

**Comparative Life Cycle Assessment of CFC-replacement
Compounds in Different Technical Applications**

Dissertation

for the award of the academic degree of
Doctor of Natural Science (Dr. rer. nat.)
from the Faculty of Biology, Chemistry, and Geosciences,
University of Bayreuth, Germany

submitted by
Monika Weckert
Dipl.-Geoökol.

born April 9, 1979
in Bayreuth, Germany

Bayreuth, October 8, 2008

Diese Arbeit wurde während meiner Anstellung am Lehrstuhl für Umweltchemie und Ökotoxikologie an der Universität Bayreuth unter der Leitung von Prof. Dr. Hartmut Frank zum Abschluss gebracht.

Vollständiger Abdruck der von der Fakultät für Biologie, Chemie und Geowissenschaften der Universität Bayreuth genehmigten Dissertation zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften (Dr. rer. nat.).

Promotionsgesuch eingereicht am: 8.10.08

Erstgutachter: Prof. Dr. H. Frank
Zweitgutachter: Prof. Dr. M. Hauhs

Tag der mündlichen Prüfung: 4.12.08

Erklärung zur vorgelegten schriftlichen Leistung

Hiermit erkläre ich an Eides statt,

dass ich die vorliegende Dissertationsschrift selbständig und ohne fremde Hilfe verfasst, andere als die angegebenen Quellen und Hilfsmittel nicht benutzt und die den benutzten Werken wörtlich oder inhaltlich entnommenen Stellen als solche kenntlich gemacht habe.

Hiermit erkläre ich an Eides statt,

dass ich weder die vorliegende noch eine gleichartige Doktorprüfung an einer anderen Hochschule endgültig nicht bestanden habe.

(gez. Monika Weckert)

Acknowledgements

I want to express my thanks to Prof. Frank who offered me the chance to work on this interesting project and who encouraged me in thinking critically. Furthermore, he gave me the opportunity to attend national and international conferences and workshops where I could present my results and could gather interesting ideas for my work.

Special thanks are given to Silke Gerstmann and Rainer Brüggemann for their help and encouragement throughout my work. They were always able to motivate me and to ask questions that enriched me and helped me in setting my work in the right direction. They were always there when I needed them most.

I would like to thank Guillermo Restrepo with whom I shared my office and many hours discussing. He was always able to translate the "Chinese" of discrete mathematics and partially ordered sets in a way that I could understand. It was always a pleasure working with him on the same project. I hope that we can keep in touch in spite of the great distance. Maybe we can see each other again and play a game of UNO together.

I like to thank some people from University Bayreuth: Mrs. Lauterbach for her patience and help with the bureaucratic aspects of my work, Benjamin Schmidt for his technical assistance with the computer, Nubia Quiroz for her friendship and enriching discussions, Likke Likke for her travel stories and friendship, Susanne Hausmann for first orientation at the university, and of course Anna Becker, Huong Ngo, Agnes Bednorz, and many others from the Department of Environmental Chemistry and Ecotoxicology.

I would like to express my thanks to Stella Pappasavva, An de Schryver, Felix Flohr, Florian Heberle, Rolf Frischknecht, Dele Fayemi, Craig Timothy, and especially to Frank Heuberger who either provided me with data or helpful information about LCA and refrigerants at times when I did not know how to continue. The Bavarian State Ministry of the Environment, Public Health and Consumer Protection is thanked for the financial support of the project.

And finally, I have to thank my parents Elisabeth and Norbert, my brother Thomas, his wife Jenny, my grandmother Marianne, and my great love, Sander, for their love and patience with me. Whenever I was at work with my thoughts and nervous or agitated about tiny things, they helped me in remembering what is really important in life. They never stopped believing in me. Thank you very much!

Content

Indexes	IV
Abbreviations	IV
Figures	VII
Tables	IX
Summary	XII
Zusammenfassung	XIV
1 Introduction & aim	1
1.1 Introduction	1
1.2 Aim	1
1.3 Layout of thesis	1
2 Background knowledge	3
2.1 Refrigerant types	3
2.2 Emissions & production rates of refrigerants	6
2.3 Refrigeration process	8
2.4 Ozone depletion & climate change	10
2.5 International & national legislation	11
3 Scope of work	14
3.1 System	14
3.2 Life cycle inventory	16
3.2.1 Introduction	16
3.2.2 Functional unit	16
3.2.3 Scope definition	17
3.2.4 Allocation	24
3.3 Impact assessment	24
3.3.1 CML02	24
3.3.2 EI99	32
3.3.3 TEWI	34
3.4 Fate modelling	37
3.5 Partial order theory	43
3.5.1 Introduction	43
3.5.2 Hasse diagram technique	43
3.5.3 METEOR	44

4	Results	47
4.1	Impact assessment	47
4.1.1	CML02	47
4.1.2	EI99	53
4.1.3	TEWI	56
4.2	Fate modelling	59
4.3	METEOR	62
5	Discussion	68
5.1	Impact assessment	68
5.1.1	Simplifications made in the life cycle inventory	68
5.1.2	Sensitivity analysis	69
5.1.3	TEWI	72
5.1.4	Comparison of additional fuel consumption	77
5.1.5	Contribution of direct refrigerant emissions to conventional CO ₂ emissions	78
5.2	Fate modelling	78
5.2.1	PFCA	78
5.2.2	TFA	79
5.2.3	Acidity	80
5.2.4	Chloride and fluoride in rainwater	80
5.3	Contribution of properties to rank distribution based on METEOR	81
5.4	Comparison of EI99, CML02, and TEWI results	84
5.5	Comparison of present LCA results with those of literature	85
5.6	Comparison of LCA with METEOR results	87
6	Recommendations & outlook	90
7	References	92
A	Attachment	A-1
A1	Property table of refrigerants	A-2
A2	Average monthly temperature of some European cities	A-4
A3	Life cycle inventory	A-5
A3-1	Production phase	A-5
A3-2	Operation phase	A-16
A3-3	Disposal phase	A-18

A4	Calculation factors of EI99 impact assessment	A-19
A5	Degradation yields of some degradation products	A-23
A6	Results of impact assessment	A-26
A6-1	CML02	A-27
A6-2	EI99	A-31
A6-3	TEWI	A-32
A7	Results of fate modelling	A-34
A8	Results of METEOR	A-47

Indexes

Abbreviations

A	-	Average scenario
A/C	-	Air conditioning
ADP	-	Impact category “Depletion of abiotic resources (excluding primary energy sources)”
AP	-	Impact category “Acidification”
AV	-	Average ranking of the 10 impact categories of CML02
BC	-	Best-case scenario
BFC	-	Bromofluorocarbons
c	-	Refrigerant loss [%] during production and charging for TEWI calculation
CC	-	Impact category “Climate change”
CFC	-	Chlorofluorocarbon
CML02	-	Dutch Handbook Method for Impact Assessment
COP	-	Coefficient of Performance
c_{ow}	-	Octanol-water partition coefficient [$\log c_{ow}$]
C_p	-	Heat capacity of vapour [J/(mol*K)]
d	-	Refrigerant loss [%] during disposal for TEWI calculation
DALYs	-	Disability Adjusted Life Years
1,4-DCB	-	1,4-Dichlorobenzene
DIN	-	German Institute for Standardization
E	-	Energy consumption [kWh/h] for TEWI calculation
EG	-	Europäische Gemeinschaft
EI99	-	Eco-indicator 99
EP	-	Impact category “Eutrophication”
eq.	-	Equivalents
e_r	-	Refrigerant emission [kg] for EI99 calculation
EU	-	European Union
E125	-	Pentafluorodimethyl ether
E134	-	1,1,1',1'-Tetrafluorodimethyl ether
E7000	-	Heptafluoropropyl methyl ether
E7100	-	Methyl nonafluorobutyl ether
E7200	-	Ethyl nonafluorobutyl ether
F	-	Radiative forcing from a pulse emissions of 1 kg gas
FAETP	-	Impact category “Fresh water aquatic toxicity”
F-gas	-	Fluorinated greenhouse gas
f_{ic}	-	Impact factor of certain impact category for EI99 calculation
FKW	-	Research center for refrigeration technique and heat pumps
g_i	-	Weight on the i-th aggregation
GWP	-	Global warming potential [kg CO ₂ eq./kg]
GWP ₁₀₀	-	Global warming potential [kg CO ₂ eq./kg], time horizon 100 years
HBFC	-	Hydrobromofluorocarbon
HC	-	Hydrocarbon
HCC	-	Hydrochlorocarbon
HCFC	-	Hydrochlorofluorocarbon
HDT	-	Hasse Diagram Technique

HFC	-	Hydrofluorocarbon
HFE	-	Hydrofluoroether
HTP	-	Impact category “Human toxicity”
IPCC	-	Intergovernmental Panel on Climate Change
L	-	Average annual loss of refrigerant [% of refrigerant charge] for TEWI calculation
LCA	-	Life cycle assessment
m	-	Refrigerant charge [kg] for TEWI calculation
METEOR	-	Method of evaluation by order theory
ODP	-	Ozone depletion potential [R11 eq.kg]
ODS	-	Ozone depleting substance
PDF	-	Potentially Disappeared Fraction of Species
PE	-	Impact category “Demand of non-renewable primary energy”
PFC	-	Perfluorocarbon
PFCA	-	Perfluorinated carboxylic acid
P _i	-	Numerical value of the i-th attribute
POCP	-	Impact category “Photo-oxidant formation”
Poset	-	Partially ordered set
Pt	-	Ecopoints of EI99
r	-	Emission of CO ₂ + other greenhouse gases by energy generation [kg CO ₂ /kWh] for TEWI calculation
ref	-	Reference gas, CO ₂ (for GWP calculation)
R11	-	Trichlorofluoromethane
R12	-	Dichlorodifluoromethane
R22	-	Chlorodifluoromethane
R23	-	Trifluoromethane
R30	-	Dichloromethane
R32	-	Difluoromethane
R116	-	Hexafluoroethane
R125	-	Pentafluoroethane
R134a	-	1,1,1,2-Tetrafluoroethane
R143a	-	1,1,1-Trifluoroethane
R152a	-	1,1-Difluoroethane
R218	-	Octafluoropropane
R227ea	-	1,1,1,2,3,3,3-Heptafluoropropane
R236fa	-	1,1,1,3,3,3-Hexafluoropropane
R290	-	Propane
R404A	-	Blend with R125 (44 %), R134a (4 %), and R143a (52 %)
R407C	-	Blend with R32 (23 %), R125 (25 %), and R134a (52 %)
R410A	-	Blend with R32 (50 %), and R125 (50 %)
R600a	-	Isobutane
R717	-	Ammonia
R718	-	Water
R744	-	Carbon dioxide
R1270	-	Propene
S _L	-	Annual operation hours [h/yr] for TEWI calculation
SOD	-	Impact category “Stratospheric ozone depletion”
T	-	Lifetime [years] for TEWI calculation
TETP	-	Impact category “Terrestrial ecotoxicity”
t _c	-	Critical temperature [°C]

TEWI	-	Total Equivalent Warming Impact [kg CO ₂ eq.]
TEWI _{direct}	-	Direct TEWI component [kg CO ₂ eq.]
TEWI _{indirect}	-	Indirect TEWI component [kg CO ₂ eq.]
TFA	-	Trifluoroacetic acid
TH	-	Time horizon (integrated time)
TWA	-	Time-weighted average exposure limit [ppm]
UNFCCC	-	United Nations Framework Convention on Climate Change
USA	-	United States of America
UV	-	Ultraviolet
WC	-	Worst-case scenario
x	-	Refrigerant loss [kg] during recharge/servicing for TEWI calculation
X	-	Gas of interest (for GWP calculation)
z	-	Number of recharges/servicing per lifetime for TEWI calculation
φ _i	-	i-th aggregation within METEOR

Figures

Figure 1:	Scheme of the direct expansion R134a A/C system in passenger cars	8
Figure 2:	Scheme of secondary loop system in passenger car A/C system	9
Figure 3:	Arctic and Antarctic ozone distribution	10
Figure 4:	Schematic of the life cycle of A/C system	15
Figure 5:	Scheme of Eco-indicator 99	31
Figure 6:	Generalized scheme for the atmospheric oxidation of halogenated organic compounds	36
Figure 7:	Scheme for atmospheric E7100 degradation	38
Figure 8:	A Hasse diagram	42
Figure 9:	Aggregation scheme of METEOR calculation	45
Figure 10:	Exemplary sketch of diagrams	46
Figure 11:	CML02 results of the impact categories ADP and PE	46
Figure 12:	CML02 results of the impact categories CC and SOD	47
Figure 13:	CML02 results of the impact categories AP and EP	48
Figure 14:	CML02 results of the impact categories POCP and HTP	48
Figure 15:	CML02 results of the impact categories FAETP and TETP	49
Figure 16:	CML02 results of the impact category ADP	50
Figure 17:	CML02 results of the impact category PE	50
Figure 18:	CML02 results of the impact category CC	51
Figure 19:	CML02 results of the impact category FAETP	51
Figure 20:	EI99 results of complete life cycle	52
Figure 21:	Contribution of production, operation, and disposal phase to EI99	53
Figure 22:	EI99 of production phase	54
Figure 23:	EI99 of operation phase	54
Figure 24:	EI99 of disposal phase	55
Figure 25:	TEWI results of complete life cycle	56
Figure 26:	Contribution of indirect TEWI component	56
Figure 27:	Contribution of direct TEWI component	57
Figure 28:	Partitioning of some degradation products into the compartments air, water, and soil under different models	58
Figure 29:	Crucial g-values of the aggregations ϕ_1 (tc, Cp), ϕ_2 (GWP, ODP), and ϕ_3 (cow, TWA)	61
Figure 30:	Linear orders of selected stability fields of aggregations ϕ_1 (tc, Cp), ϕ_2 (GWP, ODP), and ϕ_3 (cow, TWA)	62
Figure 31:	Rank distribution for each studied refrigerant	65
Figure 32:	Sensitivity analysis of different leakage rates for EI99 calculation	68
Figure 33:	Sensitivity analysis of different operation times for EI99 calculation	69

Figure 34:	Separate ranking of TEWI components	71
Figure 35:	Change of TEWIdirect (R134a) under different scenarios	71
Figure 36:	Change of TEWIindirect (R134a) under different scenarios	72
Figure 37:	Changes in refrigerant ranking due to different operating times SL under average European climate conditions	72
Figure 38:	Influence of operation time on TEWI	73
Figure 39:	Changes in refrigerant ranking due to different leakage rates during operation phase under average European climate conditions	74
Figure 40:	Influence of annual leakage rate during operation phase on TEWI	75
Figure 41:	Rank distribution pattern of specific weighted sets of stability fields, exemplary for four refrigerants	82
Figure 42:	Hasse diagram using ranks derived from EI99, TEWI, and AV (average CML02) as parameters	84

Tables

Table 1:	Example of the nomenclature of selected refrigerants	5
Table 2:	Assumptions for the annual market growth of different refrigeration sectors	6
Table 3:	Emissions of refrigerants from the refrigeration and A/C sectors in Germany, 2002	7
Table 4:	Refrigerants applied to A/C system in the present LCA study	16
Table 5:	Nominal refrigerant charge of A/C systems in a standard passenger car	18
Table 6:	Direct refrigerant emission scenarios during production phase	18
Table 7:	State description of A/C system depending on used refrigerant	20
Table 8:	Leakage scenarios during the 10 years operation of an A/C system	21
Table 9:	Impact factors for the impact category “Demand of non-renewable primary energy“	24
Table 10:	Energy content of some primary energy sources	25
Table 11:	Impact factors for the impact category “Depletion of abiotic resources”	25
Table 12:	Impact factors for the impact category “Climate change”	26
Table 13:	Impact factors for the impact category “Stratospheric ozone depletion”	27
Table 14:	Impact factors for the impact category “Human toxicity“	28
Table 15:	Impact factors for the impact categories “Fresh water aquatic toxicity” and “Terrestrial ecotoxicity”	28
Table 16:	Impact factors for the impact category “Photo-oxidant formation”	29
Table 17:	Impact factors for the impact category “Acidification”	30
Table 18:	Parameter for TEWI calculation for different emission scenarios	35
Table 19:	Refrigerant properties for TEWI calculation	35
Table 20:	Compartment properties for modelling the distribution fate of persistent degradation products	41
Table 21:	Normalized and reoriented data values of refrigerants used in the present METEOR study	44
Table 22:	Concentrations of the main degradation products of E7000, E7100, E7200, and R30 in environmental compartments [$\mu\text{g}/\text{dm}^3$] under the German model	59
Table 23:	Concentrations of the main degradation products of E125, E134, R152a, and R134a in environmental compartments [$\mu\text{g}/\text{dm}^3$] under the German model	60
Table 24:	Exemplary values of ϕ_5 for a random selection from the 749 stability fields and corresponding weights	63
Table 25:	Percentage of occupancy of certain ranks of studied refrigerants	64
Table 26:	Additional fuel consumption of studied refrigerant A/C systems under different scenarios	76
Table 27:	Average rank of refrigerants based on different sets of stability fields	80
Table 28:	Ranks of the impact categories of CML02 and its average ranking, ranks of EI99 and TEWI method for the average life cycle scenario	83

Table 29:	Spearman's rank correlation coefficient ρ	84
Table 30:	Averaged ranks derived from METEOR calculation	87
Table 31:	Property table of refrigerants	A-2
Table 32:	Average monthly temperature [$^{\circ}\text{C}$] of some European cities	A-4
Table 33:	Production of 1 kg R134a	A-6
Table 34:	Production of 1 kg R152a	A-7
Table 35:	Production of 1 kg R290	A-8
Table 36:	Production of 1 kg R600a	A-8
Table 37:	Production of 1 kg R744	A-9
Table 38:	Production of 1 kg R30	A-10
Table 39:	Production of 1 kg E125	A-11
Table 40:	Production of 1 kg E134	A-12
Table 41:	Production of 1 kg E7000	A-13
Table 42:	Production of 1 kg E7100	A-14
Table 43:	Production of 1 kg E7200	A-15
Table 44:	Energy consumption during production of one A/C system	A-16
Table 45:	Additional fuel consumption due to A/C system weight	A-16
Table 46:	Annual energy consumption due to compression of refrigerant based on worst-case, average, and best-case operation scenario	A-17
Table 47:	Input and combustion products during incineration of 1 kg refrigerant	A-18
Table 48:	Energy consumption during dismantling of one A/C system	A-18
Table 49:	Direct refrigerant emission scenarios during disposal phase	A-19
Table 50:	Normalisation and weights using hierarchist perspective combined with the default weighting	A-19
Table 51:	Damage factors for EI99 calculation	A-19
Table 52:	Standard EI99 indicators for specific processes and products	A-22
Table 53:	Atmospheric degradation products of certain refrigerants	A-23
Table 54:	Amount of refrigerant emissions and corresponding degradation products of some refrigerants from one passenger car	A-24
Table 55:	Results of studied refrigerants and contributions to different impact categories of CML02 under three different scenarios	A-27
Table 56:	Results of the studied refrigerants and contributions to different impact categories of CML02; contribution to production, operation, and disposal phase under average scenario	A-29
Table 57:	Results of EI99 assessment in Ecopoints [Pt], contribution from production, operation, and disposal phase and EI99 of the entire life cycle	A-31
Table 58:	TEWI _{indirect} , TEWI _{direct} , and TEWI values	A-32
Table 59:	TEWI _{indirect} , TEWI _{direct} , and TEWI values of different scenarios where only one parameter is changed and the others are put to average	A-33
Table 60:	Distribution [%] of some refrigerant degradation products in the environmental compartments air, water, soil/aerosol particles of four different fate models	A-34

Table 61:	Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on life cycle refrigerant emissions and German model	A-35
Table 62:	Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on refrigerant emissions during one year of operation and German model	A-36
Table 63:	Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on life cycle refrigerant emissions and Atmosphere-aerosol model	A-38
Table 64:	Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on refrigerant emissions during one year of operation and Atmosphere-aerosol model	A-39
Table 65:	Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on life cycle refrigerant emissions and Atmosphere-fog model	A-41
Table 66:	Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on refrigerant emissions during one year of operation and Atmosphere-fog model	A-42
Table 67:	Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on life cycle refrigerant emissions and Atmosphere-raining cloud model	A-44
Table 68:	Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on refrigerant emissions during one year of operation and Atmosphere-raining cloud model	A-45
Table 69:	Weights of selected stability fields	A-47

Summary

Motivation of the present study on refrigerants is the phase-out of presently used cooling agents, mainly chlorofluorocarbons, fluorocarbons, and hydrofluorocarbons, and the necessity to find environmental benign and energy efficient replacements. Aim of the present project is to compare the results of the widely used concept of life cycle assessments (LCA) with those obtained by Discrete Mathematics. Mobile air conditioning (A/C) systems in passenger cars are chosen as an example for technical application of refrigerants. The environmental impacts due to life cycles of different possible substitute refrigerants are compared with the presently used 1,1,1,2-tetrafluoroethane (R134a). Additional refrigerants included in this study comprise dichloromethane (R30), propane (R290), isobutane (R600a), carbon dioxide (R744), pentafluorodimethyl ether (E125), 1,1,1',1'-tetrafluorodimethyl ether (E134), heptafluoropropyl methyl ether (E7000), methyl nonafluorobutyl ether (E7100), ethyl nonafluorobutyl ether (E7200), and 1,1-difluoroethane (R152a).

The data interpretation is carried out by means of independent methods such as the Dutch Handbook method (CML02), Eco-indicator 99 (EI99) and Total Equivalent Warming Impact (TEWI). According to the CML02 assessment method, R290, R600a, and R744 have a lower environmental impact compared with R134a in the impact categories “Stratospheric ozone depletion” (SOD), “Climate change” (CC), “Fresh water aquatic toxicity” (FAETP), and “Terrestrial ecotoxicity” (TETP). E125, E7000, E7100, and E7200 are the refrigerants with the lowest impacts in the categories “Acidification” (AP), “Eutrophication” (EP), “Photo-oxidant formation” (POCP), and “Human toxicity” (HTP). In the impact category “Depletion of abiotic resources” (ADP), R152a has a lower impact than R134a. The operation phase is the dominant phase within the life cycle. It accounts to > 79 % for impact category ADP, 71 – 99 % for CC, and > 50 % for FAETP. By means of EI 99 and TEWI, R152a, R290, R600a, R744, and E7200 have a smaller environmental impact than R134a under average operation scenario. According to EI 99, the operation phase is with 43 – 63 % the dominating life cycle phase. Comparing the assessment of refrigerants by the three methods shows that each method ranked E134 higher than R134a. E7200, E7100, E7000, R152a, R600a, R290, and R744 are ranked lower than R134a.

The fate of some persistent degradation products of the studied refrigerants is modelled. The concentrations of perfluorinated carboxylic acids (PFCAs) in surface freshwater systems in Germany due to the annual direct refrigerant emissions of E7000, E7100, and E7200 from the A/C system of a passenger car are about the factor 10^7 to 10^9 smaller than the precautionary limit of $0.1 \mu\text{g/L}$ of the Federal Environment Agency for partly or non-assessable substances in drinking water (UBA 2003). Assuming that all 46 million German passenger cars (Destatis 2006a) are equipped with A/C systems using E7000, E7100, or E7200, the concentration of the degradation products in German surface waters will amount to $0.1 - 1 \mu\text{g/L}$. That means even under the best-case scenario the above mentioned precautionary limit will be reached and under worst-case scenario

exceeded. The acidification effect of degradation products of R30, R152a, E134, and E125 is negligible compared with the contribution of the overall acidity from other natural and anthropogenic sources.

The ranking of refrigerants due to the aggregation of six substance-intrinsic properties (critical temperature, heat capacity of vapour, global warming potential, ozone depletion potential, octanol-water partition coefficient, and toxicological exposure limits) by means of the mathematical model METEOR (**M**ET**H**od of **E**valuation by **O**Rder theory) was performed for 15 refrigerants i.e. chlorodifluoromethane (R22), difluoromethane (R32), pentafluoroethane (R125), 1,1,1-trifluoroethane (R143a), propene (R1270), ammonia (R717), R134a, R152a, R290, R30, R600a, R744, E7200, and the blends R407C and R410A. A high rank is accompanied with a high environmental impact. Considering a selection of possible aggregations, R22 is ranked to 87 % within the five highest ranks, followed by R143a with 85 %, and R32 with 71 %. Refrigerants which are ranked predominantly in the five lowest ranks include R717 (88 %), E7200 (81 %), and R290 (74 %). R744 has in ca. 40 % of the selected aggregations the highest rank and in 24 % the lowest rank. Two third of the refrigerants show a modification in their rank distribution pattern when putting an extreme low or high weight on the thermodynamic properties critical temperature and heat capacity.

Additional to the results derived by the LCA conducted in this study, literature LCA results comprising different refrigeration processes and refrigerants were included in the comparison with results from METEOR. In general, METEOR does not agree with the results from LCA. In summary, ranking of refrigerants based on substance-intrinsic properties using METEOR can only give a rough estimation about general environmental impact of a certain refrigerant compared to others. Hardly any statement can be made about the influence of the technical configuration to which the refrigerants are applied. This phenomenon is not alone due to the fact that even different LCA studies show contradicting results depending on the different applications and conditions. Considering A/C systems in passenger cars, R152a, R290, R600a, and R744 appear as the most recommendable replacements of R134a in this application taking into account the results of the present LCA study derived by the three assessment methods and the fate modelling of some refrigerant degradation products.

Zusammenfassung

Grundlage der durchgeführten Studie an Kältemitteln ist die stufenweise Einstellung der Produktion und Nutzung der derzeit verwendeten Kältemitteln, z.B. Chlorfluorkohlenwasserstoffe, Fluorkohlenwasserstoffe und teilfluorierte Kohlenwasserstoffe. Daraus ergibt sich die Notwendigkeit, umweltfreundliche und energieeffiziente Ersatzstoffe zu finden. Ziel der vorliegenden Studie ist der Vergleich von Ökobilanzergebnissen mit Ergebnissen, die anhand von Methoden der Diskreten Mathematik gewonnen wurden. Pkw-Klimaanlagen werden als Beispiel der technischen Anwendung von Kältemitteln herangezogen. Die Umweltwirkungen der Lebenszyklen verschiedener möglicher Ersatzkältemittel werden mit denen des derzeit verwendeten 1,1,1,2-Tetrafluorethans (R134a) verglichen. Neben R134a umfasst die vorliegende Studie Methylenchlorid (R30), Propan (R290), Isobutan (R600a), Kohlenstoffdioxid (R744), Pentafluordimethylether (E125), 1,1,1',1'-Tetrafluordimethylether (E134), Heptafluorpropylmethylether (E7000), Methylnonafluorbutylether (E7100), Ethylnonafluorbutylether (E7200) und 1,1-Difluorethan (R152a).

Die Auswertung erfolgt anhand unabhängiger Methoden wie die Dutch Handbook Methode (CML02), dem Eco-indicator 99 und dem Total Equivalent Warming Impact (TEWI). Nach der CML02 Bewertungsmethode haben R290, R600a und R744 in den Wirkungskategorien „Stratosphärischer Ozonabbau“ (SOD), „Treibhauseffekt“ (CC), „Aquatische Süßwassertoxizität“ (FAETP) und „Terrestrische Ökotoxizität“ (TETP) eine geringere Umweltschadwirkung als R134a. E125, E7000, E7100 und E7200 sind die Kältemittel mit den geringsten Beiträgen in den Wirkungskategorien „Versauerung“ (AP), „Eutrophierung“ (EP), „Ozonbildungspotential“ (POCP), and „Humantoxizität“ (HTP). In der Wirkungskategorie „Verbrauch abiotischer Ressourcen“ (ADP) besitzt R152a eine geringere Schadwirkung als R134a. Die Nutzungsphase ist die dominierende Phase des Lebenszyklus. Sie trägt zu > 80 % zur Wirkungskategorie ADP, zu 70 – 100 % zur Kategorie CC und zu > 50 % zu FAETP bei. Gemäß EI99 und TEWI haben R152a, R290, R600a, R744 und E7200 im Durchschnitt eine geringere Umweltschadwirkung als R134a. Bei EI99 ist die Nutzungsphase mit 43 – 63 % die dominierende Lebenszyklusphase. Ein Vergleich der Kältemittelbewertungen anhand der drei unterschiedlichen Methoden zeigt, dass alle drei Methoden E134 ein größeres Schadenspotential zuweisen als R134a. Des Weiteren besitzen E7200, E7100, E7000, R152a, R600a, R290 und R744 eine geringere Schadwirkung als R134a.

Der Verbleib einiger persistenter Abbauprodukte der betrachteten Kältemittel wird modelliert. Die Konzentration an perfluorierten Carbonsäuren (PFCA) in Oberflächengewässern in Deutschland, die aufgrund der jährlich auftretenden Kältemittelemissionen an E7000, E7100 und E7200 aus einer einzelnen Pkw-Klimaanlagen entstehen, sind um den Faktor 10^7 bis 10^9 kleiner als der Vorsorgewert von $0,1 \mu\text{g/L}$ des Umweltbundesamtes für teil- oder nicht bewertbare Stoffe im Trinkwasser (UBA 2003). Unter der Annahme, dass alle 46 Millionen deutschen Pkw (Destatis 2006a) Klimaanlagen mit E7000, E7100 oder E7200 betreiben, treten in

deutschen Oberflächengewässern PFCA-Konzentrationen von 0,1 – 1 µg/L auf. Dies bedeutet, dass sogar unter einem best-case Szenario die genannten Vorsorgewerte erreicht und unter einem worst-case Szenario sogar überschritten werden. Hingegen ist der Versauerungseffekt der Abbauprodukte von R30, R152a, E134 und E125 vernachlässigbar verglichen mit den Beiträgen aus anderen natürlichen und anthropogenen Quellen.

Ein Ranking der Kältemittel infolge der Aggregation von sechs stoffspezifischen Parametern (kritische Temperatur, Wärmekapazität, Treibhauseffekt, Ozonzerstörungspotential, Oktanol-Wasser-Verteilungskoeffizient und toxikologischer Grenzwert) mittels des mathematischen Modells METEOR (**M**ETHOD of **E**valuation by **O**Rder theory) wurde für 15 Kältemittel durchgeführt (Chlordifluormethan (R22), Difluormethan (R32), Pentafluorethan (R125), 1,1,1-Trifluorethan (R143a), Propen (R1270), Ammoniak (R717), R134a, R152a, R290, R30, R600a, R744, und E7200 sowie die Kältemittelgemische R407C und R410A). Ein hoher Rang entspricht einem großen Umweltschädigungs-potential. In der vorliegenden Studie wird eine Auswahl möglicher Aggregationen betrachtet. Diese weisen R22 mit 87 % einen Rang zwischen 11-15 zu, gefolgt von R143a mit 85 % und R32 mit 71 %. Kältemittel, die vorwiegend zwischen Rang 1-5 liegen, schließen R717 (88 %), E7200 (81 %) und R290 % ein. R744 nimmt zu ca. 40 % der ausgewählten Aggregationen den höchsten und zu etwa 24 % den niedrigsten Rang ein. Zwei Drittel der Kältemittel zeigen eine Modifikation ihrer Rangverteilung wenn die thermodynamischen Parameter kritische Temperatur und Wärmekapazität besonders hoch bzw. niedrig gewichtet werden.

Neben den Ergebnissen aus der vorliegenden Ökobilanzstudie wurden Untersuchungsergebnisse aus der Literatur, die Ökobilanzen für andere Kälteprozesse und Kältemittel umfassen, zu dem Vergleich mit Ergebnissen von METEOR hinzugezogen. Im Allgemeinen stimmen die Ergebnisse von METEOR nicht mit Ökobilanzergebnissen überein. Zusammenfassend lässt sich sagen, dass ein Ranking der Kältemittel aufgrund stoffspezifischer Eigenschaften mittels METEOR lediglich eine allgemeine Erstabseätzung hinsichtlich der Umweltschadwirkung eines Kältemittels im Vergleich zu anderen geben kann, doch ist es nicht möglich, eine Aussage bezüglich der technischen Anlagenkonfiguration, in der ein Kältemittel eingesetzt wird, zu treffen. Anhand der Ergebnisse aus der durchgeführten Sachbilanz und der Bewertung mittels der drei genannten Methoden sowie der Modellierung bestimmter Abbauprodukte konnten R152a, R290, R600a und R744 als die besten Ersatzstoffe von R134a in Pkw-Klimaanlagen identifiziert werden.

1 Introduction & aim

1.1 Introduction

Refrigeration and air conditioning (A/C) are important aspects of today's life style. Food conservation is one of the main applications of refrigeration enabling the transport of food over long distances all year. Refrigeration is also used for comfort in A/C systems. Besides comfortable effects, refrigeration and A/C also influence the environment by energy consumption and the use of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) as refrigerants.

Since 1974, the destruction of stratospheric ozone has been observed. It is mainly caused by CFCs whose chlorine atoms react catalytically with ozone. The Montreal Protocol and its amendments regulate the phase-out of CFC-production by 1996 and the phase-out of the production of HCFCs by 2030. Besides stratospheric ozone destruction, climate change is an increasingly political aspect. Especially the contribution of energy consumption to climate change is of interest. Additionally, high energy prices encourage investing in energy efficient systems. With regard to ozone depletion and climate change, substituents for the so far used refrigerants must be found.

1.2 Aim

Aim of the present project is to compare the results of the widely used concept of life cycle assessments (LCA) applied on different refrigerants with those obtained by Discrete Mathematics. The main goal is to give an estimation which refrigerant might be the environmentally least harmful replacement for CFCs in a certain application. Mobile A/C systems in passenger cars are chosen as an example for refrigerating systems. The life cycles of different possible substitute refrigerants are compared from production over operation to disposal phase. The main focus is placed on energy consumption and environmental impacts. The data interpretation is carried out by means of independent methods such as the Dutch Handbook method (CML02), Eco-indicator 99 (EI99), and Total Equivalent Warming Impact (TEWI). In addition to the results derived by the LCA conducted in this study, literature LCA results comprising different refrigeration processes and refrigerants were included in the comparison with results derived by the mathematical model METEOR (**M**ETHOD of **E**valuation by **O**RDER theory) which is based on Discrete Mathematics using refrigerant intrinsic properties.

1.3 Layout of thesis

Background information about the environmental problems caused by refrigerants, their regulation by law, types of refrigerants, emission and production rates of certain refrigerants and refrigerant techniques are described in Chapter 1.

In Chapter 1, the scope of this work is specified with the technical application and the refrigerants of interest. Furthermore, the LCA is described in detail giving functional unit, scope definition, allocations, and all assumptions that were made within this work. The impact assessment by means of CML02, EI99, and TEWI, the fate modelling, and the theory of the applied discrete mathematical models are described.

The results of the assessment (CML02, EI99, TEWI), fate modelling, and the mathematical model METEOR are included in Chapter 4. Dominance analyses on the impact assessment results were conducted in order to assign the most relevant phases within the life cycle.

Simplifications and estimations of the LCA, and finally the results are discussed in Chapter 5. Sensitivity analyses were conducted to evaluate the importance of leakage rates, damage factors, and operation time on the environmental impact. The results from the different evaluation methods are compared with each other and with results from literature that assess the environmental impact of certain refrigerants in A/C systems in passenger cars.

Finally, in Chapter 6, a recommendation and outlook are given regarding the most environmental friendly refrigerant for the application in A/C systems in cars.

2 Background knowledge

2.1 Refrigerant types

In the present study, refrigerants from different chemical groups are included. The LCA comprises hydrofluorocarbons, hydrocarbons, hydrofluoroethers, dichloromethane, and carbon dioxide. The METEOR study includes additionally mixtures of hydrofluorocarbons and ammonium. In the following paragraphs, the different groups will be shortly introduced.

Chlorofluorocarbons and hydrochlorofluorocarbons

Chlorofluorocarbons (CFCs) are hydrocarbons whose hydrogen atoms are completely replaced by chlorine or fluorine atoms. They have a high ODP and GWP due to their very long atmospheric lifetimes (Destatis 2006b).

Hydrofluorochlorocarbons (HCFCs) are hydrocarbons whose hydrogen atoms are only partially replaced by chlorine or fluorine atoms. In general, their ODPs are much lower than those of CFCs. GWPs of HCFCs are also considerably lower but can reach still relatively high values in some cases. The main advantage of HCFCs is the fact that they are decomposed in the troposphere and only a small part of their emissions enters the stratosphere (Destatis 2006b).

Fluorocarbons and hydrofluorocarbons

Perfluorocarbons (PFCs) are entirely fluorinated carbohydrates which contain no chlorine. Hydrofluorocarbons (HFCs) are not completely fluorinated, they contain hydrogen atoms. Both substance classes are relevant to global warming. GWPs of the various substances may differ greatly (Table 31). In contrast to CFCs and HCFCs, fluorocarbons have an ODP of zero (Destatis 2006b).

Hydrocarbons

Hydrocarbons (HCs) are organic compounds that consist solely of hydrogen and carbon. They all contain a carbon backbone with hydrogen atoms attached to it. The structure may be cyclic or aliphatic. The molecular structure of hydrocarbons varies from the simple methane (CH_4) to very heavy and complex molecules. Albeit this class consists of stable and unreactive molecules, the flammability and the ability to react with halons must be regarded (Destatis 2006b).

Blends

Blends are mixtures from two or more compounds, which contain at least one compound that has either an ODP or GWP₁₀₀ greater zero. They gradually replace the restricted CFCs. The values of ODP and GWP₁₀₀ are calculated on the basis of the values of the individual substances of each mixture (Destatis 2006b). For example the GWP₁₀₀ for R410A which consist to 50 % of R32 and R125 is calculated as follows:

$$\begin{aligned}\text{GWP}_{100}(\text{R410A}) &= 0.5 \cdot \text{GWP}_{100}(\text{R32}) + 0.5 \cdot \text{GWP}_{100}(\text{R125}) = && \text{Equation 1} \\ &= 0.5 \cdot 670 \text{ kg CO}_2 \text{ eq.} + 0.5 \cdot 3450 \text{ kg CO}_2 \text{ eq.} = \\ &= 2060 \text{ kg CO}_2 \text{ eq.}\end{aligned}$$

Hydrofluoroethers

Hydrofluoroethers (HFEs) are the third generation of CFC-substitutes. They are partly fluorinated ethers. Their physical and chemical properties are similar to those of CFCs and HCFCs, but their hydrogen content results in lower atmospheric lifetimes and lower GWP₁₀₀. They have a zero value of ODP, are low in toxicity, and are non-flammable. (IPCC 2006, Tsai 2005)

Natural refrigerants

Air and water are natural refrigerants with zero ODP and GWP₁₀₀ values. Conveniently, HCs, ammonia, and carbon dioxide are considered as natural refrigerants (Devotta et al. 2001, eurammon 2002, eurammon 2005a, eurammon 2005b).

Nomenclature of refrigerants

The chemical names of halogenated refrigerants are often very long. Therefore, a nomenclature system was developed to identify the different substances. It is described in DIN 8960 (1998). The number assigned to each refrigerant is related to its chemical composition and consists of four digits (Table 1). Each digit describes a characteristic of the molecule:

- 1st digit: number of carbon to carbon double bonds (if 0, not given)
- 2nd digit: number of carbon atoms minus one
- 3rd digit: number of hydrogen atoms plus one
- 4th digit: number of fluorine atoms

Any spare atoms are assumed to be chlorine unless otherwise noted.

For blends of refrigerants another nomenclature system is used. Usually, non-azeotropic mixtures are assigned numbers in the 400 series and azeotropic mixtures in the 500 series in order of their commercial introduction. Blends containing the same compounds but different mass proportions of them are distinguished by subsequent capital letters.

Other organic refrigerants, which cannot be identified by the regular numbering system because they contain nine or more hydrogen atoms, are assigned arbitrary numbers in the 600 series. Inorganic refrigerants are allocated to the 700 series. The molecular weight is used prefixed by the number 7. In Table 1 are for some refrigerants the numbers listed which arise from DIN 8960 (1998).

Table 1: Example of the nomenclature of selected refrigerants

Refrigerant type	Refrigerant number	Formula	Refrigerant name
CFC	R11	CCl_3F	Trichlorofluoromethane
HCFC	R22	CHClF_2	Chlorodifluoromethane
HFC	R32	CH_2F_4	Difluoromethane
HFC	R125	C_2HF_5	Pentafluoroethane
HC	R290	C_3H_8	Propane
HC	R600	C_4H_{10}	Butane
	R717	NH_3	Ammonia
Blend	R407C		R32 (50 %), R125 (50 %)

Properties of good refrigerants

The requirements that a substance must meet in order to be considered as a good refrigerant in vapour compression systems include its ability to absorb high amounts of energy by expanding its volume slightly, so that the work done by the compressor remains relatively low ensuring an energy efficient process and a comparable small compressor. This is influenced by the parameters latent heat of vaporisation and specific volume. A good refrigerant should have a high latent heat of vaporisation, which means that the substance can absorb high amounts of energy while changing from its liquid to its vapour phase. Additionally, it should have a low vapour specific volume meaning that a determined mass of refrigerant is occupying a reduced space.

Furthermore, a refrigerant should have a low specific heat in its liquid phase but high values in its vapour phase. The former guarantees that the refrigerant needs low amounts of energy while increasing its temperature. This is supporting its vaporisation. The latter means that the vapour can take up large amounts of energy but changes its temperature to a lesser degree. This makes the vapour condensation before approaching the compressor

and the condenser more unlikely.

All the above mentioned properties influence the efficiency of the refrigeration process in thermodynamic terms. Besides those thermodynamic aspects, toxicological and safety aspects should also be considered. Consequently, a refrigerant should favour low toxicity and low flammability as substance intrinsic attributes. Also, cost aspects are of relevance in economical terms.

2.2 Emissions & production rates of refrigerants

Consumption and emissions of refrigerants

The annual market demand for refrigeration in Europe is assumed to grow about 1 to 2 % per year from 2002 to 2015, the annual market demand in the sector of A/C is growing about 4 % per year (IPCC 2006). For the United States of America (USA) the annual market growth for that time period is believed to resemble the situation in Europe, although the annual market growth in the sectors domestic and commercial refrigeration are almost doubled (IPCC 2006). In Japan the annual market growth is supposed to be about 1 % in most sectors and in the sectors domestic and commercial refrigeration about 2 % (Table 2). For developing countries the annual market growth is assumed to be much higher than in Europe, USA, and Japan. Thus, the necessity of finding more environmental friendly refrigerants is of high relevance.

Table 2: Assumptions for the annual market growth of different refrigeration sectors (IPCC 2006)

Sector	Annual market growth 2002-2015 [%/yr]			
	Europe	USA	Japan	Developing countries
Domestic refrigeration	1	2.2	1.6	2 - 4.8
Commercial refrigeration	1.8	2.7	1.8	2.6 - 5.2
Industrial refrigeration	1	1	1	3.6 - 4
Transport refrigeration	2	3	1	3.3 - 5.2
Stationary A/C	3.8	3	1	5.4 - 6
Mobile A/C	4	4	1	6 - 8

The annual emissions of fluorinated greenhouse gases (F-gases) from different refrigeration and A/C sectors in Germany in 2002 are shown in Table 3. The table gives the mainly used F-gases in the different sectors (Schwarz 2005). Emissions from domestic refrigeration/freezing systems constitute the smallest part of the overall emissions of F-gases from refrigeration. The F-gas emissions of the sectors refrigerated vehicles, reefer containers, domestic refrigeration/freezing, and heat pumps amount

together to approx. 100 t, surpassed by both stationary A/C and mobile A/C (without passenger cars). Industrial and commercial refrigeration and freezing systems emitted together over 1 300 t F-gases in 2002. The major emission sources of F-gases were passenger car A/C systems with emissions of about 1 400 t.

Table 3: Emissions of refrigerants from the refrigeration and A/C sectors in Germany, 2002; mainly used refrigerants (Schwarz 2005) (for description of refrigerants see Attachment)

Category	Refrigerants	Emissions [t/year]
Refrigerated vehicles	R134a, R404A, R410A, R152a, R218	52
Reefer container (German share)	R134a, R404A	24
Heat pumps	R134a, R407C, R404A, R410A	22
Domestic refrigeration/freezing	R134a	1
Stationary A/C (> 60 kW cooling capacity)	R134a, R407C	116
Passenger car A/C	R134a	1405
Mobile A/C without passenger cars	R134a	173
Industrial refrigeration/freezing	R134a, R404A, R407C, R23, R227ea, R236fa, R116	222
Commercial refrigeration/freezing	R134a, R404A, R407C, R23, R125, R152a, R116, R218	814

Selection of exemplary refrigeration sector

A/C systems in passenger cars have high emission rates. In combination with the high fleet number of air conditioned cars, A/C systems in vehicles are the biggest single source of fluorinated gases in Germany. As the percentage of passenger cars equipped with A/C will finally increase to about 95 %, this sector is of main interest in regard to potential impact reduction due to ozone depleting substances (ODSs). Consequently, the main focus of the present study is laid on mobile A/C as an example for the refrigeration sector.

2.3 Refrigeration process

At present, 1,1,1,2-tetrafluoroethane (R134a) ($GWP_{100} = 1410$, IPCC 2006) is used in passenger car A/C systems. The common R134a passenger car A/C system consists of compressor, condenser, accumulator, expansion device, evaporator, tubes, and control systems (Figure 1). All components are connected within a closed cycle. The A/C unit extracts heat from the passenger's cabin and channels it outside. Usually the A/C works with the compression technology. As soon as the A/C unit is switched on at running state of the motor the compressor sucks on the cold and gaseous refrigerant from the accumulator. The refrigerant is condensed, whereby it is heated, and pressed in the condenser. The air stream of the moving car or from an extra ventilation system cools the condensed, hot gas. As soon as the pressure dependent dew point is reached the refrigerant condenses. The high pressure, liquid refrigerant streams through the expansion device and is injected into the evaporator. Here it releases tension and evaporates. The required evaporation heat is taken from the air stream that streams around the evaporation fins. In the accumulator it is collected, cleaned and dried. The main leakage points are the shaft sealing of the compressor, the tube system and the gaskets. (Schwaab et al. 2004)

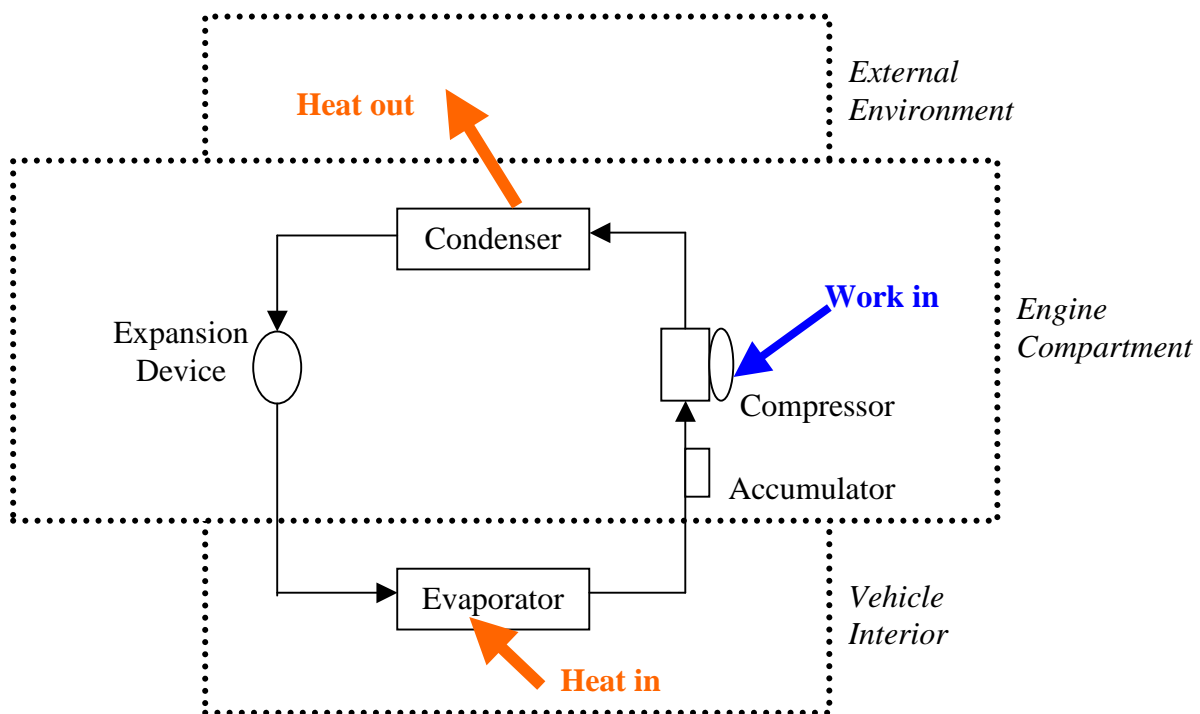


Figure 1: Scheme of the direct expansion R134a A/C system in passenger cars

Some refrigerants are not safe in a system like the one described above because they are flammable or to a certain degree toxic. In those cases, a secondary loop is applied to keep the refrigerant hermetically closed in the engine compartment (Figure 2).

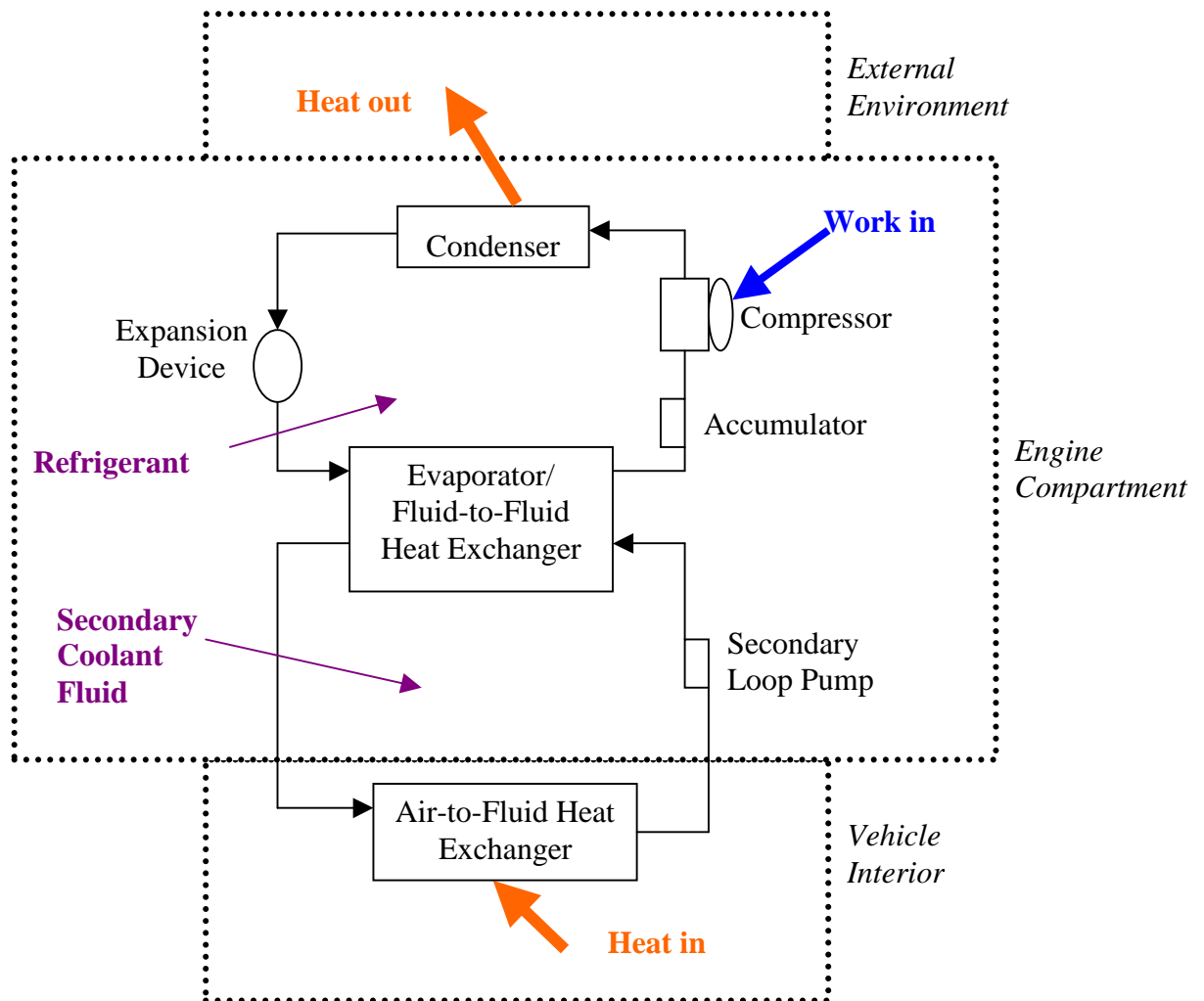


Figure 2: Scheme of secondary loop system in passenger car A/C system

2.4 Ozone depletion & climate change

Ozone depletion

Ozone plays an important role in the global climate system. Stratospheric ozone has two characteristic properties. First, it has a relatively short chemical lifetime. Therefore, it is not uniformly distributed within the atmosphere. The mixing of ozone in the atmosphere is controlled by complex dynamical and chemical processes, which are described in detail in IPCC (2006). Second, its ability to absorb ultraviolet (UV) radiation leads to an increase in stratospheric temperature with altitude. This results in a strong resistance to vertical motion. Furthermore, the stratospheric ozone layer is essential because it protects life at the Earth's surface from harmful UV radiation. (IPCC 2006)

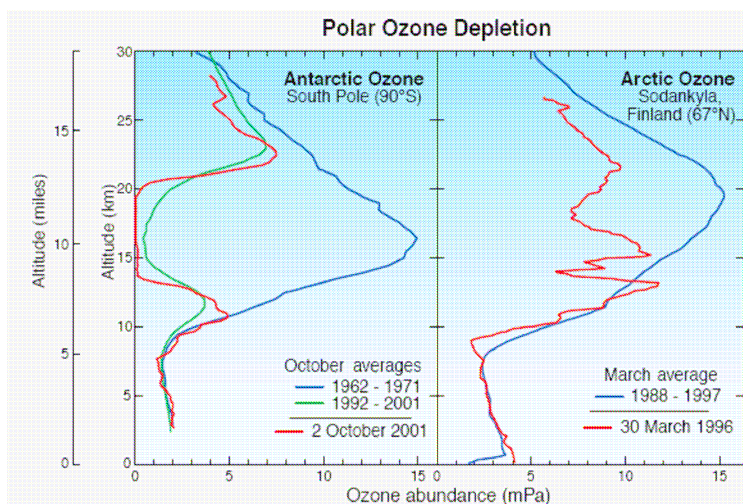


Figure 3: Arctic and Antarctic ozone distribution (IPCC 2006)

Since 1974, the destruction of the stratospheric ozone has been observed (Molina & Rowland 1974). The stratospheric ozone concentration is rapidly reduced in the 1980s (Figure 3). ODSs often contribute to the global warming by reflecting infrared radiation from the earth surface.

The major ODSs are CFCs (Molina & Rowland 1974, Harnisch et al. 2004) that are used as refrigerants, cleaning solvents, propellants, and foaming agents. In the upper stratosphere, the ozone destruction rate depends on the concentrations of radical species and temperature. A reduction of temperature slows down the destruction of ozone (IPCC 2006). In the lower stratosphere, reactions of ozone molecules with aerosols are important (IPCC 2006). The process of stratospheric ozone destruction is explained in detail in the IPCC report (2006) and therefore, is not repeated here.

Global warming potential

The Global Warming Potential (GWP) is a relative value, used to compare the impact of an emitted gas on the climate and its contribution to climate change. The standard GWP_{100} (Equation 2) is the ratio of the time-integrated radiative forcing from a pulse emission of 1 kg of a substance, relative to that of 1 kg of carbon dioxide, over a

100 year time period (IPCC 2006, Hanaoka et al. 2002). An emitted gas contributes to the global warming relative to its absorption ability to the long wave infrared radiation over a specified time period. This ability depends on its concentration and atmospheric lifetime (IPCC 2006, Highwood & Shine 2000, Good et al. 1998). GWP_{100} values can change if the radiative efficiency or the lifetime of the gas is updated (IPCC 2006).

$$GWP_x(TH) = \frac{\int_0^{TH} \Delta F_x dt}{\int_0^{TH} \Delta F_{ref} dt} \quad \text{Equation 2}$$

- TH – Time horizon (integrated time)
- F – Radiative forcing from a pulse emission of 1 kg gas
- ref – Reference gas, CO₂
- X – Gas of interest

The described methods are valid for source gases with long lifetimes for which a thorough mixing in the troposphere is to be expected but not for source gases with very short tropospheric lifetimes. Furthermore, they refer to the direct impact of source gases but do not consider degradation products which may have an additional impact on global warming. The presence of the emitted gases and their degradation products may influence the distribution of other greenhouse gases. (IPCC 2006)

2.5 International & national legislation

Global, European and national measures regulate the phase-out of production and use of ODSs. The Montreal Protocol of Beijing (1999) completely abandons ODSs according to international law (UNEP 2000). The participating countries committed themselves to stop production and use of CFCs, carbon tetrachloride, and 1,1,1-trichloroethane by January 1st, 1996. The Article 5 countries committed themselves to stop their production and application of these substances gradually by 2010. The Montreal Protocol does not include the production and application of ODSs as raw materials as - by definition - they are not emitted to the atmosphere. The Montreal Protocol allows the production and application of CFCs after January 1st, 1996, for essential-use such as medical sprays and fire extinguishers. The production and application of HCFCs will be gradually reduced and finally stopped by 2030. The application of HCFCs shall be limited to facilities where no environmental friendly substances are technical available. The ODP is the main discussed characteristic for refrigerants in the Montreal Protocol. The national implementation of the Montreal Protocol in Germany is the CFC/Halon Prohibition Ordinance (FCKW-Halon-Verbots-Verordnung 1991).

Since October 1st, 2000, the European Ordinance No. 2037/2000 (EU 2000) of the European Parliament and Council appoints the phase-out for the production of most ODSs and their handling regulations. After 2026, HCFCs are not longer permitted for production. Since January 1st, 2004, the application of HCFCs as refrigerant in new facilities, cooling and conditioning systems, and heat pumps has been prohibited. After January 1st, 2010, the application of untreated HCFCs for servicing and operation usage is prohibited. After January 1st, 2015, the application of HCFCs as refrigerant is prohibited. Besides the regulation of the production and application the EU Ordinance No. 2037/2000 regulates that ODSs have to be retrieved from certain applications and have to be recycled or destroyed.

The Kyoto Protocol (1997) is an international amendment to the United Nations Framework Convention on Climate Change (UNFCCC). The environmental focus was laid on global warming and equivalent emissions of carbon dioxide into the atmosphere. Countries that ratify this protocol commit themselves to reduce their emissions of carbon dioxide, methane, nitrous oxide, HFCs, PFCs, and sulphur hexafluoride. The Kyoto Protocol excludes CFCs, HCFCs, hydrobromofluorocarbons (HBFCs), and bromofluorocarbons (BFCs) on purpose, although the emissions of these substances were 15 % of the worldwide greenhouse gas emissions in 1990. The intention for excluding those substances was not to disturb the global phase-out process of ODSs under the Montreal Protocol (Schwarz 2004). The industry states committed themselves to reduce their combined emission by 5 % of the emissions in 1990 or 1995 for the F-gases. The EU has agreed to cut their emission levels by 8 % (Strogies et al. 2005, EG 2002). In the burden sharing agreement 2002/358/EG (EG 2002), it is regulated that Germany will reduce its emission levels by 21 %.

In relation to the Kyoto Protocol, the European Commission presented a Proposal for a Regulation of the European Parliament and of the Council on certain fluorinated greenhouse gases on August 11, 2003 (COM 2003). In further readings it was suggested to divide the regulation into two parts. First, the directive related to emissions from A/C systems in motor vehicles (EU 2006), and second, the regulation on certain F-gases (EC 2006). The first directive regulates the prohibition of F-gases with GWP₁₀₀ greater than 150 for new car models produced from 2011 onwards. But according to this directive those refrigerants may be used if the annual leakage rate does not exceed 40 g of F-gases (if only one evaporator is present) or 60 g per year (if two evaporators are present).

After January 1st, 2017, F-gases with a GWP₁₀₀ greater than 150 will be prohibited for all new cars, alternative refrigerants have to be used instead. The second ordinance will address security of system containment, recovery of F-gases for recycling or destruction, training and certification of staff, data collection and reporting of emissions, labelling, and marketing of products containing F-gases.

The EU Directive No. 2000/53 (EC 2000) is the basis for a uniform European utilisation of end-of-life vehicles. Crucial points of this ordinance are collection, reuse, and recycling of old cars. The directive states that after January 1st, 2006, not less than

85 % and after January 1st, 2015, at least 95 % of the vehicle weight must be reused or recycled. Furthermore, the member states shall ensure that vehicles put on the market after July 1st, 2003, are free of dangerous substances like lead, cadmium, mercury, and hexavalent chromium. The requirements for dismantling, reuse, and recycling of end-of-life vehicles and their components should be integrated in the design and production of new vehicles. The EU Directive was implemented to German law within the End-of-Life Vehicle Ordinance (BGB 2006).

3 Scope of work

3.1 System

Technical application

As explained in the previous chapters the A/C system in passenger cars will be the exemplary system for assessing the environmental impact of possible substitutes for HFCs. In the following chapter, the selection of refrigerants applied to the LCA of A/C systems is laid out. The technical outlay of the mobile A/C system is based on the principle of vapour compression and liquid evaporation.

Refrigerants

The Regulation of the European Parliament and of the Council on certain F-gases (COM 2003) prohibits R134a in A/C systems of new cars after 2017 because it has a GWP_{100} almost 10 times higher than 150. Therefore, the automobile industry needs substitutes for the momentarily used R134a. Presently, carbon dioxide (R744), 1,1-difluoroethane (R152a), and some HCs are regarded as possible replacements. HFEs are of increasing interest due to their thermodynamic properties and therefore five HFEs were applied to the present LCA. Besides the used refrigerant with its physical/chemical properties, several controversial aspects have to be taken into account: the main factors are weight, size, energy efficiency and cooling capacity of the whole unit, further ones are politics, costs, safety issues, and export market analyses.

The refrigerant R152a is regarded as a possible substitute because of its rather R134a like thermo-dynamic properties and lower GWP ($GWP_{100} = 122$, IPCC 2006). Being a HFC like R134a, R152a is easily adaptable to the existing technique. Merely some parts have to be changed (valves) or added (sensor). Its flammability might make it necessary to add a second refrigerant circuit if the car is to be sold in countries that have stringent safety regulations like the USA. In consequence, R152a is not economic efficient at present. Besides, the European Union plans to reduce the GWP_{100} -limit further to 120 instead of 150, and then R152a will also be prohibited.

Research and development have focused to a great extent on the climate-neutral R744 as refrigerant in A/C units in passenger cars ($GWP_{100} = 1$). The R744-based A/C system is a high pressure cooling cycle with pressures up to 135 bar (Sumantran et al. 1999, UNEP 2002). It involves super critical pressure states and therefore requires an intercooler (= interior heat exchanger) to improve capacity and coefficient of performance (COP). All components have to withstand high pressures and had to be newly developed for this system (Sumantran et al. 1999). With additional equipment the A/C system can also be used as heat pump which can heat the passenger's cabin efficiently and makes other electrical heating systems dispensable which would also save weight. Presently, the costs of the individual R744 unit are still higher than those of a

comparable R134a unit (Schwaab et al. 2004). Component improvements and mass production will make those systems economical efficient. In prototypes R744-based A/C systems have shown their potential efficiency. But some studies reveal a lack of efficiency in warmer climates (Hill & Papasavva 2005). Another problem might be the toxicity of R744 in higher concentrations, especially with regard to export to countries with high safety standards.

The replacement of fluorocarbon by HC refrigerants in passenger car A/C systems began in 1993. Reasons were the much lower GWP₁₀₀ (about 20) and the ODP of zero together with good refrigeration properties. But the flammability of HCs requires extra safety measures. HCs are more explosive than R152a. Today's system designs were not developed for the save use of flammable refrigerants. Future systems may use direct expansion systems with additional shut-off valves or use secondary loop technique. Sometimes mixtures of propane (R290) and isobutane (R600a) are used, but R600a and R290 can also be used as pure refrigerants. R290 is highly compatible with existing R134a system materials but due to its extreme flammability it might be restricted to secondary loop systems.

HFES represent the third generation of CFCs replacements. They have an ODP of zero and physical chemical properties that are similar to those of CFCs and HFCs. Their ether function causes lower atmospheric lifetimes and lower GWPs for certain HFES. The problematic of HFES might be the fact that they form perfluorinated carboxylic acids (PFCAs) during degradation in the atmosphere, which are highly acidic and persistent. This is presently not fully studied. Exemplary for the HFES, E125, E134, E7000, E7100, and E7200 are included in the present study. For reason of comparison, the impact from one hydrochlorocarbon (HCC) namely R30 with low GWP₁₀₀ is applied to the present LCA of A/C system as well.

Besides the used technology and refrigerant, the efficiency of the system depends on several parameters like ambient air temperature, relative air humidity, and driving cycle. Not every system has the same efficiency in different climates and under different user profiles. Simplifications have to be made in the frame of this work. The main focus will be laid on Germany and Europe. But as the introduction of a system depends strongly on the main export markets, US or Asian climates, driving cycles and safety standards might also be taken into consideration in further studies.

3.2 Life cycle inventory

3.2.1 Introduction

LCA is the systematic analysis of the environmental impact of products and substances. The scope of the system comprises input and output during production, operation, and disposal phase of a product or substance (Figure 4). Life cycle inventory is one main step within a LCA. It gives information about the modular structure of the system, the material and energy flow within that system, and the system boundaries (ISO 14040, ISO 14044, 2006). The present study focuses on a comparative LCA.

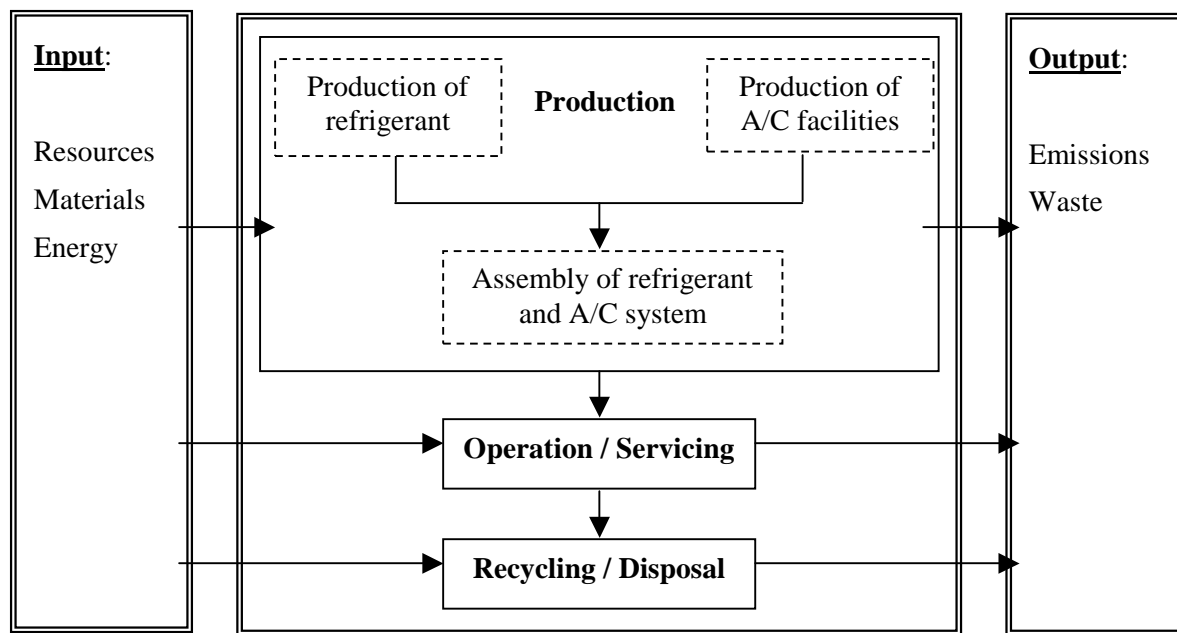


Figure 4: Schematic of the life cycle of A/C system

3.2.2 Functional unit

The functional unit used for comparing the LCA performance of different refrigerants in the present study is an A/C system in a medium-sized vehicle like a Golf from Volkswagen. Its function is to keep the passenger compartment at a comfortable temperature of about 18-20 °C. Different refrigerants are applied to the A/C system, e.g. R30, R134a, R152a, R290, R600a, R744, E125, E134, E7000, E7100 and E7200 (Table 4). The system is operated with respect to average climate conditions of some European countries. Germany was taken as example for a moderate, Sweden for a cool, and Spain for a warmer European climate region. The system is operated 10 years and than finally disposed. The compressor is driven by a motor running on petrol.

Table 4: Refrigerants applied to A/C system in the present LCA study

Refrigerant	Chemical structure	Chemical name	GWP ₁₀₀ [kg CO ₂ eq./kg]
R30	CH ₂ Cl ₂	Dichloromethane	10 ^a
R134a	C ₂ H ₂ F ₄	1,1,1,2-Tetrafluoroethane	1410 ^b
R152a	C ₂ H ₄ F ₂	1,1-Difluoroethane	122 ^b
R290	C ₃ H ₈	Propane	3 ^c
R600a	C ₄ H ₁₀	Isobutane	3 ^c
R744	CO ₂	Carbon dioxide	1 ^d
E125	CF ₃ -O-CHF ₂	Pentafluorodimethyl ether	14800 ^e
E134	CHF ₂ -O-CHF ₂	1,1,1',1'-Tetrafluorodimethyl ether	5760 ^e
E7000	C ₃ F ₇ -O-CH ₃	Heptafluoropropyl methyl ether	450 ^e
E7100	C ₄ F ₉ -O-CH ₃	Methyl nonafluorobutyl ether	410 ^e
E7200	C ₄ F ₉ -O-C ₂ H ₅	Ethyl nonafluorobutyl ether	60 ^e

^a IPCC 2001, ^b IPCC 2006, ^c Bitzer 2004, ^d Devotta et al. 2005, ^e Tsai 2005

3.2.3 Scope definition

The life cycle system comprises the following phases: production, operation (including servicing/refilling), disposal, and the fate of (highly) persistent degradation products (PFCAs, trifluoroacetic acid (TFA), and CF₂O) of emitted refrigerants. Some life cycle elements are not included in the scope, because they are not significant and/or relevant to the main question. Thus, the transport of the refrigerant and the A/C system from the manufacturer to the car production facility is not accounted for, because it is supposed to be the same for 1 kg refrigerant and one A/C system, respectively. Assuming that the energy consumption of the transport media is negligibly greater due to the 2 kg extra weight of a secondary loop A/C system, the transport of the new car to the end consumer is neglected. Because the focus of this study is the performance of different refrigerants as cooling agents in A/C systems, no inventory was conducted for the passenger car itself. As data about production and disposal of different A/C systems are rare or missing they are only partly included in this study.

Production phase

Production of refrigerants

Inventory data for refrigerant production are taken from Frischknecht (1999b), McCulloch & Lindley (2003), Krieger et al. (2004), Gover et al. (1996), Kirk-Othmer (1993), Wells (1991), ECETOC (2004, 2006), and several patents (Simons 1950, O'Neill & Holdsworth 1990, Behr & Cheburkov 2000, DuPont 2002). The inventory tables are included in the attachment (Table 33 to Table 43). Electricity values (medium voltage) were converted from MJ to kWh using the factor 3.6 (BFE 2007).

For the production of R134a three different inventories were found (Krieger et al. 2004, McCulloch & Lindley 2003, Frischknecht 1999b). Frischknecht is the only one who includes emissions of R113 and R124. Because such emissions are crucial for the environmental impact, it was decided to take the inventory from Frischknecht for comparison with other refrigerants. The inventory of R152a (Krieger et al. 2004) was supplemented by hydrochlorocarbons (HCCs) and HCFC emissions that are stated in the patent from DuPont (2002).

For the HFEs, the production energies were estimated by calculating their similarity with refrigerants for which the energies are known. Each refrigerant was described by its molecular weight, boiling temperature, freezing point, octanol-water partition coefficient, critical temperature, critical pressure, critical volume, atmospheric lifetime, global warming, and ozone depletion potential. These properties were normalized and the similarities were calculated using the Euclidean distance and single linkage technique of aggregation. It was found that all HFEs are most similar to R134a. Material input and emissions were calculated using information from patents (Simons 1950, O'Neill & Holdsworth 1990, Behr & Cheburkov 2000, DuPont 2002). The result of those calculations are listed in the attachment (Table 39 to Table 43)

Refrigerant charges of A/C systems

Refrigerant charges used in this study (Table 5) are taken from recent literature and resemble average values for A/C systems in a standard passenger car (Barrault et al. 2003, Maclaine-cross 2004, Thundiyil 2005). For the HFEs and R30, the refrigerant charges were estimated by calculating their similarity with refrigerants for which the charges are known. Each refrigerant was described by the same properties that were used for the similarity analysis of energy consumption during the production of refrigerants. These properties were normalised and the similarities were again calculated using the above mentioned technique. It was found that R30 is most similar to R152 and all HFEs are comparable to R134a.

Table 5: Nominal refrigerant charge of A/C systems in a standard passenger car

Refrigerant	Nominal charge [kg]	Refrigerant	Nominal charge [kg]
R30	0.45 ^a	E125	0.75 ^a
R134a	0.75 ^b	E134	0.75 ^a
R152a	0.45 ^c	E7000	0.75 ^a
R290	0.2 ^d	E7100	0.75 ^a
R600a	0.2 ^d	E7200	0.75 ^a
R744	0.4 ^c		

^a Similarity analysis, ^b Barrault et al. 2003, ^c Thundiyil 2005,

^d Maclaine-cross 2004

Direct refrigerant emissions (production phase)

During refrigerant production, loading of tanks and bottles, and finally charging of the A/C system, direct emissions of refrigerant occur. The refrigerant leakage within the production phase is defined independently of the refrigerant. Three different scenarios are created; worst-case, best-case, and average emission scenario. The leakage rates are shown in Table 6. They represent literature values and own assumptions (Barrault et al. 2003, Petitjean et al. 1999, Frischknecht 1999b).

Table 6: Direct refrigerant emission scenarios during production phase

Refrigerant emissions	Worst-case	Average	Best-case
	[% nominal charge]		
Refrigerant – production	1 ^a	0.5 ^d	0.1 ^b
Loading of tanks and bottles	5 ^b	2 ^b	1 ^b
Charging of A/C system	5 ^c	2 ^e	0.5 ^e

^a Frischknecht 1999b, ^b Barrault et al. 2003, ^c Own assumption: comparable to loading of tanks+bottles, ^d Own assumption: mean value, ^e Petitjean et al. 1999

Production of A/C systems

Due to scarce information about input and output of production of different A/C systems, one average energy value is included in the inventory. In average, 1 675 MJ are used for the production of a standard A/C system (Vainio 2003). The contribution of the energy consumption of the A/C system can be evaluated within the life cycle. In all cases, emissions arising from the production energy are insignificant compared with that from operating the A/C system (Campbell & McCulloch 1998).

Operation phase

Additional fuel consumption due to weight of A/C system

Regarding one standard passenger car, the additional weight of the A/C system results in increased fuel consumption. Based on different literature values (Fischer & Sand 1997, Petitjean et al. 2000, Barrault et al. 2003, Hafner et al. 2004), different weights are defined for direct expansion cycles and secondary loop systems. R134a, E125, and E7100 are used in a direct expansion system (Figure 1) which weighs approximately 15 kg; R30, R152a, R290, R600a, R744, E134, E7000, and E7200 are preferably applied to secondary loop systems (Figure 2) with a system weight of about 17 kg. The established additional fuel consumption of 57 L/ 100 kg/ 10,000 km is taken to calculate the resulting increase in litre fuel consumption (Sumantran et al. 1999). The kg CO₂ eq. emission from combustion of petrol is assumed to be 2.32 kg/L (Fischer et al. 1994). This emission factor is developed based on the fuel's heat content, the carbon content coefficient, and the carbon fraction in the fuel that is oxidized, which is assumed to be 100 % (generally approximately 99 %) (GHG 2005).

Additional fuel consumption due to compression

For simplification, the additional fuel consumption due to operating the A/C system is specified as the amount of energy necessary to compress the refrigerant under defined conditions. The energy input is represented by the change of enthalpy of the refrigerant during compression. The change of enthalpy is calculated using the "Thermophysical Properties of Fluid Systems" model from the National Institute of Standards and Technology (NIST 2005), and thermophysical property data derived from the database DIPPR (Heberle 2007) and from 3M (2007). It is assumed that the A/C circuit's temperature profile and the efficiency of the A/C compressor are constant for each refrigerant. Furthermore, it is supposed that a vapour compression cycle is most effective under certain pressure-/ temperature-conditions, and corresponding refrigerant mass flow rates. Therefore, it seems justified to use the respective pressure/temperature profiles from Ghodbane (1999) although A/C systems changed considerably in weight, size, and refrigerant charge during the last 10 years. For R744, temperature/pressure values provided by Delphi Corporation (2006), and a refrigerant mass flow rate from Hill (2006) are used in this study. Considering the specific thermophysical phase states of HFEs and R30, it was tried to use pressure and temperature states at the inlet and outlet of the compressor which are similar to those of R134a. Pressure/temperature profiles for the studied refrigerants are expressed in Table 7.

Table 7: State description of A/C system depending on used refrigerant

	R134a	R152a	R600a	R290	R744	R30
Suction pressure (kPa)	300	295	164	494	3000	103
Inlet temperature (°C)	3.6	4.4	3.9	4.4	17	3.8
Discharge pressure (kPa)	1724	1544	881	2151	12800	400
Outlet temperature (°C)	90.6	107.2	81.7	84.4	145	92.8

	E134	E125	E7100	E7200	E7000
Suction pressure (kPa)	103	103	10	10	10.0
Inlet temperature (°C)	3.8	3.8	6.8	5.9	6.9
Discharge pressure (kPa)	903	903	400	400	400
Outlet temperature (°C)	92.8	92.8	110.8	99.4	96.7

Energy consumption due to operating fans and pumps are neglected as they are assumed to be not depending on the refrigerant. The energy consumption for compression (kWh/h) is multiplied with the operation time of the A/C system. To estimate the system's operation time the A/C operating model for Europe (Duthie et al. 2002), the average monthly temperatures in some European countries (WMO 2006), and the New European Driving Cycle (NEDC) are used. Often people operate their A/C system all the time, although the outside air temperature does not justify it truly. The study concentrates on the cooling process and is neglecting the defrosting mode of A/C systems. Considering that the A/C system has to work efficiently only at temperatures higher than the desired cabin air temperature, the 90 %-percentile of the A/C operating model (Duthie et al. 2002) is taken as approximation. In Europe, 90 % of the drivers turn on their A/C system at an outside air temperature of 22 °C. For instance in Germany, 2 months or sixty days have an average daily temperature of or above 22 °C. The average mileage driven per year is 16,000 km, of which 2/3 is urban traffic (ca. 20 km/h) and 1/3 is extra-urban traffic (ca. 60 km/h). Thus, typical driving conditions in Germany are 1.5 h per day under urban and 0.2 h under extra-urban conditions. Consequently, the A/C system runs about 104 h per year in this particular scenario. To estimate the influence of the operation time of the A/C system on the amount of indirect emissions, average monthly temperatures for a warm (Spain), a cool (Sweden), and a moderate (Germany) European climate are considered (Table 32). According to the above calculation, in Germany the system is operated 104 h, in Sweden it is operated 10 h, and in Spain 260 h per year.

To account for the impact categories, the energy for compression was converted from kWh to kg CO₂ eq. and L petrol. The amount of kg CO₂ eq. associated with the energy

input (kWh) is 0.243 (Fischer et al. 1994). The amount of kg CO₂ eq. was converted to L petrol using the fuel conversion factor of petrol of 2.32 (Fischer et al. 1994).

Direct refrigerant emissions (operation phase)

Like in the production phase, the refrigerant leakage within the operation phase is defined independent of refrigerant properties. Three different scenarios are created (Table 8) using literature values and own assumptions (Barrault et al. 2003, Schwarz & Harnisch 2003). Emissions during operation are divided into regular, irregular and into emissions from servicing/refilling. Regular emissions occur because of the aging of the material and the constant vibrations and movements of the A/C components. Irregular emissions are caused by e.g. accidents and stone-hits. A 100 % emission was assumed for the worst-case scenario for irregular and regular emissions. For best-case scenario, irregular emissions of 0 % of nominal charge and regular emissions of 30 % (Barrault et al. 2003) are supposed. Emissions at servicing/refilling depend on the facilities used for recovery and refilling. Therefore, they represent constant values rather than fractions of the refrigerant charge of the A/C system (Schwarz & Harnisch 2003). The system is emptied and refilled again with new refrigerant. It is assumed that 100 g refrigerant are emitted per servicing (Barrault et al. 2003). In the average scenario, servicing/refilling takes place in the 3rd and 7th year. In the worst-case scenario, servicing/refilling takes place every second year (2nd, 4th, 6th, 8th). In the best-case scenario no servicing is necessary. The maximal amount possible to recover during servicing is the nominal charge minus the annual leakage multiplied by the years between servicings (Table 8) and minus 0.1 kg that are emitted during servicing.

Table 8: Leakage scenarios during the 10 years operation of an A/C system

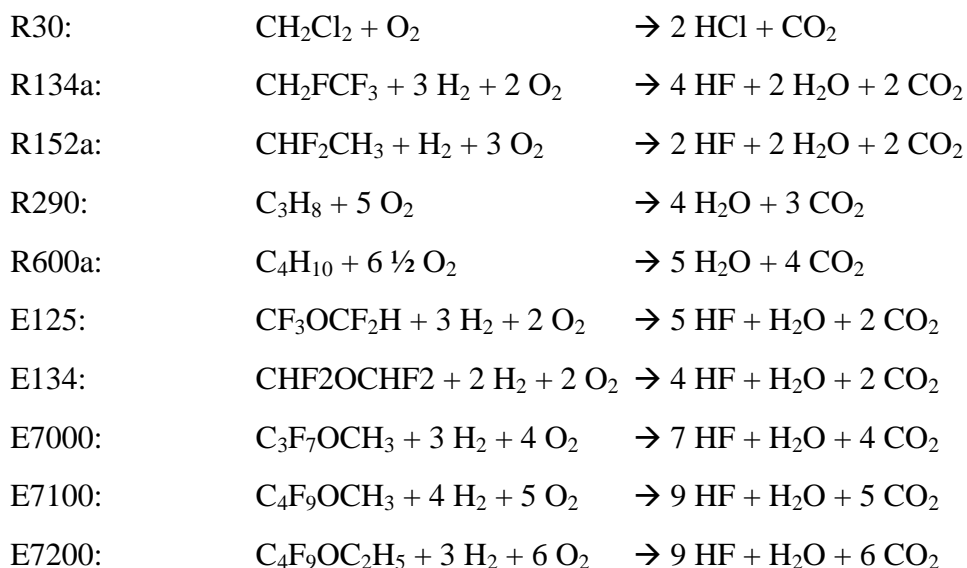
Refrigerant emissions	Worst-case	Average	Best-case
	[% of nominal charge]		
Regular emissions	100	77 ^a	30 ^a
Irregular emissions	100	33 ^a	0
	[kg]		
Emissions at servicing/refilling	0.4 ^{a*}	0.2 ^{a**}	0 ^{***}

^a Barrault et al. 2003, ^{*} Four servicing, ^{**} Two servicing, ^{***} Zero servicing

Disposal phase

Emissions due to refrigerant disposal

Like during servicing, used refrigerant is recovered during disposal processes. For example under average scenario, 50 % of the nominal charge is supposed to emit to the air and is subtracted from the charge remaining in the system in the last year resulting in the recovered refrigerant amount. The recovered refrigerants are treated differently. The partly halogenated hydrocarbons (R134a, R152a, R30), hydrofluoroethers (E125, E134, E7000, E7100, E7200), and hydrocarbons (R290, R600a) are burned under best available technology assuming total combustion. R744 is not being treated but rather released into the atmosphere. Emissions (moles) based on the combustion equation below are converted to kg CO₂ eq./refrigerant charge and added to the inventory (Table 47). The actual amount of the incineration products HF and HCl that are emitted to the atmosphere is set to 1 % of those in Table 47. The H₂O and CO₂ from incineration processes are completely released to the atmosphere. In the following, equations of complete combustion are given:



Direct refrigerant emissions (disposal phase)

The end-of-life vehicle directive requires that 95 % of a passenger car have to be reused and/or recycled (BGB 2006). With regard to the refrigerant, this means that in a best-case scenario only 5 % of the nominal refrigerant charge are being emitted during its disposal phase. Almost 46 % of the A/C systems that enter the disposal phase are already empty (Schwarz 2005). This accounts for 50 % emission of refrigerant in the average scenario. The worst-case scenario includes the export of a car into countries where no legislation exists, that would regulate the recovery of refrigerants from A/C systems, and therefore, a 100 % emission of the refrigerant charge into the atmosphere occurs.

Disposal of A/C systems

As there are only scarce information about input and output during disposal of different A/C systems, one average energy value is included in the inventory. In average, 837.5 MJ are used for the disposal of a standard A/C system (Vainio 2003). The contribution of the energy consumption of the A/C system disposal can be evaluated within the life cycle.

3.2.4 Allocation

The by-products of refrigerant production which are sold are not included in the assessment.

3.3 Impact assessment

The LCA tries to give a realistic and comprehensive evaluation of the environmental impact of a product. Life cycle inventory data will be assessed by means of the three already mentioned assessment methods. Each method is based upon a different approach. In the following chapters, the methods will shortly be introduced.

3.3.1 CML02

Introduction

The CML02 method has a problem-oriented approach to impact assessment, modelling the impacts at a midpoint somewhere in the environmental mechanism between emissions and damages and is thus called midpoint approach (Guineé et al. 2001). In this study, ten impact categories from the Dutch Handbook Method (CML02) were considered evaluating the environmental impact of certain refrigerants in A/C systems in cars:

- Demand of non-renewable primary energy (PE)
- Depletion of abiotic resources (ADP)
- Climate change (CC)
- Eutrophication (EP)
- Stratospheric ozone depletion (SOD)
- Human toxicity (HTP)
- Fresh water aquatic toxicity (FAETP)
- Terrestrial ecotoxicity (TETP)

- Photo-oxidant formation (POCP)
- Acidification (AP)

In the following chapters, reasons for the selection of those ten impact categories are given and characterization factors are given.

Selection of impact categories & impact factors

Demand of non-renewable primary energy

The energy efficiency is in many studies a main aspect; some even restrict their results to the primary energy demand (Frischknecht 1999a). Therefore, the category “Demand of non-renewable primary energy” was chosen as an impact category separate to another resource oriented indicator. It covers part of the subject of resource protection. The impact factors in Table 9 were applied to the input of energy amounting to one indicator value of “Demand of non-renewable primary energy”.

Table 9: Impact factors for the impact category “Demand of non-renewable primary energy“

Natural resource	PE [kg antimony eq./kg]
Crude oil	0.0201
Natural gas *	0.0187
Hard coal	0.0134
Soft coal	0.00671
Fossil energy **	0.000481
Uranium	0.00287

Data from Guinée et al. (2001);

* (kg antimony/m³ natural gas); ** (kg antimony/MJ fossil energy)

Assuming the German share of total primary energy supply of 2006 (BMWi 2007), the impact on this category that comes from the production of energy input in form of “primary energy sources” and “electricity” was calculated. The energy input was subdivided into the following parts: 23 % natural gas, 36 % oil, 13 % hard coal, 11 % soft coal, and 13 % nuclear. Contribution from renewable and other sources (4 %) was neglected because they account not for “non-renewable sources”. The contribution of each primary energy sector (MJ) was converted to kg using the energy content of each fuel (Goedkoop & Spriensma 2001, Frischknecht 1999b) (Table 10). For example, a consumption of 3.7 MJ electricity results in 1.33 MJ derived from oil. According to Table 10, 0.032 kg oil are needed for that amount of energy.

Table 10: Energy content of some primary energy sources

Fuel	Energy content [MJ/kg]
Natural gas	30 ^a
Oil	42 ^a
Coal	29 ^a
Uranium	460000 ^{b*}

^a Goedkoop & Spriensma 2001, ^b Frischknecht 1999b

* Equals the energy that is released from modern light water reactor, taking into account the percentage of fissionable U-235, not accounting for the uranium that is produced during enrichment and has to be disposed of

Depletion of abiotic resources (excluding energy input)

The resources necessary within the life cycle of a certain product are affecting its overall environmental impact. Therefore, next to the energy input, the “Depletion of abiotic resources (excluding energy input)” was chosen as a second resource oriented impact category in this study (Table 11).

Table 11: Impact factors for the impact category “Depletion of abiotic resources (excluding energy input)”

Alpha elements	Name	Exergy [kJ/mol]	Taken for substance (present study)	Molar mass [g/mol]	ADP [exergy in kJ/kg]
CO ₂	Carbon dioxide	20	R744	44	452
C ₂ Cl ₄	Perchloroethylene	1088	Perchloroethylene	166	6561
FH	Hydrogen fluoride	80	HF	20	3998
FK	Potassium fluoride	62	KF	58	1071
F ₂	Fluorine	466	F ₂	38	12271
Cl ₂	Chlorine	87	Cl ₂	71	1228 ^{b)}
CH ₄	Methane	832	Natural gas feedstock (90% methane)	16	51852
C ₃ H ₈	Propane	2154	R290	44	48844
C ₄ H ₁₀	Isobutane	2804	R600a	58	48245
C ₄ H ₁₀	Butane	2806		58	48276
C ₂ ClH ₃	Chloroethylene	1290	Vinylchloride	63	20640
C ₂ Cl ₃ H	Trichloroethylene	1144	Trichloroethylene	131	8707
C ₂ Cl ₃ HO	Dichloroacetyl chloride	920	Perfluorobutyric acid fluoride, pentafluoropropionyl fluoride, pentafluoropropionic acid	147	6242
C ₂ H ₆ O	Dimethyl ether	1420	Dimethyl ether	46	30812
C ₅ H ₁₂ O ₂	Ethyl propionate	2905	Methoxyfluoroisobutene	102	28443
C ₆ H ₁₂ O	Methyl isobutyl ketone	3763	Ethoxyfluoroisobutene	100	37569

C ₆ H ₁₄ O ₆	Sorbitol	3205	Diglyme	182	17592
	Petrol		Petrol	95	43543 ^a
	Diesel		Diesel	220	42960 ^a
H ₂	Hydrogen	331 ^b	H ₂	2	165500 [*]
O ₂	Oxygen	234 ^b	O ₂	32	7313 [*]
HCl	Hydrogen chloride	85 ^b	HCl	36	2361 [*]
C ₂ H ₅ OC ₂ H ₅	Diethyl ether	2707 ^b		74	36581 [*]
H ₂ O	Water	1 ^b	H ₂ O	18	56 [*]

Data from Guinée et al. (2001) or otherwise indicated; ^a BMWi (2007); ^b Ayres et al. (1996);

^{*} Recalculated from exergy (kJ/mol) values with molar mass

The calculation of the ADP factor for e.g. oxygen was as follows:

$$ADP(oxygen) = \frac{\text{exergy [kJ / mol]}}{\text{molar mass [kg / mol]}} = \frac{234 \text{ kg / mol}}{0.032 \text{ kg / mol}} = 7313 \text{ kJ / kg} \quad \text{Equation 3}$$

Climate change

The fact that some HFCs and HFEs possess a considerable direct GWP and some systems require a high amount of energy input to operate justify the consideration of “Climate change” (CC) as an individual impact category (Table 12). For substances contributing to this category, the GWP₁₀₀ are taken from IPCC (2006). The GWP₁₀₀ for the HFEs are taken from Tsai (2005). During the HFEs production, other fluorinated ether and hexafluoropivaloyl fluoride emit to the atmosphere. For those substances a GWP₁₀₀ of 1000 was assumed as a first estimation, as the average GWP₁₀₀ of the ethers in Table 12 is in the range of thousands.

Table 12: Impact factors for the impact category “Climate change”

Substance	Compartment	GWP ₁₀₀ [kg CO ₂ eq./kg]	Taken for substance (present study)
Carbon dioxide	Air	1	R744
Dimethyl ether	Air	1	
Dichloromethane	Air	10	R30
Methane	Air	23	CH ₄ , natural gas (90 % methane)
R113	Air	6030	R113
R124	Air	599	R124
R141b	Air	713	R150
R142b	Air	2270	R151a
R134a	Air	1410	R134a
R152a	Air	122	R152a
E125	Air	14800 ^a	E125

E134	Air	5760 ^a	E134
E7000	Air	450 ^a	E7000
E7100	Air	410 ^a	E7100
E7200	Air	60 ^a	E7200
Other fluorinated ether	Air	1000 ^b	Other fluorinated ether from dimethyl ether; hexafluoropivaloyl fluoride
Perfluoropropane	Air	8690	Hexafluoropropane

Data from IPCC (2006) or otherwise indicated; ^a Tsai 2005; ^b Assumption

Eutrophication

NO_x from the combustion of petrol contribute to the eutrophication process. PO₄³⁻ was taken as reference substance for the eutrophication factor. In the present study, the impact factor of NO₂, which is 0.13 kg PO₄³⁻eq./kg, was taken as approximation for NO_x (Guinée et al. 2001).

Stratospheric ozone depletion

HCFCs and HFCs are substitutes of the CFCs which have high ODP. As this study is assessing the environmental impact and occurring differences of proposed substitutes of HFCs the impact of ODP is considered.

Trichlorofluoromethane (R11) was taken as reference substance for SOD impact factor values. SOD values (Table 13) are mainly taken from IPCC (2006). For calculating the impact from hexafluoropropane, the factor of perfluoropropane was taken as a first approximation.

Table 13: Impact factors for the impact category “Stratospheric ozone depletion”

Substance	Compartment	SOD [kg R11 eq./kg]	Taken for substance (present study)
R141b	Air	0.12	R150
R142b	Air	0.07	R151a
R134a	Air	0.000015	R134a
R113	Air	1.0	R113
R124	Air	0.02	R124

Data from IPCC (2006)

Human toxicity

Some by-products formed during refrigerant manufacture possess a considerable toxicity potential to humans (Table 14). Also, degradation products of some refrigerants like HF, HCl, CF₂O, TFA, and PFCAs might pose a risk to human health. As degradation

products are not explicitly included in the CML02 method, an extra fate model (for details see Chapter 3.4) was performed assessing the impact from TFA, CF₂O, and PFCAs.

Table 14: Impact factors for the impact category “Human toxicity”

Substance	Compartment	HTP ₁₀₀ [kg 1,4-DCB eq./kg]	Taken for substance (present study)
1,1,1-Trichloroethane	Air	16.0	R113
1,2-Dichloroethane	Air	6.8	R124, R150
Nitrogen dioxide	Air	1.2	NOx
Dichloromethane	Air	2.0	R30
Hydrogen chloride	Air	0.5	HCl
Hydrogen fluoride	Air	94.0	HF

Data from Guinée et al. (2001)

Ecotoxicity

Some partly halogenated refrigerants degrade to HF and HCl, others form persistent degradation products like TFA and PFCAs, which impact category was investigated in the fate model of Chapter 3.4. For assessing the environmental impact of refrigerants, the ecotoxicological potential to fresh water and terrestrial systems is of great importance (Table 15).

Table 15: Impact factors for the impact categories “Fresh water aquatic toxicity” and “Terrestrial ecotoxicity” of the compartment air

Substance	FAETP ₁₀₀ [kg 1,4-DCB eq./kg]	TETP ₁₀₀ [kg 1,4-DCB eq./kg]	Taken for substance (present study)
1,1,1-Trichloroethane	0.00012	0.00018	R151a
1,2-Dichloroethane	0.00012	0.000026	R150
Dichloromethane	0.000033	0.0000043	R30
Hydrogen chloride			HCl
Hydrogen fluoride	4.60	0.0029	HF
R134a		2.1 ^a	R134a
R124		4.9 ^a	R124

Data from Guinée et al. (2001) or otherwise indicated; ^a Frischknecht 1999b
FAETP - Fresh water aquatic ecotoxicity; TETP - Terrestrial ecotoxicity

Photo-oxidant formation

Some substances are precursors of the tropospheric ozone formed in summer. The photochemical ozone creation potential (POCP) is considered to quantify the impact of certain substances to the environment. Ethylene is taken as reference substance for the POCP factors (Table 16).

Table 16: Impact factors for the impact category “Photo-oxidant formation” for the compartment air

Substance	POCP [kg ethylene eq./kg]	Taken for substance (present study)
1,1,1-Trichloroethane	0.009	R151a
Acetic acid	0.097	
Butane (unspec.)	0.352	
Dichloromethane	0.068	R30
Diethyl ether	0.445	
Diisopropylether	0.398	
Dimethyl ether	0.189	
CO	0.027	
Formic acid	0.032	
Isobutane	0.307	R600a
Methane	0.006	CH ₄
Methyl chloride	0.005	
Methyl tert-butyl ether	0.175	
NO ₂	0.028	NO _x
Pentane	0.395	
Propane	0.176	R290
Propanoic acid	0.15	
Hydrofluoroether	0.1 ^a	E125, E134, E7000, E7100, E7200
Hydrocarbons	0.333 ^b	Hydrocarbons (unspec.)

Data from Guinée et al. (2001) or otherwise indicated;

^a Assumption, ^b Averaged value from hydrocarbons C1-C11

Acidification

The incineration and degradation products HCl and HF of some partly halogenated refrigerants possess acidification potential (Table 17). The pH reduction even in highly buffered fresh water and soil systems due to the emissions of those and other acidifying substances can facilitate the mobilisation of heavy metals. Thus, this impact category is important to assess the overall environmental impact of one refrigerant. SO₂ was taken as reference substance for the acidification factors. The acidification potential of TFA and PFCAs were modelled in chapter 3.4.

Table 17: Impact factors for the impact category “Acidification” for the compartment air

Substance	AP [kg SO ₂ eq./kg]	Taken for substance (present study)
Hydrogen chloride	0.88	HCl
Hydrogen fluoride	1.6	HF
NO ₂	0.7	NO _x
Nitric acid	0.51 ^a	
Phosphoric acid	0.98 ^a	
Sulphuric acid	0.65 ^a	
SO ₂	1	
R123	0.42	R113
R124	0.48	R124
R125	1.35	Hexafluoropropane
R134a	0.96	R134a
R141b	0.82	R150
R142b	0.95	R151a
R152a	0.97	R152a
R22	1.11	R30

Data from Frischknecht (1999b) or otherwise indicated; ^a Guinée et al. (2001)

General assumptions

In this study, fuel consumption is not considered as a primary energy but as an abiotic resource. Thus, transport input during refrigerant production were converted from tkm to kg CO₂ eq. and kg diesel. A light truck (28 t) run by diesel consumes 15.7 L/100 km, a heavy truck (40 t) run by diesel consumes 33.6 L/100 km (GHG 2005). Hence, the amount of L diesel used was calculated and converted to kg diesel, based on the density (0.84 kg/L) of diesel (ARAL 2004). The amount of L diesel was converted to emissions of kg CO₂ eq. using the fuel conversion factor of diesel of 2.68 (GHG 2005).

Accordingly, the energy for compression was converted from kWh to kg CO₂ eq. and L petrol. The amount of kg CO₂ eq. associated with the energy input [kWh] is 0.243 (Fischer et al. 1994). The amount of kg CO₂ eq. was converted to L petrol using the fuel conversion factor of petrol of 2.32 (Fischer et al. 1994).

Thus, diesel and petrol consumption are contributing to the impact classes “Depletion of abiotic resources (excluding energy input)” and “Climate change”. The exhaust-gas limit Euro 4 (EG 1998) was taken to calculate the emissions of CO₂, HCs, CO, and NO_x for assessing the impact of burned petrol.

3.3.2 EI99

Introduction

The Eco-indicator 99 is a damage-oriented impact assessment method for LCA (Goedkoop & Spriensma 2001) which aims at modelling damage to the protection areas: Human Health, Ecosystem Quality, and Resources. The method is divided into different steps such as fate, exposure, effect, and damage analysis. The scheme of calculating EI99 is shown in Figure 5.

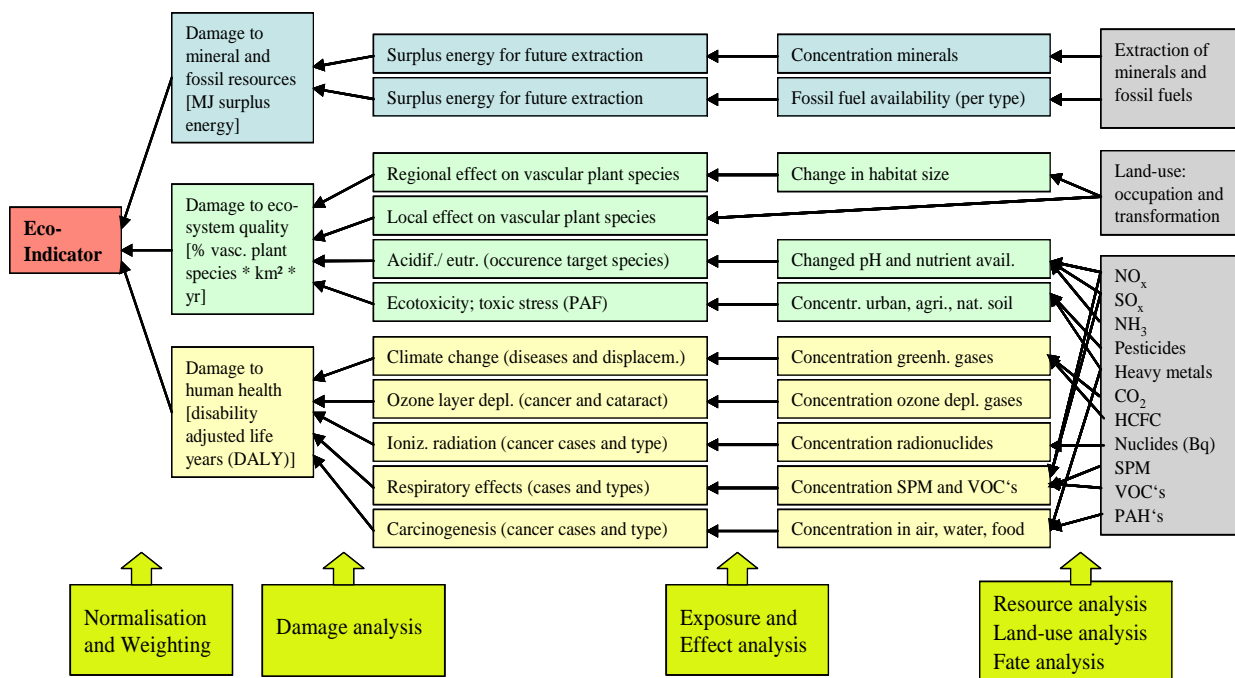


Figure 5: Scheme of Eco-indicator 99 (Goedkoop & Spriensma 2001)

The aggregation of the results from the inventory and impact assessment leads to a one-dimensional value. The aggregation includes weighting factors which affect the contribution of each damage category. Besides, the damage model determines the contribution of an impact category within a damage category. EI99 offers the opportunity to operate with three different cultural perspectives, which arise from the Cultural Theory of risk (Thompson 1990) that states that different societies fear different sorts of threats and that this is based in the different social structures. In this study, the hierarchist perspective is used as damage model combined with the default weighting factors (Goedkoop & Spriensma 2001). Hierarchists experience nature as “tolerant” (Thompson 1990): within certain limits nature can be exploited, beyond those limits the environmental system will collapse. The hierarchist perspective focuses between a short and long term time view on possible damages.

Selection of damage factors & calculation

The EI99 was calculated using inventory data, weighted damage factors listed in the “Methodology Report” (Goedkoop & Spriensma 2001) and standard indicators from the “Manual for Designers” (Pré 2000). The weighted damage factors and standard indicators used for this study are listed in Table 50. They include fate, exposure, and damage analysis as well as normalisation and weighting and have the unit ecopoints per kg (Pt/kg). The following example shall demonstrate the principles of the EI99 calculation.

If 1 kg of refrigerant R22 is emitted to the atmosphere, one has to take the weighted damage factors of the categories to which R22 contributes, here to the category “Damages to human health caused by climate change” (7.27 Pt/kg) and “Human health effects caused by ozone layer depletion” (1.09 Pt/kg). Each weighted damage factor is multiplied with 1 kg R22. Finally, the contributions are summed up to 8.36 Pt/kg (Equation 4). Consequently, for 200 g R22 emission, the EI99 is 1.67 Pt/kg.

$$EI99 = \sum_{ic} f_{ic} \cdot e_r = (7.27 \text{ Pt/kg} \cdot 1 \text{ kg}) + (1.09 \text{ Pt/kg} \cdot 1 \text{ kg}) = 8.36 \text{ Pt} \quad \text{Equation 4}$$

with

f_{ic} – Impact factor of certain impact category

e_r – Refrigerant emission [kg]

That kind of calculation is done for each emission and for material, transport, and energy input. The contribution from material input is calculated by multiplying the average standard indicators with the respective amount of material input needed. The input of transport is multiplied with the associated standard indicator (15 mPt/tkm) and added to the previous results. The contribution from energy input is derived by multiplying the weighted damage factor with the corresponding input of energy source, and adding it to the product or multiplying the electricity amount (converted to kWh) with the associated standard indicator (23 mPt/kWh). The material output is calculated by multiplication of the amount of emitted substances with the weighted damage factors of categories to which those substances contribute.

The “Methodology Report” and the “Manual for Designers” do not include damage factors and standard indicators for all substances. Therefore, preliminary estimates had to be defined. Main intention was to take damage factors from substances that are similar in respect to their chemical structure. E.g., the weighted damage factor of “HCFC-141b” (“Damages to human health caused by climatic change”) was taken for R151a, a by-product of the R152a production. The weighted damage factor of “C_xH_y halogenated” (“Respiratory effects on humans caused by organic substances”) was taken for hexafluoropivaloyl fluoride and hexafluoropropane (by-products of the manufacture of

E7000, E7100, E7200), R151a, R113, R124, R134a, and R152a. Table 51 and Table 52 show which damage factors and standard indicators were taken for each substance (right column) in the present study. The weighted damage factor for hydrocarbons (“Respiratory effects on humans caused by organic substances”) was derived by averaging over the weighted damage factors of the hydrocarbons (methane to dodecane) that are included in the list of Goedkoop & Spriensma (2001).

In some inventories (e.g. production of R152a, R134a, A/C system), the energy input is in form of one accumulated value (“Primary energy sources”). In this case, the German share of total primary energy supply of 2006 (BMWi 2007) was assumed to calculate the Eco-indicator 99 that comes from the production of energy input. The energy input was subdivided into the following parts: 23 % natural gas, 36 % oil, 24 % coal, 13 % nuclear, and 4 % other sources following the same procedure as in CML02. The resulting energy amounts were multiplied with their specific weighted damage factors (“Damage to Resources caused by extraction of fossil fuels”). The contribution from nuclear, wind, water, photovoltaic, and other sources were summed up. For this group, a weighted damage factor was calculated by averaging the damage factors of oil, natural gas, and coal. Electricity (medium voltage) was converted from MJ to kWh using the factor 3.6 (BFE 2007).

For EI99 calculation, the energy input for compression of the refrigerant [kWh] was converted to kg CO₂ eq. emissions using the conversion factor 0.243 (Fischer et al. 1994) as the car is running on petrol.

To account for the production of fuel used during the life cycle, the standard indicator (Pré 2000) was converted to mPt/L assuming that 1 L petrol weighs 0.75 kg (DIN 2006). The calculation is further based on the assumption described in Chapter 3.3.1.

3.3.3 TEWI

Introduction

The so called Total Equivalent Warming Impact (TEWI) is the sum of direct and indirect impacts on global warming. The direct TEWI component is determined by the refrigerant loss created by leakage and recovery loss, the indirect one by the energy consumption of the system during operation phase. This concept has become widely used in valuating the environmental impact of refrigerant systems (Fischer & Sand 1997, Petitjean et al. 1999, Petitjean et al. 2000, Davies & Caretta 2004, FKT 2005). It covers an important aspect of the environmental impact, although it neglects some other contributions (Frischknecht 1999a).

Computation formula

The TEWI is calculated according to Equation 5 to Equation 7. $TEWI_{direct}$ is the total amount of kg CO₂ eq. due to refrigerant loss during the whole life cycle (Equation 5). $TEWI_{indirect}$ (Equation 6) is considering the energy consumption of the system. TEWI is the overall impact on global warming (Equation 7).

$$TEWI_{direct} = \{(L/100) \cdot m \cdot T \cdot GWP_{100}\} + \{z \cdot x \cdot GWP_{100}\} + \{GWP_{100} \cdot m \cdot ((c + d)/100)\} \quad \text{Equation 5}$$

$$TEWI_{indirect} = \{E \cdot S_L \cdot r \cdot T\} \quad \text{Equation 6}$$

$$TEWI = TEWI_{direct} + TEWI_{indirect} \quad \text{Equation 7}$$

- L – Average annual loss of refrigerant [% of refrigerant charge]
- m – Refrigerant charge [kg]
- T – Lifetime [years]
- GWP_{100} – Global warming potential in units kg CO₂ eq., time horizon of 100 years
- z – Number of recharges/servicings per lifetime [kg]
- x – Refrigerant loss during recharge/servicing [kg]
- c – Refrigerant loss during production and charging [% of refrigerant charge]
- d – Refrigerant loss during disposal [% of refrigerant charge]
- E – Energy consumption [kWh/h]
- S_L – Annual operation hours [h/yr]
- r – Emission of CO₂ + other greenhouse gases by energy generation [kg CO₂ eq./kWh]

To evaluate the impact of different parameters on the ranking by TEWI, only one of the parameters in Table 18 is changed at a time, while the other parameters are set to average values. Four sets with three scenarios (worst-case, average, best-case) are created (Table 59). The average scenario is the same for all four sets. In set A, the operation time (S_L) differs notably due to different climate situations. In set B, the annual refrigerant leakage rate (L) is defined in three emission scenarios. In set C, emissions due to servicing/refilling (z) differ. Factor x , which accounts for the refrigerant loss during servicing/recharge, is 0.1 kg per servicing. In set D, emissions during production and disposal phase (c and d) are defined for three scenarios. The lifetime of an A/C system is set to be ten years. Factor r , which accounts for emissions of CO₂ and other greenhouse gases by energy production, is 0.249 kg CO₂ eq./kWh calculated from the energy content of petrol (0.0693 kg CO₂ eq./MJ) and the conversion factor 0.28 kWh/MJ (IPCC 2006). The parameter values for the different emission scenarios are shown in Table 18. Parameters related to the refrigerants are given in Table 19.

Table 18: Parameter for TEWI calculation for different emission scenarios

Parameter	Emission scenario		
	Worst-case	Average	Best-case
c [%]	11	4.5	1.6
d [%]	100	50	5
z	4	2	0
L [%/yr]	20	11	3
S _L [h/yr]	260	104	10

Table 19: Refrigerant properties for TEWI calculation

Refrigerant	GWP ₁₀₀ [kg CO ₂ eq./kg]	m [kg]	E [kWh/h]
R30	10 ^a	0.45	12.22
R134a	1410 ^b	0.75	3.20
R152a	122 ^b	0.45	2.98
R290	3 ^c	0.2	3.34
R600a	3 ^c	0.2	3.47
R744	1 ^d	0.4	4.48
E125	14800 ^e	0.75	1.83
E134	5760 ^e	0.75	8.95
E7000	450 ^e	0.75	2.35
E7100	410 ^e	0.75	2.66
E7200	60 ^e	0.75	2.40

^a IPCC 2001, ^b IPCC 2006, ^c Bitzer 2004, ^d WMO 2003, ^e Tsai 2005

The indirect and direct components of the TEWI and the total TEWI were calculated (Table 59). The TEWI of set A for R30 is exemplarily calculated under the worst-case scenario:

$$\begin{aligned}
 TEWI &= \{ L \cdot m \cdot T \cdot GWP_{100} \} + \{ z \cdot x \cdot GWP_{100} \} + \{ GWP_{100} \cdot m \cdot ((c+d)/100) \} + \{ E \cdot S_L \cdot r \cdot T \} = \\
 &= \{ 0.11 \text{ yr}^{-1} \cdot 0.45 \text{ kg} \cdot 10 \text{ yr} \cdot 10 \text{ kg CO}_2 / \text{kg} \} + \{ 2 \cdot 0.1 \text{ kg} \cdot 10 \text{ kg CO}_2 / \text{kg} \} + \\
 &+ \{ 10 \text{ kg CO}_2 / \text{kg} \cdot 0.45 \text{ kg} \cdot (0.045 + 0.5) \} + \{ 12.22 \text{ kWh/h} \cdot 260 \text{ h/yr} \cdot 0.249 \text{ kg CO}_2 / \text{kWh} \cdot 10 \text{ yr} \} \\
 &= 7920.6 \text{ kg CO}_2
 \end{aligned}$$

3.4 Fate modelling

Introduction

Due to the fact that TEWI and CML02 do not account for the persistent degradation products of the refrigerants and EI99 does not account for the PFCAs, a fate model was conducted to assess the environmental impact of those substances. First the distribution between the compartments air, water and soil was modelled and then the concentrations of the degradation products in each compartment were calculated. In the following chapters, the degradation of the studied refrigerants is shortly described and summarized in Table 53.

Degradation of refrigerants

R30

Initiating the degradation, hydroxyl (OH) radicals react with R30. Carbon dioxide (CO₂) and hydrogen chloride (HCl) are the major products of the atmospheric degradation of R30 (WHO 1996). HCl is removed from the atmosphere by wet and dry deposition.

R134a, R152a

The tropospheric degradation of R134a is most effectively initiated by OH radicals to form the CF₃CHF radical (Franklin 1993). A general scheme for the atmospheric degradation of halogenated organic compounds is given in Figure 6. The new radical reacts further with O₂ to form the CF₃CHFO₂ radical, which reacts with e.g. NO forming the alkoxy radical CF₃CFHO. This radical decomposes and reacts with O₂ to CF₃C(O)F and HO₂ radicals. Under atmospheric conditions,

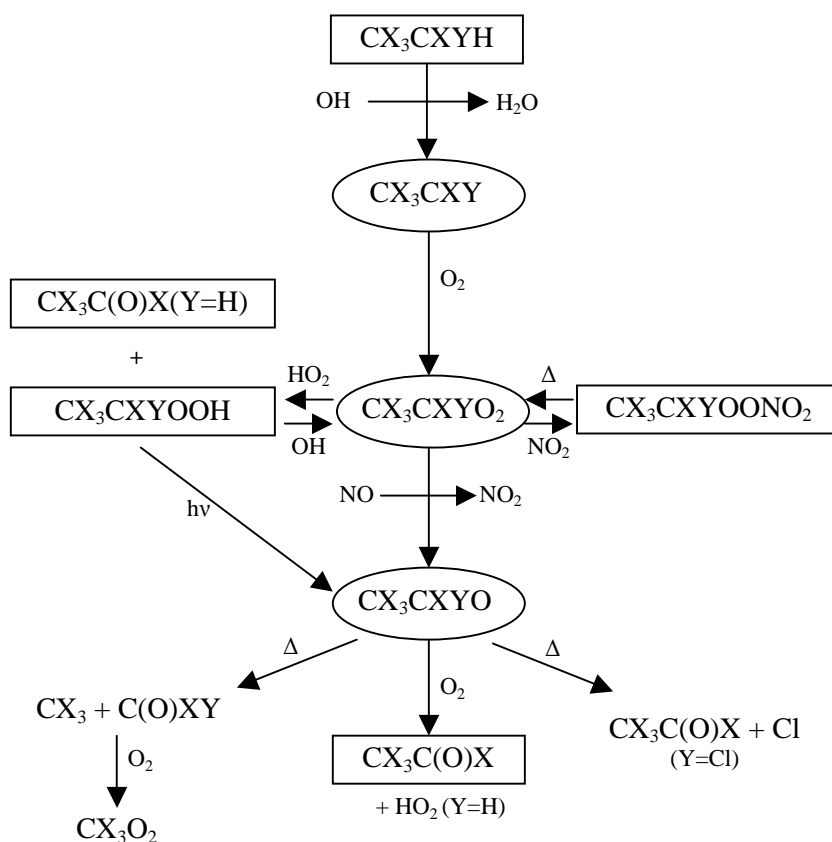


Figure 6: Generalized scheme for the atmospheric oxidation of halogenated organic compounds (X, Y = H, Cl or F); transient radical intermediates are enclosed in ellipses, products with less transitory existence are given in the boxes (IPCC 2006)

7-20 % of the CF_3CFHO radicals react with O_2 to form $\text{CF}_3\text{C(O)F}$, the remainder decompose into CF_3 radicals and HC(O)F (Wallington et al. 1996). CF_3 radicals are eventually degraded to CF_2O . After its uptake in atmospheric clouds, $\text{CF}_3\text{C(O)F}$ is hydrolysed to trifluoro-acetic acid (TFA, $\text{CF}_3\text{C(O)OH}$), a persistent degradation product that partitions into aqueous compartments of the environment (Bowden et al. 1996, IPCC 2006). The average yield of TFA from R134a is 40 %, from $\text{HC(O)F} + \text{CF}_2\text{O} + \text{HF}$ 60 % (Franklin 1993).

Atmospheric oxidation of R152a is initiated by OH radicals forming $\text{CH}_3\text{CF}_2\text{O}_2$ radicals. The dominant atmospheric degradation product of R152a is CF_2O (Hashikawa et al. 2004). Thereby, over 75 % are generated directly from R152a and less than 25 % indirectly via $\text{CHF}_2\text{C(O)H}$ (Taketani et al. 2005). A 92 % yield of CF_2O is assumed according to Tuazon & Atkinson (1993). In cloud water, CF_2O degrades further to CO_2 and hydrofluoric acid (HF) (Cavalli et al. 1998, Good et al. 1999). But there is still discussion about the importance of the uptake by cloud water (Franklin 1993).

R290, R600a, R744

Under atmospheric conditions, the main degradation processes for alkanes include reactions with OH and to a lesser extent with NO_3 radicals (Atkinson 1997, Atkinson et al. 2005). Under certain conditions, alkanes react with chlorine atoms (Atkinson 1997). The first reaction of alkanes with those three molecules is an initial H atom abstraction from C-H bonds resulting in the formation of alkyl radicals. Those react further to alkyl peroxy and alkoxy radicals and in subsequent steps to alkyl peroxy nitrates, alkyl nitrates, carbonyls, alcohols, and hydroperoxides (Atkinson et al. 2007) leading finally to the formation of CO_2 and H_2O .

Propane (R290) oxidises in the atmosphere via reaction with OH radicals and chlorine atoms. During the atmospheric degradation of R290, various carbonyl compounds are formed, like acetone, acetaldehyde, and propionaldehyde. Those carbonyl compounds are relevant because of their toxicity and ability to produce free radicals by photolysis. The exact mechanisms of the degradation pathways of R290 have not been properly characterised yet (Claudette & Francisco 2007). It is assumed that R600a follows similar degradation mechanisms. For the present study, it is assumed that R290 and R600a degrade completely to CO_2 and CO_2 (R744) is defined as not further degraded.

E125, E134

The atmospheric oxidation of E125 ($\text{CF}_3\text{OCF}_2\text{H}$) and E134 ($\text{CHF}_2\text{OCHF}_2$) is initiated by reaction with OH radicals to form the CF_3OCF_2 (Inoue et al. 2001) and CHF_2OCF_2 radical (Good et al. 1999), respectively. The dominant degradation processes of those radicals are either CO-dissociation reaction to form CF_3 and CF_2O or oxidation with O_2 resulting in alkylperoxy radicals, $\text{CF}_3\text{OCF}_2\text{O}_2$ and $\text{CHF}_2\text{OCF}_2\text{O}_2$ (Good et al. 1999).

Those radicals are degraded to CF_3O and CF_2O . Under atmospheric conditions, CF_3 and CF_3O radicals can be further oxidized to CF_2O (Good et al. 1999). The overall molar yield of CF_2O for E125 is 1.52 and for E134 it is 2 (Good et al. 1999). CF_2O is the major product of the atmospheric degradation of E134 and E125. It is removed from the atmosphere by its heterogeneous reaction with water resulting in HF and CO_2 (Cavalli et al. 1998, Good et al. 1999).

E7000, E7100, E7200

The degradation of E7000 ($\text{n-C}_3\text{F}_7\text{OCH}_3$), E7100 ($\text{C}_4\text{F}_9\text{OCH}_3$), and E7200 ($\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$) is initiated by OH radicals forming the alkyl radicals, $\text{n-C}_3\text{F}_7\text{OCH}_2\cdot$, $\text{C}_4\text{F}_9\text{OCH}_2\cdot$, $\text{C}_4\text{F}_9\text{OCHCH}_3$, and $\text{C}_4\text{F}_9\text{OCH}_2\text{CH}_2\cdot$, respectively. The scheme for atmospheric degradation of E7100 is given in Figure 7.

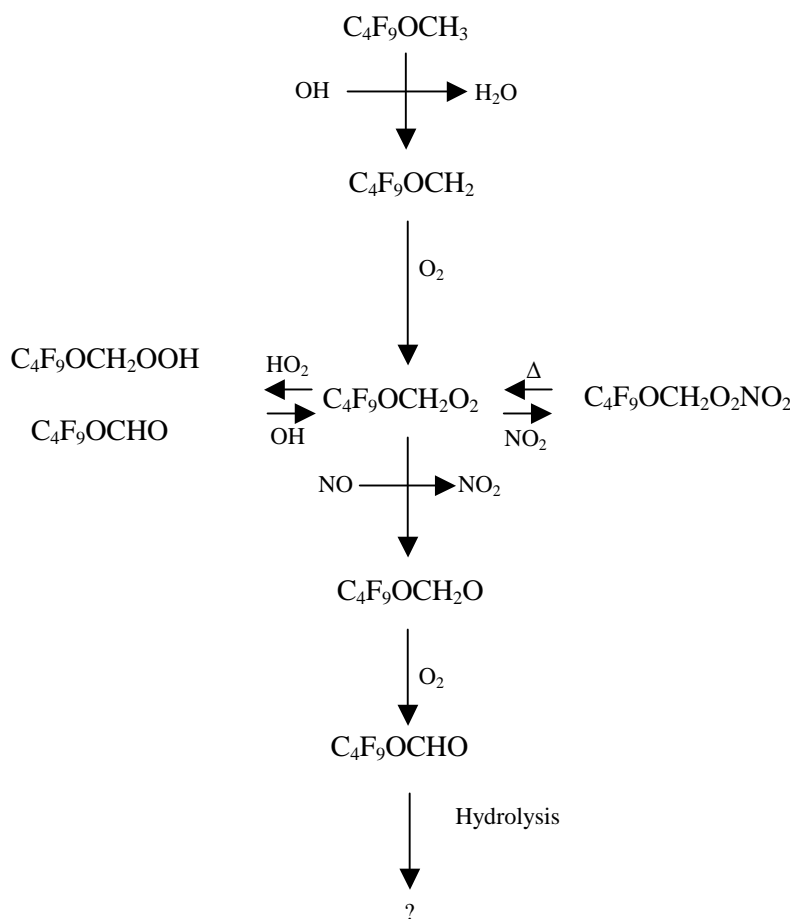


Figure 7: Scheme for atmospheric E7100 degradation (IPCC 2006)

The alkyl radicals are further oxidized by O_2 to the peroxy radicals, $\text{n-C}_3\text{F}_7\text{OCH}_2\text{O}_2$ (Ninomiya et al. 2000), $\text{C}_4\text{F}_9\text{OCH}_2\text{O}_2$ (Wallington et al. 1997), $\text{C}_4\text{F}_9\text{OCHOOCH}_3$, and $\text{C}_4\text{F}_9\text{OCH}_2\text{CH}_2\text{OO}$ (Christensen et al. 1998). The peroxy radicals react with e.g. NO to the alkoxy radicals $\text{C}_3\text{F}_7\text{OCH}_2\text{O}$ (Ninomiya et al. 2000), $\text{C}_4\text{F}_9\text{OCH}_2\text{O}$ (Tsai 2005),

$\text{C}_4\text{F}_9\text{OCHOCH}_3$, and $\text{C}_4\text{F}_9\text{OCH}_2\text{CH}_2\text{O}$ (Christensen et al. 1998). The dominant loss of the first two radicals is the reaction with O_2 under formation of perfluoropropyl formate $\text{C}_3\text{F}_7\text{OC(O)H}$ (Ninomiya et al. 2000) and perfluorobutyl formate $\text{C}_4\text{F}_9\text{OC(O)H}$ (Tsai 2005). Degradation of the $\text{C}_4\text{F}_9\text{OCHOCH}_3$ radical results in the ester $\text{C}_4\text{F}_9\text{OC(O)CH}_3$, whereas the $\text{C}_4\text{F}_9\text{OCH}_2\text{CH}_2\text{O}$ radical forms perfluorobutyl formate $\text{C}_4\text{F}_9\text{OC(O)H}$ (Christensen et al. 1998).

The perfluorobutyl formate, $\text{C}_4\text{F}_9\text{OC(O)H}$, and the perfluoropropyl formate, $\text{C}_3\text{F}_7\text{OC(O)H}$, are relatively unreactive toward Cl atoms and OH radicals (Wallington et al. 1997, Christensen et al. 1998). The main atmospheric removal processes for those formates are wet/dry deposition and possibly photolysis (Wallington et al. 1997, Ninomiya et al. 2000). At the moment, the latter aspect is rather insufficiently investigated. Nohara et al. (2001) presented results suggesting that perfluoroalkyl formates are gradually hydrolysed to PFCAs which have high acid strength, high persistence, and are likely to accumulate in the hydrosphere.

Model description

Using the distribution model *EXTND* of the software *E4CHEM* (Brüggemann et al. 1996), the thermodynamic equilibrium distribution of persistent degradation products of emitted refrigerants is calculated assuming a three compartment model.

Two different models are developed when regarding the fate of persistent chemicals. The first model describes three different media in the atmosphere; air, liquid water, and aerosol particles, and the distribution of the chemicals between those atmospheric compartments. Thereby, for the liquid water content (LWC) different values are taken, resembling the LWC in aerosol particles, fog, and raining clouds (Winkler 1986). The second model describes the distribution between the atmosphere over, and the hydro- and pedosphere of Germany. In the following paragraphs, the models are described in detail (Table 20).

As TFA and PFCAs are persistent substances, their homogenous distribution within the troposphere is assumed. Controversial statements of the uptake of CF_2O by cloud water exist (Franklin 1993). Hence, CF_2O is treated differently. In a first step, CF_2O is regarded as a persistent substance. Thus, the distribution of CF_2O is modelled in the same way as it is done for TFA and PFCAs. In a second step, the degradation of CF_2O to HF and CO_2 is considered and their distribution modelled likewise.

Air

The troposphere is in close contact with the surface of the earth. It extends to a height of 10 km. With increasing height, temperature, pressure, and density of the atmosphere decrease. For modelling purpose, a uniform density (1.2 kg/m^3) at a pressure of one

atmosphere is assumed, resulting in a reduced height of the atmosphere of 6 km (Mackay 2001). Thus, over Germany with an area of 357,000 km² the volume of air is $2.14 \cdot 10^6$ km³.

Aerosols in the atmosphere

Aerosols are ubiquitous in the atmosphere and are important in determining the fate of certain chemicals. The aerosol particles vary considerably in size and composition. They can consist of water (fog, cloud droplets), dust particles (organic matter, mineral soil), and smoke (organic combustion products). For modelling purposes, the density of 1.5 g/cm³ and the concentration of 30 µg/m³ are assumed, corresponding to a volume fraction of particles of $2 \cdot 10^{-11}$ (Mackay 2001). Consequently, in an air volume of $2.14 \cdot 10^6$ km³ over Germany the volume of solid material is $4.28 \cdot 10^{-5}$ km³.

Liquid water content in the atmosphere

The LWC of the atmosphere depends on relative humidity. For calculating the distribution of chemicals in the atmosphere, three different LWC are assumed: 30 µg/m³ in aerosol particles, 255 mg/m³ in fog, and 1 g/m³ in raining clouds (Winkler 1986). Thus, in an atmospheric volume of $2.14 \cdot 10^6$ km³ the LWC is $6.43 \cdot 10^{-5}$ km³, $5.46 \cdot 10^{-1}$ km³, and 2.14 km³, respectively.

Hydrosphere

Two percent of Germany are covered by water surfaces (Baumgartner & Liebscher 1996), resulting in an area of round 7 100 km². The average water depth is assumed to be 2 m. This yields a water volume of 14.2 km³. The water is being regarded as pure water, e.g. containing no dissolved electrolytes and suspended particles.

Pedosphere

For modelling purposes, the pedosphere is not classified into air, water, mineral and organic matter, but is regarded as homogeneous with a density of 1.5 g/cm³. The area is 349,900 km² and the depth to which chemicals intrude effectively is set to 10 cm, yielding a soil volume of 34.99 km³.

Table 20: Compartment properties for modelling the distribution fate of persistent degradation products

Compartment	Area [m ²]	Depth [m]	Density [kg/m ³]	Volume [m ³]
Water - Germany	7.10*10 ⁹	2	1000	1.42*10 ¹⁰
Soil – Germany	3.50*10 ¹¹	1*10 ⁻¹	1500	3.50*10 ¹⁰
Air	3.57*10 ¹¹	6*10 ³	1	2.14*10 ¹⁵

Compartment	Concentration [kg/m ³]	Density [kg/m ³]	Volume [m ³]
Aerosol – atmosphere	3*10 ⁻⁸	1500	4.28*10 ⁴
Water – aerosol particles	3*10 ⁻⁸	1000	6.43*10 ⁴
Water – fog	2.55*10 ⁻⁴	1000	5.46*10 ⁸
Water – raining clouds	1*10 ⁻³	1000	2.14*10 ⁹

3.5 Partial order theory

3.5.1 Introduction

The partial order theory offers the possibility to analyse a set of substances (e.g. refrigerants) which are all characterised simultaneously by several parameters (e.g. refrigerant-intrinsic properties). This method is of advantage as the parameters often do not have a common scale (Brüggemann & Bartel 1999).

A partial order on a set G , called poset (**p**artially **o**rded **s**et), with the substances x , y , and z is defined according to the following axioms of order (Brüggemann et al. 2007):

i) reflexivity: $x \leq x$

(a chemical can be compared with itself)

ii) antisymmetry: $x \leq y$ and $y \leq x \Rightarrow x = y$

(if x is better or equal than y and y is better or equal x , this implies: x equals y)

iii) transitivity: $x \leq y$ and $y \leq z \Rightarrow x \leq z$

(if x is better than y and y is better than z , then x is better than z)

The order relations are analysed component-wise, with $P_i(x)$ being the numerical value of the i -th attribute of the chemical x . If all parameters of x are lower than the respective ones of y , then x is ranked lower than y . If $P_i(x) \leq P_i(y)$ for some indices i and $P_i(y) \leq P_i(x)$ for some other indices, then x and y are “incomparable” (Brüggemann & Bartel 1999).

3.5.2 Hasse diagram technique

The graphical representation of posets is called Hasse diagram. In a Hasse diagram each substance is represented by a circle. The order relation of each pair of objects is shown by a line between them, whereby the substance which is higher ranked is placed at a higher vertical position. The diagram is greatly simplified by only drawing next neighbour links due to the transitivity relation of posets. The software *WHASSE* and *PyHasse* (software can be obtained from R. Brüggemann) permit to draw Hasse diagrams. The versatility of the Hasse diagram technique permits to combine the complete information of chemicals in order to take a decision about the priorities related to the chemicals. For instance, if a set of 6 fictitious refrigerants a , b , c , d , e , and f is defined by three parameters P_1 , P_2 , and P_3 the Hasse diagram shown in Figure 8 can be obtained.

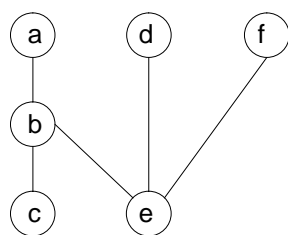


Figure 8: A Hasse diagram

From this diagram can be concluded that the most pollutant refrigerants are a, d and f since high values of P_1 , P_2 , and P_3 imply high pollution degree. In contrast, c and e are the most environmental friendly refrigerants. In addition, the Hasse diagram reveals that all the refrigerants except c are more pollutant than e.

3.5.3 METEOR

METEOR (**M**ETHOD of **E**valuation by **O**Rder theory), a mathematical method for assessing parameter prioritisation and its effect on the ranking of substances, was used to evaluate the environmental impact of refrigerants. This method is based on the Hasse diagram technique (Brüggemann & Bartel 1999, Brüggemann et al. 2007, Restrepo et al. 2008). In principle, METEOR allows a step-by-step aggregation of parameters by forming weighted sums about subsets of parameters (Brüggemann et al. 2007), thus, providing the possibility to analyse the effects of parameter weights.

In the present work, the idea of METEOR was applied considering six refrigerant-intrinsic properties (critical temperature, heat capacity of vapour, global warming potential, ozone depletion potential, octanol-water partition coefficient, and toxicological exposure limits) for a selection of 15 refrigerants, i.e. chlorodifluoromethane (R22), difluoromethane (R32), pentafluoroethane (R125), 1,1,1-trifluoroethane (R143a), propene (R1270), ammonia (R717), R134a, R152a, R290, R30, R600a, R744, E7200, and the blends R407C and R410A (Table 31). These refrigerants are used in different cooling and A/C applications.

The first step using METEOR was to normalize the values of the refrigerant-intrinsic properties to a [0,1]-scale using Equation 8 and to reorient the normalised values using Equation 9 where necessary, so that high values are associated with a negative environmental impact (Table 21).

$$P_i(x) = \frac{P'_i(x) - \min P'_i}{\max P'_i - \min P'_i} \quad \text{Equation 8}$$

$$P_{i,re}(x) = [P_i(x) \cdot (-1)] + 1 \quad \text{Equation 9}$$

For Equation 8 and Equation 9: $P'_i(x)$ is the value of property i of refrigerant x and $\min P'_i$ and $\max P'_i$ are the minimum and maximum values, $P_{i,re}(x)$ is the reoriented, normalised value of $P'_i(x)$.

Table 21: Normalized and reoriented data values of refrigerants used in the present METEOR study

Refrigerant	t_c	C_p	GWP	ODP	c_{ow}	TWA
R22	0.6837	0.6876	0.4045	1	0.5892	0.9091
R30	0	0.7814	0.0023	0.01	0.6308	1
R32	0.7718	0.9210	0.1523	0	0.3741	0.8081
R125	0.8300	0.0024	0.7841	0.0006	0.8875	0.8081
R134a	0.6596	0.1690	0.3205	0.0003	0.5844	0.8081
R143a	0.7980	0.4512	1	0	0.7506	0.8081
R152a	0.6019	0.4733	0.0277	0	0.5086	0.8081
R407C	0.7281	0.2373	0.00001	0	0.5623	0.8081
R410A	0.7985	0.6144	0.0001	0.0004	0.5330	0.8081
R290	0.6805	0.3801	0.0045	0	0.9022	0.5051
R600a	0.4951	0	0.0045	0	1	0.8485
R1270	0.7038	0.5544	0.0007	0	0.7579	0.8768
R717	0.5048	0.2861	0	0	0.3814	1
R744	1	1	0.0002	0	0	0
E7200	0.1359	0.3476	0.0136	0	0.5826	0.9697

t_c – Critical temperature, C_p - Heat capacity of vapour,
GWP - Global warming potential, ODP - Ozone depletion potential,
 c_{ow} - Octanol-water partition coefficient, TWA - Toxicological exposure limits

The second step was to aggregate two properties following Equation 10 to Equation 12 using the model *Stability* of the software *PyHasse*. The critical temperature (t_c) was aggregated with heat capacity of vapour (C_p) resulting in $\phi 1$, global warming potential (GWP) with ozone depletion potential (ODP) resulting in $\phi 2$, and octanol-water partition coefficient (c_{ow}) with exposure limit (TWA) resulting in $\phi 3$.

$$\phi 1(x) = g_1 \cdot t_c(x) + (1 - g_1) \cdot C_p(x) \quad \text{Equation 10}$$

$$\phi 2(x) = g_2 \cdot GWP(x) + (1 - g_2) \cdot ODP(x) \quad \text{Equation 11}$$

$$\phi 3(x) = g_3 \cdot c_{ow}(x) + (1 - g_3) \cdot TWA(x) \quad \text{Equation 12}$$

where g and $(1-g)$ are the selected weights for the properties. The sum of the weights must be equal to 1. An important value of g is achieved when $\phi(x) = \phi(y)$. This particular g -value is called “crucial” g -value for the pair $\{x, y\}$ (Restrepo et al. 2008).

The aggregation of METEOR followed the scheme in Figure 9. The next step was to aggregate $\varphi 2$ and $\varphi 3$ to $\varphi 4$, and finally $\varphi 4$ with $\varphi 1$ resulting in $\varphi 5$.

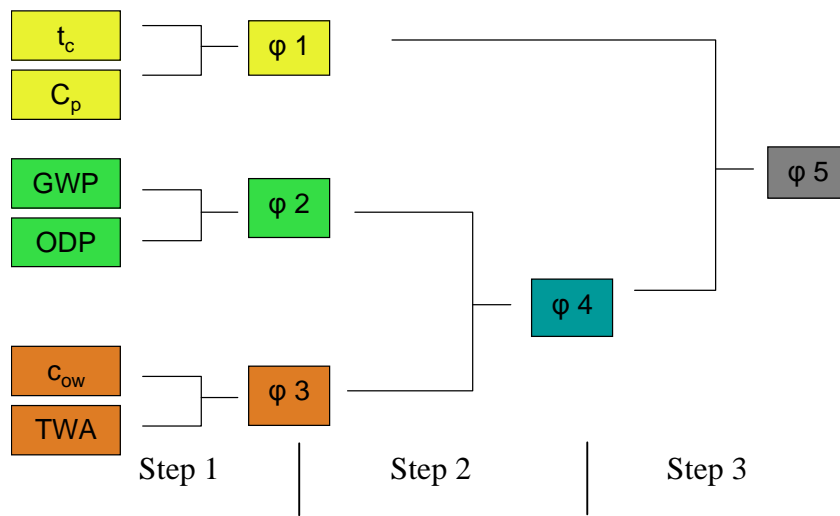


Figure 9: Aggregation scheme of METEOR calculation

4 Results

4.1 Impact assessment

4.1.1 CML02

The assessment based on CML02 includes 10 impact categories. In order to be able to show two impact categories in one figure, the results were drawn using normalised impact values. The filled bar represents the average scenario, the upper whisker the worst-case scenario, and the lower whisker the best-case scenario (Figure 10). Although two impact categories are placed in one figure they are not comparable to each other. This means that, if one refrigerant contributes more to impact category *A* than to impact category *B*, the contribution from *A* does not necessarily exert a greater negative impact on the environment than *B*. In Table 55 the non-normalised values of each category are listed.

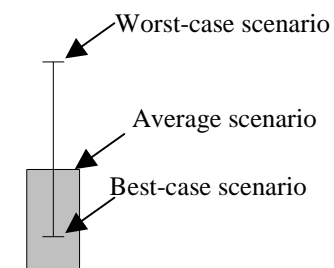


Figure 10: Exemplary sketch of diagrams

In Figure 11, the HCs R290 and R600a have a contribution to the impact category “Demand of non-renewable primary energy” (PE) of about the factor 1 000 - 4 000 smaller than those of other refrigerants. The contribution of R152a, R744, and R30 to this category that is up to 2-times smaller than those of R134a and the HFEs. Applying best-case or worst-case scenario does not change the ranking order of the refrigerants.

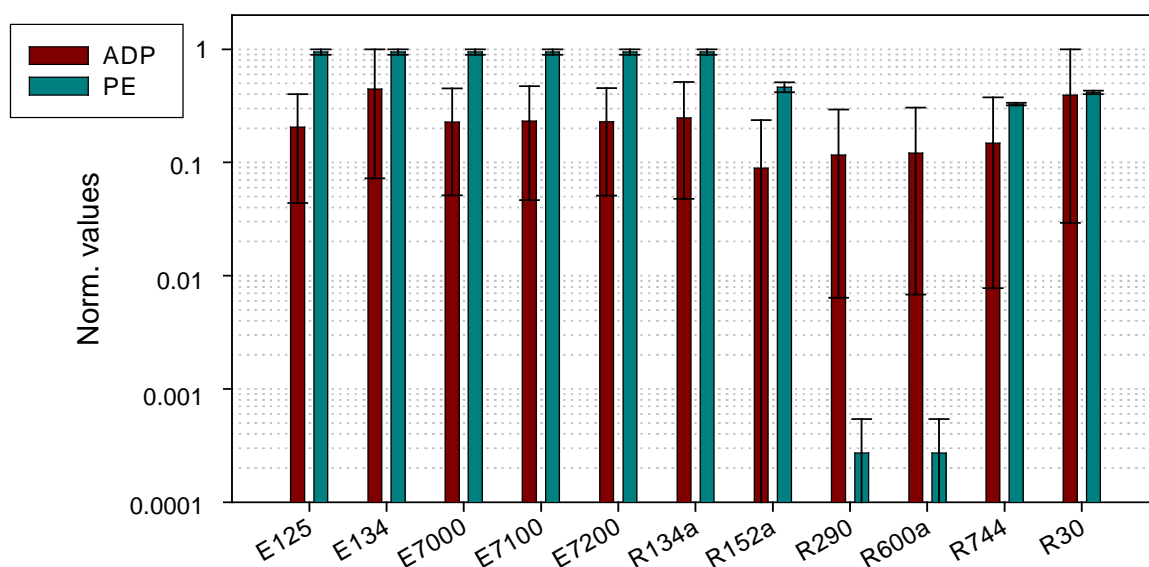


Figure 11: CML02 results of the impact categories ADP and PE

R152a has the smallest impact on the category “Depletion of abiotic resources (excluding primary energy sources)” (ADP) of the studied refrigerants under average scenario, followed by R290, R600a, and R744. E134 has the highest contribution in this category. The other HFEs have a contribution similar to that of R134a. The impact of R30 is smaller than that of E134 but greater than that of R134a (Figure 11).

Merely R134a and R152a contribute to the impact category “Stratospheric ozone depletion” (SOD). The impact of R134a is in all three scenarios 10-times higher than that of R152a (Figure 12). Considering the total life cycle, R152a has the smallest input to the category “Climate change” (CC) followed by the HCs R290 and R600a, and R744 (Figure 12). E125 and E134 have a greater impact in this category than R134a, R30, and the other HFEs.

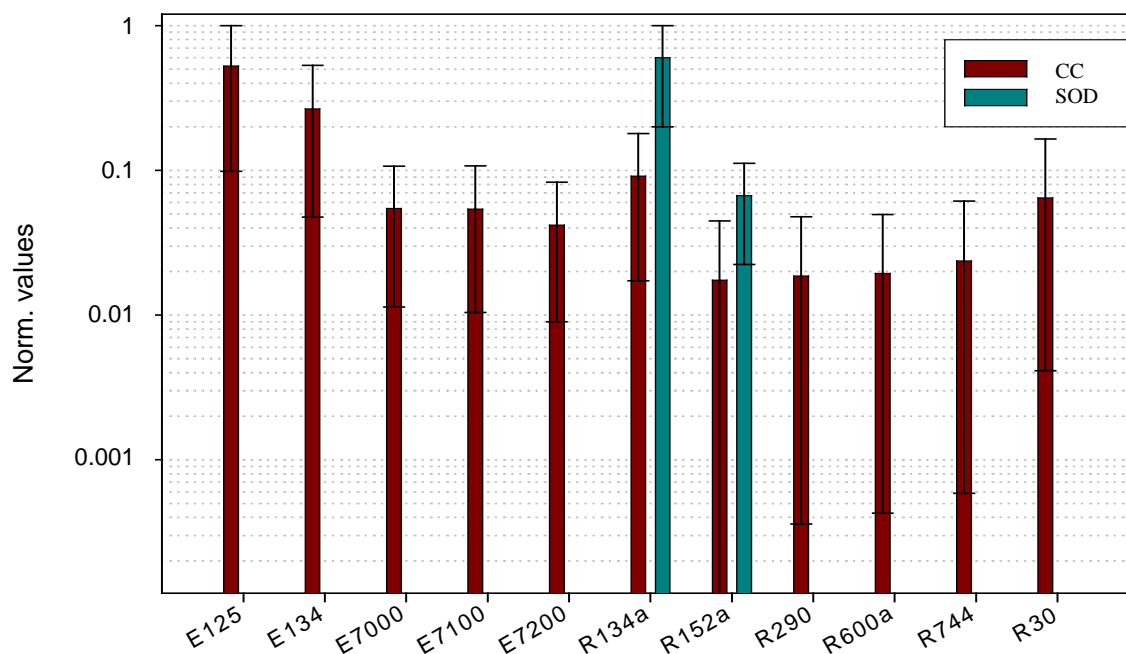


Figure 12: CML02 results of the impact categories CC and SOD

The ranking of the refrigerants is the same in the two impact categories (Figure 13) “Acidification” (AP) and “Eutrophication” (EP) because those impact categories are mainly based on fuel consumption due to compression and additional weight. Under the average scenario, E125 has the lowest impact (0.05) and R30 the greatest one (0.4) in those categories. E134 (0.3) has an impact close to R30, whereas the HFEs of the 7000-series, the HFCs, the HCs, and R744 are in the range of 0.07 – 0.15 (normalised values). Under the best-case scenario, E125 remains the least problematic refrigerant, followed by E7100 and R134a. R30 and E134a continue to be the two most problematic ones.

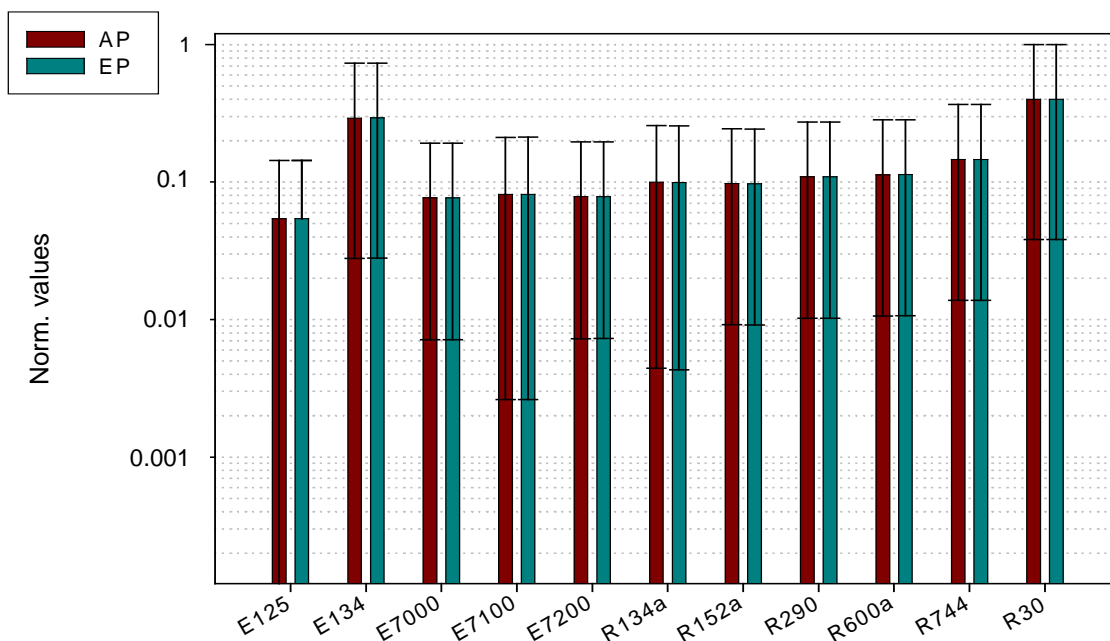


Figure 13: CML02 results of the impact categories AP and EP

The ranking of the refrigerants in the impact categories “Photo-oxidant formation” (POCP) and “Human toxicity” (HTP) is the same as in the categories AP and EP because those values are also based almost solely on the additional fuel consumption (Figure 14). The relative ranking order of the refrigerants changes equally to AP and EP in the different scenarios.

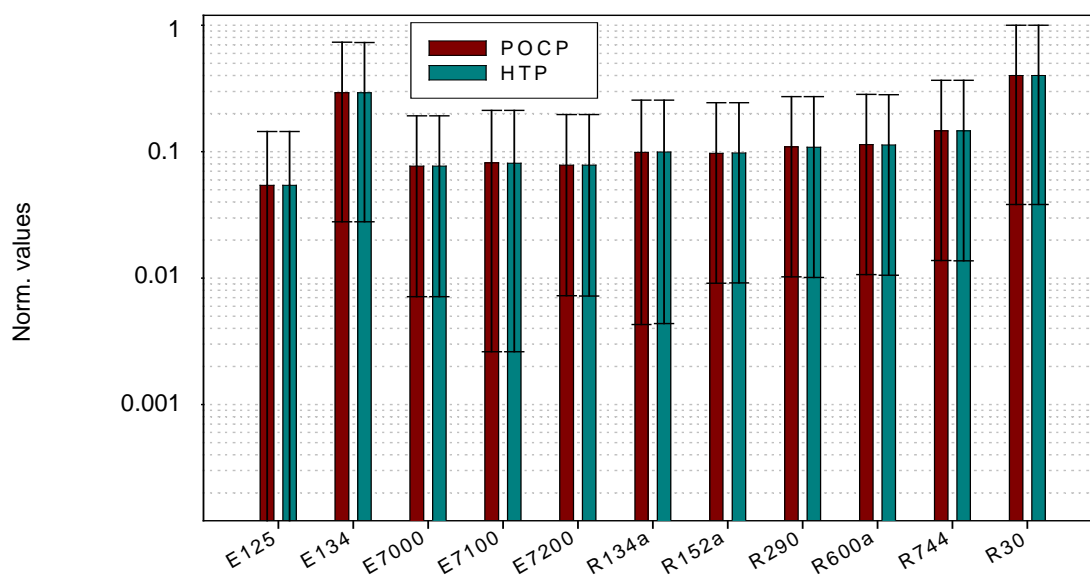


Figure 14: CML02 results of the impact categories POCP and HTP

Figure 15 depicts that R134a has the greatest impact in the categories “Fresh water aquatic toxicity” (FAETP) and “Terrestrial ecotoxicity” (TETP) of all studied refrigerants due to direct emissions. R290, R600a, and R744 do not contribute to those categories. R30 only contributes to TETP. The HFEs and R512a have impact values on FAETP and TETP which are about the factor 10^5 - 10^6 smaller than those of R134a. The relative ranking of the refrigerants does not change when regarding worst-case or best-case scenario.

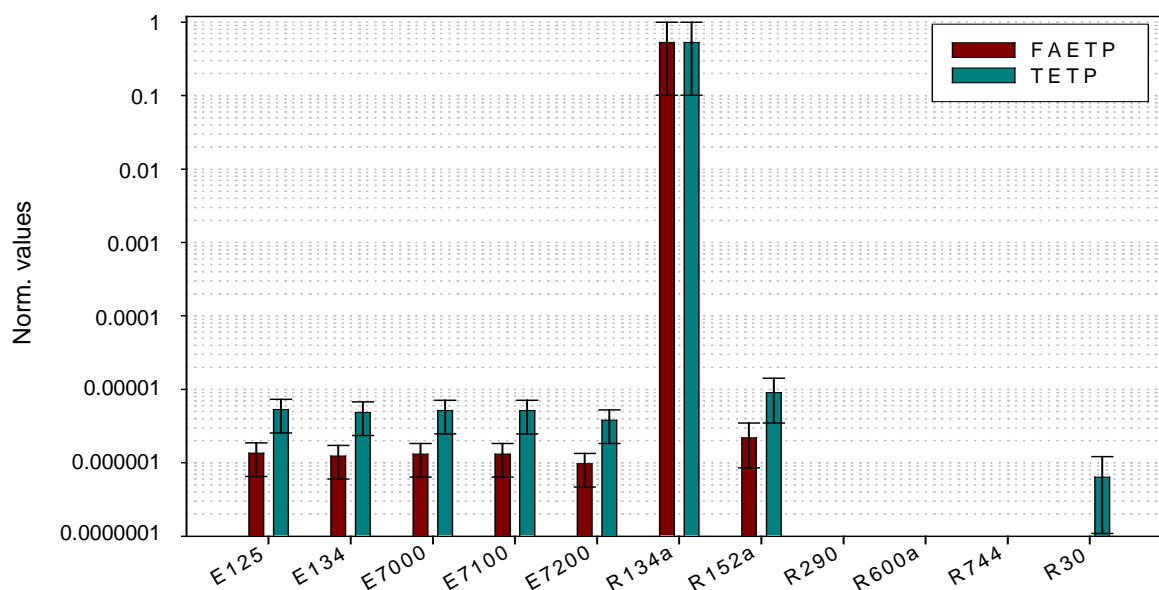


Figure 15: CML02 results of the impact categories FAETP and TETP

Dominance analysis – Contribution of life cycle phases to impact categories

For assessing the dominance of one life phase over the others, the average scenario was taken (Table 56). Within the life cycle of a passenger car, the operation phase is the longest phase with ten years. Thus, it is not surprising that this phase contributes to more than 79 % to the impact category ADP as the system that runs on petrol and petrol is defined as abiotic resource. For R152a and R30, the contribution of the production phase is smaller than 0.1 % (Figure 16). The contribution from the disposal phase is less than 0.05 % for all refrigerants as it was assumed that the recovered refrigerants - except R744 - are burned under presence of oxygen and hydrogen.

From those results, it can be concluded that the most important phase for implementing measures to reduce the environmental impact on ADP from that application is the operation phase. Main aspects are better energy efficiency and optimized tightness of the system.

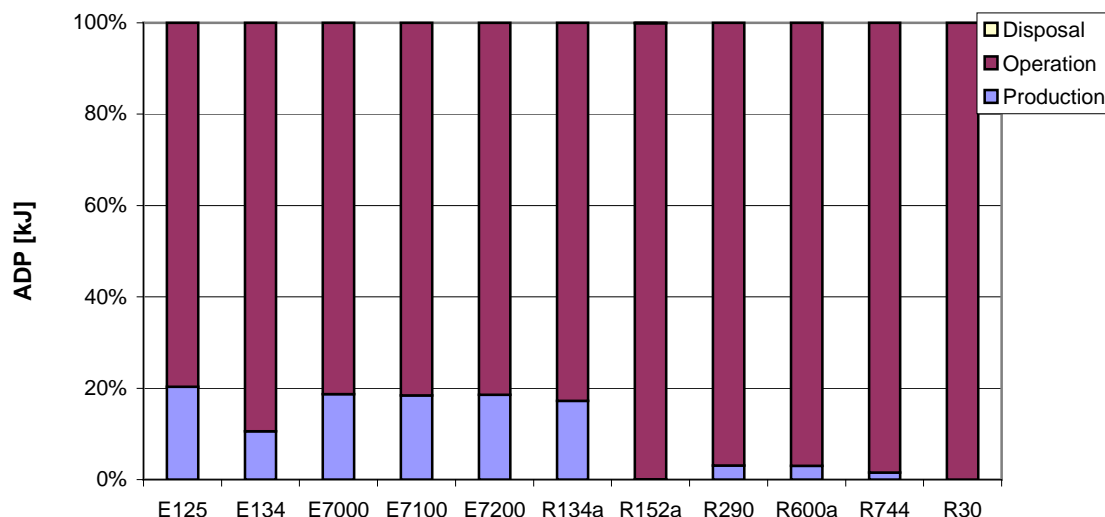


Figure 16: CML02 results of the impact category ADP

As petrol is contributing to the impact category ADP, the energy consumption of the A/C system during operation is not included in PE. In the impact category PE, the production phase is the main contributor accounting for 59 % for all studied HFEs and R134a (Figure 17). For the other refrigerants the production phase amounts to 29 – 48 %. Because of the refilling processes in the operation phase and the necessary refrigerant production, this phase is contributing up to 3 % (R152a) to PE. The HCs R290 and R600a have a contribution of almost zero to PE in the operation phase. The primary energy input to the disposal phase is about 38 % for the HFEs and R134a, and 50 - 71 % for the other refrigerants.

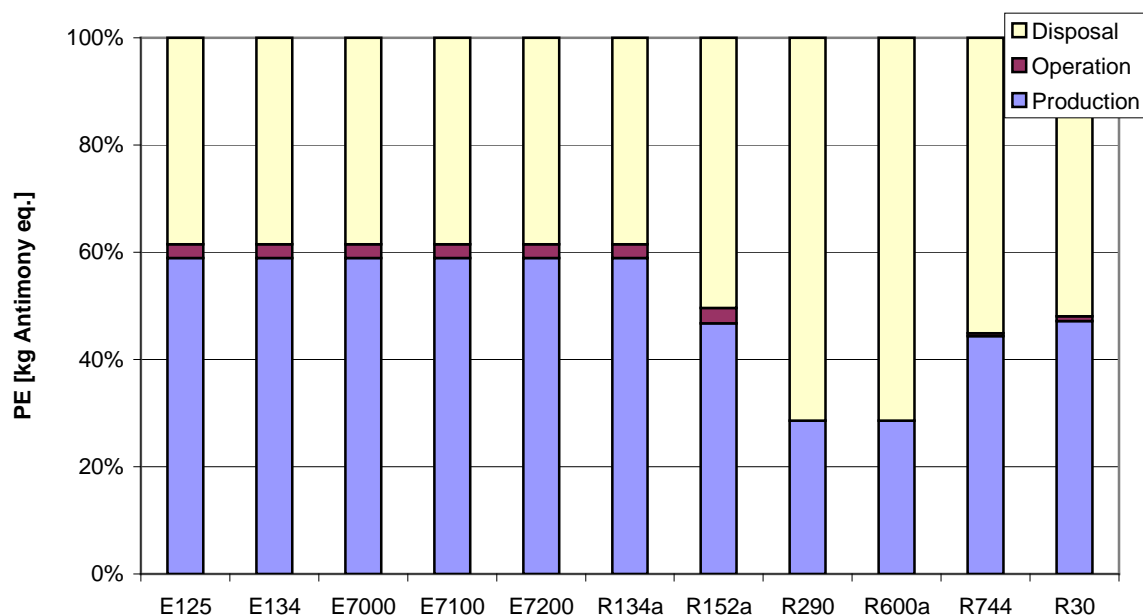


Figure 17: CML02 results of the impact category PE

The impact category CC is mainly influenced by the operation phase (71-99 %). This is, on the one hand, caused by direct emissions of refrigerants with a great GWP₁₀₀ (e.g. E125, E134, R134a) and on the other hand, due to high CO₂ emissions originating from a high energy demand of less efficient refrigerants (e.g. E134, R30, R744). Refrigerants with a great GWP₁₀₀ (e.g. E125, E134, R134a) have a relatively high contribution (up to 22 %) in the disposal phase to CC caused by direct emissions (Figure 18).

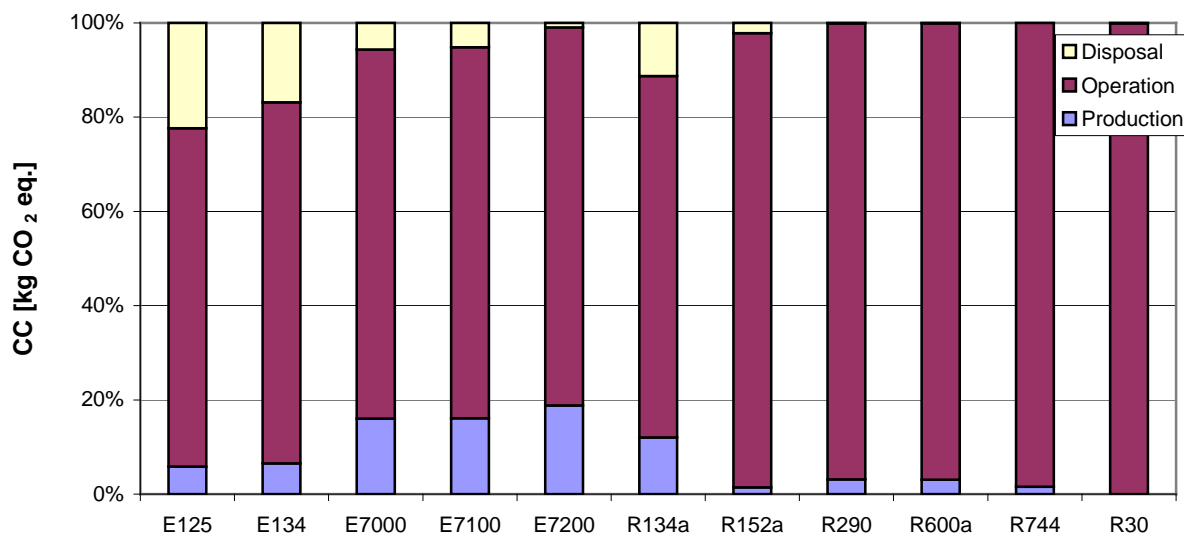


Figure 18: CML02 results of the impact category CC

R744 and the HCs R290 and R600a do not contribute to the impact category FAETP (Figure 19). For the HFEs, both disposal and operation phase add to about 50 % to this impact category. R134a, R152a, and R30 have input from all three life cycle phases. The production phase is contributing between 4-25 %, the operation phase between 61-73 %, and the disposal phase to 15-24 % to FAETP.

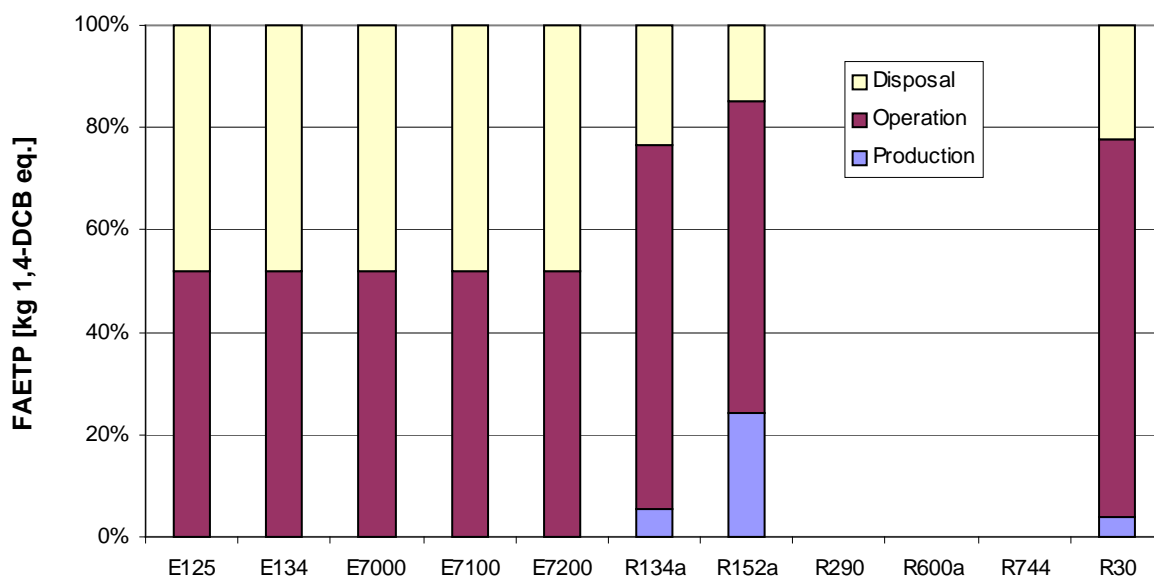


Figure 19: CML02 results of the impact category FAETP

4.1.2 EI99

Comparing EI99 of the entire life phase of the studied refrigerants (Table 57) under average scenario (Figure 20, filled bar), E134 has the greatest impact on the environment with about 54 Pt (Ecopoints), followed by R30 (44 Pt). R134a, E125, E7000, and E7100 are in the range of 40 – 41 Pt. E7200 has a little lower environmental impact (32 Pt). R152a and R744 have an environmental impact of about 30 Pt. The lowest impacts of the studied refrigerants have the HCs R290 and R600a with about 28 Pt.

Under worst-case scenario (Figure 20, upper whisker), R30 (75 Pt) stays more environmental problematic than the other refrigerants except E134 (92 Pt) which has still the greatest impact. In this particular scenario, E125 (59 Pt) becomes less problematic than E7100 and E7000 (60 and 61 Pt). The order of the other refrigerants is not influenced by this scenario.

Under best-case scenario (Figure 20, lower whisker), E7000 (25 Pt) becomes more problematic than E7100 (23.9 Pt) and R30 (24.4 Pt). R30 becomes more problematic than R134a (25 Pt). R744 (23.1 Pt) has a lesser impact than R152a (23.4 Pt). R290 stays over all scenarios the least problematic of the studied refrigerants followed by R600a.

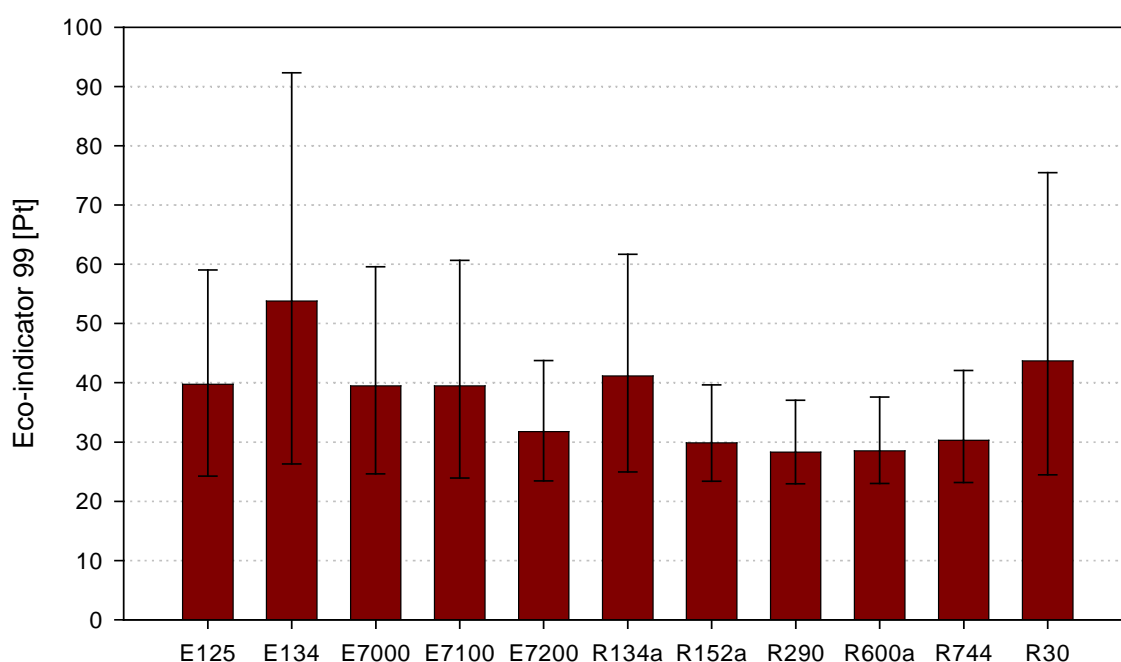


Figure 20: EI99 results of complete life cycle; filled bar – average scenario, upper whisker – worst-case scenario, lower whisker – best-case scenario

Dominance analysis – Contribution of life cycle phases to EI99

The operation phase is with 43-63 % the dominating life phase within the life cycle of A/C systems in cars, followed by the production phase (24 – 38 %). The disposal phase is the most inferior process (11 – 20 %) of the life cycle of this specific application (Figure 21).

As the EI99 is aggregating the damages of several categories, it is not so transparent which parameter is contributing the most to the final indicator. The sensitivity of specific parameters will be investigated in Chapter 5.1.

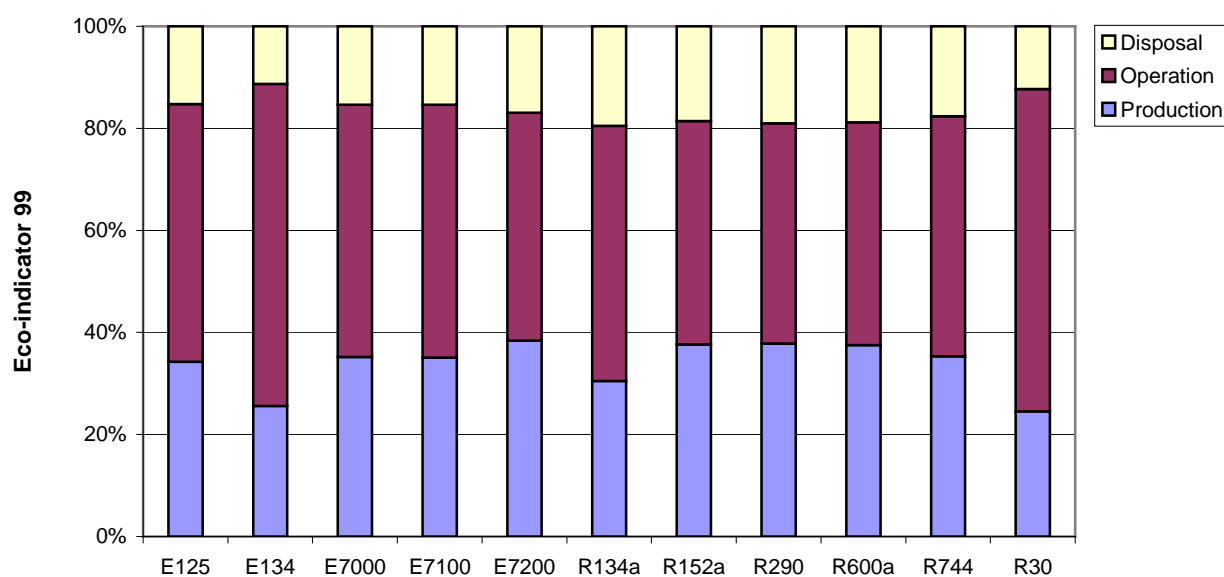


Figure 21: Contribution of production, operation, and disposal phase to EI99

Comparing the absolute EI99 values of the production phase under average scenario (Table 57), Figure 22 (filled bars) shows that the HFEs E7000, E7100, E125, and E134 have the highest values (about 14 Pt), followed by R134a (13 Pt) and E7200 (12 Pt). This is mainly caused by the energy consumption and the emissions of problematic by-products like R113, R124, hexafluoropropane, hexafluoropivaloyl fluoride, and other fluorinated ethers. R152a, R290, R600a, R30, and R744 have an impact on the environment of about 11 Pt.

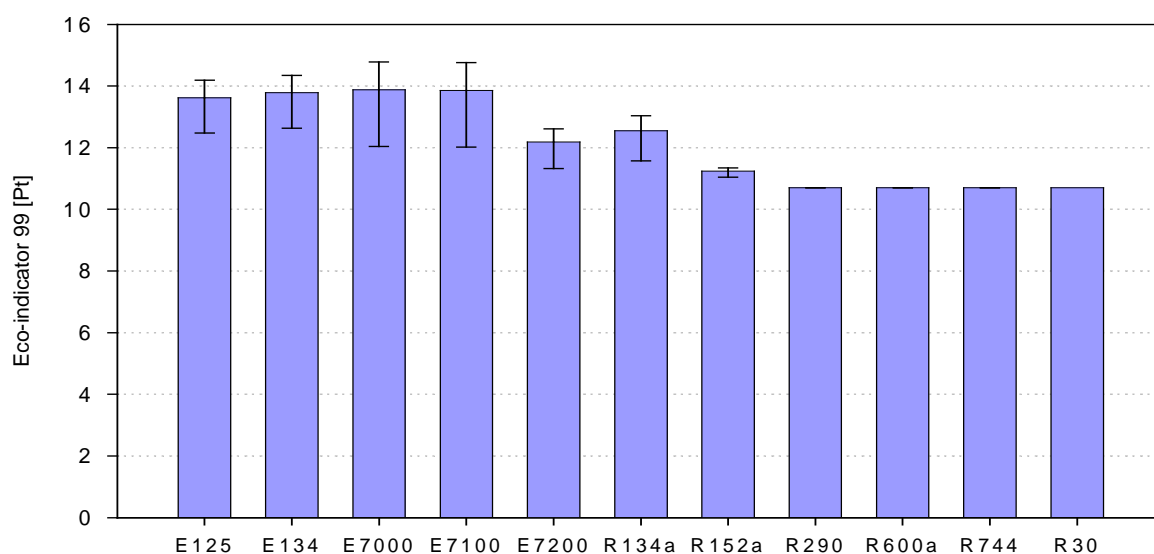


Figure 22: EI99 of production phase; filled bar – average scenario, upper whisker – worst-case scenario, lower whisker – best-case scenario

Comparing the EI99 of the operation phase under average scenario (Table 57), Figure 23 (filled bars) reveals that E134 (34 Pt) and R30 (28 Pt) have the highest values, followed by E125, E7000, E7100, and R134a, all in the range of about 20 Pt. This is partly caused by the energy consumption and the emissions of problematic by-products during the refrigerant production needed for the refilling of the system. Otherwise, the energy efficiency of the refrigerant in that particular application has a big contribution to EI99 in this life phase (R30, E134), as well as direct emissions of refrigerants (E125, E134, R134a, E7000, E7100). The other refrigerants have EI99 values in this life phase of 12 – 14 Pt. It should be mentioned that higher energy efficiency might be compensated by lower impacts on e.g. climate change due to direct emissions because of lower GWP₁₀₀ as it is the case for R744 and the HCs R290 and R600a.

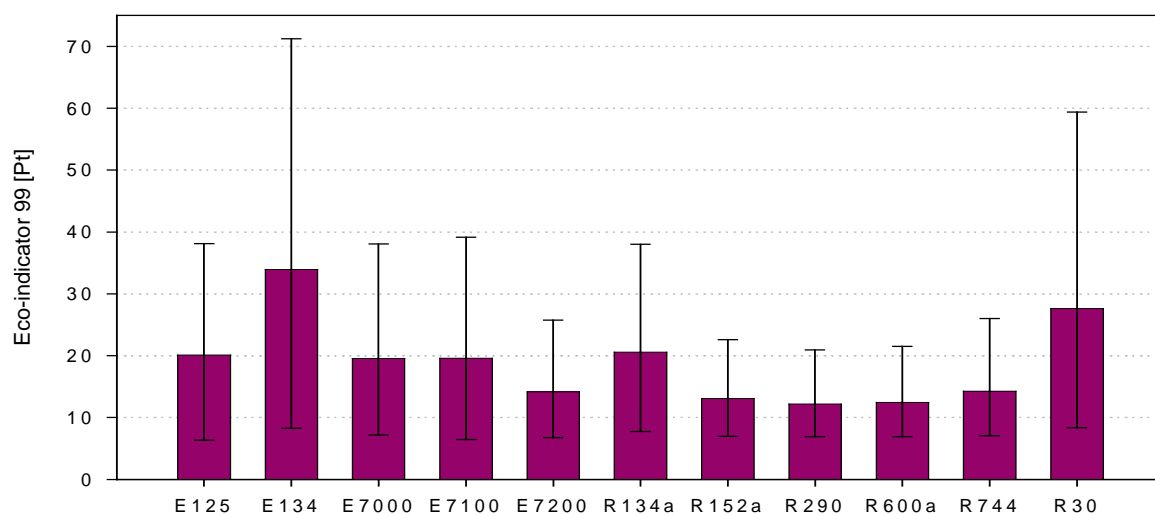


Figure 23: EI99 of operation phase; filled bar – average scenario, upper whisker – worst-case scenario, lower whisker – best-case scenario

Comparing the EI99 of the disposal phase under the average scenario (Table 57), Figure 24 (filled bars) discloses that R134a (8 Pt) has the highest value. This life phase is dominated by products formed during incineration of the recovered refrigerants and the direct emissions occurring while emptying systems. In this life phase, the other refrigerants have EI99 values between 5 – 6 Pt. Under the worst-case scenario, the impact of R134a is almost twice as high as those of other refrigerants. Under the best-case scenario, the impacts of all refrigerants are about 5 Pt.

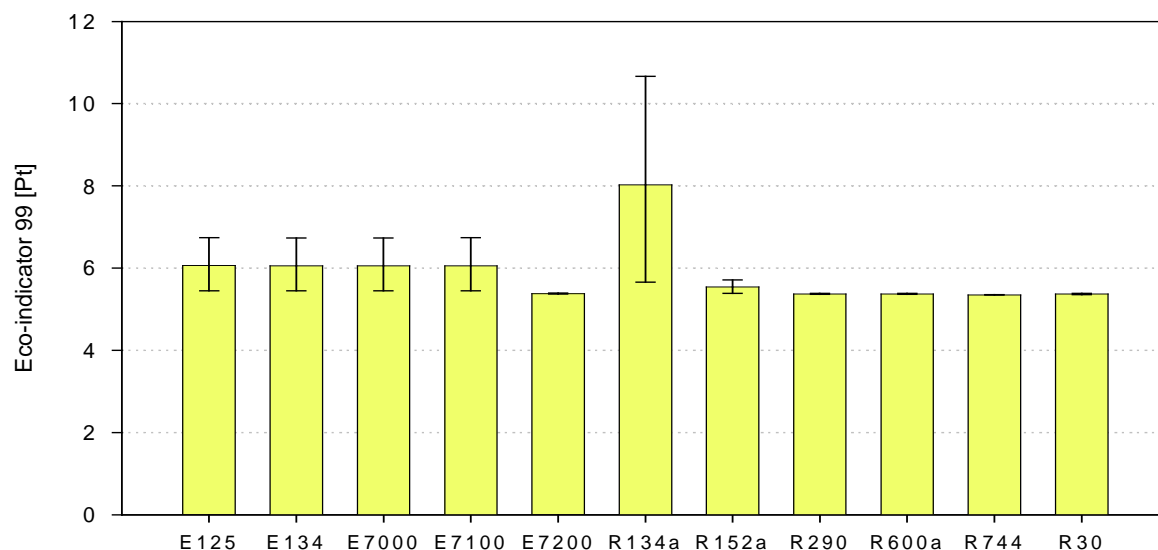


Figure 24: EI99 of disposal phase; filled bar – average scenario, upper whisker – worst-case scenario, lower whisker – best-case scenario

4.1.3 TEWI

The TEWI calculation (Table 58) showed that, under average scenario, E125 performed worst, followed by E134. R134a and R30 have almost the same environmental impact of about 3 000 kg CO₂ eq., whereas E7000, E7100, and R744 have ca. 1 000 kg CO₂ eq.. The four refrigerants with the lowest environmental impact are E7200, R290, R152a, and R600a. Under the worst-case scenario, R744 remains less problematic than R134a, R30, E134, and E125 but it becomes more problematic than E7000 and E7100. R152a becomes less problematic than R290. Under the best-case scenario, R600a becomes less problematic than R152a (Figure 25).

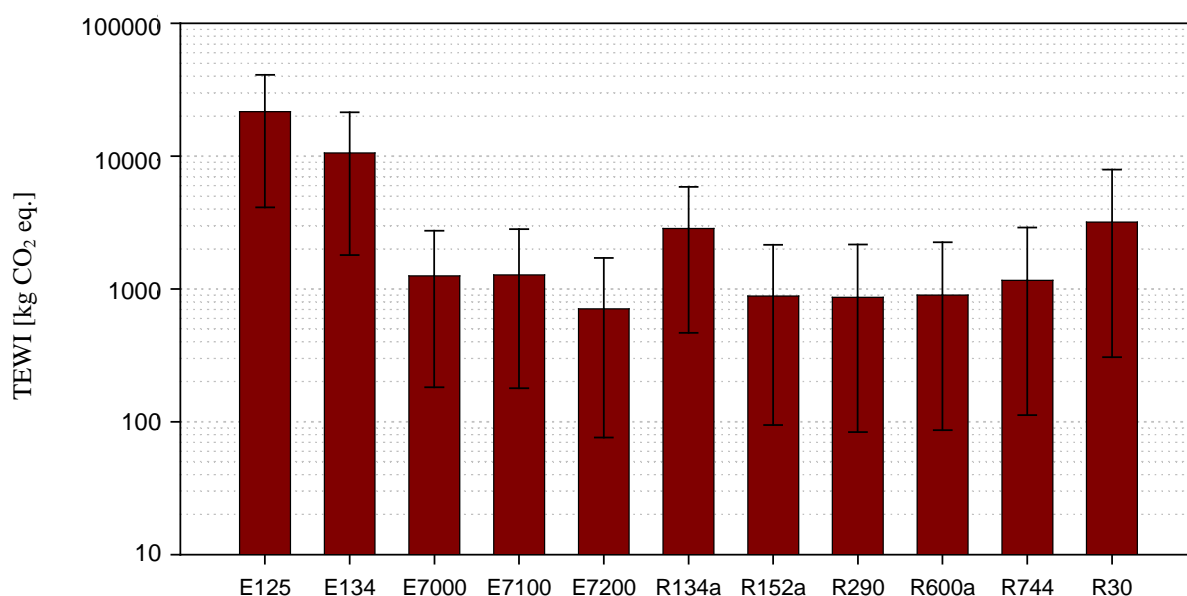


Figure 25: TEWI results of complete life cycle; filled bar – average scenario, upper whisker – worst-case scenario, lower whisker – best-case scenario

Figure 26 shows that R30, E134, and R744 have the greatest contribution (1 000 – 3 000 kg CO₂ eq.) to TEWI by the component TEWI_{indirect} under average scenario. The other refrigerant show values between 600 and 900 kg CO₂ eq., except E125 which has a contribution of 470 kg CO₂ eq.. This order is remaining the same for worst-case and best-case scenario.

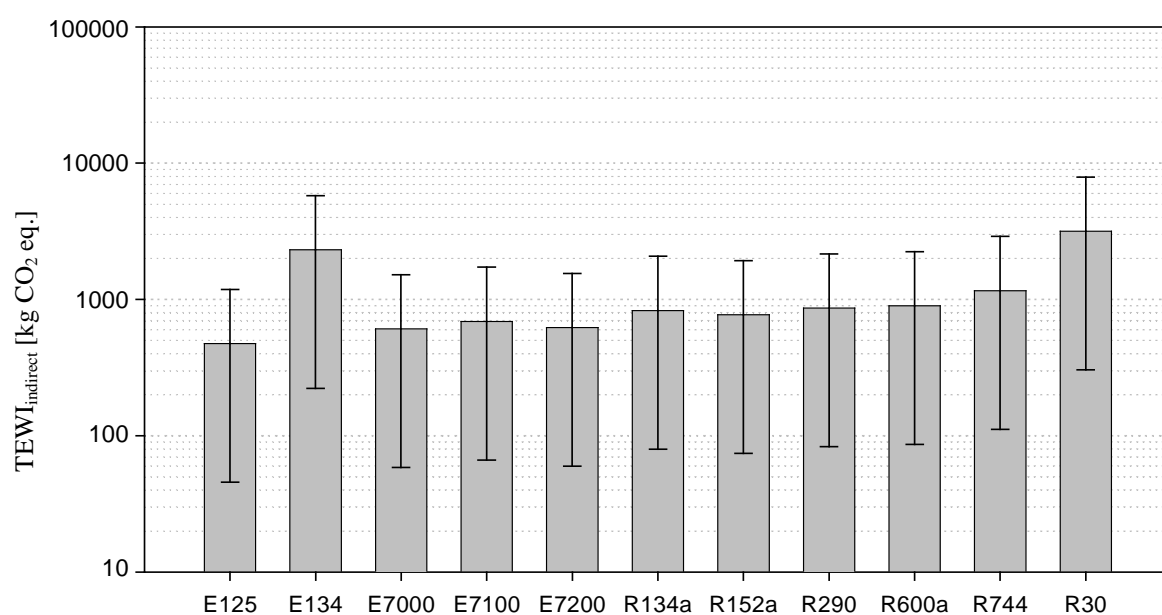


Figure 26: Contribution of indirect TEWI component; filled bar – average scenario, upper whisker – worst-case scenario, lower whisker – best-case scenario

Considering the direct component of TEWI, Figure 27 depicts that E125, E134, and R134a have the greatest contribution (2 000 – 21 000 kg CO₂ eq.) under average scenario. E7000, E7100, and R152a show values between 100 and 650 kg CO₂ eq., E7200 has an impact of 86 kg CO₂ eq.. The HCs, R30, and R744 contribute less than 10 kg CO₂ eq.. This order is remaining the same for worst-case and best-case scenario.

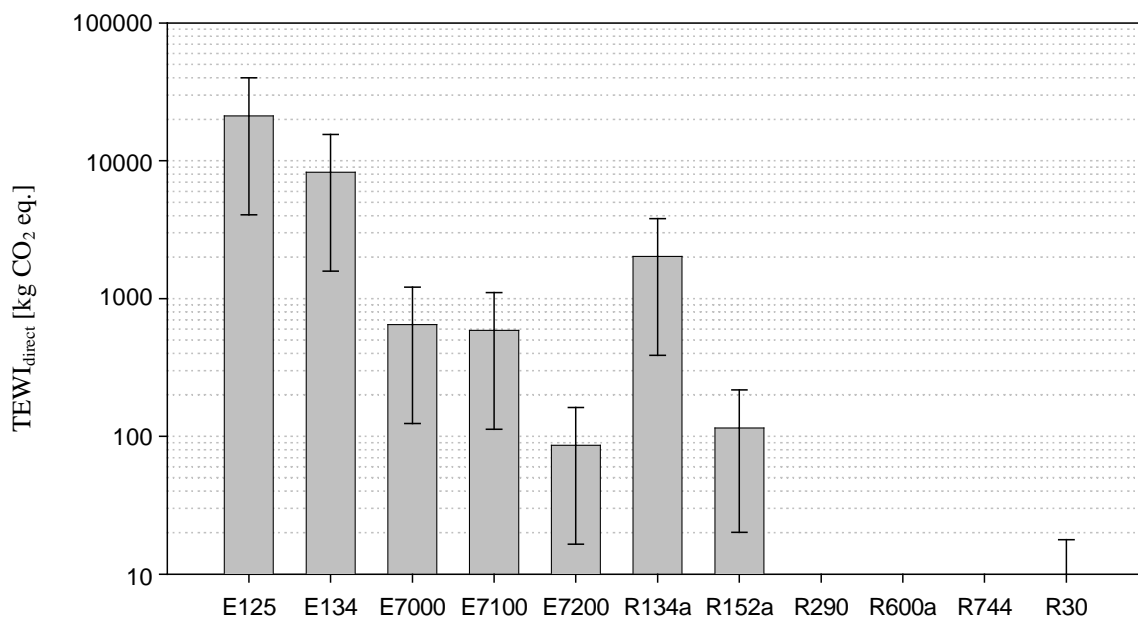


Figure 27: Contribution of direct TEWI component; filled bar – average scenario, upper whisker – worst-case scenario, lower whisker – best-case scenario

4.2 Fate modelling

Modelling the distribution of the degradation products of some of the studied refrigerants shows that under the German model, TFA is to 86 % in the atmosphere and to about 14 % in the hydrosphere (Figure 28). The PFCAs are to 98-100 % in the air compartment, to up to 0.1 % in the water compartment, and to up to 1.7 % in the soil compartment under this specific model scenario. CF_2O is to about 100 % in the air compartment.

Concentrating on the distribution of those substances in the atmosphere, different water contents were assumed. In the model “Atmosphere-aerosol particles”, all degradation products accumulated completely in the air compartment (Table 60). The higher the water content of the atmosphere the higher is the percentage of TFA and PFCAs, especially $\text{C}_4\text{F}_9\text{COOH}$, in the water phase. Under the scenario of raining cloud conditions (“Atmosphere-raining cloud”), TFA is partitioning into the water to 2.4 %, $\text{C}_4\text{F}_9\text{COOH}$ to 0.2 % (Figure 28). CF_2O stays under all regarded models predominantly in the gaseous phase.

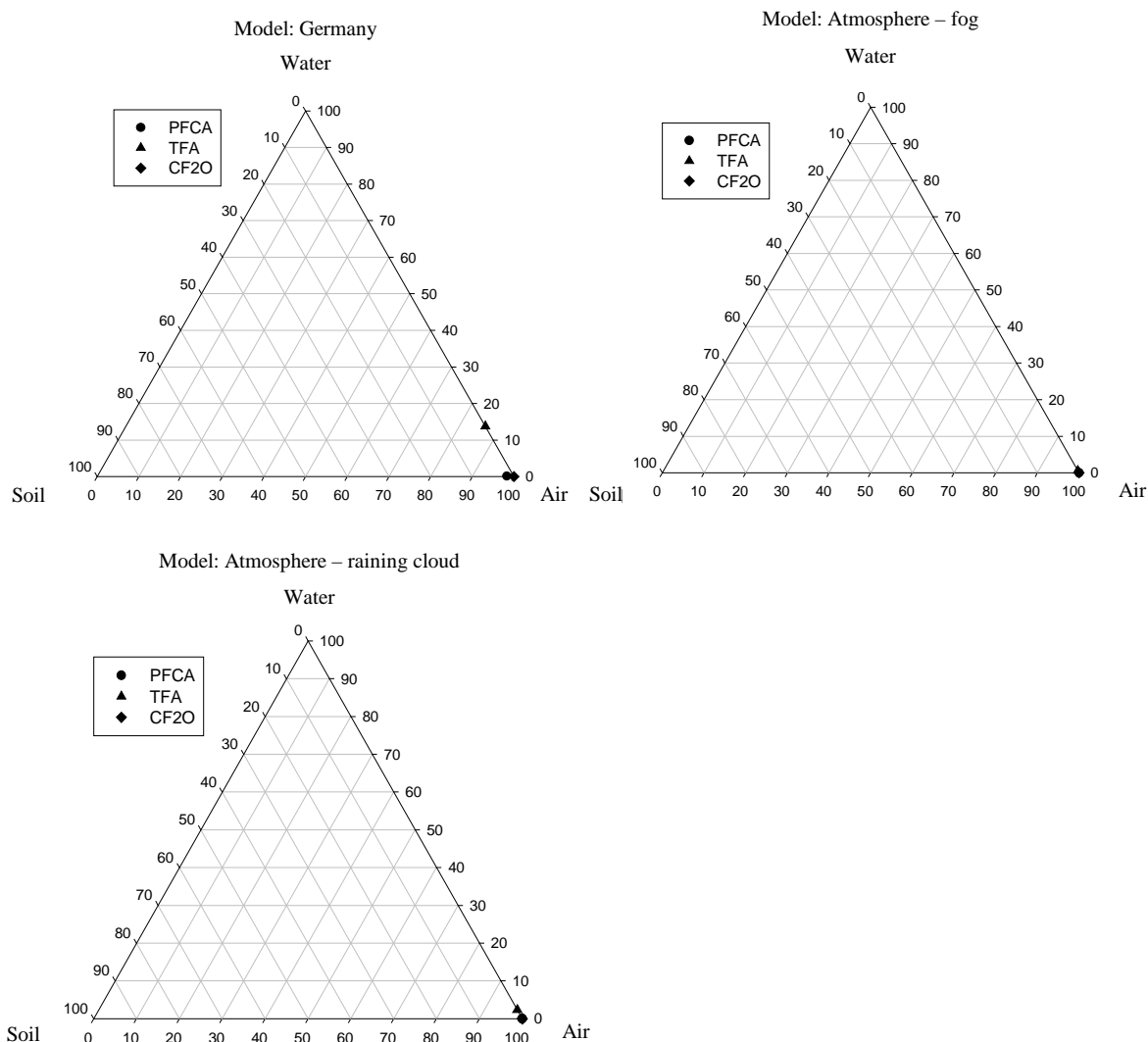


Figure 28: Partitioning of some degradation products into the compartments air, water, and soil under different models

From the amounts of refrigerants that are directly emitted to the atmosphere during the life cycle of an A/C system, the quantity of the main degradation products were calculated using the degradation yields of Chapter 3.4 (Table 54). The concentrations of the degradation products in the compartments air, water, and soil (Table 61 to Table 68) were calculated using the distribution model *EXTND* of the software *E4CHEM* (Brüggemann et al. 1996).

The refrigerant emissions (E7000, E7100, E7200) during one year of operation of the A/C system of a passenger car result in concentrations of PFCAs in air of $5 \cdot 10^{-12}$ to $1 \cdot 10^{-10} \mu\text{g}/\text{dm}^3$, in soil or on aerosol particles of $4 \cdot 10^{-10} - 7 \cdot 10^{-8} \mu\text{g}/\text{dm}^3$, and of $1 \cdot 10^{-10} - 2 \cdot 10^{-8} \mu\text{g}/\text{dm}^3$ in water (Table 22). These concentrations occur in the specific compartments of all four model scenarios (Chapter 3.4, Table 20). High values occur under worst-case and low values under best-case scenario.

Assuming complete degradation of R30 into HCl and CO_2 , the annual emissions during one year of operation of an A/C system using R30 would result in HCl concentrations of $6 \cdot 10^{-12} - 6 \cdot 10^{-11}$, $3 \cdot 10^{-9} - 3 \cdot 10^{-8}$, and $3 \cdot 10^{-11} - 3 \cdot 10^{-10} \mu\text{g}/\text{L}$ in the compartments air, water, and soil, respectively.

Table 22: Concentrations of the main degradation products of E7000, E7100, E7200, and R30 in environmental compartments [$\mu\text{g}/\text{dm}^3$] under the German model (Chapter 3.4), calculated using *EXTND* of *E4CHEM*; high values under worst-case and low values under best-case scenario

Compartment	Degradation product	$\text{C}_3\text{F}_7\text{COOH}$ from E7000	$\text{C}_4\text{F}_9\text{COOH}$ from E7100
Air		$1.13 \cdot 10^{-11} - 1.03 \cdot 10^{-10}$	$1.12 \cdot 10^{-11} - 1.01 \cdot 10^{-10}$
Water		$2.35 \cdot 10^{-9} - 2.14 \cdot 10^{-8}$	$2.32 \cdot 10^{-9} - 2.11 \cdot 10^{-8}$
Soil		$7.81 \cdot 10^{-9} - 7.10 \cdot 10^{-8}$	$7.71 \cdot 10^{-9} - 7.01 \cdot 10^{-8}$

Compartment	Degradation product	$\text{C}_4\text{F}_9\text{CH}_2\text{COOH}$ from E7200	HCl from R30
Air		$5.59 \cdot 10^{-12} - 5.12 \cdot 10^{-11}$	$5.59 \cdot 10^{-12} - 5.65 \cdot 10^{-11}$
Water		$1.37 \cdot 10^{-10} - 1.25 \cdot 10^{-9}$	$2.65 \cdot 10^{-9} - 2.68 \cdot 10^{-8}$
Soil		$4.54 \cdot 10^{-10} - 4.15 \cdot 10^{-9}$	$2.47 \cdot 10^{-11} - 2.50 \cdot 10^{-10}$

Direct emissions of R134a during one year of operation of an A/C system result in concentrations of TFA in air of about $4 \cdot 10^{-12} - 5 \cdot 10^{-11} \mu\text{g}/\text{dm}^3$, in soil or on aerosol particles of $7 \cdot 10^{-14} - 9 \cdot 10^{-13} \mu\text{g}/\text{dm}^3$, and of $9 \cdot 10^{-8} - 1 \cdot 10^{-6} \mu\text{g}/\text{dm}^3$ in water (Table 23).

Under the same scenario, an A/C system using E125, E135, and R152a, respectively, results in a CF_2O concentration in air of about $6 \cdot 10^{-12} - 1 \cdot 10^{-10} \mu\text{g}/\text{dm}^3$, in soil or on aerosol particles of $8 \cdot 10^{-14} - 2 \cdot 10^{-12} \mu\text{g}/\text{dm}^3$, and in water of about $1 \cdot 10^{-10} - 3 \cdot 10^{-9} \mu\text{g}/\text{dm}^3$ (Table 23).

Table 23: Concentrations of the main degradation products of E125, E134, R152a, and R134a in environmental compartments [$\mu\text{g}/\text{dm}^3$] under the German model (Chapter 3.4), calculated using *EXTND* of *E4CHEM*; high values under worst-case and low values under best-case scenario

Degradation product Compartment	CF_2O from E125	CF_2O from E134
Air	$7.94 \cdot 10^{-12} - 9.48 \cdot 10^{-11}$	$1.20 \cdot 10^{-11} - 1.09 \cdot 10^{-10}$
Water	$1.94 \cdot 10^{-10} - 2.32 \cdot 10^{-9}$	$2.94 \cdot 10^{-10} - 2.66 \cdot 10^{-9}$
Soil	$1.10 \cdot 10^{-13} - 1.31 \cdot 10^{-12}$	$1.66 \cdot 10^{-13} - 1.50 \cdot 10^{-12}$

Degradation product Compartment	CF_2O from R152a	TFA from R134a
Air	$6.03 \cdot 10^{-12} - 7.09 \cdot 10^{-11}$	$3.72 \cdot 10^{-12} - 4.69 \cdot 10^{-11}$
Water	$1.48 \cdot 10^{-10} - 1.74 \cdot 10^{-9}$	$8.97 \cdot 10^{-8} - 1.31 \cdot 10^{-6}$
Soil	$8.31 \cdot 10^{-14} - 9.78 \cdot 10^{-13}$	$6.82 \cdot 10^{-14} - 8.60 \cdot 10^{-13}$

4.3 METEOR

Each aggregation delivers a set of crucial g -values (Figure 29) that separates the range of g from 0 to 1 into a number of different stability fields. For further calculations, from each aggregation stability fields were chosen those whose range of g -values are equal or greater than half of the range of greatest stability field of the respective aggregation. Each of those stability fields has its characteristic linear order. The other stability fields were pooled to so called hot spots, marked with grey bars, and not further analysed. For further aggregation, the middle g -values of the selected stability fields were taken for calculation (Table 69).

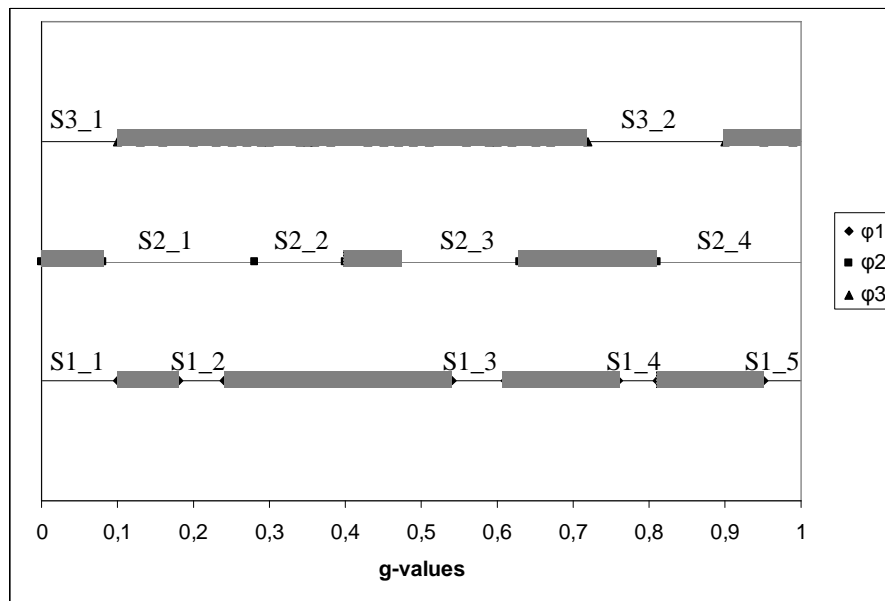


Figure 29: Crucial g -values of the aggregations $\phi 1$ (t_c , C_p), $\phi 2$ (GWP, ODP), and $\phi 3$ (c_{ow} , TWA), marked with grey bars are the stability fields that are combined to hot spots, further analysed stability fields are labelled following the scheme Sa_b where a stands for the aggregation and b for the number of stability field within that aggregation

Following the aggregation scheme in Figure 9 and the selection modulus explained above, for $\phi 1$ five stability fields were selected, for $\phi 2$ four, and for $\phi 3$ two (Figure 29). The first aggregation step (Figure 9) of two refrigerant properties at one time resulted in the linear orders shown in Figure 30.

aggregated with the five selected stability fields of $\varphi 1$. The aggregation of $\varphi 4$ and $\varphi 1$ (Equation 14) resulted in 155 g-spectra from which 749 stability fields were selected. Thus, the METEOR calculation with six refrigerant intrinsic properties resulted in a selected number of 749 linear orders whereby the refrigerant with the highest rank has the greatest impact on the environment.

$$\varphi 4(x) = g_4 \cdot \varphi 2(x) + (1 - g_4) \cdot \varphi 3(x) \quad \text{Equation 13}$$

$$\varphi 5(x) = g_5 \cdot \varphi 1(x) + (1 - g_5) \cdot \varphi 4(x) \quad \text{Equation 14}$$

Based on the data values in Table 21 and the weights of the selected stability fields (Table 69), the final aggregation ($\varphi 5$) of the six properties is achieved using Equation 10 to Equation 14. In Table 24, exemplary values of $\varphi 5$ are listed for a random selection from the 749 stability fields.

Table 24: Exemplary values of $\varphi 5$ for a random selection from the 749 stability fields and corresponding weights

Stability field Combination of stability fields of Step 1 aggregations	$\varphi 5$		
	S5_1_1	S7_31_2	S8_31_1
	S1_1 / S2_1 / S3_1	S1_3 / S2_4 / S3_2	S1_4 / S2_4 / S3_2
Weight g_1	0.05	0.575	0.785
Weight g_2	0.18	0.905	0.905
Weight g_3	0.05	0.81	0.81
Weight g_4	0.38	0.8	0.8
Weight g_5	0.31	0.965	0.06
R22	0.829	0.679	0.510
R30	0.652	0.325	0.144
R32	0.627	0.813	0.238
R125	0.398	0.488	0.737
R134a	0.416	0.448	0.369
R143a	0.537	0.659	0.867
R152a	0.489	0.533	0.160
R1270	0.547	0.623	0.188
R290	0.347	0.539	0.195
R600a	0.374	0.282	0.209
R407C	0.422	0.506	0.152
R410A	0.533	0.699	0.156
E7200	0.512	0.223	0.144
R717	0.507	0.401	0.121
R744	0.310	0.965	0.060

To summarize the results of METEOR, the percentage of occupancy of a certain rank within those 749 stability fields was calculated for each refrigerant (Table 25). R22 and R143a have in 23 % and 21 %, respectively, of the cases rank 15. R30 is ranked in position 1 in 39 % of the selected stability fields. R22 is ranked to ca. 87 % within the five highest ranks, followed by R143a with about 85 %, and R32 with 71 %. R717 is to 88 % ranked within the five lowest ranks, followed by E7200 with 81 %, and R290 with about 74 %. R744 has in nearly 40 % of the selected stability fields the highest rank and in ca. 24 % the lowest rank; the ranks 2-14 achieve together 36 %.

Table 25: Percentage of occupancy of certain ranks of studied refrigerants; high rank (15) – great environmental impact, low rank (1) – low environmental impact

Rank Refrigerant	Rank occupancy [%]														
	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1
R22	23.4	6.4	30.3	15.5	10.9	9.7	0.8	2.4	0.5	0	0	0	0	0	0
R30	0	0.9	6.3	4.9	8.3	1.9	2.9	4.1	0.7	1.2	0.9	6.7	13.1	8.7	39.4
R32	3.5	31.2	8.0	10.4	18.3	4.1	1.7	4.7	2.3	7.2	2.5	0.3	4.0	1.7	0
R125	11.2	29.5	13.9	3.2	2.5	4.0	8.0	2.4	1.5	6.8	0.1	0.3	0.4	16.2	0
R134a	0	0	0	8.4	4.8	2.5	11.7	8.5	11.6	13.9	21.0	1.2	16.2	0	0.1
R143a	21.2	24.2	19.0	11.6	8.8	1.2	13.5	0.5	0	0	0	0	0	0	0
R152a	0	0	0	0	0	0	2.7	23.5	8.0	19.9	35.8	9.5	0.7	0	0
R1270	0	0	0.4	4.1	8.7	46.5	27.1	11.2	2.0	0	0	0	0	0	0
R290	0	0	2.5	6.8	9.5	4.7	9.3	13.4	30.8	8.1	4.5	4.5	0.4	5.2	0.1
R600a	0.9	2.1	4.8	6.5	2.8	2.7	1.6	1.7	1.3	1.6	5.5	15.6	22.0	11.1	19.6
R407C	0	0	0	0	0	1.7	7.2	16.6	25.6	25.6	6.1	12.1	3.5	1.5	0
R410A	0	0	8.5	21.6	22.6	17.9	8.8	6.9	5.5	1.2	4.9	1.9	0.1	0	0
E7200	0	0	0	0	0	0.5	1.5	0.9	6.9	9.2	1.2	10.8	12.3	39.9	16.7
R717	0	0	0	0.4	0.1	0.9	1.3	2.1	2.3	4.7	15.0	33.5	24.7	14.7	0.3
R744	39.8	5.6	6.3	6.4	2.7	1.6	1.7	0.9	0.9	0.5	2.4	3.6	2.7	1.1	23.8

The rank distribution for each refrigerant is displayed in Figure 31 overlaid with the Gaussian distribution curve. R1270, R717, R407C, R22, R143a, and R152a have a narrow distribution resulting in a clear peak. R744, R30, R32, and R125, however, have a rather flat curve caused by a more even rank distribution, or, in the case of R744, by an extreme contrary distribution pattern with one peak at rank 15 and another at rank 1.

From those results, R22, R143a, and R32 would not be recommended as replacement refrigerants for R134a, whereas R717, E7200, and R290 are likely to be used as future

substitutes. R744 is mainly divided into rank 15 and 1. This contrary distribution needs further investigation. It should not be disregarded because it is the refrigerant which has the second highest occupancy (~24 %) of rank 1 after R30 (~40 %).

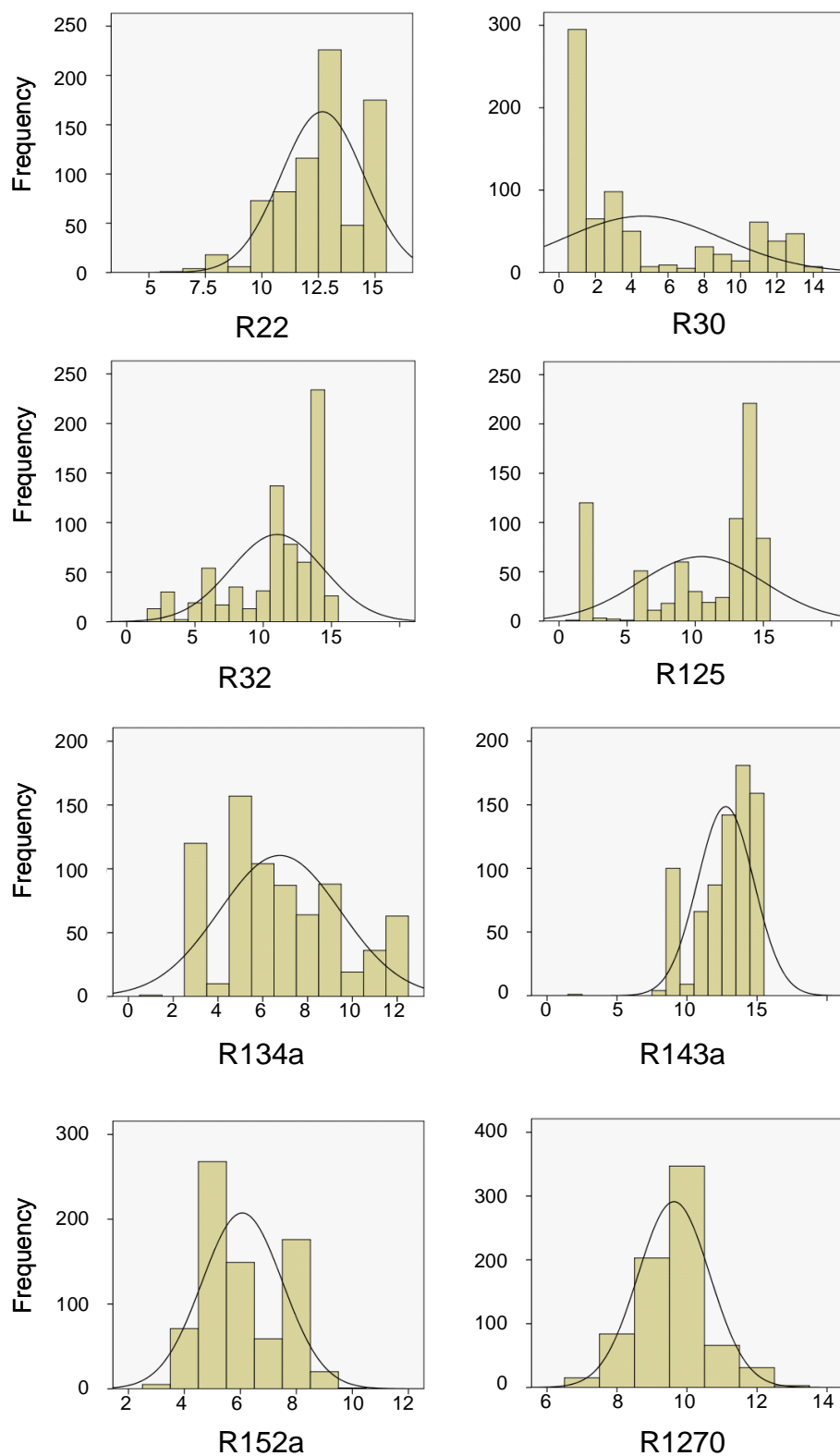
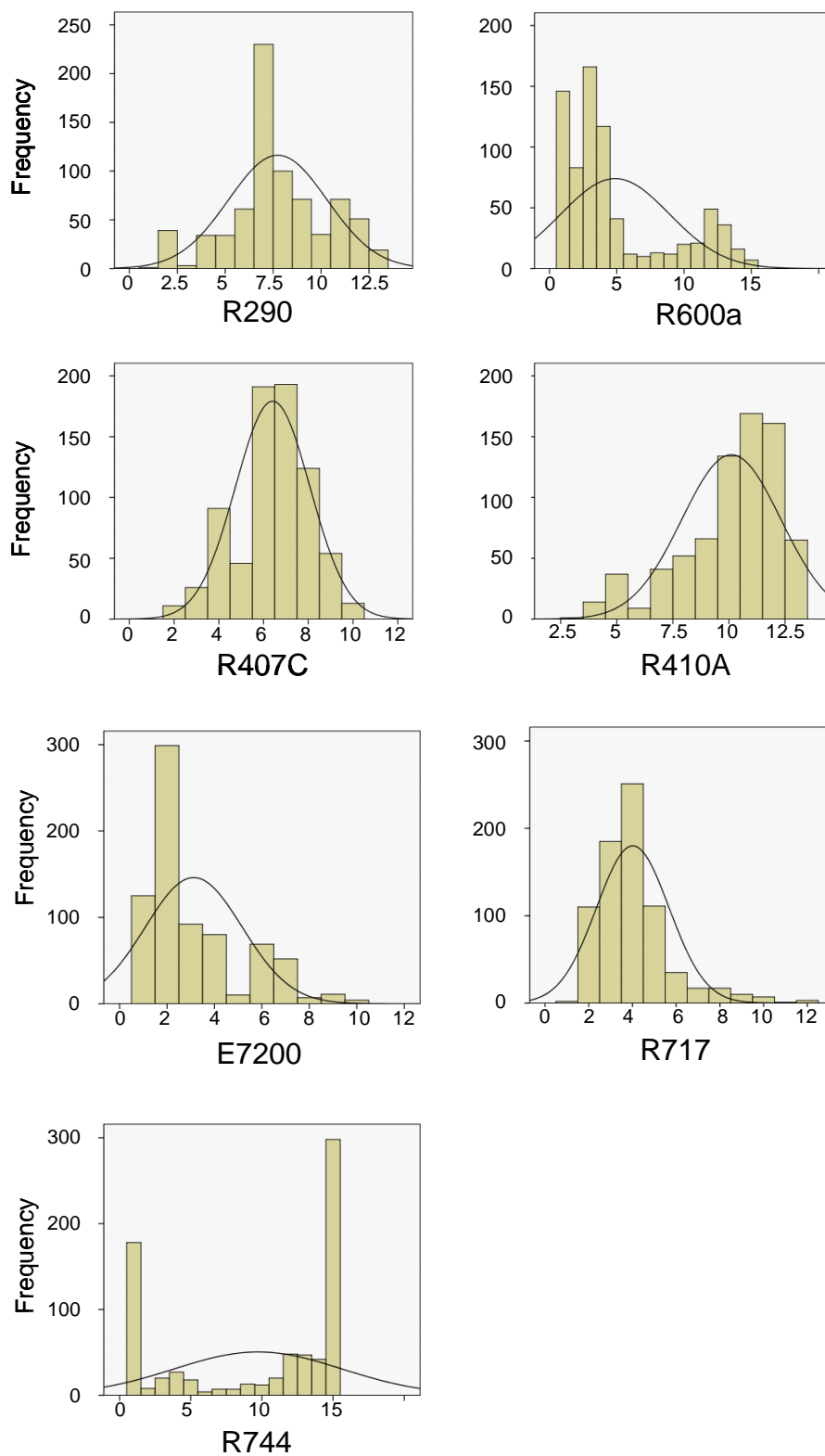


Figure 31: Rank distribution for each studied refrigerant



Cont. Figure 31: Rank distribution for each studied refrigerant

5 Discussion

5.1 Impact assessment

5.1.1 Simplifications made in the life cycle inventory

For lack of data, some simplifications and estimations were made in the life cycle inventory of this study. Thereby, the intention was to keep the simplifications for all refrigerants at the same level. Taking the change in refrigerant's enthalpy that occurs during compression is a main short coming of this study, as it does not really account for different efficiencies at varying temperature and humidity conditions and does not include different A/C system configurations. In the case of HFEs, no prototypes exist of A/C systems in passenger cars. Even for refrigerants which are presently used in A/C systems in cars let alone for prototypes, it is hard to find studies done under equal conditions. Differences in the scope of former LCA studies, in system configurations, or in outside conditions made comparable results impossible. Therefore, it was decided to use the change of enthalpy under the mentioned temperature and pressure conditions equally for all studied refrigerants as basis for the fuel consumption of A/C systems. Furthermore, the energy consumption of fans and pumps were neglected which certainly contribute to the overall energy consumption. The simplification made in this study was to assume that this contribution is equal for all refrigerants and can be neglected for comparison.

In the present study, only cooling processes were considered. Defrosting processes due to humid and cold climate conditions were ignored. But considering them would certainly increase the operation time and thus the energy consumption of A/C systems in cooler climate regions.

Inventory data for the production of HFEs was estimated from patents. Calculations on the chemical input from the yield mentioned in the patents and energy data from the production of R134a were used. Thus, the inventory data of HFEs production should be regarded as a first estimation in the exemplary LCA including new substances in the field of cooling and refrigeration. Furthermore, the refrigerant charge of A/C systems using HFEs was estimated. Based on a similarity analysis it was assumed to be equal to R134a systems.

The transportation of the refrigerants to the car manufacturer and of the finished car to the end-consumer was not included in this study. Furthermore, no inventory on the car itself was prepared, as it is assumed to be the same for all A/C systems and thus has no distinctive contribution to the overall environmental impact.

The production of the different A/C systems was omitted because no data could be gathered from industry by questionnaires. Only an average energy value was included in this inventory. The main focus of the study was on the refrigerants themselves. It was assumed that the technical configuration and material input does not vary much between the different systems. Due to the same reason, the dismantling and recycling of the A/C

system was not considered in detail. The main focus of the disposal phase was again set on the refrigerants. Here, another simplification was made. It was assumed that all refrigerants except R744 (CO₂) are burned under total combustion.

Another simplification was made regarding leakage rates of A/C systems, which were assumed to be independent of the refrigerant and vehicle age. However, some studies indicate this is not exactly true. Factors affecting the leakage rate are the pressure in the system, the type of the refrigerant, its viscosity, vehicle age, hours of vehicle and A/C operation and maintenance (Petitjean et al. 2000, Barbusse & Gagnepain 2003, Weissler 2004).

No specific damage or impact factors were available for e.g. the HFEs and some by-products during refrigerant production. In those cases, estimations or factors from other substances were taken. The influences of different estimations are discussed in Chapter 5.1.2. Replacing those simplifications by more specific data would improve the assessment done for the studied refrigerants.

5.1.2 Sensitivity analysis

Leakage rate

In the previous chapters, different scenarios were discussed. In order to determine the impact of different direct refrigerant emission scenarios on EI99 a sensitivity analysis was performed changing only this particular parameter. As expected, the direct emissions are of great relevance for refrigerants with high GWP₁₀₀ (E125, E134, E7000, E7100, E7200, R134a). In contrast, HCs, R30, and R744 show hardly any change in EI99 for different refrigerant leakage scenarios (Figure 32). Hence, the tightness of the system and its optimisation might influence the decision for the R134a substitute, but the probability of a complete leakage occurring and the corresponding environmental impact should be considered.

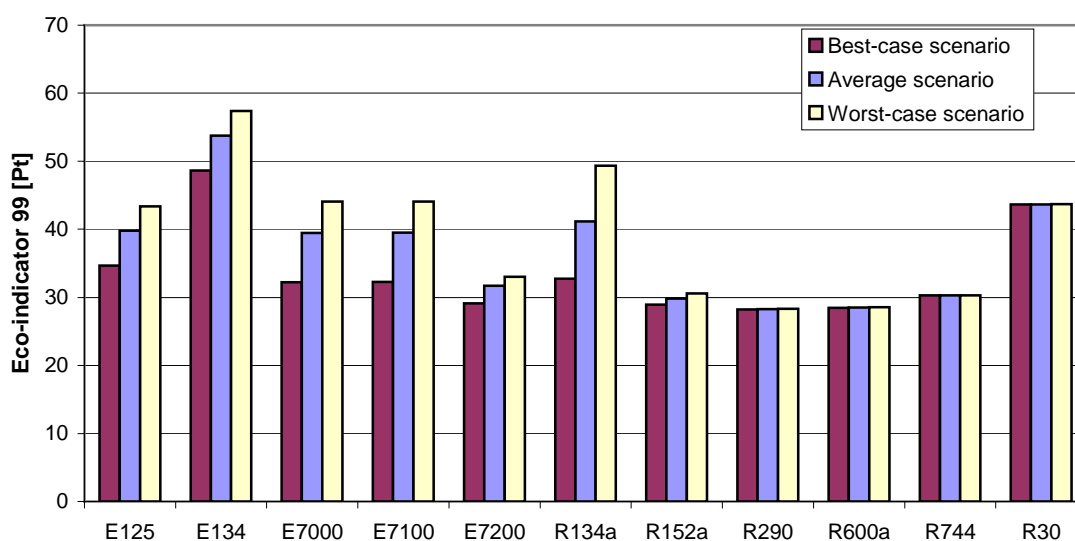


Figure 32: Sensitivity analysis of different leakage rates for EI99 calculation

The contribution of the annual operation time is important (Figure 33). EI99 for R30 under worst-case scenario is almost double that of the average scenario. With regard to the two mentioned scenarios, E134 and R744 which have rather small energy efficiencies show a similar pattern with an increase of 43 and 38 %, respectively. The other refrigerants show an increase in EI99 of 12 – 30 %. The opposite phenomenon is observed when comparing EI99 values of the average and the best-case scenario. EI99 of R30 is reduced by 44 %, a value smaller than those of most other refrigerants. Operation time effects the EI99 values of E134 and R744 more than those of the other refrigerants, except R30. Thus, the decision for the best substitute depends also on the climate region and the climate conditions where the A/C system is going to be used.

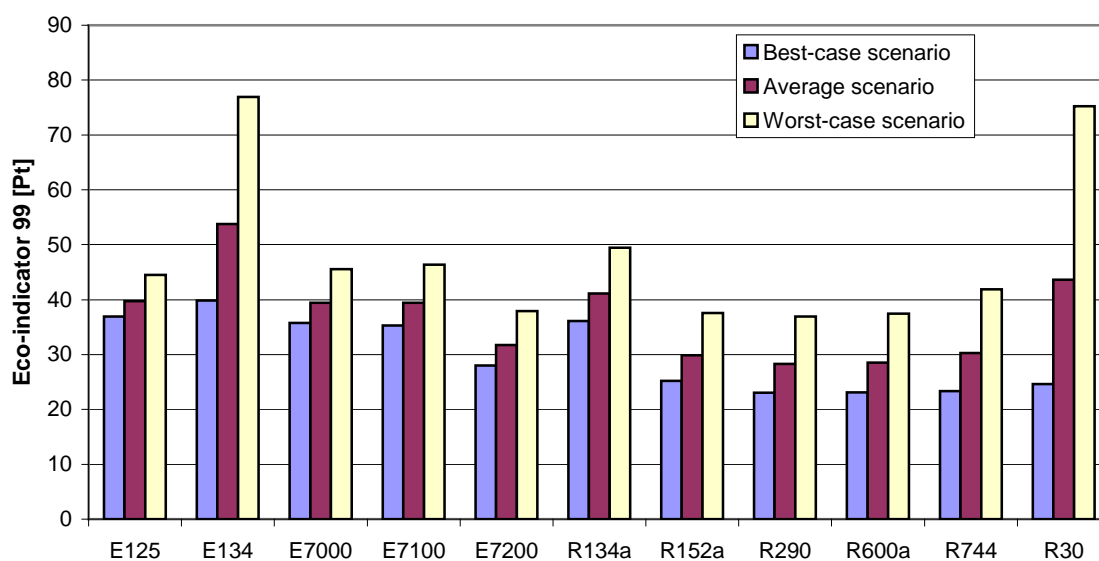


Figure 33: Sensitivity analysis of different operation times for EI99 calculation

EI99 damage factors

For some substances that are emitted to environmental compartments during the life cycle of certain refrigerants no damage factors are listed in the EI99 document. Therefore, a general decision had to be made whether to omit these emissions or to take damage factors from other substances as first estimation. In this study, the latter option was preferred.

For example hexafluoropivaloyl acid is not included in the damage factor list. Hence, an estimation was made. The influence of the estimated factor was investigated in a sensitivity analysis. Calculating EI99 for the average scenario, first the damage factor “C_xH_y halogenated” ($3.5 \cdot 10^{-7}$ DALYs/kg) was taken, second the damage factor “Propanoic acid” ($3.23 \cdot 10^{-7}$ DALYs/kg), and for the third calculation emissions of hexafluoropivaloyl acid were omitted. The difference of EI99 using these particular damage factors was less than 0.002 % and can thus be neglected.

For the hydrocarbons arising during the life cycle of A/C systems, the contribution of omitting them from the calculation or using the damage factor of “Alkanes” is for R30 about 0.1 % and for the other refrigerants between 0.02 – 0.06 %. Omitting the emissions of R151a during R152a production will result in a decrease of its EI99 of 0.6 %. This is rather small compared with the change of EI99 of 17 – 22 % when omitting the emissions of fluorinated ethers during production of E125 and E134.

The influence of taking damage factors of other substances as estimations or to omit emissions is obvious. For some substances it might be negligible, for others the contribution to EI99 is significant. It has to be carefully stated which option was chosen.

CML02 impact factors

The CML02 assessment method has the same problem with limited impact factor lists as EI99. For some substances (e.g. R113, R150, R151a, hexafluoropropane) substitute impact factors were taken from other compounds as mentioned in Chapter 3.3.1, for other substances impact factors were estimated. For example HFEs are thought to contribute to POCP but these substances are not included in the CML02 list. For this study, a first impact factor of 0.1 kg ethylene eq./kg was assumed. The contribution to the impact category POCP under average scenario is small (E125: 0.12 %, E134: 0.04 %). Increasing the impact factor to 0.5 kg ethylene eq./kg, the contribution to that impact category rises to 0.6 % for E125 and to 0.2 % for E134.

Damage and impact factors should not be omitted rather an estimation should be made. Even if each single substance is contributing only a little to the overall environmental impact indicator, neglecting all which are not listed in the factor lists might change the assessment significantly for some refrigerants, especially when assessing new substances it seems justified to use rough estimations rather than omitting occurring emissions.

5.1.3 TEWI

Considering the TEWI-components separately, rankings of $TEWI_{direct}$ and $TEWI_{indirect}$ show almost reverse order for most refrigerants (Figure 34). In the $TEWI_{direct}$ ranking, E125 is the most problematic refrigerant, followed by E134, R134a, E7000, E7100, R152a, E7200, R30, R600a, and R290. R744 is the least problematic refrigerant. This order is mainly influenced by the GWPs of the refrigerants. Thus, R290 and R600a are at the same level because they are both assigned a GWP_{100} of 3 kg CO₂/kg refrigerant. When ranking $TEWI_{indirect}$, R30 becomes the most problematic refrigerant followed by E134, R744, R600a, R290, R134a, R152a, E7100, E7200, and E7000. The refrigerant E125 is the least problematic refrigerant regarding indirect emissions from energy production. For both TEWI-components, the ranking does not change, when the different emission and operation scenarios are applied. Emission values are more or less strongly affected but the ranking stays almost the same for all scenarios.

For example, for R134a (Figure 35) a change of refrigerant loss during operation phase (L) results in a considerable change of $TEWI_{direct}$, whereas the direct emissions during servicing/refilling and production & disposal do influence $TEWI_{direct}$ less strongly. Calculating $TEWI_{indirect}$, especially the parameter annual operation time (S_L) is of importance (Figure 36). Hence, S_L and L exert the greatest effect on the calculation of the TEWI and are further discussed in this work. Nevertheless, direct emissions during production, servicing/recharge, and disposal should be minimized in order to reduce the impact of refrigerants on climate change and global warming.

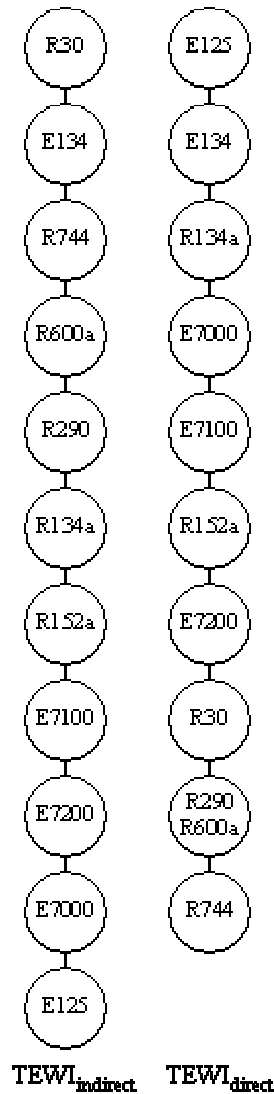


Figure 34: Separate ranking of TEWI components

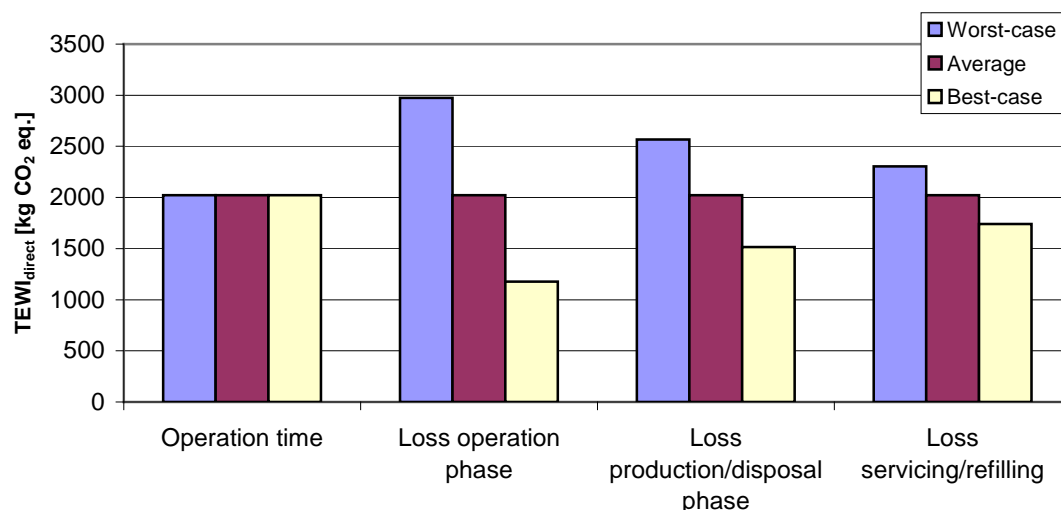


Figure 35: Change of $TEWI_{direct}$ (R134a) under different scenarios

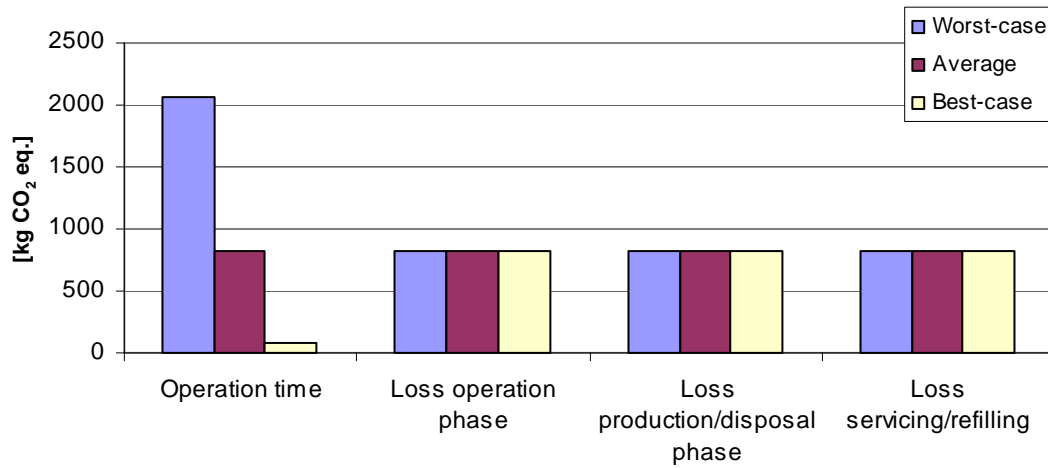


Figure 36: Change of $TEWI_{indirect}$ (R134a) under different scenarios

In Figure 37, the refrigerants are ranked according to their TEWI values. The uppermost refrigerant is the environmentally most problematic one. The lowest one is the least environmentally problematic of the refrigerants considered. For average L and S_L scenarios, the order of the refrigerants is as follows (Figure 37, linear order in the middle): E125 is the most problematic one, E134 is the second problematic one, followed by R30, R134a, E7100, E7000, R744, R600a, R152a, and R290 with E7200 being the least environmentally problematic one. An increase in S_L of the A/C system results in a change of this ranking: R600a becomes more problematic than E7000, R744 becomes more problematic than E7000 and E7100. R152a becomes less problematic than R290. E7200 remains the least environmentally problematic of those refrigerants. The increased operation time of the system causes extra energy consumption that outweighs the effect of GWP. A reduction of the operating hours and consequently of extra energy consumption, changes the order of the average scenario

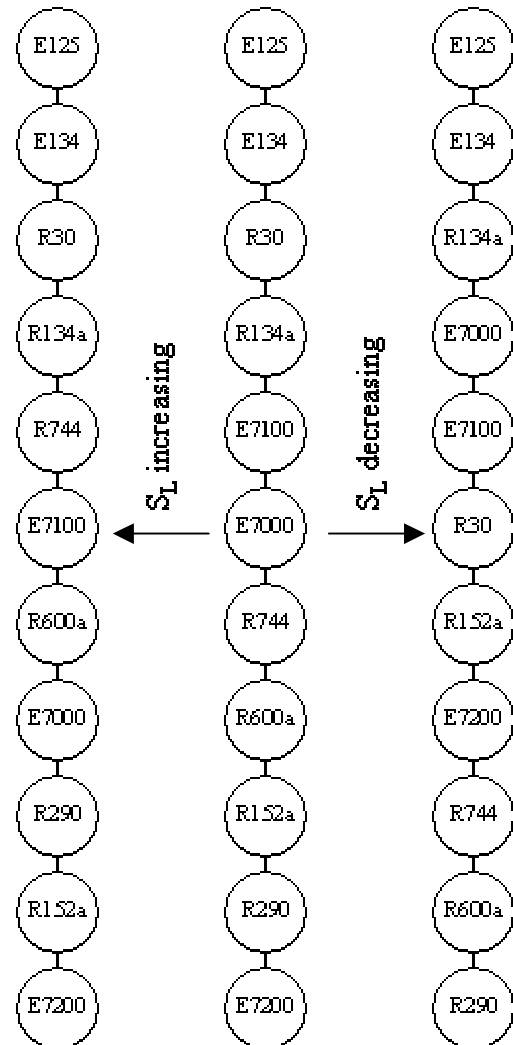


Figure 37: Changes in refrigerant ranking due to different operating times S_L under average European climate conditions

likewise. R134a, E7000, and E7100 become more problematic than R30. Due to its smaller GWP, R744 becomes less problematic than R600a, E7200, and R152a. R290 and R600a become the least environmentally problematic refrigerants.

S_L is of great influence to the overall global warming impact of a refrigerant. TEWI values increase up to 26-times (Figure 38) from best-case to worst-case scenario. Assuming a linear slope, R744 is superior to R134a under an environmental point of view up to an operation time of ca. 560 h/yr. At an operation time of 260 h/yr, both refrigerants have an impact that is 1.3 to 2.5-times greater than that of R290, R600a, R152a, E7000, E7100, and E7200. R744 is environmentally superior to E7000 until an operation time of ca. 120 h/yr. R30 is superior to E7000 until an operation time of ca. 30 h and superior to R134a until 90 h/yr. E125 and E134 have TEWI values exceeding those of the other refrigerants by factors up to 250. After an annual operation time of 36 h, E7200 is environmentally superior to the other refrigerants regarded in this study.

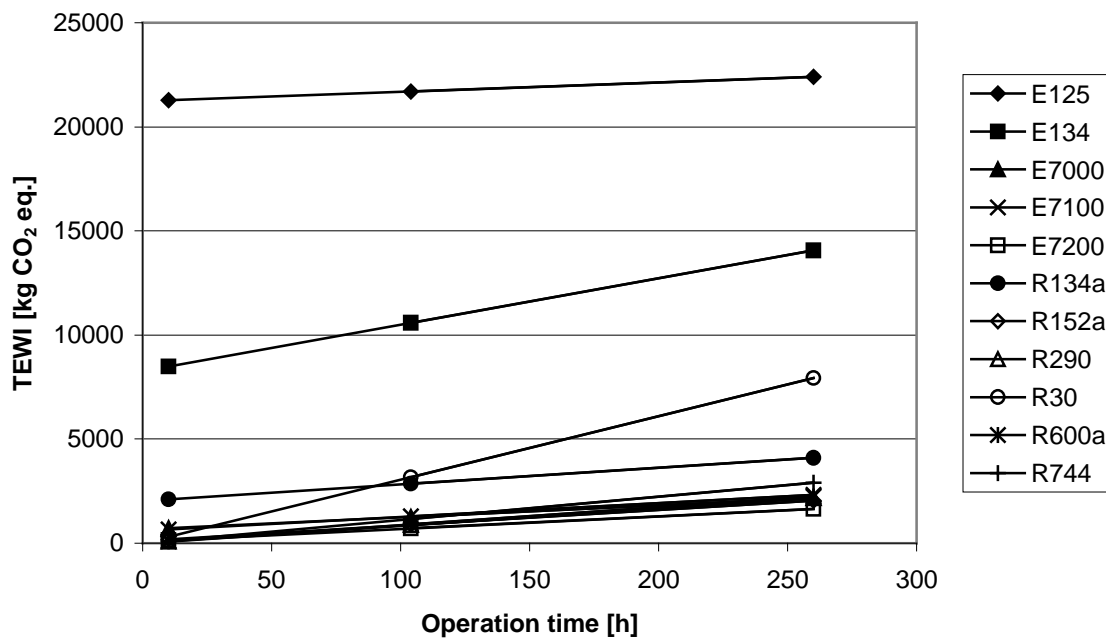


Figure 38: Influence of operation time on TEWI

Starting from the average ranking of the refrigerants (Figure 39), linear order in the middle), an increase in direct refrigerant emissions during the operating phase of the A/C system causes changes in the refrigerant ranking. E125 stays the most environmentally of the refrigerants in this study, followed by E134. But with an increasing leakage rate R134a becomes more problematic than R30. E7000 has a greater environmental impact than E7100, and R152a is ranked higher than R600a. E7200 stays the least problematic refrigerant. The CO₂ eq. emissions from the energy consumption are partly outweighed by those caused by direct refrigerant emissions. Likewise, a reduction of the annual leakage rate compared to the average scenario results in changes in the ranking: R290 becomes more problematic than R152a. E7000 and E7100 become less problematic than R744. When the annual leakage rate is above 14 % of system charge, R134a has a TEWI almost twice as high as the other refrigerants, except E125 and E134 (Figure 40).

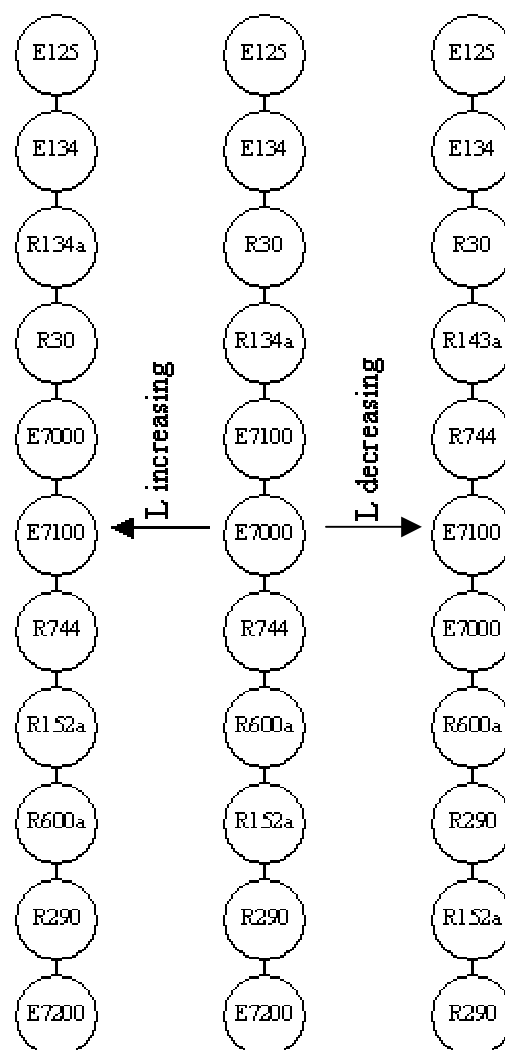


Figure 39: Changes in refrigerant ranking due to different leakage rates during operation phase under average European climate conditions

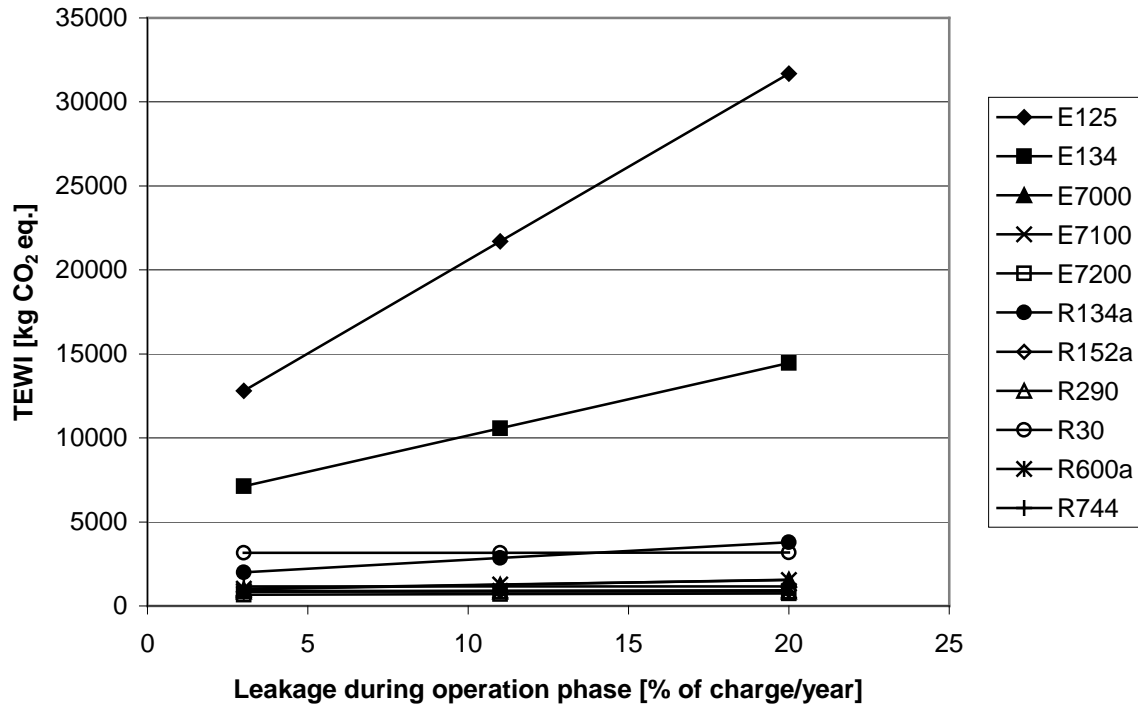


Figure 40: Influence of annual leakage rate during operation phase on TEWI

To summarize the results, E125 is under average scenario the environmentally most problematic refrigerant of those considered in this study. The parameters that have the highest impact on the refrigerant ranking are S_L and L . Considering longer operation times due to a hotter climate, the higher energy consumption of R744-systems outweighs the effect of its smaller GWP_{100} . In cooler climates with consequently shorter operating times, R744 becomes even less environmentally problematic than R152a. E7200, R152a and R290 can be considered as less problematic refrigerants under the scenarios of this study.

5.1.4 Comparison of additional fuel consumption

The additional fuel consumption is the major aspect of the life cycle of an A/C system. In order to confirm the soundness of the simplifications made, it is important to compare the additional fuel consumption that arise during the present LCA with literature values from exhaustive studies. Additional fuel consumptions calculated in this study are listed in Table 26.

Table 26: Additional fuel consumption of studied refrigerant A/C systems under different scenarios

	Refrigerant	Additional fuel consumption [L per year]	Additional fuel consumption [L per 100km]
Average scenario	E125	33.61	0.33
	E134	113.00	1.27
	E7000	41.10	0.41
	E7100	42.66	0.43
	E7200	41.65	0.41
	R134a	48.54	0.51
	R152a	47.97	0.49
	R290	51.89	0.54
	R600a	53.30	0.55
	R744	64.31	0.69
	R30	148.62	1.70
Best-case scenario	E125	15.60	0.32
	E134	24.88	1.23
	E7000	17.97	0.39
	E7100	16.47	0.42
	E7200	18.02	0.40
	R134a	17.03	0.49
	R152a	18.63	0.47
	R290	19.00	0.52
	R600a	19.14	0.53
	R744	20.20	0.66
	R30	28.30	1.64
Worst-case scenario	E125	63.52	0.33
	E134	259.24	1.27
	E7000	79.50	0.41
	E7100	86.12	0.43
	E7200	80.86	0.41
	R134a	100.82	0.51
	R152a	96.66	0.49
	R290	106.46	0.54
	R600a	110.00	0.55
	R744	137.51	0.69
	R30	348.29	1.70

The ADAC (1998) found out that A/C systems cause an extra consumption of 0.7-1.6 L/100 km under extra-urban driving conditions and 3.3-6.2 L/100 km under urban driving conditions. Values of the present study are in the range of the extra-urban driving conditions of the ADAC-study. Hill & Papasavva (2005) give approximate values for R744-, R134a-, and R152a-systems of 66 L/year, 63 L/year, and 66 L/year, respectively, under climate conditions of Frankfurt. However, for climate conditions of Phoenix Hill & Papasavva (2005) state fuel consumptions that exceed the worst-case values of the present study by factor 2-3. Fischer & Sand (1997) confirm the increase of the fuel consumption of A/C systems by the factor 2 when changing from German to Spanish climate. However, their values are about half of the values estimated in this study. Values of a study from Volkswagen are in the range of 0.4-to1.5 L/100 km (BUWAL 2002) and are in good agreement with the values in Table 26. Overall, the fuel consumptions calculated in the present study can be seen as good approximations of actually occurring ones.

5.1.5 Contribution of direct refrigerant emissions to conventional CO₂ emissions

Under average scenario, refrigerant emissions from A/C systems per operating year amount to 109 g per year for HFEs and R134a, 74 g for R152a and R30, 44 g for R290 and R600a, and 68 g for R744. Considering the specific GWP₁₀₀ of each refrigerant and the annual travel distance of 16 000 km, the amount of CO₂ eq. due to direct refrigerant emissions for R134a is about 10 g/km, for E7000 3 g/km, for E7200 0.4 g/km, for R152a 0.6 g/km, for HCs and R744 less than 0.01 g/km. The values for R134a are in agreement with literature values (Barbusse & Gagnepain 2003). Therefore, it is assumed that the calculated values for the other refrigerants resemble also realistic values.

In the worst-case scenario, the contribution to the car's CO₂ eq. emission increases to 18 g/km for R134a, 5.9 g/km for E7000, 0.8 g/km for E7200, and 1 g/km for R152a. E125 and E134 have 11 to 4-times, respectively, higher CO₂ eq. emissions per km than R134a. R744 is still adding less than 0.01 g/km to the CO₂ eq. emissions by direct refrigerant emissions. Therefore, the contribution is especially for E125, E134, E7000 and R134a not insignificant in relation to the average conventional emissions of new vehicles (120 g/km).

5.2 Fate modelling

5.2.1 PFCA

The concentrations of PFCAs in water due to the annual direct refrigerant emissions (E7000, E7100, E7200) from the A/C system of a passenger car are about the factor 10⁷ to 10⁹ smaller than the precautionary limit of 0.1 µg/L of the Federal Environment Agency for partly or non-assessable substances in drinking water (UBA 2003). The influence of one car is therefore negligible. But for the environmental impact not one

single car is of relevance but the sum of them. Therefore, a projection of the direct refrigerant emissions and their corresponding degradation products were done including all passenger cars that were registered in Germany in 2005 (Table 61 to Table 68).

Assuming that all 46 million German passenger cars (Destatis 2006a) are equipped with A/C systems using E7000, E7100, or E7200, the concentration of the degradation products in water will amount to 0.1 – 1 µg/L. That means even under the best-case scenario the above mentioned precautionary limit will be reached and under worst-case scenario exceeded. However, the limit for taking measures of the Federal Environment Agency of 5 µg/L for drinking water (UBA 2006) is not even reached under worst-case scenario. The calculated concentrations of PFCAs in surface water within this study, are in the range of PFCAs that are already measured in surface waters in Germany (Skutlarek et al. 2006). As PFCAs are persistent environmental pollutants and as the contribution of E7000, E7100, or E7200, used in A/C systems in passenger cars for one year would result in concentrations equivalent to all other sources together, those three refrigerants should not be further considered as substitutes of R134a in A/C systems in passenger cars which have relatively high direct emission rates.

5.2.2 TFA

Concentrations of TFA measured in river waters in Germany are between 0.04 and 0.28 µg/L (Klein 1997, Christoph 2002). In German lakes, TFA concentrations of 0.07 µg/L were measured (Christoph 2002). The Atlantic Ocean has TFA concentrations of 0.2 µg/L over the complete water column (Christoph 2002). TFA from direct emissions of R134a during one year operation of A/C systems, assuming that all German cars are equipped with R134a systems, will reach concentrations in German surface waters of 4.2 – 50 µg/L under best-case and worst-case scenario, respectively. This exceeds the present TFA concentration in river waters by factors 15 – 1250. Thus, considering R134a as the solely refrigerant in A/C in passenger cars and the increasing number of cars equipped with A/C systems, TFA concentrations in surface waters due to degradation of R134a will increase significantly.

In rain, TFA concentrations between 0.04 and 0.2 µg/L with an average value of 0.08 µg/L were measured in Germany (Klein 1997, Christoph 2002). In this study, concentrations of TFA in raining clouds reach 4.7 – 22.2 µg/L, assuming TFA as degradation product of directly emitted R134a during one year of operation. These concentrations are 24 to 555-times higher than the presently occurring TFA concentrations in rain water. Taking the average annual precipitation of 800 L/m², the amount of TFA which will be deposited over Germany will amount to 1 316 – 6 216 t TFA per year.

Although the acute toxicity of TFA on aquatic organisms is relatively low, the EC₅₀ for bacteria (*Pseudomonias putida*) is > 1000 mg/L, for algae (*Microcystis aeruginos*) 250 mg/L, and for protozoa (*Uronema pardueri*) 435 mg/L (AFEAS 1994), the long-term environmental effects are not exactly known which can arise from continuously

increasing TFA concentration. Thus, the phase-out of R134a is justified not only from the global warming point of view but also from an ecotoxicological perspective.

5.2.3 Acidity

Globally, the main contributors to the acidity of rain are nitric and sulphuric acids, arising from natural and anthropogenic sources. They amount to an acidity of about 10^{13} mol H^+ /year (Sidebottom & Franklin 1996). According to Franklin (1993), the amount of acidity produced per mol R134a is 3.8 mol H^+ (2.8 mol HF, 0.4 mol TFA, and 0.6 mol formic acid). At an average annual amount of 2 000 t R134a from all German A/C systems in passenger cars, the amount of acidity that could be incorporated into rainwater would be around $5.5 \cdot 10^7$ mol H^+ . The natural occurring acidity in rainwater is, thus, about the factor $1.8 \cdot 10^5$ greater than the amount that might arise in average from R134a in that particular application.

For calculating the contribution to the acidity from degradation of R152a, it is assumed that 1 mol CF_2O is degraded to 2 mol HF. Under an average annual emission scenario of R152a, 3 140 t of CF_2O are formed considering all German cars equipped with an A/C system using R152a. This would result in $9.5 \cdot 10^7$ mol H^+ possibly incorporated into rainwater.

R30 is degraded to HCl which also has an acidifying effect. From an average annual emission of A/C systems of all German cars, 3 411 t of R30 are emitted to the atmosphere resulting in $8.02 \cdot 10^7$ mol H^+ .

Thus, R30 and R152a would contribute to the acidity of rainwater to the same amount as R134a. Therefore, the contribution of degradation products from R134a, R152a, and R30 from A/C systems to “acid rain” can be seen with less than 0.001 % of the overall acidity from all other sources as negligible.

In the same manner the contributions from degradation products of E125 and E134 were calculated, assuming that 100 % of the HFEs is degraded to CF_2O . E125 form $1.2 \cdot 10^8$ mol H^+ and E134 form $1.7 \cdot 10^8$ mol H^+ . E125 and E134 contribute to the acidity of rainwater about 10-times more than R134a and R152a. Nevertheless, compared with the contribution of the overall acidity from other natural and anthropogenic sources their impact is negligible.

5.2.4 Chloride and fluoride in rainwater

Natural occurring atmospheric fluxes of chloride amount to $0.6 - 1.0 \cdot 10^{16}$ g/year (Sidebottom & Franklin 1996). Compared with those natural background fluxes, the atmospheric chloride production from R30, $2.9 \cdot 10^9$ g/year under average scenario, is insignificant.

Fluoride production from E125, E134, R134a, and R152a that is for the average

scenario in the range of 10^9 g/year is negligible compared with the estimated total atmospheric fluoride flux of $1.8 - 8.0 \cdot 10^{12}$ g/year (Sidebottom & Franklin 1996).

5.3 Contribution of properties to rank distribution based on METEOR

For evaluating the contribution of each of the six refrigerant intrinsic properties to the rank distribution, from the 749 linear orders the ones with a very low and with a very high weight on one of the six properties, respectively, were considered (Table 69). In fact, the idea was to look at the case where one property has a weight g equal zero and is therefore not further included in the calculations. But because of the fact that for the study only the most robust stability fields were further considered and because of the fact that within one stability field the linear order of refrigerants is not changing, the actual weight of the properties in the aggregation of ϕ_1 , ϕ_2 , and ϕ_3 was never equal zero. In practice that means that the lowest weight for c_{ow} was 0.05, for TWA 0.19, for GWP 0.18, for ODP 0.1, for t_c 0.05, and for C_p 0.03.

For each refrigerant, the set of linear orders with one low weighted property was compared with the complete set of linear orders. In Table 27 the average rank of those sets are listed. In Figure 41, the different distribution patterns of the above mentioned specific weighted sets of stability fields are exemplarily displayed for four refrigerants (R744, R290, R1270, R30).

Table 27: Average rank of refrigerants based on different sets of stability fields

Selection of weighted sets	All	Low weight on					
		t_c	C_p	GWP	ODP	TWA	c_{ow}
Number of stability fields	749	112	243	113	327	490	239
R22	13	13	12	14	11	12	13
R30	5	12	2	4	2	4	5
R32	11	13	9	11	9	10	13
R125	10	5	14	10	14	11	9
R134a	7	5	8	6	9	7	6
R143a	13	11	14	12	14	13	12
R152a	6	7	5	6	5	6	7
R1270	10	10	9	10	9	10	9
R290	8	7	8	8	9	9	5
R600a	5	3	7	5	7	6	3
R407C	6	4	8	7	8	6	7
R410A	10	10	10	11	10	10	11
E7200	3	6	3	3	3	3	3
R717	4	5	4	4	3	3	5
R744	10	11	7	10	7	9	10

The two main parameters influencing the rank distribution of R30 are t_c and C_p (Figure 41). A low weight on t_c is shifting the average rank from 5 up to 12, whereas a low weight on C_p is shifting the average rank to rank 2. Similar observations were made for refrigerants R32, R152a, E7200, and R744. For refrigerants R125, R134a, R143a, R600a, and R407C, a low weight on t_c is changing the average rank in the direction of lower ranks. For example, the average rank of R125 is about 10. With a low weight on t_c it is ca. 5.

Because of the relatively high *ODP* of R22 compared to the other refrigerants within the METEOR study, a low weight on *ODP* and *GWP*, respectively, is mainly influencing the rank distribution of R22. A low weight on *ODP* is decreasing the average rank of about one rank, whereas a low weight in *GWP* is resulting in an increase the average rank of about one rank.

R290 and R717 are the two refrigerants whose rank distribution is influenced by different weighting of *TWA* and c_{ow} . A low weight on *TWA* is resulting in an increase the average rank of R290, while a low weight on c_{ow} is increasing the average rank of R717.

Refrigerants that show no significant dominance of certain parameters influencing the rank distribution are R1270 (Figure 41) and R410A.

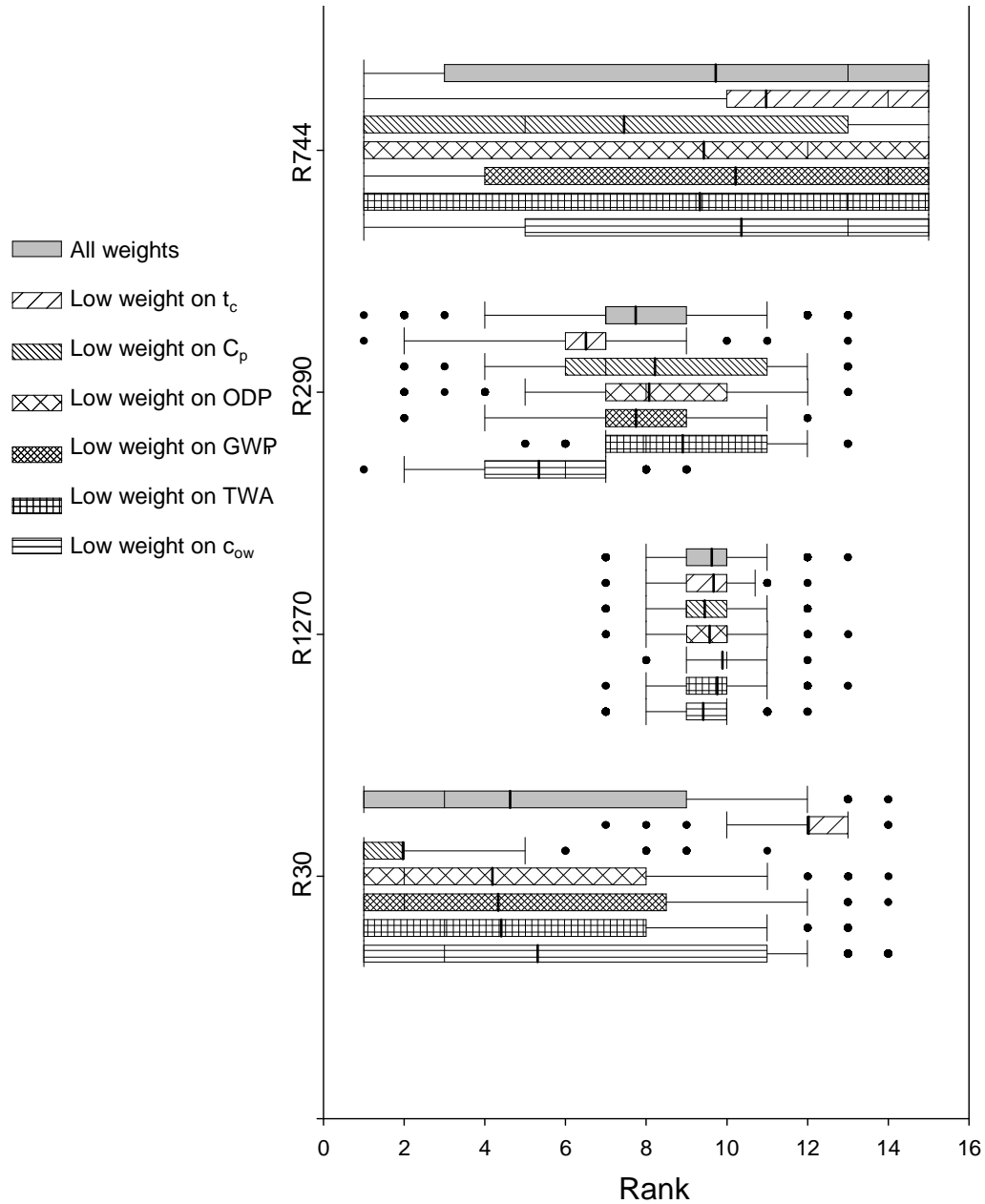


Figure 41: Rank distribution pattern of specific weighted sets of stability fields, exemplary for four refrigerants; left whisker – 10th percentile, right whisker – 90th percentile, box – 25th to 75th percentile, thick line – mean, thin line – median, points – outliers

Overall, two third of the refrigerants included in the METEOR study show a modification in their rank distribution pattern when putting an extreme low or high weight on the thermodynamic properties t_c and C_p . Moreover, because of increasing tightness of refrigeration facilities and recovery rates of refrigerants, environmental properties of refrigerants contribute less to the overall environmental impact of a refrigeration system. Thus, it might be of interest in further studies to include additional properties that are directly related to the performance of refrigerants in refrigeration systems and reduce the number of environmental properties in the METEOR calculation.

5.4 Comparison of EI99, CML02, and TEWI results

The different approaches of the three assessment methods make it difficult to perform a comparison between them based on their scores. Therefore, the results of each assessment was converted to ranks the refrigerants occupy. Exemplary, E134 which has the highest value in the impact category ADP in the CML02 method is given the rank 11 as 11 refrigerants were assessed, R152a is given the rank 1 as it has the lowest value in that category. Likewise, ranks are given to all refrigerants within the three methods. Finally, the ranks of each refrigerant of the different assessment methods will serve as basis for comparison. Thus, each impact category of CML02 resulted in a specific ranking of the refrigerants, as did EI99 and TEWI (Table 28). Based on the ten indicators ADP, PE, SOD, GWP, AP, EP, HTP, POCP, FAETP, and TETP from the impact categories of CML02 an average ranking (AV) was calculated.

Table 28: Ranks of the impact categories of CML02 and its average ranking, ranks of EI99 and TEWI method for the average life cycle scenario; high rank (11) – great environmental impact, low rank (1) – small environmental impact

Refrigerant	CML02											EI99	TEWI
	ADP	PE	CC	SOD	AP	EP	POCP	HTP	FAETP	TETP	AV		
E125	5	8.5	11	5	1	1	1	1	9	9	5.2	10	11
E134	11	8.5	10	5	10	10	10	10	6	6	8.7	11	10
E7000	6	8.5	7	5	2	2	2	2	7.5	7.5	5	7	6
E7100	8	8.5	6	5	4	4	4	4	7.5	7.5	5.9	8	7
E7200	7	8.5	5	5	3	3	3	3	5	5	4.8	5	1
R134a	9	8.5	9	11	6	6	6	6	11	11	8.4	9	8
R152a	1	5	1	10	5	5	5	5	10	10	5.7	4	3
R290	2	1.5	2	5	7	7	7	7	2	2	4.3	1	2
R600a	3	1.5	3	5	8	8	8	8	2	2	4.9	2	4
R744	4	3	4	5	9	9	9	9	2	2	5.6	3	5
R30	10	4	8	5	11	11	11	11	4	4	7.9	6	9

ADP – Depletion of abiotic resources (excluding primary energy); PE – Demand of non-renewable primary energy; CC – Climate change; SOD – Stratospheric ozone depletion; AP – Acidification; EP – Eutrophication; POCP – Photo-oxidant formation; HTP – Human toxicity; FAETP – Fresh water aquatic toxicity; TETP – Terrestrial ecotoxicity; AV – Average ranking of the 10 impact categories of CML02; EI99 – Eco-indicator 99; TEWI – Total equivalent warming impact

A Spearman correlation analysis was performed (Lyerly 1952, Kendall 1975). It showed that the AV of CML02 correlates well with the ranking of EI99 (correlation coefficient $\rho = 0.673$, at $\alpha = 0.05$) and with the ranking of TEWI ($\rho = 0.7$, at $\alpha = 0.05$). EI99 and TEWI are significantly correlated with $\rho = 0.818$ (at $\alpha = 0.01$) (Table 29).

Table 29: Spearman's rank correlation coefficient ρ

	AV	EI99	TEWI
AV	1	0.67(*)	0.7 (*)
EI99		1	0.82(**)
TEWI			1

* Correlation is significant at $\alpha = 0.05$ (two-sided)

** Correlation is significant at $\alpha = 0.01$ (two-sided)

The ranking due to AV (CML02) can be compared with the rankings resulting from EI99 and TEWI methods, respectively, applying methods of partial order theory using the software *WHASSE*. Thereby, a ranking of the

eleven refrigerants is set up without a numerical combination of these three indicators.

Using the rankings of AV, EI99, and TEWI as parameters the Hasse diagram in Figure 42 can be drawn. It shows that each method ranked E134 higher than the other refrigerants except E125. Furthermore, R290 is ranked lower than R152a, E7100, R134a, R600a, R744, R30, and E134 by all studied assessment methods. The HFEs of the 7000-series are all ranked lower than R134a. R744 has in all three assessment methods an environmental impact which is lower than that of R134a, E7100, R30, and E134, but R744 cannot be compared with R152a, E7000, E125, and E7200. R744 is ranked higher than R600a and R290. According to this, the best substitutes for R134a would be R290 and E7200, followed by R600a, R744, R152a, and E7000.

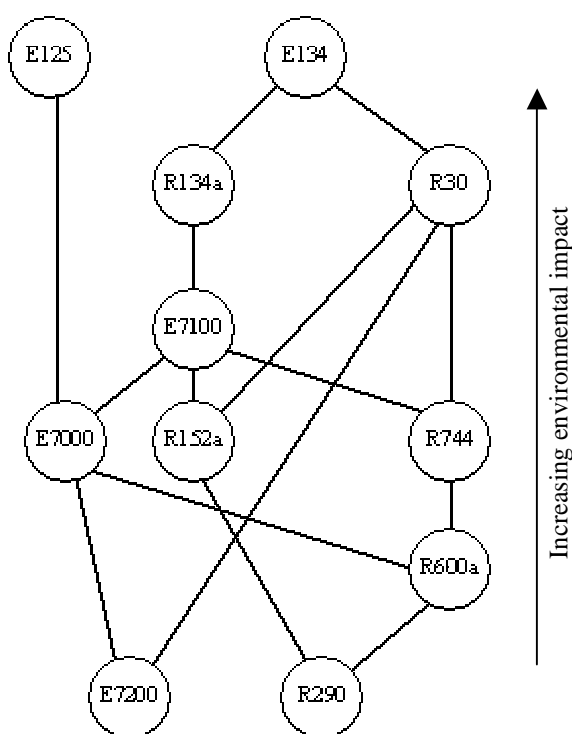


Figure 42: Hasse diagram using ranks derived from EI99, TEWI, and AV (average CML02) as parameters

5.5 Comparison of present LCA results with those of literature

The critical point of comparing the results from different LCA of A/C in passenger cars lies in the different scope definitions and the setting of frame conditions. In Chapter 5.1, it was shown how strong the results of LCA might be influenced by changing some parameters either of the scope of the LCA or the calculation factors. Therefore, it is not practicable to compare real values of different studies. Even by comparing relative orders or environmental superiority of refrigerants within one study, a faultless answer is not easy to give. In this chapter, it is tried to find common tendencies between different studies on A/C systems on cars and compare them with the results of the LCA done in

this work. No LCA has been done so far including HFEs in passenger cars. Therefore, it will be checked how good the results of the present study are compared with others regarding the commonly as substitutes proposed refrigerants and then transfer it on the ranking of HFEs.

The TEWI analysis from Sand et al. (1997) shows that the environmental impact of R134a system under European climate and driving conditions is higher than that of R290 and R744. The performance of R290 is better than the baseline R744 system. This matches the LCA results of the present study.

Ghodbane (1999) investigated the performance of R152a and hydrocarbon refrigerants in mobile A/C systems comparing it with R134a. He showed that R152a is performing better than R134a, even R290 showed marginal better performance than a R134a baseline system. R600a, however, was not seen as suitable for A/C in cars because of its low COP and high compressor displacement requirement. As those aspects are not included in the present LCA, the derived results regarding R600a are different. However, the superiority of R290 and R152a over R134a could be confirmed.

The TEWI analysis for different mobile A/C systems from Petitjean et al. (2000) used experimental data as well as simulation results. It showed very similar indirect contributions from enhanced R134a and R744 systems. Giving that the direct contributions of R744 are reasonably lower, R744 has a lower environmental impact than R134a. That is in agreement with the results of the present TEWI analysis.

Hafner et al. (2004) did a life cycle climate performance analysis of mobile A/C systems with R134a and R744. The authors showed that R744 has equal or better performance than R134a at the dominant operating conditions resembling moderate temperatures and high revolution speed of the compressor. They also indicate a reduced environmental impact by the R744 system. These findings match the results of the present LCA study where R134a is under all scenarios and with all assessment methods possessing a greater environmental impact than R744.

Hill & Papasavva (2005) did a life cycle analysis framework comprising R134a, R152a, R744, and R290 in A/C in cars including seven cities of different climate regions. For refrigerants R134a and R744, they were studying a baseline and an enhanced A/C system which possess improved compressor efficiency and heat exchanger performance, along with reduced leakage rates. The authors state that under warmer climate conditions R744 and R290 exhibit energy consumption 5 – 25 % higher than the enhanced R134a system. But the results indicate that all alternatives perform better than the baseline R134a system for all climate regions. The baseline R744 is the only exception as it has about 20 % more CO₂ emissions in Phoenix. The enhanced R134a system is under hot and humid conditions (Phoenix, Miami, Houston) better than the other alternatives. In the climate of Boston, it is better than R290 and the baseline R744 system but worse than R152a and the enhanced R744 system. Under moderate and cooler climate conditions (Tokyo, Frankfurt, Sydney), even the enhanced R134a system is performing worse than the other refrigerants. R290 is under all set scenarios performing better than baseline

R744 system. But the enhanced R744 system is under cooler climate conditions superior to R290 and R152a. Under hotter and more humid climate conditions, R152a is superior to R290 and R744.

The present LCA (EI99, TEWI) comes in some aspects to similar results, considering R134a and R744 comparable to the baseline systems of Hill & Papasavva (2005):

- R134a performs worse than the other refrigerants
- R290 always performs better than R744
- R152a performs better than R744 under worst-case and average scenario; however with EI99, R152a is under best-case scenario (representing cooler climate) worse than R744 and R290

To sum it up, for the refrigerants R134a, R152a, R290, and R744, the result of the present LCA correspond to those of LCA literature. Therefore, one can presume that the assumptions and simplifications made in this LCA study do not alter the outcome of the refrigerant performance in a way that they are far from reality. Thus, the results for the HFEs can be seen as representative estimation.

5.6 Comparison of LCA with METEOR results

In the previous chapter, results of LCA literature were compared with those of the present LCA study considering mobile A/C application. A main aim of this work was to check if results derived from mathematical models using refrigerant intrinsic properties are similar compared to those of LCA considering different technical applications. For comparison with LCA results the average ranks of METEOR calculation were used (Table 30). According to METEOR results, R143a has the greatest impact on the environment, followed by R22, R32, R125, R410A, and R744. The smallest impact has E7200 and then R717, R30, R600a, and R152a. R1270, R290, R134a, and R407C have medium environmental impacts.

In the present study, some agreements between the LCA study on mobile A/C systems and METEOR results could be found. E7200 has a smaller environmental impact than R30 and R134a. R600a is ranked lower than R744 and R134a. R290 has a lesser impact than R744, and R134a has a greater impact than R152a. Those compliances are due for all three assessment methods. For EI99 and AV (CML02), some additional agreements with METEOR results are found: R30 is ranked lower than R134a, and R600a is ranked lower than R152a.

Beside those compliances, some differences occur. In METEOR, R134a is ranked lower than R290 and R744. This is not the case for the rankings of the present LCA study. Furthermore, R30 is not ranked higher than R744, R152a, R600a, and R290. In METEOR, R600a does not have a greater environmental impact than R290. The dominance of R152a over R290 could not be confirmed by METEOR results.

Table 30: Averaged ranks derived from METEOR calculation

Refrigerant	Average rank	
R22	12.67	Yanagitani & Kawahara (2000) assessed the environmental impact of R22 and R410A in A/C systems with the performance of 4 kW. R410A showed in all studied impact categories a lower environmental impact than R22. This matches the results from METEOR.
R30	4.63	
R32	11.03	
R125	10.46	For the application of some refrigerants in residential A/C systems and heat pumps, Arthur D. Little, Inc. (2002) reported a ranking that gives greatest environmental impact to R22, followed by R407C and R410A, while R290 and R744 are the two least problematic refrigerants. The METEOR calculation compiles with the dominance of R22 over the four mentioned refrigerants, but otherwise shows a ranking of R407C that is lower than the other four refrigerants. Under METEOR, R410A is ranked higher than R290 and R744, and R744 is ranked higher than R290.
R134a	6.76	
R143a	12.76	
R152a	6.07	
R1270	9.63	
R290	7.74	
R600a	4.88	
R407C	6.41	
R410A	10.11	Similar results occur when regarding commercial A/C systems (Little 2002). R22 is ranked highest of the therein studied refrigerants. But the second highest rank of R407C does not match METEOR results which place this refrigerant at the lowest rank. Furthermore, the dominance of R134a over R290 and R744 in Little's report differs with the results of METEOR which places R134a below those two refrigerants.
E7200	3.13	
R717	4.02	
R744	9.72	

Another technical application is supermarket refrigeration in the low and medium temperature range. Bovea et al. (2007) used EI99 for assessing the environmental impact of refrigerants in a standard European supermarket (2 000 m²) with a cooling duty of 130 kW over a period of 15 years. Considering a medium temperature cooling system with direct expansion, Bovea et al. (2007) identified R744 as the refrigerant with the greatest impact followed by R134a. R22 and R410A are the two refrigerants with the lowest impact. METEOR results confirm the dominance of R744 over R134a, but rank R22 and R410A higher than R744 and R134a. In a secondary loop system under medium temperature range, Bovea et al. (2007) ranks R134a highest, followed by R717, R410A, and R22. Again, METEOR does not give the same results. Alone, that R717 is ranked lower than R134a is a common result. Bovea et al. (2007) were further considering low temperature systems. While METEOR ranks R744 higher than R407C, Bovea et al. (2007) came to the contrary result.

Zogg (1999) compared the environmental impact of natural refrigerants in heat pumps with those of refrigerant presently used. He showed that for heat pumps under comparable performance the natural refrigerants (R290, R744) have lower impact in the categories "Climate change", "Stratospheric ozone depletion", and "Terrestrial ecotoxicity" than conventionally used ones (R22, R134a, R407C). Considering the

impact categories “Non-renewable energy”, “Acidification”, “Summer smog”, “Aquatic ecotoxicity”, and “Radioactivity”, the studied refrigerants do not show great differences. METEOR ranks R744 and R290 higher than R134a and R407C but lower than R22. Thus, results from Zogg (1999) are not confirmed.

The research center for refrigeration technique and heat pumps (FKW) did a study on the replacement of R22 in existing refrigeration and A/C systems (FKW 2000). They calculated the annual TEWI for seven refrigerant including R22, R134a, R290, R407C, R410A, R717, and R1270. The systems investigated in the FKW study comprise supermarket cooling facilities in the low and medium temperature range, A/C in buildings, transport cooling in the low temperature range, and air/water heat pumps. Comparing the results of METEOR with those of FKW (2000), FKW always gave greatest environmental impact to R410A which is ranked below R22 in METEOR. In the FKW study, R717 has the smallest environmental impact in the applications supermarket refrigeration system (medium temperature), A/C system for buildings, and air/water heat pump matching the results from METEOR where it has the lowest rank of the refrigerants included in the FKW study. FKW assign in all mentioned applications a high rank to R407C which is ranked low in METEOR. Only in air/water heat pumps, R290 is assessed a greater environmental impact than R134a which is in accordance with METEOR results. However, R1270 is ranked lower than R134a in all applications except air/water heat pumps. This is in contrast to the METEOR ranking.

Frischknecht (1999a, 1999b) assessed and compared the application of natural and synthetic refrigerants finding out that the natural refrigerants (R290, R717, R744) have a smaller impact to the categories “Stratospheric ozone depletion”, “Climate change”, and “Terrestrial ecotoxicology” than the halogenated refrigerants included in his study. R290 has a slightly greater contribution to the category “Photo-oxidant formation” than synthetic refrigerants (R134a, R407C, R410A, R22). In the category “Acidification”, R717 shows similar contributions compared with the HFCs (R134a, R407C, R410A). Those results are not mirrored in METEOR where R744 and R290 show greater environmental impact than R134a and R407C, and where R22 is ranked highest and R717 lowest.

Overall, METEOR does not agree with the results from LCA. This phenomenon is not alone due to the fact that even different LCA studies show contradicting results depending on the different applications and conditions.

6 Recommendations & outlook

Ranking of refrigerants based on substance-intrinsic properties using METEOR can only give a rough estimation about general environmental impact of a certain refrigerant compared to others. Hardly any statement can be made about the influence of the technical facilities to which the refrigerants are applied. But mathematical methods based on partial order are less subjective than LCA. It might be of interest in further studies to include additional properties that are directly related to the performance of refrigerants in refrigeration systems and reduce the number of environmental properties in the METEOR calculation.

The LCA methods CML02, EI99, TEWI, and especially the calculations based on the mathematical model METEOR do not account for the impact of degradation products of HFEs. According to the fate modelling done in this work, these PFCAs will accumulate in the environment and reach concentrations which are in ranges that might cause severe ecological problems that can presently not fully be foreseen. Thus, independent from the LCA results, HFEs of that study should not be proposed as future refrigerants.

Considering the results of the present LCA study and taking from each assessment method the best four refrigerants, R152a, R290, R600a, R744, E7200, E7000, and R30 amount as the best substitutes for R134a. Eliminating E7000 and E7200 from that group because of their contribution of PFCAs to the hydrosphere will result in a remaining set of five refrigerants as possible substitutes. R30 might as well be not regarded as replacement because it has the greatest environmental impact in the categories AP, EP, POCP, and HTP. That leaves R152a, R290, R600a, and R744 as most likely replacements of R134a in A/C systems in passenger cars. Of those four refrigerants, TEWI and EI99 assign a lower environmental impact to R152a than to R744, whereas the average rank of R744 in CML02 is lower than that of R152a. R290 executes the lowest impact on the environment according to TEWI, EI99, and the average rank (AV) of CML02. R600a has the second lowest impact. Studies on R744, R152a and HC systems show no increase in loss of safety due to those refrigerants (MacLainecross 2004, Lunde & Lorentzen 1994, Clark 2005). By using secondary loop systems, the safety issue can be eliminated as relevant aspect for decision making.

It has to be stressed that the results depend generally on the scenarios and conditions for which a LCA is conducted. The setting can influence the outcome of a study in both ways. One should never look on the results alone but always consider the conditions of the study. Not one refrigerant is the best one for every application. Even if a specific study points in a specific direction. This is not likely to be true for all eternity. Public perspectives and politics are likely to change over time, as it happened throughout the past centuries, which might result in different impact and damage factors which again influence the outcome of an LCA. Priorities of some aspects might change with time as the understanding of complex relationships of ecosystems is discovered. For example, the problematic of climate change was becoming popular over the last decades. The challenge of minimizing energy consumption depends also on the kind of energy used.

When solar energy is being effectively usable, it might be that systems that possess presently a low energy efficiency are becoming more advantageous from an environmental point of view as their other environmental impacts are low. Hence, R744 and R152a should not be completely neglected as possible refrigerants in the future.

7 References

- ADAC (Editor) (1998) Klimaanlagen im Test. Gemessen und zu warm empfunden. In der Stadt deutlich höherer Kraftstoffverbrauch. Von Maurer, M., Neues vom ADAC, ND 126/98, August 1998.
- AFEAS – Alternative Fluorocarbons Environmental Acceptability Study (1994) Workshop on the Environmental Fate of Trifluoroacetic acid. 3-4 March 1994, Miami Beach, Florida, Workshop proceedings.
- ARAL (2004) Aral Diesel / Aral SuperDiesel / Aral LKW Diesel (Mindestanforderungen gem. DIN EN 590). Sicherheitsdatenblatt, Aral Aktiengesellschaft, Bochum, 27.04.2004.
- Atkinson, R. (1997) Gas-Phase Tropospheric Chemistry of Volatile Organic Compounds: 1. Alkanes and Alkenes. J. Phys. Chem. Ref. Data, Vol. 26, No. 2, pp. 215-290.
- Atkinson, R.; Arey, J.; Hoover, S.; Preston, K.; Fanning, E.; Sandy, M.S.; Sultana, D. (2005) Atmospheric Chemistry of Gasoline-related Emissions: Formation of Pollutants of Potential Concern. Draft for Public Comment, Reproductive and Cancer Hazard Assessment Branch, Office of Environmental Health Hazard Assessment, California Environmental Protection Agency.
- Atkinson, R., (2007) Atmospheric chemistry of alkanes: Review and recent developments. Atmospheric Environment, doi:10.1016/j.atmosenv.2007.08.040.
- Ayres, R.U.; Ayres, L.W.; Martinès, K. (1996) Eco-Thermodynamics : Exergy and Life Cycle Analysis, Working Paper, INSEAD's Centre for the Management of Environmental Resources, Fontainebleau, France
- Barbusse, S.; Gagnepain, L. (2003) Automobile Air-conditioning Its Energy and Environmental Impact. ADEME – Agence de l'Environnement et de la Maîtrise de l'Énergie, Transport Technologies Department, Valbonne.
- Barrault, S.; Benouali, J.; Clodic, D. (2003) Analysis of the economic and environmental consequences of a phase out or considerable reduction leakage of mobile air conditioners. Final Report ARMINES reference 30001, European Commission Service Contract B4-3040/2002/346884/MAR/C1.
- Baumgartner, A.; Liebscher, H.-J. (1996) Lehrbuch der Hydrologie, Band 1, Allgemeine Hydrologie Quantitative Hydrologie. 2. Auflage, Gebrüder Bornträger, Berlin.
- Behr, F.E.; Cheburkov, Y. (2000) Process for Preparing Hydrofluoroethers. United States Patent, Patent No. 6023002.
- BFE – Bundesamt für Energie (2007) Schweizerische Gesamtenergiestatistik 2006 Statistique globale suisse de l'énergie 2006. Schweizerische Eidgenossenschaft, BFE, Bern.
- BGB – Bürgerliches Gesetzbuch (2006) Verordnung über die Überlassung, Rücknahme und umweltverträgliche Entsorgung von Altfahrzeugen, Altfahrzeug-Verordnung. BGB1. I Nr. 41 vom 28. Juni 2002, zuletzt geändert 9. Februar 2006, BGB1. I Nr. 7 vom 13. Februar 2006.
- Bitzer International (2004): Kältemittel Report, A-500-13, 13. Auflage, Sindelfingen (<http://www.bitzer.de>).

- BMWi – Bundesministerium für Wirtschaft und Technologie (2007) Zahlen und Fakten Energiedaten Nationale und Internationale Entwicklung. Referat III A 2, Stand: 13.06.2007, (<http://www.ihl-zittau.de/de/dnl/energie-daten-gesamtpropertyblobbereichbmwisprachederwbtrue.1396.xls>)
- Bovea, M.D.; Cabello, R.; Querol, D. (2007) Comparative Life Cycle Assessment of Commonly Used Refrigerants in Commercial Refrigeration Systems. *International Journal of Life Cycle Assessment*, Vol. 12(5), pp. 299-307.
- Bowden, D.J.; Clegg, S.L.; Brimblecombe, P. (1996) The Henry's law constant of trifluoroacetic acid and its partitioning into liquid water in the atmosphere. *Chemosphere*, Vol. 32, No. 2, pp. 405-420.
- Brüggemann, R.; Drescher-Kaden, U.; Münzer, B. (1996) E4CHEM – A Simulation Program for the Fate of Chemicals in the Environment. Projektgruppe Umweltgefährdungspotential von Chemikalien, GSF-Bericht 2/96, GSF-Forschungszentrum für Umwelt und Gesundheit, Neuherberg.
- Brüggemann, R.; Bartel, H.-G. (1999) A Theoretical Concept to Rank Environmentally Significant Chemicals, *J. Chem. Inf. Comput. Sci.*, Vol. 39, pp. 211-217
- Brüggemann, R.; Voigt, K.; Restrepo, G.; Simon, U. (2007) Concept of stability fields and hot spots in ranking of environmental chemicals. *Environ. Model. Softw.*, doi:10.1016/j.envsoft.2007.11.001.
- BUWAL – Bundesamt für Umwelt, Wald und Landschaft (2002) Konzeptstudie Klimaanlage von Personenwagen Überprüfung des Fahrverhaltens von Personenwagen in der Schweiz. Arbeitsunterlage 27, Luftschadstoffemissionen des Strassenverkehrs Folgearbeiten zum BUWAL-Bericht SRU Nr. 225, erarbeitet durch Abay & Meier, Zürich.
- Calm, J.M.; Hourahan, G.C. (2001) Refrigerants Data Summary, *Engineered Systems*, Vol. 18 (11), pp. 74-88.
- Campbell, N.J.; McCulloch, A. (1998) The Climate Change Implications of Manufacturing Refrigerants A Calculation of 'Production' Energy Contents of Some Common Refrigerants. *Transactions of the Institution of Chemical Engineers*, Vol. 76, Part B, pp. 239-244.
- Cavalli, F.; Glasius, M.; Hjorth, J.; Rindone, B.; Jensen, N.R. (1998) Atmospheric Lifetimes, Infrared Spectra and Degradation Products of a Series of Hydrofluoroethers. *Atmospheric Environment*, Vol. 32, No. 21, pp. 3767-3773.
- Christensen, L.K.; Sehested, J.; Nielsen, O.J.; Bilde, M.; Wallington, T.J.; Guschin, A.; Molina, L.T.; Molina, M.J. (1998) Atmospheric Chemistry of HFE-7200 ($\text{C}_4\text{F}_9\text{OC}_2\text{H}_5$): Reaction with OH Radicals and Fate of $\text{C}_4\text{F}_9\text{OCH}_2\text{CH}_2\text{O}(\bullet)$ and $\text{C}_4\text{F}_9\text{OCHO}(\bullet)\text{CH}_3$ Radicals. *J. Phys. Chem. A*, Vol. 102, pp. 4839-2845.
- Christoph, E.H. (2002) Bilanzierung und Biomonitoring von Trifluoracetat und anderen Halogenacetaten. Dissertation zur Erlangung des Doktorgrades der Fakultät Biologie, Chemie und Geowissenschaften der Universität Bayreuth, unveröffentlicht.
- Clark, J.W. (2005) Hydrocarbon Refrigerants in Motor Vehicle Air Conditioning Systems – Reflections and Projections. Presentation to the "Natural Refrigerants Transition Board, Hydrocarbon Refrigerants Conference", June 2005, Sydney, Australia.

- Claudette, M.R.-R.; Francisco, J.S. (2007) Atmospheric oxidation pathways of propane and its by-products: Acetone, acetaldehyde, and propionaldehyde. *Journal of Geophysical Research*, Vol. 112, D14310, doi:10.1029/2006JD007566.
- COM(2003)492 final: Proposal for a Regulation of the European Parliament and of the Council on certain fluorinated greenhouse gases, 2003/0189(COD), Commission of the European Communities, Brussels, 11.8.2003
- Davies, T.W.; Caretta, O. (2004) A low carbon, low TEWI refrigeration system design. *Applied Thermal Engineering*, Vol. 24, pp. 119-1128.
- Delphi Corporation (2006) electronic communications.
- Destatis – Statistisches Bundesamt Deutschland (2006a) Verkehr in Deutschland 2006. SFG Servicecenter Fachverlage, Wiesbaden.
- Destatis – Statistisches Bundesamt (2006b) Verwendung bestimmter ozonschichtschädigender und klimawirksamer Stoffe 2004, Statistisches Bundesamt, Wiesbaden.
- Devotta, S.; Waghmare, A.V.; Sawant, N.N.; Domkundwar, B.M. (2001) Alternatives to HCFC-22 for air conditioners, *Applied Thermal Engineering*, Vol. 21, pp. 703-715.
- Devotta S., Padalkar A. S., Sane N. K. (2005) Performance assessment of HCFC-22 window air conditioner retrofitted with R-407C. *Appl. Therm. Eng.*, Vol. xxx, pp. xxx-xxx, In press.
- DIN 8960 (1998) Kältemittel – Anforderungen und Kurzzeichen, November 1998.
- DIN EN 228 (2006) Kraftstoffe für Kraftfahrzeuge - Unverbleite Ottokraftstoffe - Anforderungen und Prüfverfahren. Deutsche Fassung EN 228:2004, Berichtigungen zu DIN EN 228:2004-03; Deutsche Fassung EN 228:2004/AC:2005, Ausgabe März 2006, Beuth-Verlag GmbH, Berlin.
- DuPont (2002) Continuous Manufacture of 1,1-Difluoroethane. EP0830333B1, European Patent Office.
- Duthie, G.S.; Harte, S.; Jajashela (2002) European Average Mobile A/C Customer Usage Model, Visteon Climate Control Group, Presented at SAE Automotive Alternate Refrigerant Systems Symposium, July 2002, Scottsdale, USA.
- Duvedi, A.; Achenie, L.E.K. (1997) On the design of environmentally benign refrigerant mixtures: a mathematical programming approach, *Computers chem. Engng*, Vol. 21, No. 8, pp. 915-923.
- EC (2000) Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of life vehicles, *Official Journal of the European Communities*, No. L 269, 21 October 2000.
- EC (2006) Regulation (EC) No 842/2006 of the European Parliament and the council of 17 May 2006 on certain fluorinated greenhouse gases, *Official Journal of the European Union*, No. L 161/1, 17 May 2006.
- ECETOC – European Centre for Ecotoxicology and Toxicology of Chemicals (2004) 1,1-Difluoroethane (HFC-152a) (CAS No. 75-37-6). ECETOC JACC Report No. 45, Brussels, Belgium.

- ECETOC – European Centre for Ecotoxicology and Toxicology of Chemicals (2006) 1,1,1,2-Tetrafluoroethane (HFC-134a) (CAS No. 811-97-2). Second Edition, ECETOC JACC Report No. 50, Brussels, Belgium.
- EG – Europäische Gemeinschaft, 98/69/EG (1998) Richtlinie 98/69/EG des Europäischen Parlaments und des Rates vom 13. Oktober 1998 über Maßnahmen gegen die Verunreinigung der Luft durch Emissionen von Kraftfahrzeugen und zu Änderung der Richtlinie 70/220/EWG des Rates, Amtsblatt der Europäischen Gemeinschaft, L350, vom 28.12.1998.
- EG – Europäische Gemeinschaft, 2002/358/EG (2002): Entscheidung des Rates vom 5. April 2002 über die Genehmigung des Protokolls von Kyoto zum Rahmenübereinkommen der Vereinten Nationen über Klimaänderungen im Namen der Europäischen Gemeinschaft sowie die gemeinsame Erfüllung der daraus erwachsenden Verpflichtung, Amtsblatt der Europäischen Gemeinschaft, L130, vom 15.05.2002
- EU (2000) Verordnung (EG) Nr. 2037/2000 des Europäischen Parlamentes und des Rates vom 29. Juni 2000 über Stoffe, die zum Abbau der Ozonschicht führen, Amtsblatt der Europäischen Gemeinschaft, Nr. L244, vom 29.09.2000.
- EU (2006) Richtlinie 2006/40/EG des Europäischen Parlaments und des Rates vom 17. Mai 2006 über Emissionen aus Klimaanlage in Kraftfahrzeugen und zur Änderung der Richtlinie 70/156/EWG des Rates, Amtsblatt der Europäischen Gemeinschaft, Nr. L161/12, vom 17.05.2006.
- eurammon (2002) Kohlendioxid – CO₂ – R744 – (Kohlensäure). eurammon-Information, Nr. 11, März 2002, Frankfurt.
- eurammon (2005a) eurammon – Einsatz für natürliche Kältemittel. eurammon-Information, Nr. 1, Juli 2005, Frankfurt.
- eurammon (2005b) Das natürliche Kältemittel Ammoniak. eurammon-Information, Nr. 2, Juli 2005, Frankfurt.
- FCKW-Halon-Verbots-Verordnung (1991) Verordnung zum Verbot von bestimmten die Ozonschicht abbauenden Halogenkohlenwasserstoffen, Bundesgesetzblatt, Jahrgang 1991, Teil I, Seite 1090-1092.
- Fischer, S.K.; Tomlinson, J.J.; Hughes, P.J. (1994) Energy and Global Warming Impacts of Not-In-Kind and Next Generation CFC and HCFC Alternatives, AFEAS-Alternative Fluorocarbons Environmental Acceptability Study.
- Fischer, S.K.; Sand, J.R. (1997) Total Environmental Warming Impact (TEWI) Calculations for Alternative Automotive Air-Conditioning Systems. SAE Technical Paper Series, 970526.
- FKT – Forschungsrat Kältetechnik e.V. (2005) *TEWI-Bewertung von Kälteanlagen Werkzeug zur Berechnung des TEWI (TEWI = Total Equivalent Warming Impact)*. Bericht zum Forschungsvorhaben FKT 99/03. siccon Sicars Consulting. Frankfurt.
- FKW – Forschungszentrum für Kältetechnik und Wärmepumpen GmbH (2000): Ersatz des Kältemittels R22 in bestehenden Kälte- und Klimaanlage, Studie im Auftrag des Umweltbundesamtes, FKW, Hannover.
- Franklin, J. (1993) The Atmospheric Degradation and Impact of 1,1,1,2-Tetrafluoroethane (Hydrofluorocarbon 134a). Chemosphere, Vol. 27. No. 8, pp. 1565-1601.

- Frischknecht, R. (1999a) Umweltrelevanz natürlicher Kältemittel; Ökobilanzen von Wärmepumpen und Kälteanlagen, Schlussbericht. Bundesamt für Energie, Bern.
- Frischknecht, R. (1999b) Umweltrelevanz natürlicher Kältemittel; Ökobilanzen von Wärmepumpen und Kälteanlagen, Anhang zum Schlussbericht. Bundesamt für Energie, Bern.
- GHC – Gerling, Holz & Co (2005) R410A, EG-Sicherheitsdatenblatt gemäß Richtlinie 91/155/EWG, Gerling, Holz & Co Handels GmbH.
- GHC – Gerling, Holz & Co (2007) R407C, EG-Sicherheitsdatenblatt gemäß Richtlinie 91/155/EWG, Gerling, Holz & Co Handels GmbH.
- GHG Protocol Initiative (2005) Calculating CO₂ Emissions from Mobile Sources, Guidance to calculation worksheets. Version 1.3, Cooperation of WBCSD – World Business Council for Sustainable Development and WRI – World Resources Institute.
- Ghodbane, M. (1999) An Investigation of R152a and Hydrocarbon Refrigerants in Mobile Air Conditioning. SAE Technical Paper Series, 1999-01-0874, International Congress and Exposition, Detroit, Michigan, March 1-4, 1999.
- Goedkoop, M.; Spriensma, R. (2001) The Eco-indicator 99; A damage oriented method for Life Cycle Impact Assessment; Methodology Report. Third edition, Pré Consultants B.V., Amersfoort, in cooperation with Ministry of Housing, Spatial Planning and the Environment.
- Good, D.A.; Francisco, J.S.; Jain, A.K.; Wuebbles, D.J. (1998) Lifetimes and global warming potentials for dimethyl ether and for fluorinated ethers: CH₃OCF₃ (E143a), CHF₂OCHF₂ (E134), CHF₂OCF₃ (E125), Journal of geophysical research, Vol. 103(D21), pp. 181-186
- Good, D.A.; Kamboures, M.; Santiano, R.; Francisco, J.S. (1999) Atmospheric Oxidation of Fluorinated Ethers, E143a (CF₃OCH₃), E134 (CHF₂OCHF₂), and E125 (CHF₂OCF₃). J. Phys. Chem. A, Vol. 103, pp. 9230-9240.
- Gover, M.P.; Collings, S.A.; Hitchcock, G.S.; Moon, D.P.; Wilkins, G.T. (1996) Alternative Road Transport Fuels – A Preliminary Life-Cycle Study for the UK, Volume 2. ETSU (Energy Technology Support Unit), Harwell, United Kingdom
- Guinée, J.B.; Kleijn, R.; Gorrrée, M.; Heijungs, R.; Huppes, G.; De Koning, A.; Van Oers, L.; Wegener Sleeswijk, A.; Suh, S.; De Haes, H.A.U.; De Bruijn, H.; Van Duin, R.; Huijbregts, M.A.J. (2001) Life cycle assessment - An operational guide to the ISO standards. Final report, Part 2B, Operational Annex, Ministry of Housing, Spatial Planning and the Environment (VROM), Centre of Environmental Science, Leiden University (CML), May 2001.
- Hafner, A.; Jakobsen, A.; Neksa, P.; Pettersen, J. (2004) Life Cycle Climate Performance (LCCP) of Mobile Air-Conditioning Systems with HFC-134a and R-744. VDA Alternate Refrigerant Wintermeeting 2004, 18./19.2.2004 in Saalfelden, Austria.
- Hanaoka, T.; Ishitani, H.; Matsushashi, R.; Yoshida, Y. (2002) Recovery of fluorocarbons in Japan as a measure for abating global warming, Applied Energy, Vol. 72, pp. 705-721.

- Harnisch, J.; Höhne, N.; Koch, M.; Wartmann, S.; Schwarz, W.; Jenseit, W.; Fabian, P.; Jordan, A. (2004) Risiken und Nutzung von fluorierten Treibhausgasen in Techniken und Produkten – Bewertung technischer Fallbeispiele unter besonderer Berücksichtigung der stoffintrinsic Eigenschaften, Umweltforschungsplan des Bundesministeriums für Umwelt, Naturschutz und Reaktorsicherheit, Forschungsbericht 201 64 314, UBA-FB 000673, Berlin.
- Hashikawa, Y.; Kawasaki, M.; Sulbaek Andersen, M.P.; Hurley, M.D.; Wallington, T.J. (2004) Atmospheric chemistry of CH_3CHF_2 (R-152a): mechanism of the $\text{CH}_3\text{CF}_2\text{O}_2 + \text{HO}_2$ reaction. *Chemical Physics Letters*, Vol. 391, pp. 165-169.
- Heberle (2007) personal communication based on DIPPR 801 database, BYU-DIPPR Thermophysical Properties Laboratory Brigham Young University, Provo, Utha.
- Highwood, E.J.; Shine, K.P. (2000) Radiative forcing and global warming potentials of 11 halogenated compounds, *Journal of Quantitative Spectroscopy & Radiative Transfer*, Vol. 66, pp. 169-183.
- Hill, W.; Papasavva, S. (2005) Life Cycle Analysis Framework; A Comparison of HFC-134a, HFC-134a Enhanced, HFC-152a, R744, R744 Enhanced, and R290 Automotive Refrigerant Systems. 2005-01-1511, SAE 2005 world congress, April 11-14, SAE International.
- Hill, W.R. (2006) Industry Overview of the Environmental Performance of Non-CO2 [R744] Alternatives. Presentation at MAC Summit, 17 February 2006, Saalfelden, Austria.
- Howard, P.H. (ed.) (1990) *Handbook of Environmental Fate and Exposure Data For Organic Chemicals, Volume II, Solvents*, Lewis Publishers, Chelsea, USA.
- Howard, P.H. (ed.) (1993) *Handbook of Environmental Fate and Exposure Data For Organic Chemicals, Volume IV, Solvents 2*, Lewis Publishers, Chelsea, USA.
- Howard, P.H. (ed.) (1997) *Handbook of Environmental Fate and Exposure Data For Organic Chemicals, Volume V, Solvents 3*, Lewis Publishers, Boca Raton, USA; calculated.
- Inoue, Y.; Kawasaki, M.; Wallington, T.J.; Hurley, M.D. (2001) Atmospheric degradation mechanism of $\text{CF}_3\text{OCF}_2\text{H}$. *Chemical Physics Letters*. Vol. 343, pp. 296-302.
- IPCC – Intergovernmental Panel on Climate Change (2001) *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change* [Houghton, J.T.; Ding, Y.; Griggs, D.J.; Noguer, M.; van der Linden, P.J.; Dai, X.; Maskell, K.; Johnson, C.A. (eds.)]. Cambridge University Press, Cambridge, United Kingdom, and New York, NY, USA.
- IPCC – Intergovernmental Panel on Climate Change (2006) *Special Report on Safeguarding the Ozone Layer and the Global Climate System; Issues related to Hydrofluorocarbons and Perfluorocarbons*, [Metz, B.; Kuijpers, L.; Solomon, S.; Andersen, S.O.; Davidson, O.; Pons, J.; de Jager, D.; Kestin, T.; Manning, M.; Meyer, L. (eds.)]. Cambridge University Press (available at: www.wmo.ch)
- ISO 14040 (2006) *Environmental management – Life cycle assessment – Principles and framework*. Second edition, 2006-07-01, International Standard, Geneva.

- ISO 14044 (2006) Environmental management – Life cycle assessment – Requirements and guidelines. First edition, 2006-07-01, International Standard, Geneva.
- Kendall, M. (1975) Rank Correlation Methods. 4th edition, Charles Griffin & Company LTD, London and High Wycombe.
- Kirk-Othmer (ed.) (1993) Encyclopedia of Chemical Technology, Fourth Edition, Vol. 5, Carbon and Graphite Fibers to Chlorocarbons and Chlorohydrocarbons-C₁, John Wiley & Sons, New York and other places, S. 1028-1072.
- Klein, A. (1997) Halogenierte Essigsäuren in der Umwelt. Dissertation zur Erlangung des Doktorgrades der Fakultät Biologie, Chemie und Geowissenschaften der Universität Bayreuth, unveröffentlicht.
- Knovel (2003) Knovel Critical Tables, online version available at: <http://www.knovel.com/knovel2/Toc.jsp?BookID=761&VerticalID=0>.
- Krieger, T.M.; Bateman, D.J.; Sylvester, R.W. (2004) Life Cycle Analysis for Production of HFC-134a and HFC-152a. 15th Conference of Earth Technologies Forum and Mobile Air Conditioning Summit, April 13-15, Washington, D.C., USA.
- Kyoto Protocol (1997) Kyoto Protocol to the United Nations Framework Convention on Climate Change, United Nations Framework Convention on Climate Change – Conference of the Parties, Kyoto, 10 December 1997.
- Little, A.D., Inc. (2002) Global Comparative Analysis of HFC and Alternative Technologies for Refrigeration, Air Conditioning, Foam, Solvent, Aerosol Propellant, and Fire Protection Application. Final Report to the Alliance for Responsible Atmospheric Policy, Arthur D. Little, Inc., Reference 75966, Cambridge, Massachusetts.
- Lunde, H.; Lorentzen, G. (1994) Accidents and critical situations due to unintentional escape of refrigerants: a survey of cases in Norway over the last two decades. International Journal of Refrigeration, Vol. 17(6), pp. 371-373.
- Lyerly, S. B. (1952) The Average Spearman Rank Correlation Coefficient*. Psychometrika, Vol. 17, No. 4, pp. 421-428.
- 3M (2007) personal communication; product info sheets, 3M Electronics Markets Materials Division, Minnesota.
- Mackay, D. (2001) Multimedia Environmental Models, The Fugacity Approach. Second Edition, Lewis Publishers, Boca Raton.
- MacLaine-cross, I.L. (2004) Usage and risk of hydrocarbon refrigerants in motor cars for Australia and the United States. International Journal of Refrigeration. Vol. 27. pp. 339-345.
- McCulloch, A. (1999) CFC and halon replacements in the environment. J. Fluor. Chem., Vol. 100, pp. 163-173.
- McCulloch, A.; Lindley, A.A. (2003) From mine to refrigeration: a life cycle inventory analysis of the production of HFC-134a. International Journal of Refrigeration, Vol. 26, pp. 865-872.
- MDL Information Systems GmbH (2005): MDL CrossFire Server Software, Version 7.0SP2 (Build 37), CrossFire Beilstein Database, 2007-2008, Elsevier Information Systems GmbH.

- Molina, M. J.; Rowland, F. S. (1974): Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone, *Nature*, 249, pp. 810
- Ninomiya, Y.; Kawasaki, M.; Guschin, A.; Molina, L.T.; Molina, M.J.; Wallington, T.J. (2000) Atmospheric Chemistry of $n\text{-C}_3\text{F}_7\text{OCH}_3$: Reaction with OH Radicals and Cl Atoms and Atmospheric Fate of $n\text{-C}_3\text{F}_7\text{OCH}_2\text{O}(\bullet)$ Radicals. *Environ. Sci. Technol.*, Vol. 34, pp. 2973-2978.
- NIST – National Institute of Standard and Technology (2005) Chemistry WebBook, NIST Standard Reference Database. Number 69, June 2005 Release; copyright by the U.S. Secretary of Commerce on behalf of the United States of America.
- Nohara, K.; Toma, M.; Kutsuna, S.; Takeuchi, K.; Ibusuki, T. (2001) Cl Atom-Initiated Oxidation on Three Homologous Methyl Perfluoroalkyl Ethers. *Environ. Sci. Technol.*, Vol. 35, pp. 114-120.
- O'Neill, G.J.; Holdsworth, R.S. (1990): Bis (difluoromethyl) ether refrigerant. United States Patent, Patent No. 4961321.
- Petitjean, C.; Yahia, M.B.; Guyonvarch, G.; Beauvis, R. (1999) TEWI Analysis for Future A/C Systems Selection. Alternate Refrigerant Forum, June 30, Phoenix USA.
- Petitjean, C.; Guyonvarch, G.; Benyahia, M.; Beauvis, R. (2000) TEWI Analysis for Different Automotive Air Conditioning Systems. 2000-01-1561, 2000 Future Car Congress proceedings: April 2-6; Society of Automotive Engineers.
- Pré Consultants B.V. (2000) Eco-indicator 99; Manual for Designers. Pré Consultants B.V., Amersfoort, in cooperation with Ministry of Housing, Spatial Planning and the Environment.
- Restrepo, G. (2007) Similarity Analysis of HFE. unpublished.
- Restrepo, G.; Brueggemann, R.; Weckert, M.; Gerstmann, S.; Frank, H. (2008) Ranking Patterns, an Application to Refrigerants. *Match – communications in mathematical and in computer chemistry*, Vol. 59 (3), pp. 555-584.
- Sand, J. R.; Fischer, S. K.; Baxter, V.D. (1997) Energy and Global Warming Impacts of HFC Refrigerants and Emerging Technologies. Sponsored by AFEAS, U.S. Department of Energy, Tennessee.
- Sidebottom, H.; Franklin, J. (1996) The atmospheric fate and impact of hydrochlorofluorocarbons and chlorinated solvents. *Pure & Appl. Chem.*, Vol. 9, pp. 1757-1769.
- Schwaab, K.; Dettling, F.; Bernhardt, D.; Elsner, C.; Sartorius, R.; Reimann, K.; Remus, R.; Plehn, W. (2004): Fluorierte Treibhausgase in Produkten und Verfahren – Technische Maßnahmen zum Klimaschutz, Bericht des Umweltbundesamtes, 20. Februar 2004, Berlin
- Schwarz, W.; Harnisch, J. (2003) Establishing the Leakage Rates of Mobile Air Conditioners. Prepared for the European Commission (DG Environment), B4-3040/2002/337136/MAR/C1, Final Report.
- Schwarz, W. (2004): Der hohe und wachsende Anteil fluorierter Treibhausgase (F-Gase) an den globalen treibhauswirksamen Gesamtemissionen, Greenpeace-Studie, Öko-Recherche, Frankfurt

- Schwarz, W. (2005): Emissionen, Aktivitätsraten und Emissionsfaktoren von fluorierten Treibhausgasen (F-Gasen) in Deutschland für die Jahre 1995-2002, Umweltbundesamt, UBA-Texte 14/05
- Simons, J.H. (1950) Fluorocarbon ethers. United States Patent, Patent No. 2500388.
- Skutlarek, D.; Exner, M.; Färber, H. (2006) Perfluorierte Tenside (PFT) in der aquatischen Umwelt und im Trinkwasser. UWSF – Zeitschrift für Umweltchemie und Ökotoxikologie, Band 18, Nr. 3, pp. 151-154.
- SRC – Syracuse Research Corporation (1999): Interactive PhysProp Database Demo, (<http://www.syrres.com/esc/physdemo.htm>)
- Strogies, M.; Schiller, S.; Dreher, M. (2005): Deutsches Treibhausgasinventar 1990 – 2003, Nationaler Inventarbericht 2005, Berichterstattung unter der Klimarahmenkonvention der Vereinten Nationen, Umweltbundesamt, Berlin
- Sumantran, V.; Khalighi, B.; Saka, K.; Fischer, S. (1999): An Assessment of Alternative Refrigerants for Automotive Applications based on Environmental Impact, , SAE Automotive Alternate Refrigerant Systems Symposium, June 28 – July 1, 1999, Scottsdale, Arizona
- Taketani, F.; Nakayama, T.; Takahashi, K.; Matsumi, Y.; Hurley, M.D.; Wallington, T.J.; Toft, A.; Sulbaek Andersen, M.P. (2005) Atmospheric Chemistry of CH₃CHF₂ (HFC-152a): Kinetics, Mechanisms, and Products of Cl Atom- and OH Radical-Initiated Oxidation in the Presence and Absence of NO_x. Journal of Physical Chemistry A, Vol. 109, pp. 9061-9069.
- Thompson, M.; Ellis, R.; Wildavsky, A. (1990): Cultural Theory. Westview Print, Boulder, USA.
- Thundiyil, K. (2005) Global Progress in Improving Climate Performance of MACs. 23 February 2005, Presentation at Verband der Automobilindustrie Winter Meeting, Saalfelden, Austria.
- Tsai, W.-T. (2005): Environmental risk assessment of hydrofluoroethers (HFEs), Journal of Hazardous Materials, Vol. A119, pp. 69-78
- Tuazon, E.C.; Atkinson, R. (1993) Tropospheric transformation products of a series of hydrofluorocarbons and hydrochlorofluorocarbons. Journal of Atmospheric Chemistry, Vol. 17, No. 2, pp. 179-199.
- UBA – Umweltbundesamt (2003) Bewertung der Anwesenheit teil- oder nicht bewertbarer Stoffe im Trinkwasser aus gesundheitlicher Sicht. Empfehlung des Umweltbundesamtes, Bundesgesundheitsbl-Gesundheitsforsch-Gesundheitsschutz, Vol. 46, pp. 249-251, DOI 10.1007/s00103-022-0576-7.
- UBA – Umweltbundesamt (2006) Vorläufige Bewertung von Perfluorierten Tensiden (PFT) im Trinkwasser am Beispiel ihrer Leitsubstanzen Perfluorooctansäure (PFOA) und Perfluorooctansulfonsäure (PFOS), Stellungnahme der Trinkwasserkommission des Bundesministeriums für Gesundheit (BMG) beim Umweltbundesamt vom 21.06.06, überarbeitet am 13.07.06; <http://www.umweltbundesamt.de/uba-info-presse/hintergrund/pft-im-trinkwasser.pdf>.

- UNEP – United Nations Environment Programme (2000): The Montreal Protocol on Substances that Deplete the Ozone Layer as either adjusted and/or amended in London 1990 Copenhagen 1992 Vienna 1995 Montreal 1997 Beijing 1999, UNEP Ozone Secretariat
- UNEP - (2002): 2002 Report of the Refrigeration, Air Conditioning and Heat Pumps Technical Options Committee, 2002 Assessment, Montreal Protocol on Substances that Deplete the Ozone Layer, Ozone Secretariat, Nairobi
- Vainio, M. (2003) Life Cycle Climate Performance [LCCP] in Mobile Air Conditioning. MAC Summit, 10 February, 2003, Brussels.
- Wallington, T.J.; Hurley, M.D.; Fracheboud, J.M.; Orlando, J.J.; Tyndall, G.S.; Sehested, J.; Mogelberg, T.E.; Nielsen, O.J. (1996) Role of excited CF_3CFHO radicals in the atmospheric chemistry of HFC.134a. *Journal of Physical Chemistry*, Vol. 100, No. 46, pp. 18,116-18,122.
- Wallington T. J., Schneider W. F., Sehested J., Bilde M., Platz J., Nielsen O. J., Christensen L. K., Molina M. J., Molina L. T., Wooldridge P. W. (1997) Atmospheric chemistry of HFE-7100 ($\text{C}_4\text{F}_9\text{OCH}_3$): reaction with OH radicals, UV spectra and kinetic data for $\text{C}_4\text{F}_9\text{OCH}_2\cdot$ and $\text{C}_4\text{F}_9\text{OCH}_2\text{O}_2\cdot$ radicals, and the atmospheric fate of $\text{C}_4\text{F}_9\text{OCH}_2\text{O}\cdot$ Radicals. *J. Phys. Chem. A*. Vol. 101, pp. 8264-8274
- Weissler, P. (2004) Can R-134a be saved? *Automotive engineering international*, October Issue, pp. 151-154.
- Wells, G.M. (1991) *Handbook of Petrochemicals and Processes*. Gower Publishing Company Limited, Brookfield, Vermont, USA.
- WHO – World Health Organization (1996) *Environmental Health Criteria 164 Methylene Chloride*. Second Edition, International Programme on Chemical Safety, Geneva.
- Winkler, P. (1986) Relations Between Aerosol Acidity and Ion Balance. In: Jaeschke, W. (editor): *Chemistry of Multiphase Atmospheric Systems*. NATO ASI Series, Series G: Ecological Sciences, Vol. 6, Springer Verlag, Heidelberg.
- WMO - World Meteorological Organization (2003): *Scientific Assessment of Ozone Depletion: 2002*. Global Ozone Research and Monitoring Project – Report No. 47, World Meteorological Organization (WMO), Geneva
- WMO – World Meteorological Organization (2006) *World Weather Information Service*. <http://worldweather.wmo.int/> (Visited: 4th December 2006).
- Yanagitani, K.; Kawahara, K. (2000) LCA Study of Air Conditioners with an Alternative Refrigerant. *International Journal of Life Cycle Assessment*, Vol. 5 (5), pp. 287-290.
- Yaws, C.L. (1999) *Chemical Properties Handbook: Physical, Thermodynamic, Environmental, Transport, Safety, and Health related Properties for Organic and Inorganic Chemicals*. McGRAW-Hill, New York.
- Zogg, M. (1999) Umweltrelevanz natürlicher Kältemittel in Wärmepumpen. Vortrag am SVK-Kolloquium vom 3.November, Olten.

A Attachment

A1 Property table of refrigerants

Table 31: Property table of refrigerants

Type	Refrigerant	Chemical structure	Chemical name	GWP ₁₀₀ [kg CO ₂ eq./kg]	t _c [°C]	C _p [J/(mol*K)]	C _{ow} [log c _{ow}]	TWA [ppm]	ODP [R11 eq./ kg]
HCFC	R22	CHClF ₂	Chlorodifluoro-methane	1780 ^a	96 ^e	56.68 ⁱ	1.08 ⁿ	500 ^f	0.05 ^e
HFC	R23	CHF ₃	Trifluoromethane	14310 ^b	26 ^e	51.75 ⁱ	0.63 ⁿ	1000 ^d	0 ^s
HCC	R30	CH ₂ Cl ₂	Dichloromethane	10 ^c	238 ^d	51.20 ^j	1.25 ^o	50 ^d	0.0005 ^t
HFC	R32	CH ₂ F ₂	Difluoromethane	670 ^b	78 ^e	43.04 ^j	0.2 ^p	1000 ^d	0 ^e
HFC	R116	CF ₃ CF ₃	Perfluoroethane	11900 ^d	20 ^d	-	-	1000 ^d	0 ^d
HFC	R125	CF ₃ CF ₂ H	Pentafluoroethane	3450 ^b	66 ^e	96.74 ⁱ	2.3 ^q	1000 ^d	0.00003 ^f
HFC	R134a	C ₂ H ₂ F ₄	1,1,1,2-Tetrafluoroethane	1410 ^b	101 ^e	87.00 ⁱ	1.06 ^r	1000 ^d	0.000015 ^f
HFC	R143a	CH ₃ CF ₃	1,1,1-Trifluoroethane	4400 ^b	73 ^e	70.5 ^j	1.74 ^p	1000 ^d	0 ^f
HFC	R152a	C ₂ H ₄ F ₂	1,1-Difluoroethane	122 ^b	113 ^e	69.21 ⁱ	0.75 ⁿ	1000 ^d	0 ^g
HFC	R218	CF ₃ CF ₂ CF ₃	Perfluoropropane	8600 ^d	72 ^d	-	-	1000 ^d	0 ^d
HFC	R227ea	CF ₃ CHFCF ₃	Nonafluoropropane	3500 ^d	103 ^d	-	2.51 ^p	1000 ^d	0 ^d
HFC	R236fa	CF ₃ CH ₂ CF ₃	Hexafluoropropane	9400 ^d	125 ^d	-	2.65 ^p	1000 ^d	0 ^d
HC	R290	C ₃ H ₈	Propane	3 ^e	97 ^e	74.66 ⁱ	2.36 ^q	2500 ^d	0 ^f
HC	R600	C ₄ H ₁₀	n-Butane	20 ^f	152 ^d	100.59 ⁱ	2.89 ⁱ	800 ^d	0 ^f
HC	R600a	C ₄ H ₁₀	Isobutane	3 ^e	135 ^e	96.88 ^j	2.76 ^p	800 ^d	0 ^g
HC	R1270	C ₃ H ₆	Propene	3 ^e	92 ^e	64.47 ^k	1.77 ^p	660 ^d	0 ^f

Cont. Table 31

	R717	NH ₃	Ammonia	0 ^e	133 ^e	80.16 ⁱ	0.23 ^p	25 ^d	0 ^f
	R744	CO ₂	Carbon dioxide	1 ^g	31 ^e	38.42 ⁱ	0.83 ^p	5000 ^d	0 ^g
HFE	E125	CF ₃ -O-CHF ₂	Pentafluorodimethyl ether	14800 ^h	-	-	1.39 ^p	-	0 ^b
HFE	E134	CHF ₂ -O-CHF ₂	1,1,1',1'- Tetrafluorodimethyl ether	5760 ^h	147 ^g	-	-0.32 ^h	-	0 ^b
HFE	E7000	C ₃ F ₇ -O-CH ₃	Heptafluoropropyl methyl ether	450 ^h	165 ^g	-	0.30 ^h	-	0 ^b
HFE	E7100	C ₄ F ₉ -O-CH ₃	Methyl nonafluorobutyl ether	410 ^h	196 ^g	-	0.56 ^h	-	0 ^b
HFE	E7200	C ₄ F ₉ -O-C ₂ H ₅	Ethyl nonafluorobutyl ether	60 ^h	209 ^g	76.56 ^m	1.05 ^h	200 ^m	0 ^b
	Blend	Components	Composition [% of mass]	GWP ₁₀₀ [kg CO ₂ eq./kg]	t _c [°C]	C _p [J/(mol*K)]	c _{ow} [log c _{ow}]	TWA [ppm]	ODP [R11 eq./ kg]
HFC	R404A	R125/R143a/R134a	44/52/4	3862 ^x	72 ^d	-	3260 ^f	-	0 ^d
HFC	R407C	R32/R125/R134a	23/25/52	1750 ^x	87 ^e	83.01 ^u	0.97 ^v	1000 ^v	0.0002 ^f
HFC	R410A	R32/R125	50/50	2060 ^x	72 ^e	60.96 ^u	0.85 ^w	1000 ^f	0.000015 ^x

GWP₁₀₀ – Global warming potential, t_c – Critical temperature, C_p – Heat capacity of vapour at 25 °C, TWA – Time-weighted average exposure limit [ppm],

c_{ow} – Octanol-water partition coefficient, ODP – Ozone depletion potential,

^a WMO 2003, ^b IPCC 2006, ^c IPCC 2001, ^d Calm & Hourahan 2001, ^e Bitzer 2004, ^f FKW 2000, ^g Devotta et al. 2005, ^h Tsai 2005, ⁱ Knovel 2003,

^j MDL 2005, ^k NIST 2005, ^l Yaws 1999, ^m 3M 2007, ⁿ Howard 1993, ^o Howard 1990, ^p SRC 1999, ^q Howard 1997, ^r ECETOC 2006, ^s McCulloch 1999,

^t Duvedi 1997, ^u Calculated using mass-composition, ^v GHC 2007, ^w GHC 2005, ^x Calculated, - Not available

A2 Average monthly temperature of some European cities

Table 32: Average monthly temperature [°C] of some European cities

	Town	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Spain	Barcelona	13.4	14.6	15.9	17.6	20.5	24.2	27.5	28	25.5	21.5	17	14.3
	Sevilla	15.9	17.9	21.2	22.7	26.4	31	35.3	35	31.6	25.6	20.1	16.6
	Madrid	9.7	12	15.7	17.5	21.4	26.9	31.2	30.7	26	19	13.4	10.1
	Bilbao	13.2	14.5	15.9	16.8	20.1	22.6	25.2	25.5	24.4	20.8	16.4	14
	Malaga	16.6	17.7	19.1	20.9	23.8	27.3	23.7	29.9	30.3	23.7	19.9	17.4
Germany	Frankfurt	4	5.6	10.4	14.5	19.5	22.3	24.8	24.8	20.1	14	7.7	5
	Berlin	2.9	4.2	8.5	13.2	18.9	21.6	23.7	23.6	18.8	13.4	7.1	4.4
	Munich	2.7	4.3	9	12.5	18	20.5	23.1	23	18.8	13.2	6.9	3.7
	Hamburg	3.5	4.4	8	12.3	17.5	19.9	22.1	22.2	17.9	13	7.5	4.6
	Cologne	5.2	6.6	10.5	14.2	19	21.3	23.7	23.7	19.6	14.6	9	6.2
Sweden	Gothenburg	1	1	5	10	16	20	21	21	16	12	6	3
	Kiruna	-10	-8	-4	1	7	14	17	14	8	2	-5	-8
	Malmö	2	2	5	10	16	20	21	21	17	12	7	4
	Stockholm	-1	-1	3	9	16	21	22	20	15	10	5	1
	Sundsvall	-5	-3	2	7	14	19	21	19	14	9	2	-2

A3 Life cycle inventory

The inventory tables for the production of refrigerants are listed in the Attachment A3-1. The inventories include material input, energy consumption for production processes, and emissions (refrigerant emissions not included). For the emissions of refrigerant during production phase, three scenarios were created (worst-case, average, best-case). In Table 6, those direct emission scenarios are listed for all refrigerants. Nominal charges for each refrigerant are listed in Table 5. Energy for the production of one standard A/C system is documented in Table 44.

The inventory tables for the operation phase are listed in Attachment A3-2. They include the additional energy consumption due to the A/C system weight (Table 45), and the energy consumption due to operating the system (Table 46). The three scenarios for direct emissions of refrigerant during operation phase are listed in Table 8.

In Attachment A3-3, the inventories of the disposal phase are listed. Table 47 includes the feedstock and the resulting combustion products. The energy consumption from the disposal of the A/C system is shown in Table 48. In Table 49, the emissions of refrigerant during disposal processes are listed.

A3-1 Production phase

Production of refrigerants

Production of R134a (1,1,1,2-Tetrafluoroethane, CH₂FCF₃)

In general, the commercial production of R134a follows one of three processes (ECETOC 2006):

- Hydro-fluorination of trichloroethylene, via 1-chloro-2,2,2-trifluoroethane (R133a);
- Isomerisation/ hydro-fluorination of 1,1,2-trichloro-1,2,2-trifluoroethane (R113) to 1,1-dichloro-1,2,2,2-tetrafluoroethane (R114) followed by hydro-dechlorination of R114a;
- Hydro-fluorination of tetrachloroethylene (perchloroethylene) to 1-chloro-1,2,2,2-tetrafluoroethane (R124) and subsequent hydro-dechlorination to R134a

It should be mentioned that all production paths produce CFCs or HCFCs, which have an ozone depleting effect. The total demand of R134a in 2002 was 142 kt (IPCC 2006). If the business-as-usual scenario is applied, the IPCC predict that the demand in 2025 will rise to 446 kt, when mitigation measures are implemented the demand of R134a will be 337 kt in 2025 (IPCC 2006).

For the production of R134a, three different inventories were found (McCulloch & Lindley 2003, Krieger et al. 2004, Frischknecht 1999b). Frischknecht (1999b) is the only one who includes emissions of R113 and R124. Because such emissions are crucial for the environmental impact, it was decided to take the inventory from Frischknecht (1999b) for comparison with other refrigerants.

Electricity (medium voltage) was converted from MJ to kWh using the factor 3.6 (BFE 2007).

Table 33: Production of 1 kg R134a (Frischknecht 1999b)

Material input	Units	Quantity	
Trichloroethylene	kg	0.68	
Perchloroethylene	kg	0.9	
Hydrogen fluoride	kg	0.845	
Chlorine	kg	0.385	
Hydrogen H ₂	kg	0.02	
Transport input	Units	Quantity	Notes
Truck 40 t	tkm	0.62	Equals 558.3 kg CO ₂ or 175 kg diesel
Energy input	Units	Quantity	Notes
Natural gas	MJ	24	
Electricity (medium voltage)	MJ	3.7	Equals 1.028 kWh
Material output	Units	Quantity	Compartment of destination
R134a	kg	1	PRODUCT
Hydrochloric acid §	kg	1.64	Sold; not accounted
R113 p (Trichloro-trifluoro-ethane)	kg	0.01	Air
R124 p (Chloro-tetrafluoroethane)	kg	0.01	Air

Production of R152a (1,1-Difluoroethane, CHF_2CH_3)

R152a is produced by the reaction of hydrogen chloride (HCl), hydrogen fluoride (HF), and chloroethylene ($\text{C}_2\text{H}_3\text{Cl}$) in the presence of a tin chloride (SnCl_4) catalyst. The products react in a subsequent step with liquid phase HF. R152a is recovered from the process stream (ECETOC 2004). The annual global demand of R152a in 2002 was 4 kt (IPCC 2006). For the year 2025, the total production is estimated to be between 2-4 kt (IPCC 2006).

The inventory of R152a (Krieger et al. 2004) was supplemented by HCC and HCFC emissions that are stated in the patent from DuPont (2002). As emissions of those substances have an impact on the environment, the supplemented inventory will be used for comparing R152a with other refrigerants (Table 34).

Table 34: Production of 1 kg R152a (Krieger et al. 2004)

Material input	Units	Quantity	
Vinylchloride	kg	0.946	
Hydrogen fluoride	kg	0.606	
Energy input	Units	Quantity	
Primary energy sources	MJ	53.6	
Material output	Units	Quantity	Compartment of destination
R152a	kg	1	PRODUCT
HCl §	kg	0.552	Sold; not accounted
Hydrogen fluoride	kg	0.01	Air *
R151a (1-Chloro-1-fluoroethane)	kg	0.01	Air *
R150 (1,2-Dichloroethane)	kg	0.01	Air *

* DuPont (2002) and own assumptions

Production of R290 (Propane, C_3H_8) and R600a (Isobutane, C_4H_{10})

R290 and R600a are extracted from natural gas mixtures (IPCC 2006). Additionally electricity consumption similar to that of carbon dioxide is assumed (Frischknecht 1999b). Leakage from the production process plant comprises a variety of hydrocarbons (HC). For each kg of R290 or R600a about 0.14 kg CO_2 , 0.5 g HC, and 0.7 g methane are emitted (Gover et al. 1996). The inventories are listed in Table 35 and Table 36.

Table 35: Production of 1 kg R290 (Frischknecht 1999b)

Material input	Units	Quantity	
Propane	kg	1	
Transport input	Units	Quantity	Notes
Truck 28 t	tkm	0.5	Equals 210.4 kg CO ₂ or 66 kg diesel
Energy input	Units	Quantity	
Electricity (medium voltage)	MJ	0.72	
Material output	Units	Quantity	Compartment of destination
R290	kg	1	PRODUCT
Carbon dioxide	kg	0.14	Air *
Hydrocarbons	kg	0.0005	Air *
Methane	kg	0.0007	Air *

* Gover et al. (1996)

Table 36: Production of 1 kg R600a (Frischknecht 1999b)

Material input	Units	Quantity	
Butane	kg	1	
Transport input	Units	Quantity	Notes
Truck 28 t	tkm	0.5	Equals 210.4 kg CO ₂ or 66 kg diesel
Energy input	Units	Quantity	
Electricity (medium voltage)	MJ	0.72	
Material output	Units	Quantity	Compartment of destination
R600a	kg	1	PRODUCT
Carbon dioxide	kg	0.14	Air *
Hydrocarbons	kg	0.0005	Air *
Methane	kg	0.0007	Air *

* Gover et al. (1996)

Production of R744 (Carbon dioxide, CO₂)

Carbon dioxide is recovered from industrial exhaust gases. Some of the main industrial sources are (Kirk-Othmer 1993):

- Ammonium and hydrogen production
- Exhaust gases from incineration of coke, coal, natural gas, and fuel oil
- Lime kiln
- Production of sodium phosphate

According to data availability, the CO₂ was derived from the aluminium production process (Frischknecht 1999b). The recovered CO₂ has to be cleaned before it can be used in technical facilities.

Table 37: Production of 1 kg R744 (Frischknecht 1999b)

Material input	Units	Quantity	
Carbon dioxide	kg	2.1	
Transport input	Units	Quantity	Notes
Truck 28 t	tkm	0.15	Equals 63.1 kg CO ₂ or 20 kg diesel
Energy input	Units	Quantity	
Natural gas	MJ	1.7	
Oil	MJ	0.3	
Electricity (medium voltage)	MJ	0.72	
Material output	Units	Quantity	Compartment of destination
R744	kg	1	PRODUCT
Methane	kg	0.005	Air
Mono-ethyl-amin	kg	0.008-0.018	Not accounted for

Production of R30 (Dichloromethane, CH₂Cl₂)

Dichloromethane is produced by chlorination of methane (Wells 1991). A mixture of methane, methyl chloride, and chlorine is brought into a Ni-reactor with a temperature of 350-400 °C. Within that reactor, the compounds react to several chloromethane compounds. The gas is cooled and washed with acid. After compression, drying, and cooling, the individual substances are isolated by means of distillation.

There is no data regarding the energy consumption during production of dichloromethane. As dichloromethane is produced in the same facilities than trichloromethane, the energy consumption of the trichloromethane production is assumed to be adequate for the dichloromethane production (Frischknecht 1999b).

Table 38: Production of 1 kg R30 (Frischknecht 1999b)

Material input	Units	Quantity	Notes
Chlorine	kg	1.67	
Natural gas (feedstock) *	MJ	8.8	Equals 0.25m ³
Energy input	Units	Quantity	
Natural gas	MJ	11	
Electricity (medium voltage)	MJ	1.6	
Material output	Units	Quantity	Compartment of destination
R30	kg	1	PRODUCT
Hydrochloric acid §	kg	0.86	Sold; not accounted

* Assumption: natural gas is 100 % methane

Production of E125 (Pentafluorodimethyl ether, $\text{CF}_3\text{OCF}_2\text{H}$)

E125 is produced by electrochemical fluorination of dimethyl ether (Simons 1950). E125 has to be isolated from the mixture of fluorinated ether by means of low-temperature fractional distillation. Assuming that the molar yield of E125 is 20 %, the input of dimethyl ether and hydrogen fluoride were calculated using molar weights and the ratio 1/9 of dimethyl ether and hydrogen fluoride that is stated in the US patent No. 2,500,388 (Simons 1950). For accounting for emissions of other fluorinated ethers, 1,1,1-trifluoromethyl methyl ether (CF_3OCH_3) was taken as a representative. Emissions of fluorinated ethers are assumed to be 1 % of their molar yield that is supposed to be 80 % of the dimethyl ether input. No data was available on the transport and energy demand of the E125 production. A similarity analysis between the refrigerants of that study showed that the HFEs are most similar to R134a. Therefore, the input of energy and transport of R134a production was taken for E125. The so far developed inventory is disclosed in Table 39. Electricity (medium voltage) was converted from MJ to kWh using the factor 3.6 (BFE 2007).

Table 39: Production of 1 kg E125 (O'Neill & Holdsworth 1990, Simons 1950)

Material input	Units	Quantity	Notes
Dimethyl ether	kg	1.69	Assumption: yield = 20 % of dimethyl ether mole
Hydrogen fluoride	kg	15.25	
Transport input	Units	Quantity	Notes
Truck 40 t	tkm	0.62*	Equals 558.3 kg CO_2 or 175 kg diesel
Energy input	Units	Quantity	Notes
Natural gas	MJ	24*	Equals 1.028 kWh
Electricity (medium voltage)	MJ	3.7*	
Material output	Units	Quantity	Compartment of destination
E125	kg	1	PRODUCT
Other fluorinated ether from dimethyl ether	kg	0.029	Air, Assumption: yield of mixture of fluorinated dimethyl ether (for calculation: CF_3OCH_3) equals 80 % of dimethyl ether mole; 1 % emitted to air

* Restrepo (2007): greatest similarity with R134a, data taken from R134a (Frischknecht 1999b)

Production of E134 (Tetrafluorodimethyl ether, $\text{CHF}_2\text{OCHF}_2$)

The process of E134 production involves the fluorination of dimethyl ether. The ether may be prepared by an electrochemical fluorination process, which produces a mixture of various fluorinated methyl ethers, including E134 (O'Neill & Holdsworth 1990). The calculation was done equal to that of E125. The inventory is specified in Table 40. Electricity (medium voltage) was converted from MJ to kWh using the factor 3.6 (BFE 2007).

Table 40: Production of 1 kg E134 (O'Neill & Holdsworth 1990, Simons 1950)

Material input	Units	Quantity	Notes
Dimethyl ether	kg	1.95	Assumption: yield = 20 % of dimethyl ether mole
Hydrogen fluoride	kg	17.6	
Transport input	Units	Quantity	Notes
Truck 40 t	tkm	0.62*	Equals 558.3 kg CO ₂ or 175 kg diesel
Energy input	Units	Quantity	Notes
Natural gas	MJ	24*	Equals 1.028 kWh
Electricity (medium voltage)	MJ	3.7*	
Material output	Units	Quantity	Compartment of destination
E134	kg	1	PRODUCT
Other fluorinated ether from dimethyl ether	kg	0.033	Air; Assumption: yield of mixture of fluorinated dimethyl ether (for calculation: CF_3OCH_3) equals 80 % of dimethyl ether mole; 1 % emitted to air

* Restrepo (2007): greatest similarity with R134a, data taken from R134a (Frischknecht 1999b)

Production of E7000 (Heptafluoropropyl methyl ether, C₃F₇OCH₃)

E7000 is produced by the reaction of potassium fluoride and pentafluoropropionic acid with 1-methoxyheptafluoro-1-isobutene in the presence of diglyme, following the processes described in the US patent No. 6,023,002 (Behr & Cheburkov 2000). Besides E7000, hexafluoropivaloyl fluoride and hexafluoropropane are produced. It is assumed that 1 % of the yields of the latter substances are emitted to the atmosphere. The amount of chemicals needed to produce 1 kg E7000 were recalculated from the yields documented in the patent (Behr & Cheburkov 2000) using molar weights. No data on transport and energy input is available from the patent. Because the similarity analysis using the Euclidean distance and single linkage technique of aggregation shows E7000 similar to R134a, it was assumed that the production of E7000 requires the same amount of energy and transport that is necessary for R134a production. The full inventory is documented in Table 41. Electricity (medium voltage) was converted from MJ to kWh using the factor 3.6 (BFE 2007).

Table 41: Production of 1 kg E7000 (Behr & Cheburkov 2000)

Material input	Units	Quantity	Notes
Pentafluoropropionic acid	kg	0.953	Calculation: recalculated pentafluoropropionic acid in mole and 86 % of that as E7000, converted to kg E7000
Potassium fluoride	kg	0.369	
Diglyme	kg	2.529	
Methoxyfluoroisobutene	kg	2.183	
Transport input	Units	Quantity	Notes
Truck 40 t	tkm	0.62 ^a	Equals 558.3 kg CO ₂ or 175 kg diesel
Energy input	Units	Quantity	Notes
Natural gas	MJ	24 ^a	Equals 1.028 kWh
Electricity (medium voltage)	MJ	3.7 ^a	
Material output	Units	Quantity	Compartment of destination
E7000	kg	1 ^b	PRODUCT
Hexafluoropivaloyl fluoride [CH ₃ C(CF ₃) ₂ C(O)F]	kg	0.62	1 % emitted to air
1,1,1,3,3,3-Hexafluoropropane [CF ₃ CH ₂ CF ₃]	kg	0.4	1 % emitted to air

^a Restrepo (2007): greatest similarity with R134a, data taken from R134a (Frischknecht 1999b),

^b Recalculated pentafluoropropionic acid in mole and 86 % of that as E7000, converted to kg E7000

Production of E7100 (Methylnonafluorobutyl ether, C₄F₉OCH₃)

Using essentially the same procedure as for the production of E7000, E7100 is produced by the reaction of perfluorobutyric acid fluoride and potassium fluoride with 1-methoxyfluoro-1-isobutene in the presence of diglyme (Behr & Cheburkov 2000). This reaction produces not only E7100 but also hexafluoropivaloyl fluoride and hexafluoropropane. For the inventory, it is assumed that 1 % of the yields of the latter substances are emitted to the atmosphere. The amount of chemicals needed to produce 1 kg E7100 were recalculated from the yields documented in the patent (Behr & Cheburkov 2000) using molar weights. Like for E7000, no data on transport and energy input is available from the patent. Because the similarity analysis shows E7100 similar to R134a, it was assumed that the production of E7100 requires the same amount of energy and transport that is necessary for R134a production (Table 42). Electricity (medium voltage) was converted from MJ to kWh using the factor 3.6 (BFE 2007).

Table 42: Production of 1 kg E7100 (Behr & Cheburkov 2000)

Material input	Units	Quantity	Notes
Perfluorobutyric acid fluoride	kg	1.12	Calculation: recalculated perfluorobutyric acid in mole and 86 % of that as E7100, converted to kg E7100
Potassium fluoride	kg	0.33	
Diglyme	kg	3.59	
Methoxyfluoroisobutene	kg	2.14	
Transport input	Units	Quantity	Notes
Transport LKW 40 t	tkm	0.62 ^a	Equals 558.3 kg CO ₂ or 175 kg diesel
Energy input	Units	Quantity	Notes
Natural gas	MJ	24 ^a	Equals 1.028 kWh
Electricity (medium voltage)	MJ	3.7 ^a	
Material output	Units	Quantity	Compartment of destination
E7100	kg	1 ^b	PRODUCT
Hexafluoropivaloyl fluoride [CH ₃ C(CF ₃) ₂ C(O)F]	kg	0.52	1 % emitted to air
1,1,1,3,3,3-Hexafluoropropane [CF ₃ CH ₂ CF ₃]	kg	0.43	1 % emitted to air

^a Restrepo (2007): greatest similarity with R134a, data taken from R134a (Frischknecht 1999b),

^b Recalculated perfluorobutyric acid in mole and 86 % of that as E7100, converted to kg E7100

Production of E7200 (Ethylnonafluorobutyl ether, C₄F₉OC₂H₅)

E7200 is produced by the reaction of perfluorobutyric acid fluoride and potassium fluoride with 1-ethoxyheptafluoro-1-isobutene in diglyme (Behr & Cheburkov 2000). The reaction yields E7200 and hexafluoropropane. It is assumed that 1 % of the yielded hexafluoropropane is emitted to the atmosphere. The amount of chemicals needed to produce 1 kg E7200 were recalculated from the yields documented in the patent (Behr & Cheburkov 2000) using molar weights. Transport and energy input was assumed as being identical to that of E7000 and E71000. The full inventory is documented in Table 43. Electricity (medium voltage) was converted from MJ to kWh using the factor 3.6 (BFE 2007).

Table 43: Production of 1 kg E7200 (Behr & Cheburkov (2000))

Material input	Units	Quantity	Notes
Pentafluoropropionyl fluoride	kg	0.5995	Calculation: recalculated perfluoropropionyl in mole and 86 % of that as E7200, converted to kg E7200
Potassium fluoride	kg	0.228	
Diglyme	kg	1.806	
Ethoxyfluoroisobutene	kg	1.034	
Transport input	Units	Quantity	Notes
Truck 40 t	tkm	0.62 ^a	Equals 558.3 kg CO ₂ or 175 kg diesel
Energy input	Units	Quantity	Notes
Natural gas	MJ	24 ^a	Equals 1.028 kWh
Electricity (medium voltage)	MJ	3.7 ^a	
Material output	Units	Quantity	Compartment of destination
E7200	kg	1 ^b	PRODUCT
1,1,1,3,3,3-Hexafluoropropane [CF ₃ CH ₂ CF ₃]	kg	0.466	1 % emitted to air

^a Restrepo (2007): greatest similarity with R134a, data taken from R134a (Frischknecht 1999b),

^b Recalculate recalculate perfluoropropionyl in mole and 86 % of that as E7200, converted to kg E7200

*Production of A/C system***Table 44:** Energy consumption during production of one A/C system, taken as standard for all A/C systems (Vainio 2003)

Energy input	Units	Quantity	
Energy consumption	MJ	1675	
Material output	Units	Quantity	Compartment of destination
A/C system	Piece	1	PRODUCT

A3-2 Operation phase

*Additional fuel consumption due to weight of A/C system***Table 45:** Additional fuel consumption due to A/C system weight

Refrigerant	Weight [kg]	Fuel consumption, calculated [L/100km]
R30	17 ^a	0.0969
R134a	15 ^b	0.0855
R152a	17 ^c	0.0969
R290	17 ^c	0.0969
R600a	17 ^c	0.0969
R744	17 ^c	0.0969
E125	15 ^d	0.0855
E134	17 ^a	0.0969
E7000	17 ^a	0.0969
E7100	15 ^d	0.0855
E7200	17 ^a	0.0969

Calculation based on: 57 L/ 100 kg/ 10 000 km (Direct expansion - 15 kg;
Secondary loop - 17 kg)

^a Own assumption: cancerogen, flammable, or slightly toxic substance,

^b Petitjean et al. (2000), ^c Based on the direct expansion system of R134a (Petitjean et al. 2000) plus additional 2 kg according to Hafner et al. (2004),

^d Own assumption: non-flammable substance

*Additional fuel consumption due to compression***Table 46:** Annual energy consumption due to compression of refrigerant based on worst-case, average, and best-case operation scenario

Refrigerant	Units	Worst-case [260 h/year]	Average [104 h/year]	Best-case [10 h/year]	Data source
R30	kWh	3177	1271	122	a
R134a	kWh	832	333	32	b
R152a	kWh	775	310	30	b
R290	kWh	870	348	33	b
R600a	kWh	901	360	35	b
R744	kWh	1166	466	45	c
E125	kWh	477	191	18	a
E134	kWh	2327	931	89	a
E7000	kWh	612	245	24	d
E7100	kWh	692	277	27	d
E7200	kWh	625	250	24	d

^a Thermophysical data from DIPPR 801 database, interpolated to averaged inlet/outlet pressure and temperature values from Ghodbane (1999);

^b Inlet/outlet pressure and temperature values from Ghodbane (1999), enthalpy change calculated with NIST database, linear interpolation; ^c Inlet/outlet pressure and temperature values from Delphi (2006), enthalpy change calculated with NIST database, linear interpolation, and temperature values from Ghodbane (1999);

^d Thermophysical data from 3M (2007), interpolated to averaged inlet/outlet pressure

A3-3 Disposal phase

Emissions due to refrigerant disposal

Assuming incineration of all refrigerants recovered from A/C systems, complete combustion with oxygen is presumed (Table 47). Products of combustion are water, CO₂, HCl, and HF. Direct emissions of HF and HCl into the atmosphere are estimated to be 1 % (7.8 g HF for 1 kg R134a, 6.1 g HF for 1 kg R152a etc.). Water and CO₂ from combustion will be emitted to air to 100 %.

Table 47: Input and combustion products during incineration of 1 kg refrigerant

Refrigerant	Input [kg]			Product [kg]			
	Refrigerant	H ₂	O ₂	CO ₂	H ₂ O	HF	HCl
E125	1	0.04	0.47	0.65	0.13	0.74	
E134	1	0.03	0.54	0.75	0.15	0.68	
E7000	1	0.024	0.768	1.056	0.072	0.72	
E7100	1	0.03	0.64	0.88	0.07	0.72	
E7200	1	0.023	0.485	0.667	0.068	0.531	
R134a	1	0.06	0.63	0.86	0.35	0.78	
R152a	1	0.03	1.45	1.33	0.55	0.61	
R290	1	0.09	3.63	2.99	1.63		
R600a	1	0.03	3.58	3.03	1.55		
R744	1			1			
R30	1		0.38	0.52			0.86

Input and product values derived from stoichiometric formular

*Disposal of A/C system***Table 48:** Energy consumption during dismantling of one A/C system taken as standard for all A/C systems (Vainio 2003)

Material input	Units	Quantity
A/C system	Piece	1
Energy input	Units	Quantity
Primary energy sources	MJ	837.5

Direct refrigerant emissions (disposal phase)

Table 49: Direct refrigerant emission scenarios during disposal phase

Process step	Units	Worst-case
Dismantling	% of nominal charge	100 ^a
Process step	Units	Average
Dismantling	% of nominal charge	50 ^b
Process step	Units	Best-case
Dismantling	% of nominal charge	5 ^c

^a Own assumption : no legal regulation and/or control, ^b Barrault et al. (2003),

^c Own assumption: based on the end-of-life vehicle directive (BGB 2006)

A4 Calculation factors of EI99 impact assessment

Table 50: Normalisation and weights using hierarchist perspective combined with the default weighting

	Normalisation	Weights
Human Health	1.54E-02	400
Ecosystem Quality	5.13E+03	400
Resources	8.41E+03	200

Table 51: Damage factors for EI99 calculation; hierarchist perspective (default) (excerpt from Goedkoop & Spriensma 2001 and own changes*), all damage factors are expressed per kg emission or otherwise indicated, the unit of damage in the category Human Health is DALYs (Disability Adjusted Life Years), the unit in the category Ecosystem Quality is PDF*m²*yr (Potentially Disappeared Fraction of Species from one m² during one year), the unit in the category Resources is MJ surplus energy

Compartment	Substance (EI99 list)	Damage factor	Normalized damage factor	Weighted damage factor [Pt/kg]	Substance (present study)
-------------	-----------------------	---------------	--------------------------	--------------------------------	---------------------------

1. Damage category Human Health

1.1 Carcinogenic effects on humans

Air	1,2-Dichloroethane	2.60E-04	1.94E-03	7.74E-01	R150
Air	Dichloromethane	4.36E-07	2.83E-05	1.13E-02	R30
Water	1,2-Dichloroethane	2.98E-05	1.94E-03	7.74E-01	R150
Water	Dichloromethane	4.97E-07	3.23E-05	1.29E-02	R30

Cont. Table 51

Compartment	Substance (EI99 list)	Damage factor	Normalized damage factor	Weighted damage factor [Pt/kg]	Substance (present study)
1.2 Respiratory effects on humans caused by organic substances					
Air	Butane	7.57E-07	4.92E-05	1.97E-02	n-Butane
Air	CxHy halogenated	3.50E-07	2.27E-05	9.09E-03	Hexafluoropivaloyl fluoride, hexafluoropropane; R151a; R113, R124; R134a; R152a
Air	CxHy chloro	3.50E-07	2.27E-05	9.09E-03	R150
Air	Dichloromethane	1.45E-07	9.42E-06	3.77E-03	R30
Air	Dimethylether	3.74E-07	2.43E-05	9.71E-03	Fluorinated ether from dimethyl ether
Air	Ethers	7.40E-07	4.81E-05	1.92E-02	E125, E134, E7000, E7100, E7200
Air	i-Butane	6.64E-07	4.31E-05	1.72E-02	R600a
Air	Methane	1.28E-08	8.31E-07	3.32E-04	Methane
Air	Hydrocarbons	----	----	1.88E-02 *	Hydrocarbons
Air	Propane	3.83E-07	2.49E-05	9.95E-03	R290
Air	VOC	6.46E-07	4.19E-05	1.68E-02	Hydrocarbon VOCs
Air	Cyclohexane	6.21E-07	4.03E-05	1-61E-02	RC270

1.3 Respiratory effects on humans caused by inorganic substances

Air	SO ₂	5.46E-05	3.55E-03	1.42E+00	SO ₂
-----	-----------------	----------	----------	----------	-----------------

1.4 Damages to human health caused by climate change

Air	Carbon dioxide	2.10E-07	1.36E-05	5.45E-03	R744, E7200, R290, R600a (GWP ₁₀₀ : 20-100 years)
Air	Methane	4.40E-06	2.86E-04	1.14E-01	(GWP ₁₀₀ : <20 years)
Air	Methylene chloride	1.90E-06	1.23E-04	4.94E-02	R30
Air	CFC-113	6.30E-04	4.09E-02	1.64E+01	R113
Air	HCFC-22	2.80E-04	1.82E-02	7.27E+00	R22
Air	HCFC-124	8.50E-05	5.52E-03	2.21E+00	R124
Air	HFC-134a	2.70E-04	1.75E-02	7.01E+00	R134a
Air	HCFC-141b	5.20E-05	3.38E-03	1.35E+00	R151a
Air	HCFC-142b	3.40E-04	2.21E-02	8.83E+00	R150

Cont. Table 51

Compartment	Substance (EI99 list)	Damage factor	Normalized damage factor	Weighted damage factor [Pt/kg]	Substance (present study)
Air	HFC-152a	2.90E-05	1.88E-03	7.53E-01	R152a
Air	Nitrous oxide	6.90E-05	4.48E-03	1.79E+00	E125, E134, E7000, E7100 (GWP ₁₀₀ : >100 years)
Air	Perfluoromethane	1.40E-03	9.09E-02	3.64E+01	Fluorinated ether from dimethyl ether
Air	Perfluoropentane	1.70E-03	1.10E-01	4.42E+01	Hexafluoropivaloyl fluoride
Air	Perfluoropropane	1.50E-03	9.74E-02	3.90E+01	Hexafluoropropane

1.5 Human health effects caused by ozone layer depletion

Air	CFC-113	9.48E-04	6.16E-02	2.46E+01	R113
Air	HCFC-22	4.21E-05	2.73E-03	1.09E+00	R22
Air	HCFC-124	3.16E-05	2.05E-03	8.21E-01	R124
Air	HCFC-141b	1.05E-04	6.82E-03	2.73E+00	R151a
Air	HCFC-142b	5.26E-05	3.42E-03	1.37E+00	R150

2. Damage category Ecosystem Quality

2.1 Damage to Ecosystem Quality caused by the combined effect of acidification and eutrophication

Air	SO ₂	1.04E+00	2.03E-04	8.12E-02	SO ₂
-----	-----------------	----------	----------	----------	-----------------

3. Damage category Resources

3.1 Damage to Resources caused by extraction of fossil fuels

kg	Natural gas	4.55E+00	5.41E-04	1.08E-01	Natural gas
MJ	Natural gas (resource)	1.50E-01	1.78E-05	3.57E-03	Natural gas
m ³	Natural gas (feedstock)	5.25E+00	6.24E-04	1.25E-01	Natural gas (feedstock)
kg	Crude oil	5.90E+00	7.02E-04	1.40E-01	Crude oil
MJ	Crude oil (resource)	1.44E-01	1.71E-05	3.42E-03	Crude oil
MJ	Energy from coal	8.59E-03	1.02E-06	2.04E-04	Energy from coal
MJ	Average of oil, natural gas, and coal	----	----	2.40E-03 *	Nuclear, wind, water, photovoltaic, others

*) Calculated values

Table 52: Standard EI99 indicators for specific processes and products (excerpt from Pré 2000)

Substance (Pré 2000)	Indicator	Description	Substance (present study)
Production of chemicals and others [mPt/kg]			
Chemicals organic	99	Average value for organic chemicals	Carbon dioxide, propane, butane, trichloroethylene, perchloroethylene, dimethylether, pentafluoropropionic acid, diglyme, methoxyfluoroisobutene, perfluorobutyric acid fluoride, ethoxyfluoroisobutene, pentafluoropropionyl fluoride, vinylchloride
Chemicals inorganic	53	Average value for inorganic chemicals	Potassium fluoride, fluorspar CaF_2 , sulphur
Hydrogen fluoride	140	Fluoric acid	
Chlorine	38	Cl_2 , produced with diaphragm production process (modern technology)	
H_2	830	Hydrogen gas; used for reduction processes	
O_2	12	Oxygen gas	
NaCl	6.6	Sodium chloride	Sodium or potassium chloride
Fuel petrol unleaded	210	Production of fuel only. Combustion excluded!	
Water demineralized	0.026	Processing only; effects on groundwater table (if any) disregarded	
Electricity [mPt/kWh]			
Electr. MV Europe (UCPTE)	23	Medium voltage (1 kV – 24 kV)	
Transport [mPt/tkm]			
Truck 28t	22	Road transport with 40 % load (European average including return)	
Truck 40t	15	Road transport with 50 % load (European average including return)	

A5 Degradation yields of some degradation products

Table 53: Atmospheric degradation products of certain refrigerants

Refrigerant	Degradation product	Yield from 1 mole refrigerant [mole]
R30	HCl	1 ^a
R134a	TFA (HF, CO ₂)	0.4 (0.6) ^b
R152a	COF ₂ (HF, CO ₂)	0.92 ^c
R290	CO ₂	1 ^d
R600a	CO ₂	1 ^d
E125	COF ₂ (HF, CO ₂)	1.52 ^e
E134	COF ₂ (HF, CO ₂)	2 ^e
E7000	C ₃ F ₇ OC(O)H	1 ^f
E7100	C ₄ F ₉ OC(O)H	1 ^g
E7200	C ₄ F ₉ OC(O)CH ₃ , C ₄ F ₉ OC(O)H	0.5 ^h 0.5 ^h

^a WHO (1996); ^b Franklin (1993); ^c Tuazon & Atkinson (1993); ^d Assumption; ^e Good et al. (1999) and Inoue (2001); ^f Ninomiya et al. (2000) ; ^g Tsai (2005) ; ^h Christensen et al. (1998),

Table 54: Amount of refrigerant emissions and corresponding degradation products of some refrigerants from one passenger car, Scenario: WC – worst-case, A – average, BC – best-case

Entire life cycle emissions	Emitted refrigerant	Scenario	Refrigerant emissions [g]	Degradation products [g]					
				TFA	PFCA	CF ₂ O	HF	HCl	CO ₂
	R134a	WC	2875	1156.8			338.2		
		A	1500	603.5			176.5		
		BC	275	110.6			32.4		
	E7000	WC	2875		3076.3				
		A	1500		1605.0				
		BC	275		294.3				
	E7100	WC	2875		3036.0				
		A	1500		1584.0				
BC		275		290.4					
E7200	WC	2875		1513.7					
	A	1500		789.8					
	BC	275		144.8					
E125	WC	2875			2120.7	1285.3		1413.8	
	A	1500			1106.5	670.6		737.6	
	BC	275			202.9	122.9		135.2	
E134	WC	2875			3216.1	1949.2		2144.1	
	A	1500			1678.0	1016.9		1118.6	
	BC	275			307.6	186.4		205.1	
R152a	WC	1885			1734.2	1051.0		1156.1	
	A	980			901.6	546.4		601.1	
	BC	165			151.8	92.0		101.2	
R30	WC	1885					1620.8	976.9	
	A	980					842.6	507.9	
	BC	162					141.9	85.5	

Cont. Table 54

	Emitted refrigerant	Scenario	Refrigerant emissions [g]	Degradation products [g]					
				TFA	PFCA	CF ₂ O	HF	HCl	CO ₂
1 year operation emissions	R134a	WC	208	83.7			24.5		
		A	109	43.9			12.8		
		BC	23	9.3			2.7		
	E7000	WC	208		222.6				
		A	109		116.6				
		BC	23		24.6				
	E7100	WC	208		219.6				
		A	109		115.1				
		BC	23		24.3				
	E7200	WC	208		109.5				
		A	109		57.4				
		BC	23		12.1				
	E125	WC	208			153.4	93.0		102.3
		A	109			80.4	48.7		53.6
		BC	23			17.0	10.3		11.3
	E134	WC	208			232.8	141.0		155.1
		A	109			121.9	73.9		81.3
		BC	23			25.7	15.6		17.2
	R152a	WC	141			129.7	78.6		86.5
		A	74			68.1	41.3		45.4
		BC	14			12.9	7.8		8.6
	R30	WC	141					121.2	73.1
		A	74					63.6	38.4
		BC	14					12.0	7.3

A6 Results of impact assessment

A6-1 CML02

Table 55: Results of studied refrigerants and contributions to different impact categories of CML02 under three different scenarios; ADP – Depletion of abiotic resources (excluding primary energy sources), PE – Demand of non-renewable primary energy, CC – Climate change, SOD – Stratospheric ozone depletion, AP - Acidification, EP - Eutrophication, POCP – Photo-oxidant formation, HTP – Human toxicity, FAETP – Fresh water aquatic toxicity, TETP – Terrestrial ecotoxicity

	Refrigerant	ADP [kJ]	PE [kg antimony eq.]	CC [kg CO ₂ eq.]	SOD [kg R11 eq.]	AP [kg SO ₂ eq.]	EP [kg PO ₄ ³⁻ eq.]	POCP [kg ethylene eq.]	HTP	FAETP	TETP
									[kg 1,4-DCB eq.]		
Average scenario	E125	28163015	0.8291	24842	0	235	43.7	130.6	404.5	0.053	0.00003
	E134	54124673	0.8291	12803	0	791	146.9	438.6	1357.0	0.049	0.00003
	E7000	30607533	0.8291	2995	0	288	53.4	159.6	494.3	0.052	0.00003
	E7100	31156240	0.8291	2973	0	299	55.5	165.7	512.9	0.052	0.00003
	E7200	30695704	0.8291	2407	0	292	54.1	161.7	500.5	0.038	0.00002
	R134a	32831981	0.8291	4699	0.023	341	63.1	188.3	584.1	20672.056	3.33694
	R152a	15707107	0.6334	1276	0.003	337	62.4	186.1	577.4	0.086	0.00006
	R290	18682493	0.4465	1333	0	363	67.5	201.4	622.6	0	0
	R600a	19144514	0.4465	1365	0	373	69.3	207.0	639.6	0	0
	R744	22022147	0.5791	1569	0	450	83.6	250.0	771.7	0	0
	R30	48557100	0.6145	3458	0	1041	193.2	576.7	1785.4	0.00003	0.000004

Cont. Table 55

	Refrigerant	ADP [kJ]	PE [kg antimony eq.]	CC [kg CO ₂ eq.]	SOD [kg R11 eq.]	AP [kg SO ₂ eq.]	EP [kg PO ₄ ³⁻ eq.]	POCP [kg ethylene eq.]	HTP	FAETP	TETP
									[kg 1,4-DCB eq.]		
Best-case scenario	E125	10824299	0.8078	5043	0	109	20.3	60.5	187.7	0.026	0.00002
	E134	13867608	0.8078	2671	0	174	32.3	96.6	299	0.023	0.00001
	E7000	11597398	0.8078	996	0	126	23.4	69.7	216.1	0.025	0.00002
	E7100	11121642	0.8078	951	0	115	21.4	63.9	198.1	0.025	0.00002
	E7200	11584084	0.8078	885	0	126	23.4	69.9	216.6	0.018	0.00001
	R134a	11225736	0.8078	1268	0.008	120	22.1	66.1	205.1	3957.027	0.638
	R152a	6099391	0.6150	467	0.001	131	24.2	72.3	224.2	0.033	0.00002
	R290	6787799	0.4464	484	0	133	24.7	73.7	228	0	0
	R600a	6832080	0.4464	487	0	134	24.9	74.3	229.7	0	0
	R744	6936216	0.5756	494	0	141	26.3	78.4	242.4	0	0
	R30	9251118	0.6087	659	0	198	36.8	109.8	340	0.00001	0.0000007
Worst-case scenario	E125	49380591	0.8504	46893	0	445	82.6	246.7	763.7	0.073	0.00005
	E134	113360583	0.8504	25052	0	1815	337	1006.1	3112.2	0.067	0.00004
	E7000	54599419	0.8504	5408	0	557	103.4	308.8	955.5	0.071	0.00004
	E7100	56830009	0.8504	5450	0	603	112	334.4	1034.9	0.071	0.00004
	E7200	54895583	0.8504	4298	0	566	105.1	314	971.4	0.053	0.00003
	R134a	61221574	0.8504	8800	0.038	709	131.1	391.2	1212.3	39122.577	6.316
	R152a	31632697	0.6517	2544	0.004	679	125.7	375	1162.8	0.135	0.00009
	R290	37659007	0.4466	2685	0	745	138.4	413.3	1277.5	0	0
	R600a	38814488	0.4466	2767	0	770	143	427.1	1320	0	0
	R744	46609040	0.5826	3319	0	963	178.8	533.5	1650.1	0	0
	R30	113778305	0.6204	8100	0	2440	452.8	1351.5	4183.3	0.00006	0.00001

Table 56: Results of the studied refrigerants and contributions to different impact categories of CML02; contribution to production, operation, and disposal phase under average scenario; ADP – Depletion of abiotic resources (excluding primary energy sources), PE – Demand of non-renewable primary energy, CC – Climate change, SOD – Stratospheric ozone depletion, AP - Acidification, EP - Eutrophication, POCP – Photo-oxidant formation, HTP – Human toxicity, FAETP – Fresh water aquatic toxicity, TETP – Terrestrial ecotoxicity

	Refrigerant	ADP [kJ]	PE [kg antimony eq.]	CC [kg CO ₂ eq.]	SOD [kg R11 eq.]	AP [kg SO ₂ eq.]	EP [kg PO ₄ ³⁻ eq.]	POCP [kg ethylene eq.]	HTP	FAETP	TETP
									[kg 1,4-DCB eq.]		
Production phase	E125	5723281	0.489	1450.6	0	0	0	0.00900	0	0	0
	E134	5736336	0.489	836.6	0	0	0	0.00930	0	0	0
	E7000	5723194	0.489	480.2	0	0.004	0	0.00683	0	0	0
	E7100	5737026	0.489	478.6	0	0.004	0	0.00683	0	0	0
	E7200	5694453	0.489	453.2	0	0.005	0	0.00683	0	0	0
	R134a	5652741	0.489	564.7	0.007651	0.072	0	0.00000	0.17	1119.75	0.180075
	R152a	9877	0.296	18.4	0.000855	0.055	0	0.00008	0.45	0.020701	0.000014
	R290	576841	0.128	42.2	0	0	0	0.00324	0	0	0
	R600a	576727	0.128	42.2	0	0	0	0.00562	0	0	0
	R744	340623	0.257	25.3	0	0	0	0.00001	0	0	0
	R30	6756	0.290	0.4	0	0.045	0	0.00278	0.08	0.000001	0.0000002
Operation phase	E125	22432191	0.021	17841.4	0	235.31	44	130.53747	403.93	0.027402	0.0000173
	E134	48381651	0.021	9806.2	0	790.990	147	438.54371	1356.48	0.02518	0.0000159
	E7000	24877148	0.021	2345.3	0	287.737	53	159.58816	493.78	0.026662	0.0000168
	E7100	25411980	0.021	2339.9	0	298.608	55	165.61327	512.41	0.026662	0.0000168
	E7200	24995736	0.021	1930.5	0	291.548	54	161.70142	500.17	0.019663	0.0000124
	R134a	27168337	0.021	3605.1	0.015316	340.839	63	188.32717	583.39	14677.278883	2.3693432
	R152a	15690224	0.018	1230	0.001710	336.506	62	186.1061	576.72	0.05271	0.0000351
	R290	18100343	0	1289.5	0	363.209	67	201.39862	622.64	0	0
	R600a	18562551	0	1322.4	0	373.121	69	206.9505	639.64	0	0
	R744	21681524	0.003	1543.5	0	450.136	84	249.50383	771.66	0	0
	R30	48549094	0.006	3455.5	0	1041.144	193	576.68681	1784.89	0.000022	0.0000029

Cont. Table 56

	Refrigerant	ADP [kJ]	PE [kg antimony eq.]	CC [kg CO ₂ eq.]	SOD [kg R11 eq.]	AP [kg SO ₂ eq.]	EP [kg PO ₄ ³⁻ eq.]	POCP [kg ethylene eq.]	HTP	FAETP	TETP
									[kg 1,4-DCB eq.]		
Disposal phase	E125	7543	0.319	5550.5	0	0.009	0	0.0375	0.52	0.025530	0.0000161
	E134	6686	0.319	2160.6	0	0.008	0	0.0375	0.48	0.023460	0.0000148
	E7000	7191	0.319	169.5	0	0.009	0	0.0375	0.51	0.02484	0.0000157
	E7100	7234	0.319	154.4	0	0.009	0	0.0375	0.51	0.02484	0.0000157
	E7200	5515	0.319	23	0	0.006	0	0.0375	0.37	0.01832	0.0000115
	R134a	10902	0.319	529.4	0.000006	0.369	0	0	0.55	4875.02691	0.787517
	R152a	7006	0.319	28	0	0.223	0	0	0.26	0.012627	0.000008
	R290	5309	0.319	0.9	0	0	0	0.0176	0	0	0
	R600a	5236	0.319	0.9	0	0	0	0.0307	0	0	0
	R744	0	0.319	0.6	0	0	0	0	0	0	0
	R30	1251	0.319	2.5	0	0.253	0	0.0153	0.45	0.000007	0.0000009

A6-2 EI99

Table 57: Results of EI99 assessment in Ecopoints [Pt], contribution from production, operation, and disposal phase and EI99 of the entire life cycle under worst-case, best-case, and average scenario

	Refrigerant	Production phase	Operation phase	Disposal phase	EI99
Average scenario	E125	13.62	20.09	6.06	39.77
	E134	13.78	33.94	6.06	53.78
	E7000	13.88	19.52	6.06	39.46
	E7100	13.85	19.57	6.06	39.48
	E7200	12.19	14.17	5.38	31.74
	R134a	12.55	20.55	8.03	41.13
	R152a	11.24	13.07	5.54	29.86
	R290	10.70	12.21	5.37	28.29
	R600a	10.70	12.44	5.37	28.51
	R744	10.70	14.26	5.35	30.32
	R30	10.71	27.59	5.37	43.67
Best-case scenario	E125	12.47	6.31	5.45	24.23
	E134	12.63	8.24	5.44	26.31
	E7000	12.04	7.14	5.44	24.63
	E7100	12.02	6.45	5.45	23.91
	E7200	11.32	6.75	5.37	23.45
	R134a	11.58	7.71	5.66	24.95
	R152a	11.04	6.94	5.39	23.37
	R290	10.70	6.91	5.36	22.97
	R600a	10.70	6.93	5.36	23.00
	R744	10.71	7.09	5.35	23.15
	R30	10.71	8.38	5.36	24.44
Worst-case scenario	E125	14.19	38.13	6.74	59.06
	E134	14.34	71.23	6.74	92.31
	E7000	14.78	38.06	6.74	59.58
	E7100	14.76	39.16	6.74	60.66
	E7200	12.61	25.75	5.39	43.75
	R134a	13.03	38.00	10.66	61.70
	R152a	11.35	22.59	5.71	39.65
	R290	10.71	20.94	5.38	37.03
	R600a	10.71	21.51	5.39	37.60
	R744	10.71	26.03	5.35	42.09
	R30	10.71	59.36	5.38	75.45

A6-3 TEWI

Table 58: TEWI_{indirect}, TEWI_{direct}, and TEWI values under worst-case, best-case, and average scenario, all values expressed in kg CO₂ eq.

	Refrigerant	TEWI _{indirect}	TEWI _{direct}	TEWI
Average scenario	E125	473.9	21225.1	21699.0
	E134	2317.7	8260.6	10578.3
	E7000	608.6	645.4	1253.9
	E7100	688.8	588.0	1276.8
	E7200	621.5	86.1	707.6
	R134a	828.7	2022.1	2850.8
	R152a	771.7	114.7	886.4
	R290	864.9	1.6	866.5
	R600a	898.6	1.6	900.2
	R744	1160.1	0.9	1161.0
	R30	3164.5	9.4	3173.9
Best-case scenario	E125	45.6	4062.6	4108.2
	E134	222.9	1581.1	1804.0
	E7000	58.5	123.5	182.0
	E7100	66.2	112.6	178.8
	E7200	59.8	16.5	76.2
	R134a	79.7	387.1	466.7
	R152a	74.2	20.1	94.3
	R290	83.2	0.2	83.4
	R600a	86.4	0.2	86.6
	R744	111.6	0.2	111.7
	R30	304.3	1.7	305.9
Worst-case scenario	E125	1184.7	39886.0	41070.7
	E134	5794.2	15523.2	21317.4
	E7000	1521.4	1212.8	2734.1
	E7100	1722.1	1105.0	2827.0
	E7200	1553.8	161.7	1715.5
	R134a	2071.7	3800.0	5871.6
	R152a	1929.3	216.8	2146.1
	R290	2162.3	3.0	2165.4
	R600a	2246.5	3.0	2249.5
	R744	2900.4	1.6	2902.0
	R30	7911.2	17.8	7929.0

Table 59: TEWI_{indirect}, TEWI_{direct}, and TEWI values of different scenarios where only one parameter is changed and the others are put to average; Set A – parameter S_L (annual operation time) is changed; Set B – parameter L (annual leakage rate during operation) is changed; Set C – parameters c and d (refrigerant loss during production, charging, and disposal) are changed; Set D – parameter z (number of servicing) is changed

Scenario	Average	Set A		Set B		Set C		Set D	
		S _L		L		c+d		z	
		Worst-case	Best-case	Worst-case	Best-case	Worst-case	Best-case	Worst-case	Best-case
TEWI _{indirect} [kg CO ₂ eq.]									
E125	473.9	1184.7	45.6	473.9	473.9	473.9	473.9	473.9	473.9
E134	2317.7	5794.2	222.9	2317.7	2317.7	2317.7	2317.7	2317.7	2317.7
E7000	608.6	1521.4	58.5	608.6	608.6	608.6	608.6	608.6	608.6
E7100	688.8	1722.1	66.2	688.8	688.8	688.8	688.8	688.8	688.8
E7200	621.5	1553.8	59.8	621.5	621.5	621.5	621.5	621.5	621.5
R134a	828.7	2071.7	79.7	828.7	828.7	828.7	828.7	828.7	828.7
R152a	771.7	1929.3	74.2	771.7	771.7	771.7	771.7	771.7	771.7
R290	864.9	2162.3	83.2	864.9	864.9	864.9	864.9	864.9	864.9
R600a	898.6	2246.5	86.4	898.6	898.6	898.6	898.6	898.6	898.6
R744	1160.1	2900.4	111.6	1160.1	1160.1	1160.1	1160.1	1160.1	1160.1
R30	3164.5	7911.2	304.3	3164.5	3164.5	3164.5	3164.5	3164.5	3164.5
TEWI _{direct} [kg CO ₂ eq.]									
E125	21225.1	21225.1	21225.1	31215.1	12345.1	26936.0	15902.6	24185.1	18265.1
E134	8260.6	8260.6	8260.6	12148.6	4804.6	10483.2	6189.1	9412.6	7108.6
E7000	645.4	645.4	645.4	949.1	375.4	819.0	483.5	735.4	555.4
E7100	588.0	588.0	588.0	864.7	342.0	746.2	440.5	670.0	506.0
E7200	86.0	86.0	86.0	126.5	50.0	109.2	64.5	98.0	74.0
R134a	2022.1	2022.1	2022.1	2973.9	1176.1	2566.2	1515.0	2304.1	1740.1
R152a	114.7	114.7	114.7	164.1	70.8	143.0	88.4	139.1	90.3
R290	1.6	1.6	1.6	2.1	1.1	1.9	1.3	2.2	1.0
R600a	1.6	1.6	1.6	2.1	1.1	1.9	1.3	2.2	1.0
R744	0.9	0.9	0.9	1.2	0.5	1.1	0.7	1.1	0.7
R30	9.4	9.4	9.4	13.5	5.8	11.7	7.2	11.4	7.4

Cont. Table 59

Scenario	Average	Set A		Set B		Set C		Set D	
		S _L		L		c+d		z	
		Worst-case	Best-case	Worst-case	Best-case	Worst-case	Best-case	Worst-case	Best-case
TEWI [kg CO ₂ eq.]									
E125	21698.9	22409.8	21270.6	31688.9	12818.9	27409.9	16376.5	24658.9	18738.9
E134	10578.3	14054.8	8483.4	14466.3	7122.3	12800.9	8506.8	11730.3	9426.3
E7000	1253.9	2166.7	703.9	1557.7	983.9	1427.6	1092.1	1343.9	1163.9
E7100	1276.8	2310.1	654.2	1553.6	1030.8	1435.0	1129.4	1358.8	1194.8
E7200	707.6	1639.8	145.8	748.1	671.6	730.7	686.0	719.6	695.6
R134a	2850.8	4093.8	2101.8	3802.5	2004.8	3394.9	2343.7	3132.8	2568.8
R152a	886.4	2044.0	188.9	935.8	842.5	914.7	860.1	910.8	862.0
R290	866.5	2163.9	84.8	867.1	866.0	866.8	866.2	867.1	865.9
R600a	900.2	2248.1	88.0	900.7	899.7	900.5	899.9	900.8	899.6
R744	1161.0	2901.2	112.4	1161.4	1160.7	1161.2	1160.8	1161.2	1160.8
R30	3173.9	7920.6	313.7	3177.9	3170.3	3176.2	3171.7	3175.9	3171.9

A7 Results of fate modelling

Table 60: Distribution [%] of some refrigerant degradation products in the environmental compartments air, water, soil/aerosol particles of four different fate models

Model	Compartment	TFA	C ₃ F ₇ COOH	C ₄ F ₉ COOH	C ₄ F ₉ COOCH ₃	C ₄ F ₉ CH ₂ COOH	CF ₂ O
Atmosphere-aerosol	Air	100	100	100	100	100	100
	Water	0	0	0	0	0	0
	Soil	0	0	0	0	0	0
Atmosphere-fog	Air	99.4	100	100	100	100	100
	Water	0.6	0	0	0	0	0
	Soil	0	0	0	0	0	0
Atmosphere-raining cloud	Air	97.6	100	99.8	100	100	100
	Water	2.4	0	0.2	0	0	0
	Soil	0	0	0	0	0	0
Germany	Air	86.2	98.2	98.2	100	100	100
	Water	13.8	0.1	0.1	0	0	0
	Soil	0	1.7	1.7	0	0	0

Table 61: Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on life cycle refrigerant emissions and German model, Scenario: WC – worst-case, A – average, BC – best-case

	1 car			German cars		
	A [µg/dm ³]	WC [µg/dm ³]	BC [µg/dm ³]	A [µg/dm ³]	WC [µg/dm ³]	BC [µg/dm ³]
TFA						
Air	2.43E-10	4.66E-10	3.37E-11	1.12E-02	2.15E-02	1.56E-03
Water	5.86E-06	1.12E-05	8.13E-07	2.70E+02	5.18E+02	3.75E+01
Soil	4.45E-12	8.54E-12	6.18E-13	2.05E-04	3.93E-04	2.85E-05
C₃F₇COOH						
Air	7.39E-10	1.42E-09	1.36E-10	3.40E-02	6.46E-02	6.46E-03
Water	1.54E-07	2.96E-07	2.83E-08	7.07E+00	1.35E+01	1.35E+00
Soil	5.11E-07	9.81E-07	9.39E-08	2.35E+01	4.47E+01	4.47E+00
C₄F₉COOH						
Air	7.25E-10	1.40E-09	1.34E-10	3.35E-02	6.46E-02	6.00E-03
Water	1.51E-07	2.92E-07	2.79E-08	6.98E+00	1.35E+01	1.25E+00
Soil	5.01E-07	9.69E-07	9.25E-08	2.32E+01	4.47E+01	4.15E+00
C₄F₉COOCH₃						
Air	3.68E-10	7.06E-10	6.76E-11	1.68E-02	3.27E-02	3.11E-03
Water	9.01E-09	1.73E-08	1.65E-09	4.11E-01	7.99E-01	7.62E-02
Soil	2.99E-08	5.74E-08	5.49E-09	1.36E+00	2.65E+00	2.53E-01
C₄F₉CH₂COOH						
Air	3.68E-10	7.06E-10	6.76E-11	1.68E-02	3.27E-02	3.11E-03
Water	9.01E-09	1.73E-08	1.65E-09	4.11E-01	7.99E-01	7.62E-02
Soil	2.99E-08	5.74E-08	5.49E-09	1.36E+00	2.65E+00	2.53E-01
CF₂O from E125						
Air	5.19E-10	9.91E-10	7.15E-11	2.38E-02	4.58E-02	3.30E-03
Water	1.27E-08	2.42E-08	1.75E-09	5.83E-01	1.12E+00	8.08E-02
Soil	7.15E-12	1.37E-11	9.86E-13	3.29E-04	6.31E-04	4.56E-05
CF₂O from E134						
Air	7.85E-10	1.50E-09	1.44E-10	3.60E-02	7.01E-02	6.54E-03
Water	1.92E-08	3.68E-08	3.52E-09	8.80E-01	1.72E+00	1.60E-01
Soil	1.08E-11	2.07E-11	1.98E-12	4.96E-04	9.66E-04	9.20E-05
CF₂O from R152a						
Air	7.80E-10	8.10E-10	6.06E-11	3.61E-02	3.74E-02	2.79E-03
Water	1.91E-08	1.98E-08	1.48E-09	8.83E-01	9.15E-01	6.84E-02
Soil	1.08E-11	1.12E-11	8.36E-13	4.97E-04	5.15E-04	3.85E-05
HF from R134a						
Air	8.25E-11	1.58E-10	1.51E-11	3.80E-03	7.49E-03	6.97E-04
Water	3.51E-09	6.72E-09	6.43E-10	1.62E-01	3.10E-01	2.96E-02
Soil	7.35E-11	1.41E-10	1.35E-11	3.38E-03	6.49E-03	6.21E-04
HF from R152a						
Air	2.55E-06	4.91E-10	3.67E-11	1.18E+01	2.24E+01	1.68E+00
Water	1.09E-04	2.09E-08	1.56E-09	5.01E+02	9.54E+02	7.16E+01
Soil	2.27E-06	4.38E-10	3.27E-11	1.05E+01	2.00E+01	1.50E+00

Cont. Table 61

	1 car			German cars		
	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]
	HF from E125			HF from R152a		
Air	3.13E-10	5.88E-10	5.74E-11	1.44E+01	2.76E+01	2.66E+00
Water	1.33E-08	2.50E-08	2.44E-09	6.14E+02	1.17E+03	1.13E+02
Soil	3.59E-16	5.24E-10	5.12E-11	1.29E+01	2.46E+01	2.73E+00
	HF from E134			HF from R152a		
Air	4.75E-10	9.11E-10	8.71E-11	2.19E+01	4.20E+01	4.02E+00
Water	2.02E-08	3.87E-08	3.71E-09	9.32E+02	1.79E+03	1.71E+02
Soil	4.23E-10	8.11E-10	7.78E-11	1.95E+01	3.75E+01	3.58E+00
	HCl from R30			HCl from R30		
Air	3.93E-10	7.55E-10	6.61E-11	1.81E+01	3.49E+01	3.05E+00
Water	1.86E-07	3.59E-07	3.14E-08	8.58E+03	1.66E+04	1.45E+03
Soil	1.74E-09	3.34E-09	2.92E-10	7.98E+01	1.54E+02	1.35E+01

Table 62: Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on refrigerant emissions during one year of operation and German model,
Scenario: WC – worst-case, A – average, BC – best-case

	1 car			German cars		
	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]
	TFA			TFA		
Air	1.77E-11	4.69E-11	3.72E-12	8.13E-04	2.06E-03	1.73E-04
Water	4.26E-07	1.31E-06	8.97E-08	1.96E+01	4.95E+01	4.17E+00
Soil	3.24E-13	8.60E-13	6.82E-14	1.49E-05	3.76E-05	3.17E-06
	C₃F₇COOH			C₃F₇COOH		
Air	5.37E-11	1.03E-10	1.13E-11	2.48E-03	4.61E-03	5.19E-04
Water	1.12E-08	2.14E-08	2.35E-09	5.16E-01	9.61E-01	1.08E-01
Soil	3.71E-08	7.10E-08	7.81E-09	1.71E+00	3.19E-01	3.59E-01
	C₄F₉COOH			C₄F₉COOH		
Air	5.28E-11	1.01E-10	1.12E-11	2.43E-03	4.61E-03	5.14E-04
Water	1.10E-08	2.11E-08	2.32E-09	5.07E-01	9.61E-01	1.07E-01
Soil	3.65E-08	7.01E-08	7.71E-09	1.68E+00	3.19E+00	3.55E-01
	C₄F₉COOCH₃			C₄F₉COOCH₃		
Air	2.68E-11	5.12E-11	5.59E-12	1.21E-03	2.36E-03	2.60E-04
Water	6.55E-10	1.25E-09	1.37E-10	2.97E-02	5.76E-02	6.36E-03
Soil	2.17E-09	4.15E-09	4.54E-10	9.84E-02	1.91E-01	2.11E-02
	C₄F₉CH₂COOH			C₄F₉COOCH₃		
Air	2.68E-11	5.12E-11	5.59E-12	1.21E-03	2.36E-03	2.60E-04
Water	6.55E-10	1.25E-09	1.37E-10	2.97E-02	5.76E-02	6.36E-03
Soil	2.17E-09	4.15E-09	4.54E-10	9.84E-02	1.91E-01	2.11E-02

Cont. Table 62

	1 car			German cars		
	A [µg/dm ³]	WC [µg/dm ³]	BC [µg/dm ³]	A [µg/dm ³]	WC [µg/dm ³]	BC [µg/dm ³]
	CF₂O from E125			CF₂O from E125		
Air	3.76E-11	9.48E-11	7.94E-12	1.73E-03	4.36E-03	3.65E-04
Water	9.19E-10	2.32E-09	1.94E-10	4.23E-02	1.07E-01	8.94E-03
Soil	5.18E-13	1.31E-12	1.10E-13	2.38E-05	6.02E-05	5.04E-06
	CF₂O from E134			CF₂O from E125		
Air	5.70E-11	1.09E-10	1.20E-11	2.62E-03	5.15E-03	5.56E-04
Water	1.40E-09	2.66E-09	2.94E-10	6.40E-02	1.26E-01	1.36E-02
Soil	7.86E-13	1.50E-12	1.66E-13	3.61E-05	7.09E-05	7.67E-06
	CF₂O from R152a			CF₂O from R152a		
Air	6.45E-11	7.09E-11	6.03E-12	2.97E-03	3.27E-03	2.78E-04
Water	1.58E-09	1.74E-09	1.48E-10	7.27E-02	8.00E-02	6.79E-03
Soil	8.89E-13	9.78E-13	8.31E-14	4.10E-05	4.51E-05	3.83E-06
	HF from R134a			HF from R134a		
Air	5.98E-12	1.15E-11	1.27E-11	2.76E-04	5.28E-04	5.84E-05
Water	2.54E-10	4.87E-10	5.39E-11	1.18E-02	2.25E-02	2.49E-03
Soil	5.33E-12	1.02E-11	1.13E-12	2.46E-04	4.70E-04	5.20E-05
	HF from R152a			HF from R152a		
Air	1.93E-11	4.30E-11	3.64E-12	8.88E-01	1.96E+00	1.68E-01
Water	8.21E-10	1.83E-09	1.55E-10	3.78E+01	8.35E+01	7.16E+00
Soil	1.72E-11	3.83E-11	3.25E-12	7.91E-01	1.75E+00	1.50E-01
	HF from E125			HF from R152a		
Air	2.28E-11	4.34E-11	4.81E-12	1.05E+00	2.01E+00	2.21E-01
Water	9.68E-10	1.85E-09	2.05E-10	4.47E+01	8.55E+01	9.42E+00
Soil	2.03E-11	3.87E-11	4.29E-12	9.37E-01	1.79E+00	1.97E-01
	HF from E134			HF from R152a		
Air	3.45E-11	6.59E-11	7.29E-12	1.59E+00	3.04E+00	3.36E-01
Water	1.47E-09	2.80E-09	3.10E-10	6.78E+01	1.29E+02	1.43E+01
Soil	3.08E-11	5.87E-11	6.49E-12	1.42E+00	2.71E+00	3.66E-07
	HCl from R30			HCl from R30		
Air	2.96E-11	5.65E-11	5.59E-12	1.37E+00	2.61E+00	2.59E-01
Water	1.41E-08	2.68E-08	2.65E-09	6.48E+02	1.24E+03	1.23E+02
Soil	1.31E-10	2.50E-10	2.47E-11	6.03E+00	1.41E-05	1.14E+00

Table 63: Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on life cycle refrigerant emissions and Atmosphere-aerosol model,
Scenario: WC – worst-case, A – average, BC – best-case

	1 car			German cars		
	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]
	TFA			TFA		
Air	2.82E-10	5.41E-10	5.44E-11	1.30E-02	2.49E-02	2.38E-03
Water	6.79E-06	1.30E-05	1.31E-06	3.10E+02	6.00E+02	5.74E+01
Soil	5.16E-12	9.90E-12	9.97E-13	2.38E-04	4.56E-04	4.37E-05
	C₃F₇COOH			C₃F₇COOH		
Air	7.49E-10	1.44E-09	1.38E-10	3.46E-02	6.54E-02	6.54E-03
Water	1.56E-07	3.00E-07	2.87E-08	7.20E+00	1.36E+01	1.36E+00
Soil	5.18E-07	9.94E-07	9.51E-08	2.39E+01	4.52E+01	4.52E+00
	C₄F₉COOH			C₄F₉COOH		
Air	7.40E-10	1.42E-09	1.36E-10	3.41E-02	6.54E-02	6.08E-03
Water	1.54E-07	2.96E-07	2.82E-08	7.10E+00	1.36E+01	1.27E+00
Soil	5.11E-07	9.81E-07	9.37E-08	2.36E+01	4.52E+01	4.20E+00
	C₄F₉COOCH₃			C₄F₉COOCH₃		
Air	3.69E-10	7.07E-10	6.77E-11	1.68E-02	3.27E-02	3.12E-03
Water	9.02E-09	1.73E-08	1.66E-09	4.11E-01	8.00E-01	7.63E-02
Soil	2.99E-08	5.74E-08	5.49E-09	1.37E+00	2.66E+00	2.53E-01
	C₄F₉CH₂COOH			C₄F₉COOCH₃		
Air	3.69E-10	7.07E-10	6.77E-11	1.68E-02	3.27E-02	3.12E-03
Water	9.02E-09	1.73E-08	1.66E-09	4.11E-01	8.00E-01	7.63E-02
Soil	2.99E-08	5.74E-08	5.49E-09	1.37E+00	2.66E+00	2.53E-01
	CF₂O from E125			CF₂O from E125		
Air	5.16E-10	9.91E-10	7.15E-11	2.38E-02	4.58E-02	3.30E-03
Water	1.26E-08	2.42E-08	1.75E-09	5.23E-01	1.12E+00	8.08E-02
Soil	7.12E-12	1.37E-11	9.86E-13	3.29E-04	6.32E-04	4.56E-05
	CF₂O from E134			CF₂O from E125		
Air	7.83E-10	1.50E-09	1.44E-10	3.60E-02	7.01E-02	6.54E-03
Water	1.92E-08	3.68E-08	3.52E-09	8.80E-01	1.72E+00	1.60E-01
Soil	1.08E-11	2.07E-11	1.98E-12	4.96E-04	9.67E-04	9.02E-05
	CF₂O from R152a			CF₂O from R152a		
Air	7.80E-10	8.10E-10	6.06E-11	3.61E-02	3.74E-02	2.79E-03
Water	1.91E-08	1.98E-08	1.48E-09	8.83E-01	9.15E-01	6.84E-02
Soil	1.13E-11	1.12E-11	8.36E-13	4.98E-04	5.16E-04	3.85E-05
	HF from R134a			HF from R134a		
Air	8.25E-11	1.58E-10	1.51E-11	3.80E-03	7.29E-03	6.97E-04
Water	3.51E-09	6.72E-09	6.43E-10	1.62E-01	3.10E-01	2.97E-02
Soil	7.35E-11	1.41E-10	1.35E-11	3.39E-03	6.50E-03	6.21E-04
	HF from R152a			HF from R152a		
Air	2.55E-10	4.91E-10	1.93E-11	1.18E+01	2.24E+01	1.68E+00
Water	1.09E-08	2.09E-08	8.21E-10	5.01E+02	9.54E+02	7.16E+01
Soil	2.28E-10	4.38E-10	1.72E-11	1.05E+01	2.00E+01	1.23E+06

Cont. Table 63

	1 car			German cars		
	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]
	HF from E125			HF from R152a		
Air	3.13E-10	5.88E-10	5.74E-11	1.44E+01	2.76E+01	2.66E+00
Water	1.33E-08	2.50E-08	2.44E-09	6.14E+02	1.17E+03	1.13E+02
Soil	2.79E-10	5.24E-10	5.12E-11	1.29E+01	2.46E+01	2.37E+00
	HF from E134			HF from R152a		
Air	4.75E-10	9.11E-10	8.71E-11	2.19E+01	4.21E+01	4.02E+00
Water	2.02E-08	3.88E-08	3.71E-09	9.33E+02	1.79E+03	1.71E+02
Soil	4.24E-10	8.12E-10	7.76E-09	1.95E+01	3.75E+01	3.58E+00
	HCl from R30			HCl from R30		
Air	3.94E-10	7.58E-10	6.63E-11	1.81E+01	3.51E+01	3.06E+00
Water	1.87E-07	3.60E-07	3.15E-08	8.61E+03	1.66E+04	1.45E+03
Soil	1.74E-09	3.35E-09	2.93E-10	8.01E+01	1.55E+02	1.35E+01

Table 64: Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on refrigerant emissions during one year of operation and Atmosphere-aerosol model, Scenario: WC – worst-case, A – average, BC – best-case

	1 car			German cars		
	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]
	TFA			TFA		
Air	2.05E-11	4.15E-11	4.32E-12	9.43E-04	1.80E-03	2.01E-04
Water	4.94E-07	9.99E-07	1.04E-07	2.27E+01	4.35E+01	4.84E+00
Soil	3.76E-13	7.59E-13	7.91E-14	1.73E-05	3.31E-05	3.68E-06
	C₃F₇COOH			C₃F₇COOH		
Air	5.44E-11	1.04E-10	1.13E-11	2.52E-03	4.67E-03	5.19E-04
Water	1.13E-08	2.17E-08	2.35E-09	5.25E-01	9.74E-01	1.08E-01
Soil	3.76E-08	7.19E-08	7.81E-09	1.74E+00	3.23E-01	3.59E-01
	C₄F₉COOH			C₄F₉COOH		
Air	5.37E-11	1.03E-10	1.12E-11	2.47E-03	4.67E-03	5.14E-04
Water	1.12E-08	2.14E-08	2.32E-09	5.16E-01	9.74E-01	1.07E-01
Soil	3.72E-08	7.10E-08	7.71E-09	1.70E+00	3.23E+00	3.55E-01
	C₄F₉COOCH₃			C₄F₉COOCH₃		
Air	2.68E-11	5.12E-11	5.59E-12	1.21E-03	2.36E-03	2.60E-04
Water	6.56E-10	1.25E-09	1.37E-10	2.97E-02	5.77E-02	6.36E-03
Soil	2.18E-09	4.16E-09	4.54E-10	9.86E-02	1.92E-01	2.11E-02
	C₄F₉CH₂COOH			C₄F₉COOCH₃		
Air	2.68E-11	5.12E-11	5.59E-12	1.21E-03	2.36E-03	2.60E-04
Water	6.56E-10	1.25E-09	1.37E-10	2.97E-02	5.77E-02	6.36E-03
Soil	2.18E-09	4.16E-09	4.54E-10	9.86E-02	1.92E-01	2.11E-02

Cont. Table 64

	1 car			German cars		
	A	WC	BC	A	WC	BC
	[µg/dm³]	[µg/dm³]	[µg/dm³]	[µg/dm³]	[µg/dm³]	[µg/dm³]
	CF₂O from E125			CF₂O from E125		
Air	3.75E-11	9.48E-11	7.94E-12	1.73E-03	4.36E-03	3.65E-04
Water	9.18E-10	2.32E-09	1.94E-10	4.23E-02	1.07E-01	8.94E-03
Soil	5.18E-13	1.31E-12	1.10E-13	2.38E-05	6.02E-05	5.04E-06
	CF₂O from E134			CF₂O from E125		
Air	5.69E-11	1.09E-10	1.20E-11	2.61E-03	5.15E-03	5.56E-04
Water	1.39E-09	2.66E-09	2.94E-10	6.40E-02	1.26E-01	1.36E-02
Soil	7.85E-13	1.50E-12	1.66E-13	3.61E-05	7.09E-05	7.67E-06
	CF₂O from R152a			CF₂O from R152a		
Air	6.45E-11	7.09E-11	6.03E-12	2.97E-03	3.27E-03	2.78E-04
Water	1.58E-09	1.74E-09	1.48E-10	7.27E-02	8.00E-02	6.79E-03
Soil	8.90E-13	9.78E-13	8.31E-14	4.10E-05	4.51E-05	3.83E-06
	HF from R134a			HF from R134a		
Air	5.98E-12	1.15E-11	1.27E-12	2.76E-04	5.28E-04	5.84E-05
Water	2.55E-10	4.87E-10	5.39E-11	1.18E-02	2.25E-02	2.49E-03
Soil	5.33E-12	1.02E-11	1.13E-12	2.46E-04	4.71E-04	5.21E-05
	HF from R152a			HF from R152a		
Air	1.93E-11	4.30E-11	3.65E-12	8.88E-01	1.96E+00	1.68E-01
Water	8.21E-10	1.83E-09	1.55E-10	3.78E+01	8.35E+01	7.16E+00
Soil	1.72E-11	3.83E-11	3.25E-12	7.91E-01	1.75E+00	1.50E-01
	HF from E125			HF from R152a		
Air	2.28E-11	4.35E-11	4.81E-12	1.05E+00	2.01E+00	2.22E-01
Water	9.68E-10	1.85E-09	2.05E-10	4.47E+01	8.55E+01	9.43E+00
Soil	2.03E-11	3.87E-11	4.29E-12	9.37E-01	1.79E+00	1.97E-01
	HF from E134			HF from R152a		
Air	3.45E-11	6.59E-11	7.29E-12	1.59E+00	3.04E+00	3.36E-01
Water	1.47E-09	2.80E-09	2.63E-06	6.78E+01	1.29E+02	1.43E+01
Soil	3.08E-11	5.87E-11	6.50E-12	1.42E+00	2.71E+00	2.99E-01
	HCl from R30			HCl from R30		
Air	2.97E-11	5.67E-11	5.61E-12	1.37E+00	2.62E+00	2.59E-01
Water	1.41E-08	2.69E-08	2.66E-09	6.50E+02	1.24E+03	3.14E+01
Soil	1.31E-10	2.50E-10	2.48E-11	6.05E+00	1.16E+01	1.15E+00

Table 65: Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on life cycle refrigerant emissions and Atmosphere-fog model,
Scenario: WC – worst-case, A – average, BC – best-case

	1 car			German cars		
	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]
	TFA			TFA		
Air	4.32E-12	5.37E-10	5.41E-11	1.29E-02	2.48E-02	2.37E-03
Water	1.04E-07	1.30E-05	1.30E-06	3.11E+02	5.97E+02	5.71E+01
Soil	7.91E-14	9.84E-12	9.91E-13	2.37E-04	4.54E-04	4.34E-05
	C₃F₇COOH			C₃F₇COOH		
Air	7.50E-10	1.44E-09	1.38E-10	3.46E-02	6.54E-02	6.54E-03
Water	1.56E-07	2.99E-07	2.87E-08	7.20E+00	1.36E+01	1.36E+00
Soil	5.19E-07	9.94E-07	9.51E-08	2.39E+01	4.50E+01	4.52E+00
	C₄F₉COOH			C₄F₉COOH		
Air	7.40E-10	1.42E-09	1.36E-10	3.41E-02	6.54E-02	6.07E-03
Water	1.54E-07	2.96E-07	2.82E-08	7.11E+00	1.36E+01	1.27E+00
Soil	5.12E-07	9.81E-07	9.37E-08	2.36E+01	4.52E+01	4.20E+00
	C₄F₉COOCH₃			C₄F₉COOCH₃		
Air	3.69E-10	7.07E-10	6.77E-11	1.70E-02	3.27E-02	3.12E-03
Water	9.03E-09	1.73E-08	1.66E-09	4.16E-01	8.00E-01	7.63E-02
Soil	3.00E-08	5.74E-08	5.49E-09	1.38E+00	2.66E+00	2.53E-01
	C₄F₉CH₂COOH			C₄F₉COOCH₃		
Air	3.69E-10	7.07E-10	6.77E-11	1.70E-02	3.27E-02	3.12E-03
Water	9.03E-09	1.73E-08	1.66E-09	4.16E-01	8.00E-01	7.63E-02
Soil	3.00E-08	5.74E-08	5.49E-09	1.38E+00	2.66E+00	2.53E-01
	CF₂O from E125			CF₂O from E125		
Air	5.17E-10	9.91E-10	7.15E-11	2.38E-02	4.58E-02	3.30E-03
Water	1.27E-08	2.42E-08	1.75E-09	5.83E-01	1.12E+00	8.08E-02
Soil	7.13E-12	1.37E-11	9.86E-13	3.29E-04	6.32E-04	4.56E-05
	CF₂O from E134			CF₂O from E125		
Air	7.84E-10	1.50E-09	1.44E-10	3.61E-02	7.01E-02	6.54E-03
Water	1.92E-08	3.68E-08	3.52E-09	8.84E-01	1.72E+00	1.60E-01
Soil	1.08E-11	2.07E-11	1.98E-12	4.98E-04	9.67E-04	9.02E-05
	CF₂O from R152a			CF₂O from R152a		
Air	4.22E-10	8.10E-10	6.06E-11	1.94E-02	3.74E-02	2.79E-03
Water	1.03E-08	1.98E-08	1.48E-09	4.76E-01	9.15E-01	6.84E-02
Soil	5.81E-12	1.12E-11	8.36E-13	2.68E-04	5.16E-04	3.85E-05
	HF from R134a			HF from R134a		
Air	8.25E-11	1.58E-10	1.51E-11	3.80E-03	7.29E-03	6.97E-04
Water	3.51E-09	6.72E-09	6.43E-10	1.62E-01	3.10E-01	2.97E-02
Soil	7.35E-11	1.41E-10	1.35E-11	3.39E-03	6.50E-03	6.21E-04
	HF from R152a			HF from R152a		
Air	2.55E-10	4.91E-10	3.67E-11	1.18E+01	2.24E+01	1.68E+00
Water	1.09E-08	2.09E-08	1.84E-13	5.01E+02	9.55E+02	7.16E+01
Soil	2.28E-10	4.38E-10	3.27E-11	1.05E+01	2.00E+01	1.50E+00

Cont. Table 65

	1 car			German cars		
	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]
	HF from E125			HF from R152a		
Air	3.13E-10	6.00E-10	5.74E-11	1.44E+01	2.76E+01	2.66E+00
Water	1.33E-08	2.56E-08	2.44E-09	6.14E+02	1.17E+03	1.13E+02
Soil	2.79E-10	5.35E-10	5.12E-11	1.29E+01	2.46E+01	2.37E+00
	HF from E134			HF from R152a		
Air	4.75E-10	9.11E-10	8.71E-11	2.19E+01	4.21E+01	4.02E+00
Water	2.02E-08	3.88E-08	3.71E-09	9.33E+02	1.79E+03	1.71E+02
Soil	4.23E-10	8.12E-10	7.76E-11	1.95E+01	3.75E+01	3.58E+00
	HCl from R30			HCl from R30		
Air	3.94E-10	7.57E-10	6.63E-11	1.81E+01	3.50E+01	3.06E+00
Water	1.87E-07	3.60E-07	3.15E-08	8.60E+03	1.66E+04	1.45E+03
Soil	1.74E-09	3.35E-09	2.93E-10	8.01E+01	1.55E+02	1.35E+01

Table 66: Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on refrigerant emissions during one year of operation and Atmosphere-fog model, Scenario: WC – worst-case, A – average, BC – best-case

	1 car			German cars		
	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]
	TFA			TFA		
Air	2.04E-11	3.89E-11	4.32E-12	9.38E-04	1.79E-03	1.98E-04
Water	4.91E-07	9.37E-07	1.04E-07	2.26E+01	4.32E+01	4.78E+00
Soil	3.74E-13	7.12E-13	7.91E-14	1.72E-05	3.29E-05	3.63E-06
	C₃F₇COOH			C₃F₇COOH		
Air	5.45E-11	1.04E-10	1.13E-11	2.51E-03	4.67E-03	5.19E-04
Water	1.14E-08	2.17E-08	2.35E-09	5.24E-01	9.74E-01	1.08E-01
Soil	3.77E-08	7.19E-08	7.81E-09	1.74E+00	3.23E-01	3.59E-01
	C₄F₉COOH			C₄F₉COOH		
Air	5.38E-11	1.03E-10	1.12E-11	2.48E-03	4.67E-03	5.14E-04
Water	1.12E-08	2.14E-08	2.32E-09	5.17E-01	9.74E-01	1.07E-01
Soil	3.72E-08	7.10E-08	7.71E-09	1.72E+00	3.23E+00	3.55E-01
	C₄F₉COOCH₃			C₄F₉COOCH₃		
Air	2.68E-11	5.12E-11	5.59E-12	1.24E-03	2.36E-03	2.60E-04
Water	6.56E-10	1.25E-09	1.37E-10	3.03E-02	5.77E-02	6.36E-03
Soil	2.18E-09	4.16E-09	4.54E-10	1.01E-01	1.92E-01	2.11E-02
	C₄F₉CH₂COOH			C₄F₉COOCH₃		
Air	2.68E-11	5.12E-11	5.59E-12	1.24E-03	2.36E-03	2.60E-04
Water	6.56E-10	1.25E-09	1.37E-10	3.03E-02	5.77E-02	6.36E-03
Soil	2.18E-09	4.16E-09	4.54E-10	1.01E-01	1.92E-01	2.11E-02

Cont. Table 66

	1 car			German cars		
	A	WC	BC	A	WC	BC
	[µg/dm ³]	[µg/dm ³]	[µg/dm ³]	[µg/dm ³]	[µg/dm ³]	[µg/dm ³]
	CF₂O from E125			CF₂O from E125		
Air	3.76E-11	9.48E-11	7.94E-12	1.73E-03	4.36E-03	3.65E-04
Water	9.19E-10	2.32E-09	1.94E-10	4.24E-02	1.07E-01	8.94E-03
Soil	5.18E-13	1.31E-12	1.10E-13	2.39E-05	6.02E-05	5.04E-06
	CF₂O from E134			CF₂O from E125		
Air	5.70E-11	1.09E-10	1.20E-11	2.63E-03	5.15E-03	5.56E-04
Water	1.39E-09	2.66E-09	2.94E-10	6.43E-02	1.26E-01	1.36E-02
Soil	7.86E-13	1.50E-12	1.66E-13	3.62E-05	7.09E-05	7.67E-06
	CF₂O from R152a			CF₂O from R152a		
Air	3.18E-11	7.09E-11	6.03E-12	1.47E-03	3.27E-03	2.78E-04
Water	7.79E-10	1.74E-09	1.48E-10	3.59E-02	8.00E-02	6.79E-03
Soil	4.39E-13	9.78E-13	8.31E-14	2.02E-05	4.51E-05	3.83E-06
	HF from R134a			HF from R134a		
Air	5.98E-12	1.15E-11	1.27E-12	2.76E-04	5.28E-04	5.84E-05
Water	2.55E-10	4.87E-10	5.39E-11	1.18E-02	2.25E-02	2.49E-03
Soil	5.33E-12	1.02E-11	1.13E-12	2.46E-04	4.71E-04	5.21E-05
	HF from R152a			HF from R152a		
Air	1.93E-11	4.30E-11	3.65E-12	8.88E-01	1.96E+00	1.68E-01
Water	8.21E-10	1.83E-09	1.55E-10	3.78E+01	8.35E+01	8.43E-04
Soil	1.72E-11	3.83E-11	3.25E-12	7.91E-01	1.75E+00	1.50E-01
	HF from E125			HF from R152a		
Air	2.28E-11	4.35E-11	4.81E-12	1.05E+00	2.01E+00	2.22E-01
Water	9.68E-10	1.85E-09	2.05E-10	4.47E+01	8.55E+01	1.11E-03
Soil	2.03E-11	3.87E-11	4.30E-12	9.37E-01	1.79E+00	1.97E-01
	HF from E134			HF from R152a		
Air	3.45E-11	6.59E-11	7.29E-12	1.59E+00	3.04E+00	3.36E-01
Water	1.47E-09	2.80E-09	3.10E-10	6.78E+01	1.29E+02	5.60E+01
Soil	3.08E-11	5.87E-11	6.50E-12	1.42E+00	2.71E+00	2.99E-01
	HCl from R30			HCl from R30		
Air	2.97E-11	5.66E-11	5.61E-12	1.37E+00	2.62E+00	2.59E-01
Water	1.41E-08	2.69E-08	2.66E-09	6.50E+02	1.24E+03	3.14E+01
Soil	1.31E-10	2.50E-10	2.48E-11	6.05E+00	1.16E+01	1.15E+00

Table 67: Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on life cycle refrigerant emissions and Atmosphere-raining cloud model, Scenario: WC – worst-case, A – average, BC – best-case

	1 car			German cars		
	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]
	TFA			TFA		
Air	4.24E-12	5.28E-10	5.32E-11	1.27E-01	2.43E-02	2.33E-03
Water	1.02E-07	1.27E-05	1.28E-06	3.06E+02	5.86E+02	5.61E+01
Soil	7.78E-14	9.67E-12	9.74E-13	2.32E-04	4.46E-04	4.26E-05
	C₃F₇COOH			C₃F₇COOH		
Air	7.50E-10	1.44E-09	1.38E-10	3.46E-02	6.54E-02	6.54E-03
Water	1.56E-07	2.99E-07	2.86E-08	7.20E+00	1.36E+01	1.36E+00
Soil	5.18E-07	9.94E-07	9.51E-08	2.39E+01	4.50E+01	4.52E+00
	C₄F₉COOH			C₄F₉COOH		
Air	7.40E-10	1.42E-09	1.36E-10	3.41E-02	6.54E-02	6.07E-03
Water	1.54E-07	2.96E-07	2.82E-08	7.11E+00	1.36E+01	1.27E+00
Soil	5.12E-07	9.81E-07	9.37E-08	2.36E+01	4.52E+01	4.20E+00
	C₄F₉COOCH₃			C₄F₉COOCH₃		
Air	3.69E-10	7.07E-10	6.77E-11	1.70E-02	3.27E-02	3.12E-03
Water	9.03E-09	1.73E-08	1.66E-09	4.16E-01	8.00E-01	7.63E-02
Soil	3.00E-08	5.74E-08	5.49E-09	1.38E+00	2.66E+00	2.53E-01
	C₄F₉CH₂COOH			C₄F₉COOCH₃		
Air	3.69E-10	7.07E-10	6.77E-11	1.70E-02	3.27E-02	3.12E-03
Water	9.03E-09	1.73E-08	1.66E-09	4.16E-01	8.00E-01	7.63E-02
Soil	3.00E-08	5.74E-08	5.49E-09	1.38E+00	2.66E+00	2.53E-01
	CF₂O from E125			CF₂O from E125		
Air	5.17E-10	9.91E-10	7.15E-11	2.38E-02	4.58E-02	3.30E-03
Water	1.27E-08	2.42E-08	1.75E-09	5.83E-01	1.12E+00	8.08E-02
Soil	7.13E-12	1.37E-11	9.86E-13	3.29E-04	6.32E-04	4.56E-05
	CF₂O from E134			CF₂O from E125		
Air	7.84E-10	1.50E-09	1.44E-10	3.61E-02	7.01E-02	6.54E-03
Water	1.92E-08	3.68E-08	3.52E-09	8.84E-01	1.72E+00	1.60E-01
Soil	1.08E-11	2.07E-11	1.98E-12	4.98E-04	9.67E-04	9.02E-05
	CF₂O from R152a			CF₂O from R152a		
Air	4.22E-10	8.10E-10	6.06E-11	1.94E-02	3.74E-02	2.79E-03
Water	1.03E-08	1.98E-08	1.48E-09	4.76E-01	9.15E-01	6.84E-02
Soil	5.81E-12	1.12E-11	8.36E-13	2.68E-04	5.16E-04	3.85E-05
	HF from R134a			HF from R134a		
Air	8.25E-11	1.58E-10	1.51E-11	3.80E-03	7.29E-03	6.97E-04
Water	3.51E-09	6.72E-09	6.43E-10	1.62E-01	3.10E-01	2.97E-02
Soil	7.35E-11	1.41E-10	1.35E-11	3.39E-03	6.50E-03	6.21E-04
	HF from R152a			HF from R152a		
Air	2.55E-10	4.91E-10	3.67E-11	1.18E+01	2.24E+01	1.68E+00
Water	1.09E-08	2.09E-08	1.84E-13	5.01E+02	9.55E+02	7.16E+01
Soil	2.28E-10	4.38E-10	3.27E-11	1.05E+01	2.00E+01	1.50E+00

Cont. Table 67

	1 car			German cars		
	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]
	HF from E125			HF from R152a		
Air	3.13E-10	6.00E-10	5.74E-11	1.44E+01	2.76E+01	2.66E+00
Water	1.33E-08	2.56E-08	2.44E-09	6.14E+02	1.17E+03	1.13E+02
Soil	2.79E-10	5.35E-10	5.12E-11	1.29E+01	2.46E+01	2.37E+00
	HF from E134			HF from R152a		
Air	4.75E-10	9.11E-10	8.71E-11	2.19E+01	4.21E+01	4.02E+00
Water	2.02E-08	3.88E-08	3.71E-09	9.33E+02	1.79E+03	1.71E+02
Soil	4.23E-10	8.12E-10	7.76E-11	1.95E+01	3.75E+01	3.58E+00
	HCl from R30			HCl from R30		
Air	3.94E-10	7.57E-10	6.63E-11	1.81E+01	3.50E+01	3.06E+00
Water	1.87E-07	3.60E-07	3.15E-08	8.60E+03	1.66E+04	1.45E+03
Soil	1.74E-09	3.35E-09	2.93E-10	8.01E+01	1.55E+02	1.35E+01

Table 68: Concentrations of certain refrigerant degradation products in the environmental compartments air, water, and soil; calculation based on refrigerant emissions during one year of operation and Atmosphere-raining cloud model, Scenario: WC – worst-case, A – average, BC – best-case

	1 car			German cars		
	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]	A [µg/dm³]	WC [µg/dm³]	BC [µg/dm³]
	TFA			TFA		
Air	2.00E-11	3.82E-11	4.24E-12	9.22E-04	1.76E-03	1.95E-04
Water	4.83E-07	9.20E-07	1.02E-07	2.22E+01	4.25E+01	4.70E+00
Soil	3.67E-13	7.00E-13	7.78E-14	1.69E-05	3.23E-05	3.57E-06
	C₃F₇COOH			C₃F₇COOH		
Air	5.45E-11	1.04E-10	1.13E-11	2.51E-03	4.67E-03	5.19E-04
Water	1.14E-08	2.17E-08	2.35E-09	5.24E-01	9.70E-01	1.08E-01
Soil	3.77E-08	7.19E-08	7.81E-09	1.74E+00	3.23E-01	3.59E-01
	C₄F₉COOH			C₄F₉COOH		
Air	5.37E-11	1.03E-10	1.12E-11	2.48E-03	4.78E-03	5.14E-04
Water	1.12E-08	2.14E-08	2.32E-09	5.17E-01	9.73E-01	1.07E-01
Soil	3.72E-08	7.09E-08	7.71E-09	1.72E+00	3.23E+00	3.55E-01
	C₄F₉COOCH₃			C₄F₉COOCH₃		
Air	2.68E-11	5.12E-11	5.59E-12	1.24E-03	2.36E-03	2.60E-04
Water	6.56E-10	1.25E-09	1.37E-10	3.03E-02	5.77E-02	6.36E-03
Soil	2.18E-09	4.16E-09	4.54E-10	1.01E-01	1.92E-01	2.11E-02
	C₄F₉CH₂COOH			C₄F₉COOCH₃		
Air	2.68E-11	5.12E-11	5.59E-12	1.24E-03	2.36E-03	2.60E-04
Water	6.56E-10	1.25E-09	1.37E-10	3.03E-02	5.77E-02	6.36E-03
Soil	2.18E-09	4.16E-09	4.54E-10	1.01E-01	1.92E-01	2.11E-02

Cont. Table 68

	1 car			German cars		
	A	WC	BC	A	WC	BC
	[µg/dm³]	[µg/dm³]	[µg/dm³]	[µg/dm³]	[µg/dm³]	[µg/dm³]
	CF₂O from E125			CF₂O from E125		
Air	3.76E-11	9.48E-11	7.94E-12	1.73E-03	4.36E-03	3.65E-04
Water	9.19E-10	2.32E-09	1.94E-10	4.24E-02	1.07E-01	8.94E-03
Soil	5.18E-13	1.31E-12	1.10E-13	2.39E-05	6.02E-05	5.04E-06
	CF₂O from E134			CF₂O from E125		
Air	5.70E-11	1.09E-10	1.20E-11	2.63E-03	5.15E-03	5.56E-04
Water	1.39E-09	2.66E-09	2.94E-10	6.43E-02	1.26E-01	1.36E-02
Soil	7.86E-13	1.50E-12	1.66E-13	3.62E-05	7.09E-05	7.67E-06
	CF₂O from R152a			CF₂O from R152a		
Air	3.18E-11	7.09E-11	6.03E-12	1.47E-03	3.27E-03	2.78E-04
Water	7.79E-10	1.74E-09	1.48E-10	3.59E-02	8.00E-02	6.79E-03
Soil	4.39E-13	9.78E-13	8.31E-14	2.02E-05	4.51E-05	3.83E-06
	HF from R134a			HF from R134a		
Air	5.98E-12	1.15E-11	1.27E-12	2.76E-04	5.28E-04	5.84E-05
Water	2.55E-10	4.87E-10	5.39E-11	1.18E-02	2.25E-02	2.49E-03
Soil	5.33E-12	1.02E-11	1.13E-12	2.46E-04	4.71E-04	5.21E-05
	HF from R152a			HF from R152a		
Air	1.93E-11	4.30E-11	3.65E-12	8.88E-01	1.96E+00	1.68E-01
Water	8.21E-10	1.83E-09	1.55E-10	3.78E+01	8.35E+01	8.43E-04
Soil	1.72E-11	3.83E-11	3.25E-12	7.91E-01	1.75E+00	1.50E-01
	HF from E125			HF from R152a		
Air	2.28E-11	4.35E-11	4.81E-12	1.05E+00	2.01E+00	2.22E-01
Water	9.68E-10	1.85E-09	2.05E-10	4.47E+01	8.55E+01	1.11E-03
Soil	2.03E-11	3.87E-11	4.30E-12	9.37E-01	1.79E+00	1.97E-01
	HF from E134			HF from R152a		
Air	3.45E-11	6.59E-11	7.29E-12	1.59E+00	3.04E+00	3.36E-01
Water	1.47E-09	2.80E-09	3.10E-10	6.78E+01	1.29E+02	5.60E+01
Soil	3.08E-11	5.87E-11	6.50E-12	1.42E+00	2.71E+00	2.99E-01
	HCl from R30			HCl from R30		
Air	2.97E-11	5.66E-11	5.61E-12	1.37E+00	2.62E+00	2.59E-01
Water	1.41E-08	2.69E-08	2.66E-09	6.50E+02	1.24E+03	3.14E+01
Soil	1.31E-10	2.50E-10	2.48E-11	6.05E+00	1.16E+01	1.15E+00

A8 Results of METEOR

Table 69: Weights of selected stability fields

Aggregation					Specific weights				
$\varphi 5$	$\varphi 4$	$\varphi 3$	$\varphi 2$	$\varphi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S5_1_1	S4_1_1	S3_1	S2_1	S1_1	0.31	0.38	0.05	0.18	0.05
S5_1_2	S4_1_1	S3_1	S2_1	S1_1	0.625	0.38	0.05	0.18	0.05
S5_1_3	S4_1_1	S3_1	S2_1	S1_1	0.69	0.38	0.05	0.18	0.05
S5_1_4	S4_1_1	S3_1	S2_1	S1_1	0.795	0.38	0.05	0.18	0.05
S5_1_5	S4_1_1	S3_1	S2_1	S1_1	0.94	0.38	0.05	0.18	0.05
S5_2_1	S4_1_2	S3_1	S2_1	S1_1	0.235	0.62	0.05	0.18	0.05
S5_2_2	S4_1_2	S3_1	S2_1	S1_1	0.695	0.62	0.05	0.18	0.05
S5_2_3	S4_1_2	S3_1	S2_1	S1_1	0.855	0.62	0.05	0.18	0.05
S5_2_4	S4_1_2	S3_1	S2_1	S1_1	0.96	0.62	0.05	0.18	0.05
S5_3_1	S4_2_1	S3_2	S2_1	S1_1	0.095	0.29	0.81	0.18	0.05
S5_3_2	S4_2_1	S3_2	S2_1	S1_1	0.54	0.29	0.81	0.18	0.05
S5_3_3	S4_2_1	S3_2	S2_1	S1_1	0.8	0.29	0.81	0.18	0.05
S5_4_1	S4_2_2	S3_2	S2_1	S1_1	0.625	0.46	0.81	0.18	0.05
S5_4_2	S4_2_2	S3_2	S2_1	S1_1	0.845	0.46	0.81	0.18	0.05
S5_4_3	S4_2_2	S3_2	S2_1	S1_1	0.93	0.46	0.81	0.18	0.05
S5_5_1	S4_2_3	S3_2	S2_1	S1_1	0.65	0.65	0.81	0.18	0.05
S5_5_2	S4_2_3	S3_2	S2_1	S1_1	0.845	0.65	0.81	0.18	0.05
S5_6_1	S4_3_1	S3_1	S2_2	S1_1	0.095	0.45	0.05	0.34	0.05
S5_6_2	S4_3_1	S3_1	S2_2	S1_1	0.225	0.45	0.05	0.34	0.05
S5_6_3	S4_3_1	S3_1	S2_2	S1_1	0.31	0.45	0.05	0.34	0.05
S5_6_4	S4_3_1	S3_1	S2_2	S1_1	0.51	0.45	0.05	0.34	0.05
S5_6_5	S4_3_1	S3_1	S2_2	S1_1	0.63	0.45	0.05	0.34	0.05
S5_6_6	S4_3_1	S3_1	S2_2	S1_1	0.69	0.45	0.05	0.34	0.05
S5_6_7	S4_3_1	S3_1	S2_2	S1_1	0.79	0.45	0.05	0.34	0.05
S5_6_8	S4_3_1	S3_1	S2_2	S1_1	0.84	0.45	0.05	0.34	0.05
S5_6_9	S4_3_1	S3_1	S2_2	S1_1	0.905	0.45	0.05	0.34	0.05
S5_6_10	S4_3_1	S3_1	S2_2	S1_1	0.97	0.45	0.05	0.34	0.05
S5_7_1	S4_3_2	S3_1	S2_2	S1_1	0.68	0.67	0.05	0.34	0.05
S5_7_2	S4_3_2	S3_1	S2_2	S1_1	0.855	0.67	0.05	0.34	0.05
S5_8_1	S4_4_1	S3_2	S2_2	S1_1	0.03	0.09	0.81	0.34	0.05

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S5_8_2	S4_4_1	S3_2	S2_2	S1_1	0.895	0.09	0.81	0.34	0.05
S5_9_1	S4_4_2	S3_2	S2_2	S1_1	0.8	0.3	0.81	0.34	0.05
S5_9_2	S4_4_2	S3_2	S2_2	S1_1	0.905	0.3	0.81	0.34	0.05
S5_10_1	S4_4_3	S3_2	S2_2	S1_1	0.135	0.47	0.81	0.34	0.05
S5_10_2	S4_4_3	S3_2	S2_2	S1_1	0.71	0.47	0.81	0.34	0.05
S5_10_3	S4_4_3	S3_2	S2_2	S1_1	0.785	0.47	0.81	0.34	0.05
S5_10_4	S4_4_3	S3_2	S2_2	S1_1	0.85	0.47	0.81	0.34	0.05
S5_10_5	S4_4_3	S3_2	S2_2	S1_1	0.93	0.47	0.81	0.34	0.05
S5_11_1	S4_5_1	S3_1	S2_3	S1_1	0.36	0.3	0.05	0.55	0.05
S5_11_2	S4_5_1	S3_1	S2_3	S1_1	0.695	0.3	0.05	0.55	0.05
S5_11_3	S4_5_1	S3_1	S2_3	S1_1	0.825	0.3	0.05	0.55	0.05
S5_11_4	S4_5_1	S3_1	S2_3	S1_1	0.92	0.3	0.05	0.55	0.05
S5_12_1	S4_5_2	S3_1	S2_3	S1_1	0.03	0.52	0.05	0.55	0.05
S5_12_2	S4_5_2	S3_1	S2_3	S1_1	0.51	0.52	0.05	0.55	0.05
S5_12_3	S4_5_2	S3_1	S2_3	S1_1	0.795	0.52	0.05	0.55	0.05
S5_12_4	S4_5_2	S3_1	S2_3	S1_1	0.92	0.52	0.05	0.55	0.05
S5_13_1	S4_5_3	S3_1	S2_3	S1_1	0.065	0.7	0.05	0.55	0.05
S5_13_2	S4_5_3	S3_1	S2_3	S1_1	0.21	0.7	0.05	0.55	0.05
S5_13_3	S4_5_3	S3_1	S2_3	S1_1	0.55	0.7	0.05	0.55	0.05
S5_13_4	S4_5_3	S3_1	S2_3	S1_1	0.68	0.7	0.05	0.55	0.05
S5_13_5	S4_5_3	S3_1	S2_3	S1_1	0.795	0.7	0.05	0.55	0.05
S5_13_6	S4_5_3	S3_1	S2_3	S1_1	0.875	0.7	0.05	0.55	0.05
S5_13_7	S4_5_3	S3_1	S2_3	S1_1	0.945	0.7	0.05	0.55	0.05
S5_14_1	S4_6_1	S3_2	S2_3	S1_1	0.125	0.18	0.81	0.55	0.05
S5_14_2	S4_6_1	S3_2	S2_3	S1_1	0.33	0.18	0.81	0.55	0.05
S5_14_3	S4_6_1	S3_2	S2_3	S1_1	0.805	0.18	0.81	0.55	0.05
S5_14_4	S4_6_1	S3_2	S2_3	S1_1	0.91	0.18	0.81	0.55	0.05
S5_15_1	S4_6_2	S3_2	S2_3	S1_1	0.775	0.32	0.81	0.55	0.05
S5_15_2	S4_6_2	S3_2	S2_3	S1_1	0.905	0.32	0.81	0.55	0.05
S5_16_1	S4_6_3	S3_2	S2_3	S1_1	0.105	0.61	0.81	0.55	0.05
S5_16_2	S4_6_3	S3_2	S2_3	S1_1	0.59	0.61	0.81	0.55	0.05
S5_16_3	S4_6_3	S3_2	S2_3	S1_1	0.82	0.61	0.81	0.55	0.05

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S5_16_4	S4_6_3	S3_2	S2_3	S1_1	0.875	0.61	0.81	0.55	0.05
S5_16_5	S4_6_3	S3_2	S2_3	S1_1	0.945	0.61	0.81	0.55	0.05
S5_17_1	S4_6_4	S3_2	S2_3	S1_1	0.035	0.85	0.81	0.55	0.05
S5_17_2	S4_6_4	S3_2	S2_3	S1_1	0.11	0.85	0.81	0.55	0.05
S5_17_3	S4_6_4	S3_2	S2_3	S1_1	0.295	0.85	0.81	0.55	0.05
S5_17_4	S4_6_4	S3_2	S2_3	S1_1	0.365	0.85	0.81	0.55	0.05
S5_17_5	S4_6_4	S3_2	S2_3	S1_1	0.395	0.85	0.81	0.55	0.05
S5_17_6	S4_6_4	S3_2	S2_3	S1_1	0.485	0.85	0.81	0.55	0.05
S5_17_7	S4_6_4	S3_2	S2_3	S1_1	0.545	0.85	0.81	0.55	0.05
S5_17_8	S4_6_4	S3_2	S2_3	S1_1	0.635	0.85	0.81	0.55	0.05
S5_17_9	S4_6_4	S3_2	S2_3	S1_1	0.68	0.85	0.81	0.55	0.05
S5_17_10	S4_6_4	S3_2	S2_3	S1_1	0.745	0.85	0.81	0.55	0.05
S5_17_11	S4_6_4	S3_2	S2_3	S1_1	0.795	0.85	0.81	0.55	0.05
S5_17_12	S4_6_4	S3_2	S2_3	S1_1	0.85	0.85	0.81	0.55	0.05
S5_17_13	S4_6_4	S3_2	S2_3	S1_1	0.91	0.85	0.81	0.55	0.05
S5_17_14	S4_6_4	S3_2	S2_3	S1_1	0.96	0.85	0.81	0.55	0.05
S5_18_1	S4_7_1	S3_1	S2_4	S1_1	0.21	0.28	0.05	0.905	0.05
S5_18_2	S4_7_1	S3_1	S2_4	S1_1	0.6	0.28	0.05	0.905	0.05
S5_18_3	S4_7_1	S3_1	S2_4	S1_1	0.69	0.28	0.05	0.905	0.05
S5_18_4	S4_7_1	S3_1	S2_4	S1_1	0.825	0.28	0.05	0.905	0.05
S5_18_5	S4_7_1	S3_1	S2_4	S1_1	0.925	0.28	0.05	0.905	0.05
S5_18_6	S4_7_1	S3_1	S2_4	S1_1	0.98	0.28	0.05	0.905	0.05
S5_19_1	S4_7_2	S3_1	S2_4	S1_1	0.03	0.46	0.05	0.905	0.05
S5_19_2	S4_7_2	S3_1	S2_4	S1_1	0.925	0.46	0.05	0.905	0.05
S5_20_1	S4_7_3	S3_1	S2_4	S1_1	0.07	0.66	0.05	0.905	0.05
S5_20_2	S4_7_3	S3_1	S2_4	S1_1	0.925	0.66	0.05	0.905	0.05
S5_21_1	S4_8_1	S3_2	S2_4	S1_1	0.03	0.04	0.81	0.905	0.05
S5_21_2	S4_8_1	S3_2	S2_4	S1_1	0.895	0.04	0.81	0.905	0.05
S5_22_1	S4_8_2	S3_2	S2_4	S1_1	0.8	0.15	0.81	0.905	0.05
S5_22_2	S4_8_2	S3_2	S2_4	S1_1	0.905	0.15	0.81	0.905	0.05
S5_23_1	S4_8_3	S3_2	S2_4	S1_1	0.79	0.24	0.81	0.905	0.05
S5_23_2	S4_8_3	S3_2	S2_4	S1_1	0.905	0.24	0.81	0.905	0.05

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S5_24	S4_8_4	S3_2	S2_4	S1_1	0.905	0.3	0.81	0.905	0.05
S5_25	S4_8_5	S3_2	S2_4	S1_1	0.9	0.37	0.81	0.905	0.05
S5_26	S4_8_6	S3_2	S2_4	S1_1	0.905	0.43	0.81	0.905	0.05
S5_27_1	S4_8_7	S3_2	S2_4	S1_1	0.115	0.49	0.81	0.905	0.05
S5_27_2	S4_8_7	S3_2	S2_4	S1_1	0.76	0.49	0.81	0.905	0.05
S5_27_3	S4_8_7	S3_2	S2_4	S1_1	0.91	0.49	0.81	0.905	0.05
S5_28_1	S4_8_8	S3_2	S2_4	S1_1	0.085	0.57	0.81	0.905	0.05
S5_28_2	S4_8_8	S3_2	S2_4	S1_1	0.92	0.57	0.81	0.905	0.05
S5_29_1	S4_8_9	S3_2	S2_4	S1_1	0.8	0.66	0.81	0.905	0.05
S5_29_2	S4_8_9	S3_2	S2_4	S1_1	0.935	0.66	0.81	0.905	0.05
S5_30_1	S4_8_10	S3_2	S2_4	S1_1	0.06	0.75	0.81	0.905	0.05
S5_30_2	S4_8_10	S3_2	S2_4	S1_1	0.13	0.75	0.81	0.905	0.05
S5_30_3	S4_8_10	S3_2	S2_4	S1_1	0.51	0.75	0.81	0.905	0.05
S5_30_4	S4_8_10	S3_2	S2_4	S1_1	0.81	0.75	0.81	0.905	0.05
S5_30_5	S4_8_10	S3_2	S2_4	S1_1	0.94	0.75	0.81	0.905	0.05
S5_31_1	S4_8_11	S3_2	S2_4	S1_1	0.035	0.8	0.81	0.905	0.05
S5_31_2	S4_8_11	S3_2	S2_4	S1_1	0.355	0.8	0.81	0.905	0.05
S5_31_3	S4_8_11	S3_2	S2_4	S1_1	0.945	0.8	0.81	0.905	0.05
S6_1_1	S4_1_1	S3_1	S2_1	S1_2	0.875	0.38	0.05	0.18	0.21
S6_1_2	S4_1_1	S3_1	S2_1	S1_2	0.965	0.38	0.05	0.18	0.21
S6_2_1	S4_1_2	S3_1	S2_1	S1_2	0.815	0.62	0.05	0.18	0.21
S6_2_2	S4_1_2	S3_1	S2_1	S1_2	0.945	0.62	0.05	0.18	0.21
S6_3	S4_2_1	S3_2	S2_1	S1_2	0.915	0.29	0.81	0.18	0.21
S6_4	S4_2_2	S3_2	S2_1	S1_2	0.89	0.46	0.81	0.18	0.21
S6_5	S4_2_3	S3_2	S2_1	S1_2	0.89	0.65	0.81	0.18	0.21
S6_6_1	S4_3_1	S3_1	S2_2	S1_2	0.865	0.45	0.05	0.34	0.21
S6_6_2	S4_3_1	S3_1	S2_2	S1_2	0.96	0.45	0.05	0.34	0.21
S6_7_1	S4_3_2	S3_1	S2_2	S1_2	0.705	0.67	0.05	0.34	0.21
S6_7_2	S4_3_2	S3_1	S2_2	S1_2	0.83	0.67	0.05	0.34	0.21
S6_7_3	S4_3_2	S3_1	S2_2	S1_2	0.94	0.67	0.05	0.34	0.21
S6_8	S4_4_1	S3_2	S2_2	S1_2	0.915	0.09	0.81	0.34	0.21
S6_9	S4_4_2	S3_2	S2_2	S1_2	0.915	0.3	0.81	0.34	0.21

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S6_10	S4_4_3	S3_2	S2_2	S1_2	0.895	0.47	0.81	0.34	0.21
S6_11_1	S4_5_1	S3_1	S2_3	S1_2	0.825	0.3	0.05	0.55	0.21
S6_11_2	S4_5_1	S3_1	S2_3	S1_2	0.895	0.3	0.05	0.55	0.21
S6_11_3	S4_5_1	S3_1	S2_3	S1_2	0.97	0.3	0.05	0.55	0.21
S6_12_1	S4_5_2	S3_1	S2_3	S1_2	0.025	0.52	0.05	0.55	0.21
S6_12_2	S4_5_2	S3_1	S2_3	S1_2	0.495	0.52	0.05	0.55	0.21
S6_12_3	S4_5_2	S3_1	S2_3	S1_2	0.78	0.52	0.05	0.55	0.21
S6_12_4	S4_5_2	S3_1	S2_3	S1_2	0.875	0.52	0.05	0.55	0.21
S6_12_5	S4_5_2	S3_1	S2_3	S1_2	0.96	0.52	0.05	0.55	0.21
S6_13_1	S4_5_3	S3_1	S2_3	S1_2	0.56	0.7	0.05	0.55	0.21
S6_13_2	S4_5_3	S3_1	S2_3	S1_2	0.845	0.7	0.05	0.55	0.21
S6_13_3	S4_5_3	S3_1	S2_3	S1_2	0.94	0.7	0.05	0.55	0.21
S6_14	S4_6_1	S3_2	S2_3	S1_2	0.92	0.18	0.81	0.55	0.21
S6_15	S4_6_2	S3_2	S2_3	S1_2	0.91	0.32	0.81	0.55	0.21
S6_16	S4_6_3	S3_2	S2_3	S1_2	0.94	0.61	0.81	0.55	0.21
S6_17_1	S4_6_4	S3_2	S2_3	S1_2	0.425	0.85	0.81	0.55	0.21
S6_17_2	S4_6_4	S3_2	S2_3	S1_2	0.51	0.85	0.81	0.55	0.21
S6_17_3	S4_6_4	S3_2	S2_3	S1_2	0.695	0.85	0.81	0.55	0.21
S6_17_4	S4_6_4	S3_2	S2_3	S1_2	0.955	0.85	0.81	0.55	0.21
S6_18_1	S4_7_1	S3_1	S2_4	S1_2	0.345	0.28	0.05	0.905	0.21
S6_18_2	S4_7_1	S3_1	S2_4	S1_2	0.825	0.28	0.05	0.905	0.21
S6_18_3	S4_7_1	S3_1	S2_4	S1_2	0.895	0.28	0.05	0.905	0.21
S6_18_4	S4_7_1	S3_1	S2_4	S1_2	0.97	0.28	0.05	0.905	0.21
S6_19_1	S4_7_2	S3_1	S2_4	S1_2	0.32	0.46	0.05	0.905	0.21
S6_19_2	S4_7_2	S3_1	S2_4	S1_2	0.8	0.46	0.05	0.905	0.21
S6_19_3	S4_7_2	S3_1	S2_4	S1_2	0.845	0.46	0.05	0.905	0.21
S6_19_4	S4_7_2	S3_1	S2_4	S1_2	0.895	0.46	0.05	0.905	0.21
S6_19_5	S4_7_2	S3_1	S2_4	S1_2	0.96	0.46	0.05	0.905	0.21
S6_20_1	S4_7_3	S3_1	S2_4	S1_2	0.555	0.66	0.05	0.905	0.21
S6_20_2	S4_7_3	S3_1	S2_4	S1_2	0.955	0.66	0.05	0.905	0.21
S6_21	S4_8_1	S3_2	S2_4	S1_2	0.915	0.04	0.81	0.905	0.21
S6_22	S4_8_2	S3_2	S2_4	S1_2	0.915	0.15	0.81	0.905	0.21

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S6_23	S4_8_3	S3_2	S2_4	S1_2	0.91	0.24	0.81	0.905	0.21
S6_24	S4_8_4	S3_2	S2_4	S1_2	0.91	0.3	0.81	0.905	0.21
S6_25	S4_8_5	S3_2	S2_4	S1_2	0.925	0.37	0.81	0.905	0.21
S6_26	S4_8_6	S3_2	S2_4	S1_2	0.935	0.43	0.81	0.905	0.21
S6_27	S4_8_7	S3_2	S2_4	S1_2	0.94	0.49	0.81	0.905	0.21
S6_28_1	S4_8_8	S3_2	S2_4	S1_2	0.07	0.57	0.81	0.905	0.21
S6_28_2	S4_8_8	S3_2	S2_4	S1_2	0.695	0.57	0.81	0.905	0.21
S6_28_3	S4_8_8	S3_2	S2_4	S1_2	0.95	0.57	0.81	0.905	0.21
S6_29_1	S4_8_9	S3_2	S2_4	S1_2	0.615	0.66	0.81	0.905	0.21
S6_29_2	S4_8_9	S3_2	S2_4	S1_2	0.725	0.66	0.81	0.905	0.21
S6_29_3	S4_8_9	S3_2	S2_4	S1_2	0.955	0.66	0.81	0.905	0.21
S6_30_1	S4_8_10	S3_2	S2_4	S1_2	0.14	0.75	0.81	0.905	0.21
S6_30_2	S4_8_10	S3_2	S2_4	S1_2	0.405	0.75	0.81	0.905	0.21
S6_30_3	S4_8_10	S3_2	S2_4	S1_2	0.535	0.75	0.81	0.905	0.21
S6_30_4	S4_8_10	S3_2	S2_4	S1_2	0.735	0.75	0.81	0.905	0.21
S6_30_5	S4_8_10	S3_2	S2_4	S1_2	0.9	0.75	0.81	0.905	0.21
S6_30_6	S4_8_10	S3_2	S2_4	S1_2	0.96	0.75	0.81	0.905	0.21
S6_31_1	S4_8_11	S3_2	S2_4	S1_2	0.46	0.8	0.81	0.905	0.21
S6_31_2	S4_8_11	S3_2	S2_4	S1_2	0.55	0.8	0.81	0.905	0.21
S6_31_3	S4_8_11	S3_2	S2_4	S1_2	0.74	0.8	0.81	0.905	0.21
S6_31_4	S4_8_11	S3_2	S2_4	S1_2	0.96	0.8	0.81	0.905	0.21
S7_1_1	S4_1_1	S3_1	S2_1	S1_3	0.285	0.38	0.05	0.18	0.575
S7_1_2	S4_1_1	S3_1	S2_1	S1_3	0.675	0.38	0.05	0.18	0.575
S7_1_3	S4_1_1	S3_1	S2_1	S1_3	0.77	0.38	0.05	0.18	0.575
S7_1_4	S4_1_1	S3_1	S2_1	S1_3	0.86	0.38	0.05	0.18	0.575
S7_1_5	S4_1_1	S3_1	S2_1	S1_3	0.935	0.38	0.05	0.18	0.575
S7_2	S4_1_2	S3_1	S2_1	S1_3	0.855	0.62	0.05	0.18	0.575
S7_3_1	S4_2_1	S3_2	S2_1	S1_3	0.36	0.29	0.81	0.18	0.575
S7_3_2	S4_2_1	S3_2	S2_1	S1_3	0.77	0.29	0.81	0.18	0.575
S7_3_3	S4_2_1	S3_2	S2_1	S1_3	0.835	0.29	0.81	0.18	0.575
S7_4_1	S4_2_2	S3_2	S2_1	S1_3	0.105	0.46	0.81	0.18	0.575
S7_4_2	S4_2_2	S3_2	S2_1	S1_3	0.645	0.46	0.81	0.18	0.575

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	g5	g4	g3	g2	g1
S7_4_3	S4_2_2	S3_2	S2_1	S1_3	0.805	0.46	0.81	0.18	0.575
S7_4_4	S4_2_2	S3_2	S2_1	S1_3	0.885	0.46	0.81	0.18	0.575
S7_4_5	S4_2_2	S3_2	S2_1	S1_3	0.965	0.46	0.81	0.18	0.575
S7_5_1	S4_2_3	S3_2	S2_1	S1_3	0.61	0.65	0.81	0.18	0.575
S7_5_2	S4_2_3	S3_2	S2_1	S1_3	0.675	0.65	0.81	0.18	0.575
S7_5_3	S4_2_3	S3_2	S2_1	S1_3	0.765	0.65	0.81	0.18	0.575
S7_5_4	S4_2_3	S3_2	S2_1	S1_3	0.875	0.65	0.81	0.18	0.575
S7_5_5	S4_2_3	S3_2	S2_1	S1_3	0.97	0.65	0.81	0.18	0.575
S7_6_1	S4_3_1	S3_1	S2_2	S1_3	0.26	0.45	0.05	0.34	0.575
S7_6_2	S4_3_1	S3_1	S2_2	S1_3	0.86	0.45	0.05	0.34	0.575
S7_7_1	S4_3_2	S3_1	S2_2	S1_3	0.535	0.67	0.05	0.34	0.575
S7_7_2	S4_3_2	S3_1	S2_2	S1_3	0.665	0.67	0.05	0.34	0.575
S7_7_3	S4_3_2	S3_1	S2_2	S1_3	0.665	0.67	0.05	0.34	0.575
S7_7_4	S4_3_2	S3_1	S2_2	S1_3	0.875	0.67	0.05	0.34	0.575
S7_7_5	S4_3_2	S3_1	S2_2	S1_3	0.97	0.67	0.05	0.34	0.575
S7_8	S4_4_1	S3_2	S2_2	S1_3	0.925	0.09	0.81	0.34	0.575
S7_9_1	S4_4_2	S3_2	S2_2	S1_3	0.145	0.3	0.81	0.34	0.575
S7_9_2	S4_4_2	S3_2	S2_2	S1_3	0.365	0.3	0.81	0.34	0.575
S7_9_3	S4_4_2	S3_2	S2_2	S1_3	0.855	0.3	0.81	0.34	0.575
S7_9_4	S4_4_2	S3_2	S2_2	S1_3	0.95	0.3	0.81	0.34	0.575
S7_10_1	S4_4_3	S3_2	S2_2	S1_3	0.03	0.47	0.81	0.34	0.575
S7_10_2	S4_4_3	S3_2	S2_2	S1_3	0.21	0.47	0.81	0.34	0.575
S7_10_3	S4_4_3	S3_2	S2_2	S1_3	0.31	0.47	0.81	0.34	0.575
S7_10_4	S4_4_3	S3_2	S2_2	S1_3	0.36	0.47	0.81	0.34	0.575
S7_10_5	S4_4_3	S3_2	S2_2	S1_3	0.655	0.47	0.81	0.34	0.575
S7_10_6	S4_4_3	S3_2	S2_2	S1_3	0.735	0.47	0.81	0.34	0.575
S7_10_7	S4_4_3	S3_2	S2_2	S1_3	0.78	0.47	0.81	0.34	0.575
S7_10_8	S4_4_3	S3_2	S2_2	S1_3	0.845	0.47	0.81	0.34	0.575
S7_10_9	S4_4_3	S3_2	S2_2	S1_3	0.9	0.47	0.81	0.34	0.575
S7_10_10	S4_4_3	S3_2	S2_2	S1_3	0.965	0.47	0.81	0.34	0.575
S7_11_1	S4_5_1	S3_1	S2_3	S1_3	0.3	0.3	0.05	0.55	0.575
S7_11_2	S4_5_1	S3_1	S2_3	S1_3	0.735	0.3	0.05	0.55	0.575

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S7_11_3	S4_5_1	S3_1	S2_3	S1_3	0.925	0.3	0.05	0.55	0.575
S7_12_1	S4_5_2	S3_1	S2_3	S1_3	0.02	0.52	0.05	0.55	0.575
S7_12_2	S4_5_2	S3_1	S2_3	S1_3	0.52	0.52	0.05	0.55	0.575
S7_12_3	S4_5_2	S3_1	S2_3	S1_3	0.63	0.52	0.05	0.55	0.575
S7_12_4	S4_5_2	S3_1	S2_3	S1_3	0.74	0.52	0.05	0.55	0.575
S7_12_5	S4_5_2	S3_1	S2_3	S1_3	0.885	0.52	0.05	0.55	0.575
S7_12_6	S4_5_2	S3_1	S2_3	S1_3	0.94	0.52	0.05	0.55	0.575
S7_12_7	S4_5_2	S3_1	S2_3	S1_3	0.98	0.52	0.05	0.55	0.575
S7_13_1	S4_5_3	S3_1	S2_3	S1_3	0.18	0.7	0.05	0.55	0.575
S7_13_2	S4_5_3	S3_1	S2_3	S1_3	0.02	0.7	0.05	0.55	0.575
S7_13_3	S4_5_3	S3_1	S2_3	S1_3	0.61	0.7	0.05	0.55	0.575
S7_13_4	S4_5_3	S3_1	S2_3	S1_3	0.735	0.7	0.05	0.55	0.575
S7_13_5	S4_5_3	S3_1	S2_3	S1_3	0.79	0.7	0.05	0.55	0.575
S7_13_6	S4_5_3	S3_1	S2_3	S1_3	0.87	0.7	0.05	0.55	0.575
S7_13_7	S4_5_3	S3_1	S2_3	S1_3	0.915	0.7	0.05	0.55	0.575
S7_13_8	S4_5_3	S3_1	S2_3	S1_3	0.97	0.7	0.05	0.55	0.575
S7_14	S4_6_1	S3_2	S2_3	S1_3	0.935	0.18	0.81	0.55	0.575
S7_15_1	S4_6_2	S3_2	S2_3	S1_3	0.045	0.32	0.81	0.55	0.575
S7_15_2	S4_6_2	S3_2	S2_3	S1_3	0.33	0.32	0.81	0.55	0.575
S7_15_3	S4_6_2	S3_2	S2_3	S1_3	0.765	0.32	0.81	0.55	0.575
S7_15_4	S4_6_2	S3_2	S2_3	S1_3	0.945	0.32	0.81	0.55	0.575
S7_16_1	S4_6_3	S3_2	S2_3	S1_3	0.115	0.61	0.81	0.55	0.575
S7_16_2	S4_6_3	S3_2	S2_3	S1_3	0.15	0.61	0.81	0.55	0.575
S7_16_3	S4_6_3	S3_2	S2_3	S1_3	0.185	0.61	0.81	0.55	0.575
S7_16_4	S4_6_3	S3_2	S2_3	S1_3	0.215	0.61	0.81	0.55	0.575
S7_16_5	S4_6_3	S3_2	S2_3	S1_3	0.255	0.61	0.81	0.55	0.575
S7_16_6	S4_6_3	S3_2	S2_3	S1_3	0.445	0.61	0.81	0.55	0.575
S7_16_7	S4_6_3	S3_2	S2_3	S1_3	0.475	0.61	0.81	0.55	0.575
S7_16_8	S4_6_3	S3_2	S2_3	S1_3	0.515	0.61	0.81	0.55	0.575
S7_16_9	S4_6_3	S3_2	S2_3	S1_3	0.585	0.61	0.81	0.55	0.575
S7_16_10	S4_6_3	S3_2	S2_3	S1_3	0.695	0.61	0.81	0.55	0.575
S7_16_11	S4_6_3	S3_2	S2_3	S1_3	0.745	0.61	0.81	0.55	0.575

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	g5	g4	g3	g2	g1
S7_16_12	S4_6_3	S3_2	S2_3	S1_3	0.79	0.61	0.81	0.55	0.575
S7_16_13	S4_6_3	S3_2	S2_3	S1_3	0.835	0.61	0.81	0.55	0.575
S7_16_14	S4_6_3	S3_2	S2_3	S1_3	0.89	0.61	0.81	0.55	0.575
S7_16_15	S4_6_3	S3_2	S2_3	S1_3	0.925	0.61	0.81	0.55	0.575
S7_16_16	S4_6_3	S3_2	S2_3	S1_3	0.97	0.61	0.81	0.55	0.575
S7_17_1	S4_6_4	S3_2	S2_3	S1_3	0.37	0.85	0.81	0.55	0.575
S7_17_2	S4_6_4	S3_2	S2_3	S1_3	0.605	0.85	0.81	0.55	0.575
S7_17_3	S4_6_4	S3_2	S2_3	S1_3	0.685	0.85	0.81	0.55	0.575
S7_17_4	S4_6_4	S3_2	S2_3	S1_3	0.765	0.85	0.81	0.55	0.575
S7_17_5	S4_6_4	S3_2	S2_3	S1_3	0.825	0.85	0.81	0.55	0.575
S7_17_6	S4_6_4	S3_2	S2_3	S1_3	0.975	0.85	0.81	0.55	0.575
S7_18	S4_7_1	S3_1	S2_4	S1_3	0.905	0.28	0.05	0.905	0.575
S7_19_1	S4_7_2	S3_1	S2_4	S1_3	0.02	0.46	0.05	0.905	0.575
S7_19_2	S4_7_2	S3_1	S2_4	S1_3	0.26	0.46	0.05	0.905	0.575
S7_19_3	S4_7_2	S3_1	S2_4	S1_3	0.52	0.46	0.05	0.905	0.575
S7_19_4	S4_7_2	S3_1	S2_4	S1_3	0.765	0.46	0.05	0.905	0.575
S7_19_5	S4_7_2	S3_1	S2_4	S1_3	0.83	0.46	0.05	0.905	0.575
S7_19_6	S4_7_2	S3_1	S2_4	S1_3	0.92	0.46	0.05	0.905	0.575
S7_19_7	S4_7_2	S3_1	S2_4	S1_3	0.98	0.46	0.05	0.905	0.575
S7_20_1	S4_7_3	S3_1	S2_4	S1_3	0.525	0.66	0.05	0.905	0.575
S7_20_2	S4_7_3	S3_1	S2_4	S1_3	0.78	0.66	0.05	0.905	0.575
S7_21	S4_8_1	S3_2	S2_4	S1_3	0.925	0.04	0.81	0.905	0.575
S7_22	S4_8_2	S3_2	S2_4	S1_3	0.94	0.15	0.81	0.905	0.575
S7_23_1	S4_8_3	S3_2	S2_4	S1_3	0.04	0.24	0.81	0.905	0.575
S7_23_2	S4_8_3	S3_2	S2_4	S1_3	0.76	0.24	0.81	0.905	0.575
S7_23_3	S4_8_3	S3_2	S2_4	S1_3	0.945	0.24	0.81	0.905	0.575
S7_24_1	S4_8_4	S3_2	S2_4	S1_3	0.035	0.3	0.81	0.905	0.575
S7_24_2	S4_8_4	S3_2	S2_4	S1_3	0.225	0.3	0.81	0.905	0.575
S7_24_3	S4_8_4	S3_2	S2_4	S1_3	0.32	0.3	0.81	0.905	0.575
S7_24_4	S4_8_4	S3_2	S2_4	S1_3	0.875	0.3	0.81	0.905	0.575
S7_24_5	S4_8_4	S3_2	S2_4	S1_3	0.95	0.3	0.81	0.905	0.575
S7_25_1	S4_8_5	S3_2	S2_4	S1_3	0.025	0.37	0.81	0.905	0.575

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S7_25_2	S4_8_5	S3_2	S2_4	S1_3	0.74	0.37	0.81	0.905	0.575
S7_25_3	S4_8_5	S3_2	S2_4	S1_3	0.82	0.37	0.81	0.905	0.575
S7_25_4	S4_8_5	S3_2	S2_4	S1_3	0.955	0.37	0.81	0.905	0.575
S7_26_1	S4_8_6	S3_2	S2_4	S1_3	0.18	0.43	0.81	0.905	0.575
S7_26_2	S4_8_6	S3_2	S2_4	S1_3	0.255	0.43	0.81	0.905	0.575
S7_26_3	S4_8_6	S3_2	S2_4	S1_3	0.475	0.43	0.81	0.905	0.575
S7_26_4	S4_8_6	S3_2	S2_4	S1_3	0.78	0.43	0.81	0.905	0.575
S7_26_5	S4_8_6	S3_2	S2_4	S1_3	0.835	0.43	0.81	0.905	0.575
S7_26_6	S4_8_6	S3_2	S2_4	S1_3	0.955	0.43	0.81	0.905	0.575
S7_27_1	S4_8_7	S3_2	S2_4	S1_3	0.775	0.49	0.81	0.905	0.575
S7_27_2	S4_8_7	S3_2	S2_4	S1_3	0.845	0.49	0.81	0.905	0.575
S7_27_3	S4_8_7	S3_2	S2_4	S1_3	0.96	0.49	0.81	0.905	0.575
S7_28_1	S4_8_8	S3_2	S2_4	S1_3	0.535	0.57	0.81	0.905	0.575
S7_28_2	S4_8_8	S3_2	S2_4	S1_3	0.79	0.57	0.81	0.905	0.575
S7_28_3	S4_8_8	S3_2	S2_4	S1_3	0.96	0.57	0.81	0.905	0.575
S7_29_1	S4_8_9	S3_2	S2_4	S1_3	0.185	0.66	0.81	0.905	0.575
S7_29_2	S4_8_9	S3_2	S2_4	S1_3	0.475	0.66	0.81	0.905	0.575
S7_29_3	S4_8_9	S3_2	S2_4	S1_3	0.8	0.66	0.81	0.905	0.575
S7_29_4	S4_8_9	S3_2	S2_4	S1_3	0.96	0.66	0.81	0.905	0.575
S7_30_1	S4_8_10	S3_2	S2_4	S1_3	0.815	0.75	0.81	0.905	0.575
S7_30_2	S4_8_10	S3_2	S2_4	S1_3	0.965	0.75	0.81	0.905	0.575
S7_31_1	S4_8_11	S3_2	S2_4	S1_3	0.815	0.8	0.81	0.905	0.575
S7_31_2	S4_8_11	S3_2	S2_4	S1_3	0.965	0.8	0.81	0.905	0.575
S8_1_1	S4_1_1	S3_1	S2_1	S1_4	0.815	0.38	0.05	0.18	0.785
S8_1_2	S4_1_1	S3_1	S2_1	S1_4	0.965	0.38	0.05	0.18	0.785
S8_2_1	S4_1_2	S3_1	S2_1	S1_4	0.2	0.62	0.05	0.18	0.785
S8_2_2	S4_1_2	S3_1	S2_1	S1_4	0.365	0.62	0.05	0.18	0.785
S8_2_3	S4_1_2	S3_1	S2_1	S1_4	0.56	0.62	0.05	0.18	0.785
S8_2_4	S4_1_2	S3_1	S2_1	S1_4	0.645	0.62	0.05	0.18	0.785
S8_2_5	S4_1_2	S3_1	S2_1	S1_4	0.79	0.62	0.05	0.18	0.785
S8_2_6	S4_1_2	S3_1	S2_1	S1_4	0.85	0.62	0.05	0.18	0.785
S8_2_7	S4_1_2	S3_1	S2_1	S1_4	0.9	0.62	0.05	0.18	0.785

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S8_2_8	S4_1_2	S3_1	S2_1	S1_4	0.96	0.62	0.05	0.18	0.785
S8_3_1	S4_2_1	S3_2	S2_1	S1_4	0.04	0.29	0.81	0.18	0.785
S8_3_2	S4_2_1	S3_2	S2_1	S1_4	0.29	0.29	0.81	0.18	0.785
S8_3_3	S4_2_1	S3_2	S2_1	S1_4	0.91	0.29	0.81	0.18	0.785
S8_4_1	S4_2_2	S3_2	S2_1	S1_4	0.23	0.46	0.81	0.18	0.785
S8_4_2	S4_2_2	S3_2	S2_1	S1_4	0.02	0.46	0.81	0.18	0.785
S8_4_3	S4_2_2	S3_2	S2_1	S1_4	0.61	0.46	0.81	0.18	0.785
S8_4_4	S4_2_2	S3_2	S2_1	S1_4	0.71	0.46	0.81	0.18	0.785
S8_4_5	S4_2_2	S3_2	S2_1	S1_4	0.78	0.46	0.81	0.18	0.785
S8_4_6	S4_2_2	S3_2	S2_1	S1_4	0.915	0.46	0.81	0.18	0.785
S8_4_7	S4_2_2	S3_2	S2_1	S1_4	0.975	0.46	0.81	0.18	0.785
S8_5_1	S4_2_3	S3_2	S2_1	S1_4	0.14	0.65	0.81	0.18	0.785
S8_5_2	S4_2_3	S3_2	S2_1	S1_4	0.51	0.65	0.81	0.18	0.785
S8_5_3	S4_2_3	S3_2	S2_1	S1_4	0.565	0.65	0.81	0.18	0.785
S8_5_4	S4_2_3	S3_2	S2_1	S1_4	0.625	0.65	0.81	0.18	0.785
S8_5_5	S4_2_3	S3_2	S2_1	S1_4	0.68	0.65	0.81	0.18	0.785
S8_5_6	S4_2_3	S3_2	S2_1	S1_4	0.79	0.65	0.81	0.18	0.785
S8_5_7	S4_2_3	S3_2	S2_1	S1_4	0.96	0.65	0.81	0.18	0.785
S8_6_1	S4_3_1	S3_1	S2_2	S1_4	0.28	0.45	0.05	0.34	0.785
S8_6_2	S4_3_1	S3_1	S2_2	S1_4	0.93	0.45	0.05	0.34	0.785
S8_7_1	S4_3_2	S3_1	S2_2	S1_4	0.195	0.67	0.05	0.34	0.785
S8_7_2	S4_3_2	S3_1	S2_2	S1_4	0.665	0.67	0.05	0.34	0.785
S8_7_3	S4_3_2	S3_1	S2_2	S1_4	0.795	0.67	0.05	0.34	0.785
S8_7_4	S4_3_2	S3_1	S2_2	S1_4	0.845	0.67	0.05	0.34	0.785
S8_7_5	S4_3_2	S3_1	S2_2	S1_4	0.95	0.67	0.05	0.34	0.785
S8_8	S4_4_1	S3_2	S2_2	S1_4	0.91	0.09	0.81	0.34	0.785
S8_9_1	S4_4_2	S3_2	S2_2	S1_4	0.025	0.3	0.81	0.34	0.785
S8_9_2	S4_4_2	S3_2	S2_2	S1_4	0.3	0.3	0.81	0.34	0.785
S8_9_3	S4_4_2	S3_2	S2_2	S1_4	0.935	0.3	0.81	0.34	0.785
S8_10_1	S4_4_3	S3_2	S2_2	S1_4	0.035	0.47	0.81	0.34	0.785
S8_10_2	S4_4_3	S3_2	S2_2	S1_4	0.215	0.47	0.81	0.34	0.785
S8_10_3	S4_4_3	S3_2	S2_2	S1_4	0.635	0.47	0.81	0.34	0.785

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S8_10_4	S4_4_3	S3_2	S2_2	S1_4	0.78	0.47	0.81	0.34	0.785
S8_10_5	S4_4_3	S3_2	S2_2	S1_4	0.975	0.47	0.81	0.34	0.785
S8_11_1	S4_5_1	S3_1	S2_3	S1_4	0.29	0.3	0.05	0.55	0.785
S8_11_2	S4_5_1	S3_1	S2_3	S1_4	0.915	0.3	0.05	0.55	0.785
S8_12_1	S4_5_2	S3_1	S2_3	S1_4	0.27	0.52	0.05	0.55	0.785
S8_12_2	S4_5_2	S3_1	S2_3	S1_4	0.455	0.52	0.05	0.55	0.785
S8_12_3	S4_5_2	S3_1	S2_3	S1_4	0.555	0.52	0.05	0.55	0.785
S8_12_4	S4_5_2	S3_1	S2_3	S1_4	0.675	0.52	0.05	0.55	0.785
S8_12_5	S4_5_2	S3_1	S2_3	S1_4	0.875	0.52	0.05	0.55	0.785
S8_12_6	S4_5_2	S3_1	S2_3	S1_4	0.955	0.52	0.05	0.55	0.785
S8_12_7	S4_5_2	S3_1	S2_3	S1_4	0.415	0.52	0.05	0.55	0.785
S8_13_1	S4_5_3	S3_1	S2_3	S1_4	0.355	0.7	0.05	0.55	0.785
S8_13_2	S4_5_3	S3_1	S2_3	S1_4	0.445	0.7	0.05	0.55	0.785
S8_13_3	S4_5_3	S3_1	S2_3	S1_4	0.58	0.7	0.05	0.55	0.785
S8_13_4	S4_5_3	S3_1	S2_3	S1_4	0.905	0.7	0.05	0.55	0.785
S8_13_5	S4_5_3	S3_1	S2_3	S1_4	0.97	0.7	0.05	0.55	0.785
S8_14_1	S4_6_1	S3_2	S2_3	S1_4	0.035	0.18	0.81	0.55	0.785
S8_14_2	S4_6_1	S3_2	S2_3	S1_4	0.3	0.18	0.81	0.55	0.785
S8_14_3	S4_6_1	S3_2	S2_3	S1_4	0.775	0.18	0.81	0.55	0.785
S8_14_4	S4_6_1	S3_2	S2_3	S1_4	0.93	0.18	0.81	0.55	0.785
S8_15_1	S4_6_2	S3_2	S2_3	S1_4	0.05	0.32	0.81	0.55	0.785
S8_15_2	S4_6_2	S3_2	S2_3	S1_4	0.26	0.32	0.81	0.55	0.785
S8_15_3	S4_6_2	S3_2	S2_3	S1_4	0.87	0.32	0.81	0.55	0.785
S8_16_1	S4_6_3	S3_2	S2_3	S1_4	0.03	0.61	0.81	0.55	0.785
S8_16_2	S4_6_3	S3_2	S2_3	S1_4	0.155	0.61	0.81	0.55	0.785
S8_16_3	S4_6_3	S3_2	S2_3	S1_4	0.205	0.61	0.81	0.55	0.785
S8_16_4	S4_6_3	S3_2	S2_3	S1_4	0.48	0.61	0.81	0.55	0.785
S8_16_5	S4_6_3	S3_2	S2_3	S1_4	0.565	0.61	0.81	0.55	0.785
S8_16_6	S4_6_3	S3_2	S2_3	S1_4	0.64	0.61	0.81	0.55	0.785
S8_16_7	S4_6_3	S3_2	S2_3	S1_4	0.705	0.61	0.81	0.55	0.785
S8_16_8	S4_6_3	S3_2	S2_3	S1_4	0.79	0.61	0.81	0.55	0.785
S8_16_9	S4_6_3	S3_2	S2_3	S1_4	0.84	0.61	0.81	0.55	0.785

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	g5	g4	g3	g2	g1
S8_16_10	S4_6_3	S3_2	S2_3	S1_4	0.905	0.61	0.81	0.55	0.785
S8_16_11	S4_6_3	S3_2	S2_3	S1_4	0.975	0.61	0.81	0.55	0.785
S8_17_1	S4_6_4	S3_2	S2_3	S1_4	0.085	0.85	0.81	0.55	0.785
S8_17_2	S4_6_4	S3_2	S2_3	S1_4	0.195	0.85	0.81	0.55	0.785
S8_17_3	S4_6_4	S3_2	S2_3	S1_4	0.27	0.85	0.81	0.55	0.785
S8_17_4	S4_6_4	S3_2	S2_3	S1_4	0.37	0.85	0.81	0.55	0.785
S8_17_5	S4_6_4	S3_2	S2_3	S1_4	0.435	0.85	0.81	0.55	0.785
S8_17_6	S4_6_4	S3_2	S2_3	S1_4	0.53	0.85	0.81	0.55	0.785
S8_17_7	S4_6_4	S3_2	S2_3	S1_4	0.605	0.85	0.81	0.55	0.785
S8_17_8	S4_6_4	S3_2	S2_3	S1_4	0.67	0.85	0.81	0.55	0.785
S8_17_9	S4_6_4	S3_2	S2_3	S1_4	0.79	0.85	0.81	0.55	0.785
S8_17_10	S4_6_4	S3_2	S2_3	S1_4	0.93	0.85	0.81	0.55	0.785
S8_17_11	S4_6_4	S3_2	S2_3	S1_4	0.98	0.85	0.81	0.55	0.785
S8_18_1	S4_7_1	S3_1	S2_4	S1_4	0.35	0.28	0.05	0.905	0.785
S8_18_2	S4_7_1	S3_1	S2_4	S1_4	0.63	0.28	0.05	0.905	0.785
S8_18_3	S4_7_1	S3_1	S2_4	S1_4	0.945	0.28	0.05	0.905	0.785
S8_19_1	S4_7_2	S3_1	S2_4	S1_4	0.275	0.46	0.05	0.905	0.785
S8_19_2	S4_7_2	S3_1	S2_4	S1_4	0.89	0.46	0.05	0.905	0.785
S8_19_3	S4_7_2	S3_1	S2_4	S1_4	0.97	0.46	0.05	0.905	0.785
S8_20_1	S4_7_3	S3_1	S2_4	S1_4	0.19	0.66	0.05	0.905	0.785
S8_20_2	S4_7_3	S3_1	S2_4	S1_4	0.345	0.66	0.05	0.905	0.785
S8_20_3	S4_7_3	S3_1	S2_4	S1_4	0.435	0.66	0.05	0.905	0.785
S8_20_4	S4_7_3	S3_1	S2_4	S1_4	0.545	0.66	0.05	0.905	0.785
S8_20_5	S4_7_3	S3_1	S2_4	S1_4	0.605	0.66	0.05	0.905	0.785
S8_20_6	S4_7_3	S3_1	S2_4	S1_4	0.67	0.66	0.05	0.905	0.785
S8_20_7	S4_7_3	S3_1	S2_4	S1_4	0.915	0.66	0.05	0.905	0.785
S8_20_8	S4_7_3	S3_1	S2_4	S1_4	0.98	0.66	0.05	0.905	0.785
S8_21_1	S4_8_1	S3_2	S2_4	S1_4	0.81	0.04	0.81	0.905	0.785
S8_21_2	S4_8_1	S3_2	S2_4	S1_4	0.925	0.04	0.81	0.905	0.785
S8_22_1	S4_8_2	S3_2	S2_4	S1_4	0.02	0.15	0.81	0.905	0.785
S8_22_2	S4_8_2	S3_2	S2_4	S1_4	0.07	0.15	0.81	0.905	0.785
S8_22_3	S4_8_2	S3_2	S2_4	S1_4	0.175	0.15	0.81	0.905	0.785

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S8_22_4	S4_8_2	S3_2	S2_4	S1_4	0.255	0.15	0.81	0.905	0.785
S8_22_5	S4_8_2	S3_2	S2_4	S1_4	0.295	0.15	0.81	0.905	0.785
S8_22_6	S4_8_2	S3_2	S2_4	S1_4	0.335	0.15	0.81	0.905	0.785
S8_22_7	S4_8_2	S3_2	S2_4	S1_4	0.385	0.15	0.81	0.905	0.785
S8_22_8	S4_8_2	S3_2	S2_4	S1_4	0.445	0.15	0.81	0.905	0.785
S8_22_9	S4_8_2	S3_2	S2_4	S1_4	0.485	0.15	0.81	0.905	0.785
S8_22_10	S4_8_2	S3_2	S2_4	S1_4	0.515	0.15	0.81	0.905	0.785
S8_22_11	S4_8_2	S3_2	S2_4	S1_4	0.69	0.15	0.81	0.905	0.785
S8_22_12	S4_8_2	S3_2	S2_4	S1_4	0.79	0.15	0.81	0.905	0.785
S8_22_13	S4_8_2	S3_2	S2_4	S1_4	0.835	0.15	0.81	0.905	0.785
S8_22_14	S4_8_2	S3_2	S2_4	S1_4	0.93	0.15	0.81	0.905	0.785
S8_22_15	S4_8_2	S3_2	S2_4	S1_4	0.98	0.15	0.81	0.905	0.785
S8_23_1	S4_8_3	S3_2	S2_4	S1_4	0.04	0.24	0.81	0.905	0.785
S8_23_2	S4_8_3	S3_2	S2_4	S1_4	0.23	0.24	0.81	0.905	0.785
S8_23_3	S4_8_3	S3_2	S2_4	S1_4	0.285	0.24	0.81	0.905	0.785
S8_23_4	S4_8_3	S3_2	S2_4	S1_4	0.485	0.24	0.81	0.905	0.785
S8_23_5	S4_8_3	S3_2	S2_4	S1_4	0.81	0.24	0.81	0.905	0.785
S8_23_6	S4_8_3	S3_2	S2_4	S1_4	0.94	0.24	0.81	0.905	0.785
S8_23_7	S4_8_3	S3_2	S2_4	S1_4	0.98	0.24	0.81	0.905	0.785
S8_24_1	S4_8_4	S3_2	S2_4	S1_4	0.04	0.3	0.81	0.905	0.785
S8_24_2	S4_8_4	S3_2	S2_4	S1_4	0.25	0.3	0.81	0.905	0.785
S8_24_3	S4_8_4	S3_2	S2_4	S1_4	0.465	0.3	0.81	0.905	0.785
S8_24_4	S4_8_4	S3_2	S2_4	S1_4	0.57	0.3	0.81	0.905	0.785
S8_24_5	S4_8_4	S3_2	S2_4	S1_4	0.73	0.3	0.81	0.905	0.785
S8_24_6	S4_8_4	S3_2	S2_4	S1_4	0.775	0.3	0.81	0.905	0.785
S8_24_7	S4_8_4	S3_2	S2_4	S1_4	0.9	0.3	0.81	0.905	0.785
S8_24_8	S4_8_4	S3_2	S2_4	S1_4	0.98	0.3	0.81	0.905	0.785
S8_25_1	S4_8_5	S3_2	S2_4	S1_4	0.035	0.37	0.81	0.905	0.785
S8_25_2	S4_8_5	S3_2	S2_4	S1_4	0.18	0.37	0.81	0.905	0.785
S8_25_3	S4_8_5	S3_2	S2_4	S1_4	0.24	0.37	0.81	0.905	0.785
S8_25_4	S4_8_5	S3_2	S2_4	S1_4	0.44	0.37	0.81	0.905	0.785
S8_25_5	S4_8_5	S3_2	S2_4	S1_4	0.56	0.37	0.81	0.905	0.785

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	g5	g4	g3	g2	g1
S8_25_6	S4_8_5	S3_2	S2_4	S1_4	0.72	0.37	0.81	0.905	0.785
S8_25_7	S4_8_5	S3_2	S2_4	S1_4	0.785	0.37	0.81	0.905	0.785
S8_25_8	S4_8_5	S3_2	S2_4	S1_4	0.84	0.37	0.81	0.905	0.785
S8_25_9	S4_8_5	S3_2	S2_4	S1_4	0.905	0.37	0.81	0.905	0.785
S8_25_10	S4_8_5	S3_2	S2_4	S1_4	0.98	0.37	0.81	0.905	0.785
S8_26_1	S4_8_6	S3_2	S2_4	S1_4	0.03	0.43	0.81	0.905	0.785
S8_26_2	S4_8_6	S3_2	S2_4	S1_4	0.19	0.43	0.81	0.905	0.785
S8_26_3	S4_8_6	S3_2	S2_4	S1_4	0.725	0.43	0.81	0.905	0.785
S8_26_4	S4_8_6	S3_2	S2_4	S1_4	0.905	0.43	0.81	0.905	0.785
S8_26_5	S4_8_6	S3_2	S2_4	S1_4	0.975	0.43	0.81	0.905	0.785
S8_27_1	S4_8_7	S3_2	S2_4	S1_4	0.03	0.49	0.81	0.905	0.785
S8_27_2	S4_8_7	S3_2	S2_4	S1_4	0.115	0.49	0.81	0.905	0.785
S8_27_3	S4_8_7	S3_2	S2_4	S1_4	0.155	0.49	0.81	0.905	0.785
S8_27_4	S4_8_7	S3_2	S2_4	S1_4	0.21	0.49	0.81	0.905	0.785
S8_27_5	S4_8_7	S3_2	S2_4	S1_4	0.335	0.49	0.81	0.905	0.785
S8_27_6	S4_8_7	S3_2	S2_4	S1_4	0.365	0.49	0.81	0.905	0.785
S8_27_7	S4_8_7	S3_2	S2_4	S1_4	0.49	0.49	0.81	0.905	0.785
S8_27_8	S4_8_7	S3_2	S2_4	S1_4	0.565	0.49	0.81	0.905	0.785
S8_27_9	S4_8_7	S3_2	S2_4	S1_4	0.62	0.49	0.81	0.905	0.785
S8_27_10	S4_8_7	S3_2	S2_4	S1_4	0.66	0.49	0.81	0.905	0.785
S8_27_11	S4_8_7	S3_2	S2_4	S1_4	0.725	0.49	0.81	0.905	0.785
S8_27_12	S4_8_7	S3_2	S2_4	S1_4	0.8	0.49	0.81	0.905	0.785
S8_27_13	S4_8_7	S3_2	S2_4	S1_4	0.845	0.49	0.81	0.905	0.785
S8_27_14	S4_8_7	S3_2	S2_4	S1_4	0.915	0.49	0.81	0.905	0.785
S8_27_15	S4_8_7	S3_2	S2_4	S1_4	0.975	0.49	0.81	0.905	0.785
S8_28_1	S4_8_8	S3_2	S2_4	S1_4	0.155	0.57	0.81	0.905	0.785
S8_28_2	S4_8_8	S3_2	S2_4	S1_4	0.66	0.57	0.81	0.905	0.785
S8_29_1	S4_8_9	S3_2	S2_4	S1_4	0.1	0.66	0.81	0.905	0.785
S8_29_2	S4_8_9	S3_2	S2_4	S1_4	0.29	0.66	0.81	0.905	0.785
S8_29_3	S4_8_9	S3_2	S2_4	S1_4	0.51	0.66	0.81	0.905	0.785
S8_29_4	S4_8_9	S3_2	S2_4	S1_4	0.585	0.66	0.81	0.905	0.785
S8_29_5	S4_8_9	S3_2	S2_4	S1_4	0.64	0.66	0.81	0.905	0.785

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S8_29_6	S4_8_9	S3_2	S2_4	S1_4	0.72	0.66	0.81	0.905	0.785
S8_29_7	S4_8_9	S3_2	S2_4	S1_4	0.79	0.66	0.81	0.905	0.785
S8_29_8	S4_8_9	S3_2	S2_4	S1_4	0.86	0.66	0.81	0.905	0.785
S8_29_9	S4_8_9	S3_2	S2_4	S1_4	0.98	0.66	0.81	0.905	0.785
S8_30_1	S4_8_10	S3_2	S2_4	S1_4	0.1	0.75	0.81	0.905	0.785
S8_30_2	S4_8_10	S3_2	S2_4	S1_4	0.415	0.75	0.81	0.905	0.785
S8_30_3	S4_8_10	S3_2	S2_4	S1_4	0.48	0.75	0.81	0.905	0.785
S8_30_4	S4_8_10	S3_2	S2_4	S1_4	0.555	0.75	0.81	0.905	0.785
S8_30_5	S4_8_10	S3_2	S2_4	S1_4	0.65	0.75	0.81	0.905	0.785
S8_30_6	S4_8_10	S3_2	S2_4	S1_4	0.795	0.75	0.81	0.905	0.785
S8_30_7	S4_8_10	S3_2	S2_4	S1_4	0.86	0.75	0.81	0.905	0.785
S8_30_8	S4_8_10	S3_2	S2_4	S1_4	0.93	0.75	0.81	0.905	0.785
S8_30_9	S4_8_10	S3_2	S2_4	S1_4	0.98	0.75	0.81	0.905	0.785
S8_31_1	S4_8_11	S3_2	S2_4	S1_4	0.06	0.8	0.81	0.905	0.785
S8_31_2	S4_8_11	S3_2	S2_4	S1_4	0.205	0.8	0.81	0.905	0.785
S8_31_3	S4_8_11	S3_2	S2_4	S1_4	0.27	0.8	0.81	0.905	0.785
S8_31_4	S4_8_11	S3_2	S2_4	S1_4	0.345	0.8	0.81	0.905	0.785
S8_31_5	S4_8_11	S3_2	S2_4	S1_4	0.4	0.8	0.81	0.905	0.785
S8_31_6	S4_8_11	S3_2	S2_4	S1_4	0.46	0.8	0.81	0.905	0.785
S8_31_7	S4_8_11	S3_2	S2_4	S1_4	0.51	0.8	0.81	0.905	0.785
S8_31_8	S4_8_11	S3_2	S2_4	S1_4	0.55	0.8	0.81	0.905	0.785
S8_31_9	S4_8_11	S3_2	S2_4	S1_4	0.585	0.8	0.81	0.905	0.785
S8_31_10	S4_8_11	S3_2	S2_4	S1_4	0.645	0.8	0.81	0.905	0.785
S8_31_11	S4_8_11	S3_2	S2_4	S1_4	0.685	0.8	0.81	0.905	0.785
S8_31_12	S4_8_11	S3_2	S2_4	S1_4	0.72	0.8	0.81	0.905	0.785
S8_31_13	S4_8_11	S3_2	S2_4	S1_4	0.8	0.8	0.81	0.905	0.785
S8_31_14	S4_8_11	S3_2	S2_4	S1_4	0.93	0.8	0.81	0.905	0.785
S8_31_15	S4_8_11	S3_2	S2_4	S1_4	0.985	0.8	0.81	0.905	0.785
S9_1_1	S4_1_1	S3_1	S2_1	S1_5	0.215	0.38	0.05	0.18	0.975
S9_1_2	S4_1_1	S3_1	S2_1	S1_5	0.475	0.38	0.05	0.18	0.975
S9_1_3	S4_1_1	S3_1	S2_1	S1_5	0.595	0.38	0.05	0.18	0.975
S9_1_4	S4_1_1	S3_1	S2_1	S1_5	0.685	0.38	0.05	0.18	0.975

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S9_1_5	S4_1_1	S3_1	S2_1	S1_5	0.86	0.38	0.05	0.18	0.975
S9_2_1	S4_1_2	S3_1	S2_1	S1_5	0.275	0.62	0.05	0.18	0.975
S9_2_2	S4_1_2	S3_1	S2_1	S1_5	0.345	0.62	0.05	0.18	0.975
S9_2_3	S4_1_2	S3_1	S2_1	S1_5	0.48	0.62	0.05	0.18	0.975
S9_2_4	S4_1_2	S3_1	S2_1	S1_5	0.58	0.62	0.05	0.18	0.975
S9_2_5	S4_1_2	S3_1	S2_1	S1_5	0.405	0.62	0.05	0.18	0.975
S9_2_6	S4_1_2	S3_1	S2_1	S1_5	0.645	0.62	0.05	0.18	0.975
S9_2_7	S4_1_2	S3_1	S2_1	S1_5	0.73	0.62	0.05	0.18	0.975
S9_2_8	S4_1_2	S3_1	S2_1	S1_5	0.785	0.62	0.05	0.18	0.975
S9_2_9	S4_1_2	S3_1	S2_1	S1_5	0.91	0.62	0.05	0.18	0.975
S9_3_1	S4_2_1	S3_2	S2_1	S1_5	0.04	0.29	0.81	0.18	0.975
S9_3_2	S4_2_1	S3_2	S2_1	S1_5	0.145	0.29	0.81	0.18	0.975
S9_3_3	S4_2_1	S3_2	S2_1	S1_5	0.175	0.29	0.81	0.18	0.975
S9_3_4	S4_2_1	S3_2	S2_1	S1_5	0.205	0.29	0.81	0.18	0.975
S9_3_5	S4_2_1	S3_2	S2_1	S1_5	0.25	0.29	0.81	0.18	0.975
S9_3_6	S4_2_1	S3_2	S2_1	S1_5	0.325	0.29	0.81	0.18	0.975
S9_3_7	S4_2_1	S3_2	S2_1	S1_5	0.28	0.29	0.81	0.18	0.975
S9_3_8	S4_2_1	S3_2	S2_1	S1_5	0.445	0.29	0.81	0.18	0.975
S9_3_9	S4_2_1	S3_2	S2_1	S1_5	0.475	0.29	0.81	0.18	0.975
S9_3_10	S4_2_1	S3_2	S2_1	S1_5	0.52	0.29	0.81	0.18	0.975
S9_3_11	S4_2_1	S3_2	S2_1	S1_5	0.565	0.29	0.81	0.18	0.975
S9_3_12	S4_2_1	S3_2	S2_1	S1_5	0.745	0.29	0.81	0.18	0.975
S9_3_13	S4_2_1	S3_2	S2_1	S1_5	0.88	0.29	0.81	0.18	0.975
S9_4_1	S4_2_2	S3_2	S2_1	S1_5	0.195	0.46	0.81	0.18	0.975
S9_4_2	S4_2_2	S3_2	S2_1	S1_5	0.28	0.46	0.81	0.18	0.975
S9_4_3	S4_2_2	S3_2	S2_1	S1_5	0.435	0.46	0.81	0.18	0.975
S9_4_4	S4_2_2	S3_2	S2_1	S1_5	0.48	0.46	0.81	0.18	0.975
S9_4_5	S4_2_2	S3_2	S2_1	S1_5	0.62	0.46	0.81	0.18	0.975
S9_4_6	S4_2_2	S3_2	S2_1	S1_5	0.68	0.46	0.81	0.18	0.975
S9_4_7	S4_2_2	S3_2	S2_1	S1_5	0.81	0.46	0.81	0.18	0.975
S9_4_8	S4_2_2	S3_2	S2_1	S1_5	0.86	0.46	0.81	0.18	0.975
S9_4_9	S4_2_2	S3_2	S2_1	S1_5	0.915	0.46	0.81	0.18	0.975

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S9_5_1	S4_2_3	S3_2	S2_1	S1_5	0.02	0.65	0.81	0.18	0.975
S9_5_2	S4_2_3	S3_2	S2_1	S1_5	0.2	0.65	0.81	0.18	0.975
S9_5_3	S4_2_3	S3_2	S2_1	S1_5	0.325	0.65	0.81	0.18	0.975
S9_5_4	S4_2_3	S3_2	S2_1	S1_5	0.65	0.65	0.81	0.18	0.975
S9_5_5	S4_2_3	S3_2	S2_1	S1_5	0.74	0.65	0.81	0.18	0.975
S9_5_6	S4_2_3	S3_2	S2_1	S1_5	0.78	0.65	0.81	0.18	0.975
S9_5_7	S4_2_3	S3_2	S2_1	S1_5	0.85	0.65	0.81	0.18	0.975
S9_6_1	S4_3_1	S3_1	S2_2	S1_5	0.2	0.45	0.05	0.34	0.975
S9_6_2	S4_3_1	S3_1	S2_2	S1_5	0.365	0.45	0.05	0.34	0.975
S9_6_3	S4_3_1	S3_1	S2_2	S1_5	0.435	0.45	0.05	0.34	0.975
S9_6_4	S4_3_1	S3_1	S2_2	S1_5	0.485	0.45	0.05	0.34	0.975
S9_6_5	S4_3_1	S3_1	S2_2	S1_5	0.585	0.45	0.05	0.34	0.975
S9_6_6	S4_3_1	S3_1	S2_2	S1_5	0.675	0.45	0.05	0.34	0.975
S9_6_7	S4_3_1	S3_1	S2_2	S1_5	0.79	0.45	0.05	0.34	0.975
S9_6_8	S4_3_1	S3_1	S2_2	S1_5	0.865	0.45	0.05	0.34	0.975
S9_6_9	S4_3_1	S3_1	S2_2	S1_5	0.92	0.45	0.05	0.34	0.975
S9_7_1	S4_3_2	S3_1	S2_2	S1_5	0.26	0.67	0.05	0.34	0.975
S9_7_2	S4_3_2	S3_1	S2_2	S1_5	0.335	0.67	0.05	0.34	0.975
S9_7_3	S4_3_2	S3_1	S2_2	S1_5	0.47	0.67	0.05	0.34	0.975
S9_7_4	S4_3_2	S3_1	S2_2	S1_5	0.58	0.67	0.05	0.34	0.975
S9_7_5	S4_3_2	S3_1	S2_2	S1_5	0.63	0.67	0.05	0.34	0.975
S9_7_6	S4_3_2	S3_1	S2_2	S1_5	0.7	0.67	0.05	0.34	0.975
S9_7_7	S4_3_2	S3_1	S2_2	S1_5	0.825	0.67	0.05	0.34	0.975
S9_7_8	S4_3_2	S3_1	S2_2	S1_5	0.915	0.67	0.05	0.34	0.975
S9_8_1	S4_4_1	S3_2	S2_2	S1_5	0.02	0.09	0.81	0.34	0.975
S9_8_2	S4_4_1	S3_2	S2_2	S1_5	0.06	0.09	0.81	0.34	0.975
S9_8_3	S4_4_1	S3_2	S2_2	S1_5	0.15	0.09	0.81	0.34	0.975
S9_8_4	S4_4_1	S3_2	S2_2	S1_5	0.205	0.09	0.81	0.34	0.975
S9_8_5	S4_4_1	S3_2	S2_2	S1_5	0.255	0.09	0.81	0.34	0.975
S9_8_6	S4_4_1	S3_2	S2_2	S1_5	0.285	0.09	0.81	0.34	0.975
S9_8_7	S4_4_1	S3_2	S2_2	S1_5	0.34	0.09	0.81	0.34	0.975
S9_8_8	S4_4_1	S3_2	S2_2	S1_5	0.395	0.09	0.81	0.34	0.975

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S9_8_9	S4_4_1	S3_2	S2_2	S1_5	0.455	0.09	0.81	0.34	0.975
S9_8_10	S4_4_1	S3_2	S2_2	S1_5	0.485	0.09	0.81	0.34	0.975
S9_8_11	S4_4_1	S3_2	S2_2	S1_5	0.525	0.09	0.81	0.34	0.975
S9_8_12	S4_4_1	S3_2	S2_2	S1_5	0.765	0.09	0.81	0.34	0.975
S9_8_13	S4_4_1	S3_2	S2_2	S1_5	0.87	0.09	0.81	0.34	0.975
S9_8_14	S4_4_1	S3_2	S2_2	S1_5	0.945	0.09	0.81	0.34	0.975
S9_9_1	S4_4_2	S3_2	S2_2	S1_5	0.02	0.3	0.81	0.34	0.975
S9_9_2	S4_4_2	S3_2	S2_2	S1_5	0.25	0.3	0.81	0.34	0.975
S9_9_3	S4_4_2	S3_2	S2_2	S1_5	0.395	0.3	0.81	0.34	0.975
S9_9_4	S4_4_2	S3_2	S2_2	S1_5	0.525	0.3	0.81	0.34	0.975
S9_9_5	S4_4_2	S3_2	S2_2	S1_5	0.885	0.3	0.81	0.34	0.975
S9_9_6	S4_4_2	S3_2	S2_2	S1_5	0.95	0.3	0.81	0.34	0.975
S9_10_1	S4_4_3	S3_2	S2_2	S1_5	0.03	0.47	0.81	0.34	0.975
S9_10_2	S4_4_3	S3_2	S2_2	S1_5	0.295	0.47	0.81	0.34	0.975
S9_10_3	S4_4_3	S3_2	S2_2	S1_5	0.445	0.47	0.81	0.34	0.975
S9_10_4	S4_4_3	S3_2	S2_2	S1_5	0.915	0.47	0.81	0.34	0.975
S9_11_1	S4_5_1	S3_1	S2_3	S1_5	0.06	0.3	0.05	0.55	0.975
S9_11_2	S4_5_1	S3_1	S2_3	S1_5	0.425	0.3	0.05	0.55	0.975
S9_11_3	S4_5_1	S3_1	S2_3	S1_5	0.86	0.3	0.05	0.55	0.975
S9_12_1	S4_5_2	S3_1	S2_3	S1_5	0.465	0.52	0.05	0.55	0.975
S9_12_2	S4_5_2	S3_1	S2_3	S1_5	0.67	0.52	0.05	0.55	0.975
S9_12_3	S4_5_2	S3_1	S2_3	S1_5	0.875	0.52	0.05	0.55	0.975
S9_13_1	S4_5_3	S3_1	S2_3	S1_5	0.04	0.7	0.05	0.55	0.975
S9_13_2	S4_5_3	S3_1	S2_3	S1_5	0.135	0.7	0.05	0.55	0.975
S9_13_3	S4_5_3	S3_1	S2_3	S1_5	0.175	0.7	0.05	0.55	0.975
S9_13_4	S4_5_3	S3_1	S2_3	S1_5	0.205	0.7	0.05	0.55	0.975
S9_13_5	S4_5_3	S3_1	S2_3	S1_5	0.27	0.7	0.05	0.55	0.975
S9_13_6	S4_5_3	S3_1	S2_3	S1_5	0.335	0.7	0.05	0.55	0.975
S9_13_7	S4_5_3	S3_1	S2_3	S1_5	0.375	0.7	0.05	0.55	0.975
S9_13_8	S4_5_3	S3_1	S2_3	S1_5	0.425	0.7	0.05	0.55	0.975
S9_13_9	S4_5_3	S3_1	S2_3	S1_5	0.475	0.7	0.05	0.55	0.975
S9_13_10	S4_5_3	S3_1	S2_3	S1_5	0.515	0.7	0.05	0.55	0.975

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S9_13_11	S4_5_3	S3_1	S2_3	S1_5	0.56	0.7	0.05	0.55	0.975
S9_13_12	S4_5_3	S3_1	S2_3	S1_5	0.595	0.7	0.05	0.55	0.975
S9_13_13	S4_5_3	S3_1	S2_3	S1_5	0.625	0.7	0.05	0.55	0.975
S9_13_14	S4_5_3	S3_1	S2_3	S1_5	0.69	0.7	0.05	0.55	0.975
S9_13_15	S4_5_3	S3_1	S2_3	S1_5	0.74	0.7	0.05	0.55	0.975
S9_13_16	S4_5_3	S3_1	S2_3	S1_5	0.775	0.7	0.05	0.55	0.975
S9_13_17	S4_5_3	S3_1	S2_3	S1_5	0.82	0.7	0.05	0.55	0.975
S9_13_18	S4_5_3	S3_1	S2_3	S1_5	0.89	0.7	0.05	0.55	0.975
S9_13_19	S4_5_3	S3_1	S2_3	S1_5	0.93	0.7	0.05	0.55	0.975
S9_14_1	S4_6_1	S3_2	S2_3	S1_5	0.035	0.18	0.81	0.55	0.975
S9_14_2	S4_6_1	S3_2	S2_3	S1_5	0.145	0.18	0.81	0.55	0.975
S9_14_3	S4_6_1	S3_2	S2_3	S1_5	0.175	0.18	0.81	0.55	0.975
S9_14_4	S4_6_1	S3_2	S2_3	S1_5	0.21	0.18	0.81	0.55	0.975
S9_14_5	S4_6_1	S3_2	S2_3	S1_5	0.25	0.18	0.81	0.55	0.975
S9_14_6	S4_6_1	S3_2	S2_3	S1_5	0.285	0.18	0.81	0.55	0.975
S9_14_7	S4_6_1	S3_2	S2_3	S1_5	0.33	0.18	0.81	0.55	0.975
S9_14_8	S4_6_1	S3_2	S2_3	S1_5	0.39	0.18	0.81	0.55	0.975
S9_14_9	S4_6_1	S3_2	S2_3	S1_5	0.485	0.18	0.81	0.55	0.975
S9_14_10	S4_6_1	S3_2	S2_3	S1_5	0.535	0.18	0.81	0.55	0.975
S9_14_11	S4_6_1	S3_2	S2_3	S1_5	0.705	0.18	0.81	0.55	0.975
S9_14_12	S4_6_1	S3_2	S2_3	S1_5	0.76	0.18	0.81	0.55	0.975
S9_14_13	S4_6_1	S3_2	S2_3	S1_5	0.89	0.18	0.81	0.55	0.975
S9_14_14	S4_6_1	S3_2	S2_3	S1_5	0.945	0.18	0.81	0.55	0.975
S9_15_1	S4_6_2	S3_2	S2_3	S1_5	0.345	0.32	0.81	0.55	0.975
S9_15_2	S4_6_2	S3_2	S2_3	S1_5	0.875	0.32	0.81	0.55	0.975
S9_16_1	S4_6_3	S3_2	S2_3	S1_5	0.035	0.61	0.81	0.55	0.975
S9_16_2	S4_6_3	S3_2	S2_3	S1_5	0.13	0.61	0.81	0.55	0.975
S9_16_3	S4_6_3	S3_2	S2_3	S1_5	0.25	0.61	0.81	0.55	0.975
S9_16_4	S4_6_3	S3_2	S2_3	S1_5	0.385	0.61	0.81	0.55	0.975
S9_16_5	S4_6_3	S3_2	S2_3	S1_5	0.64	0.61	0.81	0.55	0.975
S9_16_6	S4_6_3	S3_2	S2_3	S1_5	0.73	0.61	0.81	0.55	0.975
S9_16_7	S4_6_3	S3_2	S2_3	S1_5	0.79	0.61	0.81	0.55	0.975

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	g5	g4	g3	g2	g1
S9_16_8	S4_6_3	S3_2	S2_3	S1_5	0.905	0.61	0.81	0.55	0.975
S9_17_1	S4_6_4	S3_2	S2_3	S1_5	0.435	0.85	0.81	0.55	0.975
S9_17_2	S4_6_4	S3_2	S2_3	S1_5	0.58	0.85	0.81	0.55	0.975
S9_17_3	S4_6_4	S3_2	S2_3	S1_5	0.64	0.85	0.81	0.55	0.975
S9_17_4	S4_6_4	S3_2	S2_3	S1_5	0.735	0.85	0.81	0.55	0.975
S9_17_5	S4_6_4	S3_2	S2_3	S1_5	0.83	0.85	0.81	0.55	0.975
S9_17_6	S4_6_4	S3_2	S2_3	S1_5	0.925	0.85	0.81	0.55	0.975
S9_18_1	S4_7_1	S3_1	S2_4	S1_5	0.435	0.28	0.05	0.905	0.975
S9_18_2	S4_7_1	S3_1	S2_4	S1_5	0.535	0.28	0.05	0.905	0.975
S9_18_3	S4_7_1	S3_1	S2_4	S1_5	0.655	0.28	0.05	0.905	0.975
S9_18_4	S4_7_1	S3_1	S2_4	S1_5	0.855	0.28	0.05	0.905	0.975
S9_18_5	S4_7_1	S3_1	S2_4	S1_5	0.96	0.28	0.05	0.905	0.975
S9_19_1	S4_7_2	S3_1	S2_4	S1_5	0.21	0.46	0.05	0.905	0.975
S9_19_2	S4_7_2	S3_1	S2_4	S1_5	0.25	0.46	0.05	0.905	0.975
S9_19_3	S4_7_2	S3_1	S2_4	S1_5	0.36	0.46	0.05	0.905	0.975
S9_19_4	S4_7_2	S3_1	S2_4	S1_5	0.45	0.46	0.05	0.905	0.975
S9_19_5	S4_7_2	S3_1	S2_4	S1_5	0.585	0.46	0.05	0.905	0.975
S9_19_6	S4_7_2	S3_1	S2_4	S1_5	0.77	0.46	0.05	0.905	0.975
S9_19_7	S4_7_2	S3_1	S2_4	S1_5	0.865	0.46	0.05	0.905	0.975
S9_19_8	S4_7_2	S3_1	S2_4	S1_5	0.965	0.46	0.05	0.905	0.975
S9_20_1	S4_7_3	S3_1	S2_4	S1_5	0.26	0.66	0.05	0.905	0.975
S9_20_2	S4_7_3	S3_1	S2_4	S1_5	0.355	0.66	0.05	0.905	0.975
S9_20_3	S4_7_3	S3_1	S2_4	S1_5	0.565	0.66	0.05	0.905	0.975
S9_20_4	S4_7_3	S3_1	S2_4	S1_5	0.675	0.66	0.05	0.905	0.975
S9_20_5	S4_7_3	S3_1	S2_4	S1_5	0.73	0.66	0.05	0.905	0.975
S9_20_6	S4_7_3	S3_1	S2_4	S1_5	0.86	0.66	0.05	0.905	0.975
S9_20_7	S4_7_3	S3_1	S2_4	S1_5	0.905	0.66	0.05	0.905	0.975
S9_21_1	S4_8_1	S3_2	S2_4	S1_5	0.15	0.04	0.81	0.905	0.975
S9_21_2	S4_8_1	S3_2	S2_4	S1_5	0.215	0.04	0.81	0.905	0.975
S9_21_3	S4_8_1	S3_2	S2_4	S1_5	0.335	0.04	0.81	0.905	0.975
S9_21_4	S4_8_1	S3_2	S2_4	S1_5	0.395	0.04	0.81	0.905	0.975
S9_21_5	S4_8_1	S3_2	S2_4	S1_5	0.53	0.04	0.81	0.905	0.975

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	$g 5$	$g 4$	$g 3$	$g 2$	$g 1$
S9_21_6	S4_8_1	S3_2	S2_4	S1_5	0.76	0.04	0.81	0.905	0.975
S9_21_7	S4_8_1	S3_2	S2_4	S1_5	0.88	0.04	0.81	0.905	0.975
S9_22_1	S4_8_2	S3_2	S2_4	S1_5	0.02	0.15	0.81	0.905	0.975
S9_22_2	S4_8_2	S3_2	S2_4	S1_5	0.2	0.15	0.81	0.905	0.975
S9_22_3	S4_8_2	S3_2	S2_4	S1_5	0.245	0.15	0.81	0.905	0.975
S9_22_4	S4_8_2	S3_2	S2_4	S1_5	0.275	0.15	0.81	0.905	0.975
S9_22_5	S4_8_2	S3_2	S2_4	S1_5	0.315	0.15	0.81	0.905	0.975
S9_22_6	S4_8_2	S3_2	S2_4	S1_5	0.355	0.15	0.81	0.905	0.975
S9_22_7	S4_8_2	S3_2	S2_4	S1_5	0.395	0.15	0.81	0.905	0.975
S9_22_8	S4_8_2	S3_2	S2_4	S1_5	0.445	0.15	0.81	0.905	0.975
S9_22_9	S4_8_2	S3_2	S2_4	S1_5	0.475	0.15	0.81	0.905	0.975
S9_22_10	S4_8_2	S3_2	S2_4	S1_5	0.52	0.15	0.81	0.905	0.975
S9_22_11	S4_8_2	S3_2	S2_4	S1_5	0.755	0.15	0.81	0.905	0.975
S9_22_12	S4_8_2	S3_2	S2_4	S1_5	0.87	0.15	0.81	0.905	0.975
S9_22_13	S4_8_2	S3_2	S2_4	S1_5	0.94	0.15	0.81	0.905	0.975
S9_23_1	S4_8_3	S3_2	S2_4	S1_5	0.035	0.24	0.81	0.905	0.975
S9_23_2	S4_8_3	S3_2	S2_4	S1_5	0.34	0.24	0.81	0.905	0.975
S9_23_3	S4_8_3	S3_2	S2_4	S1_5	0.5	0.24	0.81	0.905	0.975
S9_23_4	S4_8_3	S3_2	S2_4	S1_5	0.875	0.24	0.81	0.905	0.975
S9_24_1	S4_8_4	S3_2	S2_4	S1_5	0.035	0.3	0.81	0.905	0.975
S9_24_2	S4_8_4	S3_2	S2_4	S1_5	0.24	0.3	0.81	0.905	0.975
S9_24_3	S4_8_4	S3_2	S2_4	S1_5	0.305	0.3	0.81	0.905	0.975
S9_24_4	S4_8_4	S3_2	S2_4	S1_5	0.47	0.3	0.81	0.905	0.975
S9_24_5	S4_8_4	S3_2	S2_4	S1_5	0.79	0.3	0.81	0.905	0.975
S9_24_6	S4_8_4	S3_2	S2_4	S1_5	0.14	0.3	0.81	0.905	0.975
S9_24_7	S4_8_4	S3_2	S2_4	S1_5	0.88	0.3	0.81	0.905	0.975
S9_24_8	S4_8_4	S3_2	S2_4	S1_5	0.93	0.3	0.81	0.905	0.975
S9_25_1	S4_8_5	S3_2	S2_4	S1_5	0.035	0.37	0.81	0.905	0.975
S9_25_2	S4_8_5	S3_2	S2_4	S1_5	0.305	0.37	0.81	0.905	0.975
S9_25_3	S4_8_5	S3_2	S2_4	S1_5	0.925	0.37	0.81	0.905	0.975
S9_26_1	S4_8_6	S3_2	S2_4	S1_5	0.03	0.43	0.81	0.905	0.975
S9_26_2	S4_8_6	S3_2	S2_4	S1_5	0.145	0.43	0.81	0.905	0.975

Cont. Table 69

Aggregation					Specific weights				
$\phi 5$	$\phi 4$	$\phi 3$	$\phi 2$	$\phi 1$	g5	g4	g3	g2	g1
S9_26_3	S4_8_6	S3_2	S2_4	S1_5	0.195	0.43	0.81	0.905	0.975
S9_26_4	S4_8_6	S3_2	S2_4	S1_5	0.27	0.43	0.81	0.905	0.975
S9_26_5	S4_8_6	S3_2	S2_4	S1_5	0.315	0.43	0.81	0.905	0.975
S9_26_6	S4_8_6	S3_2	S2_4	S1_5	0.425	0.43	0.81	0.905	0.975
S9_26_7	S4_8_6	S3_2	S2_4	S1_5	0.475	0.43	0.81	0.905	0.975
S9_26_8	S4_8_6	S3_2	S2_4	S1_5	0.535	0.43	0.81	0.905	0.975
S9_26_9	S4_8_6	S3_2	S2_4	S1_5	0.74	0.43	0.81	0.905	0.975
S9_26_10	S4_8_6	S3_2	S2_4	S1_5	0.8	0.43	0.81	0.905	0.975
S9_26_11	S4_8_6	S3_2	S2_4	S1_5	0.855	0.43	0.81	0.905	0.975
S9_26_12	S4_8_6	S3_2	S2_4	S1_5	0.925	0.43	0.81	0.905	0.975
S9_26_13	S4_8_6	S3_2	S2_4	S1_5	0.97	0.43	0.81	0.905	0.975
S9_27_1	S4_8_7	S3_2	S2_4	S1_5	0.035	0.49	0.81	0.905	0.975
S9_27_2	S4_8_7	S3_2	S2_4	S1_5	0.13	0.49	0.81	0.905	0.975
S9_27_3	S4_8_7	S3_2	S2_4	S1_5	0.26	0.49	0.81	0.905	0.975
S9_27_4	S4_8_7	S3_2	S2_4	S1_5	0.4	0.49	0.81	0.905	0.975
S9_27_5	S4_8_7	S3_2	S2_4	S1_5	0.795	0.49	0.81	0.905	0.975
S9_27_6	S4_8_7	S3_2	S2_4	S1_5	0.85	0.49	0.81	0.905	0.975
S9_27_7	S4_8_7	S3_2	S2_4	S1_5	0.97	0.49	0.81	0.905	0.975
S9_28_1	S4_8_8	S3_2	S2_4	S1_5	0.015	0.57	0.81	0.905	0.975
S9_28_2	S4_8_8	S3_2	S2_4	S1_5	0.1	0.57	0.81	0.905	0.975
S9_28_3	S4_8_8	S3_2	S2_4	S1_5	0.155	0.57	0.81	0.905	0.975
S9_28_4	S4_8_8	S3_2	S2_4	S1_5	0.23	0.57	0.81	0.905	0.975
S9_28_5	S4_8_8	S3_2	S2_4	S1_5	0.295	0.57	0.81	0.905	0.975
S9_28_6	S4_8_8	S3_2	S2_4	S1_5	0.35	0.57	0.81	0.905	0.975
S9_28_7	S4_8_8	S3_2	S2_4	S1_5	0.41	0.57	0.81	0.905	0.975
S9_28_8	S4_8_8	S3_2	S2_4	S1_5	0.46	0.57	0.81	0.905	0.975
S9_28_9	S4_8_8	S3_2	S2_4	S1_5	0.54	0.57	0.81	0.905	0.975
S9_28_10	S4_8_8	S3_2	S2_4	S1_5	0.605	0.57	0.81	0.905	0.975
S9_28_11	S4_8_8	S3_2	S2_4	S1_5	0.645	0.57	0.81	0.905	0.975
S9_28_12	S4_8_8	S3_2	S2_4	S1_5	0.705	0.57	0.81	0.905	0.975
S9_28_13	S4_8_8	S3_2	S2_4	S1_5	0.735	0.57	0.81	0.905	0.975
S9_28_14	S4_8_8	S3_2	S2_4	S1_5	0.88	0.57	0.81	0.905	0.975

Cont. Table 69

Aggregation					Specific weights				
$\varphi 5$	$\varphi 4$	$\varphi 3$	$\varphi 2$	$\varphi 1$	$g5$	$g4$	$g3$	$g2$	$g1$
S9_28_15	S4_8_8	S3_2	S2_4	S1_5	0.965	0.57	0.81	0.905	0.975
S9_29_1	S4_8_9	S3_2	S2_4	S1_5	0.19	0.66	0.81	0.905	0.975
S9_29_2	S4_8_9	S3_2	S2_4	S1_5	0.35	0.66	0.81	0.905	0.975
S9_29_3	S4_8_9	S3_2	S2_4	S1_5	0.4	0.66	0.81	0.905	0.975
S9_29_4	S4_8_9	S3_2	S2_4	S1_5	0.475	0.66	0.81	0.905	0.975
S9_29_5	S4_8_9	S3_2	S2_4	S1_5	0.64	0.66	0.81	0.905	0.975
S9_29_6	S4_8_9	S3_2	S2_4	S1_5	0.71	0.66	0.81	0.905	0.975
S9_29_7	S4_8_9	S3_2	S2_4	S1_5	0.88	0.66	0.81	0.905	0.975
S9_29_8	S4_8_9	S3_2	S2_4	S1_5	0.97	0.66	0.81	0.905	0.975
S9_30_1	S4_8_10	S3_2	S2_4	S1_5	0.485	0.75	0.81	0.905	0.975
S9_30_2	S4_8_10	S3_2	S2_4	S1_5	0.7	0.75	0.81	0.905	0.975
S9_31_1	S4_8_11	S3_2	S2_4	S1_5	0.445	0.8	0.81	0.905	0.975
S9_31_2	S4_8_11	S3_2	S2_4	S1_5	0.61	0.8	0.81	0.905	0.975
S9_31_3	S4_8_11	S3_2	S2_4	S1_5	0.68	0.8	0.81	0.905	0.975
S9_31_4	S4_8_11	S3_2	S2_4	S1_5	0.745	0.8	0.81	0.905	0.975