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Best available practice in life cycle assessment of climate change, stratospheric ozone depletion, photo-oxidant formation, acidification, and eutrophication

Backgrounds on specific impact categories

W. Klöpffer, J. Potting (eds.), J. Seppälä, J. Risbey,
S. Meilinger, G. Norris, L.G. Lindfors, and M. Goedkoop

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RIVM, P.O. Box 1, 3720 BA Bilthoven, telephone: 31 - 30 - 274 91 11; telefax: 31 - 30 - 274 29 71

Corresponding address:

Center for Energy and Environmental Studies IVEM
University of Groningen
Nijenborgh 4
9747 AG Groningen
The Netherlands

Telephone: 00 31 50 363 46 05
Fax: 00 31 50 363 71 68

Email: J.Potting@fwn.rug.nl

Abstract

This report has been prepared by the SETAC Europe **S**cientific **T**ask **G**roup on **G**lobal **A**nd **R**egiona**L** **I**mpact **C**ategories (SETAC-Europe/STG-GARLIC) that is installed by the 2nd SETAC Europe working group on life cycle impact assessment (WIA-2). This document is background to a chapter written by the same authors under the title "Climate change, stratospheric ozone depletion, photo-oxidant formation, acidification and eutrophication" in Udo de Haes et al. (2002)[1]. The chapter summarises the work of the STG-GARLIC and aims to give a state-of-the-art review of the best available practice(s) regarding category indicators and lists of concomitant characterisation factors for climate change, stratospheric ozone depletion, photo-oxidant formation, acidification, and aquatic and terrestrial eutrophication. Backgrounds on a selection of general issues relevant in relation to LCA and characterisation of impact in LCA are given in another background report from Potting and Klöpffer (2001)[2].

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[1] Udo de Haes, H.A., G. Finnveden, M. Goedkoop, M. Hauschild, E.G. Hertwich, P. Hofstetter, O. Jolliet, W. Klöpffer, W. Krewitt, E. Lindeijer, R. Müller-Wenk, S.I. Olsen, D.W. Pennington, J. Potting and B. Steen. Life-cycle impact assessment: Striving towards best practice. ISBN 1-880611-54-6. Pensacola (Florida, United States of America), SETAC-Press, 2002.

[2] Potting, J., W. Klöpffer (eds.), J. Seppälä, J. Risbey, G. Norris, L.G. Lindfors, and M. Goedkoop. Best available practice in life cycle assessment of climate change, stratospheric ozone depletion, photo-oxidant formation, acidification and eutrophication. Backgrounds on general issues. Report by SETAC Europe Scientific Task Group on Global And Regional Impact Categories (SETAC-Europe/STG-GARLIC). RIVM-report 550015002. Bilthoven (RIVM), National Institute of Public Health and the Environment (RIVM), 2001.

Preface

Methods like integrated modelling of the chain from cause to environmental effect are of growing importance for the support of European Environmental policy. RIVM explores the potential of broadening the basis of such integrated environmental assessment methods with knowledge and conventions applied in Life Cycle Assessment and Substance Flow Analysis in close collaboration with the Center for Environmental Science of the University of Leiden, and the dept. of Science, Technology and Society of Utrecht University, and SETAC[3]. We are therefore happy to publish this document as a RIVM report.

This document is prepared by SETAC's Europe **S**cientific **T**ask **G**roup on **G**lobal **A**nd **R**egiona**L** **I**mpact **C**ategories (SETAC-Europe/STG-GARLIC) that is installed by the second SETAC Europe working group on life cycle impact assessment (WIA-2). This working group has adopted as a priority aim to establish best available practice(s) regarding impact categories, category indicators, and equivalency factors to be used in impact in Life Cycle Assessment. Scientific Task Groups are formed around groups of impact categories to start this process. SETAC-Europe/STG-GARLIC deals with acidification, aquatic and terrestrial eutrophication, photo-oxidant formation, stratospheric ozone depletion and climate change.

The ultimate aim is to develop general indicators that integrate environmental side-effects of economic activities, which can be used in decision-making by governments, companies and consumers.

Drs. Rob Maas
(Head of the Environmental Assessment Bureau of RIVM)

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[3] SETAC is the acronym for Society of Environmental Toxicology and Chemistry.

Contents

Samenvatting

Dit document geeft informatie over de karakterisatie van klimaatverandering, stratosferische ozonafbraak, formatie van foto-oxidanten, verzuring en aquatische en terrestrische vermesting. Per milieu-effectcategorie wordt een overzicht gegeven van de stand van zaken met betrekking tot karakterisatie van deze categorie in LCA.

Summary

This document provides information about characterisation of climate change, stratospheric ozone depletion, acidification, troposheric photo-oxidant formation, and terrestrial and aquatic eutrophication. For each impact category, an overview of the state-of-the-art is given about characterisation of the given impact category in LCA.

1 Climate change

(written by W. Klöpffer and S. Meilinger)

1.1 Background

The physical basis of this area of public environmental concern is the so-called greenhouse effect or, more specifically, the **enhanced, anthropogenic** greenhouse effect. The natural greenhouse effect, which has been known for more than hundred years, is mainly due to the gas carbon dioxide in its pre-industrial concentration and water vapour. The natural greenhouse effect ensures higher life on earth, since without it the average temperature at the surface of the earth would be about -18°C, compared to the actual global average of +15°C. This actual average is due to the absorption infrared radiation sent back from the surface of the earth toward the space.

The additional or enhanced anthropogenic greenhouse effect, which in the last 100 years is considered by many scientists to have already caused an increase of the average surface temperature of about 0.5 to 1 °C [1], is due to the increase of the atmospheric concentrations of several trace gases, which are partly identical with the "natural" greenhouse gases:

- Carbon dioxide (CO_2)
- Methane (CH_4)
- Nitrous oxide (N_2O)
- Synthetic, persistent, especially halogenated chemicals (e.g. tetrachloro- and tetrafluoromethane, sulfurhexafluoride).

The mechanism causing the warming effect is called “radiative forcing” and consists essentially in infrared absorption in the spectral region between 10 and 15 µm, the “spectral window” of the atmosphere. The enhanced radiative forcing and thereby enhanced global warming can be seen as the primary effect from the increase of greenhouse gases in the atmosphere.

Besides primarily emitted gases being greenhouse gases, greenhouse gases may also be produced as secondary products (e.g. ozone). Such secondary greenhouse gas formation can be due to natural as well as anthropogenic sources and contribute to the enhanced radiative forcing. In addition to gases, aerosol particles also have a radiative forcing effect which, depending on the particle properties, can have a positive or negative sign, leading to warming or cooling.

Several secondary and tertiary effects have been identified, which may follow the primary radiative forcing and warming, such as climatic instabilities (e.g. storms), increasing sealevel, changing of oceanic streams etc. Therefore, the more general name “Climate change” replaced the formerly used “Greenhouse effect” as a description of the environmental theme and the impact category.

1.2 Climate change as an impact category

As an impact category, climate change was introduced into LCIA in the early 90’s [2,3]. The quantification proposed for this category is based on IPCC’s Global Warming Potentials (GWP) [1,3]. It became the model for quantifying or characterising most of the other impact categories. In the fundamental paper of WIA-2 [4], Climate change has been described as follows:

This category is generally known under the heading “global warming”; it can better be called “Climate change” because also storms or regional cooling can be part of the impacts. The modelling at the level of radiative forcing is rather well underpinned, less so impacts further along the impact network (displacement of Gulf Stream; release of methane from tundra’s?). Therefore there is as yet no basis for choosing the category indicator further along the impact network. It should be mentioned however, that in the ExternE programme modelling at the level of endpoints is taken (Eyre et al., 1997 [5]). The choice of the most appropriate time period has to be considered; depending on the choice to be made regarding the temporal aspects (see question in section 3.3).

Proposal:
a) Areas of protection: human health, natural environment, man-made environment
b) Content of impact category: all impacts related to climate change caused by changes in radiative forcing
c) Category indicator: radiative forcing

Climate change is an output-related impact category, describing global impacts [6] and many identified “endpoints”, some of them likely, others still speculative. The relevant gaseous emissions, quantified as mass per functional unit in the inventory, originate from many human activities, e.g.:

- burning of fossil fuels (CO_2)
- calcination of minerals (CO_2)
- agriculture (CH_4, N_2O)
- losses during extraction and transport of fuels (CH_4)
- industrial processes (chlorinated solvents, CF_4, SF_6, N_2O)
- private use (freons, chlorinated solvents)
- waste dumping (CH_4, CO_2)

Not quantified in life cycle inventory are CO_2-emissions from burning or aerobic metabolism of renewable raw materials and fuels that have been produced recently from atmospheric CO_2 via assimilation.This is not true, however, for methane formed anaerobically from the same sources, e.g. in landfills. This is due to the much higher Global Warming Potential (GWP) of methane relative to carbon dioxide, the end product of atmospheric oxidation of methane.

1.3 Positioning of the indicator

The positioning of the indicator between the “elementary flows” quantified in the inventory and the "endpoints" or potential effects within an impact category is free according to ISO 14042 [7c]. Selecting an indicator near to the elementary flows has the following advantages:

- The endpoints have not to be known in detail, i.e. the causal chains have not to be established quantitatively
- The indicators can often be defined rigorously and derived from basic laws
- The precautionary principle is in general better taken into account, since (still) unknown secondary and tertiary effects are automatically included if they are related to the primary effect and this primary effect is used for the indicator model. Even if some secondary effects are definitely known and may be modelled with a reasonably accuracy, other effects not known today may surface in the future.
- The number of effective categories is not increased by the introduction of subcategories (inevitable if several endpoints are modelled as indicators)

The main advantage of selecting the indicator near to the endpoints is the completeness of the analysis (at the present state of knowledge), especially if no common primary effect can be identified. In this case, however, the question is allowed whether the impact category itself has been selected and defined properly.

In the case of “Climate change” it is consensus within the community of atmospheric scientists that the midpoint “enhanced radiative forcing” (i.e. the absorption of infrared radiation in the spectral “window” from about 10 to 15 μm) is the common and global primary effect which may cause several serious secondary and tertiary effects whose actual regional consequences may dramatically endanger the future existence of humankind. The enhanced radiative forcing is linked to the “global warming”, i.e. the increase of the average temperature near the surface of the earth. That is why this impact category has formerly been called “Global warming”. For this reason and the general arguments given above, it is advisable to select enhanced radiative forcing as the midpoint to be modelled and characterised as the indicator for the renamed impact category “Climate change”. The new name, which implies a broader definition, gives the option of defining new indicators closer to the endpoint in the future, if atmospheric sciences sufficiently progressed in order to present simple and yet accurate calculations for well defined secondary or tertiary effects.

1.4 Selection of the indicator model and of characterisation factors

1.4.1 The global warming effect

As proposed in section 1.3, radiative forcing by (anthropogenic) emissions is the most appropriate midpoint for the impact category “Climate change”. For modelling purposes, however, the closely related global warming effect is used as the indicator.
Substances which are able to contribute to radiative forcing have to be sufficiently stable (persistent) in the troposphere and to have absorption bands in the spectral region between about 10 and 15 µm. Since both the absorption cross section (absorption coefficient) and the lifetime or persistence contribute to the effect, there is no simple way to calculate the global warming caused by a specific compound. Due to the effect of the lifetime which differs from compound to compound, a time-dependency becomes evident which is more pronounced for substances with relatively short lifetimes (e.g. methane [8]).

To complicate things further, several indirect effects have been identified which presently cannot quantified with sufficient precision. To give an example, the chlorofluorocarbons (CFC) show a pronounced radiative forcing due to strong absorption in the spectral window **and** high persistence; the depletion of the stratospheric ozone layer caused by these substances (see chapter 2), however, is believed to have an indirect cooling effect and thus counteracts the warming effect due to radiative forcing [10]. Since this cooling effect cannot be quantified, the Intergovernmental Panel on Climate change (IPCC) decided to exclude the freons from the list of global warming gases in the 1996 Report [1c].

Since furthermore the prediction of temperature increases depends on the further development of the emissions - especially of CO_2 - and thus also on the measures taken (or not taken) in order to reduce the emissions, scenarios for this development enter into the calculations of further temperature increases and the contribution of the individual “greenhouse”-gases. Due to the scenarios, the different lifetimes of the gases and other related effects, a time dependence of the contributions is introduced into the results of the calculations, known as the “time horizon” of the Global Warming Potentials (GWP) to be discussed below.

1.4.2 The IPCC model

According to ISO 14042 [7c], the indicator model chosen for an impact category should ideally be based on scientific evidence and be supported by an international organisation. In the case of the category Climate change, the second condition is fulfilled by IPCC, working under the auspices of UNEP and WMO. The reports published by IPCC [1] are peer-reviewed by a panel consisting of several hundred leading experts world-wide. For this reason, it can be assumed that the models and the results obtained are based on the best scientific evidence available at present. However, a fully objective scientific theory cannot be expected presently due to assumptions in the scenarios needed, as mentioned in section 1.4.1. The unprecedented effort made by the scientific community, which is focussed in IPCC, guaranties that the best scientific evidence presently available is used and that the scenarios are realistic to the extent possible.

The models used by IPCC serve different purposes. One purpose is the prediction of future and the explanation of past temperature increases due to the anthropogenic greenhouse effect. Actually, the known development since the beginning of the industrialisation is used for the calibration of the models and their predictive power. A second purpose, which is of paramount importance for the environmental policy, aims at proposing reduction rates and political and technical measures for the most important greenhouse-gas-emissions. For this purpose, different scenarios are calculated, showing the temperature increase after a given time horizon. A third purpose, which is the most important for LCIA, is to calculate the relative contribution of the different gases at the basis of equal weight. The question to be answered here is: how much more (or less) contributes one mass unit of gas A relative to one mass unit gas B to the global warming at a given time horizon.

The form chosen by IPCC for quantifying these ratios is ideally suited for the characterisation of Climate change or - actually the other way round - since the form given by IPCC is so well suited for LCIA, this form has been adopted as the general model of the characterisation of basically all impact categories [3]. The ratios calculated for different time horizons are called Global Warming Potentials (GWP) and are normalised with regard one mass unit of carbon dioxide. A GWP of 100 says that 1 kg of the substance has the same global warming effect (at a given time horizon, e.g. 100 years) as 100 kg CO_2. It is immediately clear that a list of GWPs including those greenhouse gases quantified in the inventory [7b], allows the aggregation of the masses per functional unit into one figure, the GWP [kg CO_2-equivalents] per functional unit (f.u.).

1.4.3 Numerical values of GWP for greenhouse gases

In Table 1.1, the GWPs of the most important greenhouse gases are presented for three time horizons. As can be seen from the data, the GWP of some compounds is several orders of magnitude higher compared to CO_2 (GWP 10^3 to 10^4). The main overall contribution to global warming is nevertheless due to CO_2 (61 % [1f]) due to its high anthropogenic emission (26000 Tg in 1990 [1f]). This is true in a global perspective; for certain product systems other greenhouse gases may be much more important.

Table 1.1: GWP and Lifetimes of Greenhouse Gases after IPCC and WMO [1c,10] in [kg CO_2-equivalents/kg] and Lifetimes

Compound (i)	Lifetime [a] τ_i [years]	Lifetime (OH) [b] τ_i [years]	GWP_i [c] Time Horizon 20 yr	GWP_i [c] Time Horizon 100 yr	GWP_i [c] Time Horizon 500 yr
Carbondioxide (CO_2)	determined acc. to the Bern C-model		1	1	1
Methane (CH_4)	8.9 ± 0.6		64 *	24 *	7.5 *
Dinitrogenoxide, nitrous oxide (N_2O)	120		330	360	190
HCFC-22 ($CHClF_2$)	11.8	12.3	5200	1900	590
HFC-23 (CHF_3)	243	255	11700	14800	11900
HFC-32 (CH_2F_2)		5.6	2900	880	270
HFC-41 (CH_3F)		3.7	460	140	43
HCF-125 (C_2HF_5)		32.6	6100	3800	1200
HFC-134 ($C_2H_2F_4$)		10.6	3400	1200	370
HFC-134a (CH_2FCF_3)	13.6	14.1	4100	1600	500
HFC-152a ($C_2H_4F_2$)		1.5	630	190	58
HCF-143 ($C_2H_3F_3$)		3.8	1200	370	120
HCF-143a (CH_3CF_3)		48.3	6800	5400	2000
Sulphurhexafluoride (SF_6)		3200	15100	22200	32400
CFC-11 (CCl_3F)	45	> 6400 **	6300	4600	1600
CFC-12 (CCl_2F_2)	100	> 6400 **	10200	10600	5200
CFC-113 ($C_2Cl_3F_3$)	85		6100	6000	2700
Dichloromethane (CH_2Cl_2)		0.4 to 0.5	35	10	3
Chloroform ($CHCl_3$)		ca. 0.5	55	16	5
Tetrachloromethane, Carbon tetrachloride (CCl_4)	35	≥ 130 **	2100	1400	450
1,1,1-Trichloroethane, Methyl chloroform (CCl_3CH_3)	4.8	5.7	450	140	42
Tetrafluoromethane (CF_4)		50000	3900	5700	8900
Hexafluoroethane (C_2F_6)		10000	7700	11400	17300
Perfluoropropane (C_3F_8)		2600	5900	8600	12400

Compound (i)	Lifetime [a] τ_i [years]	Lifetime (OH) [b] τ_i [years]	GWP_i [c] Time Horizon 20 yr	GWP_i [c] Time Horizon 100 yr	GWP_i [c] Time Horizon 500 yr
Perfluorobutane (C_4F_{10})		2600	5900	8600	12400
Perfluoropentane (C_5F_{12})		4100	6000	8900	13200
Perfluorohexane (C_6F_{14})		3200	6100	9000	13200

a Tropospheric residence time after [10] or [1c]; in case of non-coincidence the more recent value is given [10]

b Tropospheric chemical lifetime calculated from the rate constant of reaction with OH-radicals and average OH-concentration in the troposphere; data after IPCC 1996 [1c] and WMO 1999 [10]. The tropospheric (OH) lifetime gives an upper limit for the tropospheric residence time, since all degradation- and other (physical) removal processes shorten the average time spent by a molecule in the troposphere

c Most recent data after WMO 1999 [10]; in this compilation of direct GWPs more data on CFCs, HFCs and other halogenated compounds are available. The data of CH_4 and N_2O are basically those of IPCC 1996 [1c], but re-scaled according to new scientific evidence. IPCC 1996 [1c] does not include substances degrading the stratospheric ozone; they are included in IPCC 1990 [1a] and WMO 1999 [10]; the values given here [10] are typically 10 to 20% higher compared to [1a]

* Includes indirect effects as tropospheric ozone formation and stratospheric water formation

** Calculated according to experimental k_{OH}-values [9] at 298 K; actual lifetimes are higher due to the lower average temperature of the troposphere

The time horizon chosen for the calculation influences the GWP values significantly only in the case of relatively short lifetimes (up to about 100 years). The typical uncertainty of the GWP of individual greenhouse gases is in general about ± 35 %. Since GWPs of individual gases are relative numbers, this uncertainty does not contain the absolute uncertainty of climate modelling of carbon dioxide; this, however, is no concern to LCIA since only relative values are necessary in the indicator model chosen.

In Table 1.1 some GWP-values of persistent chlorinated gases are included. As discussed in section 1.4.1, using these data may overestimate the GWP, since the compensating effect is not taken into account. Their use or not-use in a specific LCA has to be discussed in the goal and scope definition of that study. It may be argued that the precautionary principle is better fulfilled if the GWP of chlorofluorocarbons (CFC, freons) and chlorinated persistent solvents is taken into account, although the calculated total GWP may be too high.

1.4.4 Selection of the time horizon

For principal reasons, a large time horizon should be chosen in LCIA [4] in order to prevent a too restricted impact assessment, not taking into account possible negative effects for the coming generations. For this reason, the longest horizon used in the calculations (500 years) would be appropriate. However, scenarios defined today are very unlikely to hold true for the future and seem to be most accurate for the time being. It may therefore be a good compromise to use GWP data calculated for a time horizon of 100 years, as has been done in most LCIAs in the past.

For special LCAs, dealing explicitly with products under the aspect of, e.g. reducing global warming, a more detailed handling of this question may be necessary. In these cases, the goal definition may include requirements for using several time horizons or, at least, to include the uncertainty introduced by using one fixed time horizon.

1.4.5 Calculation of the indicator result

The formula used for calculating the indicator result from the inventory data classified for the impact category “Climate change” is given in equation (1.1).

$$\mathbf{GWP} = \sum_i (\mathbf{m_i} \times \mathbf{GWP_i}) \qquad (1.1)$$

GWP: Indicator result for the impact category Climate change [kg CO_2-equivalents/functional unit]
m_i: Mass of greenhouse gas i assigned to the impact category Climate change during “classification” [kg i /functional unit]
GWP_i: Global warming potential of gas i [kg CO_2 equivalents/kg i] for time horizon 100 years (if not otherwise requested)

In using (1.1) the most recent list of GWP_i -values published by IPCC or WMO should be used. The data selection in Table 1 taken from WMO 1999 [10].

Due to the long lifetime of all greenhouse gases (the inter-hemispheric exchange time is in the order of one year), a good mixing in the troposphere can be expected. Therefore, as an approximation for LCIA, no regional effects have to be taken into account.

1.5 Further developments and recommendations

In the future, reliable calculations linking the emission of greenhouse gases with potential secondary effects of global warming may become possible (see [5,8]). Depending of the goal definition, such indicators nearer to endpoints affecting human life and ecosystems more directly than radiative forcing as such may be useful in LCA to facilitate weighting across impact categories. Radiative forcing itself is not well suited as an indicator for aggregating the climatic effects of emissions since the lifetime of the molecules does not enter into the calculation [10]. The closely related global warming effect is therefore a much better indicator and should be retained in LCIA.

Considering the rules given by ISO 14042 [7c], indicators nearer to the endpoints may be used in special LCAs. For the time being, however, we propose to practitioners to use

- The IPCC global warming model as the indicator model which is based on radiative forcing
- A time horizon of 100 years, if not required otherwise in the goal definition of the LCA
- The latest GWP_i-list published by IPCC or WMO, and
- Equation (1.1) for calculating the indicator result

Atmospheric/environmental researchers and LCA-developers should

- Provide GWP_i-values for all chemicals persistent in the troposphere
- Investigate the indirect effects (including particles) and provide modified GWP_i-values where necessary
- Investigate the effect of changing time horizons in real-life LCAs
- Consider requirements for the inventory (greenhouse gases not generally contained in present-day inventories, CH_4 from anaerobic processes et cetera)

As in the case of the other impact categories, Climate change should be developed further and adjusted to the scientific progress that is fast in this area. Care should be taken, however, not to complicate more than necessary this category and the indicator recommended which for the reasons given is ideally suited for LCIA.

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2 Stratospheric ozone depletion

(written by W. Klöpffer and S. Meilinger)

2.1 Introduction

The environmental concern about the impact category “Stratospheric ozone depletion” is based on the UV-absorption capacity of the ozone present in the stratosphere, which hinders radiation below 300 nm from reaching the troposphere and the surface of the earth. The ozone molecules are present in the stratosphere in very low concentration, but the layer thickness to be passed by the photons is very large (about 25 km), so that the absorption of short wavelength radiation is complete despite the small concentration of O_3. This absorption capacity, among other beneficial properties of the stratospheric ozone layer is at stake if ozone is depleted by anthropogenic emissions.

According to Chapman (1930), formation and decay of O_3 in the stratosphere are in a dynamic equilibrium (2.1, 2.2):

Formation of Ozone:

$O_2 + h\nu \text{ -----> } 2\,O \quad (\lambda = c/\nu < 240 \text{ nm})$ (2.1a)

$O + O_2\ (+M) \text{ -----> } O_3\ (+M)$ (2.1b)

Destruction of Ozone:

$O + O_3 \text{ --------> } 2\,O_2$ (2.2a)

$O_3 + h\nu \text{ --------> } O + O_2 \quad (\lambda = c/\nu < 1140 \text{ nm})$ (2.2b)

In addition to these reactions there are several additional formation- and degradation processes going on, which are catalysed by trace constituents of the atmosphere (HO_x, NO_x). As early as 1970, the possible depletion of the ozone layer by supersonic jets emitting NO_x during flights in the lower stratosphere have been discussed. An extension of this work to the ClO_x cycle, which was new at that time, by Rowland and Molina was presented in two papers (1974, 1975 [1,2]) which had a high impact. In this work, a possible connection between the emission of freons or chlorofluorocarbons (CFC) and the postulated ozone depletion has been outlined and supported with reasonable data and assumptions.

Chlorine cycle of the catalytic ozone degradation [1], equation (2.3):

$Cl + O_3 \text{ -----> } ClO + O_2$ (2.3a)

$O_3 + O \text{ -----> } 2\,O_2$ (2.3b)

$ClO + O \text{ -----> } Cl + O_2$ (2.3c)

$2\,O_3 \text{ -----> } 3\,O_2$

The chlorine atom needed for initiating this cycle (2.1a) stems from the photolysis of longlived (persistent) organic chlorinated compounds of predominantly anthropogenic origin.

These compounds are able to penetrate the stratosphere, since reactions in the troposphere and washout processes (high Henry coefficient) are inefficient. Since the crossing of the tropopause is a slow process (characteristic time about 10 years for substances emitted at the surface of the earth), there is a time lag between emission and effect.

In addition to this mechanism of homogeneous catalysis, which leads to a more or less equal and slow depletion of stratospheric ozone around the globe, the so called “ozone hole” was detected over Antarctica 1985 [4] and found to be due to heterogeneous catalysis [5-7]. It is important to know that this effect was **not** predicted by Roland and Molina`s theory, although the chemicals causing it are the same. This shows the importance of the precautionary principle and our limited knowledge of complex reactions in the environment.

The heterogeneous reactions take place at acidic hydrate or ice particles and ternary solution droplets present in the lower stratosphere during the Antarctic winter and, to a lesser degree, also during the arctic winter. The effect is observed during Spring when the solar radiation liberates chlorine. Since the temperatures are lower in the Antarctic stratosphere, the effect is more pronounced there compared to the Arctic and thus has been detected earlier. According to a recent report by WMO [13] it was a series of exceptionally cold winters which increased the springtime ozone hole over the Arctic.

2.2 Stratospheric ozone depletion as an impact category

The impact category “Stratospheric ozone depletion” was introduced into LCIA together with the first list of categories and based on the “Ozone Depletion Potentials” (ODP) from the beginning [8]. In the basic paper of WIA-2, this category is described as follows:

Depletion of the stratospheric ozone layer leads to an increase of UV-B intensity at the surface of the earth, causing a number of radiation impacts: on algae and arctic flora, on crops, on wildlife and on humans. The first three are as yet rather uncertain; the latter can already be modelled with considerable certainty (cf. Müller-Wenk, 1997 [10]). As to the time period, a choice has to be made, depending on the choice to be made in section 3.3. In as far as relevant, possibly new modelling of background concentrations is necessary due to envisaged emission reduction.

Proposal:
a) *Areas of protection: human health, natural environment, man-made environment, natural resources*
b) *Content of category: all impacts due to Stratospheric ozone depletion (including possible impacts on human health)*
c) *Category indicator: stratospheric ozone depleting potency of substances; in addition it will be analysed whether impacts on human health can be modelled in a comparable way to the human toxicity indicators.*

Stratospheric ozone depletion is an output-related impact category, describing global and regional impacts due to the increased UV-radiation below about 300 nm. This radiation carries more energy per photon compared to the UV-radiation reaching the surface of the earth with an intact ozone layer. Therefore, many possible adverse effects can occur, leading to a multitude of potential endpoints from potential human toxicological effects to disturbances of ecosystems exposed to solar irradiation.

The relevant gaseous emissions, quantified as mass per functional unit in the inventory, originate from many human activities, e.g.:

- aerosol sprays
- polymer foam production (e.g. polyurethanes)
- cooling agents for refrigerators and small air conditioners (cars)
- cleaning agents (e.g. in the electronic industry)
- smaller applications in medicine (asthma sprays), analytical chemistry (extraction agents, solvents for IR-spectroscopy) et cetera
- fire extinguishing (Halons)
- agriculture, pesticides (CH_3Br)

Most of these uses have in the past been performed with CFCs and similar chlorinated solvents. The majority of these chemicals are now forbidden in the industrialised countries as a consequence of the Protocol of Montreal (1987) and its subsequent adjustments and amendments of London (1990), Copenhagen (1992), Vienna (1995) and again Montreal (1997) [13]. For some uses there are exceptions from the general ban; this together with the production going on in developing countries, some smuggling etc. causes still emissions of freons and similar ozone depleting substances. Some of the substitutes for CFCs might cause similar problems as well.

These facts have to be considered in the inventory component of LCA. The reference year of the data is especially important, since production and use of ozone depleting substances has changed dramatically in the last years.

2.3 Positioning of the indicator

The reasons for positioning the indicator near to “elementary flows” have been given in Section 1.3 for “Climate change”; they are equally valid for “Stratospheric ozone depletion”, since the secondary effects and possible endpoints are equally uncertain. This is especially true for damages of ecosystems and species exposed to solar radiation (air, surface waters, and oceans near to the surface, vegetation, surface of bare soils).

There is one effect that is reasonably well known in order to be considered as a separate endpoint: human skin cancer as a consequence of increased UV-B radiation. UV-B is the medical expression for this part of the solar radiation that is near to the natural edge at 290-300 nm. This part of the spectrum is the one that increases in intensity due to Stratospheric ozone depletion. Thus, in principal, a causal chain can be constructed which links the emission of ozone depleting substances with increased UV-B radiation and the likelihood of skin cancer incidents.
Two different situations have to be considered, however:

- the general increase of UV-B intensity due to photolyses of long-lived organic chlorinated compounds initiating the Rowland and Molina mechanism (homogenous catalysis)
- the temporary and regional increase of UV-B radiation during “ozone hole” events in the most southern and to a smaller degree also in the most northern regions of the globe during the southern or northern early springtime.

It should however be noted that the global effect of homogeneous ozone depletion is less severe with respect to increasing UV-B radiation than the regional ozone hole effect.

The common primary effect of Stratospheric ozone depletion is the increased ozone destruction in itself. Increased UV-B radiation at the surface of the earth is already a secondary effect, and not the only one. Since absorption of solar radiation (not only UV) by stratospheric ozone contributes significantly to the warming of the stratosphere (the tropopause being the thermocline between the stratosphere and the colder upper troposphere), ozone depletion may also cool the stratosphere and possibly change the stratification of the atmosphere. Possible tertiary effects from this are not calculable and belong into the realm of “Climate change”.

Due to the unforeseeable consequences of the primary ozone depletion (both global/homogeneously catalysed and ozone-hole type/regional/heterogeneously catalysed) it is suggested to position the indicator near the elementary flows. As discussed for the closely related category "Climate change", the precautionary principle is best taken into account in that way.

2.4 Selection of the indicator model and of characterisation factors

2.4.1 The ozone depletion effect

As discussed in the proceeding sections, Stratospheric ozone depletion by halogen (chlorine- and bromine-) containing molecules occurs by two related but different mechanisms

- homogeneous catalysis (less important)
- heterogeneous catalysis (more important)

where the first mechanism can occur globally in the whole stratosphere (although depending on the height and latitude) and the second one only temporarily during the Antarctic (and, to a minor degree, also arctic) spring. The common link between the mechanisms is the intermediate ClO (and BrO), the main difference consists in the formation of this active species.

In order to be active as halogen (Cl,Br) carriers, organic substances have to be persistent (tropospheric lifetimes of several years) in order to reach the stratosphere before degradation occurs on the way up. This precondition is ideally fulfilled in perhalogenated compounds, e.g. CFC-11 (chlorotrifluoromethane) and CFC-12 (dichlorodifluoromethane) and to a minor degree also in partially halogenated compounds, as methylchloroform (1,1,1-trichloroethane) or methylbromide.

Fluor as substituent is not active per se, but increases the persistence by lowering the OH-reaction rate. Freon (CFC) substitutes have therefore be chosen among the fluorocompounds with residual H-atoms in order to enable the reaction with OH-radicals (HFC). As shown in chapter 1, however, the residual persistence in connection with IR-absorption is sufficient for the global warming effect.

2.4.2 The WMO-model

According to ISO 14042 [11], the indicator model chosen for an impact category should ideally be based on scientific evidence and be supported by an international organization of high reputation. In the case of the category “Stratospheric ozone depletion”, the second condition is fulfilled by the Global Ozone Research and Monitoring Project of the World Meteorological Organization (WMO), the United Nations Environment Program (UNEP) and other national and international bodies, [12,13]. The scientific evidence accumulated within this program endorses the causal relationships outlined in the proceeding chapters, i.e. the halogen input by man-made persistent Cl- and Br- containing chemicals and the catalytic destruction of the stratospheric ozone.

As in the case of "Climate change", modelling plays a major role in predicting the further development of the ozone layer as a function of the further development of the critical emissions and for identifying and quantifying the contributions of the individual substances which cause the adverse effects. It is this latter point which makes the models applicable to LCIA. Two basic models were developed in order to quantify the ozone depletion capacity of chemicals [12]:

- Chlorine Loading Potential (CLP) [14]
- Ozone Depletion Potential (ODP) [15]

The CLP is the simplest model and considers only tropospheric lifetimes of the compound (relative to CFC-11), the molar mass and the number of Cl-atoms in the molecule considered. Since bromine is also - and even more - effective in degrading ozone, a Bromine Loading Potential (BLP) was defined in an analogous manner. The ozone depletion efficiency in the stratosphere, however, does not only depend on the factors included in the calculation of CLP and BLP, but also on the stratospheric lifetime which is controlled mainly by photolysis, not by the OH-reaction which dominates the tropospheric degradation of organic chemicals. Hence, the Ozone Depletion Potential (ODP) has been defined as a relative measure of the ozone depletion capacity [15] which avoids the deficiencies of CLP and BLP and allows the description of chlorine- and bromine-containing molecules in one parameter. The ODP is - in analogy to the older parameters - a **relative** number and uses the ozone depletion capacity of CFC-11 (trichlorofluoromethane) as a reference.

The ODP is defined by equation (2.4) [12]:

$$\mathrm{ODP}_i = (\text{Global } \Delta\, O_3 \text{ due to i}) / (\text{Global } \Delta\, O_3 \text{ due to CFC-11}) \qquad (2.4)$$

ODP_i: Ozone Depletion Potential of compound i

The verbal definition reads [13]:

The ODP represents the amount of ozone destroyed by emission of a gas over the entire atmospheric lifetime (i.e. at steady state) relative to that due to emission of the same mass of CFC-11, and is defined in modelling calculations as [see equation (2.4)].

It is clear from the discussion above that the ODP is superior to the chlorine and bromine loading potentials, since it allows to characterise both chlorine- and bromine- containing molecules in one parameter and includes differences in stratospheric as well as tropospheric lifetimes. Its determination requires models, however, whereas the loading potentials can be calculated from basic chemical knowledge and the OH-reaction rate constant. Several atmospheric models were used for the calculation of ODP-values [13] resulting in similar, but not identical ODPs. The uncertainty is in the range of 20 to 50 %.

Table 2.1: ODP_i of some ozone depleting gases after World Meteorological Organization [13]

Compound (i)	Lifetime [a] τ_i [years]	Lifetime (OH) [b] τ_i [years]	ODP_i (kg CFC-11 Equivalents per kg i)
CFC-11, Trichlorofluoromethane (CCl_3F). Reference substance	45	< 6400	1.0
CFC-12, Dichlorodifluoromethane (CCl_2F_2)	100	< 6400	0.82
CFC-113, Trichlorotrifluoroethane, (CCl_2FCClF_2)	90		0.90
CFC-114 1,2-Dichloro-1,1,2,2-terafluoroethane (CF_2Cl CF_2Cl)			0.85
CFC-115 1-Chloro-1,1,2,2,2-pentafluoroethane (CF_2ClCF_3)			0.40
Tetrachloromethane (CCl_4)	35	> 130	1.20
Methylchloride (CH_3Cl)	ca. 1.3	1.3	0.02
HCFC-22, Chlorodifluoromethan ($CHClF_2$)	11.8	12.3	0.034
HCFC-123, 2,2-Dichloro-1,1,1-trifluoroethane (CF_3CHCl_2)			0.012
HCFC-124, 2-Chloro-1,1,1,2-tetrafluoroethane (CF_3CHClF)			0.026
HCFC-141b, 1,1,-Dichloro-1-fluoroethane ($CFCl_2$ CH_3)	9.2	10.4	0.086
HCFC-142b, 1-Chloro-1,1-difluoroethane (CF_2Cl CH_3)	18.5	19.5	0.043
1,1,1-Trichloroethane, (CH_3CCl_3)	4.8	5.7	0.11
Halon 1301, Bromotrifluoromethane ($CBrF_3$)	65		12
Halon 1211, Bromochlorodifluoromethane ($CBrClF_2$)	11		5.1
Halon 2402, 1,2-Dibromo-1,1,2,2-tetrafluoroethane ($CBrF_2CBrF_2$)			6.0
Methylbromide (CH_3Br)	0.7	1.8	0.37 (0.2-0.5)

a Tropospheric residence time after [13]

b Tropospheric chemical lifetime calculated from the rate constant of reaction with OH-radicals and average OH-concentration in the troposphere; data after WMO 1999 [13].

In Table 2.1 a selection of numerical ODP values are given from recent sources. Due to the refereeing process of the WMO/UNEP-reports they may be considered as the best available figures at present. Future improvements and adjustments are likely and should be taken into account in actual LCIAs.

2.4.3 Numerical values of ODP for ozone depleting gases

As can be seen from the data, the highest values are those of the halons due to the about tenfold catalytic activity of bromine, compared to chlorine. The other perhalogenated compounds (Cl,F) are in the range of ODP 0.5 to 1.1. Compounds containing H-atoms that can react with OH in the troposphere and are therefore less persistent show much smaller ODP-values. The ODP-values of compounds containing only F as halogen are zero by definition, since F does not catalyse the ozone destruction. Iodine acts as catalyst, but I-containing compounds have a very short tropospheric lifetime due to photolysis (hours to a few days [13]) and therefore only a very small fraction enters the stratosphere.

2.4.4 Selection of the time horizon

The ODP-values given in Table 2.1 are calculated for the steady-state over a time horizon that is theoretically infinite. Since, however, the input into the environment of many compounds is not constant but changes rapidly due to the enactment of the protocol of Montreal and its amendments, this time horizon does not reflect a good representation of the “real” value.

The question of time-dependency is discussed in [22]. According to this discussion, ODP (stationary) values of relatively short-lived compounds (e.g. HCFCs) are small, since they are derived with regard to CFC-11 whose steady-state - assuming constant emissions - will be reached in centuries. The short-term impact of not highly persistent ozone depleting substances is therefore underestimated. If ODP is calculated for a short time-horizon of a few years, the ODP of relatively short lived compounds may be higher by an order of magnitude (but still smaller than that of CFC-11 due to the shorter tropospheric lifetimes).

In LCAs in which the goal definition specifically involves the comparison of different agents including freons and their substitutes, the time dependency should be taken into account. Time-dependent ODPs have been calculated for the most important compounds and a formula for the calculation is given [22]. For LCAs not dealing specifically with such problems, stationary ODP-values should be used. The data given in Table 2.1 is only an extract of ODPs available.

2.4.5 Calculation of the indicator result

The formula used for calculating the indicator result from the inventory data classified for the impact category “Stratospheric ozone depletion” is given in equation (2.5).

$$\mathbf{ODP} = \sum_i (\mathbf{m_i} \times \mathbf{ODP_i}) \qquad (2.5)$$

ODP: Indicator result for the impact category Stratospheric ozone depletion [kg CFC-11 equivalents/functional unit]
m_i: mass of ozone depleting gas i assigned to the impact category Stratospheric ozone depletion during “classification” [kg i /functional unit]
ODP_i: ozone depletion potential of gas i [kg CFC-11 equivalents/kg i] for steady state (if not requested otherwise)

The ODP_i-values should be taken from the most recent WMO/UNEP report. If time-dependent data are used, the model used for the calculation should be given.

Due to the long lifetime of most ozone depleting gases, a good mixing in the troposphere can be expected. Therefore, as an approximation for LCIA, no regional dependence of emissions has to be taken into account. This is also true if secondary effects (e.g. UV-B exposure of humans) should be considered. Whereas the effects show spatially differentiation ("ozone hole"), the responsible agents still distribute globally after emission and the spatial differentiated effects can thus not be traced back to a specific region of emission. In case of quantifying secondary effects, other indicators have to be defined, which are not considered in this chapter.

2.5 Ozone depletion not related to Halogens

As mentioned in section 2.1, environmental concerns about ozone depletion by NO_x preceeded the now accepted mechanism of halogen-induced stratospheric ozone depletion. The entrance path considered in the early 70's was air traffic by supersonic aircraft [23]. This is still or again a matter of concern, since plans exist for a new generation of supersonic passenger aircraft.

The main source of nitrogen oxides in the stratosphere is N_2O that has natural as well as anthropogenic sources [13,22,17]. N_2O is highly persistent in the troposphere, (non polar molecule, no chemical sink) and thus reaches the stratosphere. The total column mixing ratio increased from 299 ppbv in 1976 to 310 ppbv in 1993, the growth rate is 0.2 to 0.3 % per year (3.1-4.7 Tg N/yr) [22]. The anthropogenic sources are not yet well understood, but nitrogen fertilising seems to play a major role [17]. In addition, some industrial processes (polyamide 66 and nitric acid production) contribute to the N_2O emissions.
In the stratosphere N_2O forms NO and secondary reactive NO-species which can degrade ozone by a well known catalytic mechanisms [24]. This mechanism is shown in equation (2.6):

$$NO + O_3 \text{ ------> } NO_2 + O_2 \qquad (2.6a)$$

$$O_3 + h\nu \text{ ------> } O + O_2 \qquad (2.6b)$$

$$NO_2 + O \text{ -----> } NO + O_2 \qquad (2.6c)$$

$$2\,O_3 + h\nu \text{ -----> } 3\,O_2$$

This mechanism of ozone depletion prevails in the middle stratosphere (25-35 km).
At lower altitudes, however, where the concentration of free oxygen atoms is lower, photo dissociation of NO_2 ($NO_2 \rightarrow NO + O$ for $\lambda = c/\nu < 405$ nm) exceeds reaction (2.6c) and a photochemical equilibrium between O_3, NO and NO_2 establishes.

At even lower altitude, in the region of the tropopause (in the upper troposphere and the lowest part of the stratosphere), photosmog chemistry (see Chapter 3) might give rise to ozone production and to the oxidation of CO, CH_4 and other hydrocarbons. Detailed studies by Ehhalt and Rohrer (1995) [18], Brasseur et al. (1996) [19] and Grooß et al. (1998) [20] show that the formation and decay of ozone in this region depends in a non-linear way on the availability of NO_x. Further influencing factors are ozone, water, CO, hydrocarbons and solar radiation, all of which have strong gradients at the tropopause. An additional complication is given by heterogeneous chemistry on cirrus cloud particles. Depending on the local and temporal conditions, ozone depletion as well as ozone formation may prevail.

A further influence of NO_x on the ozone dynamics in the lower stratosphere consists in the formation of reservoir species (e.g. HNO_3 from NO_2 and OH). These reservoir species slowly regenerate NO_x by photolysis and OH. Active halogen species may also be stored as relatively inactive species, which can, however, be activated by heterogeneous catalysis and contribute to ozone degradation in the ozone-hole formation. Thus, the increase of nitrogen compounds may decrease the global ozone destruction, however, it's removal in the polar regions (e.g. via washout into the troposphere) might increase ozone destruction by the heterogeneous mechanism.

The effect of NO_x by aircraft depends on the altitude. Subsonic aircraft fly at altitudes of 9-13 km and thus partly in upper troposphere (circa 60 %) and partly in the lower stratosphere (circa 40 %). As discussed above, NO_x in these altitudes may increase (locally) the ozone concentration. Since this effect depends on various factors, it cannot be modelled in a simple way to be useful for LCIA. Supersonic aircraft fly at about 17-20 km; NO_x-emissions at this altitude may decrease the ozone at a global level, IPCC 1999 [21]. No simple quantitative relationship exists at present that could be used as indicator model in LCIA.

2.6 Further developments and recommendations

One further development of the impact category Stratospheric ozone depletion in LCIA could be the modelling of the impact closer to or at the endpoint, e.g. known adverse effects of increased UV-B radiation. This endpoint could be treated as a subcategory of the existing category. Alternatively, it could be treated as a subcategory of human toxicology. Keeping this endpoint in the category would give much more weight to human effects, compared to the possibly much more far reaching effects to the ecosystems exposed to increased UV-B radiation, which cannot be protected by any means. In contrast, humans can protect themselves against solar radiation.

We therefore propose to keep the category indicator for "Stratospheric ozone depletion" essentially at the level of the primary effect.

We propose to practitioners to use:

- the WMO/UNEP model as the indicator model
- an infinite time horizon (steady state model), if not required otherwise in the goal definition of the LCA
- the latest ODP_i-list published by WMO/UNEP, and
- equation (2.5) for calculating the indicator result

Atmospheric/environmental researchers and LCA-developers should:

- investigate the effects leading to ozone depletion by other mechanisms, especially by nitrogen oxides and
- provide ODP_i-values for N_2O and NO_x (for supersonic aircraft) to be used in addition to the established values of the halogen-containing gases, or
- alternatively create a subcategory and an indicator dealing with these effects
- investigate the need for shorter time horizons in real-life LCAs and the consequences for the results
- consider requirements for the inventory (ozone depleting gases not generally contained in present-day inventories)

As in the case of the other impact categories, Stratospheric ozone depletion should be developed further and adjusted to the scientific progress. It should be taken into consideration, however, that the indicator used in this category is very well suited for LCIA, as formalised in ISO 14042.

Since the ozone layer is not expected to fully recover before the end of the 21st century, the environmental concern underlying this category is not likely to vanish soon. New challenges will appear if the supersonic aircraft is to be developed beyond the not successful “Concorde”.

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3 Photo-oxidant formation

(written by W. Klöpffer, J. Potting and S. Meilinger)

3.1 Background

The photochemical smog, also known as “Los Angeles smog”, has been known for about 50 years [1]. Its popular name is derived from the air quality problems in the metropolitan area of Los Angeles that are connected with the high density of car traffic in this area in combination with the high solar irradiance and a high frequency of meteorological situations that inhibit the exchange of air. These factors form the basis for a sequence of chemical reactions in the lower troposphere leading to the formation of ozone and other reactive and toxic/ecotoxic reaction products. The sum of the products formed in this photochemical oxidation process are called “photo-oxidants”, hence the name of this impact category.

The primary step of the smog formation is shown in equ. (3.1) [2]:

$$NO_2 + h\nu \text{ ----> } NO + O \quad (\lambda = c/\nu < 405 \text{ nm}) \qquad (3.1a)$$
$$O + O_2 \text{ ----> } O_3 \qquad (3.1b)$$

As long as NO (emitted from the cars and other combustion processes) is present in the reacting atmosphere, ozone is spent by the reaction with NO to give NO_2, i.e. no net formation of ozone would occur in an atmosphere consisting of NO, O_2 and non reactive gases as N_2. In order to form a surplus of ozone, other trace gases, especially the highly OH-reactive hydrocarbons and carbon monoxide (CO) are needed which remove NO from the reaction mixture and thus eliminate the main reductive agent which reacts with the strong oxidant ozone. This reaction sequence is shown for CO in equation (3.2):

$$CO + OH + O_2 (+M) \text{ ----> } CO_2 + HO_2 \quad (+M) \qquad (3.2a)$$
$$NO + HO_2 \text{ -----> } NO_2 + OH \qquad (3.2b)$$
$$NO_2 + h\nu \text{ -----> } NO + O \quad (\lambda = c/\nu < 405 \text{ nm}) \qquad (3.2c)$$
$$O + O_2 \ (+M) \text{ -----> } O_3 + (+M) \qquad (3.2d)$$

$$\text{net: } CO + 2O_2 + h\nu \text{ -----> } CO_2 + O_3$$

The reactions depicted in (3.2) show the great importance of the trace radicals OH and HO_2 as intermediates in the formation of ozone and it depicts the central role of NO_x. The function of the VOCs is similar to the one shown in (3.2) for CO.

The latter leads to a time lag of several hours between the emission of precursors and the formation of ozone that is due to reactions removing NO (3.2b). As a consequence of this time lag, a corresponding spatial shift is often observed, leading to high ozone levels downwind from the areas of highest precursor emissions. This local phenomenon is blurred, however, in densely populated areas. Since solar irradiation is necessary for driving the processes (3.2c), a characteristic diurnal development of photo-oxidant formation can be observed. During the night, the ozone formed may react with NO_2 to form reactive NO_3 radicals that can be compared with the OH-radicals active during day light.

In addition to such local features of ozone formation, photo-oxidants do not only occur in typical smog events, but there is evidence of a general increase in ozone concentrations especially on the Northern hemisphere. Thus, a pre-industrial level of about 10 ppbv has increased to 30-50 ppbv found now in the lower atmosphere globally [2b]. Peak values observed in severe smog events amount to 450 to 500 ppbv, clearly above the WHO published guideline values of 100 to 120 ppbv (8 hrs average; 1 ppbv $\approx$ 2 $\mu g/m^3$ at ground level). [2b].

As noted by Finlayson-Pitts and Pitts [2], tropospheric ozone is involved in the general tropospheric chemistry, especially since O_3 photolysis (followed by $O(^1D)+H_2O \rightarrow 2OH$) is the main precursor of the reactive OH-radical (see Levy, 1971). It is also emphasised by these authors that the control of **both** VOC (+ CO) and NO_x is crucial for decreasing the formation of photo-oxidants. They also state that the amount of VOC has been strongly underestimated in the past so that some conclusions with regard to a minor role of NO_x are obsolete.

The mechanism shown in equation (3.1) and (3.2) has been known for several decades [2]. The “ingredients” for the formation of photo-oxidants according to the smog mechanism are:

- short wavelength solar radiation
- reactive nitrogen oxides ($NO + NO_2 = NO_x$)
- reactive volatile organic compounds (VOC) and CO

Intense solar radiation with a high fraction of UV is ideally suited for smog formation; however, also less intense radiation, as in middle Europe, is sufficient for photo-oxidant formation. NO_x is primarily emitted from cars and trucks, but it is also present - in smaller concentrations - in remote areas and is partly transported down from the stratosphere. NO_x in the tropopause region originates from aircraft emissions as well as from NO_x-formation due to lightening, from stratospheric injections and advected surface pollution. Reactive organic compounds and CO on the surface originate from car-traffic, too, but also in this case there are sources in non-industrialised areas, e.g. isoprene and terpenes (especially α-pinene) emitted by forests [2b]. It is the **combination** of the three essential factors which makes a real environmental problem and a threat to human health, the environment and the man-made environment, e.g. crops (ozone is strongly phytotoxic and so are other photo-oxidants).

Since this environmental problem was recognised early, technical and legislative measures have been taken in many countries to minimise the effect, but only with moderate success. Even very strict regulations, as in California, have only reduced the number and strength of peak events, but not removed the smog problem. In conclusion, photochemical ozone formation is still a world-wide problem; peak events in highly populated sunny areas constitute only “the peak of the iceberg”.

3.2 Photo-oxidant formation as an impact category

The impact category ”Photo-oxidant formation” was introduced into LCIA together with the first list of categories (see Section1.2) and based on the “Photochemical Ozone Creation Potentials” (POCP) from the beginning [3]. In the basic paper of WIA-2, this category is described as follows [4]:

As indicated above this category will be dealt with as a unity, including impacts on human health. For the total of impacts the oxidant creation potentials are proposed as category indicator. Today, there are two approaches available:

1. *Firstly, there are the photochemical ozone creation potentials (POCPs), which are developed for the European situation, taking into account average concentration levels of the relevant substances concerned (Derwent et al., 1998 [5]).*
2. *Secondly, there are the Maximum Incremental Reactivity (MIRs), developed in the US, which are of a more generic character as they are adapted to conditions of maximum oxidant creation (Carter, 1994 [7]). At a later stage a choice has to be made here. An important point is that these oxidant creation potentials must be extended to include* NO_x *as catalyst in the process (Nichols et al. 1996 [8]); this is now being accomplished in the running Danish LCA programme.*

Proposal:

- a) *Areas of protection: human health, man-made environment, natural environment and natural resources*
- b) *Content of category: all impacts related to tropospheric oxidant formation, including impacts from* NO_x *emissions. There may be a need for distinguishing between two subcategories:*
  - *the short term and local impacts contributing to photo smog in the close vicinity of the source, primarily affecting human health and mainly caused by the more reactive VOCs)*
  - *the medium term and more regional impacts primarily affecting crops and possibly natural vegetation, to a higher degree due to the more long-lived VOCs (alkanes)*
- c) *Category indicators: either the POCPs, i.e., the photochemical ozone creation potentials adapted to specific European conditions or the more generic MIRs; in both also* NO_x *is to be included, which may be more easily achievable under the above distinction of subcategories. Furthermore there is also a high need for a sum-parameter regarding VOCs because their composition is generally not given. In addition it is likely that impacts on human health can be characterised further in a comparable way to the human toxicity indicators*

Photo-oxidant formation is an output-related impact category, describing local as well as regional potential impacts due to the formation of ozone and other photo-oxidants from precursors, as described in section 3.1. These compounds can act on humans as well as ecosystems and plants and animals.

The relevant gaseous emissions, quantified as mass per functional unit in the inventory, originate from many human activities, e.g.:

- traffic by cars, trucks, ships and airplanes (hydrocarbons and other VOC, NO_x and CO)
- use of solvents in industry (VOC)
- energy-related processes based on fossil fuels (NO_x, CO)
- heating of homes et cetera

The most important single source for local smog events, most likely to cause adverse effects to human health, is road traffic. Regional effects may in addition to traffic (in that case also including ships and aeroplanes) be caused by other emission sources.

Ideally, the inventory should list individual volatile organic compounds, so that the different reactivities can be taken into account. Unfortunately, emissions of hydrocarbons and other volatile organic compounds are often only poorly defined and given as the sum of volatile organic compounds (VOC), sum of hydrocarbons (HC) or sum of non-methane hydrocarbons (NMHC) or organic gases (NMOG). NO_x is part of each inventory, but this information has not been used in most LCIAs that have been published.

3.3 Positioning of the indicator

The positioning of the indicator is much more difficult in the case of this category compared to global categories. The general increase in global ozone concentrations has not yet reached a level that poses a concern with regard to the (known) human toxic effects. Ozone is a greenhouse gas, however, and interferes with the tropospheric chemistry in a complex manner [2]. It may be considered therefore also as a global effect, although not yet for human health outside the densely populated areas.

The reason for the difficulties of this category has been outlined in section 3.2: the effects (endpoints) are local to regional and range from acute toxic toward humans in smog situations to chronic ecotoxic (possible contribution to forest die-back). The definition of two sub-categories has therefore been envisaged by SETAC-Europe (WIA-1 [9]):

- *Photosmog (local)*
- *Tropospheric Ozone formation (regional)*

Alternatively, one indicator near to the “elementary flows” may be maintained. The general arguments put forward in section 1.3 are in favour of such a decision. However, unlike the situation in the “global” categories, where in a first approximation each molecule of an active chemical species contributes an equal share to the effect (e.g. CH_4 to global warming), ozone precursors emitted in different geographical regions or at different times may have either a strong effect or none at all. That means, due to spatial differences, tropospheric chemistry will more or less transform precursors in ozone and other photo-oxidants and, more important, the number of endpoints will be very different between regions).
Choosing the indicator in the same way as for the global categories requires a stricter interpretation of the precautionary principle, since the effect from precursors released in the one region may namely be larger than from precursors in another region. In a precautionary approach one would therefore like to prioritise the most severe situations above others to be improved, since general pollution prevention would lead to sub-optimisation. Such spatial resolved assessment would require an indicator differentiated towards human beings and the natural environment. We therefore will consider both possible choices (one category as it is established practice or at least two subcategories) in section 3.4.

3.4 Selection of indicator models and of characterisation factors

3.4.1 The photochemical ozone formation indices (MIR, POCP)

The basic photochemical reaction sequence leading to ozone and other photo-oxidants in the troposphere has been given in section 3.1. Ozone is often considered to be the characteristic reaction product, since its formation and effects are well known.
While local smog events strongly depend on local conditions as solar irradiance, amount of emissions, direction and speed of wind etc., the local conditions should not be considered for the use of model calculations in LCIA, especially not if one indicator is to be created for this impact category. For this purpose, a model yielding the relative efficiency in photo-oxidant or ozone formation for the substances classified should be available.

The earliest approach to classify reactive hydrocarbons with regard to their ozone forming potential is the one by Darnall et al. 1976 [11]. These authors defined groups of different reactivy (reactivity scale) based on k_{OH}, the most OH-reactive substances belonging to the most efficient ozone-forming hydrocarbons and vice versa. This is only partly true, however, since the secondary processes also contribute to the overall ozone efficiency of a particular compound [2b].

More advanced methods try to calculate the contribution of individual compounds to the formation of ozone (or peroxyacetylnitrate, another important photo-oxidant). The approach developed in the US is based on Incremental Reactivities (IR), as defined in equ. (3.3) [2b]:

$$IR = \Delta [O_3] \; / \; \Delta [\text{C atom of VOC added}] \qquad (3.3)$$

This index, in contrast to the k_{OH}-reactivity scale, may even be negative if the secondary reactions hinder the development of the smog, e.g. for benzaldehyde which removes NO_x without radical formation [2b]. The IR-values still depend on the special characteristics of a smog event and thus cannot be used for a general ranking of VOC with regard to ozone formation. Therefore, a peak IR value can be defined, called Maximum Incremental Reactivity (MIR) [mg O_3 formed / mg VOC added]. For the special case of fuels, a RAF (Reactivity Adjustment Factor) is defined, which can be calculated from the MIR-values of the compounds emitted. This, however, seems to be too special for LCIA in general purpose LCAs.

MIR-values can be converted to relative values, taking the MIR of one characteristic compound equal to 1. This would be in complete accordance with the procedure observed in the global impact categories (GWP and ODP)

The European counterpart of MIR is the Photochemical Ozone Creation Potential (POCP) according to Derwent et al. [5,6,12]. These relative reactivities have been calculated for ozone formation in an air-parcel travelling through Western Europe, i.e. in a moderate climate and without peak ozone formation (smog formation in the local sense). Relative POCP-values were derived from the model calculations. These values [12] were proposed for the characterisation step of LCIA [3] and used in many LCAs. The photochemical ozone creation of ethylene, a strong ozone forming compound, was defined as reference (POCP of 1 kg ethylene = 1). The POCP-value for a given hydrocarbon assesses its ability to form ozone relative to ethylene for an identical atmospheric mass emission.

A drawback of both MIR [2b] and early POCP [12] consists in the restriction to organic compounds as the only candidates for assessing the photo-oxidant formation. The assumption that composition and amount of VOC are the only chemical smog-controlling factors seems to be wrong, however. In addition to VOC and CO, NO_x is the second controlling factor both in polluted and in rural/background atmospheres.

A minimum requirement to the indicator chosen is therefore the inclusion of both VOC + CO and NO_x.

This requirement is fulfilled by recent recalculations of POCP-values by Derwent et al. [5,6], including POCP-values for NO_x, CO and SO_2. Derwent et al [6] also checked for the robustness of POCP-values to changes in the NO emission densities across Europe accounting for the general increase of ozone formation efficiency of VOCs if background NO_x increases. It is not clear at the moment whether MIR-values can be adjusted to NO_x.

Table 3.1: POCP- and MIR-values of several volatile organic compounds after CML/Derwent and Derwent et al.

VOC (class)	VOC (compound)	POCP [kg ethylene-equ. Per kg VOC]		MIR (relative to ethylene)	MIR (absolute) [mg O_3/mg VOC]
		CML/Derwent [3,12]	Derwent et al. [6]		
Alkanes	Methane (CH_4)	0.007	0.034	0.002	0.0148
	Ethane (C_2H_6)	0.082	0.14	0.034	0.25
	Propane (C_3H_8)	0.42	0.41	0.066	0.48
	n-Butane (C_4H_{10})	0.41	0.60		
	n-Pentane (C_5H_{12})	0.41	0.62	0.14	1.02
	n-Hexan (C_6H_{14})	0.42	0.65		
	Cyclohexane (C_6H_{12})	-	0.60		
	n-Heptane (C_7H_{16})	0.53	0.77		
	average (alkanes)	0.40 (n=23)	0.60 (n=25)		
Alkenes	Ethylene (C_2H_4)	1	1	1	7.29
	Propene (C_3H_6)	1.03	1.08	1.29	9.40
	1-Butene (C_4H_8)	0.96	1.13	1.22	8.91
	iso-Butene (C_4H_8)			0.73	5.31
	1,3-Butadiene (C_4H_6)			1.49	10.89
	Isoprene (C_5H_8)	-	1.18	1.25	9.08
	α-Pinene (C_5H_8)			0.45	3.28
	Styrene ($C_6H_5C_2H_3$)	-	0.077		
	Average	0.91 (n=10)	0.91 (n=12)		
Alkine	Acetylene (C_2H_2)	0.17	0.28	0.069	0.50
Aromatic Hydrocarbons	Benzene (C_6H_6)	0.19	0.33	0.058	0.42
	Toluene ($C_6H_5CH_3$)	0.56	0.77	0.37	2.73
	o-Xylene ($C_6H_4(CH_3)_2$)	0.67	0.83		
	m-Xylene	1.0	1.09	1.12	8.15
	p-Xylene	0.89	0.95		
	Ethylbenzene ($C_6H_5(C_2H_5)$)	0.60	0.81		

VOC (class)	VOC (compound)	POCP [kg ethylene-equ. Per kg VOC] CML/Derwent [3,12]	Derwent et al. [6]	MIR (relative to ethylene)	MIR (absolute) [mg O_3/mg VOC]
	1,3,5-Trimethyl-benzene (C_9H_{12})			1.39	10.12
Aromatic Hydrocarbons	Average	0.76(n=14)	0.96 (n=16)		
Hydrocarbons	Average	0.38			
Non-methane-hydrocarbons	Average	0.42			
Alcohols	Methanol (CH_3OH)	0.12	0,21	0.077	0.56
	Ethanol (C_2H_5OH)	0.27	0.45	0.18	1.34
	iso-Propanol (C_3H_7OH)	-	0.22		
	Ethyleneglycol (CH_2OHCH_2OH)	-	0.2		
Alcohols	Average	0.196	0.44 (n=9)		
Aldehydes	Acetaldehyde (CH_3CHO)	0.53	0.65	0.76	5.52
	Formaldehyde (HCHO)	0.42	0.55	0.98	7.15
	Benzaldehyde (C_6H_5CHO)			0	-0.55
	Average	0.443	0.75 (n=6)		
Ketones	Acetone (CH_3COCH_3)	0.18	0.18	0.077	0.56
	Average	0.326	0.52 (n=4)		
Organic acids	Acetic acid (CH_3COOH)	-	0.16		
Halogenated Hydrocarbons	Methylchloride (CH_3Cl)	-	0.04		
	Methylenechloride (CH_2Cl_2)	0.01	0,03		
	Vinylchloride (C_2H_3Cl)	-	0.27		
	Trichloroethylene/Tri (C_2HCl_3)	0.07	0.08		
	Tetrachloroethylene/Per (C_2Cl_4)	0.005	0.04		

VOC (class)	VOC (compound)	POCP [kg ethylene-equ. Per kg VOC] CML/Derwent [3,12]	Derwent et al. [6]	MIR (relative to ethylene)	MIR (absolute) [mg O_3/mg VOC]
	1,1-Dichloroethylene	-	0.23		
	1,2-Dichloroethane	-	0.04		
	Average	0.021	0.11 (n=9)		
Inorganic oxides	Nitrogendioxide (NO_2)	-	0.028		
	Carbonmonoxide (CO)	-	0.027	0.0074	0.054
	Sulphurdioxide (SO_2)	-	0.048		

3.4.3 Numerical values of MIR and POCP for ozone forming gases

In Table 3.1 a selection of numerical MIR and POCP-values is given from recent sources. The MIR-values have been recalculated from data presented in [2b] setting MIR (ethylene) =1 arbitrarily in order to facilitate the comparison with Derwent´s POCP values and - at the same time - to bring them in a form usable in the characterisation step of LCIA.

As can be seen from Table 3.1, only the more recent data by Derwent et al. include data on NO_2, as required by Finlayson-Pitts and Pitts [2b]. CO is covered by MIR as well as by Derwent. Surprisingly, SO_2 also interferes with photo-oxidant formation (no MIR-value). As can be seen from the data, the results obtained by the different models do not coincide exactly. The total range does not exceed 2-3 orders of magnitude and most of the reactive compounds are in a range of about 0.1 to 1 (POCP) and 0.1 to 1.5 (MIR). This means that the exact composition of the mixtures “VOC” et cetera is not very important for the results; the methane should not be included, however, since this compound is, due to its small reactivity toward OH, much less reactive according to both models.

3.4.4 Calculation of the indicator result

The formula used for calculating the indicator result from the inventory data classified for the impact category “Photo-oxidant formation” is given in equation (3.4):

$$\mathbf{POP_{reg} = \sum_i (m_i \times POCP_i)} \qquad (3.4)$$

POP_{reg}: Photo-oxidant formation potential (regional) (regional means e.g. Western Europe).

Alternatively, the relative MIR_i -values may be used if local ozone formation is defined as the indicator in the goal definition phase (3.5).

$$\mathbf{POP_{loc} = \sum_i (m_i \times MIR_i)} \qquad (3.5)$$

POP_{loc}: Photo-oxidant formation potential (local) (local means e.g. a metropolitan area of the LA-type)

m_i: mass of ozone forming gas i assigned to the impact category Photo-oxidant formation during “classification” [kg i /functional unit]

3.5 Regionalization

As already indicated in 3.3, the extent to which precursors lead to adverse effects on human beings and natural environment depends on spatial differences in meteorological conditions, source density and resulting “background concentrations” of relevant precursors, and in receptor density. The effect from precursors released in the one region may therefore be larger than from precursors in another region. The RAINS[4] model, as used in and established under the UNECE convention on long-range transboundary air pollution, estimates ozone formation spatially resolved over the full European domain by taking into account the pattern of regional emissions and spatial differences in meteorology and tropospheric chemistry. Next, the spatial resolved ozone levels are compared with critical ozone values (AOT60 for human beings and AOT40) for natural environment). The areas where critical values are exceeded are next multiplied with receptor density to arrive at the total number of receptors exposed above critical ozone levels. The RAINS model is used by Hauschild and Potting (2003) [10] to arrive at simple factors that relate the emission of a given ozone precursor in a given region to its effect on the full impact area (i.e., the total number of receptors exposed above critical levels is quantified). These spatially resolved factors can be used to modify the ozone formation as calculated with help of the POCP's into their actual effects on human beings and natural environment. The results show that the uncertainty in the calculated effect from refraining of spatial resolved modelling of the actual effect (factor 100 between smallest and largest factor) is far larger than the uncertainty ignoring the ozone formatting potential of different precursors (factor 2 difference for majority of VOC's). The results also show that NO_x as a precursor of ozone and its effects is far more important than VOCs. This ones again underlines to also take NO_x into account in LCA as precursor of ozone.

3.6 Recommendations

For practitioners:

- use the most recent set of POCP- or MIR-values, depending on the aim and scope of the study - considering also the main geographical locations covered by the study.
- depending on aim and scope of the study, it is recommended to use the spatial resolved modifiers from Hauschild and Potting (2003) [10] to arrive at a more accurate estimate of ozone formation and its actual effect

For researchers:

- check relevance of MIR-values for European (and other) conditions
- check relevance of POCP-values for North American (and other) conditions
- compare results obtained with both reactivity scales in real-life LCAs
- reconsider the influence of different definitions and measurement practices of sum parameters as VOC, HC, NMVOC et cetera on the results
- give POCP- and MIR-values as a function of NO_x
- consider the inclusion of increased ozone (local) into the impact category "Human health"

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[4] RAINS is an integrated assessment model that combines information on national emission levels with information on long range atmospheric transport in order to estimate patterns of deposition and concentration for comparison with critical loads and thresholds for acidification, terrestrial eutrophication-via-air and tropospheric ozone formation.

- consider the inclusion of increased ozone (regional to global) into the impact category "Climate change"
- develop spatial resolved characterisation factors for other regions than those in Europe (i.e., a global set of spatially resoved characterisation factors).
- Explore the relevance and feasibility of temporal resolved characterisation factors

3.7 References

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4 Acidification

(taken from G. Norris)[5]

4.1. Basic Equivalency Factors

The basis for the acidification equivalency factors reported in [Heijungs et al. 1992], as well as two variations which have been proposed since (reviewed below) is the number of hydrogen ions that can theoretically be formed per mass unit of the pollutant X released. This number is given by the stoichiometric coefficient v in the chemical reaction equation

$$X + \ldots \rightarrow vH^+ + \ldots \tag{1}$$

From this basis, the equivalency factors assume that one mole of SO_2 will produce two moles of H^+; one mole nitrogen oxide compounds (NO_x) will produce one mole of H^+; and one mole reduced nitrogen compound (NH_x) will produce one mol H^+ equivalent. Since pollutant releases are specified in mass of emissions rather than moles, the coefficient v must be divided by the molecular weight of the pollutant.

Then, analogous to global warming potentials or ozone depletion potentials, the characterization factors are developed relative to one of the acidifying substances. Sulfur dioxide was (arbitrarily) selected, so LCIA acidification characterization expresses acidification potential in terms of "SO_2 equivalents." On this basis, Heijungs et al. [1992] calculated the acidification potentials shown in Table 2-1. Recently, Hauschild and Wenzel [1997] applied the same method to calculate acidification potentials for five additional releases, which are also shown in Table 2-1.

Table 4.1: Acidification potentials for a range of acidifying substances

Substance	Equivalency factor [Heijungs et al., 1992]	Equivalency factor [Hauschild and Wenzel, 1997]
Sulfur dioxide (SO_2)	1.00	1.00
Nitric oxide (NO)	1.07	1.07
Nitrogen dioxide (NO_2)	0.70	0.70
Nitrogen oxides (as NO_2)	0.70	0.70
Ammonia (NH_3)	1.88	1.88
Hydrochloric acid (HCl)	0.88	0.88
Hydrofluoric acid (HF)	1.60	1.60
Sulfur trioxide (SO_3)		0.80
Nitric acid (HNO_3)		0.51
Sulfuric acid (H_2SO_4)		0.65
Phosphoric acid (H_3O_4P)		0.98
Hydrogen sulfide (H_2S)		1.88

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[5] This text is a verbatim version of Section on Acidification in the report written by Gregory Norris and published under the title "Background Report on Life Cycle Impact Assessment Methods for Acidification, Eutrophication, and Photochemical Oxidant Formation".

4.2 Limitations

The most significant limitation in the basic acidification characterization method is its lack of attention to spatial variability in the sensitivity of the receiving environment [Udo de Haes, 1996].

Related to this regional variability in effects is the fact that in some regions, nitrogen deposition to soils is only partially leached out (at least for a period of years until soil capacity to retain nitrogen is exceeded).

4.3 Recently proposed enhancements

To address the issue of incomplete leaching of nitrogen anions, [Finnveden et al., 1992] suggested that minimum and maximum scenarios of N deposition effects be characterized simultaneously, to bracket actual results. The maximum N-influence characterization analysis would employ the factors reported in [Heijungs et al., 1992], while minimum N-influence factors would be zero for nitrogen compounds.

To address the issue of spatial variability in the sensitivity of the receiving environment, a number of approaches have been proposed and some provisionally demonstrated.
Hogan et al., [1996] presented a “Threshold Inventory Interpretation Methodology” (TIIM) which neglected process emissions from the inventory analysis for which the emissions sources were located in areas not sensitive for the subject impact category. In the case of acidification, emissions occurring in states west of the Minnesota/Iowa/Missouri/Arkansas/ Louisiana border were neglected entirely, while those east of this line were included in full. To estimate the location of processes within the life cycle, the authors suggested the use of Federal data indicating the percentage of production capacity in specific economic sectors which is located inside/outside the regions which were defined as sensitive or otherwise.

Missing from this approach is any use of information on atmospheric transport of pollutants, and any information on the relative sensitivity of receiving areas to deposition. Obviously the 100% and 0% adjustment factors and spatial boundaries described above are very crude. But the principal of using data on the locations of sectoral output capacity shares to help determine *ex-post* location shares of processes within the inventory model is a useful one.

An approach similar to TIIM was demonstrated by Tolle [1997], who developed and applied qualitative scaling factors (using a 1-9 scale) on a state by state basis for the US. For acidification, he developed qualitative scores for states using maps of acid-sensitive soil types and of regions likely to have acid-sensitive freshwater lakes based on bedrock geology, combined with information on the existence within each state of very large point source emitters of acidification precursors. Then, as in TIIM, emission sources within the life cycle

inventory were weighted based on their location within "sensitive regions", rather than making use of information or modeling of atmospheric transport processes.
Blau and Seneviratne, [1995] reviewed issues surrounding regionalization of acidification analysis in LCIA, and concluded by proposing an approach for Europe which was very anticipatory of the two US applications described above. They proposed three categories (rather than the 9 of Tolle, [1997] or the 2 of Hogan et al., [1996]) of regional acidification sensitivity, based on both environmental sensitivity and current loading. In their method, standard acidification potential scores [Heijungs et al. 1992] would then be scaled by 100% for high-sensitivity areas, 50% for moderate areas, and 0% for low-sensitivity areas. The method was not operationalized.

The single example of regionalizing acidification analysis for LCIA in a way that includes attention to atmospheric dispersion processes is an approach proposed by Potting and Hauschild [1997] and demonstrated in Potting et al., [1998]. Atmospheric transport processes are addressed using region-to-grid atmospheric transfer matrices derived from simulations using the EMEP single layer trajectory model [e.g., Barret et al., 1996]. The transfer matrices relate emissions from 44 European regions to deposition in 612 grid elements (150x150 km) superimposed on the same 44-regions.
Spatially-dependent sensitivity of the receiving environment is characterized by the methods and spatial databases developed under the on-going European "critical loads" research program (e.g., Posch et al., 1995, 1997]. The critical loads framework takes joint account the acidifying influence and environmental sensitivity associated with sulfur and nitrogen deposition for a given ecosystem. As one EMEP grid element may contain multiple ecosystems with differing critical load functions, these functions can be superimposed and used to derive "protection percentage isolines" (e.g., Posch et al., 1997) which bound the deposition levels below which a given percentage of the contained ecosystems will not exceed critical loads. Alternatively – and as used by Potting et al., [1998] -- the superimposed curves for a grid element allow calculation of an estimated change in "unprotected" ecosystem area (where critical loads are exceeded) in response to specified changes in sulfur and/or nitrogen deposition rates.

The critical load functions spatial database and the atmospheric transfer matrices jointly allow calculation of spatial acidification factors, in units of hectares (of ecosystem) per tonne (of emission), relating emission changes within one of the 44 regions to changes in total acreage of protected ecosystems across the 44-region area. As with the more simplistic acidification regionalization approaches described earlier, the only additional data needed from the life cycle inventory analysis is the location of the emissions source (at roughly the European country level in this case). Differences among the resulting source-regional acidification factors obtained by Potting et al. were commonly on the order of a factor of 5-10, and ranged up to a factor of 1 thousand. One limitation of the method is that it only estimates total acreage pushed beyond critical loads thresholds (which the authors term "a change in risk"), rather than estimating changes in damages.

4.4 Towards an improved US approach for acidification characterization analysis

Many decisions are before us regarding development of a new acidification characterization method for the US. I would make the following suggestions towards a staw-man approach:

First, I suggest the use of a source-receptor matrices which will translate state level emissions of NO_x and SO_2 emissions into state level deposition estimates. I would further suggest that the best available such matrices are those developed from the ASTRAP (Lagrangian) model which supported the National Acid Precipitation Assessment Program (NAPAP). This model was recently used to generate up-do-date source-receptor matrices for acidifying substances as part of the US Department of Energy's Tracking and Analysis Framework (TAF) integrated assessment of Title IV of the Clean Air Act Ammendments [Bloyd et al., 1996].

Next, I suggest the use of a reduced-form soil/aquatic acidification effects model which was also developed for the TAF integrated assessment. This model relates wet and dry deposition of sulfur, nitrogen, and other constituents (results obtained from source-receptor matrix modeling) to changes in watershed chemical properties, including acid-neutralizing capacity, calcium, pH, aluminum, soil base saturation, and the measures of the ability of a lake to support fish species of differing acid sensitivity. The TAF soil/aquatic effects model is a reduced-form model developed from the Model of Acidification of Groundwater in Catchments (MAGIC) (e.g., [Crosby et al., 1995], [Sullivan et al., 1996]). The assumptions, methods, capabilities and limitations of this model should be discussed at the workshop.

Note that the effects model includes multiple endpoints. We need to discuss whether one or possibly some function of these effects serves as a reasonable endpoint for acidification characterization analysis. We should also discuss whether a critical loads framework is in development for the US, and the relative merits of using critical load outcomes versus modeled soil/aquatic effects outcomes, or other outcomes altogether.
Of course, a third and simpler approach might be to undertake (or borrow from existing) efforts to qualitatively score the states in terms of their relative sensitivity to acidic deposition, and to use such a simple scoring system together with the atmospheric transport transfer matrices. This might help gain an initial sense of the relative importance of taking emissions source location into account, but only in a qualitative way if we have only qualitative scoring of the receptor regions.

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5 Eutrophication

(taken from G. Finnveden and J. Potting)[6]

5.1 Abstract

State of the art and research needs for the impact category eutrophication are discussed. Eutrophication is a difficult impact category because it includes emissions to both air and water - both subject to different environmental mechanisms - as well as impacts occurring in different types of terrestrial and aquatic ecosystems. The possible fate processes are complex and include transportation between different ecosystems.

In some recent approaches, transportation modelling of air emissions has been included. However, in general, the used characterisation methods do not integrate fate modelling, which is a limitation. The definition of the impact indicator needs further research, too. The inclusion of other nutrients than those typically considered should also be investigated.

Keywords: Air emissions; aquatic systems; biomass production; ecosystems; eutrophication; fate modelling; impact category; nitrogen; nutrients; phosphorous; terrestrial systems; transportation; water emissions

5.2 Introduction

State of the art and research needs for Life Cycle Impact Assessment (LCIA) in general have recently been reviewed (Barnthouse et al., 1997; Finnveden and Lindfors, 1997; Udo de Haes, 1996; Udo de Haes et al., 1999). Eutrophication is generally regarded as one of the impact categories to be considered in the impact assessment. The aim of this paper is to review the state of the art and discuss research needs for the impact category Eutrophication.

5.3 On Eutrophication

It is sometimes suggested that the term “eutrophication” only refers to impacts on the aquatic systems. However, in this paper, the term refers to both impacts on aquatic and terrestrial systems. This is in line with the use of the term in many other publications (e.g. Grennfelt and Thörnelöf, 1992). Other terms are sometimes used, notably “nutrient enrichment”, “nutrification” and “oxygen depletion”, typically referring to the same group of impacts that are discussed here, or to some of them.

Eutrophication is a difficult impact category for several reasons. Substances that may cause the impact can be emitted to both air and water. Impacts can occur in many different types of terrestrial and aquatic systems. The fate processes are site dependent as are the impacts. The

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[6] Göran Finnveden and José Potting. Eutrophication as an Impact Category. State of the Art and Research Needs. Int. Journal of LCA, Vol. 4 (1999), Issue 6, pp311-314.

fate processes depend on different characteristics of the emitting source, environmental media, and receiving environments. The impacts depend on background loads and different sensitivities of different ecosystems. As discussed below, different nutrients may limit the growth in different ecosystems. Another complicating factor is that some impacts, e.g. increased growth, in some cases may be regarded as a positive impact rather than a negative one.

The inventory parameters that are typically assigned to "Eutrophication" are emissions of nitrogen, phosphorous and organic materials. Several methods for life-cycle impact assessment distinguish between emissions to air and water.

Other nutrients which locally could be limiting, or which could be of relevance to a specific LCA case study, are typically not considered. This is further discussed below.

The concept of “limiting nutrient” is essential when discussing eutrophication. In principle, it states that, in an ecosystem, one nutrient is limiting the growth, and that there is an excess of all other nutrients. If an additional amount of the limiting nutrient is added, this will lead to increased growth. An additional amount of the other nutrients will, however, not lead to increased growth, since they are already in excess.

Terrestrial systems are often limited by nitrogen. This, for example, is the case in many ecosystems in Europe and North America (Nillson and Grennfelt, 1988). For aquatic systems, the situation is more complex (e.g. Grennfelt and Thörnelof, 1992). Freshwater systems are often limited by phosphorous, although there are exceptions *(ibid.)*. Marine systems are often limited by nitrogen, again with exceptions.

Coastal and brackish water can be limited by either phosphorous or nitrogen, or both. Other nutrients, such as silicon, can also be of importance.

The concept of “the limiting nutrient”, however, is a simplification (Grennfelt and Thörnelof, 1992) and can be misleading. Examples of complications are that the limiting nutrient may change over seasons. The limiting nutrient may also change over the years, for example as an effect of earlier loadings. The balance between different nutrients is also of importance. Since different species have different nutrient requirements, different species may be limited by different nutrients. A change in the balance between nutrients may therefore lead to a shift in species composition. Another important aspect is the possibility of the transportation of nutrients from one ecosystem to another one. Thus, even if a nutrient is emitted to an ecosystem where it has no impact, it may be transported to another ecosystem where it can have an impact. It might therefore be that the contribution from an emission to eutrophication is always larger than zero.

5.4 An example

To illustrate the complexity and some possible fate processes, examples of the possible fate of nitrogen emitted to air will be discussed. The example is not exhaustive, since it does not describe all possible processes.

After emission to air, nitrogen can be deposited on surface water. Its subsequent fate is further discussed below. It can also be deposited on soil or vegetation. If so, it can be fixated by biomass or leached out to surface waters. The fraction being leached out in relation to the input depends on site-specific aspects. In Europe it varies between approximately 5 and 80% (Grennfelt et al., 1994). If not immediately leached out, it can be taken up by growing vegetation, thus contributing to terrestrial eutrophication. The vegetation (with the nitrogen) may be exported from the ecosystem, for example, as timber or it may instead degrade. After degradation, the released nitrogen can be taken up again by growing vegetation, thus contributing to eutrophication a second time. It can, however, also be leached out to surface waters, become immobilised for some time in the soil, or be denitrified and leave the system as nitrogen gas. This nitrogen circulation can occur in every subsequent ecosystem to which it will be transported.

If the nitrogen reaches surface waters, either through direct deposition or after leaching from a terrestrial system, the surface water may be strictly phosphorous limited. In this water, the nitrogen will not contribute to eutrophication, but it can undergo further processes. It can be denitrified and thus leave the system completely, or it can be transported to another surface water that perhaps is nitrogen limited.

The nitrogen can thus be transported to nitrogen surface waters through a number of different ways, for example, direct deposition, leaching from terrestrial systems, or by transportation from other surface waters. The nitrogen may be taken up by phytoplankton, thus contributing to eutrophication.

The nitrogen may in subsequent steps be exported from the system, for example together with fish. The phytoplankton may also undergo degradation, making the nitrogen available again. After this, a number of things can happen, e.g. the nitrogen can be taken up by growing phytoplankton again, it can be transported to other waters, be buried in sediments, or be denitrified and leave the system as nitrogen gas.

5.5 Overview of Suggested Methods

Around 1992-93, three methods were suggested approximately at the same time, largely independently of each other. Jensen et al. (1992) discuss eutrophication but conclude that aggregation into one impact category is difficult, because of the different types of impacts and because different nutrients are limiting in different cases. Instead they advocate an approach without any aggregation of different compounds resulting in an approach with four subcategories:

- emissions of nitrogen to air
- emissions of nitrogen to water
- emissions of phosphorous to water
- emissions of BOD to water (Biological Oxygen Demand)

Heijungs et al. (1992) draw the opposite conclusion, suggesting a complete aggregation into one impact score. The definition of the impact indicator is biomass production. All emissions of nitrogen (to both air and water), phosphorous and organic material are assumed to contribute once (and only once) to the same impact. The weighting factors are based on the

Redfield ratio describing the approximate stoichiometric ratio between carbon, nitrogen and phosphorous in phytoplankton.
An approach that partly can be seen as a compromise between the two earlier approaches was suggested by Finnveden et al. (1992) and further developed by Samuelsson (1993) and Lindfors et al. (1995). In this approach, terrestrial and aquatic systems are treated separately. For terrestrial systems, the impact indicator is simply the amount of nitrogen emissions to air. For aquatic systems, the definition of the impact indicator is oxygen consumption resulting from the degradation of organic material. The weighting factors are also in this case based on the Redfield ratio. It is assumed that emissions can contribute once, and only once, but sometimes may not at all contribute to the impact. Four different scenarios, or subcategories, were defined: One for the phosphorous limited case, where emissions of phosphorous and organic material are aggregated. Two for the nitrogen limited case; in one of them nitrogen emissions to water plus organic material are aggregated, and in the second also nitrogen emission to air is included in the aggregation. The separation of these two nitrogen limited-scenarios is motivated because it is unknown to what extent emissions of nitrogen to air will actually reach nitrogen limited surface waters. In the final, maximum scenario, all emissions are aggregated. This last scenario is then identical to the method suggested by Heijungs et al. (1992).
After 1992, the development of methods was somewhat slowed down for a couple of years. In the discussions there were demands for site specific assessments and factors (e.g. Pujol and Boidot Forget, 1994; Potting and Blok, 1994; Blau and Seneviratne, 1995).
Hauschild and Wenzel (1996) suggested a method similar to the previous ones put forward by Heijungs et al. and Finnveden et al. They excluded organic material from the impact category and suggested an aggregation with nitrogen and phosphorous, either separately or combined. Tolle (1997) suggested the incorporation of a regional scaling factor (1-9) increasing with present loadings. According to this approach for the U.S., large regions (e.g., the size of most states) currently receiving high nutrient loads to soils and surface water are allocated the largest potential for eutrophication. That is because already polluted regions are supposed to have already largely used the carrying capacity of the ecosystems in these regions. Additional airborne nutrient releases would then actually affect these sensitive systems.

In a recent work by Seppälä (1998), two impact categories were used for aquatic ecosystems: Oxygen Depletion and Aquatic Eutrophication. For Oxygen Depletion, emissions of BOD were used as the category indicator. For Aquatic Eutrophication, the definition of the impact indicator is increased production based on the Redfield ratio. For water emissions of nitrogen and phosphorous, site dependent transport and effect factors were determined by experts. For air emissions of nitrogen, transport factors were based on EMEP-data. It can be interesting to note that in the case study by Seppälä (1998) 6-7% of the nitrogen emitted to air was deposited in nitrogen sensitive areas. Only a small fraction of the air emissions was thus important.
For calculation of ecoprofiles intended for third party certified environmental product performance declarations, a new approach for aquatic oxygen depletion has been suggested by Lindfors et al. (1998) and Pleijel et al. (1998). Also in this case the definition of the effect is

oxygen depletion, and the characterisation factors are based on the Redfield ratio. However, this approach requires a site-dependent assessment in which emissions are only considered for receiving environments, where the effect of pollutants is determined by expert judgements. No guidance is given for the situation in which a site-dependent assessment is impossible. Characterisation factors to assess the impact from atmospheric nitrogen emission on terrestrial ecosystems are discussed and presented by Potting and Hauschild (2003). Transportation modelling is taken from the EMEP-models in a similar way as for acidification (Potting et al., 1998). The effect is defined using a marginal approach based on the concept of critical loads. The effect is defined as the area of ecosystem that becomes unprotected as a result of that emission. This means that emissions falling on areas that are (far) below the critical load are not considered. Also emissions falling on areas which are already (far) above the critical load (i.e. they are already unprotected) are not considered. See the contribution of Potting and Hauschild (1999) for a discussion on background levels, thresholds and the different ways in which these can be taken into account in impact assessment.

5.6 Discussion and Research Issues

The SETAC-Europe working group on Life Cycle Impact Assessment discussed eutrophication (Nichols et al., 1996). They asked for an adaptation of earlier approaches. They concluded that several subcategories are probably necessary. A distinction between terrestrial and aquatic systems has already been suggested and this is probably a minimum requirement. A further distinction between different types of aquatic systems should also be investigated. An important aspect here is the requirement that a distinction between different ecosystems will pose on the inventory analysis.

Another issue that requires further attention is the question whether other nutrients should also be considered (Nichols et al., 1996). For example, not only nitrogen and phosphorous but also silicon are important parameters when determining the limiting factors for marine systems (Grennfelt and Thörnelöf, 1992).

The definition of the category indicators may also need some further discussion. For aquatic systems, so far oxygen consumption or biomass production has been used. Other approaches could be worthwhile exploring. An open question is whether the definition should take into account the sensitivity of different systems. Except for the approach of Potting and Hauschild (2003), the present approaches do not integrate sensitivity.

For terrestrial systems, one possible, simple category indicator can be the emitted amount of nitrogen, as long as only nitrogen compounds are considered. More sophisticated indicators, taking into account differences in regional atmospheric conditions, background levels, and the difference in sensitivity of the several ecosystems in the deposition area, have been developed by Potting and Hauschild (2003) based on the concept of critical loads, still only considering nitrogen compounds. Potting and Hauschild consider the area that becomes unprotected due to the emission (a curvilinear marginal approach).

Different modifications of definitions of their indicator can be developed. Another approach is to look at the unprotected area which receives emission (i.e. the area which already receives emissions on or above the critical load) (a similar approach was used by Lindfors et al., 1998, for acidification). Careful considerations of these, and possibly other options, should be made. For discussion, see the contribution by Potting and Hauschild (1999).

A discussion of the definition of the category indicator is also linked to more general discussion points for the whole Life Cycle Impact Assessment. One such question is whether a marginal or an average approach based on a linear or curvilinear dose/effect curve should be used. The answer on this question may depend on the goals of a specific case study (see, e.g. Udo de Haes et al., 1999). A closely related question concerns the issue of thresholds. Should a threshold-approach like that of Lindfors et al (1998) and Potting and Hauschild (2003) be used, or should both below and above thresholds be considered, perhaps in separate subcategories.

For discussion, see again Potting and Hauschild (1999) and also Finnveden and Potting (1999).

In the earlier approaches suggested by Jensen et al. (1992), Finnveden et al. (1992), Samuelsson et al. (1993), Heijungs et al. (1992), Hauschild and Wenzel (1996) and Tolle (1997), no fate and target modelling is included. The lack of fate and target information is a drawback of all these methods. It is still largely an open question how the modelling could be incorporated.

For emissions to air, both Seppälä (1998) and Potting Hauschild (2003) use integrated assessment models for nitrogen emission. In this type of modelling, regional emission projections and modelling of fate and target systems are integrated. Background concentrations are thus included. Also target sensitivity can be included. The integrated assessment models used by both Seppälä (1998) and Potting and Hauschild (2003) also assess leaching to water systems, but they do not yet use this information in their impact modelling. This information is important for the assessment of impacts on aquatic systems from emissions to air.

For emissions to water, very few attempts have been made to model the fate. Both Seppälä (1998) and the IVL researchers (Lindfors et al., 1998; Pleijel et al., 1998) use expert judgements for transport and fate assessment. A potentially useful research project would be to study some site-specific cases carefully in order to get an understanding of the processes involved and the possible variability between different sites. Work in this direction is in process by Potting and Hauschild (2003).

Another issue for general discussion of Life Cycle Impact Assessment concerns the spatial differentiation (e.g. Udo de Haes, 1996; Udo de Haes et al., 1999). In most LCA case studies typically some, but not all, spatial information will be available. Important questions are then how to make optimal use of the spatial information that is available and the possible requirements towards the inventory analysis, if more information is wanted. A useful result would be if characterisation factors could be developed where spatially differentiated and spatially non-differentiated factors could be compatible so that the spatially differentiated factors could be used when relevant information is available.

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Call for Comments: Comments on this paper from the LCA readership are appreciated.

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