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**TNO-report**

**R 2004/347**

**Improvement of LCA characterization factors and  
LCA practice for metals**

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Order no.	35468
Keywords	LCA Characterisation factors Essential metals Non-ferrous metals Ecotoxicity
Intended for	International Council on Mining and Metals (ICMM)



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## Summary

Toxic impacts from metals are treated in life cycle impact assessment (LCIA) in a way that has evoked quite some criticism. This document reviews the principles, the state-of-the-art and the current development of LCIA and contrasts it with the physical, chemical and biological aspects of metals in the environment and the progress that is being made to cast these aspects in models. The main issues addressed are:

- Persistence;
- Bio-availability;
- Speciation;
- Essentiality.

Two types of conclusions are presented:

1. Guidelines for treating metal emissions in the present framework of LCIA are given for different levels of sophistication;
2. A research agenda is drafted to steer a more scientifically founded adoption and adaptation of the new and emerging metal-specific knowledge by the LCIA-modellers.



## Preface

This report is the result of a project carried out by CML and TNO for ICMM. It grew out of the mutual recognised discomfort with the way toxic impacts of metals are presently treated in life cycle impact assessment (LCIA).

This report reviews the current status of LCIA and current developments within the risk assessment of metals. It then investigates the extent to which these developments can be accommodated in LCIA. A first version of this report has been discussed at a workshop in Apeldoorn, The Netherlands, on 15 April 2004. After comments by reviewers and other experts, some adaptations has been made. The workshop was co-sponsored by the UNEP/SETAC Life Cycle Initiative. The results have been submitted to their process of establishing the best available practice for LCA and drafting a research agenda. Part of this has been the establishment of the so-called *Declaration of Apeldoorn on LCIA of Non-Ferro Metals*, which has been published in the SETAC Globe, and which has been added as Appendix I of this report.

The authors are grateful to commissioners, reviewers and the participants that attended the workshop in Apeldoorn. Special words of thanks go to Katrien Delbeke, Wim van Tilborg and John Atherton for initiating this project, to Olivier Jolliet, Michael Hauschild, William Adams and Nico van Straalen for providing detailed comments to the draft version, and to Helias Udo de Haes for chairing the workshop and acting as a liaison to the UNEP/SETAC Life Cycle Initiative.



## Table of contents

Summary .....	3
Preface .....	5
1. Introduction.....	9
1.1 Background.....	9
1.2 Objectives .....	9
1.3 Metals and LCA: some examples from practice.....	10
1.4 Structure of the report.....	12
2. Life cycle assessment.....	13
2.1 Overview .....	13
2.2 Life cycle impact assessment .....	14
2.3 Characterisation.....	16
2.4 Fundamental limitations of characterisation.....	19
2.4.1 Aggregation over space, time and substance variety.....	20
2.4.2 The less-is-better paradigm and potential versus actual impacts.....	21
2.4.3 The linearity of the dose-response relationship.....	22
2.4.4 Mass loading (pulse) versus flow rate (flux), and time-integration .....	24
2.4.5 Trade-off between substances and comparisons across substances.....	27
2.5 A historical overview of approaches .....	28
2.5.1 Model developments .....	28
2.5.2 Numerical comparison .....	30
3. Metals and the environment.....	33
3.1 HSE, RA and LCA .....	33
3.2 Speciation .....	34
3.3 Evaluative environment.....	36
3.4 Speciation processes to include .....	37
3.4.1 Sorption processes.....	37
3.4.2 Complexation, hydrolysis and redox reactions .....	40
3.4.3 Precipitation and dissolution .....	42
3.4.4 Methylation .....	42
3.4.5 Activity correction .....	42
3.5 Bioavailability .....	43
3.6 Essential elements.....	45
3.7 Life cycle inventory data and metal emissions.....	46

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4.	Developments in characterisation .....	47
4.1	Regionalised models .....	47
4.2	Non-linear models and background-dependency .....	48
4.3	Non-steady-state models .....	49
4.4	Metabolites .....	50
4.5	Metals and LCIA of toxics .....	51
5.	Characterisation of ecotoxicity impacts of metals .....	53
5.1	Possibilities and limitations .....	53
5.1.1	Persistence .....	53
5.1.2	Bio-availability .....	54
5.1.3	Speciation .....	54
5.1.4	Essentiality .....	55
5.2	Recommended practice .....	55
5.2.1	Guidelines for simplified LCA .....	56
5.2.2	Guidelines for detailed LCA .....	57
5.2.3	Guidelines for optional extensions .....	57
5.3	A research agenda .....	57
6.	Concluding remarks .....	59
6.1	Human health impacts .....	59
6.2	Non-toxic impacts .....	59
6.3	Beyond the metals .....	59
7.	Abbreviations and symbols .....	61
8.	References .....	63
9.	Authentication .....	67

Appendix 1    Declaration of Apeldoorn on LCIA of Non-Ferro Metals



## **1. Introduction**

### **1.1 Background**

The International Council on Mining and Metals (ICMM) has commissioned TNO (Netherlands Organisation for Applied Scientific Research) and CML (Institute of Environmental Sciences, Leiden University) to organise a workshop, on the inclusion of state-of-the-art expertise and current expert knowledge on risk assessment of metals in life cycle impact assessment. The workshop was held on 15 April 2004 in Apeldoorn, The Netherlands. It was based on the preliminary results of a recent concise study addressing the scientific issues and practical dilemmas encountered in the development or use of characterisation factors for life-cycle impact assessment purposes. The preliminary study also offered a number of directions for improvement. The workshop was co-sponsored by the UNEP/SETAC Life Cycle Initiative. The aim of the workshop was to make an inventory of what is needed to define and develop a recommended practice for the characterisation of metals in LCIA (Life Cycle Impact Assessment). The workshop also drafted a declaration on LCIA of non-ferro metals (see Appendix I), and commented on the preliminary report of the position paper. The present report is the revised version of this concise study.

Life cycle impact assessment (LCIA) is part of the life cycle assessment procedure (LCA). It is a procedure aimed at assessing the environmental consequences of extractions of natural resources and emission of chemicals in terms of contributions to so-called environmental impact categories, such as climate change, acidification, ecotoxicity and resource depletion. Although the LCIA procedure was developed and is used by a large array of groups, ranging from universities, multinationals, and ministries to NGOs, its fundamentals are not yet entirely clear. Environmental experts often have problems with the way LCIA deals with specific issues, such as non-linear dose-response relationships, dynamic variations of concentrations of pollutants, regional or local conditions, thresholds and essentiality, and many more. One important group of problems is created by the way metals, and in particular non-ferrous metals, are addressed. Risk assessment specialists have a large body of knowledge on metal-specific behaviour (complexation, bio-availability, essentiality, etc.) that is largely or even entirely ignored in the current models for LCIA.

### **1.2 Objectives**

The objectives of this report are:

- to investigate the extent to which results from LCAs are (rightly or wrongly) dominated by metals;
- to give an overview of metal-specific issues not (properly) accounted for in current LCIA procedures;

- to explore the extent to which these issues are in principle compatible with the axioms of LCA;
- to investigate which changes would be needed with respect to models, software, data and databases to implement these issues into LCA;
- to draft an agenda of research needed to solve the problems in an appropriate way;
- to make an inventory of the issues needed to define and develop a recommended practice for the characterisation of metals in LCIA;
- to provide guidance for LCA practitioners on possible impacts of the R&D results on LCA conclusions.

This report does not contain new characterisation factors for LCIA. Neither does it include a description of an improved model for calculating new factors. Rather, it focuses on a discussion of the aspects that could be included in new models.

### **1.3 Metals and LCA: some examples from practice**

Before going into detail on life cycle impact assessment and the environmental effects of non-ferrous metals we would like to show two examples in order to investigate the extent to which the present treatment of metals is troublesome.

#### *Example 1.*

The models suggest that it is better to empty a jerrycan of benzene into a fountain than to throw a nickel coin into it. After all, Guinée et al. (2002) ascertained that 5 kg benzene has a fresh water aquatic ecotoxicity potential of 0.45 kg 1,4 DB equivalent while 10 g of nickel scores a 32 kg 1,4 DB equivalent.

#### *Example 2.*

By way of example, Figure 1 shows the environmental impact of the sewage wastewater treatment plant (SWTP) in The Netherlands for 2001. It is clear that the marine aquatic ecotoxicity potential (MAETP) dominates the environmental profile of the characterised emissions.

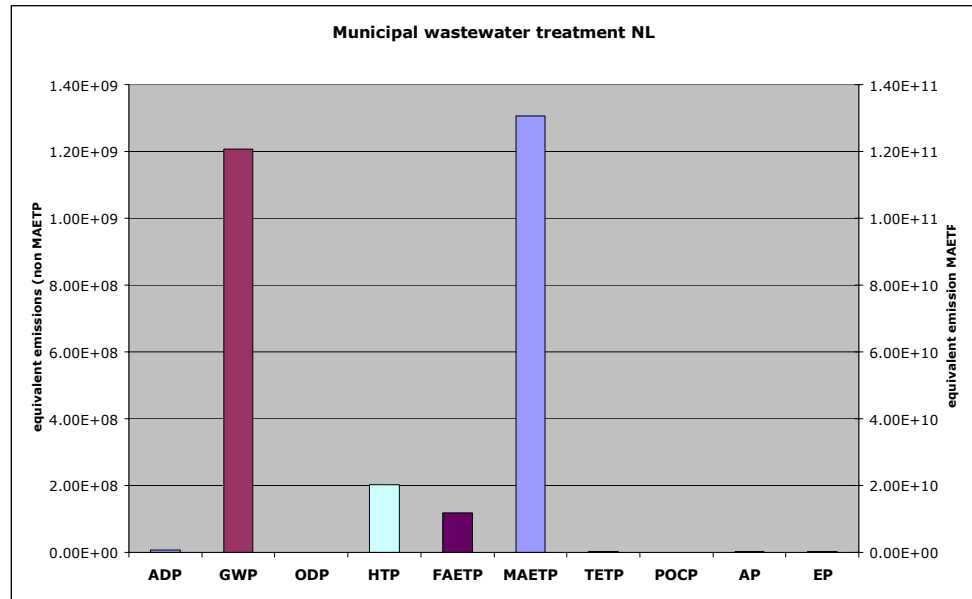


Figure 1 Environmental profile of municipal wastewater treatment in The Netherlands in 2001. Note that the equivalent emissions for MAETP are given on the right axis.

A contribution analysis shows that the use of electricity dominates, its contribution is over 90%, the MAETP impact category. Analysis of the substances mainly responsible (see Table 1) clearly shows that non-ferrous metals are in fact the only relevant substances.

Table 1 Main contributing substances to Marine Aquatic Ecotoxicity Potential.

No	Substance	Initial Compartment	Amount (kg 1,4-DB eq)	Cumulative contribution
	Total of all compartments	-	1.31E+11	100%
1	Se	Water	3.57E+10	27%
2	Ni	Water	3.47E+10	27%
3	Ba	Water	2.07E+10	16%
4	V	Air	1.27E+10	10%
5	V	Water	1.24E+10	9%
6	Cu	Water	5.15E+09	4%
7	Co	Water	2.51E+09	2%
8	Mo	Water	1.61E+09	1%
9	Zn	Water	1.56E+09	1%
10	Ni	Air	1.09E+09	1%
11	Se	Air	9.79E+08	1%
	Above substances	-	2.60 E+11	99%

It appears that for the fresh water aquatic ecotoxicity potential (FAETP), a less dominant impact category in Figure 1, more than 99% of the total is related to non-

ferrous metals. The effluent of the SWTP is, however, the main contributing process for this impact category.

From the above examples it is clear that emissions of non-ferrous metals can thus dominate the environmental profiles of many processes and products. The question has arisen whether this dominance of metals reflects reality.

## 1.4 Structure of the report

Chapter 2 gives an account of LCA, both in general terms and in more specific terms as to those parts of LCA that play a central role in this report: characterisation models and characterisation factors. Chapter 3 presents some critical issues and developments in the environmental assessment of metals. Chapter 4 discusses developments and explorations that are taking place within the field of LCIA, as far as they provide interesting connections for the developments in the environmental assessment of metals. This paves the ground for Chapter 5, in which a judgement is made to which extent the metal-specific knowledge is, can or should be incorporated in LCIA, and to which extent such developments are fundamentally incompatible with the philosophical, conceptual or mathematical structure of LCA. Here, we distinguish two lines:

- a short-term solution, in the form of guidelines for carrying out LCAs now;
- a long-term solution, in the form of a research agenda for identifying and prioritising developments in LCIA.

We end up with some final reflections in Chapter 6.

This report, although addressing issues that are of strategic interest, is not written from a managerial point of view. The problems related to unifying the LCA model and the advanced metal-specific models can only be discussed in relation to the fundamental set-up of both families of models, because incorporation of metal-specific models can only be done by adapting the fundamentals of LCA. This requires a thorough presentation of selected elements of these two families. At many places, the discussion is quite technical and involves the use of mathematical notation. This applies to large parts of Chapters 2, 3 and 4. Main points and conclusions can be singled out by concentrating on Sections 2.1, 2.2, 3.1 and Chapter 5.

## 2. Life cycle assessment

This chapter will provide a concise picture of LCA, with a focus on the elements of LCA that are important within the scope of the present subject, i.e. incorporation of metal-specific knowledge in the assessment of toxic impacts. The metal-specific issues themselves will not be discussed here, but are specifically addressed in Chapter 3.

### 2.1 Overview

LCA is an abbreviation of life cycle assessment, but it must be made clear from the outset that we have a more precise concept in mind. In this report, the term LCA will primarily refer to the ISO-standardised quantitative environmental life cycle assessment of products.

Life cycle assessment, then, is defined as the “compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle” (ISO 14040, p. 2). In life cycle assessment, the central objects of analysis are a product function and the industrial and other processes connected to it. Thus, the function of lighting a room can be fulfilled with a lamp, wiring and electricity, but the system extends to the transportation of coal from mines to power plants, the production of electric wires and glass, the mining of fossil fuels and metals, the disposal of used lamps, the recycling of copper wires, etc. It is immediately clear that LCA is a complicated exercise:

- A life cycle easily involves hundreds of processes;
- These processes emit a large variety of chemicals, from CO<sub>2</sub> to mercury, and from phenol to SO<sub>2</sub>;
- These processes use a large variety of natural resources, from iron ore to crude oil, and from trees to arable land;
- These processes take place throughout a long span of time (decades may elapse between the production of machinery and the final disposal of the recycled glass);
- These processes take place in a large geographical setting (although part of the life cycle may be localised in one country or region, many of the resources come from all over the world).

Obviously, simplifications are necessary to make LCA analysis feasible. The analysis must also follow a clear and transparent protocol.

In developing a method for LCA, a general framework has been set up. The ISO 14040 standard distinguishes four main phases in LCA:

- Goal and scope definition
- Inventory analysis
- Impact assessment
- Interpretation.

The phase of goal and scope definition largely deals with formulating the precise question to be answered, e.g. what is the exact function of the system and where do its boundaries lie. This phase also involves setting some a priori restrictions.

Inventory analysis focuses on outlining the structure and interdependency of the processes in relation to the product function analysed. Quantification of emissions and resource extractions per process finally lead to the overall emissions and resource extractions for the entire product system. The emissions and resource extractions together are referred to as the environmental interventions of the product system.

The third phase, impact assessment, aims at aggregating and interpreting the results of the inventory analysis. For instance, emissions of greenhouse gases are converted into one score for climate change; emissions of acidifying substances are converted into one score for acidification, etc.

Interpretation, finally, provides an array of possibilities for investigating the consequences and solidity of the results. This phase can include uncertainty and sensitivity analyses, comparison of the results with previous results, decomposition into contributing parts, etc.

In this report, the emphasis will be on impact assessment. This phase will be discussed in more detail below.

## **2.2 Life cycle impact assessment**

Life cycle impact assessment is traditionally divided into a number of elements (ISO 14042, Guinée et al., 2002):

- Selection of impact categories;
- Selection of characterisation methods: category indicators, characterisation models and factors;
- Classification;
- Characterisation;
- Normalisation;
- Grouping;
- Weighting.

The first element, the selection of impact categories, deals with the identification and definition of relevant impact categories. The CML Handbook (Guinée et al., 2002) distinguishes baseline impact categories, study-specific impact categories, and other impact categories (see below).

The selection of characterisation methods, secondly, deals with the identification and definition of appropriate category indicators, characterisation models and characterisation factors. An example may provide some clarity here. Climate change is a baseline impact category in the CML Handbook (Guinée et al., 2002). But this is only the name that we are to attach to a numerical result that must be calculated. In other words, behind an impact category there is a mathematical structure: a number, a model, or several of these. For climate change, we have the choice of modelling infrared absorption, temperature increase, sea-level rise, change in life-expectancy, etc. The chosen endpoint of the model is referred to as the category indicator. For climate change, Guinée et al. (2002) choose infrared radiative forcing as the category indicator. The model, which translates emissions of greenhouse gases into changes in infrared radiative forcing, has been developed by IPCC, the International Panel on Climate Change. Characterisation factors that are used to calculate the increase in infrared radiative forcing as the result of a unit emission of a certain greenhouse gas, can be derived from this model. IPCC refers to these factors as the GWPs, the global warming potentials. It should be mentioned that IPCC in fact provides several sets of GWPs, for different time horizons. In choosing a baseline characterisation method for climate change, Guinée et al. (2002) had to choose among the various models available and within the chosen model among the various variants available.

Guinée et al. (2002) provide an overview of baseline impact categories and associated baseline characterisation methods, such as:

- Depletion of abiotic resources;
- Impacts of land use: land competition;
- Climate change;
- Stratospheric ozone depletion;
- Human toxicity;
- Ecotoxicity: freshwater aquatic ecotoxicity;
- Ecotoxicity: marine aquatic ecotoxicity;
- Ecotoxicity: terrestrial ecotoxicity;
- Photo-oxidant formation;
- Acidification;
- Eutrophication.

During the third step in life cycle impact assessment, classification, the results from the inventory analysis are assigned to the impact categories in a qualitative way. Guinée et al. (2002) propose to skip this step once the previous steps have been reported.

In the characterisation phase, fourthly, the indicator results are calculated. These are obtained by applying the characterisation model to the inventory results. Alternatively phrased, one multiplies each environmental intervention with the corresponding characterisation factor, and aggregates the results within each impact category. In the section below we will discuss the characterisation step in more detail.

The remaining elements within life cycle impact assessment, normalisation, grouping and weighting, are beyond the scope of this report. ISO 14042 and Guinée et al. (2002) provide definitions and interpretations.

### 2.3 Characterisation

Traditionally, characterisation proceeds by a simple formula:

$$IR_c = \sum_s CF_{cs} \times m_s$$

where  $IR_c$  is the indicator result for impact category  $c$ ,  $CF_{cs}$  the characterisation factor that connects intervention  $s$  with impact category  $c$ , and  $m_s$  the size of intervention  $s$  (i.e. the mass of substance  $s$  emitted). This approach has been used in formulas such as

$$CC = \sum_s GWP_s \times m_s$$

where  $CC$  is the indicator result for climate change, and  $GWP_s$  the global warming potential for substance  $s$ .

The IPCC model, from which the GWPs are derived, is a large model. Most LCA practitioners and even LCA experts have never seen or studied it in detail. The model yields GWPs which can be interpreted as a characterisation factor and then added to a formula for characterisation. For a small number of impact categories, such ready-made characterisation factors from authoritative bodies are available. Apart from GWPs for climate change, there are ODPs for stratospheric ozone depletion and POCPs for photo-oxidant formation. For many impact categories, however, characterisation factors are not directly available. In these cases, they must be constructed from models, either existing or self-constructed. Thus, Guinée et al. (2002) present APs for acidification, HTPs for human toxicity, etc. In discussing characterisation factors, it is thus necessary to discuss the underlying characterisation models, and the way characterisation factors are derived from such models.

As a general recipe for deriving characterisation factors from characterisation models, the following equation is used:



$$CF_{cs} = \frac{\partial I_c(m_1, m_2, \dots)}{\partial m_s}$$

where  $I_c$  is the indicator for impact category  $c$ . We see that the impact principle is based on two assumptions:

- The intervention is small in comparison with a background, hence the use of infinitesimal calculus;
- The background of other substances is kept constant, hence the use of a partial derivative.

Technically speaking, we treat characterisation factors as the first-order approximation from a Taylor series of the characterisation model (Heijungs & Suh, 2002).

This means, among other things, that the validity of the characterisation factors critically depends on two issues:

- The validity of using a first-order Taylor approximation;
- The validity of the characterisation model, embodied by the indicator  $I_c(m_1, m_2, \dots)$ .

The first of the two is a general LCA issue and touches the foundations of LCA, as it is related to the purpose and realm of application of LCA. Although we will occasionally touch upon this problem, we will generally consider the context of LCA as a given for this project. The second issue is one that should be studied for every impact category. In this report, a discussion of the characterisation model and indicator for toxic impacts of pollutants, and of metals in particular, receives a central position.

The section on historical approaches will provide some concrete examples of the construction of characterisation factors. It should be stressed that not all texts on characterisation give a clear specification of the underlying characterisation models. In fact, the entire concept of an underlying characterisation model has emerged only recently, and in the past many tables with characterisation factors were constructed without a proper discussion of the characterisation model.

Given the scope of this report, a brief consideration of toxicity-related principles is inevitable. Models for toxicity assessment often stem from the field of risk assessment (RA); see also Section 3.1. Given the fact that RA has many meanings and can take on many forms, we will restrict the discussion here to a specific form of chemical risk assessment, in which risk has the meaning of high probability and low risk. The type of risk assessment we will be dealing with is the type of study that is used by the EU, the OECD, US-EPA and other regulating bodies for controlling the admission of chemicals and setting policy priorities. Well-known models in this field are IMPACT 2002+ (Jolliet et al., 2003), USES/EUSES (Huijbregts, 1999) and CalTOX (Hertwich et al., 2001); see De Koning et al. (2002). These models attempt to answer questions such as: what is the risk to ecosystems of the continuous release of a defined chemical in a defined amount? Besides a model for emission estimation, risk assessment models developed to answer this type of questions contain:

- A model for estimating the pathway of the chemical through the environment (the fate model);
- A model for estimating the exposure of target organisms to the chemical (the exposure model); and
- A model for estimating the dose-response characteristics (the effect model).

In many models for risk assessment, the exposure model for ecotoxicity is skipped; it is used solely for human toxicity, to model the pathways from air, water and soil to the human body through consumption of crops, meat and milk. However, there is reason to believe that for certain target ecosystems the prevailing concentration of pollutants (which is the outcome of the fate model) cannot be directly connected to the dose-response relationship. In those cases, a more sophisticated exposure model should be included. On the other hand, the effect measure for ecosystems is often determined with the underlying exposure pathway as part of the experimental set-up.

A key element in the USES/EUSES and related models is the so-called PEC/PNEC approach. For a specific substance,  $s$ , the fate model translates a given continuous release  $\Phi_{is}$  into a steady-state concentration in one or more compartments. This is referred to as the predicted environmental concentration, the PEC:

$$PEC_{cs} = C_{cs} = \sum_i T_{ics} \Phi_{is}$$

The coefficients  $T_{ics}$  reflect the modelling structure of the multimedia fate model. The effect model translates toxicity information (like NOELs and EC50s) for a variety of species into a predicted no-effect concentration, a PNEC, for a specified target ecosystem. PEC and PNEC are subsequently compared to each other.<sup>1</sup> Their ratio, PEC/PNEC, is referred to as the risk characterisation ratio (RCR):

$$RCR_{cs} = \frac{PEC_{cs}}{PNEC_{cs}}$$

The RCR is a dimensionless pure number. It should be below 1 in risk management. A value of 1 or higher indicates a possibly problematic situation, a value below 1 but close to 1 indicates that more detailed research is needed. Besides being used for regulating permits, the RCR can be used for comparing a range of substances, in order to set priorities in substance policy. In LCIA, the RCR can be calculated for a unit emission. It then provides a characterisation factor that can be tabulated. See Guinée et al. (2002) for extensive examples of such tables.

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<sup>1</sup> The PEC/PNEC approach has been set up for ecotoxicity, most notably concerning aquatic and terrestrial ecosystems, but to an increasing extent also for marine and sediment ecosystems. For human toxicity, the additional exposure step leads to a reinterpretation of PEC and PNEC into PDI and ADI, the predicted daily intake and the acceptable daily intake.

In USES-LCA, the effect parameter in the denominator is the PNEC, a presumed no-effect concentration which represents a concentration at which a negligible part (e.g., 5%) of the ecosystem is exposed to a stressful level of contaminants (the concentration being referred to as the HC5). In IMPACT 2002+ (Jolliet et al., 2003), the no-effect concentration that is used for the PNEC is replaced by an effect concentration that yields a so-called AMI. For this, the concentration at which half the ecosystem is affected, the HC50, forms the basis. It is presumed that a HC50 is a better and more stable indicator to compare the intrinsic toxicity of chemicals than the HC5. The SETAC Workshop in Lausanne has recommended the use of the HC50.

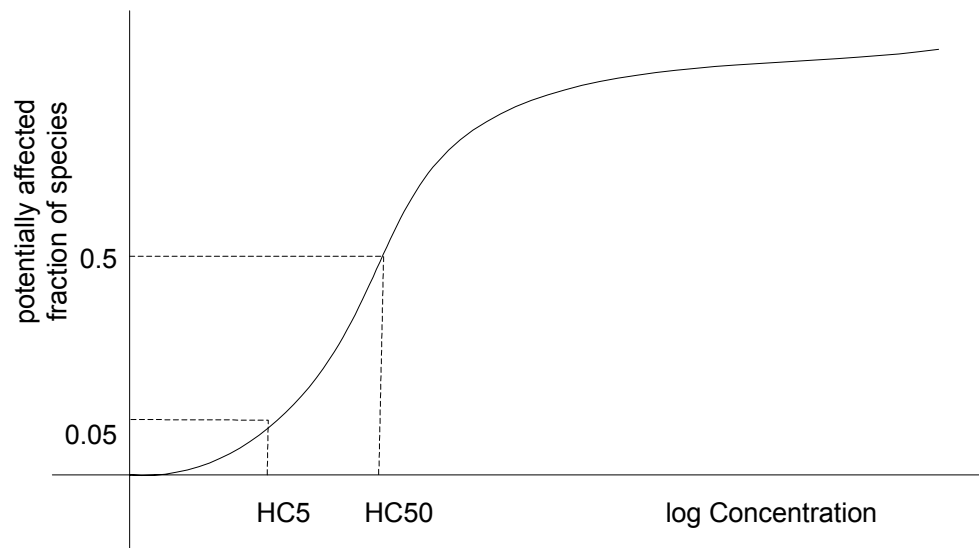


Figure 2 The dose-response relationship for ecosystems. Indicated are the HC5, which forms the basis of the PNEC in USES-LCA, and the HC50, which forms the basis of the AMI in IMPACT 2002+.

## 2.4 Fundamental limitations of characterisation

Above, the fundamental equation for characterisation was presented as:

$$IR_c = \sum_s CF_{cs} \times m_s$$

This equation, although deceptively simple, reflects some fundamental principles of characterisation. The following sections will discuss these principles as far as they are relevant to the problems addressed in this report.

### 2.4.1 Aggregation over space, time and substance variety

First, it should be noted that  $m_s$ , the size of intervention  $s$  (i.e. the mass of substance  $s$  emitted), has only one subscript:  $s$ . Typically, this index  $s$  runs over combinations of substance and emission compartment. Thus at the intervention level, phenol to air, phenol to water, mercury to water, mercury to soil, etc. are distinguished. The exact specifications of the substances and compartments differ per inventory and per characterisation method. The Handbook on LCA (Guinée et al., 2002) distinguishes the following emission compartments for ecotoxicity:

- Air;
- Fresh water;
- Seawater;
- Agricultural soil;
- Industrial soil.

As to substances, a few hundred are distinguished. Below, we list just a few to give an impression of the level of detail:

- 1,1,1-trichloroethane;
- 1,2,3,4-tetrachlorobenzene;
- 1,2,3,5-tetrachlorobenzene;
- acephate;
- acrolein;
- beryllium;
- carcinogenic PAHs;
- chromium III;
- chromium VI;
- copper;
- di(2-ethylhexyl)phtalate;
- mercury;
- dust (PM10);
- naphthalane;
- styrene;
- tin;
- zinc.

The intervention of a certain type is usually the result of the aggregation over the processes  $p$  along the entire life cycle:

$$m_s = \sum_p m_{sp}$$

Thus, no space-time characteristics are provided. Although the emission compartment may provide some information on the spatial details (e.g., emission to fresh water or to seawater), there is no information on whether an intervention takes place in a cold or a warm region, in a densely or sparsely populated area, near a nature area or at an industrial park, in a polluted environment or in a pristine area, in

a soil with a high or a low organic fraction, concentrated in one place or diffused over a long road, etc. Similarly, there is no information on the temporal scale: Is an emission taking place in summer or in winter, on a rainy or a dry day, concentrated in a few seconds or stretched out over a few weeks, etc.

To a large extent, the aggregation over processes is necessary for keeping the analysis feasible. Partly, it is even inevitable. A typical life cycle may involve hundreds or thousands of processes. Many of these processes do not take place at manageable facilities, but represent national or even global averages. For instance, the life cycle of a television set contains electricity generation for using the set, but this electricity does not come from your nearest power plant. All national power plants are connected with one another, so that any additional MJ of electricity tends to be produced by a weighted mix of all national power plants. This argument applies even more strongly to the required fuel: the oil market is a world market, and the oil needed to generate an MJ tends to come from all oil wells in the world. It is therefore fundamentally impossible to specify where a certain release takes place.

The level of detail as to the substances illustrated above, shows a distinct imbalance between certain organic chemicals. We see a distinction between 1,2,3,4-tetrachlorobenzene and 1,2,3,5-tetrachlorobenzene, and inorganic chemicals, whereas mercury is not further specified as to its form: metallic, ionic, methylated, complexed or as a compound. On the other hand, the fact that chromium III and VI are mentioned suggests that the other metals should be regarded as ions as well. Yet, metal ions are often not emitted directly; rather, they are formed by processes that take place in the environment. Some industrial processes, such as galvanic processes, emit metals in ionic forms. Care should thus be taken in specifying the form of metal emissions. On the other hand, one should acknowledge that many toxicity tests –used to derive HC5s and HC50s – disregard the speciation issue as well.

#### **2.4.2 The less-is-better paradigm and potential versus actual impacts**

The lack of space-time detail on the intervention side necessarily has consequences for the possibilities and the meaning of the results of the impact assessment. The possibilities for including threshold levels in LCIA are rather limited: for most non-global pollutants, the question as to whether or not threshold levels are surpassed depends on the location. In some places, thresholds are exceeded, in other places they are not. Such subtleties are beyond the resolution of a global inventory, in which releases of identical substances emitted at different places have been added. Consequently, most methods for LCIA are fairly global in nature: no distinct characterisation factors are provided for different regions or times. All kilograms of a certain pollutant are treated in the same way, irrespective of the environmental conditions, background levels, and so on. The corresponding paradigm has been coined 'the less-is-better principle' (White et al., 1995), and the impacts indicated

have been referred to as potential impacts (Guinée & Heijungs, 1993), to stress the fact that one is in fact looking at pollutants that have the potential to exhibit adverse effects, regardless of whether this potential is likely to be realised or not.

Understandably, the concept of potential impacts and the less-is-better paradigm have been criticised for generating false incentives (Perriman (1995), Owens (1996)). A feasible and operational alternative has not been developed, although several authors have proposed or even elaborated on models for particular substance groups or impact types (Potting (1998), (1996), Hogan et al. (1996), Krewitt et al. (1998), Wegener Sleeswijk (2003)). Whether or not potential impacts become actual impacts, generally depends on exposure conditions, background levels, presence of vulnerable species, and other local conditions.

In the case of metals, an additional complication is essentiality: some metals do not only have the potential to cause adverse effects, but also to cause beneficial effects (Van Tilborg, 1995?). Which of the two effects will operate depends on local circumstances.

### 2.4.3 The linearity of the dose-response relationship

Another related aspect that is implied by the general characterisation formula is the linearity of the effects. The indicator result that is calculated is a linear aggregation of interventions. Thus, non-linearities contained in the dose-response curve are excluded, and the possibility of synergistic or antagonistic effects due to toxicity mixes is not taken into account. Obviously, non-linear responses require more locally specified information than can be delivered by current LCA methods.

It is important to specify what exactly is meant by linearity. Even when the underlying fate models contain non-linear relationships, in the sense that for instance the Octanol-Water Partition Coefficient  $K_{ow}$  enters the model in a logarithmic form, the relation between emission size and concentration may still be linear. As shown in Section 2.3, characterisation factors represent a first-order Taylor approximation, and are calculated from characterisation models by means of partial derivatives. No second-order terms are involved, and no cross-dependency of input parameters is taken into account. Thus, the characterisation step involves a linear calculus, even though the underlying characterisation model may or may not be linear. Whether or not the linear calculus of characterisation is appropriate remains an important question.

Another question, of course, is whether the underlying characterisation model is linear or non-linear. The IPCC model for climate change and the different models for photo-oxidant formation are non-linear models in the sense that doubling the emission will not double the impact. The multimedia fate models and the

PEC/PNEC dose-response models are linear in this sense. We will discuss these two briefly.

Multimedia fate models (also called evaluative fate models, fugacity models, box models, or Mackay models) are models that aim to predict the fate of chemicals in the environment. Fate is here understood to mean: Where will a chemical emitted to an initial compartment end up after a specified time? The models consider a number of compartments (typically air, water, soil and sediment) and specify mathematical equations for the transport between compartments and the degradation within a compartment. Typical transport processes modelled include: evaporation from water to air, advection with rain from air to water and soil, run-off from soil to water, sedimentation from water to sediment, re-suspension from sediment to water and a few more. Degradation processes may include biotic and abiotic degradation. Mass balance equations are set up for every compartment. Then a system of differential equations is defined. These describe the time-pattern of concentration in the various compartments:

$$\begin{aligned}\frac{\partial C_a}{\partial t} &= -T_a C_a(t) + T_{wa} C_w(t) + \dots + \Phi_a \\ \frac{\partial C_w}{\partial t} &= T_{aw} C_a(t) - T_w C_w(t) + \dots + \Phi_w \\ \dots &= \dots\end{aligned}$$

where  $C_a$  and  $C_w$  denotes the chemical's concentration in air and water,  $t$  is time, the various  $T$ s represent transport and degradation coefficients, and  $\Phi_a$  and  $\Phi_w$  denote emission fluxes to air and water. The ellipsis (...) indicate that similar terms and equations are to be supplied for soil, sediment and so on, with additional subscripts.

The system of differential equations may next be considered in two different ways:

- as defining a dynamic trajectory  $C_a(t)$ ,  $C_w(t)$ , etc. either with a continuous time parameter, or at discrete time intervals, say every day, week or year;
- as defining a steady-state condition, by putting the left-hand side at zero, and solving for  $C_a(\infty)$ ,  $C_w(\infty)$ , etc.

The second option is by far the form most frequently seen both in RA and in LCA. It is based on the possibility of writing all coefficients  $T$  in a matrix  $\mathbf{T}$  and arranging the concentrations  $C$  and emission fluxes  $\Phi$  in vectors  $\mathbf{C}$  and  $\Phi$ . The system of differential equations then becomes:

$$\frac{\partial \mathbf{C}}{\partial t} = \mathbf{T}\mathbf{C}(t) + \Phi$$

and the steady-state condition  $\partial \mathbf{C} / \partial t = \mathbf{0}$  easily provides a solution for  $\mathbf{C}$ :

$$\mathbf{C}(\infty) = -\mathbf{T}^{-1}\Phi$$

where the superscript -1 denotes the inverse of the matrix.

A similar analysis holds for the effect part of the characterisation. In the usual PEC/PNEC setup, a fully linear dose-response is assumed; see Figure 3. A general formula is:

$$RCR = \frac{C}{PNEC}$$

and the  $1/PNEC$  is a simple constant of proportionality.

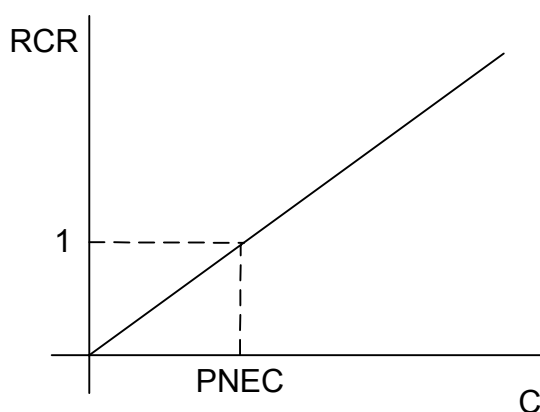


Figure 3 The dose-response relationship for the PEC/PNEC approach.

Obviously, modelling non-linear responses requires more locally specified information than can be delivered by current LCA and even more by available information on dose-response and effect data.

#### 2.4.4 Mass loading (pulse) versus flow rate (flux), and time-integration

A further observation is the fact that the characterisation formula contains a mass loading term (in kg) intervention. Most multimedia fate models require the specification of a mass flow rate (in kg/s). Most dose-response relationships are based on concentrations (in kg/m<sup>3</sup>). Hence, there is a mismatch between what LCI delivers and what RA models require. The incompatibility of the mass loading (emission pulse) and the mass flow rate (emission flux), especially, has given rise to the flux-pulse debate. Although the debate has settled by now, one must still be careful in specifying and interpreting the use of RA models for LCA.

In relation to persistent chemicals, the use of multimedia fate models requires some further consideration at this point. LCA may be conceived in two different ways:

- There is a constant background of anthropogenic and non-anthropogenic pollution, and LCA deals with the modelling of the additional impacts of one extra product;



- There is an initial background of anthropogenic and non-anthropogenic pollution, and LCA deals with the modelling of the change to a new state with one extra product per time unit.

We will discuss and illustrate these two approaches briefly.

In the first case, the extra product leads to extra emissions at a certain point in time. These extra emissions induce a temporary increase in the ambient concentration of certain chemicals. After some time, removal mechanisms, like biodegradation and immobilisation, will have been effective in re-establishing the old steady-state background level. The LCA then focuses on the time-integrated increase of concentration and/or impact due to the temporary increase in concentration and/or impact. The integration begins at the onset of the change. The end time may be set to infinity to ensure that all distortions of the steady-state have been put to an end. For several reasons, a finite time horizon, such as 100 years, is sometimes used.

The second case is addressed by the comparison of an initial and a final steady state. The difference in concentrations and/or impacts is expressed in terms of a difference per unit of product. The initial concentration is the concentration before the change; the final concentration is the concentration measured when all changes have come to rest. As in the first case, this may require an infinite time, but in some situations a finite time is used.

General formulas<sup>1</sup> for these two interpretations are:

$$IR = \int_{t_0}^{t_1} C(t) dt$$

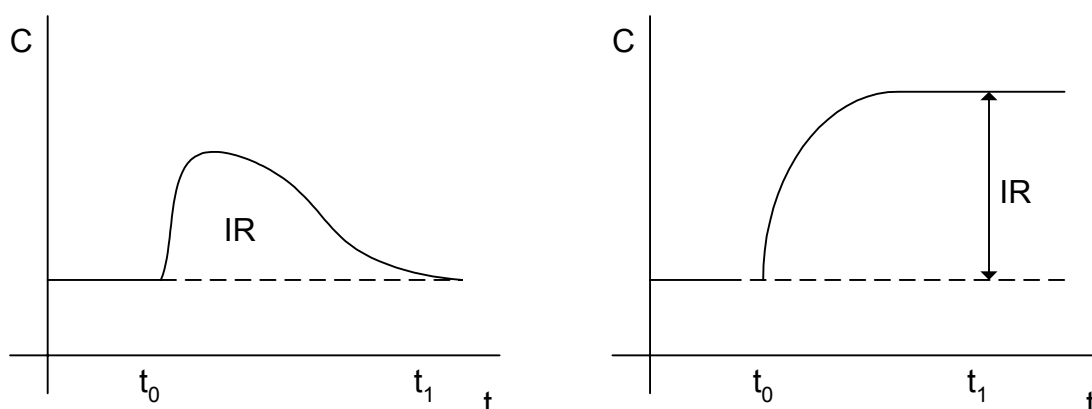
for the dynamic case, and:

$$IR = C(t_1) - C(t_0)$$

for the comparison of steady states. The two forms are illustrated in Figure 4.

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<sup>1</sup> In practice, the situation is slightly more complicated: the indicator is not a concentration, but some measure of impact, say, the concentration divided by the PNEC or a different threshold value.



*Figure 4 Illustration of the two interpretations of the dose-response relationship: in terms of the time-integrated deviation of the indicator (here: the concentration C) from the steady-state level (left) and in terms of the difference between an old and a new steady-state level of the indicator C (right).*

Although both forms contain the term  $IR$ , it should be observed that the dimensions of these quantities differ. When  $C$  is measured in  $\text{kg}/\text{m}^3$ , and  $t$  in s, the first expression for  $IR$  yields  $\text{kg}\cdot\text{s}/\text{m}^3$ , and the second one a form that corresponds with a concentration:  $\text{kg}/\text{m}^3$ . The second form is easily connected with a PEC/PNEC effect assessment, for the first form this is not clear.

Under certain conditions, the two approaches and interpretations give identical results. But both approaches pose problems when the equilibration time is very long. Consider, for instance, the release of metals to the environment, and the impacts on marine ecosystems. One may argue that there is no empirical evidence that atmospheric emissions lead to increased concentrations in seawater, although the models suggest there is. One should, however, bear in mind that the models are steady-state models, and that predicted changes in concentrations in seawater are changes that may become apparent in the long term only. It may very well be that we have been measuring only before the onset of changes.

This is not the place to settle these controversies. Our purpose here is only to point out the sometimes counter-intuitive interpretations of a steady-state model in LCA.

For both interpretations, an infinite time is required: infinite time-integration guarantees that long-lasting impacts are also fully taken into account, and an infinite waiting time guarantees that the new state is indeed a steady state. However, infinite is sometimes too long. For instance, the climate change models take into account future emission scenarios to determine the effects of releases currently taking place. Predicting emissions a hundred years in advance is not easy, but predicting emissions for eternity is obviously nonsensical. Therefore, in certain cases, a finite time horizon is chosen in impact assessment. Global warming potentials are available for different time horizons, and a choice of 100 years is quite normal.

Another example is related to the impacts of radioactive substances. Time-integration of impacts for isotopes with a half-life time of several billions of years requires the inclusion of impacts at dates so remote that by then the sun will have ceased to burn. The infinite time horizon for ecotoxicological impacts could also be considered inappropriate, as the species on which the PNECs are based may have become extinct by then due to other causes, or evolutionary mechanisms may have led to an adaptation of the target organisms. An alternative to a finite time-horizon is time-discounting, where every future year has a lower weight. Incorporating autonomous or forced changes of ecosystem composition and discounting schemes requires, besides the technical knowledge, an ethical discussion on the desirability and consequences of such methodological modifications.

#### **2.4.5 Trade-off between substances and comparisons across substances**

LCA usually deals with product comparisons. Product A is compared to product B, or a redesigned product is compared to the original one. In comparisons, high scores for one chemical may be compensated by low scores for another chemical within the same impact category. A product life cycle that emits small amounts of a large number of chemicals may be worse than a product life cycle that emits vast amounts of only one chemical. In other words, there is a trade-off between substances contributing to the same impact category, and LCA may be said to be based on compensatory indicators. This compensatory effect is sometimes a source of misunderstanding.

One of the fundamental consequences of this trade-off mechanism is that the use of threshold values and toxicologically safe levels is problematic. In assessing the hazard of a chemical, regulating bodies want to know the reference dose at which no adverse effects to ecosystems (or to human beings) are observed. In determining these levels, safety factors are often used to extrapolate from single species to ecosystems, and from a laboratory to the field. In this way, threshold values are artificially reduced by a factor of 10 or 100 in order to be sure that no impacts will show up. It is like building a bridge with oversized materials, in order to be sure that the structure will not collapse. Although this deliberate oversetting<sup>1</sup> of acceptable levels may be defensible from a security point of view, its use in compensatory and comparative evaluative tools creates problems. In comparisons, and therefore also in compensatory indicators, balance is the keyword. A comparison of two products makes little sense if one of the products has been assessed on the basis of exaggerated safety factors, while the other product has been assessed with the best-available data, without any safety correction.

This applies to safety factors, but also to the level of sophistication of the models. If a poor model is used for the majority of substances, and a good model for only a

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<sup>1</sup> Note that in certain cases safety factors are not conservative, but may turn out to represent underestimates or quite good approximations.

few substances, the resulting analysis will be out of balance. The poor model may give an over- or underestimation of the results that would have been obtained with the more sophisticated model.

A general conclusion is that one should not automatically use the best model and state of knowledge in a model with compensatory mechanisms, like LCA. On the other hand, if one uses the lowest quality model, a large amount of useful information will be wasted. One of the problems of LCA is striking the balance between consistent use of bad models and inconsistent use of the best available models.

## 2.5 A historical overview of approaches

This section gives a brief tour through the library of models for LCIA of toxic releases. It does not give a systematic account, but focuses on the historical development and the resulting changes in characterisation factors. For an overview and comparison of the currently used models, we refer to De Koning et al. (2002).

### 2.5.1 Model developments

The oldest form of life cycle impact assessment for toxic substances is to lump the masses released. Pollutants are simply treated in a less-is-better paradigm, without any consideration of differences in inherent hazard or persistence. This form can be written as:

$$IR = \sum_i m_i$$

so without a distinction of impact categories, with effectively all characterisation factors being equal to 1:

$$CF_i = 1$$

As characterisation factors can in retrospect be seen as being derived from a characterisation model, the apparent characterisation model is here:

$$I(m_1, m_2, \dots) = m_1 + m_2 + \dots = \sum_i m_i$$

An improvement came with the advent of so-called critical-volume approaches (see, e.g., Mekel and Huppes, 1990). The basic idea of a critical-volume approach is that 1 kg of a chemical with a threshold value of 1 mg/l can pollute 1,000,000 l up to the threshold, while 1 kg of a chemical with a threshold value of 2 mg/l can pollute 500,000 l. Hence, the threshold value may serve as the basis for a measure of hazard. The characterisation factors are:

$$CF_i = \frac{1}{TV_i}$$

where  $TV_i$  is the threshold value for substance  $i$ . Such characterisation factors point towards a characterisation model:

$$I(m_1, m_2, \dots) = \frac{m_1}{TV_1} + \frac{m_2}{TV_2} + \dots = \sum_i \frac{m_i}{TV_i}$$

Several developments can be distinguished within the critical-volume approach, for instance older forms on the basis of legal standards, and newer forms on the basis of purely toxicological laboratory or even field data.

The incorporation of a fate model meant another step forward (see, e.g., Guinée and Heijungs, 1993). Fate information as to persistence and multimedia transport was combined with critical-volume-like toxicity information. Characterisation factors are constructed by multiplying a fate factor ( $FF$ ) and an effect factor ( $EF$ ):

$$CF_{ijk} = EF_{ij} \times FF_{ijk}$$

Here,  $CF_{ijk}$  denotes the characterisation factor for substance  $i$  affecting target ecosystem  $j$ . The subscript  $k$  indicates the initial emission compartment. Thus, chemicals released to air may deposit to soil or water where they affect terrestrial or aquatic ecosystems. Effect factors are in most cases defined in a critical-volume method. Hence:

$$EF_{ij} = \frac{1}{TV_{ij}}$$

where  $TV_{ij}$  is the threshold value for substance  $i$  and target ecosystem  $j$ . Fate factors are obtained from an environmental box model. This may be a very simple one, in which only degradation is accounted for:

$$FF_{ijk} = \begin{cases} \frac{1}{DT50_{ij}} & j = k \\ 0 & j \neq k \end{cases}$$

where  $DT50_{ij}$  is the half-life time of substance  $i$  in compartment  $j$ . More sophisticated models include the multimedia transport between compartments:

$$FF_{ijk} = \begin{cases} T_k & j = k \\ T_{kj} & j \neq k \end{cases}$$

where  $T_{kj}$  indicates the transport coefficient for transport from compartment  $k$  to compartment  $j$  and  $T_k$  the removal from compartment  $k$  by means of degradation and transport. In general, Mackay-type multimedia models (see, e.g., Mackay, 1991 for an overview) are used to find expressions for the transport coefficients. These

models are based on first-order kinetics, steady state partitioning, and instantaneous homogeneous mixing within each compartment. The underlying characterisation models that give rise to these characterisation factors can be written as:

$$I_j(m_1, m_2, \dots) = \frac{C_{1j}(m_1)}{TV_{1j}} + \frac{C_{2j}(m_2)}{TV_{2j}} + \dots = \sum_i \frac{C_{ij}(m_i)}{TV_{ij}}$$

where  $C_{1j}$  is the steady-state concentration of substance 1 in compartment  $j$ . These concentrations are obtained from the fate model. For substance 1, for instance, we have:

$$C_{1j} = \sum_{k \neq j} T_{1kj} \frac{m_{1k}}{t} + T_{1j} \frac{m_{1j}}{t}$$

where  $T_{1kj}$  is the above-mentioned transport coefficient for transport from compartment  $k$  to compartment  $j$  for substance 1, and  $T_{1k}$  the removal from compartment  $k$  for substance 1. Note the introduction of the symbol  $t$  in the last equation. It represents an arbitrary time, such as 1 second or 1 day, which makes it possible to connect the intervention, the mass load or emission pulse  $m$ , to the steady-state fate model, which requires a flow rate or emission flux  $m/t$ . More information on the background and implications of this flux-pulse conversion is presented in Section 2.4.2.

Of a somewhat different nature is the method by Hauschild & Wenzel (1998), that is known as the EDIP-method. It is a semi-quantitative method, that combines toxicity, persistence and bioaccumulation, where the toxicity component is based on a PNEC, and the persistence, cross-media transport and bioaccumulation components are based on categorical variables, such as: the biodegradability factor is 0.2 if less than 60% degrades within 28 days.

## 2.5.2 Numerical comparison

From a theoretical perspective, there is a large difference between aggregating emitted masses, correcting for differences in toxicity, and correcting for differences in effect and toxicity. This does not tell us anything about numerical differences. Table 2 shows the characterisation factors for a selection of chemicals according to a number of characterisation methods. To dispose of the disturbing effect of differences in units and other irrelevant scale factors, all characterisation factors have been rescaled.

*Table 2 Characterisation factors for a selection of chemicals according to three different characterisation methods.*

<b>Substance</b>	<b>Mass</b>	<b>Threshold(a)</b>	<b>Effect(b) kg/mg</b>	<b>Fate and effect(c) (kg DCB-eq/kg)</b>
benzene	1	–	0.029	9.1E-2
aldicarb	1	–	3.1	4.4E5
DDT	1	–	1.3	2.9E4
TEQ	1	–	–	1.7E8
1,4-DCB	1	–	0.16	1.0
zinc	1	1/1000	0.38	9.2E1
copper	1	1/50	2.0	1.2E3
cadmium	1	1/3	200	1.5E3
chromium (VI)	1	1/50	1.0	2.8E1
lead	1	1/50	2.0	9.6
nickel	1	–	0.33	3.2E3
mercury	1	1/0.3	500	1.7E3

(b) Source: Mekel & Huppel, 1990, Appendix, p.36-37.

(c) Source: Heijungs et al, 1992, Vol II, p. 77-83. The number represents the ECA for emissions to water in kg/mg.

(d) Source: Guinée et al., 2002, Vol IIa, p.228-248. The number represents the FAETP for emissions to fresh water in kg DCB-eq/kg.

We see that the characterisation factors of substances over the years has changed considerably. But, more importantly, the ranking of substances has changed as well. Benzene has become less important, while aldicarb has become more important. Similar – and sometimes dramatic – changes can be seen for metals.

Changes in scale or units are unimportant, as LCA does not address actual risks and absolute values play no role. But relative changes will show up in results, decomposition of results, and recommendations. Such changes may lead to doubts on credibility and on the use of LCA as tool for decision-support. But one should not forget that LCA is a young discipline, involving a large set of disciplines and requiring many submodels and data. It is natural that the practice and the results of LCA change in the course of the years. In fact, even this reports aims to induce more changes, as will be clear from the final recommendations in Section 5.3.





### 3. Metals and the environment

This chapter provides an overview of some metal-specific issues in relation to environmental assessment. The purpose of this chapter is not to provide an overview of all issues, but only to the extent that is of interest in a discussion of possible LCA shortcomings in treating impacts from metals.

#### 3.1 HSE, RA and LCA

The first thing to note is that company-internal environmental practice is often anchored in an HSE unit, which is a staff department dealing with health, safety and environmental issues. These HSE units tend to focus exclusively on the ecological impacts, for instance on aquatic and/or terrestrial ecosystems, and not on human health. This is in contrast to LCA, where human toxicological and ecotoxicological impacts are addressed in conjunction and in quite similar ways. Safety, on the other hand, is an aspect that is most often ignored in LCAs, where the emphasis is on the impacts of regular operation, and incidences are only included on a statistical basis and to the extent to which they increase normal emission rates.

Most modern chemical regulating practices are based on information generated by risk assessments. These RA studies follow a standardised framework, consisting of the following steps (Van Leeuwen & Hermens, 1995):

- Hazard identification
- Dose-response assessment
- Exposure assessment
- Risk characterisation.

Hazard identification focuses on the identification of potentially adverse effects of the chemical. A well-known form of hazard identification is based on the so-called PBT aspects, i.e. persistence, bioaccumulation and toxicity.

Dose-response assessment tends to focus on the establishment of a PNEC, a predicted no-effect concentration, which is the concentration at which 95% of the species within an ecosystem are not expected to be affected.

Exposure assessment focuses on the establishment of the PEC, the predicted environmental concentration, which is the (steady-state) concentration that is measured or calculated given an emission scenario.

Risk characterisation finally proceeds to compare PEC and PNEC values. If the ratio between PEC and PNEC exceeds 1, problems may be expected. If the ratio is far below 1, the RA procedure suggests a safe situation. If values very close to 1 occur, further investigation is recommended.

Risk assessment and the models developed to perform the calculations originate from the necessity to regulate primarily non-polar organic chemicals. Many of the estimation routines are valid for chemicals with physico-chemical parameters that fall within a certain range. Use of the models outside those ranges, for instance for polar organics, inorganics or metals, may lead to serious under- or overestimates of PECs and/or PNECs. In the sections below, some processes and properties that are typical for metals or that work differently for metals than for non-polar organics will be discussed.

### 3.2 Speciation

The term speciation is not well defined. In its narrow “definition” it is used to describe the ability of elements to exist in different species with a single medium (e.g.  $\text{Cu}^{+2}_{\text{aq}}$ ,  $\text{Cu}(\text{OH})^{-1}_{\text{aq}}$  etc.). However, the concept speciation is also given a broader meaning. In LCIA it is often used to indicate the ability of substances (even organics) to exist in different forms in the environment in general (Birkved *et al.*, 2003). For example, sorption of the copper-ion to colloidal matter or the volatilisation of mercury are referred to as speciation processes. In this paper we will use the term speciation in this broader meaning.

One of the processes that make the behaviour of metals/elements stand out from that of non-polar organics is their ability to speciate much more extensively. Speciation can affect the fate of substances to a very large extent. Speciation processes include (without being complete) sorption of metals to dissolved colloidal organic matter, sorption to suspended particulate matter, precipitation, hydrolysis, redox and complexation reactions. In Figure 5 some of these speciation processes are shown, according Di Toro *et al.*, 2001. Some metals can also be methylated e.g. Hg and Ni (this is not shown in Figure 5).

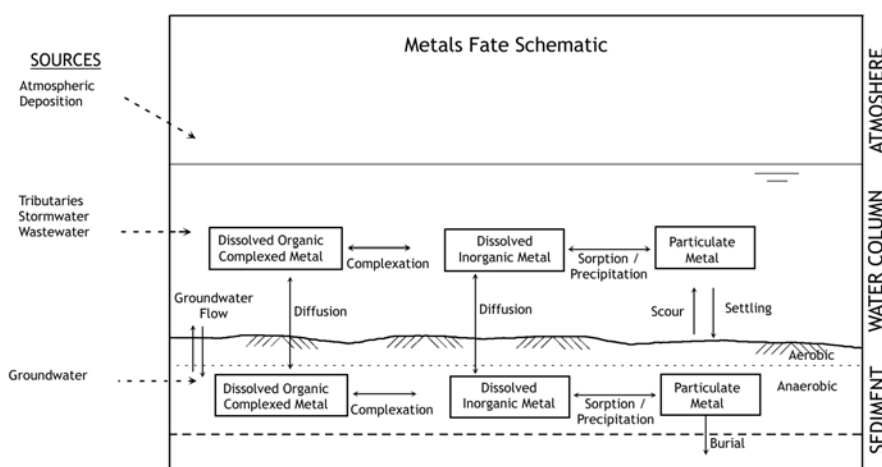


Figure 5 Fate of metals in the aquatic environment, adapted from Di Toro *et al.*, 2001.

All these speciation processes can affect the activity of the “free” metal ion and the transfer of the substance between soil, water, sediment and air. The speciation process is dependent on the kind of metal considered, the metal concentration, the reaction rate and the environmental conditions. See for example Figure 6, the influence of the different sorption properties of the metals on the residence time of the metal in a lake. In Figure 6 the residence time of metals in the water column is plotted as fraction of metals adsorbed to suspended particulate matter. The data have been taken from Diamond *et al.* (1990).

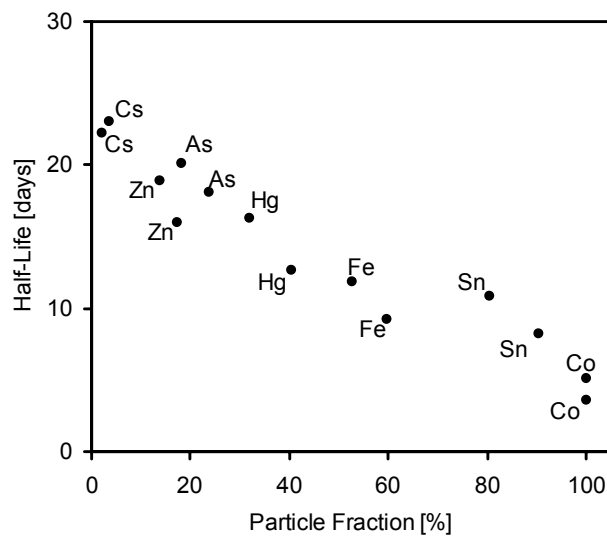


Figure 6 Summary of Half-Life versus particulate fraction for Perch Lake, Canada (Diamond *et al.*, 1990).

The trend shown in Figure 6 can be explained as follows. Metals can adsorb to suspended particulate matter. As the particulate matter with attached metals sinks to the bottom of the lake, the adsorbed metals are removed from the water column. If a larger fraction of the total metal concentration in solution is adsorbed to the suspended particulate matter, it will be removed more quickly from the water column; hence its residence time in the water column will be smaller.

Multimedia models cannot fully cover the complex process of speciation. Although there are software packages that can, MINTEQ (Allison *et al.*, 1991) or PHREEQ C (Parkhurst&Appelo, 1999) and their descendants probably being the most well known, these models cannot readily be incorporated into multimedia models. One fundamental problem is that the processes are often highly non-linear. Operational problems include the computing time needed for solving speciation problems, especially for spatially resolved multimedia models, and the lack of knowledge on speciation among general LCIA practitioners. Additionally the speciation process is strongly location dependent as local pH and Eh may strongly influence a metals species.

Fortunately, however, a correct assessment of the impact of metals in LCIA does not require full inclusion of the complex speciation process. The multimedia models only have to predict realistically the “free” concentration of the metal ion and the transfer of the metals through the environment. The multimedia models do not have to predict the correct concentration of every possible species. Other models, specifically targeted at this task, should be used for that. The “free” concentration of the metal ion has to be assessed correctly as it is one of the important parameters predicting the toxicological effect of the metal. There are exceptions to this general rule, but for reasons of simplicity they will not be considered here for the moment. The transfer of the metal ion between different media must be modelled correctly for correct assessment of the total concentration in the media and residence time of the metals in a specific medium.

A practical implementation of the speciation process in multimedia models which follows the above line of reasoning, has been worked out by Birkved and coworkers (Birkved et al., 2003; Birkved 2004). They suggest to give the individual compartments of the multimedia models a specific composition (salinity, temperature, pH etc.) which depends on the spatial composition. The inorganic species distribution in each compartment is fixed according to model results from advanced speciation models like PREEQ C. This approach is termed decoupled multi species by the authors.

### 3.3 Evaluative environment

The multimedia models used in LCIA (and RA) should be considered an evaluative environment which has fictitious but realistic environmental conditions such as volume, composition and temperature (Mackay, 2001). The multimedia models are given desired environmental conditions and then the behaviour of the substances of interest are mathematically explored. However, the environmental conditions should resemble the average environmental conditions of the area of interest (e.g. average World, average Europe, average Rhine catchment area).

As noted in the previous section, speciation of metals is highly dependent on these environmental conditions. If speciation of metals is to be taken into account in a consistent way, the environmental properties of the evaluative environment in the multimedia models must be defined rather precisely, at least in much more detail than is now customary.

A list of environmental properties to be specified for the fresh and marine water compartment includes:

- pH;
- Eh;
- Suspended particulate matter concentration;
- Dissolved organic matter concentration;

- Temperature;
- Etc.

A list of environmental properties for the soil environment to be specified includes:

- Colloidal matter concentration in pore water;
- pH
- Eh
- Soil moisture content
- Etc.

### **3.4 Speciation processes to include**

In Section 3.2 it was noted that for a correct assessment of the impact of metals in LCIA it is not necessary to include the complex speciation process in all its details. The speciation process need only be taken into account as far as speciation affects the “free” concentration of the metal and the transfer through compartments.

Below we suggest which speciation processes should and can be incorporated in the multimedia models for the correct assessment of the impact of the metals in LCIA. The list does not cover physical processes like diffusion across sediment-water interface, but only includes chemical processes. The list is a first attempt to specify the most important processes to be taken into account and is open for discussion.

#### **3.4.1 Sorption processes**

Sorption of metals to organic and inorganic material is one of the important processes responsible for reducing the bioavailability of metals in the environment. Sorption of metals to soils, sediments, suspended particulate matter etc. is a highly non-linear process. Generally speaking, metal ions are very strongly bound to the surface of the solids if the surface concentrations are very low. At increasing surface loading the metal ion becomes less specifically bound to the surface, meaning that a higher fraction of the metal remains in solution and hence remains (bio)available. As an example Cu sorption to a clay soil is shown in Figure 7, data from Sposito (1984).

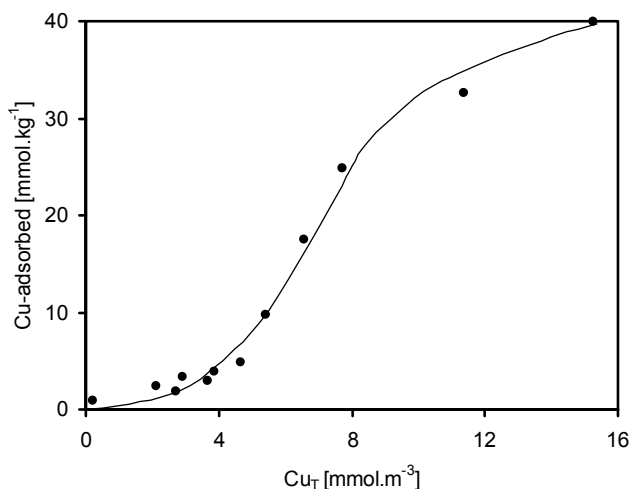


Figure 7 Non-linear sorption of copper to a clay soil.  
Figure adapted from Sposito, 1984.

Sorption of metals to solids is extremely dependent on environmental properties like pH, concentration of counter-ions and specific properties of the adsorbate, such as sorption capacity. For instance, adsorption of caesium to anoxic sediments is very much influenced by the ammonium concentration in these sediments, as caesium and ammonium compete for the same adsorption sites. An example is shown in, data from Comans *et al.*, (1989) and Comans (1999).

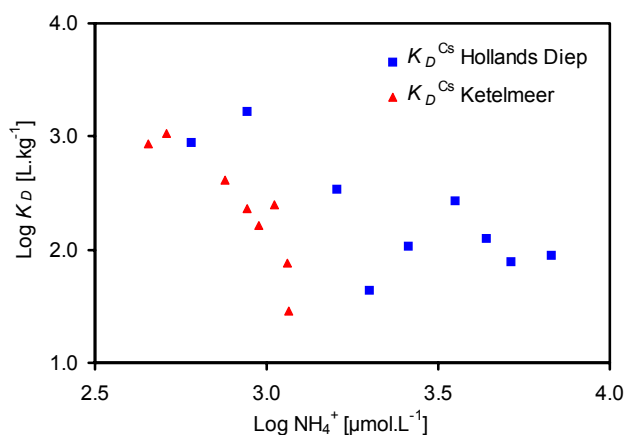


Figure 8 In-situ measurement of the adsorption of caesium to two freshwater sediments in the Netherlands as a function of pore-water ammonium concentrations. Data on Ketelmeer sediment from Comans *et al.*, (1989) and data on Hollands Diep sediment from Comans (1999).

Sorption is also very much dependent on the adsorption time. See, for example, the adsorption of trace amounts of caesium as a function of time (De Koning & Comans, 2004).

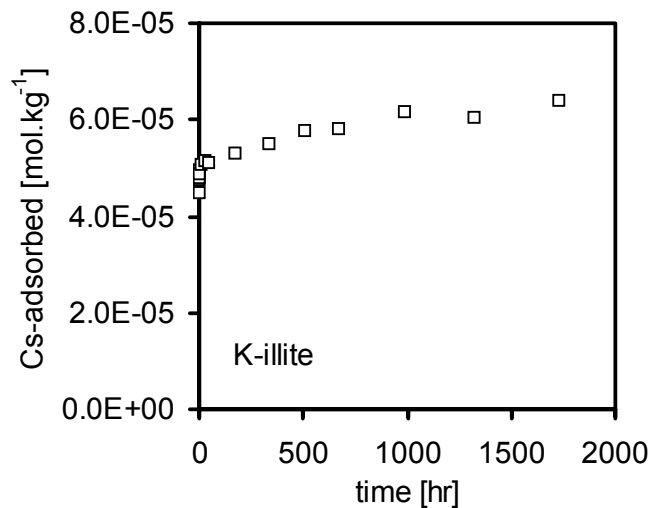


Figure 9 *Ceasium adsorption to a clay mineral as a function of time. Measured on a K-saturated illite in the presence of  $1 \times 10^{-4}$  M KCl environment at a total caesium concentration of  $3.3 \text{ nmol.L}^{-1}$  in the experiment.*

In summary; sorption is highly non-linear, extremely dependent on environmental conditions and very much dependent on the sorption time.

Detailed modelling of this non-linear sorption process cannot be done within the multimedia models for application in LCIA, but the non-linear adsorption process can be approximated on small concentration ranges by a linear adsorption isotherm, which is defined by the  $K_D$ .

In the current multimedia models the  $K_D$  is one of the most common parameters significantly influencing the calculated characterisation factor. Hence it is important to select the right value for this parameter. The  $K_D$  to be used in the models should be applicable to the “evaluative” environment selected. This means that the  $K_D$  selected should be chosen at a relevant loading level of the sorbate with the substance and under the relevant environmental conditions. The  $K_D$  should also be applicable to steady-state conditions.

In as far as appropriate<sup>1</sup>, the sorbates that have to be included into the multimedia models should at least be:

- Soil (particulate);
- Sediment (particulate);
- Suspended particulate matter;
- Colloidal organic matter<sup>2</sup>;
- Particulate matter in air.

Generally speaking, the current multimedia models do not consider adsorption of metals to colloidal organic matter in the water-phase. This is probably due to the limited amount of knowledge available on metal sorption to colloidal organic matter. The authors think that recent progress made in the field of metal sorption to humic acid/fulvic acids, may make it possible to include this process into state-of-the-art multimedia models.

### 3.4.2 Complexation, hydrolysis and redox reactions

In the water phase, metals can form complexes with many of the available anions like  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ . For instance,  $\text{Cd}^{+2}$  can very easily form chloride species according to:



The stability constants have been taken from Lindsay (1979). In seawater, which has a chloride concentration of  $19344 \text{ mg.L}^{-1}$  (Chester, 1990), the above reactions are responsible for the decrease of the "free"  $\text{Cd}^{+2}$  concentration of 96 % (at a total Cd concentration of  $1 \times 10^{-5} \text{ mol.L}^{-1}$ )  $\text{Cd}^{+2}$ .

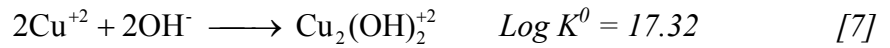
Other metals like  $\text{Cu}^{+2}$  can form hydrolysis species. A well-known example is the  $\text{Cu}^{+2}$  ion:



<sup>1</sup> E.g. if a multimedia model only focuses on the fresh water environment, sorption to soil is not included.

<sup>2</sup> The difference between suspended particulate matter (which often has an high organic matter content) and colloidal organic matter is their size. Suspended particulate matter can be retained with a  $0.45 \mu\text{m}$  or  $0.2 \mu\text{m}$  while colloidal organic matter passes these filters. Suspended particulate matter is subject to sedimentation while colloidal organic matter is not.





All stability constants have been taken from Lindsay (1979) except the one for  $\text{Cu}(\text{OH})_2^0$ , which has been taken from Morel & Hering (1993). It shows how Cu speciation is influenced by the pH of the medium, calculated with the equations given above.

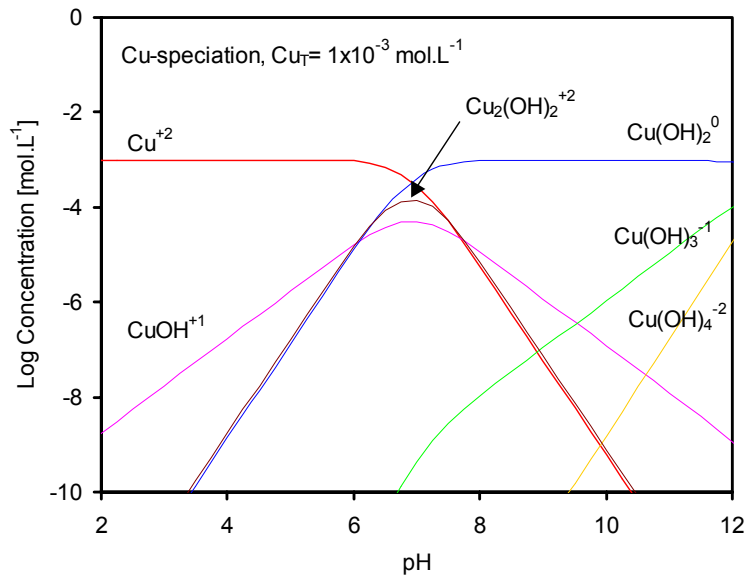


Figure 10 Calculated speciation of copper as a function of pH at a total copper concentration of  $1 \times 10^{-3} \text{ mol.L}^{-1}$  using Equations 4 to 7 given above.

According to hypothetical calculations, at a pH of 7, only 27 per cent of the copper is in the  $\text{Cu}^{+2}$  species.

Again, it is not feasible to include these complexation and hydrolysis reactions into the multimedia models. However, given the fact that the evaluative multimedia environment is a fixed evaluative environment it does seem feasible to calculate only once for each metal the “free” fraction of the metal in the water phase and to use this fixed factor in the model. Alternatively, measured values for the free ion activity could be used. How this simplification affects diffusion across sediment-water interface or air-water interface is not known.

### 3.4.3 Precipitation and dissolution

Many metals can form precipitates. In anoxic fresh water sediments, heavy metals are often precipitated in the form of sulphides, which have a very low solubility. Examples are CuS, ZnS etc. (Groenendijk, 1990).

The formation of these precipitates can cause the concentration of the metal in the sediment compartment to be independent of the load to the compartment.

Considering the fact that the typical characterisation factor is derived from the predicted environmental concentration after long reaction times (> 100 year), a lot of slow but eventually (if enough time elapses) important reactions can take place. Clay mineral formation, for instance, is a process that is usually not taken into account in short-term speciation calculations. However, on somewhat longer time-scales this process can withdraw significant amounts of metals from solution. On the other hand, weathering can cause minerals to completely disintegrate in the long run. How this phenomenon should be dealt with in LCIA procedures is not clear.

### 3.4.4 Methylation

Only a few metals can be methylated. The formation of methyl mercury is the most well-known example. If the toxicity of a metal is determined by several “metabolites”, as they are called in LCIA, the concentration of these metabolites should be calculated. The feasibility of such calculations has been shown on several occasions, e.g. by Diamond *et al.* (1992) or Dekeling (2002). The only operational problem is the collection of properties of all individual species.

### 3.4.5 Activity correction

Until now we have rather loosely spoken of the “free” concentration of the metal ion. However, it is the activity of the metal ions that is important. The activity coefficient is dependent on the ionic strength and is routinely taken into account in the models used to calculate speciation, such as MINTEQA2. Calculating and applying the activity can be done easily for environments with low ionic strength (< 0.1 M), like fresh water environments.

For environments with a high ionic strength, such as seawater, the calculation routines used for calculating the activity coefficients are not appropriate. In these cases, it is advised to use measured activity coefficients instead. This is not a trivial matter! The activity coefficients have quite a large influence in these environments especially for higher charged metal ions

### 3.5 Bioavailability

In our discussion of speciation in a previous section, it was noted that the process of speciation determines the fate of the metals and the concentration of the free metal ion. We did not discuss the extent to which speciation influences bioavailability and toxicity<sup>1</sup>.

The total concentration of a metal in the water phase is often not the most relevant indicator for assessing the toxic impact of the metal. The free metal ion activity is often a much better predictor of the toxic pressure to an aquatic organism.

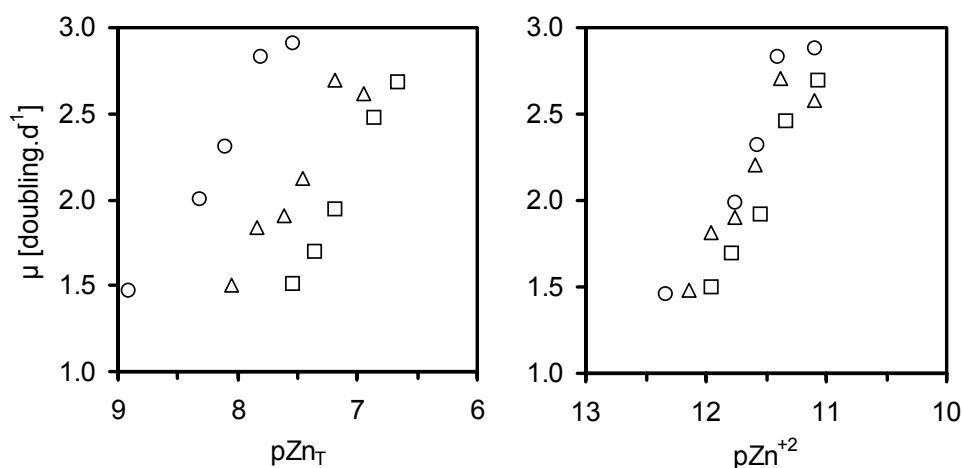


Figure 11 Variation in the growth rate of *A* marine diatom, as a function of total Zn,  $[Zn]_T$ , or free-Zn concentration,  $[Zn^{+2}]$ . Three different EDTA concentrations were used:  $10^{-5}$  M (○);  $10^{-4.3}$  M (Δ), and  $10^{-4}$  M (□). Modified from Campbell (1995).

See, for example, the variation in the growth rate of a marine diatom as a function of total Zn and as a function the free-Zn concentration in Figure 11. Data have been taken from Campbell (1995). In this case the effects of Zn as a micronutrient were investigated. More details on essential metals are given in Section 3.6. The marine diatom was grown in a Zn deficit environment. After harvesting these marine diatoms and resuspending them in a medium with different Zn concentrations, their growth rate was measured. More details of this experiment can be found in Campbell (1995). It must be noted that growing the diatoms in a Zn-deficit environment may make the diatoms very efficient in obtaining Zn from their environment. Placing these diatoms in an environment with a normal Zn availability may than lead to toxic effects.

<sup>1</sup> The discussion on the toxicity of metals is limited to aquatic ecotoxicity, which is sufficient for demonstrating the influence of speciation processes on toxicity. The authors lack knowledge to discuss human toxicity in this context.

The data in Figure 11 show that under different environmental conditions (in this case different concentrations of the organic substance EDTA) the same total concentration of Zn can have completely different effects. However, if the growth rate of the marine diatom is plotted as a function of the free concentration, the growth rate is perfectly correlated with the free concentration of the metal.

In 1983, Morel introduced the free-ion activity model (FIAM), which states that the biological effect of a metal is fully correlated to the activity of the free metal ion. This model was a first important step towards understanding and interpreting the results from toxicity studies. However, it was soon found out that the biota do not passively take up free metal ions from solution but that the interaction between metal ions and proteins on cell surfaces, which are responsible for the active transport of the hydrophilic ions across the cell wall, determines the bioavailability.

The interaction between metals, background ion concentrations ( $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{H}^+$ ) and the transport proteins is modelled with the so-called biotic ligand model (BLM). The BLM encompasses both models for speciation and interaction with the biotic ligands. The model is very successful in predicting toxicity to some fish species for some metals under different environmental conditions. Currently the BLM is operational for the following metals: Cu, Ag, Zn, Cd.

As the BLM is operational for a small number of metals only, it is questionable if it can be used at all in LCIA where the potential impact of all kinds of metals has to be assessed. According to risk assessment specialists (ICMM workshop as mentioned in Section 1.1 of this document) it might be possible to both use BLM and the simpler FIAM model in LCIA. The BLM can be used for the few metals for which parameters are available to populate the BLM, the FIAM can be used for the other metals. The BLM will likely give more accurate predictions of metals toxicity than the FIAM but no bias in the comparative assessment of the potential impact of the metals will be introduced when using the BLM for one metal and the FIAM for the other metal. More research is necessary to prove the validity of this approach.

Of course when applying the BLM or FIAM it is necessary to review the (aquatic) ecotoxicity.

Another approach was suggested to account for speciation and bioavailability (Van Straalen, 2004). Perhaps it is possible to discern, for each environmental compartment, two pools of metals: 1) a "readily available" pool and 2) a "scarcely available" pool. Emissions are assumed to enter the "readily available" pool first. This pool is connected to the "scarcely available" pool with very small time constants (slow exchange rates). Eventually equilibrium will be achieved between the two pools (Van Straalen, 2004).

### 3.6 Essential elements

Many elements are essential nutrients for most organisms (for instance  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{K}^{+}$  and  $\text{Na}^{+}$ ). Even many heavy metals, like  $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$  and  $\text{Co}^{+2}$ , are micronutrients without which most organisms cannot survive.

Organisms can often regulate their intake of essential metals although some organisms do not regulate the uptake of essential metals (e.g. zinc and copper in many crustaceans, Van Straalen, 2004). Within certain bounds varying environmental concentrations will not influence the concentration of the metal within the organism. The ability of the organism to adapt to different environmental conditions is called homeostasis. However, homeostasis has its limitations. If the concentration of a metal in the environment is too low the development of the organism is reduced. If the metal concentration becomes too high, toxic effects may occur. Considering the fact that organisms may develop under (micro)nutrient limiting conditions an addition of the limiting (micro)nutrient may be fatal to the organism.

Thus there is a concentration range in which addition is beneficial, a concentration range in which addition has no effect, as it is in the range within which homeostasis can regulate the metal uptake and a concentration range in which addition has harmful effects. This concept is also called the deficiency-toxicity model (DT model). It is illustrated in Figure 12.

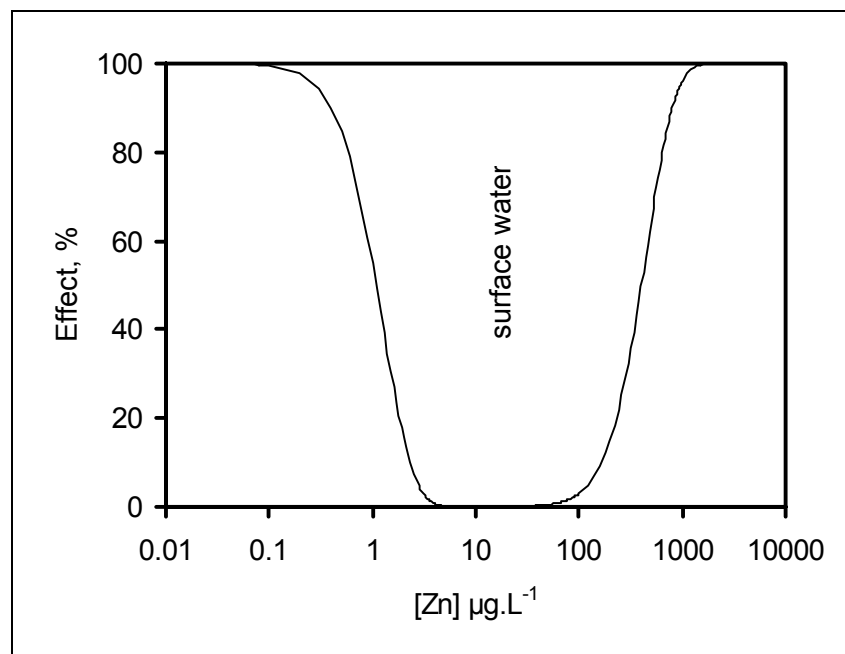


Figure 12 Schematic picture of the Deficiency-Toxicity model (Van Tilborg, 1995?).

In current LCIA practice, every addition of a metal is considered detrimental. A similar problem occurs in the impact category eutrophication.

Most organisms are well adapted, due to natural selection, to the background concentrations in the environment. A significant change in the concentration may thus have adverse effects.

The assessment of essential elements has parallels with the assessment of nitrogen and phosphorous enrichment. Consistent assessment of both types of impacts is desirable.

### **3.7 Life cycle inventory data and metal emissions**

One of the issues related to in the impact assessment of metals in LCA is the way in which metal emissions are reported. In life cycle inventories, it is currently customary to report emissions as the metal ion only, like Cu or Cu<sup>+2</sup>-ion. See for instance the LCI Ecoinvent database (<http://www.ecoinvent.ch/>). Because of this method of reporting, the LCIA practitioner has no data on the form in which the metal is emitted. Thus it is often assumed that the metal released is in soluble form, which might be a worst-case assumption.

## 4. Developments in characterisation

Chapter 2 presented the standard practice of LCA and the characterisation step in LCIA. Although this standard practice has proved informative and valuable in numerous applications, its limitations have become apparent as well. These have spawned new developments. This chapter presents some of these new developments as far as they relate to the subject matter of this report. We will discuss:

- The advent of regionalised models for LCIA;
- The use of non-linear dose-response relationships;
- The use of non-steady state models;
- The incorporation of metabolites of breakdown processes.

It should be noted that there are other developments underway in the LCIA field as well. For instance, instead of the baseline impact categories according to Guinée et al. (2002), one may well choose more endpoint-oriented impact categories at a more aggregated level, such as ecosystem damage (Goedkoop & Spriensma, 1999). Although the choice of impact categories and category indicators is obviously an important aspect of LCIA, the discussion in this chapter is restricted to those topics that immediately relate to the toxicity models.

### 4.1 Regionalised models

An important development in LCA is the introduction of regional differentiation. A first thing to discuss is the meaning of regional differentiation.

Space, as a distance-defining concept, was introduced into LCIA from the outset in the form of transport requirements between producing and using facilities. Spatial differentiation, however, is something different. It refers to the fact that the world is not uniform, but that there are spatial patterns in activity and sensitivity. This applies to inventory analysis, where, for instance, regional differences occur between electricity mixes and agricultural practices. More importantly for this document, however, spatial differentiation applies to impact assessment. Consider, for instance:

- Regional differences between environmental conditions, like temperature, wind speed, soil composition, and water depths;
- Regional differences between target ecosystems, most notably the occurrence of sensitive species;
- For human toxicity, regional differences between consumption patterns, body weight, degree of drinking water purification, etc.

Potting (2000) offers some interesting elaborations of site-dependent characterisation models, on the basis of the RAINS model for acidification. The development of regionalised or nested multimedia models has led to other developments, such

as the characterisation models for toxicity on regional and continental scale by Huijbregts (1999), the ongoing work on water catchment-based models (Bachmann (in progress) and Hollander (in progress)) and the ongoing work on county-based models (Wegener Sleswijk (in progress)).

It should be noted that the realm of spatial variation differs over geographical scales. A parameter like the pH or the organic content of soil will have more or less the same average and standard deviation whether we consider the world or one continent. Only if we descend into the level of countries, provinces or smaller will we see a real distinction in parameter values and a subsequent reduction of standard deviations.

## 4.2 Non-linear models and background-dependency

It may be observed that the so-called critical-volumes approach (see Section 2.5.1), which entered LCA around 1990, is still the prevailing line of thought in LCIA, at least for the effect part. Roughly stated, the fate aspect has undergone a far more profound development than the effect aspect. However, the development of models for the risk assessment of chemicals has enabled a number of interesting elements to penetrate LCA as well. Let us revisit the PEC/PNEC approach:

$$I_c(m_1, m_2, \dots) = \sum_s \frac{PEC_{sc}(m_s)}{PNEC_{sc}}$$

The critical points in this justification are of course two aspects in the central formula for the indicator namely:

- The justification of the PEC/PNEC concept;
- The justification of the aggregation of PEC/PNEC ratios for different chemicals *i*.

The former is an issue that has been discussed at length in the RA-community. The latter point has been discussed to a lesser extent, but here, too, some progress has been reported. Below, we will give a brief review of some recent developments.

New developments in RA have concentrated on improving the crude linear dose-response relationship encapsulated by the PEC/PNEC principle. Sigmoidal dose-response curves, for instance on the basis of lognormal or loglogistic distributions, are increasingly entering the domain of risk assessment and LCA. Posthuma et al. (2002) extensively discuss these so-called species sensitivity distributions, or SSD curves. The use of such non-linear dose-response models in the context of LCA can be found in Huijbregts et al. (2002) with applications in Eco-indicator 99 (Goedkoop & Spriensma, 1999) and in Payet et al. (2003), with applications in IMPACT 2002+ (Jolliet et al., 2003).



The SSD concept offers a variety of improvements on the PEC/PNEC approach. We mention two of them:

- They offer a more realistic modelling of dose-response relationships;
- They offer the possibility to address impacts of combinations of substances.

They clearly have also some disadvantages, such as:

- They have a larger data demand;
- They are more difficult to interpret, especially when used for LCA.

For this latter point, it will suffice to point out that the relatively simple formula:

$$I_c(m_1, m_2, \dots) = \sum_s \frac{PEC_{sc}(m_s)}{PNEC_{sc}}$$

has been replaced by a formula in which the term  $1/PNEC$  is replaced by a non-linear function  $\zeta$ :

$$I_c(m_1, m_2, \dots) = \sum_s \zeta(PEC_{sc}(m_s))$$

and that the characterisation factor is based on an even more difficult form, involving  $\partial\zeta/\partial m$  (see Posthuma et al., 2002, p.426). It should be noted that the calculation of a derivative in a non-linear dose-response setting requires knowledge of the working point, i.e. the background concentration of the substance. In the case of the multi-substance SDD, it requires knowledge of the background impact level.

Although the SDD approach is still based on a less-is-better paradigm, the introduction of non-linear dose-response curves offers additional insights. One of these is the incorporation of the deficiency-toxicity model (see Section 3.6), in which an emission of the substance may be seen as beneficial below a certain point, and detrimental above that point. One should, however, bear in mind the ethical problems that arise from the question of to which extent industrial in the past are to some extent responsible for a certain background pattern (Van Straalen & Souren, 2002).

### 4.3 Non-steady-state models

As noted in Section 2.4.4, the normal use of characterisation can be interpreted in two different ways: as a time-integrated deviation of a steady-state situation, or as a difference between two steady-state situations. In traditional LCA, there is integration over space and over time. With the advent of regionalised models, the integration over space is increasingly being refined. The situation for time integration is subtler.

First, one should distinguish between two types of time-integration:

- time-integration of emissions;
- time-integration of impacts.

The former integration is the aggregation of unit processes throughout the life cycle: mining, production, use, disposal are aggregated, even though mining may take place many years before disposal. The latter integration has to do with the fact that a pollutant may have a long time of impact, starting at the time of release. For instance, impacts of greenhouse gases are usually assessed on the basis of global warming potentials with a time horizon of 100 years.

It is especially this second form of time-integration that is of interest in impact assessment. Huijbregts (1999) gives toxicity characterisation factors that are obtained by a dynamic characterisation model, with a finite integration time (20, 100 and 500 years). Others (for instance Hellweg et al., 2003) propose a more continuous temporal cut-off by introducing a time-discounting scheme, in which every next year counts a bit less. Underlying these models are time series of impact indicators, which are then aggregated with some specific rule. A full presentation of the time series of indicator results has, as far as we know, not been encountered in LCA. Of course, specifying the effects per year cannot be meaningfully done as long as the temporal separation between mining, manufacture, use and disposal has not been made. This poses so many data and model complications, that we do not expect that LCA will soon proceed in this direction.

With respect to the temporal integration of impacts, an often forgotten aspect is the evolutionary property of organisms and ecosystems. An exposure during several hundred years to a particular pollutant will lead to an increased mortality and morbidity in the first few years, but will gradually lead to a genetic adaptation of the organisms or a structural shift in the species composition of the ecosystem. In other words, the PNEC will increase as the result of a high PEC. A time-integrated PEC/PNEC ratio will then need to account for this changed PNEC.

#### **4.4 Metabolites**

Multimedia fate and exposure models for chemical risk assessment usually focus on one single chemical; it is the life cycle of the chemical that assumes a central position (cf. USES). Processes within that life cycle include production, use, waste treatment, and so on. The link with the environment is provided by emissions. Once released into the environment, a different life cycle takes place: consisting of diffusion, transport, uptake by vegetation, degradation, and so on. Although the atomic theory of matter does not allow for degradation, a particular substance can disappear as such. For instance, the pesticide aldicarb breaks down into aldicarb-sulphoxide and aldicarbsulphone (Vink & Van der Zee, 1997). A risk assessment that aims at monitoring or predicting concentrations of aldicarb will naturally exclude other substances.

In life cycle assessment, the scope is different. By definition, all substances and impacts that are related to a product are taken into account. Thus, when aldicarb is

released into the environment, the breakdown of aldicarb should not merely be seen as a disappearance, but as the simultaneous disappearance of aldicarb and the formation of aldicarbsulphoxide, aldicarbsulphone or other substances. These secondary substances can have impacts on the environment as well, they can be more or less toxic than the original substance, or they can have a completely different type of impact (e.g., acidification or climate change). The breakdown processes may be biotic (e.g., bacterial) or abiotic (e.g., by photolysis). The secondary substances are variously called transformation products, breakdown products, metabolites, etc.

The fact that models for the risk assessment of a specific chemical are almost by definition restricted to the analysis of that chemical implies that the use of such models for the more integrative purposes of LCIA is cumbersome. Although LCIA should address the impacts of metabolites, in practice it does not. Only a few exploratory studies have addressed this topic (Fenner et al. (2000); Dekeling (2002)). Addressing metabolites is definitely not in a stage of best available practice within LCIA.

#### **4.5 Metals and LCIA of toxics**

The problems of incorporating metals in the characterisation of toxic releases from metals have been recognised and addressed by a couple of authors. Payet & Jolliet (2003) discuss the effect measure to be used for metals on the basis of the median impact. Wegener Sleeswijk et al. (2003) have developed a model with characterisation factors for the North Sea, with special attention for the activity correction and availability of metals in sea water. Birkved et al. (2004) link various speciation-specific multi-media models to each other to address the issue of speciation. Workshop from ICM in Montreal in 2002 and SETAC/UNEP in Lausanne in 2003 specifically addressed the problems of metals in LCIA. This provides a host of ideas and general recommendations for treating metals in a proper way in the context of LCIA. Nevertheless, a definite set of principles and an operational model are still lacking.



## 5. Characterisation of ecotoxicity impacts of metals

Chapter 2 gave a survey of the current status of life cycle impact assessment. Chapter 3 introduced a number of metal-specific issues and developments in the risk assessment of metals. Chapter 4, finally, gave an overview of developments taking place in LCIA towards inclusion of more sophisticated models. This chapter will further explore the possibilities and limitations for incorporating metal-specific knowledge and developments in LCIA in its present form, or in a modified LCA setup, in line with developments that are taking place within LCIA.

### 5.1 Possibilities and limitations

The metal-specific developments sketched in Chapter 3 are of the following types:

- Persistence;
- Bio-availability;
- Speciation;
- Essentiality.

We will discuss these issues separately in the following paragraphs.

#### 5.1.1 Persistence

From an atomic point of view, metals are persistent. But mere persistence is not the problem that LCIA is supposed to address. Concrete waste is very persistent as well, but is treated very differently than metals in LCIA are. The point in current LCIA practice is that metals can have a toxic impact, and that therefore persistence seems to matter. But a more consistent argument would be, that metals can have a toxic impact at certain places. Hence, we open the possibility of excluding metals that are unable to exert toxic impacts on ecosystems because they are too far removed from those ecosystems. They may be buried in deep sediment or otherwise unavailable.

Current multimedia fate models are developed around organic chemicals. Typical environmental half-lives are between one hour and several years. The processes included in the multimedia fate models are those that make sense within this time period: rain, wind, soil run-off, erosion, and sedimentation. Other processes, most notably geological processes like rock formation, are not included, because they tend to take much longer. Omission of such processes does not invalidate the results for most organic chemicals, but creates problems for substances that are in themselves persistent, like metals.

Solving this problem requires the critical examination and improvement of multimedia models with the specific purpose of including more processes that operate on a longer time scale.

### 5.1.2 Bio-availability

The bioligand model (BLM) appears to provide a good model for accounting for the difference between laboratory conditions and field conditions of the toxic effects of heavy metals. Although the results are encouraging, a few problems should be emphasised in connection with LCIA:

- the model is very sensitive to ambient conditions, and even the most advanced forms of data collection in life cycle inventory analysis cannot supply the detailed information required;
- the model is applicable to very few substances, whereas similar corrections would be needed for many other substances.

With respect to the first point, the current state of life cycle inventory practice is to specify emission sources at country level or even on a continental level. It is uncertain how meaningful the BLM will be if average European conditions are entered as the environmental parameters.

### 5.1.3 Speciation

As we have seen, the term “speciation” can be used in a stricter or a wider sense. Depending on our choice, the need for dealing with speciation is larger or smaller, and so are the possibilities. Some current issues in LCIA can be connected to speciation. Dekeling (2002) discusses the transformations between metallic mercury, ionic mercury, and (di-)methylmercury in the context of accounting for metabolites in LCIA. As mentioned earlier, metals may become less available by transformation and binding, e.g. to organic carbon. A proper account of the impact of metals would necessarily include multiple speciation pathways.

To quite some extent, solving the speciation problem is a key to many other problems addressed in this report. Modelling speciation of metals would to a certain extent provide a solution to the problem of quasi-infinite half-life times that are now entered in certain models to account for the fact that metals do not disappear. The BLM would most probably deliver many useful modelling elements for a multispeciation multimedia fate and exposure model.

At the same time, a similar type of inclusion of metabolites would have to be implemented for organic chemicals. In the present situation, the characterisation factor of aldicarb is underestimated because the impact of metabolites has been left out, and the characterisation factor of metals is overestimated because the transformation of metals into a less mobile or less harmful form has been left out. It

would at least be a research topic to investigate to what extent the metabolite issue of organics is as important as the speciation issue of metals.

In principle, both problems could be solved at the same time by implementing coupled multimedia fate models for cascades of substances that are coupled by transformation processes. In practice, however, this is not so simple. Even if the qualitative features of transformation processes are known, the quantitative details are often not. For instance, the fraction of aldicarb that transforms into the different metabolites is not well known. Moreover, it is highly dependent on environmental conditions. The same applies to the speciation of metals, for instance to mercury.

#### **5.1.4 Essentiality**

The idea that substances can be beneficial in low concentrations and harmful in high concentrations is a valuable and perhaps provoking idea to the LCIA community, which has thus far been educated with either the less-is-better paradigm, or the only-above-threshold paradigm. A problem with accounting for different regimes of effect is that the dose-response relationship is strongly non-linear. However, with the advance of the SSD curve in risk assessment (Posthuma et al., 2002), and its application in LCIA (Huijbregts et al, 2002), the possibilities for dealing with non-linear relationships have come within reach.

This does not mean that there are no practical problems in applying these concepts. In particular, the working point of the dose-response curve is a locally determined variable, and all local variations are almost by definition beyond the scope of LCA. In its present form LCA can only deal with this issue when regions of deficiency are prevalent in large regions (e.g., entire countries). It may well be the case that solving the essentiality issue calls for a treatment at the level of the individual receiving lake or river.

## **5.2 Recommended practice**

In recommending a certain practice, one is faced with the diversity of questions that can be approached with LCA. Metals play a role in all of them, but a central in only a few of them. The Handbook on LCA (Guinée et al., 2002, p.465) distinguishes a number of methods for LCA:

- Simplified LCA: an LCA based on practical guidelines not fully complying with ISO standards, for reasons associated with time and resource constraints;
- Detailed LCA: an LCA based on practical guidelines complying with ISO standards, where time and resource constraints do not play a dominant role;
- Options for extensions: options for extending a detailed LCA to include, for example, elaboration of new impact categories, development of new characterisation methods and/or calculation of associated factors.

The Handbook on LCA provides specific guidelines for detailed and simplified LCA, and suggests some guidelines for extending detailed LCA.

Within the characterisation step of the LCIA, the Handbook on LCA (Guinée et al., 2002, p.70) distinguishes:

- A baseline characterisation method, i.e. the method recommended as the current best available practice;
  - Alternative characterisation methods, which may be adopted instead of the baseline method if duly justified and documented, or may be used in tandem with the baseline method, as a sensitivity analysis;
  - Additional characterisation methods, which may be applied like the alternative methods but require additional effort (e.g., collection of additional data, development of additional models);
  - Variant characterisation methods, which start from entirely different principles.
- For characterising ecotoxic and human toxic effects, the baseline characterisation method is the USES-LCA model (Huijbregts, 1999). This method is ultimately based on the USES 2.0 model. It has an infinite time horizon and is evaluated on a global scale. Alternative characterisation methods are based on the same model, but with different time horizons (20, 100 and 500 years) and evaluated on a continental scale.

The Handbook on LCA proposes that in simplified and detailed LCA, the baseline characterisation method is to be preferred, but that alternative characterisation methods may be used as well. Other methods are also allowed, but their use requires a much more extensive description and justification. For the optional extensions, this latter line is followed more consistently: new methods and/or factors are allowed, but their rationale should be discussed according to the ISO 14042 principles, and sensitivity and uncertainty analyses should play a larger role.

Following the logic of distinguishing three scopes and four different groups of characterisation methods, and bearing in mind the possibilities and limitations of including the metal-specific developments into LCIA, we are now in a position to formulate new guidelines.

### 5.2.1 Guidelines for simplified LCA

- Use the baseline characterisation methods for ecotoxicity (FAETP<sub>∞,global</sub> for freshwater aquatic ecotoxicity, MAETP<sub>∞,global</sub> for marine aquatic ecotoxicity, TETP<sub>∞,global</sub> for terrestrial ecotoxicity. (see the Handbook on LCA for more details).



### 5.2.2 Guidelines for detailed LCA

The guideline given before for simplified studies applies here as well. In addition, the following guidelines apply.

- Discuss in conjunction with the numerical results of the baseline characterisation methods the shortcomings with respect to the following points: persistence of elements (such as metals), bioavailability (in particular in relation to the difference between laboratory and field conditions), speciation (in particular for metals) and metabolites (in particular for organic chemicals) and essentiality (of substances such as nitrogen, phosphorous, potassium, iron, zinc and so on).
- Determine and discuss in a contribution analysis the extent to which indicator results for ecotoxicity are – rightly or wrongly – dominated by metals, organic chemicals or other clusters of mutually comparable substances.

### 5.2.3 Guidelines for optional extensions

The guidelines given above for simplified and detailed studies apply here as well. In addition, the following guidelines apply.

- Consider the development of more sophisticated models to account for the fate, exposure and/or effect of toxic substances. In particular, consider the development of approaches to incorporating persistence, bioavailability, speciation/metabolites, and essentiality. In the development of such models, the balance between chemicals should be kept in mind, so that biased sophistication is avoided.
- Consider the development of a number of scenarios for uncertainty and sensitivity analysis, in particular for issues not fully resolved, such as the time horizon considered, the mechanisms included, and the ambient conditions that influence the model results.

## 5.3 A research agenda

From the preceding sections, it is clear that interesting and relevant metal-specific knowledge is available, but that the incorporation of this knowledge into LCIA is hampered by the unbalanced status of this knowledge. In a compensatory system in which different types of substances are to be aggregated, balance in the sophistication of the models is of prime importance. We therefore suggest a research agenda aimed at providing a more balanced state of knowledge.

- The inclusion of highly persistent substances in models for LCIA should be more closely investigated. This applies to the empirical content of the models (for instance, if processes that act on almost geological time scales are included) as well as to more ethical questions (for instance, if accounting for impacts that take place in the very far future should be included, and if so, with a weight equal to that of the present impacts).

- The bioavailability aspect of a metal like copper appears to be addressed quite successfully with the BLM. The extension of this type of model to other substances, at least to metals but probably to other types of substances as well, should be investigated from a theoretical perspective. The practical modelling and data availability aspects should be kept in mind.
- The question how to deal with speciation and metabolites has only superficially been discussed in LCIA. Here, in particular, the question of balance between degradable compounds and indestructible elements creates a large bias. This bias may already be reduced by either including the transformation products of organic chemicals, or by somehow accounting for the forms in which metals appear in the environment. A more encompassing approach to accounting for both problems simultaneously would, however, be even more effective in reducing or removing this bias. Accounting for speciation also sheds additional light on the issue of persistence and bioavailability. We expect this to be a crucial development for the proper development of LCIA.
- The distinction between deficiency and abundance of substances should be addressed. The newly emerging approaches to dealing with non-linear dose-response curves (like the SSD curves) provide a good starting point.

This is a report on issues and approaches to solutions. It is not a project proposal, with time schedules and required budgets. Any of the raised issues might require a full PhD period.

The list of research to be carried out is long. Yet, pessimism is not appropriate. We think that the analysis presented in Chapters 3 and 4 show that there is a large potential for a more scientific re-erection of the foundations of LCA and LCIA in particular. Construction of bridges is an art that began as intuitive craftsmanship and developed into a scientifically founded discipline of civil engineering. Likewise, the first intuitive LCAs of the 1980s, lumping mass loads of pollutants by adhering to a simple less-is-better paradigm, is starting to evolve in a scientifically founded discipline, involving complicated mathematical models, sophisticated bio-availability models, and advanced dose-response relationships. The progress can be easily judged by comparing the literature of 1980 or 1990 by that of 2004.

## 6. Concluding remarks

This final chapter contains some further reflections that are not entirely within the scope of the report, but that nevertheless have connections with the subject matter discussed.

### 6.1 Human health impacts

The previous material has focussed on ecological impacts, with an emphasis on aquatic ecosystems. Obviously, impacts on human health are an additional important impact category for LCIA. There are some important differences between humans and ecosystems in their sensitivity to substances and to metals in particular. This report does not address these issues, but reasserts the importance of considering sophisticated and dedicated models for each target separately.

### 6.2 Non-toxic impacts

Besides the focus on ecological impacts, this report is restricted to addressing toxic impacts. There are various non-toxic impacts of substances, and of metals in particular. One of these has been mentioned in Section 3.6: a deficiency of metals may lead to adverse effects. High concentrations of essential elements may, in turn, lead to eutrophication. Although this phenomenon is most well-known for macronutrients like nitrogen and phosphorous, and has been taken into account in LCIA for these substances, the possibility of eutrophication by an excess concentration of metals should be considered, if only for reasons of consistency in the treatment of substances and impacts.

There are quite a few heavy metal isotopes that are radioactive as well as toxic. LCAs tend to specify the releases of such substances in terms of becquerel, but this unit is less suitable as an input to toxicity models. Conversion from releases in terms of Bq to releases in terms of kg (and *vice versa*) has been described by Guinée et al. (2002, p.137-138).

### 6.3 Beyond the metals

Some of the problems that have been discussed for metals are present – although sometimes in a different form – for other substances as well. At some places, we already pointed out the similarity of including speciation with that of accounting for metabolites and other degradation products. Also, the similarity of deficiency/toxicity of metals with that of macronutrients, like nitrogen and phosphorous, has been mentioned. There are more places at which an improved LCIA prac-

tice for metals may intensify the need for improvements in other areas, either other chemicals or other impact categories.

## 7. Abbreviations and symbols

### *Abbreviations*

BLM	biotic ligand model
FIAM	free ion activity model
ISO	International Organization for Standardization
LCA	life cycle assessment
LCIA	life cycle impact assessment
PEC	predicted environmental concentration
PNEC	predicted no-effect concentration
RA	risk assessment
RCR	risk characterisation ratio
SSD	species sensitivity distributions

### *Symbols*

<i>m</i>	mass (or more general: size of intervention)
<i>CF</i>	characterisation factor
<i>EF</i>	effect factor
<i>FF</i>	fate factor
<i>XF</i>	exposure factor
<i>iF</i>	intake fraction
<i>I</i>	indicator
<i>IR</i>	indicator result
<i>PEC</i>	predicted environmental concentration
<i>PNEC</i>	predicted no-effect concentration
<i>RCR</i>	risk characterisation ratio
<i>TV</i>	threshold value

### *Subscripts*

p	process
s	substance
c	impact category



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Date upon which, or period in which, the research took place:

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## Appendix 1 Declaration of Apeldoorn

### Declaration of Apeldoorn on LCIA of Non-Ferro Metals

April 15<sup>th</sup>, 2004, a group of specialists in the areas of LCA (Life Cycle Assessment), LCIA (Life Cycle Impact Assessment) and Risk Assessment came together at TNO in Apeldoorn, The Netherlands, to discuss the current practices and complications of LCIA methodologies for non-ferro metals (including essential metals such as zinc and copper). The workshop was commissioned by ICMM (International Council on Mining and Metals), ECI (European Copper Institute) and DBM (Dutch Duurzaam BouwMetaal Foundation), co-sponsored by the UNEP/SETAC (United Nations Environment Programme / Society of Environmental Toxicology and Chemistry) Life Cycle Initiative, and was organized by TNO (Netherlands Organisation for Applied Scientific Research) and CML (Institute of Environmental Sciences, Leiden University). The purpose of the workshop was to provide input to the UNEP/SETAC Life Cycle Initiative on issues surrounding the characterisation of metals by currently available ecotoxicity-based LCIA methods. The group, originating from industry, academia, government, research and consultancy, recognised that current ecotoxicity LCIA methods often produce a probably incorrect emphasis on the impact of metals.

Even though LCIA can use the models and the methodologies developed for Risk Assessment, *LCA is designed to compare different products and systems and not to predict the maximal risks associated with single substances*. However, LCIA models are still in development and do not yet take all important metal-specific properties and processes into account. They can be improved to provide a more meaningful result in ecotoxicity assessment by critically adopting and adapting advanced knowledge and models from risk assessment.

Agreement was reached that the following aspects are of major relevance for a correct understanding of the fate and toxicity of essential elements and need further elaboration:

- Speciation. This feature of metals, which determines their bioavailability and toxicity, was regarded as a highly desirable extension of LCIA, both in fate and effect modelling. The present focus on total metals concentrations in LCA and LCIA could be overly conservative.
- Persistence. Although metals may remain in a certain compartment of a model or ecosystem for a long time, they are usually not present in their bio-available form, but are rather converted to other species and/or adsorbed to particulate matter (e.g., soils, sediments, suspended matter). Infinite time horizons in steady state effect models could only be appropriate if bio-availability is properly considered.
- Essentiality. Within the essentiality window of essential metals, the possibility of adverse biological effects should be set at zero. Adverse effects may occur above or below that window. Below and within that window the LCA general principle of “less is better” does not apply.
- Bioavailability. As noted above, metals speciation determines bioavailability, which also needs to be included in LCIA. For this purpose the Biotic Ligand

Model (BLM) should be used preferentially, with the Free-Ion Activity Model (FIAM) used in cases where the BLM has not been fully developed.

- Characterisation. Because LCA is used for comparative rather than predictive purposes or determinations of absolute risk, it is appropriate to use robust measures of toxicity rather than the lowest measures of toxicity, which are generally interpolated rather than directly measured. On this basis, the characterisation factor should be chosen at the HC<sub>50</sub> (geometric mean of EC<sub>50</sub>) level rather than the HC<sub>5</sub> or the NOEC level, based on the most representative, not the most sensitive species.
- Compartments in the multimedia model. A distinction should be made between compartments in the fate model (which should be as inclusive as possible) and in the effect model. If effects are negligible in a given effect compartment, there is no need to consider effects. This may well be the case for essential metals in the ocean.
- Spatial aspects. The consequences of regional differences in bioavailability, background concentrations, and therefore toxicity need to be further elaborated.

The UNEP/SETAC Life Cycle Initiative was asked to provide recommendations on the integration of the above factors into LCIA methodology. On some issues further research may be necessary beyond these recommendations. The Apeldoorn workshop participants recommend the following working procedures until final recommendations from the UNEP/SETAC Life Cycle Initiative are issued:

1. The fact that a number of critical issues regarding metals are imperfectly dealt with by present characterisation models for ecotoxicity, should be clearly communicated as part of LCIA reporting. Additionally, business or policy decisions should not without further discussion be made based on the results of the currently available (deficient) methods for assessing ecotoxicity in LCIA.
2. The chemical speciation of metals should be taken into account from the inventory phase onwards; emissions should be reported in terms of metal species, preferably in terms of dissolved metal instead of total metal.
3. If the contribution analysis of the LCIA shows that metals have a dominant influence on the results (and conclusions), a sensitivity analysis should be made with the time horizon for the toxicity impact categories set to 100 years when applicable or with excluding the metals from the impact assessment.
4. The oceans are deficient in essential metals. Therefore additional inputs to the ocean will probably not lead to toxic effects. The characterisation factor for toxicity in oceans of essential metals should be set at zero. For coastal seas, this may well be different.

A full report of the workshop, the underlying scientific report and presentations can soon be found at [www.mep.tno.nl](http://www.mep.tno.nl) by using the search function for 'Apeldoorn Declaration'.

Apeldoorn, April 15<sup>th</sup>, 2004

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