved organic carbon. For a typical scenario, the median value of each relevant ECD is used. The choice of a low, high or typical value is relevant to perform the uncertainty analysis.

More information on the way bioavailability is incorporated in the risk assessment can be found in Fact Sheets 5 and 6. An overview of the different refinement levels is given in Figure 6. Depending on the scenario, low/high (reference) or typical (at regional or local scale) concentrations of the modifiers of metal-toxicity should be selected.

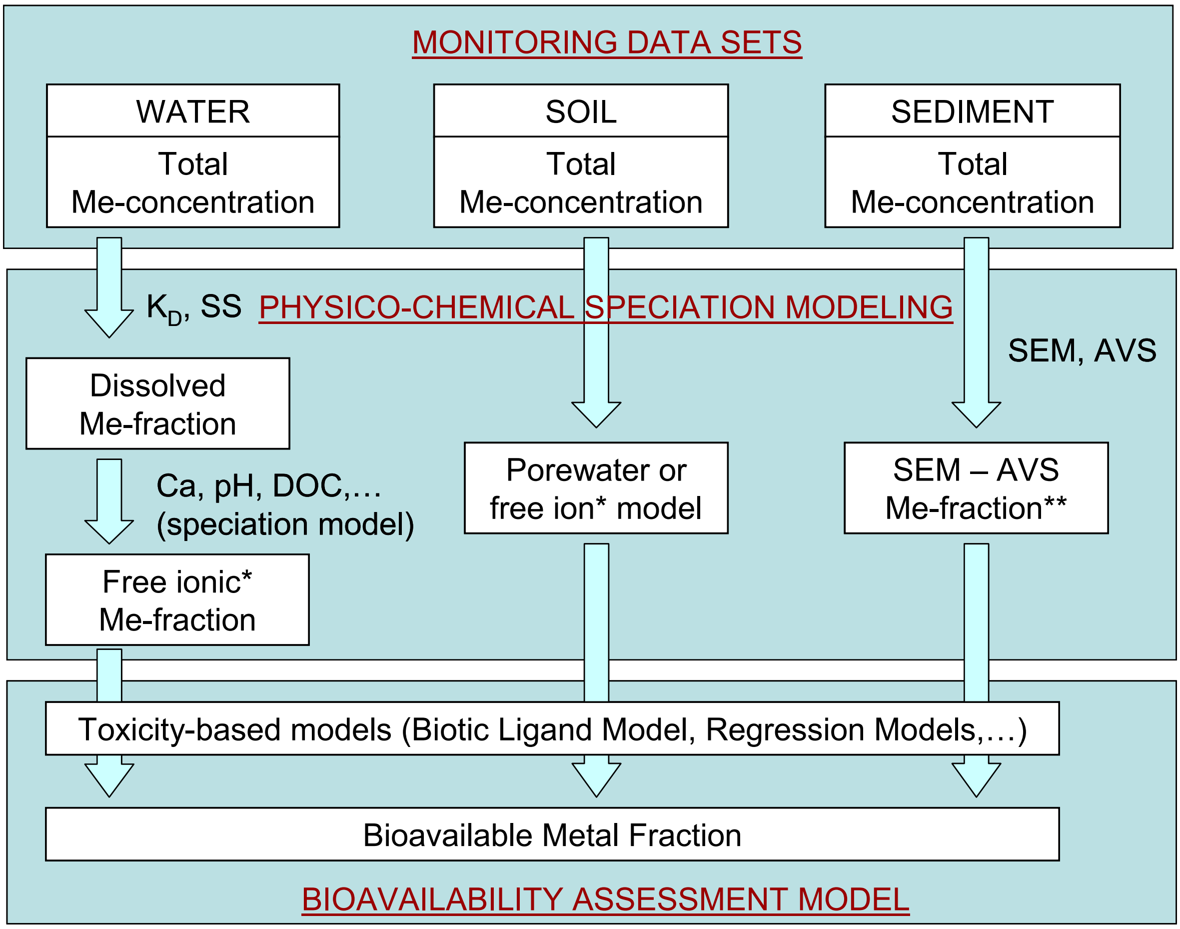

Figure 6: Refinement levels for the incorporation of bioavailability concept for the water, sediment and soil compartment (from fact sheet 5).

3. EXPOSURE ASSESSMENT USING MEASURED DATA

3.1 General recommendations

With regard to the risk characterization of metals, monitoring data are generally preferred over model calculations when sufficient representative and reliable data are available[1]. For metals, however, these data represent the sum of three different fractions: 1) the natural (background) concentration, 2) the diffuse anthropogenic input due to human activities, and 3) the site-specific anthropogenic input due to human activities. Fractions two and three can be further divided into historical and recent inputs. Elevated metal concentrations in the proximity of an identified point source can be used to describe the site-specific scenario, but are not representative for deriving diffuse ambient metal concentrations and to avoid interference must therefore be excluded from monitoring data sets used in a diffuse ambient exposure assessment. The diffuse ambient concentration in a specific area includes both the natural background and the diffuse anthropogenic input. More information on the background issue can be found in Annex 2 and in the background document.

In addition, the fraction of the metal present in the environment that is available for biological uptake depends on various biotic and abiotic parameters. Therefore, for risk assessment purposes of metals it is recommended that, beside background and ambient site-specific/diffuse metal concentrations, the distribution of parameters that determine metal bioavailability are also described and integrated in the exposure assessment (see section 2.4.6).

An additional recommendation that should be made is that emission balances based on monitoring data should not be used to identify sources that could lead to a local risk. Nevertheless regulating authorities tend to rely on these to establish risk reduction measures on the most import emission source. For example if 50 % of the emissions are due to certain source, the focus will be on that source. This observation, however, does not mean that there is a local risk; neither does a low emission estimate (e.g. 1 %) exclude a local risk. The concentrations that are monitored are only the reflection of local input (diffuse and point).

3.2 Data selection and handling

Metal concentrations in the environment can be affected by a large number of parameters and processes: the natural background, storm water events, release of sediments, the spatial and temporal distributions of the releases, and the results of the action of a large number of geochemical transportation and transformation processes on the substance. The likelihood and extent to which all these different parameters affect the total or dissolved metal quantity in the environment can be described by means of particular frequency distributions of exposure concentrations in the environment. Many physical, chemical, biological, toxicological, and statistical processes tend to create random variables that follow Log-Normal distributions although it should always be tested whether these functions actually are appropriate for describing a given data set, or whether a different type of distribution (Log-Logistic, Log-Weibull, Log-Beta,…) better fits the measured data.

The amount of measurements in monitoring data sets is strongly dependent on the compound of interest. For a number of metals, large data sets are available (e.g., Cd, Pb, Zn, Cu, Ni). On the other hand, more rare elements are not determined on a regular basis in monitoring programs or are present in the environment at an ambient concentration well below the detection limit of standard analytical methods. The local or regional exposure assessment of such data-poor metals should be based on modeled data until reliable measured data become available from (targeted) monitoring programs.

Because the quality of the extracted information can vary considerably, only the most relevant and reliable monitoring data should be incorporated into the risk assessment.

Most of the attention points given below are not metal specific but simply present general guidance on how to use and select monitoring data, although metal specific points are discussed when appropriate. The evaluation of the data should take into account the following points:

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[1] For the soil/sediment compartment it is preferable to have both in order to better understand the importance of historical pollution

- Sample treatment and analysis of reported metal concentrations should be in line with international accepted Standard Guidelines (ISO, ASTM Standards,…). Several analytical techniques are used in literature to measure metal concentrations. Most analytical techniques are quite precise (i.e., able to generate a similar value when measurement of the sample is repeated), but have different accuracies (i.e., how close the measurement is to the real value) and detection levels. Good quality assurance of selected monitoring data should also be ensured, e.g. by randomizing the sampling during the measurement procedure. The quality of trace level metal data, especially below 1 µg/L, may be compromised due to contamination of samples during collection, preparation, storage and analysis. Therefore depending on the level of metal present, the use of "clean" and "ultraclean" techniques for sampling and analysis may be critical to have accurate data. (US-EPA, 1994). For the aquatic environment, metal concentrations can be reported as the total or dissolved fraction. The latter fraction is preferred as it is the dissolved fraction that is calculated in the modeling section of the exposure analysis or that is used in the effect assessment. It is therefore important to ensure that reported monitoring data refer to the dissolved fraction. Water samples should be 0.45 µm filtered prior to analysis and sampling handling should not have affected the dissolved metal fraction in any way (e.g., acidification). If no dissolved data are available, an estimate of this fraction may be possible using the total metal concentrations, amount of particulate material in the water sample and relevant physicochemical parameters such as the Kd. With regard to the soil and sediment compartment, the digestion procedure of the samples is rarely similar between different studies. Depending on the applied extraction procedure, different metal fractions can be obtained: exchangeable, acetate-extractable, reducible, oxidizable and residual fraction. The metal fraction which is released after aqua regia digestion, is recommended for use in a regional exposure assessment. The aqua regia (HCl + HNO_3) digestion method releases all bioavailable metal fractions but does not takes into account all the metal fractions build into the crystal structure of the soil. The latter fraction would contribute more to the total amount of measured metal when other digestion methods are applied (HF, X-Ray Fluorescence). The mineral fraction is not expected to be released in solution over a reasonable time span under conditions normally encountered in nature (Tessier et al., 1979). Other acids, like NaOAc or $NH_2OH.HCl$, are less strong than aqua regia and will not release all relevant metal fractions. Secondly, the aqua regia digestion method is harmonized as an International Standard (ISO 11466) and is applied in most EU-15 countries (ESB, 1999)]. Finally, most data sets that result from national or international monitoring programs report metal concentrations obtained after digestion with aqua regia. Other analytical methods that assess the bioavailable fraction have been developed (DGT, voltametry), but the generated values only represent the labile metal fraction under a specific environmental condition.

- The most reliable and relevant data (i.e., obtained preferably within the last five years) should be used for the determination of site-specific and diffuse ambient exposure concentrations. Data generated in earlier sampling exercises should only be used for the derivation of site-specific or region-specific metal distributions if no (or few) recent data are available. Use of older measurements should be avoided if temporal analysis indicates that the older exposure data for a specific area do not reflect the current environmental distribution or if analytical methods are not explained in sufficient detail to validate approach and detection limits. With regard to the soil and sediment compartment, the total metal concentration remains independent of possible transformation processes of metals and metal compounds that may occur, regardless of any temporal changes of its bioavailability due to complexation and ageing processes. Processes like leaching, however, may reduce the soil concentration of metals with high leaching, and older data may therefore not reflect the current situation for this type of metals. In general, physicochemical and transformation processes have a larger effect on measured metal concentrations in the aquatic environment: the dissolved metal concentration, for instance, is determined by processes like precipitation and binding to particulate material.

- The sampling points within a data set for a specific area should not only represent this area in the most optimal way with regard to geographical and temporal aspects, but should also reflect the typical environmental conditions (e.g., types of surface waters, types of soils, etc.).

- The data should be assigned to site specific or regional scenarios by taking into account the sources of exposure and the environmental fate(s) of the substance. In this regard it should also be noted that typically monitoring programs are set up in contaminated areas which may result in data skewed towards the higher end.

- It may occur that in data sets where both the dissolved and total concentration are reported, the reported dissolved concentration is higher that the total. In such cases, it should be investigated whether different water samples – possibly taken at a different time, where used for the analysis. If this is not the case, such data points should be excluded and the quality of the whole data set should be questioned and further investigated.

- Measurements that fall below the detection limit (DL) should always remain included in the exposure analysis. With respect to the treatment of such values, it is suggested to set those entries to DL/2. This value represents the median of all values below DL when an uniform distribution between zero and DL is assumed, and these 'generic' values are assumed to optimize the parametric fit through the complete data set. Some of the other statistical methods available to estimate a mean and variance for each year are: maximum likelihood (ML), iterative methods (Gleit), regression methods, bias corrected ML, Schneider's One-Step, Helsel's robust method, winsorization, EPA delta log method[1]. But if the number of censored data is larger than 40%, the estimates of the mean and variance calculated according to these methods are not reliable.

- The presence of measured values below some of the reported detection limits can occur if data are obtained using different analytical procedures. If a substantial amount of measured values are below the detection limit of a method with lower sensitivity, a derived ambient PEC (e.g. 90th percentile) may be governed by the 'uncertain' value of DL/2 rather than by the measured metal concentrations obtained with a more sensitive analytical procedure. A data set can not be used for the derivation of an environmental distribution if the 90th percentile of all data is determined by the generic DL-value (DL/2) or if the 90th percentile is lower than the highest reported DL. With regard to impact assessment (comparing a DL-driven 90P-value with a PNEC or WQC) this type of data sets can be used to establish the absence of risk for a specific site or area (DL < PNEC, WQC), but not for the reverse (determination of a potential impact/risk).The quality of the derived 90P-value can be evaluated by means of graphical methods that can reveal important characteristics of a data set, including skewness (asymmetry), number of peaks (multi-modality), behavior in the tails, and data outliers. A schematic overview of how to deal with values below the detection limit is given in Figure 7.

[1] UNCENSOR. 2003. The Uncensor program estimates the mean, standard deviation, variance, and the confidence interval on the mean of left-censored data sets. http://www.vims.edu/env/research/software/vims_software.html#uncensor

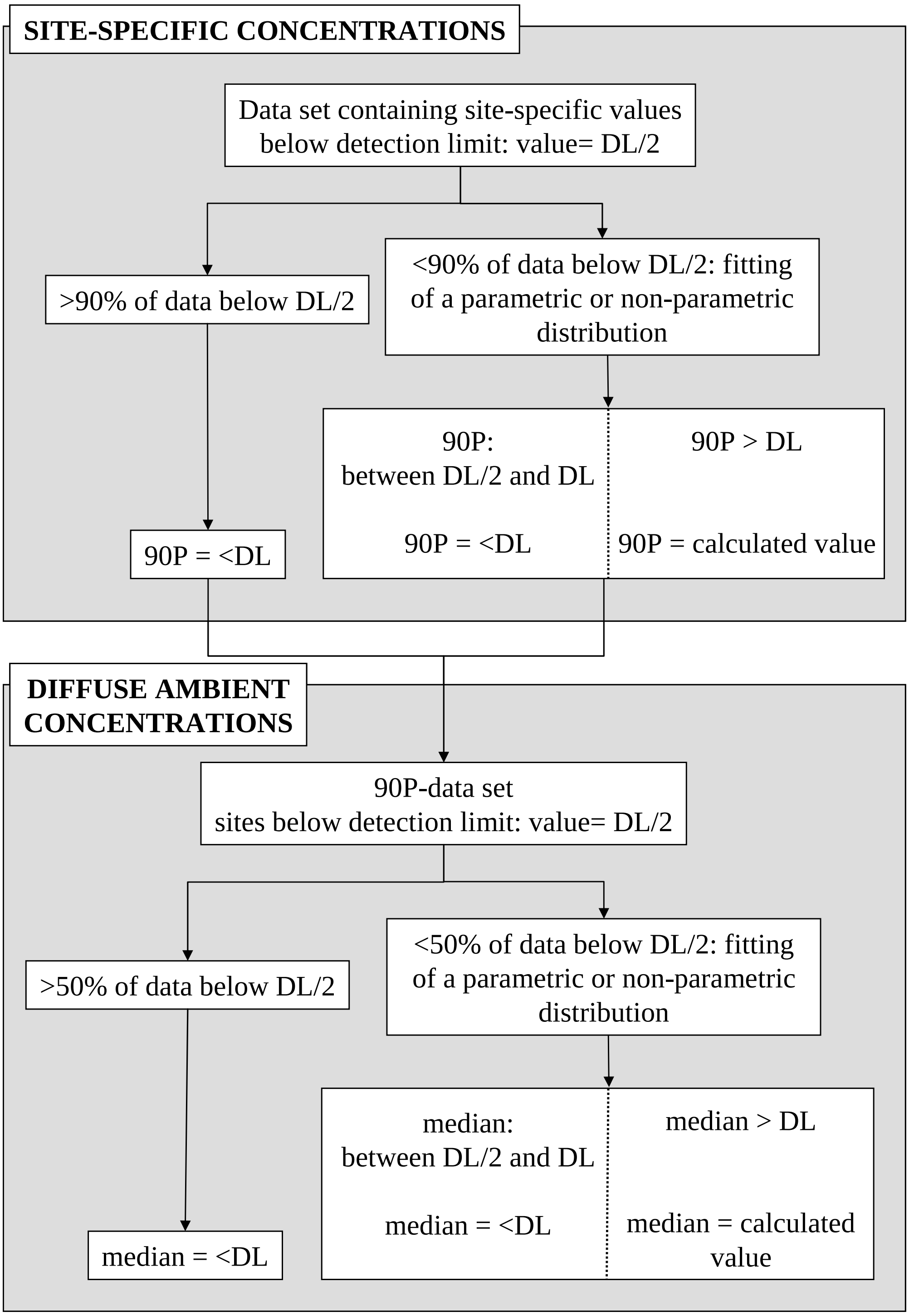

Figure 7: Handling of data below the detection limit

Outlier values due to site-specific conditions in the proximity of a point source should in general be discarded for diffuse ambient exposure assessment purposes, but not when site-specific conditions are considered. Outliers can be identified according to the statistical approach proposed in the TGD (EC, 2003), i.e., $\mathrm{Log}_{10}(X_i) > \log_{10}(p_{.75}) + K(\log_{10}(p_{.75}) - \log_{10}(p_{.25}))$ with X_i being the concentration above which a measured concentration may be considered an outlier, p_i the value of the i^{th} percentile of the distribution and K a scaling factor. A scaling factor K=1.5 is applied, as this value is used in most statistical packages. High ambient metal concentrations that are caused by natural processes (e.g., high background concentrations in soil samples of geological active areas, rivers flowing through metal-rich areas) should not be discarded from the data set, but their use in a diffuse ambient concentration assessment needs to be considered carefully because differences between modeled and measured ambient metal concentrations may occur due to these elevated background levels. If necessary and appropriate, the natural elevated metal concentration should be assessed in a separate scenario for this specific biogeochemical region.

Sometimes elevated metal levels are caused by a historical pollution. If so these data should not be taken into account for the chemical assessment of the diffuse ambient metal concentration. They can, however, be useful in the framework of an 'ecological risk assessment'.

3.3 Determination of Environmental Concentration Distribution (ECD) and Predicted Environmental Concentration (PEC) from measured data

From the collected monitoring data, it is possible to generate realistic distributions of environmental parameters that follow a statistical distribution. From these environmental concentration distributions (ECD), it is possible to assign probabilities to the likelihood that a measure will exceed a certain value. In a probabilistic framework, the whole ECD in itself is used in the risk characterization instead of 10^{th}, 50^{th} or 90^{th} percentiles. A deterministic framework will only derive a Predicted Environmental Concentration (single PEC value) from the ECD that is constructed with monitoring data.

3.3.1 Site-specific exposure assessment

On a site-specific scale (single site), the variation among the measured data typically reflects the temporal variability of the local conditions. Downstream river concentrations in the proximity of an industrial site, for example, can fluctuate due to changes in the amount of emitted metal, (the activity in some years may be higher or smaller compared to other years), variation in the flow of the receiving surface water (the flow and the dilution is typically larger in winter), etc.

Using a statistical computer package the distribution that most likely reproduces the monitoring data for a specific location is identified. Goodness-of-fit tests are formal statistical tests of the hypothesis that the data represent an independent sample from an assumed distribution. These tests involve a comparison between the actual data and the theoretical distribution under consideration. The goodness-of-fit tests used for screening the selected distribution are Kolmogorov-Smirnov and Anderson-Darling. The latter test is mainly focused on the goodness-of-fit in the tails of the distribution, and is therefore the most appropriate test when high end values (e.g. 90 percentiles) are considered, i.e., reasonable worst-case (RWC) ambient PEC. When a median value of a distribution is calculated, the goodness-of-fit test used for screening the selected distribution is Kolmogorov-Smirnov. Additional support for the selection or rejection of a fitted distribution is provided by Cullen & Frey (1999), Vose (1996), EPA (1999) and the background document.

Non-parametric distributions are used when no parametric distribution can be fitted significantly ($p<0.05$) to the data points. To calculate a 90^{th} percentile non-parametrically, an empirical distribution function needs to be constructed first. Cullen & Frey (1999) summarize several possible methods for constructing an empirical distribution function of an observed data set. Once the observed data set is plotted, percentiles can be calculated taking the inverse interpolated empirical distribution function. Most statistical software packages provide the necessary functions to calculate a non-parametrical distribution.

3.3.2 Diffuse ambient concentration exposure assessment

On a larger scale scale, the variance of the measured data typically reflects the spatial and/or temporal variability (e.g., seasonal) of an area (state, country, biogeochemical region). Soil conditions, for example, may vary widely within such an area due to different geological and climatic conditions. The approach to derive a regional PEC value is very similar to the site specific exposure assessment. However, the additional complexity is added in dealing with both temporal and spatial variability in the ECD. A diffuse ambient 'reasonable worst-case' (RWC) PEC concentration for a certain area can be derived as follows:

Diffuse ambient PECarea = median value of all site-specific 90th percentiles that have been derived within the area of interest and that are not affected by the anthropogenic input of nearby point-sources.

It is recommended that the median value of site-specific 90P-values be used for diffuse ambient exposure assessment purposes. There are some important arguments that support the preference for using the median of all 90P-values over the average value (as in TGD-methodology; EC, 2003) for the determination of a RWC-ambient PEC. Firstly, the use of a mean value assumes that none of the data points is affected by any point sources: environmental parameters are considered to be log-normally distributed, in which case the mean and median value of log-transformed monitoring data are the same. However, the effect of point source contamination – often too small to be detected with the conventional outlier-analysis, will stretch the upper part of the log-distribution to the right, resulting in a higher mean, but the median will be less affected by this single value. Secondly, the presence of site-specific 90P-values that are <DL (i.e., 90P= DL/2) will always cause an uncertainty with regard to the average value, whereas the median is determined by measured data if less than 50% of all 90P-values are <DL. When the median is equal to the DL/2, the diffuse ambient RWC-PEC is not quantified but reported as <DL.

It is, however, not always feasible to perform this type of data treatment:

- no site-specific 90P can be calculated when insufficient site-specific data points are available;
- when the number of site-specific measurements are different for each sampling location (between 1 and >20), it is not possible to derive 90P-values for each location; in such cases the derived 90P-values (where possible) or average value (if no reliable distribution can be fitted due to insufficient data points) are considered as a single measurement for that site.

When the absence of reliable data prevents estimation of a diffuse ambient RWC-PEC for the area of interest on a site-specific 90P-basis, a river- or sub-area-specific approach may be applied: data are grouped according to different rivers or sub-areas within the area of interest, and river/sub-area-specific 90th percentiles are calculated. Subsequently these 90P-values are used for the determination of the diffuse ambient RWC-PEC. An example of an area and its sub-areas are a country and its provinces/states, respectively.

An overview of both approaches to derive ambient diffuse RWC-PECs is presented in Figures 8. Both approaches are very similar but the decision whether to follow the procedure described in Figure 8a or 8b depends on the aims of the performed exposure analysis. For the derivation of a diffuse ambient PEC for a geopolitical area (e.g., country, state), calculations are based on all site-specific 90P-values within the area of interest (Figure 8a).

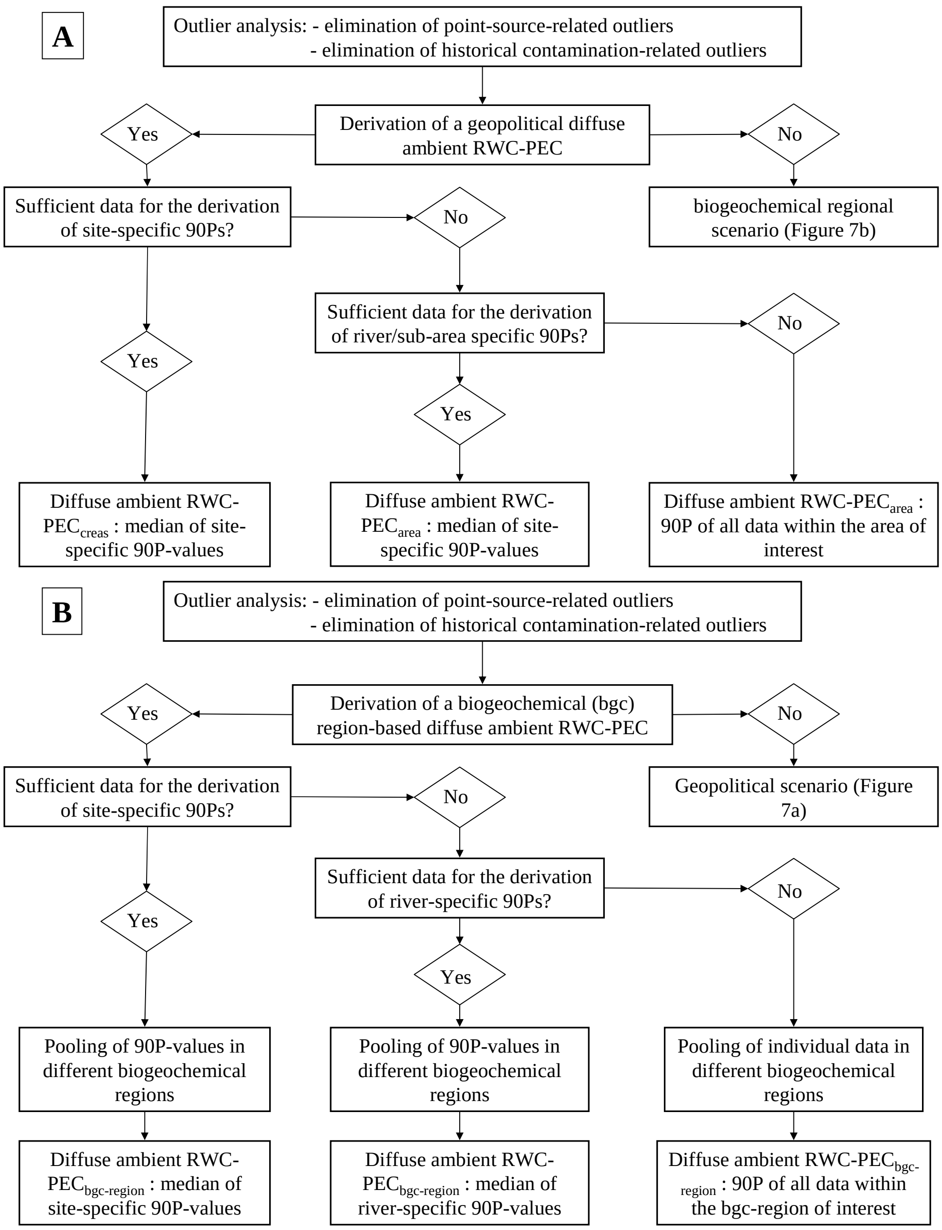

Figure 8: Schematic overview of the derivation of a diffuse ambient RWC-PEC. A) geopolitical assessment; B) Ecological assessment for specific biogeochemical areas.

This approach allows comparison of the measured data with the modelled diffuse metal concentrations, as the derivation of the latter concentrations is also based on emission data for a geopolitical area. For the performance of an ecological-based assessment, however, it is recommended that the exposure risk characterization be based on biogeochemical region-specific RWC-ambient PECs (Figure 7B). These biogeochemical regions can be river catchments or areas that represent different geological conditions and background concentrations. In this case the diffuse ambient RWC-PEC is represented by the median value of all site-specific 90P-values within that biogeochemical region.

3.4 Bioavailability

Analysis can be performed on available monitoring data for the physicochemical parameters that affect metal bioavailability and that are required for the incorporation of bioavailability in the risk assessment according to a BLM-approach: pH, major ions (Ca, Mg, Na, K, Cl, SO_4,…), alkalinity, dissolved organic carbon. Reported monitoring data that comply with the data selection criteria mentioned in section 3.2, can be used to define country-specific or biogeochemical region-specific distributions for these parameters. The 50^{th}, 10^{th} or 90^{th} percentiles that are extracted from these distributions represent typical (50P) or worst-case (10P, 90P) conditions, and can be used in the (eco)-regional risk characterization and uncertainty analysis. Additionally, site-specific environmental data can also be used in local risk assessment scenarios.

4. COMPARISON AND SELECTION MODELLED VERSUS MEASURED DATA

For data rich metals, a range of concentrations from measured data or modelled data will be available. It may be assumed that measurements may always give more reliable results than model estimations. However, measured concentrations can have a considerable uncertainty associated with them due to temporal and spatial variations as well as differences in analytical methods. Therefore, both approaches complement each other and a comparison is necessary for a proper understanding of the data.

4.1 Comparison modelled versus measured data

To facilitate the comparison between modelled and measured environmental concentrations, it is recommended to include all products (even if excluded from the regulatory framework (such as biocides, pesticides, medical product applications) in the emission inventory and subsequent calculated regional PEC derivation to avoid missing important sources. It is also recommended that the metal of concern and its compounds be assessed as a group. Since the modelled diffuse ambient metal concentrations are typically calculated using a country specific approach, the comparison with the measured data can best be based on all site-specific 90P-values within a geopolitical area (e.g., country, state).

If the outcome of the comparison indicates that the PEC calculated/modelled is not of the same order of magnitude as the PEC value derived from measured data, a further in depth analysis and critical discussion of divergences are important steps. For this, both the calculated and measured PEC values need to be reconsidered, re-evaluated (see next sections) and, if possible, further refined. In general, the following cases can be distinguished:

- Modelled PEC ~= PEC based on measured concentrations: The result indicates that the most relevant sources of exposure and fate processes were taken into account.
- Modelled PEC > PEC based on measured concentrations: This result might indicate that relevant elimination processes were not considered in the PEC calculation or that the employed model did not simulate the real environmental conditions for the regarded substance. On the other hand, measured data may not be reliable or may represent only the background concentration or diffuse ambient RWC-PEC in the regarded environmental compartment. If the PEC based on measured data has been derived from a sufficient number of representative samples then they should override the model predictions.
- Modelled PEC < PEC based on measured concentrations: This can be caused by failure to take all relevant sources of emission into account when calculating the PEC, or that the used models were not suitable for the conditions/metal. Another explanation is that the higher ambient measured concentrations are due to a natural high background or reflect historical pollution (especially on a local scale), are caused by spillage, are the result of a recent change in use pattern, or reflect the recent introduction of emission-reducing measures that have not yet affected the environmental concentrations of the metal/metal compounds.

If no further refinements are possible or if the modelled PEC is similar to the measured PEC, a weight-of-evidence approach is recommended to finally select the modelled or measured PEC for further risk characterization.

4.2 Re-evaluation modelled PEC

A sensitivity analysis can be conducted to identify the most important parameters and their associated processes. Alternatively, the different components of the mass balances in steady-state can be assessed for each compartment. For example, the mass balance for the water compartment can be:

$$\frac{dC}{dt} = Emission + \mathrm{Im}\,port - Export + Deposition + Runoff - Volatilisation - Adsorption + Desorption$$

The most important processes can then each be identified and verified by comparison with measured data or other lines of evidence. In this way, insufficiently considered relevant elimination processes or important emission sources or environmental conditions can be detected and, if possible, refined.

4.3 Re-evaluation measured PEC

For this, the scope of the monitoring study should be verified in detail. Sources of natural (or ambient), historical and recent contributions should be carefully re-analysed following the guidance given in section 3.

5. TARGETED APPROACHES

In some cases, there could be a need to develop specific scenarios in a more targeted way which could be use driven and/or compartment driven: e.g., waste scenario, road border scenario, shooting range scenario. A balance between generic scenarios and specific scenarios is recommended in such cases. Specific attention should be paid to:

- Many metals are used in alloy form. The type of alloy could lead to different exposure releases.
- Other environmental fate processes, which are negligible in the standard local exposure scenarios of the TGD, may be relevant in specific cases.
- Attention needs to be paid to the definition of a "technical area". In the TGD, technical areas are not considered for risk assessment as they are not considered as "the environment" and they typically fall under different directives in which remediation is needed when the site is closed. It is obvious that industrial sites are considered as technical areas. Shooting ranges, for example, can also be considered as technical areas. Only emission to the environment outside of the technical area need to be further considered for risk assessment.

ANNEX 1 : QUESTIONNAIRE

Questionnaire - regional exposure analysis

Hereunder a not-exhaustive overview is provided of the information needed to evaluate the emission inventory data:

- national emission data by source category (e.g., industry, households, agriculture, etc…):
  - for metal under investigation; please mention the speciation if available;
  - for the most recent year available;
  - allocated to the different compartments (air, water, soil).
- Industry information should be provided by sector. If available we prefer data on company level;
- For sewage treatment plants (STP) the following information by installation is preferred:
  - number of inhabitant equivalents (domestic/industrial) connected to the installation;
  - total annual load of each heavy metal in the influent of the installation;
  - purification yield of the installation;
  - total annual load of each heavy metal in the effluent of the installation;
  - total annual load of each heavy metal in the sludge of the installation;
- a detailed description of the methodology used to set up this emission inventory, which allows us to recalculate the emission data:
  - the way the data were collected (calculated or measured);
  - if calculated: the emission factors (EF) used (the exact EF + literature references) and the calculation method;
  - if measured: the analytical method used and detection limit for each compound and medium (soil, water, sediment);
  - the methodology used to allocate the total emissions to the different compartments (air, water and soil);
  - all information that could help us to compare your emission data with methodologies used in other member states;
- an overview of the different international institutions, to whom your country has to report their emissions of heavy metals (e.g., Eurostat, OSPAR, International Commission for the Protection of the Rhine, HELCOM,…);
- any information, necessary to understand the emission data.

The questionnaire also request information on the physicochemical characteristics of the receiving surface water, sediment and soil. With this information, it will be possible to include bioavailability in the local risk assessment scenario.

A distinction can be made between various 'levels of information' with regard to the exposure modelling. The tiered approach is:

Level I: minimum data set to avoid full default (generic) scenario
Level II: allowing refinement of level I by correcting for local conditions
Level III: allowing refinement of level II by including measurements or local bioavailability factors

Emission source	Total emissions in reference year (kg)				Specification of the calculation method				
	Air	Water	Soil	STP	calculated (C) OR measured (M)	Emission factor (EF) + reference OR detection limit (DL)	Information source for activity unit (when calculated)	Calculation method	Allocation method (air, water, soil)
Industry: - non ferro - refineries - etc…									
Traffic: - navigation - etc…									
Agriculture: - run-off manure - soil erosion - etc…									
Etc…									

Questionnaire - local exposure analysis

1. Total metal or metal compound production/use (t / y) (Level I)

Site (or division)	Form of metal	T_{r-2}	T_{r-1}	Reference year T_r

2. Working days (Level I)

Number of working days (*that emissions may have occurred)*	T_{r-2}	T_{r-1}	Reference year T_r
Remarks			

3. Metal emissions to the environment

<u>3.1 Air</u>

- **<u>Point source emissions to air</u> (Level I)**
-

Total annual emissions to air from point sources (kg metal / year).	T_{r-2}		T_{r-1}	Reference year T_r
Calculated emission factors (g metal emitted to air / t metal produced or used) for EACH STAGE OF PROCESSING.	**Production stage**	T_{r-2}	T_{r-1}	Reference year T_r
	smelting			
	refining			
	downstream use			
Sampling device (e.g., type, is sampling conducted isokinetically)				
Analytical method				
Remarks:				

- **<u>Fugitive Emissions</u> (Level I)**

What measures are taken to minimise fugitive emissions (e.g., covered storage areas, water spraying of open areas etc.)?			
Has amount of fugitive emissions been estimated (yes/no)? If yes, estimate total annual tonnage and briefly describe method of calculation below (*).			
	T_{r-2}	**T_{r-1}**	**Reference year T_r**
Description of calculation method (*)			
Remarks:			

- **<u>Metal in air monitoring data (on-site or surrounding area)/ Metal in suspended/deposited dust</u> (Level III)**
-

For each measurement point give name or reference number, location description, distance from emission point (m) and location relative to prevailing wind direction.					
Results: Metal in air levels (µg/m^3) given as 90^{th} percentile (daily basis), and geometric annual average	**Statistics**	**Name/Ref Number**	**T_{r-2}**	**T_{r-1}**	**Reference year T_r**
	90 % upper (daily basis)				
	geometric annual mean				
	90 % under (daily basis)				
Sampling device: type, flow rate (high or low volume sampler), filter used (PM2.5, PM10 or others)					
Sampling duration :					

3.2 Water

- **<u>Emissions to Water</u> (Level II)**

<table>
<tr><td rowspan="4">Average concentration of metal in effluent (90th percentile, upper and lower limit and geometric average in mg/l)</td><td></td><td colspan="2">T_{r-2}</td><td colspan="2">T_{r-1}</td><td>Reference year T_r</td></tr>
<tr><td>90% upper (monthly basis)</td><td colspan="2"></td><td colspan="2"></td><td></td></tr>
<tr><td>Geometric annual mean</td><td colspan="2"></td><td colspan="2"></td><td></td></tr>
<tr><td>90% lower (monthly basis)</td><td colspan="2"></td><td colspan="2"></td><td></td></tr>
<tr><td></td><td colspan="2">T_{r-2}</td><td colspan="2">T_{r-1}</td><td colspan="2">Reference year T_r</td></tr>
<tr><td>Total emissions to water from point sources (total and/or soluble fraction) (kg metal year): (Level I)</td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td></tr>
<tr><td>Average effluent flow rate (m^3/day)</td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td></tr>
<tr><td>Calculated emission factors (total and/or soluble fraction) (g metal emitted to water / t metal produced or used) for each production stage including method of calculation.</td><td colspan="2"></td><td colspan="2"></td><td colspan="2"></td></tr>
<tr><td>Sample collection method (grab samples, automatic sampler, volume driven sampler etc):</td><td colspan="6"></td></tr>
<tr><td>Sampling frequency (no. of times/year, continuous etc.):</td><td colspan="6"></td></tr>
<tr><td>Analytical method used:
● total and soluble metal measured?
● techniques used to determine total and/or soluble (give literature reference, standard method or description of method)
● filter type and pore size used?</td><td colspan="6"></td></tr>
</table>

- **<u>Characteristics of receiving water</u> (Level II)**

Is the effluent discharged to:	
➢ river (specify flow of receiving water m^3/day as annual mean and 10^{th} percentile, if possible)	
➢ estuary (specify flow of receiving water m^3/day as annual mean and 10^{th} percentile, min. and max. if possible)	
➢ canal (specify water renewal rate as annual mean and 10^{th} percentile, if possible)	
➢ lake (specify volume and water renewal rate as annual mean and 10^{th} percentile, if possible)	
➢ To community sewer system	
➢ Sea	
➢ other (please specify)	
Remarks:	

- **<u>Monitoring of receiving waters</u> (Level III)**

		T_{r-2}	T_{r-1}	Reference year T_r
Results: Metal levels in receiving water AFTER plant emissions (in mg/ l given as 90^{th} percentile, upper and lower limits and geometric annual average).	**90% upper (monthly basis)**			
	Geometric annual mean			
	90% lower (monthly basis)			
Specify whether total and/or soluble fractions are measured and give location relative to plant discharge point.				
Sample collection method (grab samples, automatic sampler, volume driven sampler etc):				
Sampling frequency (no. of times/year):				
Analytical method used: ● total and soluble metal measured? ● techniques used to determine total and/or soluble (give literature reference, standard method or description of method) filter type and pore size used?				

		T_{r-2}	T_{r-1}	Reference year T_r
Results: **Background metal levels** in water BEFORE plant emissions (in mg/l given as 90^{th} percentile, upper and lower limits and geometric annual average).	**90% upper (monthly basis)**			
	Geometric annual mean			
	90% lower (monthly basis)			
Specify whether total and/or soluble fractions are measured and give location relative to plant discharge point.				

<table>
<tr><td rowspan="13">Also provide details of pH, major cation concentrations, hardness, and dissolved organic carbon (including analytical technique used for each) for the receiving water (if available).</td><td>Phys-chem</td><td>T_{r-2}</td><td>T_{r-1}</td><td>Reference year T_r</td></tr>
<tr><td>pH</td><td></td><td></td><td></td></tr>
<tr><td>Hardness (mg $CaCO_3$/L)</td><td></td><td></td><td></td></tr>
<tr><td>DOC</td><td></td><td></td><td></td></tr>
<tr><td>Suspended solids</td><td></td><td></td><td></td></tr>
<tr><td>Alkalinity (mg $CaCO_3$/L)</td><td></td><td></td><td></td></tr>
<tr><td>Ca (mg/L)</td><td></td><td></td><td></td></tr>
<tr><td>Mg (mg/L)</td><td></td><td></td><td></td></tr>
<tr><td>Na (mg/L)</td><td></td><td></td><td></td></tr>
<tr><td>K (mg/L)</td><td></td><td></td><td></td></tr>
<tr><td>SO_4 (mg/L)</td><td></td><td></td><td></td></tr>
<tr><td>Cl (mg/L)</td><td></td><td></td><td></td></tr>
<tr><td>Others if deemed appropriate (e.g., F for Al) (mg/L)</td><td></td><td></td><td></td></tr>
<tr><td>After the effluent has been discharged, does the receiving river water undergo any further treatment (yes/no)?</td><td colspan="4"></td></tr>
<tr><td>If yes, what is the destination of the municipal sludge from this water treatment center (disposed, incinerated or recycled to agricultural land?)</td><td colspan="4"></td></tr>
<tr><td>Remarks:</td><td colspan="4"></td></tr>
</table>

3.3 Waste water treatment at production site (Level II)

<table>
<tr><td>Is there a treatment system for process waste water at the site? If yes, briefly describe the waste water treatment system</td><td colspan="4"></td></tr>
<tr><td>What is the average efficiency of waste water treatment? (e.g., in % of metal in water before and after treatment).</td><td colspan="4"></td></tr>
<tr><td>Can this efficiency figure be proven by measured data or is it based on modelling assumptions?</td><td colspan="4"></td></tr>
<tr><td rowspan="3">How much metal-containing sludge/cake is produced by the waste water treatment plant (in dry weight)</td><td></td><td>T_{r-2}</td><td>T_{r-1}</td><td>Reference year T_r</td></tr>
<tr><td>total amount (t/y)</td><td></td><td></td><td></td></tr>
<tr><td>metal content (g/t)</td><td></td><td></td><td></td></tr>
<tr><td>What is the destination/handling of the sludge/cake produced by the on-site treatment plant, i.e., is the sludge disposed, incinerated or recycled (give details)?
If disposed of, is the sludge landfilled or used on agricultural land?</td><td colspan="4"></td></tr>
</table>

Give details of any rainwater treatment at site	
Remarks:	

3. Sediment monitoring (Level III)

Give details of representative metal levels and other physicochemical characteristics in sediment monitored UPSTREAM of plant discharge points including location relative to discharge point (incl. year and method of sampling) (in mg/kg dry weight)	**SEM (Cu, Ni, Pb, Zn, Cd) (µmol/L)**	
	AVS (µmol/L)	
	OC (%)	
Give details of metal levels and other physicochemical characteristics in sediment monitored AFTER and close to plant discharge points including location relative to discharge point, year of measurement and method of sampling) (in mg/kg dry weight)	**SEM (Cu, Ni, Pb, Zn, Cd) (µmol/L)**	
	AVS (µmol/L)	
	OC (%)	
Would your company be prepared to take part in a monitoring programme to establish the bioavailable fraction of metal in local sediments if the draft risk assessment should indicate a potential local risk?		
If available give details of representative metal levels and other physicochemical characteristics in porewater of the sediments UPSTREAM or DOWNSTREAM of plant discharge point (in µg/L)		
Remarks:		

4. Waste

4.1 Solid Waste Emissions (Level II)

	T_{r-2}	T_{r-1}	Reference year T_r
Type and quantity (t) of industrial wastes produced: **(Level I)** - For final disposal (burning or landfilling)			
For reuse (please indicate what type of reuse) (e.g., slag products used in building or construction materials):			
Average concentration of metal in industrial wastes (mg metal/g): (specify if dry or wet weight)			
Leachability of the metal (including details of the test methods used and whether these comply with any test standards):			
Total waste produced (kg dry weight/year):			
Kg (total weight) of waste produced / t metal produced or used:			
Permanent **on-site** waste storage arrangements for metal-containing wastes (e.g., type, lining material used, leachate recovery system):			
Describe any monitoring programmes used to monitor leakage from permanent on-site waste storage sites:			

What **off-site** waste disposal arrangements are in place? For each type, indicate the waste management systems that are in place (e.g., information from local authorities on disposal sites)	
Remarks:	

5. <u>Other general data</u> (Level III)

<u>5.1 Monitoring</u>

Other monitoring data on metal levels in the local environment, e.g environmental monitoring in crops, fish, soil, groundwater, street dust, household dust etc.

For each study please describe:

- Type of exposure studied
- Sampling methods used
- Summary of results
- Reference.

<u>5.2 Socio-economic information</u> (Level III)

Company location (city, industrial estate, rural, coastal etc.)	

ANNEX 2: DEALING WITH THE NATURAL BACKGROUND

Introduction

Naturally-occuring background concentrations of metals in different environmental compartments (water, sediment, soil) are the concentrations that existed before any human activities (Gough, 1993). These naturally-occurring background concentrations vary markedly between geologically disparate areas, and are determined by various factors like the site/regional-specific bedrock composition, effects of climate on the degree of weathering etc. The variation in site-specific conditions has resulted in ranges of naturally-occuring background levels that span several orders of magnitude. Regulatory bodies, however, are not always aware of these significant natural variations, which should be taken into account in defining action limits. There are already examples of action limits that are lower than natural concentrations.

With exception for some remote and unpopulated area’s, true natural background concentrations can hardly be found in the aquatic and terrestrial compartment as a result of historical and current anthropogenic input from diffuse sources. Human processes that have altered natural metal levels (enrichment, depletion) can be categorized into two different classes, i.e., agricultural activities and industrial activities. For example, background levels of Pb in the environment are commonly elevated due to long-term usage of Pb-based gasoline and paints. On the other hand, levels of e.g., cobalt, nickel and zinc have slightly depleted by agricultural practices

Since it is becoming more and more difficult to determine natural background levels of certain elements, the baseline concentration of a metal has been recognized as a means to establish reliable worldwide elemental concentrations in natural materials (Gough et al., 1988; Kabata-Pendias and Pendias, 1992). The term “baseline concentration” or “baseline concentration range” is often used to express an expected range of element concentrations around a mean in a “normal” sample medium. Ma et al (1997) defined the baseline concentration of a metal as 95% of the expected range of background concentration. Baseline concentrations of metals were also determined in the FOREGS Geochemical Baseline Mapping programme, a monitoring campaign that sought to provide high quality environmental geochemical baseline data for Europe based on samples of stream water, stream sediment, floodplain sediment, soil, and humus collected all over Europe. In this study, the baseline concentration was defined as that concentration in the present or past corresponding to very low anthropogenic pressure.

Figure A1 illustrates the different metal fractions from a different origin that are measured in an environmental sample.

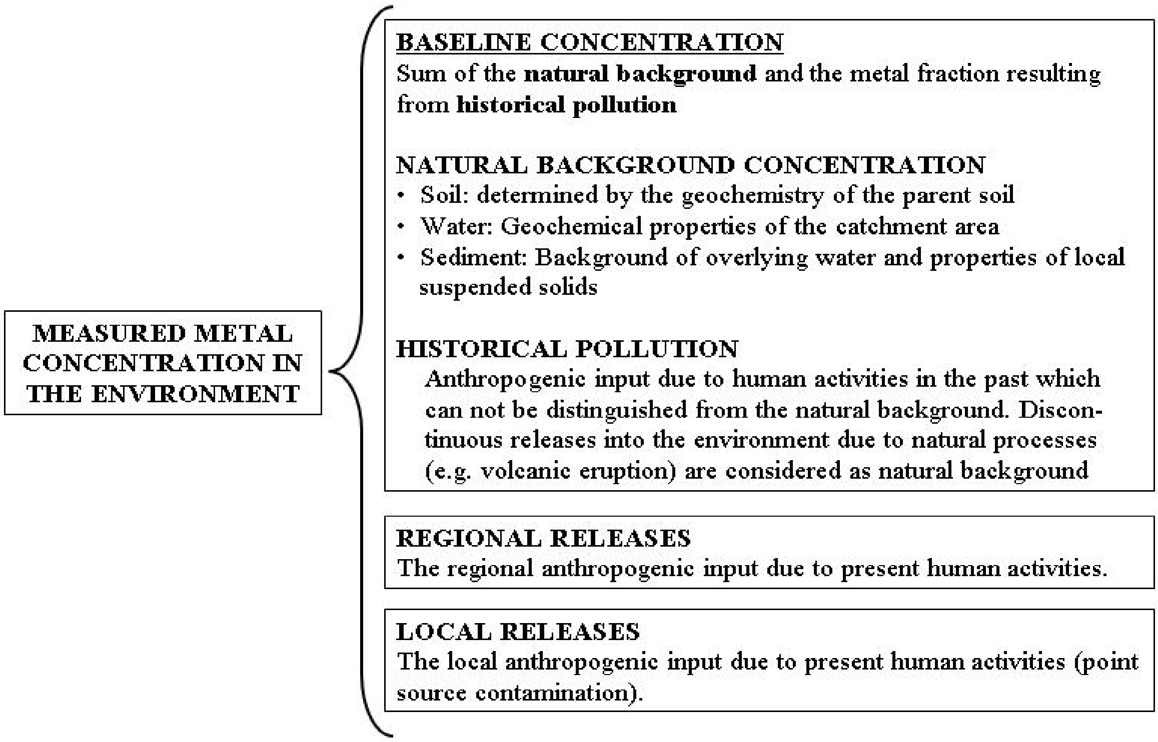

Figure A1: Different origins of metal fractions in the environment

The **natural background** refers to the metal fraction that originates from natural and geological processes. This fraction is region-dependent and should therefore be the primary parameter for the identification of metallo-regions. The determination of natural background concentrations in the different environmental compartments (water, soil, sediment) of a specific area could be done directly if representative pristine areas are available. Such areas can be defined as locations that have been free from any anthropogenic impact in the past or present, but can hardly be found in regions with large populations and substantial industrial or agricultural activities.

As human presence has caused a profound effect on land use, landscape, emissions, he natural biocycle of metals, with emphasis on essential elements like copper, zinc and nickel, has been altered dramatically. For instance, the introduction of agriculture did not only alter the natural soil composition, but also changed erosion rates and, hence, the amount of metals in river waters and sediments (Van Tilborg, 2002).

The baseline concentration is therefore the sum of the natural background and the fraction of metal that has been introduced (or removed) in the environment by men during the past decades or even centuries. The added fraction is often referred to as historical pollution. In many cases this historical pollution can not be distinguished from the natural background concentration.

Regional and local anthropogenic releases of metals to the environment are the remaining two components that determine the observed metal concentrations. In theory, the ambient concentration of a metal is the sum of the background concentration, the contribution of historical pollution and the regional emissions. In practice, however, it is not always possible to eliminate any possible influence of local emissions into the environment

Using conventional analytical techniques, it is not possible to make a distinction between the different metal fractions in environmental samples, which complicates the identification of natural metal backgrounds in different (eco-) regions. Structural differences of metal particles emitted from smelters vs. those found in natural soils, can be detected by means of electron microscopic examination of soil particles. This type of techniques can be a helpful tool for differentiating the natural and added metal fraction quantitatively.

Compartment-specific considerations for the different metal fractions

Water compartment

Due to the dynamics and the limited residence time of water in the aquatic compartment (fast renewal of the water), the total metal background concentration in uncontaminated surface water can be assumed to be close to the natural background. Metal background concentrations are determined by the metal content of well water (geochemical composition of source-area), the geochemical properties of the area through with the water body flows, introduction of natural organic material (leaves), erosion from natural (uncontaminated) river banks and atmospheric deposition from natural origin[8]. When well water or groundwater is used for estimating natural background levels, is it essential to verify that these samples are free of current or historic pollution. Moreover, due do their contact with deeper, mineral rocks, metal background concentrations in these waters can be higher than that in surface waters where there is an additional dilution with rain water.

It is expected that the effect of historical pollution on the natural metal background level will be very limited due to the high dynamics of the aquatic compartment, and measured baseline levels in pristine areas will therefore be close to the natural background.. The contribution of historical pollution to the measured baseline concentration could become important when enclosed water bodies with low turnover (e.g., lakes, reservoirs) are considered that have been affected by important anthropogenic inputs in the past. This type of waterbodies should therefore only be used for the determination of baseline levels when there is no indication that metal levels have been affected by anthropogenic contributions in the past.

[8] It should be noted that some part of household emissions also originates from natural sources, and must therefore be considered as part of the natural background

Historical pollution will be restricted to processes like the introduction of soil-related historical pollution through erosion processes. With regard to regional and local emissions, it is expected that ambient metal concentrations will increase downstream from the spring: effluent emissions, erosion from agricultural areas, human (industrial) activities in the proximity of the water body, etc., can add substantial amounts of metal in the aquatic compartment.

A number of natural processes determine the variation found in natural background concentrations in surface water:

- Seasonal variation of the precipitation (rainfall) affects the amount of metal that enters the aquatic compartment through erosion and run off;
- Introduction of metal-containing organic material (leaves) becomes more important in the autumn;
- Flow rates, and hence, the metal concentration in the water show seasonal variation due to changes in rainfall, etc.
- Biological processes like algal blooms affect the amount of free metal in the water column.

These natural processes will not only affect the amount of metal on in the water column, but may also affect the metal speciation in the water (binding to suspended solids, presence of dissolved organic matter). Due to their complexity it is currently not possible to quantify the effect of each of these processes on the natural background in water

Soil compartment

In general, the residence time of metals in soil is much longer compared to that in the water compartment. Some metals, however, are hardly adsorbed to soil compounds and are quickly transported into the groundwater (e.g., selenium, boron, arsenic). For other metals the added amount to the top soil (historical pollution, anthropogenic inputs) remains present in the measured concentration over a long period of time. It is therefore difficult to allocate the measured metal concentration to the different fractions that are presented in Figure 1.

The natural metal background concentration of top soils is determined by the metal content of the parent soil material, the removal by biological (uptake by plants in a non-agricultural contex) and physicochemical (run-off, leaching to ground water) processes, the input by organic material (remains of plants) and air deposition(e.g., volcanic deposition). In most cases, however, the measured baseline concentration in pristine soils exceeds the natural background. For example, historical metal emissions by man affect ambient metal concentrations in soils, even far away from point sources such as smelters.

Due to the lower mobility of metals in the soil compartment compared to the aquatic phase, it is easier to assess whether the measured ambient metal content of a soil sample might be due to a local emission source. If no potential point sources are identified in the proximity of the sampling location, it can be assumed that the observed metal concentration is the sum of the natural, historical and regional emission fractions.

The very same processes that play a role in the natural variation of the background in water, will also affect the metal content of the top soil layer:

- The seasonal-dependent amount of precipitation determine the loss of metals from soil by leaching (vertical water movement), run off (horizontal water movement) and erosion (loss of soil solids);
- Uptake of metals from the soil by plants occurs during spring and summer;
- Enrichment of the soil with metals from organic debris (leaves etc.) is a typical phenomenon for the autumn.

Sediment compartment

The sediment layer in freshwater bodies is mainly formed by the deposition of organic matter from which the metal content is in equilibrium with the surface water concentration. In decaying, metals will partly be given back to the water phase, but also become entrapped in the sediment (e.g., metal sulfides). In time, this process extracts large amounts of metals from surface waters.

As a result of this accumulation process, the background concentration of metals in the sediment can be biased by an unidentified pollution of the overlying water in the past (historical, recent point source contamination), although this contamination may not affect the metal concentration of the surface water at the time of sampling. Therefore measured background concentrations in the sediment of ‘clean’ surface waters may not always reflect the natural background levels.

Regional and local anthropogenic inputs of metals into the water column will also add to the total metal concentration in the sediment layer. This enrichment will mainly take place at the upper part of the sediment and the influence of these anthropogenic contributions will diminish with increasing depth. Due to the dynamics of the aquatic compartment (constant renewal of the overlying water, sediment transport), it may sometimes difficult to relate elevated metal concentrations in the sediment to a previous local (point source) emission. A better insight into the history of sediment contamination can be obtained by investigating the evolution of metal sediment concentrations with increasing depth (sediment stratification).

The observed metal concentration in the top layers of the sediment may also be subject to seasonal variation. Changes of the oxic/anoxic conditions in this layer can induce the release of metals from the sediment to the aquatic compartment.

Air compartment
Background metal concentrations in air originate from natural processes such as volcanic eruptions, bush fires, etc. These diffuse sources are not included in the anthropogenic emission inventory.

Determination of baseline metal concentrations in different environmental compartments
Baseline metal concentrations within an environmental compartment may vary from site to site by several orders of magnitude. Also, due to natural dynamic processes these levels may change over time. This means that it is impossible to attribute single values to natural background concentrations of specific metals within a certain compartment. It should be noted that under natural conditions, clearly elevated natural background concentrations can be encountered in certain regions. When assessing a representative baseline concentration for a defined area, these “outliers” should not be used or included in the calculation of a generic baseline level as they would give a non-representative picture thereof. Some guidance to determine background concentration can be found in the paper of Reimann and Garret, 2005.

An important data set containing recent, reliable baseline concentrations in different environmental compartments has been developed from the results of the FOREGS Geochemical Baseline Programme (FGBP) published in March 2004 (http://www.gsf.fi/foregs/geochem/). FOREGS (Forum of European Geological Surveys) Geochemical Baseline Programme sought to provide high quality environmental geochemical baseline data for Europe based on samples of stream water, stream sediment, floodplain sediment, soil, and humus collected all over Europe. The high quality of the generated data in this programme was ensured by treating and analysing all samples in the same laboratories and by using standardised sampling methods:

- running stream water was collected form small, second order drainage basins (<100 km²) that are pristine or nearly so;
- whenever possible, sampling was performed during winter and early spring months, and was avoided during rainy periods and flood events;
- a full description of sampling materials and sampling volumes is provided, and all materials were rinsed twice with unfiltered or filtered stream water (depending on the type of water sample);
- all potential contaminating factors were reduced during the sampling period (wearing of gloves, no smoking in the area allowed, no hand jewelry was allowed , running vehicles during sampling was prohibited, etc..).
- water samples were analysed by ICP-MS, and the following elements were determined: Ag, Al, As, B, Ba, Be, Bi, Br, C, Ca, Cd, Ce, Cl, Co Cr, Cs, Cu, Dy, Er, Eu, F, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb,Nd, Ni, P, Pb, Pr, Rb, S, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V,W, Y, Yb, Zn, Zr.

The following sections give an overview of some reported baseline or natural background concentrations of metals in the different evironmental compartments

Surface water

Table A.1 presents the range of observed metal baseline concentrations that were determined in Europe during the FOREGS program. Similar data sets for other regions or continents are currently not available.

Table A.1: Ranges of some baseline metal concentrations in European surface waters (data from the FOREGS-program (http://www.gsf.fi/foregs/geochem/)

Element	Min	Median	Max	Element	Min	Median	Max
	µg/L				µg/L		
As	<0.01	0.63	273	Ni	0.03	1.91	24.6
Cd	<0.002	0.01	1.25	Pb	<0.005	0.093	10.6
Co	0.01	0.16	15.7	Sb	<0.002	0.07	2.91
Cr	<0.01	0.38	43	V	<0.05	0.46	19.5
Cu	0.08	0.88	14.6	W	<0.002	0.007	3.47
Mo	<0.002	0.22	16	Zn	0.09	2.68	310

From the data given in Table A2.1 it can be concluded that baseline-concentrations for a specific metal in the aquatic compartment (surface water) can vary up to 4 orders of magnitude (e.g., As, Mo, Pb).

Apart from the straightforward method of measuring metal levels at selected sites that are considered to be undisturbed by human activities, several additional methods are available:

- Geochemical modeling: estimation methods on the basis of the contribution of weathering processes (erosion). This method is shown to be well applicable for assessing natural background concentration in aqueous systems (rivers).
- Calculation based on background sediment concentration and the equilibrium coefficient. This may not be applicable if metal has been redistributed significantly in sediment column by diagenesis.
- For surface water having ground water as its origin: assessment of the metal concentrations in the deeper ground water.

An overview of total and dissolved background concentrations in freshwater surface waters presented by Zuurdeeg et al. (1992) and is given in Table A.2. In the absence of local- or (eco-) region-specific background levels, the values proposed by Zuurdeeg (1992) can be used as default background values in the local or regional risk characterization of metals.

Values were derived from measured data representing areas that are considered to be relatively unpolluted (NH_4-N: < 0.1 mg/L; BOD: < 2 mg/L; O_2: > 8 mg/L). Data were obtained form literature searches and results from monitoring programs that were performed in relatively unpolluted surface waters. A second selection of the data was done by using the following criteria: NO_3: < 15 mg/L; Cl: <15-35 mg/L; Zn: < 100 µg/L);

Data for the Northern European lowland originated from the following areas: Belgium (Ardennes), The Netherlands (some areas in the Veluwe), Germany (Eiffel, Sauerland, Arnsberg, Harz, Luneburger Heather) and Poland (High Tatra, Mazury). Due to different data sources between reported total and dissolved metal concentrations, the average total concentration is sometimes lower than the average dissolved concentration (e.g., Mo, Zn). In those cases, it is recommended to use the dissolved background concentration as the total metal levels may be influenced by the applied method for releasing metals from the suspended solid phase.

Table A.2: Overview of natural background concentrations in freshwater surface waters (data from Zuurdeeg et al., 1992)

	WORLD				N-EUROPEAN LOWLAND			
Element	Dissolved (filtered) (µg/L)		Total (unfiltered) (µg/L)		Dissolved (filtered) (µg/L)		Total (unfiltered) (µg/L)	
	average	Range (± 1 σ)	average	Range (± 1 σ)	Average	Range (± 1 σ)	average	Range (± 1 σ)
As	1.24	0.28 – 5.42	0.78	0.60 – 1.02			1.0	0.59 – 1.9
Ba	19.8	9.49 – 41.4	78	49 – 126			76	48 – 121
Be	0.020	0.007 – 0.056						
Cd	0.053	0.010 – 0.15	0.27	0.09 – 0.82	0.12	0.04 – 0.35	0.41	0.22 – 0.78
Co	0.031	0.010 – 0.098	1.03	0.21 – 5.01				
Cr	0.097	0.024 – 0.39	2.03	0.68 – 6.05			1.6	0.62 – 4.2
Cu	1.18	0.55 – 2.57	1.78	0.72 – 4.41	2.0	0.8 – 5.3	1.1	0.56 – 2.5
Hg	(0.004)		0.049	0.011 – 0.21			0.060	0.028 – 0.13
Mo	0.78	0.26 – 2.32	3.94	1.66 – 9.35	2.0	0.6 – 7.0	1.4	0.38 – 4.8
Ni	0.25	0.064 – 0.99	3.03	1.88 – 4.89	3.6	1.0 – 13.3	4.1	2.3 – 7.9
Pb	0.52	0.13 -2.02	1.48	0.52 – 4.18	3.1	1.1 – 8.4	3.1	1.9 – 5.2
Sb	0.42	0.16 – 1.09						
Se	(0.16)	0.084 – 0.29						
Sn	(0.002)	0.001 – 0.003						
Tl			0.040	0.023 – 0.90	0.016	<0.01 – 0.035		
V	0.30	0.14 – 0.63					0.96	0.38 – 2.4
Zn	3.25	0.64 – 16.6	20.6	12.3 – 34.6	18.5	8.0 – 42.7	12.0	5.1 – 27

Sediment
Table A.3 presents the range of observed metal baseline concentrations in European sediments, as determined during the FOREGS program. Similar data sets for other regions or continents are currently not available.

Table A.3: Ranges of some baseline metal concentrations in European freshwater stream sediments (data from the FOREGS-program (http://www.gsf.fi/foregs/geochem/). Values determined after aqua regia extraction, with exception of Cd, Mo, Sb and W.

Element	Min	Median	Max	Element	Min	Median	Max
	mg/kg				mg/kg		
As	<5.0	6.0	231	Ni	2.0	16.0	1,200
Cd	<0.02	0.28	43.1	Pb	<3.0	14.0	4,880
Co	<1.0	8.0	245	Sb	<0.02	0.615	34.1
Cr	2.0	21.0	1,750	V	4.0	29.0	306
Cu	1.0	14.0	998	W	<0.05	1.24	81.5
Mo	0.12	0.63	117	Zn	7.0	60.0	11,400

From the data given in Table A3 it can be concluded that baseline-concentrations for a specific metal in the sediment compartment (freshwater streams) mostly vary up to 3 orders of magnitude.

A number of model-based approaches for the estimation of background metal concentrations have been summarized by Van Tilborg (2002). Apart from the straightforward method of measuring metal levels at selected sites considered to be undisturbed by human activities, additional methods include:

- Assessment of metal concentrations in the deeper sediment layers, taking into account anthropogenic contributions and vertical distributrion of metals towards these deeper layers.
- Calculation based on background surface water concentration and the equilibrium coefficient.
- For local assessment, the difference between upstream and downstream sediment concentrations could be taken. However, this method only excludes historical emission from the local site and not from other sites or diffuse pollution.

Soil
Table A.4 presents the range of observed metal baseline concentrations in European soil samples, as determined during the FOREGS program. Similar data sets for other regions or continents are currently not available.

Table A.4: Ranges of some baseline metal concentrations in European soil samples (data from the FOREGS-program (http://www.gsf.fi/foregs/geochem/). Values determined after aqua regia extraction, with exception of Cd, Mo, Sb and W.

Element	Min	Median	Max	Element	Min	Median	Max
	mg/kg				mg/kg		
As	<5.0	6.0	220	Ni	<2.0	14.0	2,560
Cd	<0.01	0.145	14.1	Pb	<3.0	15.0	886
Co	<1.0	7.0	255	Sb	0.02	0.60	31.1
Cr	1.0	22	2,340	V	1.0	33.0	281
Cu	1.0	12	239	W	<5.0	<5.0	14.0
Mo	<0.1	0.62	21.3	Zn	4.0	48.0	2,270

From the data given in table A2.3 can be concluded that baseline-concentrations for a specific metal in the terrestrial compartment (freshwater streams) mostly vary up to 3 orders of magnitude.

The degree of variation depends on factors like soil composition (sandy soil, clayey soils) and geochemical origin of the soil. Sandy and loamy soils, for instance, contain lower concentrations of trace metals than clay soils. Several countries (Belgium, The Netherlands, Denmark) have reported regression lines that predict (background) metal concentrations as a function of soil texture: most often the clay content and the organic matter content (VLAREBO, VROM, Lexmond et al., 1986, Tjell and Hovmand, 1978). Both parameters mainly determine the natural binding capacity of different soils parameters. As regressions were based on measured data, reported metal concentrations may be influenced by historical pollution (e.g., atmospheric deposition) and may therefore be more representative for the baseline concentration than for the natural background.

Equation 1 presents a regression line for copper that was generated on Dutch soil data (VROM). Equation 2 is a second example, predicting the background of Pb in Flemish soils.

$$C_{Cu}\ (mg/kg) = 15 + 0.6 \times (Clay(\%)) + 0.6 \times (OM(\%)) \quad (1)$$

$$C_{Pb}\ (mg/kg) = 33 + 0.3 \times (Clay(\%)) + 2.3 \times (OM(\%)) \quad (2)$$

The metal-specific coefficients for clay and OM that are used for the determination of metal background concentrations in Flanders are summarized in Table 4.

The coefficients of Table A.5 actually reflect the 90th percentile upper regression line to account for the variations of the background concentrations. Note that the regression coefficients (square of correlation coefficients) R^2 are low, indicating that the proposed regression lines only explain a minor part of the observed variation in metal concentrations in soils. As a result the use of these reference lines for predicting background concentration for a specific soil may lead to substantial over- or underestimations**.**

Table A.5: Overview of the coefficients for the reference lines to calculate a soil background concentration in Flanders (OVAM, 1996)

	Constant	Clay-coefficient	OM-coefficient	R^2
As	14	0.5	0	0.39
Cd	0.4	0.03	0.05	0.39
Cr(III)	31	0.6	0	0.37
Cu	14	0.3	0	0.24
Hg	0.5	0.0046	0	0.08
Pb	33	0.3	2.3	0.15
Ni	6.5	0.2	0.3	0.48
Zn	46	1.1	2.3	0.26

The same type of reference lines for the derivation of metal background concentrations in The Netherlands are also presented in Crommentuyn et al. (1997), and the metal coefficient values are summarized in Table A.6. The use of these reference lines for estimating natural background concentrations, however, appears to be questionable:

- reference lines were all based on older measurements in soil samples from a large number of **relatively unpolluted** areas in the Netherlands, i.e., some of the data will most likely include some regional anthropogenic input by human activities and should therefore be considered as baseline concentration data

Derived background concentrations for a standard soil do not seem to be representative for the European situation. For copper, the Dutch standard background of 36 mg/kg in Crommentuyn et al. (1997) is a factor of 3 higher than the median concentration of 12 mg/kg (n=835, 2 outliers were discarded) that was derived with the recent data generated in the recent FOREGS-monitoring program (see Table A.2.3)

Table A.2.5: Overview of the coefficients for the conversion regressions to calculate a soil background concentration in The Netherlands (BIM, 1995; RIVM, 2004 http://www.rivm.nl/stoffen-risico/NL/ond_4_0_1.html)

	Constant	Clay-coefficient	OM-coefficient
As	15	0.4	0.4
Ba	30	5	0
Be	0.3	0.033	0
Cd	0.4	0.007	0.021
Cr (tot)	50	2	0
Co	2	0.28	0
Cu	15	0.6	0.6
Hg	0.2	0.0034	0.0017
Pb	50	1	1
Mo	1	0	0
Ni	10	1	0
Sb	1	0	0
V	12	1.2	0
Zn	50	3	1.5

Implementation of background concentrations for risk characterization

With regard to the use of the term 'background', it should be noted that this tern refers to the baseline concentration, as the natural background can not be determined anymore in many cases and because it is assumed that the baseline values are close to natural background levels.

The risk characterization of regional exposure concentrations in the different environmental compartments can be performed according to two different concepts: the Added Risk approach (ARA) or the Total Risk approach (TRA) (see MERAG fact sheet 3). The Added Risk approach assumes that only the anthropogenic added fraction of a natural element attributes to the risk for the environment, i.e., the amount of metal that is added to the background concentration. The total risk assessment approach assumes that "exposure" and "effects" are compared on the fraction compiling the natural and the added anthropogenic background. The risk characterization can be done at different levels like on total fraction, on dissolved or on the bioavailable fraction.

The added risk approach is recommended for those substances where a) no bioavailability model/data are available, b) the natural background is close to the PNEC and c) the $PNEC_{total}$ does not remains above the calculated or measured RWC-ambient PECs. A more thorough discussion on these criteria is provided in fact sheet 3.

The RWC-ambient PEC_{added} is defined as the difference between the RWC-ambient PEC (regional, local) and the background concentration. The use of a single number that represents the background concentration of a metal in a large region (e.g., continental scale) is of limited value due to high variability across such a large geographic area. Consequently, averages/medians (depending on the amount of available data) and ranges of background concentrations for various (eco-) regions should be defined.

The background value that needs to be used for the translation of PEC_{total} to PEC_{added}, is dependent on the available information. The use of reliable local-specific or regional-specific background concentrations is recommended for the derivation of the added local/regional PEC. If such information is not on hand, a generic background concentration is applied. This value represents the median value of all available (eco)region specific background concentrations within the area of interest (e.g., Europe for EU-risk assessment purposes).

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