

METALS ENVIRONMENTAL RISK ASSESSMENT GUIDANCE

# MERAG

## Exposure assessment

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*The content of the Metal Risk Assessment Guidance (MERAG) fact sheets reflect the experiences and recent progress made with environmental risk assessment methods, concepts and methodologies used in Chemicals Management programs and Environmental Quality Standards setting (soil, water, sediments, ...) for metals. Because science keeps evolving, these fact sheets will be updated on a regular basis to take into account new developments.*

## 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 local and diffuse emissions associated with the use pattern (anthropogenic) and the complete life cycle of the metal (ie, from mining to waste disposal). Collecting information on anthropogenic emissions of pollutants to surface water, wastewater air and soil through the different life stages is, hence, crucial for chemicals management purposes because it allows regulators, industry, and government agencies to estimate concentrations and potential risks related to the presence of pollutants in the environment and helps to identify the most efficient risk management option(s). Due to the inherent variation of metal concentration in the natural environment (eg different natural background concentrations) and the variability in anthropogenic input, large differences in metal concentrations can be observed among different locations. Taking into account, the relative contribution of the different anthropogenic inputs as well as local natural background, the exposure assessment can be performed combining both modelled data and measured data.

The information presented in this document serves as guidance both for the national governmental institutions, industrial users and evaluating experts faced with conducting exposure assessment for inorganic substances. Because exposure data are a key component of compliance checking and risk assessments in general, this guidance focuses on how exposure data should be compiled taking into account relevant facts when dealing with metal exposure data (ie, natural background, local and diffuse emissions, bioavailability, availability of large monitoring data sets, etc).

The structure of this guidance is the following. Section 2 gives a brief overview of the terminology and definitions used, and introduces the main advantages/disadvantages of using modelled or measured metal concentrations. Section 3 is dedicated to exposure assessment using modelled data. Section 3.1 outlines in detail how diffuse sources analysis can be used to discern the relative contribution of the different anthropogenic inputs with respect to natural background/natural sources. These diffuse emissions are important to calculate the emissions on a regional and continental scale. In addition, tools, such as specific environmental release categories (SPERCS) are presented in Section 3.2 which may be used to calculate local emissions. In Section 3.4, different multi-media fate models (EUSES, Unit World Model, etc) and their usefulness and parameterization for metals are discussed. Finally, Section 4 reviews

the wealth of measured data which are available for some metals and how these data can be screened for fit for purpose and how reliable exposure estimates can be derived.

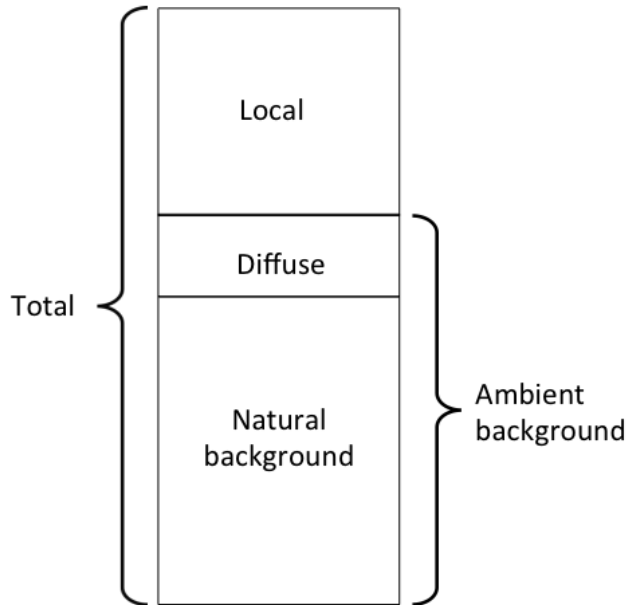
## 2. Concepts and overview

### 2.1 Terminology and Definitions

The presence of metals in the environment due to natural processes (resulting in a natural background concentration of metals in all environmental compartments, including organisms) and the chemical processes that affect the speciation of metals in the environment have implications for both the environmental exposure and effects assessment of metals and thus for the risk characterisation/environmental quality setting of metals in general. Regarding the background concentration of metals in the environment, a distinction must be made between (ECHA 2008):

- **natural background concentration:** the natural concentration of an element in the environment that reflects the situation before any human activity disturbed the natural equilibrium. As a result of historical and current anthropogenic input from diffuse sources, the direct measurement of natural background concentrations is challenging in the European environment;
- **ambient background concentration:** the sum of the natural background of an element with diffuse anthropogenic input in the past or present (ie, influence of point sources not included);
- **baseline background concentration:** the concentration of an element in the present or past corresponding to very low anthropogenic pressure (ie, close to the natural background).

Figure 1 gives the relation of these definitions with the total and local contributions.



**Figure 1:** Breakdown of metal concentrations in the environment

Definitions of some terms that are used in this document are given below:

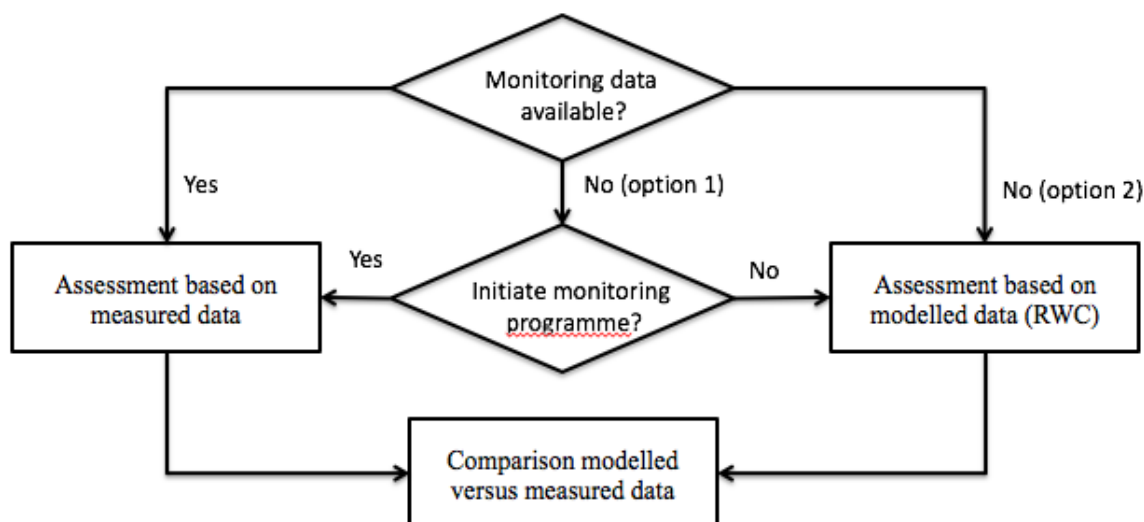
- **Bioavailability:** (or biological availability) means the extent to which a substance is taken up by an organism, and distributed to an area within the organism. It is dependent upon physico-chemical properties of the substance, anatomy and physiology of the organism, pharmacokinetics, and route of exposure.” (UN-GHS 2013). Hence, metal bioavailability refers to the fraction of the bioaccessible metal pool that is available to elicit a potential effect following internal distribution; metabolism, elimination and bioaccumulation. For the purpose of this guidance, the term “metal bioavailability” is used more as a conceptual term as initially proposed by Meyer (2002).
- **Biogeochemical region:** Fairbrother and McLaughlin (2002) initially referred to this concept as metallo-regions where on a regional scale separate sub-regions are being defined using suitable methods to aggregate spatially explicit environmental variables. Another term frequently used in this regard is “ecoregion”. At the moment the biological/ecological-part has been a bit underrated because the current existing biogeochemical regions are based on abiotic factors rather than quantified ecological metrics. If ecology can be considered, that approach further suggests that instead of

using 'generic' species, it is preferable to use 'endemic' test organisms representative for the natural environment under investigation to characterise the sensitivity of the ecosystem.

- **Environmental Exposure Concentration (EEC):** is an exposure benchmark value, which is compared with an Environmental Threshold Value in a risk assessment framework or for compliance checking. The Environmental Exposure Concentration is typically calculated from all individual measured or modelled metal concentrations for a predefined environment taking a high end value (eg, the 90<sup>th</sup> percentile) of the environmental concentration distribution at a site/region.
- **Environmental Threshold Value (ETV):** is an environmental effects concentration below which adverse effects on the environment are not expected to occur. Examples of ETVs are Predicted No Effect Concentrations (PNEC), Environmental Quality Standards (EQS), Water Quality Criteria (WQC), Water Quality Standards, etc.
- **Reasonable Worst Case Conditions (RWC):** considered to be the environmental conditions that maximises bioavailability.

## 2.2 Use of Modelled Versus Measured Data

The exposure assessment can be performed using a combination of modelled data and measured data (Figure 2).



**Figure 2:** Use of measured and modelled data

Figure 2 starts off with the question if adequate monitoring data are available. For quite a number of metals, a large data set of measured environmental concentrations exists. However, care needs to be taken that the measurements were properly done, notably when the dissolved fraction is measured (see Section 4.1). Given the fact that metals are naturally occurring, the possible influence of local geological conditions (possibility for local metal-containing mineralogy) should also be taken into account. Another factor often influencing local metal levels is historical contamination. 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 a Realistic Worst Case (RWC) modelling approach as a way forward for carrying out the exposure assessment.

The decision to embark or not on a monitoring program, 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 (eg, 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. Recognising that both modelling approaches and the use of measured data (when available) have their advantages and disadvantages (Table 1), it is recommended to use both approaches in parallel.

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

MODELLING	MEASURED DATA
Possibility of unintentionally <ul style="list-style-type: none"> <li>• missing unidentified sources,</li> <li>• missing metal compounds or</li> <li>• excluding sources due to regulatory issues (eg, biocides, mining, medical use, ...)</li> </ul>	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: reality-check, realistic reflection of environmental exposure
Advantage: typically low resource allocation	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 predicted environmental concentrations (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
	Disadvantage: measured concentrations can



	have a considerable uncertainty associated with them due to temporal and spatial variations as well as differences in analytical methods
Advantage: can be used for projection and to test management scenarios	Disadvantage: limited to retrospective evaluations

To facilitate the comparison between modelled and measured environmental concentrations, all products, even if excluded from the regulatory framework for which the exposure assessment is being conducted (eg, biocides, pesticides, and medical product applications are not covered under the REACH framework), should be included in the emission inventory and subsequent derived environmental exposure concentration (EEC) to avoid missing important sources. It is also recommended that the metal of concern and its compounds be assessed as a group. Because the modelled diffuse ambient metal concentrations are typically calculated using a country-specific approach (Section 3.2), the comparison with the measured data can best be based on all site-specific 90P-values within a geopolitical area (eg, country, state).

If the outcome of the comparison indicates that the calculated/modelled EEC is not of the same order of magnitude as the EEC 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 EEC values need to be reconsidered, re-evaluated and, if possible, further refined. In general, the following cases can be distinguished:

- $EEC_{\text{modelled}} \approx EEC_{\text{measured}}$ : The result indicates that the most relevant sources of exposure and fate processes were taken into account.
- $EEC_{\text{modelled}} > EEC_{\text{measured}}$ : This result might indicate that relevant elimination processes were not considered in the EEC 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-EEC in the regarded environmental compartment. It may also indicate a slow time response to a new external load. If the PEC based on measured data has been derived from a sufficient number of representative samples, then they should override the model predictions.
- $EEC_{\text{modelled}} < EEC_{\text{measured}}$ : This can be caused by failure to take all relevant sources of emission into account when calculating the EEC, or that the used models were not suitable for the conditions/metal. Another explanation is that the higher ambient

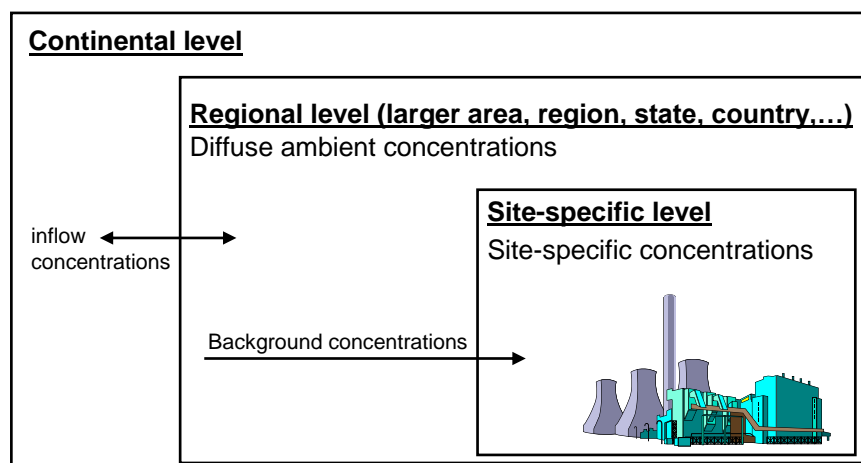
measured concentrations are due to a natural high background or reflect historical pollution (especially on a local scale), are caused by spillage, are the result of a recent change in use pattern, or reflect the recent introduction of emission-reducing measures that have not yet affected the environmental concentrations of the metal/metal compounds.

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

### 3. EXPOSURE ASSESSMENT USING MODELLED DATA

#### 3.1 Introduction

With regard to the modelled exposure analysis for risk assessment purposes, a distinction can be made between different spatial scales. The 'site-specific' or local 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<sup>1</sup> 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 the European Union System for the Evaluation of Substances (EUSES). An overview of the different interactions between the different spatial scales is presented in Figure 3.



**Figure 3:** 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

#### 3.2 Diffuse Source Emission Inventory

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<sup>1</sup> 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 (eg, residential heating, wastewater discharge, agriculture, traffic, ...). In the exposure assessment, diffuse sources include all sources, not included in the local RAR

### **3.2.1 General**

Human society uses many chemical compounds for the production of goods, health care, and agriculture. These chemical compounds can be either synthetically produced or be of natural origin. The latter group is mostly comprised of metals (including metalloids like arsenic and antimony). These metals are a part of a natural biogeochemical cycle of elements. Within this cycle, the metals are exchanged between the geosphere, hydrosphere, and biosphere. Metals originating from natural sources are released into the environment through a variety of processes including volcanic eruption, forest and brush fires, and wind-blown suspension of dust and sea salt spray (Nriagu 1989; Lin and Pehkonen 1998).

Collecting information on anthropogenic emissions of pollutants to surface water, wastewater, air, and soil through the different life stages is crucial for chemicals management purposes because it allows for the rational estimation of concentrations and potential risks related to the presence of pollutants in the environment and helps in identifying the most efficient risk management option(s), if relevant. A detailed investigation and analysis of diffuse sources further allows for understanding their relative contribution to regional/continental emissions, thereby providing crucial and complementary information to environmental compartment monitoring data. Indeed, the comparison of the two often allows a better insight into the relative contribution of the different anthropogenic inputs, also with respect to local natural background. In addition, diffuse source analyses enable generic source type allocation (eg, impurities in inorganic fertilizers, corrosion from metallic structures, releases from brake pads) to be made as well as to define their underlying drivers of release. It therefore provides clear insights about the metals emissions originating from products (eg, corrosion from building materials, tire wearing) and non-product use (eg, from impurities in oil, from steel/fertiliser manufacturers).

The relative contribution of product and non-product-related metal emissions are dependent on the environmental compartment and metal considered. For example, the current emissions of Pb to the soil compartment could almost fully be attributed to the use of Pb-shot (product-related emission), while for Ni, the soil emissions could almost fully be attributed to the use of manure/fertilizer on agricultural land (Figure 4). Emissions of Ni from these sources are typically non-product related emissions because Ni is present as an impurity in manure/fertilizer.

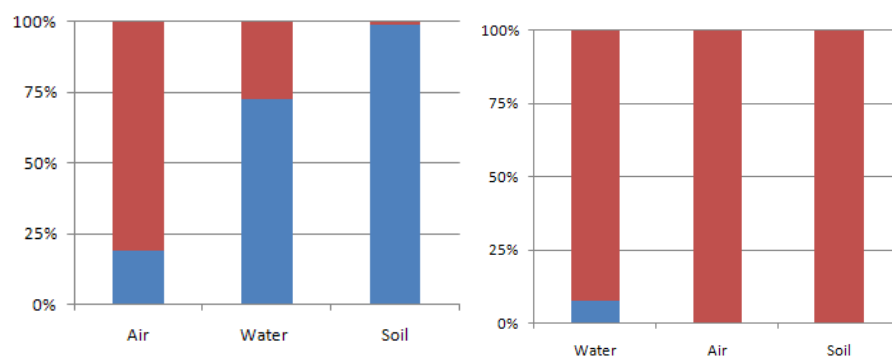


Figure 4: Product (blue bars) and non-product releases (red bars) for Pb (left figure) and Ni (right figure)

In terms of absolute quantity, the contribution of diffuse sources can in certain cases be large compared to point sources or releases from natural background. However, it is noted that diffuse emissions are by definition dispersive and will as such be spread over large areas. Therefore, their influence on environmental exposure concentrations and risk is often less important than emissions from point sources which only influence environmental exposure concentrations at a specific location. Therefore, environmental concentrations that are monitored are the only reflection of local input from diffuse and point sources.

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 (eg, ECHA 2012; TGD 2003; EEA 2003; US EPA 1996). However, some metals may require specific or targeted assessments (eg, highway or road border scenario). 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/states and the selection of a representative area/region/state;

- Quantification of regional and continental metal emissions (in the EU, the scope of the assessment is limited to current emissions).

Ideally, biogeochemical regions (metallo-regions) that take the geochemical and ecological dimensions into account should be used instead of regions based solely on social, demographic, economical, and geographical factors (eg, countries, states). Different background concentrations and bioavailability corrections can then be used in correspondence with such regions. In practise, this may not always be feasible. As an alternative, a well-defined area (region, state, country) that is representative of the global area under consideration (ie, the continent) could be used for the modelling of diffuse ambient concentrations. For such areas, physico-chemical conditions should be documented and defined. 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 (ie, also those governed by other laws and regulatory statutes).

### ***3.2.2 Identification of all relevant sources***

A first step in the diffuse source analysis is the identification of the relevant sources that could result in releases of metals to the environment. A list of potential emission uses/sources for a specific metal should be developed based on the knowledge of the mass-flow of the specific metal. Further information on the use, sources and emissions could be gathered from national emission inventories available for those countries/states within the area of interest, from international organizations (Box 1), from available emission inventory guidelines, or from the open literature. 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 relevant in terms of emissions is the European Pollutant Emission Register (e-PRTR-). Other data, compiled for the European Commission (Directive 76/464/EEC, Water Framework Directive (WISE, Eionet databases), 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 can be useful sources of exposure emissions.

An overview of the most important identified sources for Cd, Co, Cu, Mo, Ni, Pb, Sb, V and Zn is shown in Table 2. The cradle-to-grave overview of emission sources covers the emissions during production (manufacturing and use), product use and waste management.

**Table 2:** Overview of relevant metal specific sources of emissions

Category	Sub-category	Point source	Cd	Co	Cu	Mo	Ni	Pb	Sb	V	Zn
Industry	Non-combustion	Manufacture and industrial use of metal and metal compounds	X	X	X	X	X	X	X	X	X
	Combustion	Power production, refineries	X	X	X		X	X	X	X	X
Product use	Households	Residential heating		X	X		X	X	X	X	
		Domestic waste water		X	X	X	X	X	X	X	X
		Use of fishing weights						X			
	Agriculture	Heating of buildings		X	X		X	X	X	X	
		Use of	X	X	X	X	X	X	X	X	X

		fertilisers/manure/ sewage sludge									
		Use as feed component (essential elements)		X	X						X
	Transport	Exhaust fumes (road transport, shipping,...)	X	X	X		X	X	X	X	
		Brake wear	X	X	X		X	X	X	X	X
		Tire wear		X	X		X	X	X	X	X
		Road surface wear		X	X		X	X			X
		Motor oil leakage		X	X		X	X			X
		Use of wheel balance weights						X			
		Use of grease				X		X			
		Use of antifouling paints			X						X
		Wear of collector shoes/overhead wires			X						
Waste management		Sewage treatment plants	X	X	X	X	X	X	X	X	X
		Landfills	X	X	X	X	X	X	X		X
		Waste incineration	X	X	X	X	X	X	X		X
Other sources		Use of shot/ammunition						X	X		
		Fireworks	?		X						
		Wood preservatives			X						
		Corrosion of materials			X	X	X	X		X	X



### 3.2.2.1 *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, those products that are excluded from the regulatory framework (for example, industrial/consumer chemicals versus biocides, plant protection products, medical product applications) in the emission inventory and subsequent regional EEC derivation. In case not enough information is available on the emissions of these sources or because the use of these products is very specific and therefore the available 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 characterisation. If any risks are identified under this scenario, then it can be further investigated if more realistic use patterns apply in the region of interest.

### 3.2.2.2 Selection 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:** ie, specific value of an emission, mostly given in physical terms, related to the respective sectoral or process activity rate (eg, for energy-related emissions (Mg/GJ) (EMEP/Corinair 2009). Most often, average emission factors are used in this perspective.
- **The means of expressing/describing activity data:** ie, quantitative representation of the variable that “explains” the emissions in a source category, preferably in physical dimensions (eg, produced mass of cement [Mg/year] or otherwise in monetary dimensions (eg, value of glass production [ECU/year]), either in emission inventories or in emission projections (EMEP/Corinair 2009).
- **The choice of the distribution factor:** ie, the partitioning of total emissions to the environmental compartments.

Criteria for evaluating the quality of the emission data have been proposed by US EPA (2009) and EMEP/Corinair (EEA 2009). 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 (D and E) increases the uncertainty with regard to the outcome of the modelled exposure assessment and, subsequently, the risk characterisation based here upon. Based on the quality assessment of the emission inventory, sources and quantification methodologies can further be identified but which have to be studied in-depth because of their importance and/or low-quality quantification method.. It is recommended that the quantification method with the highest quality score A 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.

Preference is given to the quantification of emissions that are based on semi-measured/measured data (eg, individual reporting of measured industrial emissions to E-PRTR). In some cases (eg, % filter dust), data contained on the E-PRTR database are not always measured, or have been derived indirectly. In the absence of measured data, emissions should be quantified based on detailed substance-specific modelled data (eg, emissions quantified by a detailed sewage system model or road traffic model). Finally, in the absence of such measured and/or substance-specific modelled data, emissions could be estimated using a more generic default approach based upon the following quantification equation (Eq-1):

$$E = A \times EF \times DF \times 'X' \quad (\text{Eq-1})$$

where A is the activity data and can be defined as a quantitative representation of the variable that “explains” the emissions in a source category, usually in physical dimensions; EF represents the emission factor, the factor that quantifies the emission of a metal/product/debris per unit of A; DF represents the distribution factor or the partitioning of the total emissions to the environmental compartments (air, surface water, soil) and ‘X’ relates to the concentration of the metal in the exposed product, or connection rate to the sewage system. The quantification equation for very relevant and important sources of metals are provided hereunder:

- Emissions of metals from combustion processes:

$$E_{\text{combustion}} = \sum(C_f) \times Me_f \quad (\text{Eq-2})$$

Where  $E_{\text{combustion}}$  (in kg) is the emissions from industrial/residential combustion processes;  $C_f$  (in kg fuel) is the industrial/domestic consumption of fossil fuel type  $f$  and  $Me_f$  (in kg metal/kg fuel) is the metal content per fuel type.

- Emissions of metals from households not connected to a sewage system:

$$E_{\text{domestic}} = (\text{INH} \times W_d) \times Me_d \times (1 - CR_s) \times DF_d \quad (\text{Eq-3})$$

Where  $E_{\text{domestic}}$  (in kg) is the emissions from the discharge of domestic wastewater, INH is the number of inhabitants in a region;  $W_d$  (in L) is the water consumption per inhabitant;  $Me_d$  (in mg/L) is the average metal concentration in the emitted wastewater from households;  $CR_s$  (in %) is the relative number of inhabitants not connected to a sewage system (ie, connection rate); and  $DF_d$  the distribution coefficient (in %).

- Emissions of metals from sewage treatment plants (STP):

$$E_{\text{sewage}} = W_s \times Me_w \times (1 - R_s/100) \quad (\text{Eq-4})$$

Where  $E_{\text{sewage}}$  (in kg) is the emissions of metals from STP;  $W_s$  is referring to the amount of wastewater connected to sewage treatment plants (in L);  $Me_w$  (in mg/L) to the concentration of metals in influent water of the STP; and  $R_s$  refers to the removal efficiency for metals of the waste water treatment plant (in %).

- Emissions of metals from the use of fertilizers/manure in agriculture:

$$E_{\text{agriculture}} = ((Q_f \times Me_f) + (Q_m \times Me_m)) - (\text{drift} + \text{runoff} + \text{leaching} + \text{uptake by crops}) \quad (\text{Eq-5})$$

The estimation of the input of metals from mineral fertilisers is based on a mass balance model by multiplying the average metal content of fertilisers ( $Me_f$  in mg/kg) and the amount of fertiliser used on agricultural soil (quantities  $Q_f$  in kg). The input of metals through manure to agricultural soil is the sum of the amount of manure applied (quantities  $Q_m$  in kg) and the average metal content in roughage (in most cases, feed produced at the farm) and the concentrated feed that is used as a supplement ( $Me_m$  in mg/kg) taking into account removal of metals through animal products, feed for household animals and the net export of concentrate

feed and manure. On the other hand, leaching of metals to groundwater and uptake of metals by crops growing on the land may decrease the metal accumulation in soils. Other processes resulting in an output of metals from the soil compartment are related to drift (ie, the physical movement of droplets or particles through the air at the time of fertiliser/manure application or soon thereafter) and run-off from agriculture land that can cause an emission to the surface water. Such processes resulting in a decrease of the metal accumulation in soils could be calculated using multi-media modelling.

- Emissions of metals from tyre wear/brake wear:

$$E_{\text{wear}} = K_v \times EF_w \times CF_w \times DF_w \quad (\text{Eq-6})$$

Where  $E_{\text{wear}}$  (in kg dust) is the metal emission from tyre wear/brake wear/road wear  $K_v$  (in km) is the amount of kilometres driven per vehicle type  $v$  (passenger car, truck, motorcycle,..);  $EF_w$  (in mg dust/km) is the emission factor for dust per vehicle type  $v$ ;  $CF_w$  (in mg metal/mg dust) is the concentration factor for metals; and  $DF_w$  (in %) is the distribution factor for dust to air, water, soil

- Emissions of metals from the corrosion of materials:

The approach used to estimate the metal emissions from the corrosion of material uses the following equation:

$$E_{\text{corrosion}} = \sum (M_m) \times R_m \times DF_c \quad (\text{Eq. 7})$$

Where  $E_{\text{corrosion}}$  (in kg) is the emissions of metals from the corrosion of materials;  $M_m$  (in m<sup>2</sup>/y) is the amount of material  $m$  exposed to open air;  $R_m$  (in g metal/m<sup>2</sup>/y) the run-off factor or emission factor for metals per material  $m$  and  $DF_c$  the distribution factor to air, water, soil (in %). It should be stressed that the emission factor for metals should be based on the quantification of the “run-off” rather than on the corrosion rate of the metal. Indeed, the corrosion process takes place at the interface between the metal substrate and the corrosion product (patina or passive film), whereas the runoff process takes place at the interface between the atmosphere and the corrosion product. Hence, it follows that corrosion and runoff proceed independently of each other and with rates that are not necessarily equal or even proportional (He et al, 2001; Verbiest et al, 1997; Cramer et al 1988). The runoff rate is mainly determined by precipitation volume and the concentrations of acid pollutants (SO<sub>2</sub> and chlorides in particular) in the atmosphere. For Zn, the empirical equation of Wallinder et al

(1998-2000) as presented in Table 3 is at present the best descriptor for the runoff rate and is related to the SO<sub>2</sub> concentration in the air. For copper, the runoff rate could be calculated as a function of the annual precipitation volume, pH and the angle of inclination (Zhang et al, 2002).

**Table 3:** Overview of the runoff equations for Zn and Cu

<b>Metal</b>	<b>Material</b>	<b>Runoff equation and driver</b>
Cu	Roofs	Runoff rate = $(0.97 + 0.95 \times V \times 10^{-0.62\text{pH}}) \times \text{COS}(\theta)/\text{COS}45^\circ$ with V the annual precipitation volume (mm/y), pH and $\theta$ the angle of inclination
Zn	Roofs	Runoff rate = $1.36 + 0.16 [\text{SO}_2] \times \text{COS}(\theta)/\text{COS}45^\circ$ and $\theta$ the angle of inclination with SO <sub>2</sub> a measured regional year-average concentration level ( $\mu\text{g}/\text{m}^3$ )

### **3.2.3 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 (eg 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 summarising 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 (eg mileage driven for tyre wear) and used as a translator to extrapolate the emissions to a continental scale. This methodology can be summarised by the following equation (Eq-8). Due to the structure of the exposure model ("nested multi-media model"), the continental concentration serves as a background for the regional scale. Therefore, double counting would occur if the regional emission is not subtracted in Eq-8, which would lead to a significant overestimation of the regional PEC.

$$Emission_{continental} = (Extrapolation\ factor \times Emissions_{regional})_{source\ specific} - Emission_{regional} \text{ (Eq-8)}$$

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 where 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<sup>1</sup>. 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 because quite often the country-specific extrapolation factors are larger.

### 3.2.4 Calculations of environmental concentrations on a regional and continental scale

Multi-media fate models (eg, EUSES 2.0) can be used for calculating the regional Environmental Exposure Concentrations at the regional ( $EEC_{regional}$ ) and continental scale ( $EEC_{continental}$ ) for each environmental compartment, ie, air, water, and soil (see also section 3.2.5).

The inputs for the regional assessment are the anthropogenic point and diffuse emissions of metals to air, wastewater, surface water, agricultural soil, and industrial/urban soil. The  $PEC_{regional}$  also provides the ambient background concentration (ie, concentration in environmental compartments that enter the local system) that is incorporated in the calculation of the EEC at a local scale ( $EEC_{local}$ ), while the  $EEC_{continental}$  provides the 'background' for the regional scale, ie, for the  $EEC_{regional}$ .

Metal concentrations at the continental level ( $EEC_{continental}$ ) are calculated based on the combined anthropogenic metal emissions from all countries within the continent ( $C_{continental}$ ) and on the natural/pristine ambient background.

$$EEC_{continental} = C_{continental} + \text{natural/pristine ambient background} \text{ (Eq-9)}$$

---

<sup>1</sup> Eg,, 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<sup>2</sup> and 20 million inhabitants, located in the margin of Western Europe.

The  $EEC_{\text{regional}}$  is calculated from

$$EEC_{\text{regional}} = C_{\text{regional}} + EEC_{\text{continental}} \quad (\text{Eq-10}).$$

The  $C_{\text{regional}}$  is the metal concentration at the regional scale that is calculated, using a multi-media fate model, from the anthropogenic metal emissions by man.

Calculation of the  $EEC_{\text{regional}}$  from metals emissions is usually achieved by considering a general standard region that is typically represented by a representative, usually densely populated, area. In the EU, such area is defined as an area of 200 x 200 km<sup>2</sup> and 20 million inhabitants, located in the margin of Western Europe with well-defined model parameters such as area fraction of water/soil, depth of water/sediment, residence time of air/water.

### **3.2.5 Calculation of local emissions from wide dispersive uses**

Since the 1990s, the contribution of industrial discharges to the overall metal load discharged by Sewage Treatment Plants (STP) has decreased significantly due to the fact that more and more industries were being disconnected from the municipal STP network in favour of implementing company-owned water treatment systems. However, the overall diffuse emissions of metal compounds from domestic and urban sources have become increasingly important over time as a result of the growth of the general population in urban settings and the increased use of metal compounds in consumer applications (CBS 2011). The wide dispersive use of a metal can thus entail an increase in metal of a local municipal STP that can be considered as a point source release. This observation has triggered some chemical agencies to require the development and modelling of a specific local STP scenario for those substances with a wide dispersive use pattern (ECHA 2012).

Example of the methodology used in the EU:

The proposed methodology is starting from the total registrant's tonnage at EU level for an identified use. A fraction of this tonnage is then assumed to be entering a default municipal STP of a typical town of 10,000 inhabitants. On top of this, by default a safety factor of 4 is applied to take into account geographical or temporal peaks in the use and the release of a substance (for example, the use of metals in sunscreen). This calculation is repeated for each



identified wide dispersal use of the substance and because all these releases will by default enter into the same sewage system, combined risk is considered.

Applying this approach for high-volume chemicals like metals will most often overestimate emissions due to the overly conservative approach taken. For example, the extrapolation factor used to translate from an overall EU tonnage to a region is still based on conditions when the EU consisted only of 15 member states (EU15). In the meantime, the EU tonnage represents 27 member states (EU 27). Also, many consumer applications like everyday cosmetics (shampoos) do not show geographical or temporal peaks that would justify the use of an additional safety factor.

The use of measured data instead of modelling could be a more appropriate way to avoid some of the uncertainties associated with the modelling approach. In order to demonstrate safe use, an approach using measured data is proposed. The risk characterisation for the STP, aquatic and sediment compartments are all directly (STP) or indirectly (aquatic and sediment) based on the effluent concentration of a STP. Measured effluent concentrations are hence the most appropriate parameters to collect. Measured effluent concentrations will take into account the true dimensions of an STP and cover all possible consumer and professional sources discharging to a STP. Any additional measures that might have been taken for STPs receiving larger volumes of metals are also taken into account. Indirect STP parameters such as influent concentrations, sludge concentrations or removal percentages can eventually be converted to effluent concentrations but would decrease the overall quality of the risk characterisation. Ideally, information is available for different seasons (temporal peaks) and different regions (geographical peaks), but to avoid those peaks, a large data set from a particular region would skew the distribution. The data should be weighted per region when percentiles are derived. To be conservative but still exclude any remaining industrial sources, the 90<sup>th</sup> percentile of the data set should be the starting point for modelling exposure concentrations in the STP, aquatic and sediment compartments.

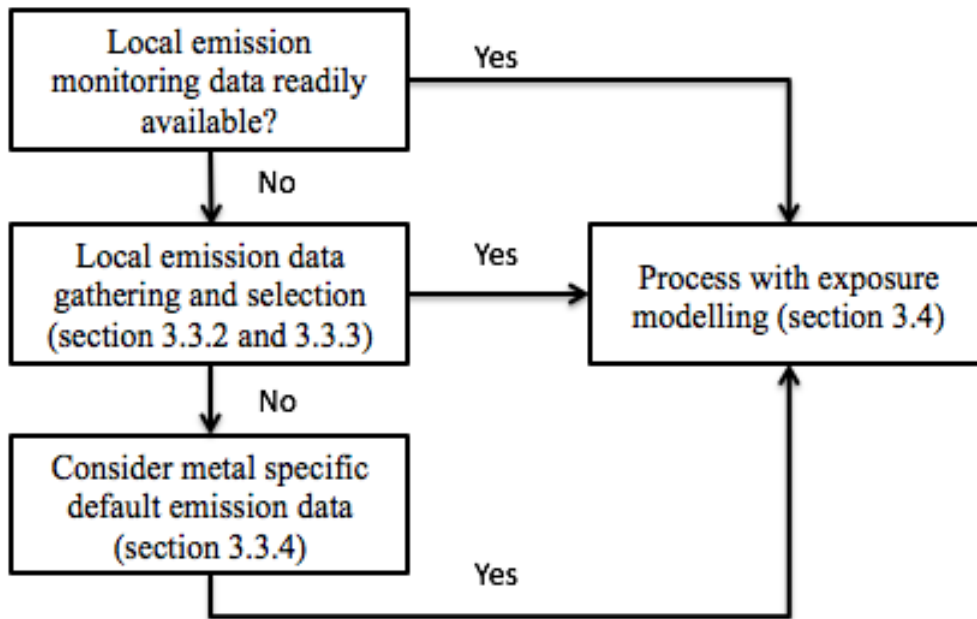
### **3.3 LOCAL EMISSION INVENTORY**

#### **3.3.1 General**

In analogy with the diffuse source emission inventory, emission data have to be collected on a site-specific (local) scale for companies that mine, produce, refine or use the metal/metal compounds in their industrial processes (ie, downstream users) (Section 3.3.2). Special attention points here are the representativeness of the release factors in 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 (Section 3.3.3).

In the absence of measured emissions/releases of a specific substance, an exposure assessor would rely on default release factors as proposed in the literature or guidance documents. For example, the OECD Emission Scenario Documents (ESD) are international documents that describe the sources, production processes, pathways, and use patterns of a chemical, ideally for the entire life-cycle, with the aim of quantifying the emissions (or releases) into water, air, soil and/or solid waste. In general, OECD (2000) prefers “hard” data, based on measurements, and statistically derived values. Often, the best available values are those based on the experience of experts working in the area. The concept of ESD has been widely used in national and regional contexts (OECDa 2013). Also, the US EPA has developed a number of generic scenarios to be used as default release scenarios in risk assessment (OECDb 2013). The European Chemicals Agency (ECHA) has introduced the environmental release categories (ERCs) to standardise the description of environmental emissions for different manufacture and use processes under REACH Regulation (EC) 1907/2006 (EU 2006; ECHA 2012) Chapter R.16 on Environmental Exposure Estimation). Default worst-case release factors to the environmental compartments water, air and soil are provided for each ERC, enabling first-tier emission estimations for different steps of the lifecycle. In response to the conservatism included in these default release factors, a significant number of sector groups of the chemical industry and their downstream user industries in the EU developed the so-called Specific Environmental Release Categories (SPERCs) (Sättler et al 2012). SPERCs are intended to be used as refinement of default release factors, as an advanced tier instrument in environmental safety assessment, increasing realism and accuracy of the resulting environmental emissions, and exposure estimates. The metals industry developed realistic environmental release factors for metals and metal compounds (Section 3.3.4). Because it can be expected that emissions are technology-driven, the EU SPERCs may be transferred to other regions in the world if technology and maintenance of equipment are comparable.



**Figure 5:** Tiered approach for assessing local emissions

### **3.3.2 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 (ie, 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:

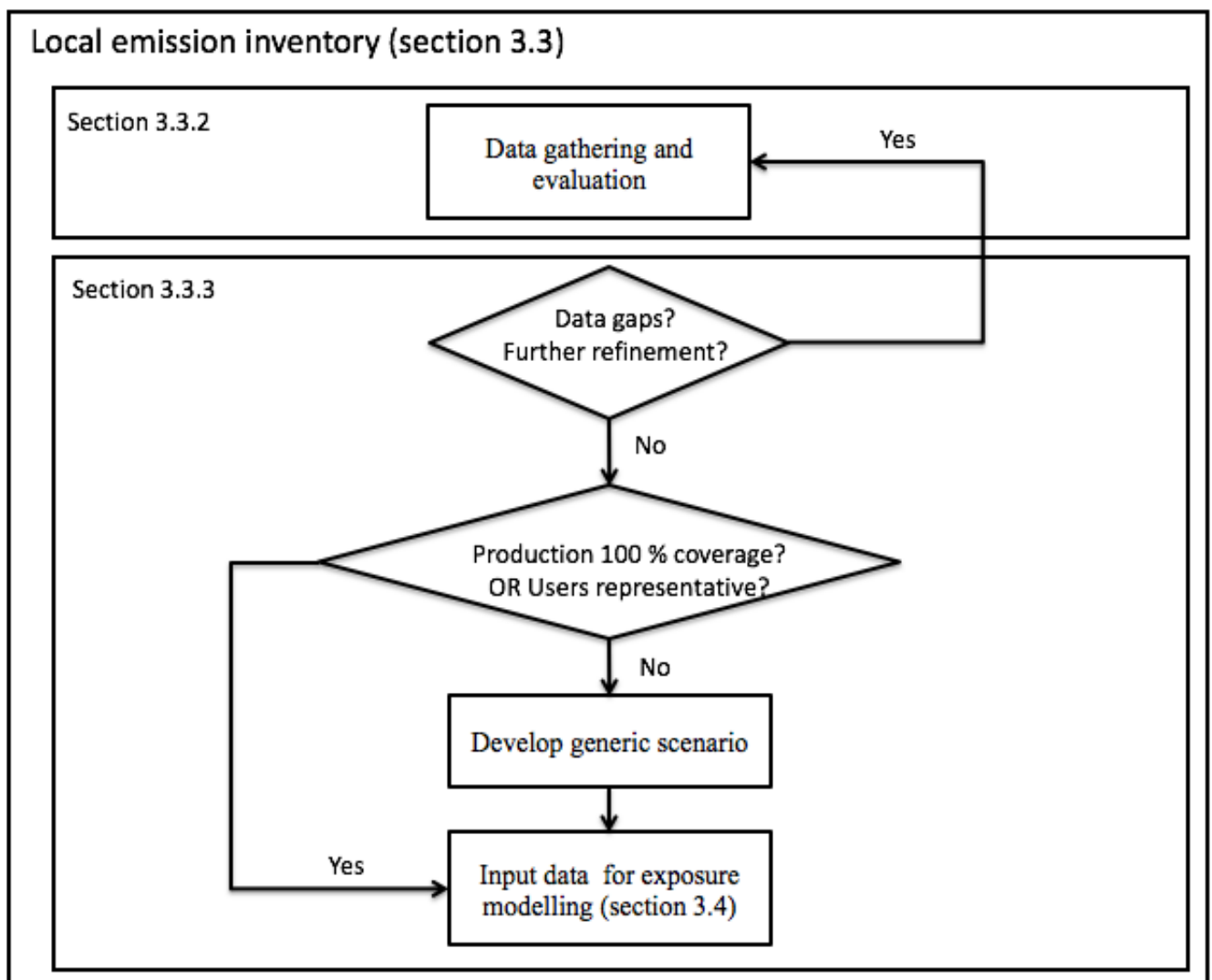
- Production/use data: tonnage, number of production days;
- Environmental exposure data;
- Conditions of use: operational conditions (eg, dry/wet process, process losses, etc...) and risk management measures (eg, on-site treatment with efficiencies,...)
- Emissions to all environmental compartments (kg/y), emission factors (g/t);
- Flow rate of the receiving water (or better dilution factor<sup>1</sup>) for all water discharges (m<sup>3</sup>/s);

<sup>2</sup> For example, a dispersion model such as CHEMSIM can be useful.

- Is sludge used on agricultural land, put into a landfill, or other route of disposal (tonnes/y/use);
- Effluent concentration ( $\mu\text{g/L}$ , on daily basis).

### 3.3.3 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 summarise data gaps. This data gap analysis should give insight on what additional local exposure data needs to be additionally compiled by industry (Figure 6).

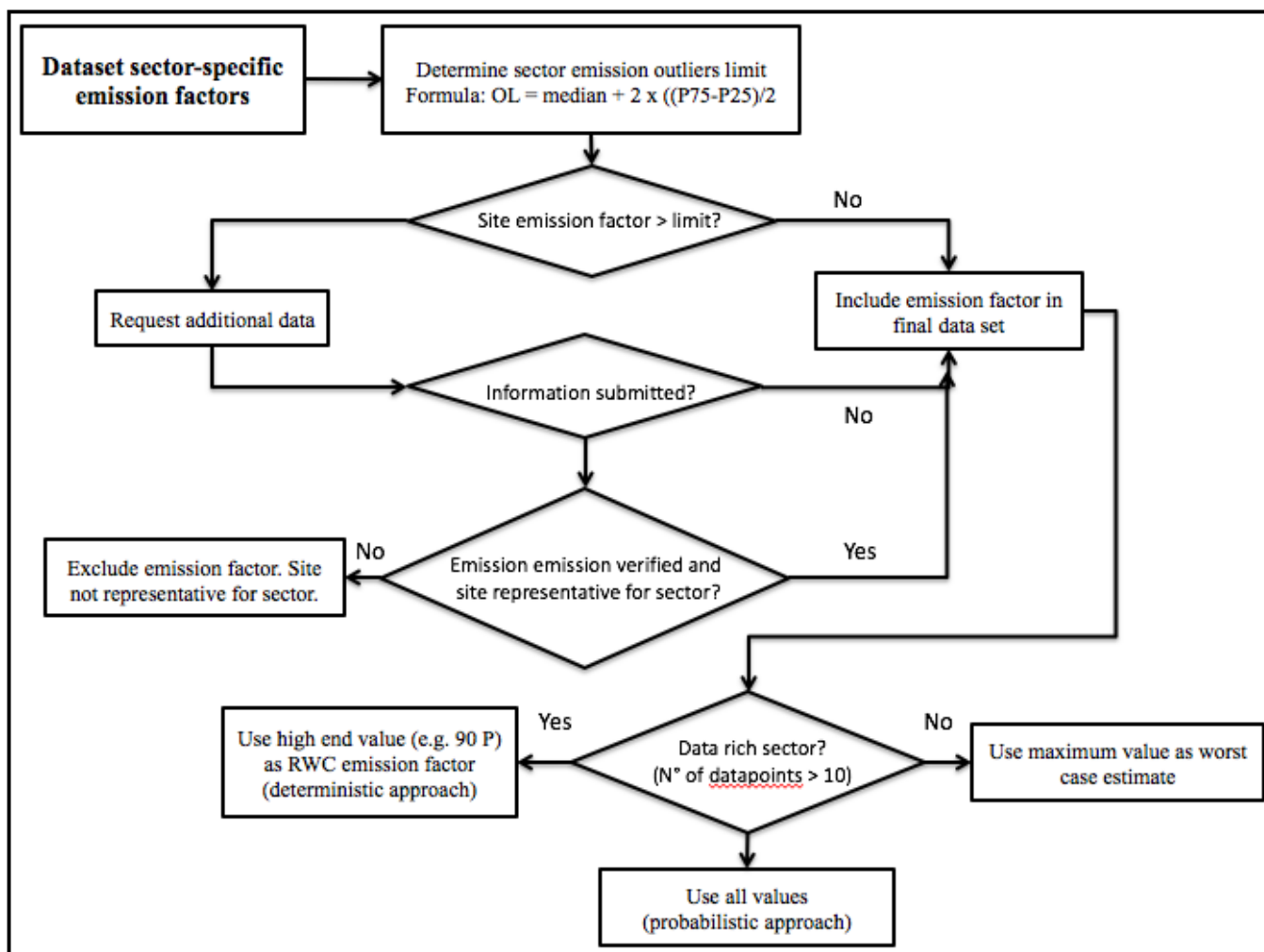


**Figure 6:** Overview of local emission inventory

\* For one representative country in case of many downstream users

## Selection emission factor

Reliable and representative emission factors can be extracted from the collected site-specific information<sup>3</sup> (Figure 7).



**Figure 7:** 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 data set. For each site emission factor, it should be verified whether the specific emission

<sup>3</sup> Next to sector-specific information made available by industry, regulatory sector documents -eg, IPPC (Integrated Pollution Prevention and Control) Reference Documents for different industry sectors ie, BREFs-(define BREF) 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; ie, companies that follow BAT (Best Available Techniques) requirements. For non-compliant companies, industry information should be provided in order to estimate emission factors.

factor exceeds the outlier limit value. If this is the case, a request for additional specific emission/exposure data (ie, production tonnage, emissions, detailed process activities, emission reduction measures) should be directed to the 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 data set. 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 data set.

From the 'reliable and representative emission factor data set'--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 datapoints (emission factors) available is sufficiently large (>10); a high-end value (eg 90<sup>th</sup> percentile) of the data set is proposed as a reasonable worst-case emission factor for the sector (deterministic approach) or all data can be used in a probabilistic assessment. In the other case—number of data points <10--the maximum emission factor is used. Alternatively, multiple statistics (eg, medium value and high end value (eg, 90th percentile)) can be derived for use in probabilistic assessment or uncertainty/sensitivity analysis.

#### *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) as well as similarity of conditions of use 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, conditions of use, 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 (eg, 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 is recommended if risks are shown from the worst-case scenario.

#### ***3.3.4 Realistic environmental release factors for metals and metal compounds***

Although developed in the EU, this approach can be used also in other regions world wide, and in other chemical management systems addressing metals, especially when similar technology and conditions of use are applicable. A database consisting of more than 1,300 recent (1993-2010) for site-specific measured release factors to air and water of 18 different metals from various EU Member States was compiled and used to calculate average and reasonable worst-case release factors for multiple metal manufacture and industrial use processes. The parameters influencing releases to water were found to depend predominantly on life-cycle step (manufacture/use), the sector, and/or the solid/water partition coefficient for suspended matter ( $K_d$ ). The release factors can be used as advanced tiered instruments in environmental safety assessments, increasing the realism of the estimates while still keeping a sufficient level of conservatism. The approach is described in Verdonck et al (2014).

For each life-cycle step, average (50th percentile) and reasonable worst-case empirical 90th percentile of the release factors to air and to wastewater of all metals were calculated. The resulting values can be found in Table 4. For the release factors to wastewater, further differentiation was made. The release to water and air depends on life-cycle step/use and sector in some cases and solid/water partition coefficients for suspended matter in other cases.

### Example use of release factors to water and air for an alloy producer

An alloy producer, located in the EU, formulates 100 tonnes/year of Zn with other metals into a special alloy preparation. There is no Zn release information available to air and water. The release factors (90th percentiles) contained in the Table below can be considered. First, the relevant category is formulation in alloys. Secondly, the reasonable worst-case release factor (based on the 90th percentile) is selected because the release estimates will be used in a risk assessment context. Thirdly, the available process conditions and on-site risk management measures of wet electrostatic precipitator (to treat air releases) and the chemical precipitator (to treat water releases) have equivalent removal efficiencies and correspond to the conditions of use of the release factors derived in Table 2. Fourth, even though the release factors of the Table below are equally applicable to any metal, the presence of Zn data in the underlying release factor database gives additional support. Therefore, the release factors of 0.005% to air and 0.005% to water can be used to estimate the releases of this site: 5 kg/year and 5 kg/year to air and water, respectively.



Life-cycle step / category		Sub-category	Typical (50 <sup>th</sup> percentile) release factor (after on-site treatment)		Reasonable worst-case (90 <sup>th</sup> percentile) release factor (after on-site treatment)	
			Water	Air	Water	Air
Manufacture and recycling of	massive metal and metal powder	Kd: 10,000 - 25,000 L/kg	0.01%	0.002%	0.03%	0.03%
		Kd: 25,000 - 60,000 L/kg	0.002%		0.01%	
		Kd: 60,000 - 190,000 L/kg	0.0005%		0.005%	
		Kd: 190,000 - 400,000 L/kg	0.0001%		0.002%	
Manufacture of	metal compounds	Kd: 1,000 - 10,000 L/kg	0.02%	0.003%	0.2%	0.03%
		Kd: 10,000 - 25,000 L/kg	0.02%		0.2%	
		Kd: 25,000 - 60,000 L/kg	0.005%		0.04%	
		Kd: 60,000 - 100,000 L/kg	0.002%		0.01%	
		Kd: 100,000 - 190,000 L/kg	0.0007%		0.005%	
		Kd: 190,000 - 250,000 L/kg	0.0003%		0.002%	
Formulation	in alloys		0.0002%	0.0001%	0.005%	0.005%
Industrial use: shaping	massive metal		0.00001%	0.0001%	0.02%	0.003%
Industrial use in batteries	metals (compounds)		0.0001%	0.0006%	0.003%	0.003%
Industrial use in metallic coating	metal (compounds)		0.02%	0%	0.5%	0.2%
Formulation of	metal compounds	Plastics and rubber	0%	0%	0.0002%	0.005%
		Paints and coatings	0.001%	0.0005%	0.01%	0.005%
		Other sectors	0.1%*	0.00002%	2%*	0.01%
Industrial use of	metal compounds	Plastics and rubber	0%	0%	0.001%	0.001%
		Textile	0.002%	0%	0.007%	0.001%
		Glass	0.007%*	0.004%*	0.5%*	2%*

\* Before on-site RMM/STP

Kd: Partitioning coefficient for suspended solids

Table 4: Overview default release estimates for different life cycle steps

### 3.4 DERIVATION OF THE ENVIRONMENTAL EXPOSURE CONCENTRATION USING EXPOSURE MODELS

Environmental concentrations of a substance in the environment can be calculated using multi-media fate models. However, most of these multi-media models have been developed mainly from the experience gained on individual organic substances (for example, FOCUS models (FOCUS 1997 and 2001; EUSES 1996; etc). This implies (“means”? “implies” is waffling, uncertain) that the methodology/assumptions used cannot always be applied directly to metals without any kind of modifications. For example, gas-plume models ignore the fact that most metals present in the atmosphere are bound to aerosols and some of the fate parameters included in FOCUS/EUSES (such as log  $K_{ow}$ ) are not fit for purpose. A more refined analysis that includes processes that affect fate and potential exposure of organisms (bioavailability), such as inter-compartment transfer, complexation adsorption, and precipitation reactions, is often required for metals

Although it is recognised that metal concentrations in the environment are subject to variation due to topographical and climatological regional and local differences, the modelled PEC calculations using multi-media fate models such as EUSES, Unit World Model, TRIM.FaTE<sup>4</sup> etc 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. Generic 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 (eg., 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.

Such a refined fate and transport model for metals is the “TICKET Unit World” model, developed in the US and Canada and which 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 (eg, the Biotic Ligand Model) and sediment (eg, Acid Volatile Sulfides and Simultaneously Extractable Metal) ((Diamond et al 1990; Bhavsar et al 2004; Harvey et al 2007; Farley et al 2011).

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<sup>4</sup> Multi-media air deposition models [http://www.epa.gov/ttn/fera/trim\\_fate.html](http://www.epa.gov/ttn/fera/trim_fate.html) .

Specific guidance and background on how to run the different models in order to derive modelled EEC concentrations can be found in the original documents dealing with the subject (TGD 2003; EUSES 1996). If these models are to be used, their parameterization should be properly done with regard to the main metal-specific attention points that should be taken into account when conducting the modelling. These aspects are discussed in more detail below:

### **3.4.1 Adsorption/desorption processes**

For organic non-ionic chemicals, adsorption/desorption processes are often based on octanol-water partition coefficients ( $K_{OW}$ ) and the assumption that all adsorption is related to the organic matter or lipid matter (fat).  $K_{OW}$ s cannot be used to describe the partitioning of inorganic metal compounds in the different environmental compartments for the following reasons:

- The  $K_{ow}$  and  $K_{oc}$  concept is not applicable for inorganic compounds such as metals and most of the metal compounds are hydrophilic polar entities. The hydrocarbon phase of octanol is thermodynamically very unfavourable towards polar compounds (similar to the core of biomembrane lipid bilayers).
- Sorption is not controlled only by organic matter, but also by other inorganic solid phase constituents like clay minerals and oxides.
- The distribution of metals over the solid and liquid phase is not solely controlled by pure adsorption/desorption mechanisms. Other processes like precipitation or encapsulation in the mineral fraction also play a role.
- Environmental conditions (pH, redox conditions, temperature, ionic strength) and the composition of the liquid and solid phase have a strong effect on the  $K_d$  of inorganic substances. As a result, a wide range of  $K_d$  values have been reported.

Consequently, the distribution of metals between the aqueous phase and soil/sediment/suspended matter should be preferentially described on the basis of measured soil/water, sediment/water, and suspended matter/water equilibrium distribution coefficients ( $K_d$ ; also called partition coefficient,  $K_p$ ).

Most  $K_d$  values are expressed in terms of total metal concentrations present in the solid phase (mg/kg, determined by eg, aqua regia extraction) and total dissolved concentrations in the aquatic phase (mg/L, Eq-11).

$$K_d = \frac{\text{Total concentration in the solid phase}}{\text{Dissolved concentration in the aqueous phase}} \quad (\text{Eq-11}).$$

It should, however, be acknowledged that Kd values cannot 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), ionic strength, redox conditions, or the composition of the liquid phase (DOC or dissolved organic carbon concentration, other complexing ions) and solid phase [organic matter, clay, oxides, sulphides (only for sediment)]. Consequently, Kd's may differ from site to site and can change over time. This explains the wide range in Kd values observed for metals. Table 5 gives an overview of Kd values for several metals (ECHA 2007).

Table 5: Overview of metal partition coefficients for suspended matter, sediment (freshwater environment) and soil (median, 10P, 90P) (L/kg) (ECHA 2008)

Metal	Kp suspended matter (L/kg)				Kp sediment (L/kg)			
	N° of data	50P	10P	90P	N° of data	50P	10P	90P
Cadmium (Cd)	6	130,00 0 Log Kp=5.1 1	Min: 17,000 Log Kp=4.2 3	Max: 224,00 0 Log Kp=5.3 5	-	Cfr. Kpsusp . matter	Cfr. Kpsusp . matter	Cfr. Kpsusp. matter
Copper (Cu)	24	30,246 Log Kp=4.4 8	5,752 Log Kp=3.7 6	194,22 8 Log Kp=5.2 9	11	24,409 Log Kp=4.3 9	8,934 Log Kp=3.9 5	99,961 Log Kp=5.0
Lead (Pb)	19	295,12 1 Log Kp=5.4 7	50,119 Log Kp=4.7 0	1,698, 244 Log Kp=6.2 3	5	154,88 2 Log Kp=5.1 9	35,481 Log Kp=4.5 5	707,946 Log Kp=5.8 5
Nickel (Ni)	39	26,303 Log Kp=4.4 2	5,754 Log Kp=3.7 6	117,49 0 Log Kp=5.0 7	17	7,079 Log Kp=3.8 5	2,138 Log Kp=3.3 3	16,982 Log Kp=4.2 3

Zinc (Zn)	14	110,00 0 Log Kp=5.0 4	Min: 64,000 Log Kp=4.8 1	Max: 176,00 0 Log Kp=5.2 5	-	73,000* Log Kp=4.8 6	42,667* Log Kp=4.6 3	117,333 * Log Kp=5.0 7
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\* Kp sediment derived as Kp suspended matter / 1.5

Metal	N° of data	Kpsoil L/kg		
		50P	10P	90P
Cadmium (Cd)		280 Log Kp=2.45	ND	ND
Copper (Cu)	70 studies	2,120 Log Kp=3.33	Min: 6.8 Log Kp=0.83	Max: 82,850 Log Kp=4.92
Lead (Pb)	60	6,400 Log Kp=3.81	600 Log Kp=2.78	43,000 Log Kp=4.63
Nickel (Ni)	46	631 Log Kp=2.86	Min: 9 Log Kp=0.95	Max: 3,547 Log Kp=3.55
Zinc (Zn)	11	158 Log Kp=2.2	ND	ND

### Selection of Kd values

The choice of the Kd values has important consequences for the outcome of the exposure and risk assessment. Small Kd values will predict a larger EEC and higher risk in water, and large Kd values will lead to a large PEC in soils and sediments. 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.

Because 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. In order to judge quality and usefulness, further information must be available on:

- Analytics:
  - extraction of the metal content of the solid phase (eg, with aqua regia)
  - sampling techniques of the solution phase (extraction of pore water for soil and sediment, filtration, etc)
  - analytical techniques

- Key drivers determining the Kd value:
  - composition of the solid phase (organic matter, clay, AVS (sediments))
  - pH
  - equilibration period after addition of metals
  - metal loading

Preference should always be given to Kd values based on paired measured data in the solid and solution phase and 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 (2009). If no coupled data on metal concentrations in corresponding solid and solution phases are available, an alternative approach that can be used as a screening method 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. The combination of low-end and high-end values can be used to estimate a realistic range of variation between Kd-values. This approach has the disadvantage that the values are not coupled.

When sufficient distribution coefficients (more than 4 data points) 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/are selected for further assessment. From these distributions, it is possible to determine the probability that a Kd-value measure will exceed a certain value and a realistic range of Kd values can be estimated based on the 10<sup>th</sup> and 90<sup>th</sup> percentiles.

When only few distribution coefficients are available ( $\leq 4$  data points), only summary statistics (average, median, minimum and maximum) are calculated. The geometric mean Kd-value should be used in the exposure assessment. In case percentiles cannot be calculated, the minimum and the maximum values are taken forward to the uncertainty analysis.

For the risk assessment at local scale, the Kd values should, as far as possible, be representative of 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 soil properties into account (pH, organic matter content, clay content, metal loading). For the aquatic compartment, Kd values should be derived under similar water quality parameters (pH, ionic strength, concentration of adsorbing phase) as those prevailing in the region of interest.

For sediments, partition coefficients are redox dependent. This can be taken into account using different redox-specific partition coefficients. These partition coefficients analysed in oxygen-rich and anoxic (N<sub>2</sub>-atmosphere) sediments can be measured or can sometimes be found also in the literature. The choice of a representative realistic worst-case K<sub>d</sub> will have to be made case by case. Some metals form insoluble sulphide complexes in anoxic systems yielding higher K<sub>d</sub> values. Other metals shift in redox state (Cr<sup>6+</sup>:Cr<sup>3+</sup>) with different sorption capacities.

Besides measuring site-specific K<sub>d</sub> values, those may also be indirectly estimated using field-validated models.

- *Models based on an established empirical relationship between measured K<sub>d</sub> values and soil properties.* Such regression models usually take the form of a linear relation between log K<sub>d</sub> and soil properties or a Freundlich type equation (eg, Sauvé et al 2000 and Degryse et al 2009). These models are simplifications of the complex soil system, and should not be extrapolated beyond the range of soil properties for which they were originally developed. Regression models should be based on data sets of high quality that cover a large range of soil properties. From a practical point of view, it is preferable that only routinely measured soil properties (eg, pH, % organic matter) are included in the model. An advantage of regression models is that these models may be calibrated on a large number of real soils.
- *Field-validated surface complexation models.* Surface complexation models such as WHAM/SCAMP (Tipping 1994 & 1998; Lofts and Tipping 1998) consider the soil or sediment as a set of independent reactive surfaces, and combine several models to describe sorption on (solid and dissolved) organic matter, oxides, and clay. These models are conceptually more attractive compared to the empirical regressions. However, extensive input information is needed, and assumptions about the relative reactivity of surfaces compared with model constituents (eg, % active organic matter) are required. Because these models are derived for pure model constituents under laboratory conditions, an essential condition for their application is their validation for real soil/sediments systems. **The use of modelled K<sub>d</sub> values can therefore, at present, be used for estimation purposes only. Further research in this area may, however, allow appropriate use of modelled K<sub>d</sub> values for future risk assessments.**

#### Uncertainty analysis

A  $K_d$  value for metals is not one single value and a wide range of  $K_d$  values is often observed. Using a representative range of  $K_d$  values will help to highlight if the adsorption coefficient is an important factor for the environmental behaviour of the substance and to evaluate if the adsorption coefficient will not affect the outcome of the exposure and risk assessment. Typically, uncertainty over the use of a particular value for a specific assessment is investigated by varying the value between high and low extremes – in a kind of sensitivity analysis. If a  $K_d$  distribution is available, a low-end value (eg, 10<sup>th</sup> percentile) and a high-end value (eg, 90<sup>th</sup> percentile) are selected for the sensitivity analysis. In the case of a limited data set, the minimum and maximum must be used as lower and upper bounds as worst-case scenarios. The representativity of the data available for the sites under assessment must also be discussed. The results of the uncertainty analysis can be used to check the robustness of the risk evaluation and could trigger further refinements when needed.

### **3.4.2 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  $K_d$  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.

### **3.4.3 Volatilization**

For a few metals and metal compounds (eg, mercury-compounds,  $AsH_3$  and stibnite), 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 some exposure models (eg, EUSES) 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 eg,  $10E^{-20}$  Pa. If a valid measured value is available, this value can be used.

#### **3.4.4 Degradability**

Biotic degradation rates should be set to zero for metals as metals do not biodegrade. However, the lack of degradation of metal ions does not exclude that metals can be removed from the water column towards the sediment compartment, change speciation, and stored there in a less or non-bioavailable form.

A distinction can be made between 3 groups of metals in respect of the assessment of the degradability principle:

1. Metals that readily methylate, such as Hg, Se and others.
2. Metals that rapidly hydrolyse under a range of relevant aquatic conditions and that form different non-toxic chemical forms that precipitate in the water column, such as Fe, Sb, Mo, Al, Sn, Cr and others. Hydrolysis and precipitation to form different species is a very significant removal process from the aquatic system.
3. Metals that partition to suspended matter and precipitate to sediment and bind to ligands such as (mainly) AVS. This group includes metals such as Ag, Cu, Zn, Ni, Co, Pb and others. The rate and “irreversibility” of the process (ie, binding to a non-bioavailable form under a range of environmental conditions) are critical in determining the toxic substance removal from the aquatic compartment.

These processes have recently been built into the TICKET<sup>5</sup> Unit World Model (UWM) (Farley et al 2011, see section 3.4.5). The TICKET-UWM was used to assess the “degradation” of soluble metal salts in a generalized aquatic environment resulting from metal removal from the water column and sequestration in sediment. To estimate the rate and fate of the “degradability” of metals released to the aquatic column, two processes were modelled with the TICKET UWM:

- A) removal of soluble metal salts from the water column through speciation transformations and sedimentation of particulate metal, and
- B) metal speciation transformations and remobilization potential in sediments.

The removal of metals from the water column depends on the extent to which they bind to suspended particles (ie, particle-reactivity, expressed as  $K_d$  for suspended matter). Elimination

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<sup>5</sup> Tableau Input Coupled Kinetic Equilibrium Transport-Unit World Model.

from the water column is fast and extensive for highly particle-reactive metals (high  $K_d$ ), while less particle-reactive metals (with low  $K_d$ ) tend to remain in the water column for longer periods. For copper, zinc, lead, cobalt, cadmium, and silver, model-predicted metal precipitation as metal sulphides maintained a diffusive flux directed into the sediment when sufficient AVS was present to bind all sediment metal. This supports field data showing that remobilization (flux) to the water column contributes to a very small percentage of what is in the water column. On the other hand, metals that will not bind to AVS (or only bind under a restricted set of conditions), will not be rapidly removed from the water column unless other insoluble species are formed.

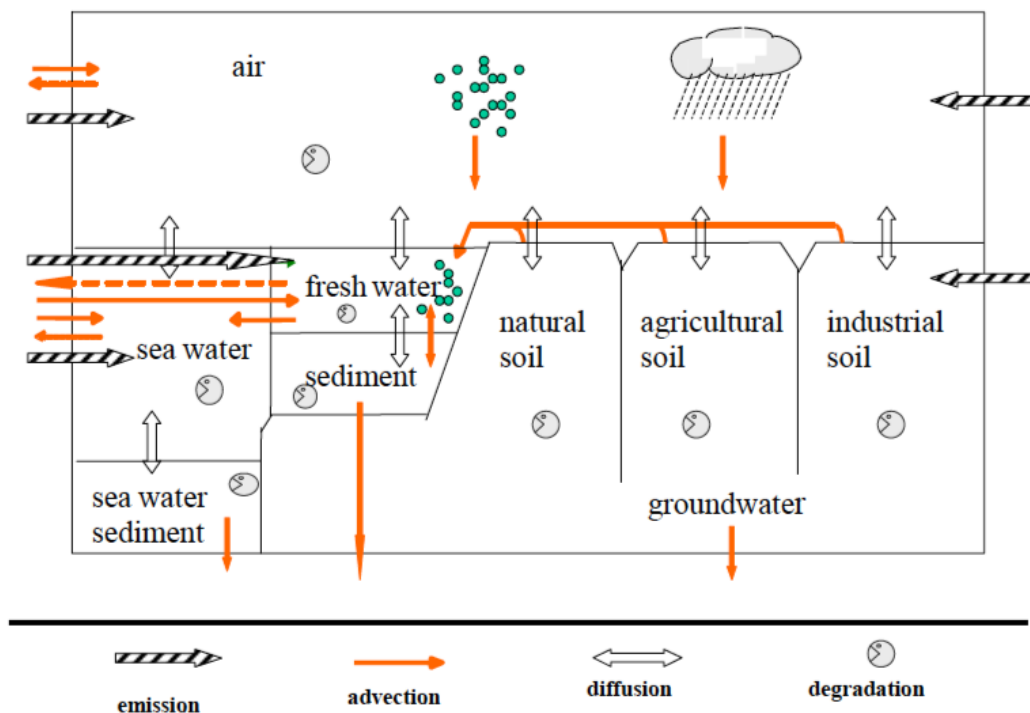
The behaviour of a substance in a wastewater treatment plant can be modelled using, for example, the SimpleTreat module of EUSES (European Union System for Evaluation of Substances). Irrespective of the model used to assess the partitioning between the sludge phase and water compartment, measured  $K_d$  values should be used to explain the removal of the metal from the water column in a wastewater treatment. 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.

#### **3.4.5 Multi-media fate models: estimating fate and distribution between compartments**

Multi-media fate models (eg, EUSES 2.0, TICKET-UWM) can be used for calculating the Predicted Environmental Concentrations (PEC) at the local, regional and continental scale for different environmental compartments, .ie, air, water, sediment and soil.

EUSES is the multi-media fate model used as a decision-support instrument in the European REACH and Biocides Regulations. It is a typical Mackay level 3-based model to predict the steady-state distribution of substances between the water, sediment, soil and air compartments. The model, which enables the user to calculate the risk for man and environment, has been developed for organic substances and is therefore less fit to predict the fate and exposure of metals.

All releases to each environmental compartment for each use, assumed to constitute a constant and continuous flux, are summed and averaged over the year, and steady-state concentrations in the environmental compartments are calculated. **Figure 7** gives a general overview of the distribution processes in the regional model as used in the EU.



**Figure 7:** Schematic representation of the fate and transport processes included in the EUSES model for calculating the regional PECs

As this model is developed for organic substances, it should be noted that some fate parameters of the model should be adapted to reflect metal-specific properties. As described above, for modelling the behaviour of metals in the environment, the octanol-water partition coefficient ( $K_{ow}$ ) and the solubility are not appropriate. For metals, all individual compounds are assumed to transform into the ionic species and therefore the solubility is set to maximum value of  $1 \times 10^5$  mg/L. To replace the  $K_{ow}$ , it is recommended to use measured solids-water partition coefficients for sediment, suspended matter and soil. Volatilisation of metals is usually ignored, therefore the Henry Law-coefficient should be minimised. The vapour pressure is set to  $10^{-10}$  Pa to ensure that the metal fraction associated to aerosols was equal to one. Biotic and abiotic degradation rates were considered not to be relevant and have been minimised.

The metal-specific features are nevertheless very limited in the current EUSES 2.1.2 model. Indeed, for metal risk assessment purposes, the model can only consider the selection of metal-specific partition coefficients ( $K_p$ ) instead of the octanol-water partition coefficient in the model. The distribution of metals over the solid and liquid phase is, however, not only controlled by pure adsorption/desorption mechanisms, but other processes like precipitation or encapsulation in the mineral fraction also play a role. Environmental conditions (pH, redox conditions, temperature, ionic strength) and the composition of the liquid and solid phase have

a strong effect on the  $K_p$  of inorganic substances. As a result, a wide range of  $K_p$  values have been reported and it is not always clear which value to select in a generic assessment with the EUSES model.

The TICKET-UWM is a similar Mackay-based screening model for water and sediment, but is capable of assessing the long-term fate and effects of metals in the environment by explicitly considering the effects of chemical speciation on metal partitioning, transport and bioavailability in the lake water column and underlying sediments. The TICKET-UWM is capable of conducting both steady-state calculations with a continuous load of metal(loid), as well as time-variable simulations to model the response of a standard water column to a continuous or instantaneous load of a metal(loid). In the TICKET-UWM model, the following additional features for metals are specifically included (Figure 8):

- dissolved and particulate phase transport between the overlying water and sediment;
- metal binding to inorganic ligands, dissolved organic carbon (DOC) and particulate organic carbon (POC) (using WHAM V, Tipping 1994), and hydrous ferric oxide (HFO) and hydrous manganese oxide (HMO);
- metal binding to biological receptors using information from the Biotic Ligand Model;
- metal precipitation as (hydr)oxides, carbonates and sulphides, using information from MINEQL+ software;
- dissolution kinetics for metal powders, massives, etc;
- average annual cycling of organic matter and sulphide production; and
- simplified hydrous ferric oxide (HFO) and hydrous manganese oxide (HMO) interactions with metal ion.

These features allow better prediction of the fate and behaviour of metals depending on the characteristics of the water column. The following metals are currently included in the TICKET-UWM model: Cd, Co, Cu, Ni, Pb, Zn, Al, Ba, Ag, As<sup>3+</sup>, As<sup>5+</sup>, Cr<sup>6+</sup>. The latest version of the TICKET-UWM software is available free of charge at <http://unitworldmodel.net>.

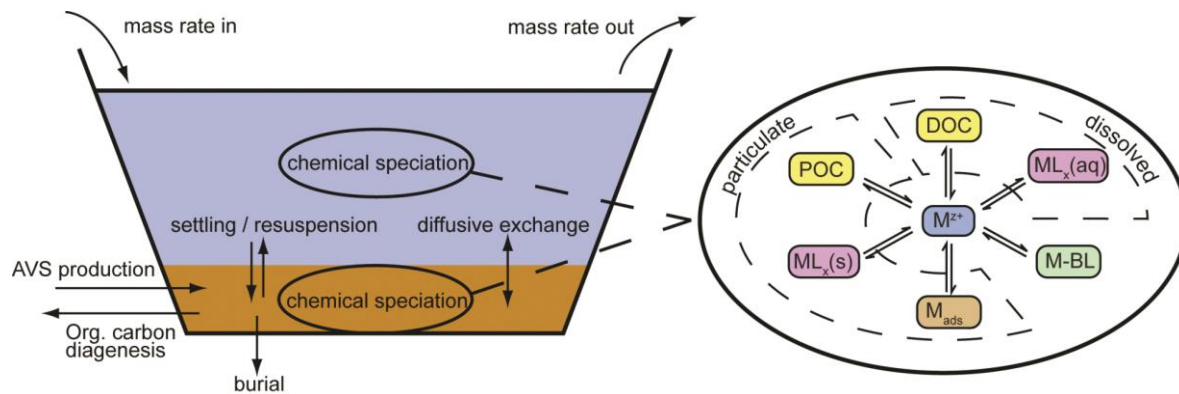
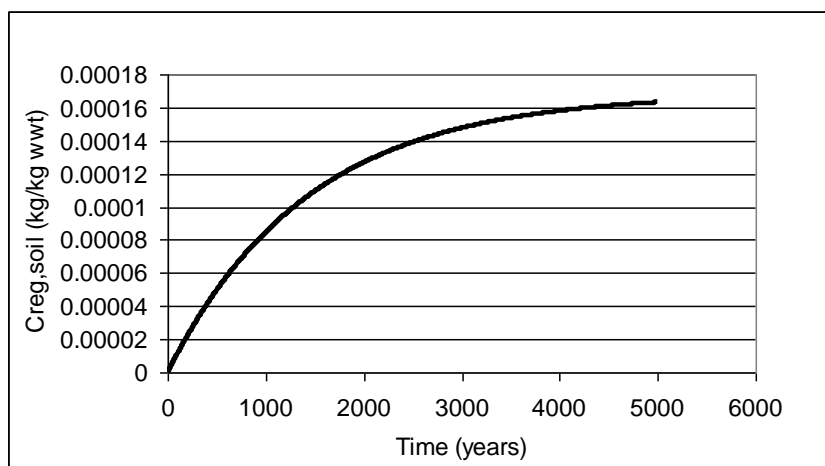


Figure 8: Conceptual model for the TICKET Unit World Model for Metals in Lakes (TICKET-UWM); where POC = particulate organic carbon, DOC = dissolved organic carbon, ML = metal ligands; M-BL = metal-biotic ligand

### 3.4.6. Steady state assumption

In many multi-media models, PEC values for every compartment on a regional/continental scale are calculated as steady-state concentrations (eg, EUSES). However, for metals, steady-state is typically only reached after several decades or even thousands of years (see example in Figure 9 where long-term mineralisation processes are not included in the model). 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 9:** Regional steady-state metal concentrations are typically reached after an unsurveyable time period (example calculation in multi-media model EUSES for lead, note: long-term mineralisation fate processes are not included in EUSES leading to an “accumulation” prediction)

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 factors are taken into account.

If possible, crop uptake can 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.

## **4. EXPOSURE ASSESSMENT USING MEASURED DATA**

### **4.1 Introduction**

When conducting a risk assessment for metals, quite often a wealth of monitoring data are available. 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 ambient metal concentrations. To avoid interference, they must therefore be excluded from monitoring data sets used in an ambient exposure assessment. The diffuse ambient concentration in a specific area includes both the natural background and the diffuse anthropogenic input. Natural background concentrations are spatially variable. More information on the background issue can be found in Annex 2.

In addition, the fraction of the metal present in the environment that is available for biological uptake depends on various biotic and abiotic parameters (section 4.4). Therefore, for risk assessment purposes of metals, it is recommended that, beside background and ambient metal concentrations, the distribution of parameters that determine metal bioavailability are also described and integrated in the exposure assessment (Oorts and Schoeters 2014).

## 4.2 Data Selection and Handling

Metal concentrations in the environment can be affected by a large number of parameters and processes: the natural background, stormwater events, release from 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 (eg, Cd, Pb, Zn, Cu, Ni). On the other hand, 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.

Some of the attention points given below are not restricted to metals only but simply present general guidance on how to use and select monitoring data, although metal specific points are highlighted when appropriate. General guidance on data selection and handling can also be found in the OECD guidance document for exposure assessment based on environmental monitoring (OECD 2013) and the reader is referred to this document for further details not covered in the present guidance.

The evaluation of the data should take into account the following points:

- Sample treatment and analysis of reported metal concentrations should be in line with international accepted Standard Guidelines (ISO, ASTM Standards, etc). Several analytical techniques are used in the literature to measure metal concentrations. Most

analytical techniques are quite precise (ie, able to generate a similar value when measurement of the sample is repeated), but have different accuracies (ie, 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.

- For the aquatic environment, metal concentrations can be reported as the total or dissolved fraction. The latter fraction is preferred for risk assessment because as a rule, water-quality standards for metals are expressed on a dissolved ion basis. It is the dissolved fraction that is also preferred in the modeling section of the exposure analysis, although both total and dissolved metal can be calculated. It is therefore important to ensure that reported monitoring data refer to the dissolved fraction. Sometimes it has added value to measure both dissolved and total because both may be significantly different for some metals.
- If no dissolved metal 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  $K_d$ . Due to variability of the parameters involved, this approach results in a higher level of uncertainty than the accurate measurement of the dissolved fraction as described above. Still, in many cases only total concentration is monitored. In such cases, the calculation of the dissolved fraction from the total concentration should be performed in any case, before the data are used for risk assessment. The dissolved concentration can be calculated from the total by using the partition coefficient between metal in water and suspended matter:  $[Me]_{diss} = [Me]_{total} / (1 + K_p * C_s)$ , where  $K_p$ : *water-suspended matter partition coefficient for metal*  $X C_s =$  *suspended matter concentration (for this general analysis, the TGD default value of 15 mg/L is used)*. The use of total metal concentration data for metal risk assessment should be avoided.
- Crompton (2015) pointed out that it is not possible at present to recommend a filtration procedure known to be suitable for all metals. In general, the use of membrane filters with a pore size of 0.45  $\mu m$  is considered to give a separation of practical utility. This pore size and type of filter has been chosen by the US EPA as the basis of its standard separation techniques, and similar filters have been recommended in a number of authoritative texts (Crompton 2015). Depending on the use and interpretation of the data, filtration through pore sizes other than 0.45  $\mu m$ , as well as using different type of filters (glass fiber filters), may be required. It should be taken into account, however, that an increase or decrease of the pore size can have a significant impact on the measured trace element concentrations. Filtration is preferably done on the



sampling site or as soon as possible after sampling. After filtration, filtered samples can be stabilized with nitric acid. **(Such stabilization should never be done before filtering the sample).**

- The trace level metal data may be significantly compromised due to contamination or adsorption during collection, preparation, storage and analysis. Therefore “clean” and “ultraclean” techniques for sampling and analysis are critical to have accurate data (US EPA 1994). It is emphasised that apart from the glassware used for sampling, other sampling materials eg, plastics, filters, rubber tubes and gloves can significantly alter the metal concentration in the samples. Salmela and Vuori (1979), for instance, reported on Cd contamination related to the use of yellow Eppendorf micropipettes. To check for overall contamination, sampling blanks (distilled water samples that go in parallel through the whole procedure) should regularly be included. Coupled data indicating a higher dissolved concentration than total concentration, are obviously the result of contamination and should be disregarded. In general, it may occur that in data sets where both the dissolved and total concentrations are reported, the reported dissolved concentration is higher than the total. In such cases, it should be investigated whether different water samples – possibly taken at a different time, were used for the analysis. If this is not the case, such data points should be excluded (see above) from the data analysis. The quality of the whole data set should be questioned and further investigated.
- The most reliable, relevant and most recent data (ie, 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 be considered with caution because they may reflect earlier situations and ignore recent developments in eg, emission control technology or use pattern of the substance. Older data can 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, however, 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, physico-

chemical 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 and can strongly vary in time.

- Because “dissolved” concentrations of metal in overlying water and porewater provide a more relevant exposure metric for risk assessments, the use of Passive Sampling Methods (PSMs) for metals have gained interest (Peijnenburg et al 2014). Examples of PSM are Diffuse Gradients in Thin films (DGT), diffusion samplers, Chemcatcher etc for overlying water sampling and DGT, porewater peepers, Diffuse equilibration in a thin film (DET), and Teflon® sheets for sediments. A correspondence between metal bioavailability and PSM-measured metal has been demonstrated for the water column. For sediments, the results are less persuasive. At the moment, it is unclear if this is due to the fact that PSMs are restricted to aqueous metals and thus can only indirectly account for the uptake of dietborne metals (eg, ingesting sediment particles).
- The sampling points within a data set for a specific area should not only represent this area in the most relevant way with regard to spatial (geographical) and temporal aspects, but should also reflect the typical environmental conditions (eg, 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.
- 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 a uniform distribution between zero and DL is assumed. These DL/2 values can then be included in the exposure distributions, and these ‘generic’ values are assumed to optimize the parametric fit through the complete data set.
- Care should also be taken that DLs are 1/10th below the PNEC or EQS in order to be of direct use for risk assessment purposes.
- 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 exposure summary statistic (eg, 90<sup>th</sup> percentile, 50<sup>th</sup> percentile, minimum, maximum) may be governed by the ‘uncertain’ value of DL/2 rather than by the measured metal concentrations obtained with a more sensitive analytical procedure. If the summary statistic is lower than the reported DL, the summary statistic will be a

“lower than” value. Some legislations limit the amount of censored data allowed (eg, EU Water Framework Directive allow 30% of censored values).

- 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.

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 statistical approaches (eg, proposal in ECHA (2012),  $\log_{10}(X_i) > \log_{10}(p_{.75}) + K(\log_{10}(p_{.75}) - \log_{10}(p_{.25}))$ ) with  $X_i$  being the concentration above which a measured concentration may be considered an outlier,  $p_i$  the value of the  $i^{\text{th}}$  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 (eg, 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 used for the chemical assessment of the diffuse ambient metal concentration. They can, however, be useful when seen from a historical perspective.

#### **4.3 Determination of Environmental Concentration Distribution (ECD) and Estimation Environmental Exposure Concentration (EEC) 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 characterisation instead of 10<sup>th</sup>, 50<sup>th</sup> or 90<sup>th</sup> percentiles. A deterministic framework will only derive an estimated Environmental Exposure Concentration (single EEC value) from the ECD that is constructed with monitoring data.

##### **4.3.1 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), and other factors that might be influencing downstream metal concentrations can also fluctuate.

#### ***4.3.2 Diffuse ambient concentration exposure assessment: dealing with spatial and temporal variability***

On a larger scale, the variance of the measured data typically reflects the spatial and/or temporal variability (eg, 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.

##### *4.3.2.1. Temporal variability*

Both events within season (eg, diurnal variation, low vs high flows) as events driven by seasonal variability may cause temporal variability in concentrations of the metal of concern and/or abiotic factors is well documented (Oste et al 2012; Verschoor et al 2011; Prokovsky and Shirokova 2012). Greater variability is often linked to events that occur within seasons. Short-term fluctuations are more likely to occur in the water column than in the sediment/soil compartment, which are more buffered systems. In sediments, flushing or run-off events may lead to sudden increases in exposure, which could even have the tendency to last longer than in the water column (ECHA 2014). On the other hand, flushing events may also flush away all of the important surficial sediments. In that case, any established AVS-metal relationships have to re-establish. Therefore, it is critical that metals concentrations and related bioavailability controls are tied to low vs high flow (preferably first flush) conditions. The amount of Total Suspended Solids (TSS) and Dissolved Organic Carbon (DOC) are, for example, other important parameters governing metals transport and availability during these events.

Various seasonal-related biotic and abiotic processes may affect the concentration of a metal in the water column such as the amount of rainfall and related river flow rates (changing water

physico-chemistry), water runoff (eg, rainfall intensity, absence of vegetation on soil during winter season, soil type) and biological activity in the water (eg, algal growth). Seasonal and spatial variation (4.3.2.2) in DOC and living organisms, for instance, can influence the background concentrations due to binding/uptake of metals (eg, Van Stolwijk et al 2000; Verschoor et al 2011).

Van Tilborg (Tilborg 2000) demonstrated that Dutch surface water concentrations of essential elements (eg, zinc) are, within certain limits, governed by biological activity; zinc concentrations peaked in January and reached their lowest level in August when biotic activity and biological zinc uptake was at its highest. Van der Weijden and Middelburg (1989) also reported on long-term and seasonal variations in the composition of water (metals, nutrients, major ions) and suspended matter in the River Rhine. Consequently, without mentioning the covered period of monitoring, measured field concentrations may have limited relevance for exposure assessment purposes. Therefore, data sets that represent a sampling period that covers a complete year (or more) will take all seasonal-related variability into account. Secondly, the availability of data sets where individual sampling locations are monitored frequently throughout a year will potentially allow the identification of seasonal trends of metal concentration levels in surface water. If identified, this type of information can contribute to a refined assessment of data sets that only cover a specific season.

Some of the processes mitigating metal toxicity in sediments [eg, Acid Volatile Sulfides (AVS) see Factsheet 5] are microbial-mediated processes that are known to be variable in activity over the year. This is reflected in the fact that AVS concentrations tend to be higher at the end of the summer and during fall and lower in winter and spring (microbial activity depends on water temperature and higher temperatures in spring and summer will result in increased microbial activity yielding a higher sulfate reduction rate) (Howard and Evans 1993; Van Den Hoop et al 1997; Grabowski et al 2001). Temporal variability of AVS has been addressed by several authors (Van den Berg et al 1998; Van Griethuysen et al 2006). The results indicate that seasonal variability is closely linked to microbial activity. Care should be taken in extrapolating the results of floodplain soils (eg, Van Griethuysen et al 2005; Poot et al 2007). In fact some of the floodplain soils showed an opposite AVS seasonality because of preferential inundation and concomitant AVS formation in winter as was observed by Poot et al (2007). The sampling strategy used for most of the AVS databases used in metal risk assessment took this seasonality factor into account as much as possible. Samples were taken by preference in springtime when AVS levels are expected to be the lowest. It should be noted that most often the above-mentioned phenomena are strongly influenced by dynamic behavior of the overlying water stream (Poot et al 2007).

Next to this temporal variability in AVS concentrations, the reproducibility and accuracy of AVS and SEM measurements may also be a large source in variability. Hammerschmidt and Burton (2010) observed that the observed large interlaboratory variations of AVS and SEM were most likely from either AVS oxidation during sample preparation/analysis or operational differences in extraction. It is recommended that these types of analysis are only performed following rigid and correct guidance on how to handle samples in order to reduce uncertainty.

#### *4.3.2.2 Spatial variability of the natural background concentrations: defining biogeochemical regions*

Even without seasonal variability or anthropogenic influences, concentrations and hotspots will always be variable depending on the geochemical location. This spatial variation is caused not only by differences in the original rock formations and the pathways to the surface water, but also by the proportion of different water sources (rain, groundwater, melting water, upstream river water) (Oste et al 2012). In sediments, metal concentrations are closely tied to sediment grain-size distributions such as the < 63 µm (Strom et al 2011). Spatial heterogeneity is observed at small local scales (eg, cms to 1-3 m) and regional scales (river basins).

Variations in metal background concentrations and variability in the presence of abiotic factors governing the bioavailability of a metal complicates the way a generic risk assessment is applied to metals. For example, organisms could have been conditioned to changing backgrounds and these acclimation/adaptation phenomena may influence the sensitivity of an organism and changing abiotic factors may increase or decrease the bioavailability of a metal. From a practical standpoint, this means that a single ETV is inadequate to accurately assess the risk of metals for systems that have different geochemical parameters and that reasonable ranges of ETVs are needed to account for potential differences in metal risk. Geostatistics and appropriate sampling strategies could be used to capture this variability. In this context, the “biogeochemical region” concept has been introduced. Fairbrother and McLaughlin (2002) initially referred to this concept as metallo-regions where on a regional scale separate sub-regions are being defined using suitable methods to aggregate spatially explicit environmental variables. Another term frequently used in this regard is “ecoregion”. At the moment, the biological/ecological-part has been a bit underrated because the current existing biogeochemical regions are based on abiotic factors rather than quantified ecological metrics. Nevertheless, the ecological dimension of the ecoregion concept may have significant implications in terms of regional risk assessment. This is particularly true for data-rich metals, where the Species Sensitivity Distributions (SSDs) are often comprised of a diverse taxonomic range of test species that are drawn from various geographical origins and different habitats.

If the bioavailability normalisation approach is being applied to a geographic region that is well characterised from the ecological perspective, it would be appropriate to modify the SSD by removing species that are clearly not representative of the region. For example, if bioavailability normalisation was applied to a tropical lentic system, then ecotoxicity data for cold water lotic systems could be considered to be irrelevant, and therefore removed from the SSD. Such modifications should be performed as a second-tier refinement, and without consideration of the rank sensitivity of organisms in question. Any modified SSD should be evaluated against relevant acceptance criteria, including minimum numbers of species, inclusion of key taxonomic groups for the system in question, statistically significant fit, and so on.

One of the first applications of the biogeochemical region concept was used in the environment section of the EU's Existing Substance Risk Assessment of Nickel (RAR Ni), and specifically in the assessment of risk of nickel to aquatic ecosystems. The toxicity of nickel to aquatic organisms was shown to be influenced by three main geochemical parameters--dissolved organic carbon (DOC), pH, and water hardness (and specifically the concentrations of Ca and Mg) (Deleebeeck et al 2008). The distributions of these parameters in EU surface waters were well documented in national and international databases. Using these data, it was possible to identify relevant points on the distribution, including the 10<sup>th</sup>, 50<sup>th</sup>, and 90<sup>th</sup> percentile.

The RAR of Ni was a generic risk assessment, which in the Existing Substances regulation was defined as the 10<sup>th</sup> to the 90<sup>th</sup> percentile of conditions. One approach to incorporate bioavailability in a generic assessment would be to define a reasonable worst-case bioavailability scenario, in which the 10<sup>th</sup> or 90<sup>th</sup> percentile of the relevant geochemical parameters were used in the bioavailability normalisation process. The selection of the 10<sup>th</sup> or 90<sup>th</sup> percentile would depend on the relationship between that parameter and observed toxicity. For example, Ni toxicity increases with increasing pH, decreases with increasing hardness, and decreases with increasing DOC. The reasonable worst case could therefore be defined as follows: 10<sup>th</sup> percentile hardness, 10<sup>th</sup> percentile DOC, 90<sup>th</sup> percentile pH. The problem with this approach is that geochemical parameters in EU surface waters co-vary. This is particularly true for pH and hardness, such that there are no situations that show the combination of 10<sup>th</sup> percentile hardness and 90<sup>th</sup> percentile pH.

To address this issue, while still addressing the goal of a generic risk assessment, the ecoregion concept utilized actual European water bodies that reflected the range of expected variability in terms of Ni bioavailability. To this end, seven well-characterised systems were



identified that, together, exhibited the relevant ranges of bioavailability normalised ecotoxicity threshold values (ETVs). The chosen scenarios included both lentic and lotic systems, showed a range of flow rates, and were geographically distributed across Europe (Table 6). Of equal importance, the ranges of pH, hardness (H), and DOC were within the boundaries of the Ni Biotic Ligand Models (BLMs), which were used to normalise the Ni ecotoxicity database.

The outcome of this exercise was a range of bioavailability-normalised ETVs that were representative of typical conditions found in European surface waters. The ETVs ranged from 7.1 µg Ni/L for the oligotrophic lake to 43.6 µg Ni/L for the ditch scenario. Relevant Ni exposure data were then used in a semi-probabilistic way to estimate risk for each scenario.

**Table 6:** Summary of the physico-chemical characteristics of the different selected scenarios

	Type	pH	H (mg/L CaCO <sub>3</sub> )	DOC (mg/L)
Rivers (Lotic system)	Small (ditches with flow rate of ± 1,000 m <sup>3</sup> /d)	6.9	260	12.0
	Medium (rivers with flow rate of ± 200,000 m <sup>3</sup> /d)	8.1	165	3.2
		7.6	159	8.0
	Large (rivers with flow rate of ± 1,000,000 m <sup>3</sup> /d)	7.8	217	2.8
Lakes (Lentic system)	Oligotrophic lakes	7.7	48.3	2.5
	Neutral-acidic lakes	6.7	27.8	3.8

The biogeochemical region approach can be applied to different environmental matrices and to metals other than Ni. For example, the ecoregion concept was used in the assessment of Ni risks to European soils, where the geochemical parameters of note included soil pH and effective cation exchange capacity (eCEC). Similarly, the ecoregion concept was applied to the environment section of the Existing Substances Risk Assessment of Cu. Similar testing programs were set up for implementation of metal bioavailability in regulatory frameworks in China and Australia (see eg, Ma et al 2012; NEPC 2011). Copper and nickel toxicities to plants and microbial endpoints were tested in 17 Chinese soils, after different spiking treatments (with and without leaching) (Li et al 2010, 2013).

In theory, the ecoregion concept can be applied to any new geographic regions provided that supporting information is available, such as:

- o Does the area have equal/comparable physico-chemical conditions (eg pH, hardness, temperature)?
- o Are the taxonomic levels/functional systems similar?

- o Are metal background levels equal?

A last step could be an additional validation step (eg, measuring bioavailability fractions, measurements of taxonomic groups).

Recently, a study was initiated to confirm the validity of the Ni BLMs to Australian waters (Peters et al 2014). Distributions of DOC, pH, and water hardness values in Australian surface waters were collected, and the results demonstrated the critical nature of this step. First, the distributions were quite different than EU or North American surface waters, with lower distributions of water hardness and pH, and higher DOC distributions (Peters et al, 2013). Secondly, the ratios of Ca:Mg within water hardness were different from those observed in the EU. In general, a 3:1 ratio of Ca:Mg is observed in EU surface waters. In Australian surface waters, the Ca:Mg ratio was closer to 1:1. Especially for Ni BLMs, where both Ca and Mg have been observed to affect Ni toxicity to freshwater organisms, this information is important in terms of defining relevant and typical bioavailability scenarios.

#### ***4.3.3 Diffuse ambient concentration exposure assessment: derivation reasonable worst-case (RWC) EEC***

A diffuse ambient 'reasonable worst-case' (RWC) EEC concentration for a certain area can be defined as follows:

*Diffuse ambient EEC<sub>area</sub> = 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 an RWC-ambient EEC. Firstly, the use of a mean value assumes that none of the data points are 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 (ie, 90P= DL/2) will always cause an uncertainty with regard

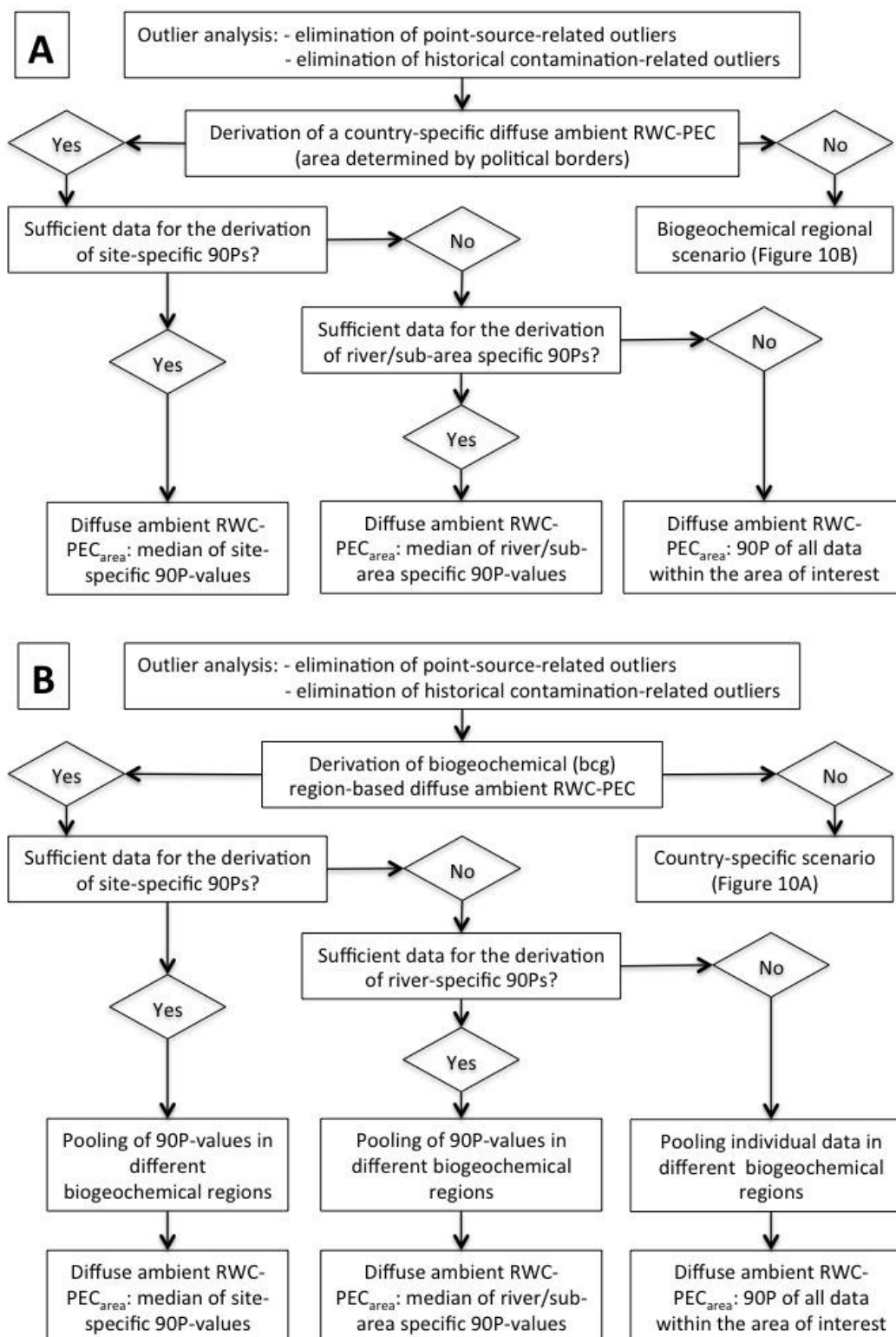
to the average value, whereas the median is determined by measured data if less than 50% of all 90P-values are <DL. When the median is equal to the DL/2, the diffuse ambient RWC-EEC is not quantified but reported as <DL.

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-EEC 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 90<sup>th</sup> percentiles are calculated. Subsequently, these 90P-values are used for the determination of the diffuse ambient RWC-EEC. 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-EECs is presented in Figure 10. Both approaches are very similar but the decision whether to follow the procedure described in Figure 10a or 10b depends on the aims of the performed exposure analysis. For the derivation of a diffuse ambient PEC for an area that is defined by political borders (eg, country, state), calculations are based on all site-specific 90P-values within the area of interest (Figure 10a).



**Figure 10:** Schematic overview of the derivation of a diffuse ambient RWC-PEC. A: country-based assessment (based on political borders); 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 characterisation be based on biogeochemical region-specific RWC-ambient PECs (Figure 10B). 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.

#### **4.4 DATA AVAILABILITY FOR THE BIOAVAILABILITY ASSESSMENT/NORMALISATION)**

The way bioavailability should be taken into account is described in detail in Factsheet 5 *“Incorporation of bioavailability concepts into environmental quality standard setting of metals and inorganic metal compounds” (version 1 December 2015)*. In order to normalise toxicity data towards physico-chemical conditions, different data sets for abiotic factors (and environmental concentrations) should be considered depending on the goal of the assessment (ie, threshold derivation, site-specific assessment etc). More specifically, datasets of abiotic factors as well as environmental concentrations should be representative of the area under investigation. The breadth of the datasets will usually be proportional to the scope of the assessment, ie, broader datasets will be necessary for regional assessments with national to continental scales due to spatial variability, compared to local assessments which address site-specific operational scales. It is particularly important to take relevant abiotic factors into account for the metal under investigation. In Tables 7 and 8, an overview is given of the relevant importance of the physico-chemical parameters for the different metal species that influence their bioavailability. For most metals, DOC, pH, and hardness are key parameters in the water compartment.

**Table 7:** Overview of the most relevant parameters that influence the bioavailability of metal species in the water compartment. Those indicated moderate and major should be measured. Minor is nice to have. Shaded area gives the magnitude of importance.

Water compartment		Relative importance		
Metal	Physico-chemical parameter	Minor	Moderate	Major
Cu	DOC			
	Hardness (Ca <sup>2+</sup> , Mg <sup>2+</sup> )			
	pH			
	Other inorganic ligands (SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> , Na <sup>+</sup> , K <sup>+</sup> , etc)			
Zn	DOC			
	Hardness (Ca <sup>2+</sup> , Mg <sup>2+</sup> )			
	pH			
	Other inorganic ligands (SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> , Na <sup>+</sup> , K <sup>+</sup> , etc)			
Ni	DOC			
	Hardness (Ca <sup>2+</sup> , Mg <sup>2+</sup> )			
	pH			
	Alkalinity			
	Other inorganic ligands (SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> , Na <sup>+</sup> , K <sup>+</sup> , etc)			
Pb	DOC			
	Hardness (Ca <sup>2+</sup> , Mg <sup>2+</sup> )			
	pH			
	Other inorganic ligands (SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> , Na <sup>+</sup> , K <sup>+</sup> , etc)			

	Na <sup>+</sup> , K <sup>+</sup> , etc)			
Mn	DOC			
	Hardness (Ca <sup>2+</sup> , Mg <sup>2+</sup> )			
	pH			
	Other inorganic ligands (SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> , Na <sup>+</sup> , K <sup>+</sup> , etc)			
Ag	DOC			
	Hardness (Ca <sup>2+</sup> , Mg <sup>2+</sup> )			
	pH			
	Sulfides			
	Chlorides			
	Other inorganic ligands (SO <sub>4</sub> <sup>2-</sup> , , Na <sup>+</sup> , K <sup>+</sup> , etc)			
Cd	DOC			
	Hardness (Ca <sup>2+</sup> , Mg <sup>2+</sup> )			
	pH			
	Chlorides			
	Other inorganic ligands (SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> , Na <sup>+</sup> , K <sup>+</sup> , etc)			

**Table 8:** Overview of the most relevant parameters that influence the bioavailability of metal species in the sediment/soil compartment

	<b>Sediment</b>	<b>Soil</b>
Required	Total Organic Carbon (TOC)	Total Organic Carbon (TOC)
	Acid Volatile Sulfides (AVS)*	pH
	Al/Fe/Mn oxides	Effective Cation Exchange Capacity (eCEC, ie, CEC at prevailing soil pH)*.
		Al/Fe/Mn Oxides
		Particle size (sand, silt and clay content)
Supportive information	Particle size (sand, silt and clay content)	Pore water chemistry (total and dissolved metal concentrations, pH, DOC, hardness, conductivity/salinity, etc)
	Pore water chemistry (total and dissolved metal concentrations, DOC, hardness, conductivity/salinity, ammonium etc)	

\* Mainly for divalent metals (Ag, Hg, Cu, Pb, Cd, Zn, Ni)

Because 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 physico-chemical 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 optimise 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 (eg, 10<sup>th</sup> P) or high (eg, 90<sup>th</sup> 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.

There are several publicly available data bases that report on typical values of the main physico-chemical properties of water, sediment, and soil, as well as baseline levels or inorganic elements for these different environmental compartments (section 4.5). Additionally, site-specific environmental data can also be used in local risk assessment scenarios (see Factsheet 1).

#### **4.5 Database(s)**

Available databases with harmonised monitoring data on a continental scale are listed in Table 9 below.

Harmonised monitoring data on a continental scale for both metal concentrations and general physico-chemical properties of water, sediment, or soil, are critical for a realistic assessment of risk of metals towards organisms in the various compartments. Such data provide a strong basis for taking into account the spatial variability of both exposure (metal concentrations) and effect concentrations (considering bioavailability through variation in physico-chemical properties) in a risk assessment for metals in the environment. Availability of these data therefore avoids the need for (worst-case) assumptions in both exposure and effects assessments and, thereby, increasing the transparency and reliability of the regional risk characterisation. Harmonised data, with respect to land-use, sampling, and analytical methods, facilitate a consistent approach at the European scale, enabling direct comparison of results for various regions.

**Table 9:** Summary of continental monitoring data for metals

Database	Environmental compartment	Geographical area	Parameters analysed	Reference
FOREGS	Water Sediment Soil	Europe	<ul style="list-style-type: none"> <li>• Total + aqua regia extractable element content (&gt;40 elements)</li> <li>• pH</li> <li>• Total Carbon content (sediment, soil)</li> <li>• Dissolved Carbon content (water) – NDIR detection</li> <li>• Sulphate, nitrate (water)</li> <li>• Inorganic elements in water (ICP-QMS, ICP-AES),</li> </ul>	<a href="http://weppi.gtk.fi/publ/foregsatlas/">http://weppi.gtk.fi/publ/foregsatlas/</a>
NAWQA	Groundwater, streams, sediment, fish and clam tissue	USA		<a href="http://water.usgs.gov/nawqa/">http://water.usgs.gov/nawqa/</a>  Mahler et al (2006); Ayotte et al (2011); De Weese et al (2007).
GEMAS	Soil (arable land 0-20 cm) and grazing land (0-10 cm)	Europe	<ul style="list-style-type: none"> <li>• Total + aqua regia extractable element content (&gt;40 elements)</li> <li>• General soil properties (pH, organic carbon, clay, CEC)</li> </ul>	Reimann et al (2014) <a href="http://gemas.geolb.a.ac.at/">http://gemas.geolb.a.ac.at/</a>
USGS	Soil, ambient background (0-5 cm, A-horizon and C-horizon)	USA	(near) total element content (>40 elements)	Smit et al (2013) <a href="http://pubs.usgs.gov/ds/801">http://pubs.usgs.gov/ds/801</a>

National Geochemical Survey of Australia	Soil, ambient background (0-10 cm and 60-80 cm depth)	Australia	<ul style="list-style-type: none"> <li>• Total + aqua regia extractable element content (&gt;40 elements)</li> <li>• pH</li> </ul>	Caritat and Cooper (2011)
...				

## Annex 1. Questionnaire for regional exposure analysis

Hereunder a non-exhaustive overview is provided of the information needed to evaluate the emission inventory data:

- National emission data by source category (eg, 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, data on company level is preferred;
- 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 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 (eg, Eurostat, OSPAR, International Commission for the Protection of the Rhine, HELCOM,...);
- Any information necessary to understand the emission data.

The questionnaire also requests information on the physico-chemical 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 dataset 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 for local exposure analysis

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

Site (or division)	Form of metal	T <sub>r-2</sub>	T <sub>r-1</sub>	Reference year T <sub>r</sub>

### 2. Working days (Level I)

Number of working days ( <i>that emissions may have occurred</i> )	T <sub>r-2</sub>	T <sub>r-1</sub>	Reference year T <sub>r</sub>
Remarks			

### 3. Metal emissions to the environment

#### 3.1 Air

##### - Point source emissions to air (Level I)

-

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

- **Fugitive Emissions (Level I)**

What measures are taken to minimise fugitive emissions (eg, 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 (*)	<b>T<sub>r-2</sub></b>	<b>T<sub>r-1</sub></b>	<b>Reference year T<sub>r</sub></b>
Description of calculation method (*)			
Remarks:			

- **Metal in air monitoring data (on-site or surrounding area)/ Metal in suspended/deposited dust (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 ( $\mu\text{g}/\text{m}^3$ ) given as 90 <sup>th</sup> percentile (daily basis), and geometric annual average	<b>Statistics</b>	<b>Name/Ref Number</b>	<b>T<sub>r-2</sub></b>	<b>T<sub>r-1</sub></b>	<b>Reference year T<sub>r</sub></b>
	<b>90 % upper (daily basis)</b>				
	<b>geometric annual mean</b>				
	<b>90 % under (daily basis)</b>				
Sampling device: type, flow rate (high or low volume sampler), filter used (PM2.5, PM10 or others)					
Sampling duration :					



### 3.2 Water

- **Emissions to Water (Level II)**

Average concentration of metal in effluent (90 <sup>th</sup> percentile, upper and lower limit and geometric average in mg/L)		<b>T<sub>r-2</sub></b>	<b>T<sub>r-1</sub></b>	<b>Reference year T<sub>r</sub></b>
	<b>90% upper (monthly basis)</b>			
	<b>Geometric annual mean</b>			
	<b>90% lower (monthly basis)</b>			
	<b>T<sub>r-2</sub></b>	<b>T<sub>r-1</sub></b>	<b>Reference year T<sub>r</sub></b>	
Total emissions to water from point sources (total and/or soluble fraction) (kg metal year): <b>(Level I)</b>				
Average effluent flow rate (m <sup>3</sup> /day)				
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				
Sample collection method (grab samples, automatic sampler, volume driven sampler etc):				
Sampling frequency (no. of times/year, continuous etc):				
Analytical method used: <ul style="list-style-type: none"> <li>● total and soluble metal measured</li> <li>● techniques used to determine total and/or soluble (give literature reference, standard method or description of method)</li> </ul>				

- filter type and pore size used

- **Characteristics of receiving water (Level II)**

Is the effluent discharged to:	
➤ River (specify flow of receiving water m <sup>3</sup> /day as annual mean and 10 <sup>th</sup> percentile, if possible)	
➤ Estuary (specify flow of receiving water m <sup>3</sup> /day as annual mean and 10 <sup>th</sup> percentile, min. and max. if possible )	
➤ Canal (specify water renewal rate as annual mean and 10 <sup>th</sup> percentile, if possible )	
➤ Lake (specify volume and water renewal rate as annual mean and 10 <sup>th</sup> percentile, if possible )	
➤ To community sewer system	
➤ Sea	
➤ Other (please specify)	
Remarks:	

- **Monitoring of receiving waters (Level III)**

	<b>T<sub>r-2</sub></b>	<b>T<sub>r-1</sub></b>	<b>Reference year T<sub>r</sub></b>
Results: Metal levels in receiving water AFTER plant emissions (in mg/L given as 90 <sup>th</sup> percentile, upper and lower limits and geometric annual average)	<b>90% upper (monthly basis)</b>		
	<b>Geometric annual mean</b>		
	<b>90% lower (monthly basis)</b>		
	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: <ul style="list-style-type: none"> <li>total and soluble metal measured</li> <li>techniques used to determine total and/or soluble (give literature reference, standard method or description of method)</li> </ul> filter type and pore size used	

Results: <b>Background metal levels</b> in water BEFORE plant emissions (in mg/L given as 90 <sup>th</sup> percentile, upper and lower limits and geometric annual average)  Specify whether total and/or soluble fractions are measured and give location relative to plant discharge point		<b>T<sub>r-2</sub></b>	<b>T<sub>r-1</sub></b>	<b>Reference year T<sub>r</sub></b>
	<b>90% upper (monthly basis)</b>			
	<b>Geometric annual mean</b>			
	<b>90% lower (monthly basis)</b>			
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).	<b>Phys-chem</b>	<b>T<sub>r-2</sub></b>	<b>T<sub>r-1</sub></b>	<b>Reference year T<sub>r</sub></b>
	<b>pH</b>			
	<b>Hardness (mg CaCO<sub>3</sub>/L)</b>			
	<b>DOC</b>			
	<b>Suspended solids</b>			
	<b>Alkalinity (mg CaCO<sub>3</sub>/L)</b>			
	<b>Ca (mg/L)</b>			

	<b>Mg (mg/L)</b>			
	<b>Na (mg/L)</b>			
	<b>K (mg/L)</b>			
	<b>SO<sub>4</sub> (mg/L)</b>			
	<b>Cl (mg/L)</b>			
	<b>Others if deemed appropriate (eg, F for Al) (mg/L)</b>			
After the effluent has been discharged, does the receiving river water undergo any further treatment (yes/no)?				
If yes, what is the destination of the municipal sludge from this water treatment center (disposed, incinerated or recycled to agricultural land?)				
Remarks:				

### 3.3 Waste water treatment at production site (Level II)

Is there a treatment system for process waste water at the site? If yes, briefly describe the waste water treatment system				
What is the average efficiency of waste water treatment? (eg, in % of metal in water before and after treatment)				
Can this efficiency figure be proven by measured data or is it based on modelling assumptions?				
How much metal-containing sludge/cake is produced by the waste water treatment plant (in dry weight)?		<b>T<sub>r-2</sub></b>	<b>T<sub>r-1</sub></b>	<b>Reference year T<sub>r</sub></b>
	<b>total amount (t/y)</b>			

	metal content (g/t)			
What is the destination/handling of the sludge/cake produced by the on-site treatment plant, ie, is the sludge disposed, incinerated or recycled (give details)? If disposed of, is the sludge landfilled or used on agricultural land?				
Give details of any rainwater treatment at site				
Remarks:				

### 3. Sediment monitoring (Level III)

Give details of representative metal levels and other physico-chemical characteristics in sediment monitored UPSTREAM of plant discharge points including location relative to discharge point (include year and method of sampling) (in mg/kg dry weight)	<b>SEM (Cu, Ni, Pb, Zn, Cd) (<math>\mu\text{mol/L}</math>)</b>	
	<b>AVS (<math>\mu\text{mol/L}</math>)</b>	
	<b>OC (%)</b>	
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)	<b>SEM (Cu, Ni, Pb, Zn, Cd) (<math>\mu\text{mol/L}</math>)</b>	
	<b>AVS (<math>\mu\text{mol/L}</math>)</b>	
	<b>OC (%)</b>	
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		

physico-chemical 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)**

Type and quantity (t) of industrial wastes produced: <b>(Level I)</b>	<b>T<sub>r-2</sub></b>	<b>T<sub>r-1</sub></b>	<b>Reference year T<sub>r</sub></b>
- For final disposal (burning or landfilling)			
For reuse (please indicate what type of reuse) (eg, 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 <b>on-site</b> waste storage arrangements for metal-containing wastes (eg, type, lining material used, leachate recovery system):			
Describe any monitoring programmes used to monitor leakage from permanent on-site waste storage sites:			
What <b>off-site</b> waste disposal arrangements are in place? For each			

type, indicate the waste management systems that are in place (eg, information from local authorities on disposal sites)	
Remarks:	

## 5. Other general data (Level III)

### 5.1 Monitoring

Other monitoring data on metal levels in the local environment, eg, 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.

### 5.2 Socio-economic information (Level III)

Company location (city, industrial estate, rural, coastal etc)	
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## **Annex 2: Dealing with the natural background**

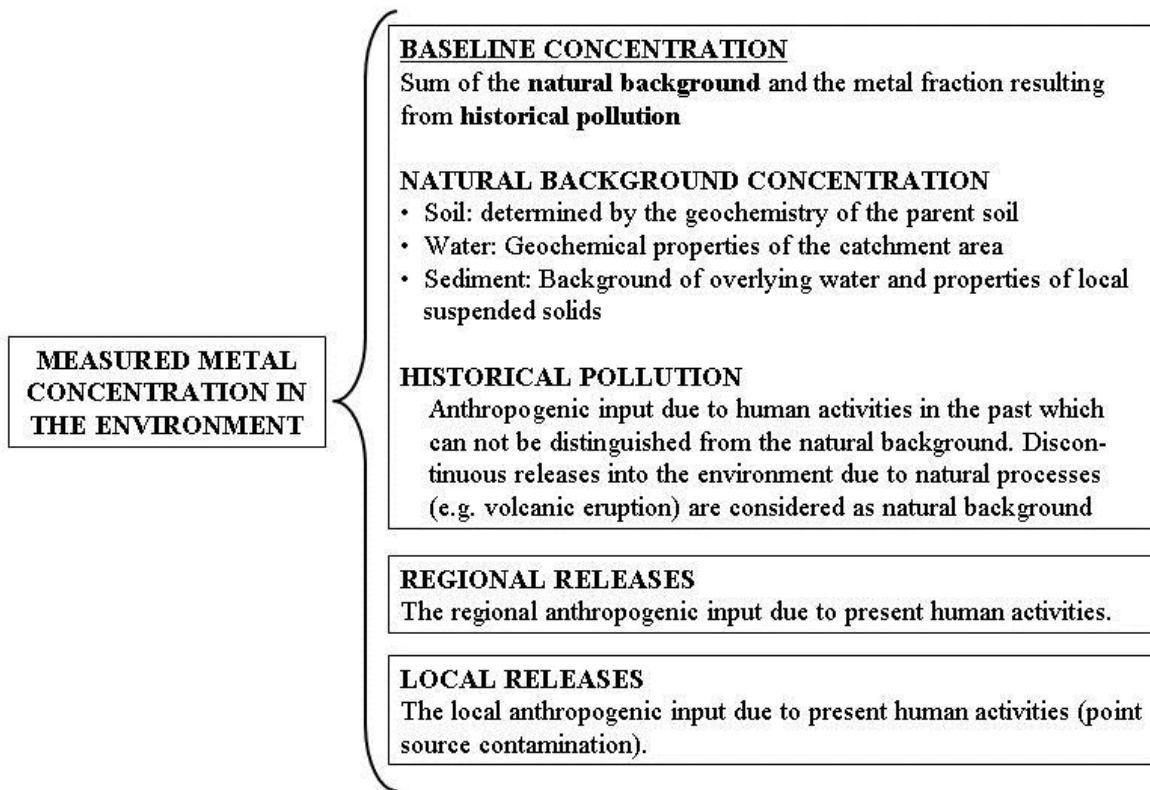
### **Introduction**

Naturally occurring 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 occurring 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 areas, 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, ie, 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 eg, cobalt, nickel, and zinc are slightly depleted by agricultural practices

Because it is becoming more and more difficult to determine natural background levels of certain elements, the baseline concentration of a metal has been recognised 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, the 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 humans during the past decades or even centuries. The added fraction is often referred to as historical pollution. In many cases this historical pollution cannot 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 technique can be a helpful tool for differentiating the natural and added metal fractions 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 which the water body flows, introduction of natural organic material (leaves), erosion from natural (uncontaminated) river banks, and atmospheric deposition from natural origin<sup>7</sup>. When well water or groundwater is used for estimating natural background levels, it is essential to verify that these samples are free of current or historic pollution. Moreover, due to 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.

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<sup>7</sup>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.

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 (eg, lakes, reservoirs) are considered that have been affected by important anthropogenic inputs in the past. These type 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.

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 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 (eg, selenium, boron, arsenic). For other metals, the added

amount to the topsoil (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 context) and physico-chemical (run-off, leaching to ground water) processes, the input by organic material (remains of plants) and air deposition( eg, 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 in temperate climates:

- 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. When organic material is decaying, metals will partly be given back to the water phase, but also become entrapped in the sediment (eg, metal sulphides, binding to settling solids, incorporation into Fe/Mn oxy hydroxide precipitates etc). In time, these processes extract 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 be 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, brush 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 from small, second order drainage basins (<100 km<sup>2</sup>) that are pristine or nearly so;
- whenever possible, sampling was performed during winter and early spring months, and was avoided during heavy rainy periods and flood events.. Consequently, some critical periods (first flush events, low summer flow rates) were not sampled and hence metal concentrations may underestimate metal exposures to aquatic biota;
- 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 environmental 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 A.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 (eg, 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 the 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 metals 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 et al (1992) can be used as default background values in the local or regional risk characterisation of metals.

Values were derived from measured data representing areas that are considered to be relatively unpolluted ( $\text{NH}_4\text{-N}$ : < 0.1 mg/L; BOD: < 2 mg/L;  $\text{O}_2$ : > 8 mg/L). Data were obtained from 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:  $\text{NO}_3$ : < 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 (eg, Mo, Zn). In those cases, it is recommended to use the dissolved background concentration because 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)

Element	WORLD				N-EUROPEAN LOWLAND			
	Dissolved (filtered)		Total (unfiltered)		Dissolved (filtered)		Total (unfiltered)	
	(µg/L)		(µg/L)		(µg/L)		(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 A.3 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 has been summarised 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 distribution 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 presented in Table A.4, it can be concluded that baseline-concentrations for a specific metal in the terrestrial compartment (top soil) mostly vary up to 3 orders of magnitude.

The degree of variation depends on factors like soil composition (sandy soil, clay soil) 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. Because regressions were based on measured data, reported metal concentrations may be influenced by historical pollution (eg 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.

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

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

The metal-specific coefficients for clay and OM (organic matter) that are used for the determination of metal background concentrations in Flanders are summarised in Table A.5.

The coefficients of Table A.5 actually reflect the 90<sup>th</sup> 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 under-estimations.

**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 <sup>2</sup>
<b>As</b>	14	0.5	0	0.39
<b>Cd</b>	0.4	0.03	0.05	0.39
<b>Cr(III)</b>	31	0.6	0	0.37
<b>Cu</b>	14	0.3	0	0.24
<b>Hg</b>	0.5	0.0046	0	0.08
<b>Pb</b>	33	0.3	2.3	0.15
<b>Ni</b>	6.5	0.2	0.3	0.48
<b>Zn</b>	46	1.1	2.3	0.26

The same type of reference lines for the derivation of metal background concentrations in The Netherlands is also presented in Crommentuijn et al (1997), and the metal coefficient values are summarised 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, ie, 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 Crommentuijn 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.6:** 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](http://www.rivm.nl/stoffen-risico/NL/ond_4_0_1.html) )

	Constant	Clay-coefficient	OM-coefficient
<b>As</b>	15	0.4	0.4
<b>Ba</b>	30	5	0
<b>Be</b>	0.3	0.033	0
<b>Cd</b>	0.4	0.007	0.021
<b>Cr (tot)</b>	50	2	0
<b>Co</b>	2	0.28	0

<b>Cu</b>	15	0.6	0.6
<b>Hg</b>	0.2	0.0034	0.0017
<b>Pb</b>	50	1	1
<b>Mo</b>	1	0	0
<b>Ni</b>	10	1	0
<b>Sb</b>	1	0	0
<b>V</b>	12	1.2	0
<b>Zn</b>	50	3	1.5

### Implementation of background concentrations for risk characterisation.

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

The risk characterisation 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, ie, 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 characterisation 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<sub>total</sub> does not remain 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<sub>added</sub> 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 (eg, 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 (eg, Europe for EU-risk assessment purposes).

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