Guidance on the Chemical Safety Assessment for metals

Introduction

A chemical safety assessment and its associated report (CSR) for metals and metal compounds (inorganics) requires special attention to ensure that hazard, exposure and risk assessments meet the requirements for a CSR under REACH Article 14. The major areas of concern include:

- determination of natural background levels and historical emissions since metals are known to be persistent in the environment;
- for data rich metals, the use of statistical and probabilistic tools will be required for quantifying import/export tonnage within the exposure assessment;
- speciation is of paramount importance: metals can occur in different valences, associated with different anions or cations, and can be associated to adsorptive agents, such as Dissolved Organic Matter (DOM) in water, or bound to minerals in sediment or soil. Speciation highly depends on environmental conditions and chemistry;
- the adsorption/desorption behaviour of a metal strongly depends on prevailing environmental conditions.
- differences in physicochemical properties such as (bio)availability and partitioning coefficients.

For most metals and metal compounds, the availability of data will be limited and the approach taken in the CSA will consider the situation that no data or only limited data are available.

Metals and metal compounds will be assessed to determine if they meet the criteria for classification as hazardous, persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB) under Article 14 (3). If all potential risks are adequately assessed and controlled the CSA ends. If the registrant concludes that the metal meets the criteria as hazardous or assessed to be a PBT or vPvB, then an exposure assessment, and risk assessment is required. The methodologies required for conducting the exposure assessment and risk assessment differs somewhat from the traditional CSA approach and will be discussed further.

Exposure Assessment

Metal-specific considerations that should be considered when estimating the predicted environmental concentration (PEC) for the exposure assessment of a CSA:

<u>Exposure modelling for metals and metal compounds</u>

Most of the current guidance on CSA has been developed mainly from the experience gained on individual organic substances. Therefore, the methodology used and assumptions made cannot always be applied directly to metals without modification.

Parameter	Metals and metal compounds
Water solubility	Prediction should be based on the relevant soluble metal ion /or other metal species that is bioavailable or may become available through transformation processes. Where the metal is poorly soluble and sufficiently stable to not rapidly transform to a water soluble form, the metal itself should be assessed taking into account its specific partitioning characteristics
Vapour pressure	**$1x10^{-06}$Pa** Most metals, except for mercury compounds and several organometallo compounds, have a very low vapour pressure. Therefore adjusting the vapour pressure will ensure that modelled distribution to air is negligible.
Henry coefficient	**$4x10^{-06}$ $Pa.m^3.mol^{-1}$** Volatilisation can be ignored for metals except for mercury compounds and several organometallo compounds. Consequently, the Henry-coefficient should be set to a very low value
Adsorption to aerosol particles	Metal present in the atmosphere will normally be bound to aerosols, hence an extremely low value should be used for the vapour pressure to ensure that the metal fraction associated to aerosols is almost equal to one. If a valid measured value is available, this value should be used.
Octanol-water partitioning coefficient	Modelled / measured partition coefficients Kp should be used instead of the K_{ow}, taking into account environmental conditions.
Biotic and abiotic degradation rates	**0** Biotic and abiotic degradation rates should be set to zero for metals.
Elimination in STP	Measured/modelled partition coefficient for water-sludge should be used. These values are difficult to find and it may be easier to use the removal efficiency rates (expressed in percent) than sludge-water partition coefficients.
Time scale	**20-100 years** Steady-state concentrations takes several decades, hundreds or even thousands of years, hence time scale is no longer relevant for risk assessments. It is therefore necessary to calculate both the PEC values after a surveyable time period of 100 years and the PEC at steady-state. The time period at which PEC equals PNEC should also be calculated for risk management purposes
Adsorption-desorption	The transport of metals between the aqueous phase and soil/sediment/suspended matter should be described on the basis of measured soil/water, sediment/water and suspended matter/water equilibrium distribution coefficients (Kd also called partition coefficient Kp)

Use of monitoring data for metals

Monitored or measured environmental concentration (MEC) can be used to replace the PEC for the CSA where this data is available for metals. However, care should be taken as measured data sets represent the sum of three different fractions: the natural (background) concentration, the dispersive anthropogenic input due to human activities (historical and recent) and the site-specific anthropogenic input due to human activities (historical and recent).

Background metal concentration can be determined by data collected in pristine (uncontaminated) areas. The FOREGS Geochemical Baseline Programme (FGBP) database can be used to acquire data and contains recent, baseline concentrations for various environmental compartments. (http://www.gsf.fi/foregs/geochem/). For example, the MEC in surface waters in upstream areas (as measured in FOREGS) could be retained as an estimate for the natural background for the aquatic

environment. It has been common practice to report/use the 10-90th percentiles of the baseline concentrations as regional background ranges.

Historical contamination can also contribute significantly to MECs for metals and hence must also be estimated. The influence from historical contamination is not readily identifiable, since there is usually mix of influences but can be determined from historical records that may provide information on former activities at sites, collecting detailed information on local water concentration profiles, evaluating information about local geology and the presence of elevated metal levels that cannot be explained by identified sources (may suggest influence from historical contamination) or the use of ratios of stable lead isotopes.

Further work for the determination of natural metal background and historical concentrations is currently ongoing.

Choosing abiotic parameters that drive metal bioavailability

Bioavailability of metals and metal compounds is an important criterion when estimating exposure, as the dissolved free ionic metal species is far more bioavailable than most complexed metal species. Additionally, geochemical factors in water, sediment, and soil influence metal speciation. Some abiotic factors influencing bioavailability for metals include pH, presence of cations, dissolved organic carbon (DOC) and organic carbon (OC). These parameters should be carefully considered when collecting data for MEC for metals and metal compounds.

Risk Assessment

In order to calculate the risk characterisation ratio (RCR) to assess the potential environmental risks of metal and metal compounds the predicted no effect concentration (PNEC) has to be derived. Similarly as in the exposure assessment, various metal specific considerations should be taken into account in the effects assessment for estimating PNEC (see Appendix). If ecotoxicity data is not available, read-across ecotoxicity data from other inorganic compounds of the same metal could be considered or Quantitative Ion Character-Activity Relationships (QICARs) and Quantitative Cationic-Activity Relationships (QCARs) can be used to extrapolate ecotoxicity values. More research efforts are needed to develop and validate appropriate models.

The RCR is then calculated by determining the PEC_{metal} : $PNEC_{metal}$ ratio as outlined in the ECHA guidance. However, the risk characterisation for metals and metal compounds depends to a large extent on how bioavailability can be incorporated into the process which in turn depends on the availability of data on the abiotic factors. More information on can be found in the Guidance on information requirements and chemical safety assessment: Appendix R.7.13-2: Environmental risk assessment for metals and metal compounds.

Metals in nanoform

The European Commission has adopted a definition on nanomaterials to mean “A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one

or more external dimensions is in the size range 1 nm to 100 nm. In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50 % may be replaced by a threshold between 1 and 50 %".

Most of the CSR refinement tools for metals are only applicable for data-rich metals, hence the introduction of 'nano' sized particles (e.g. ZnO, CEO_2, Al_2O_3) further complicates the CSA process. Specific guidelines for defining and assessing metals in nanoform are currently in progress. However, based on tonnage, at present some nano materials may be able to evade the CSA process, thus not requiring a CSR.

Appendix

Metal-specific points for selecting ecotoxicity data

Parameter	**Metals and metal compounds**
Description of the physico-chemical test conditions	These include DOC, OC, water hardness, pH, alkalinity, presence of complexing agents such as humic acids and EDTA
Test media for ecotoxicity testing	Measured data of the metal concentrations instead of artificial media should be used because of the potential issues related to natural background, analytical errors and the limited solubility of some metals and inorganic metal compounds. Measured data on dissolved metal fractions are always required in order to obtain reliable toxicity test data A proper description of the culture conditions specifically related to the level of essential metals and inorganic metal compounds added or is already present in the culture media should be given Test media containing chelators (e.g. EDTA) should be excluded from PNEC derivation.
Calculating toxicity value	The possibility of hormesis (dose-response) effects needs to be considered when evaluating the calculation of EC10 values beyond the lowest tested concentration.