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Risks and Benefits of Fluorinated Greenhouse Gases in Techniques and Products under Special Consideration of the Properties Intrinsic to the Substance

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16. Abstract This study characterises the risk emanating from the application of fluorinated GHG in greater detail and weighs this against the benefit of the substances in example applications. This study comes to the conclusion that especially effects on climate and persistence stand out as negative properties intrinsic to the examined fluorinated substances. On the positive side, their generally low direct toxicity and their very low specific contribution to the formation of photosmog were identified. In the exemplary applications examined in the study (PU-insulation panels, PU insulation in refrigerated vehicles and interconnected supermarket refrigeration systems) but also in other relevant analyses it became clear that already today the use of fluorinated GHG in applications earlier being the domain of CFC is not or only marginally economical in comparison to new alternative technologies. In the comparison and evaluation of technical systems in which fluorinated GHG and relevant alternative substances are applied, a significant dynamic can be observed in the changes of technical properties and cost data as well as in the widening of the portfolio of technologies available.		
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16. Kurzfassung Die Studie charakterisiert das vom Einsatz fluorierter Treibhausgase ausgehende Risiko nach aktuellem Forschungsstand und wägt es gegen den Nutzen der Substanzen in exemplarisch ausgewählten Anwendungen ab. Diese Studie kommt zu dem Ergebnis, dass als stoffintrinsische Eigenschaften der untersuchten fluorierten Substanzen insbesondere ihre Klimawirksamkeit und ihre Persistenz negativ hervorstechen. Auf der Positivseite wurden ihre i.d.R. gering ausgeprägte Toxizität und Brennbarkeit identifiziert. Im Rahmen der in dieser Studie untersuchten Anwendungsbeispielen (PU-Dachdämmplatten, PU-Dämmung im Kühlaufleger und Supermarkt-Verbundkälte) aber auch anderer einschlägiger Analysen zeigt sich, dass bereits heute in vielen früher den FCKW angestammten Anwendungen für fluorierte Treibhausgase die Wirtschaftlichkeit im Vergleich zu neuen Alternativtechnologien nicht oder nur marginal gegeben ist, dass es ebenso weiterhin Anwendungsfälle gibt, in denen fluorierte Treibhausgase gegenüber Alternativsubstanzen deutliche Wirtschaftlichkeitsvorteile aufweisen. Beim Vergleich und der Bewertung technischer Systeme, in denen fluorierte Treibhausgase und entsprechende Alternativstoffe zur Anwendung kommen, zeigt sich eine erhebliche Dynamik, mit der sich technische Eigenschaften und Kostendaten verändern und sich das Portfolio verfügbarer Technologien erweitert.		
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Risks and Benefits of Fluorinated Greenhouse Gases in Processes and Products under Special Consideration of the Properties Intrinsic to the Substance

Summary

1 Objective of the study

Fluorinated greenhouse gases (GHG) are used in a multitude of applications to date. Next to perfluorinated compounds (e.g. CF_4 , C_2F_6 or SF_6), especially the fluorinated hydrocarbons (HFC) are of relevance by means of volume. HFCs represent the special focus of this study. They are mainly applied as a substitute for fluorinated and chlorinated hydrocarbons (HCFC) which are internationally banned under the Montreal protocol because of their role in the destruction of stratospheric ozone. Since 1993, several different HFC were step by step introduced into the market as substitutes in the framework of phasing out the use of HCFC.

From the beginning the application of fluorinated GHG was discussed controversial in the expert public. There were special concerns that one environmentally problematic substance class is replaced by another without being able to assess the specific problems of their environmental behaviour.

It was the objective of the research project to characterize the risks emanating from the application of fluorinated GHG according to present state of research and weigh it against the use of substances in exemplary applications including cost considerations. In this, the research project is geared towards giving assistance to decision makers in administration and economy in the designing of a long-term product policy in view of the application of fluorinated GHG.

The project consisted of the following Steps:

- Development of an application-specific evaluation methodology on the basis of a list of criteria
- Overview over the present and forecasted future application patterns for fluorinated GHG
- Summarizing discussion of the present state of scientific knowledge on the environmental behaviour of fluorinated GHG
- Examination of selected application examples (blowing agent in polyurethane rigid foam and refrigerant in supermarket refrigeration)
- Conclusions for a precautionary environmental policy.

For the first time, this study compiles the scientific and technological knowledge on the environmental importance accumulated during the first decade after commercial introduction of fluorinated GHG relevant for both private and public decision makers. For the evaluation a pragmatic approach was developed, which accounts for the complexity of the application fields but offers assistance in decision situations at the same time.

2 Methodology

In this study, the following questions should be examined:

- Which are the environmental and health-related risks deriving from the application of (H)FC under consideration of their properties intrinsic to the substance?
- Which environment- and health-related advantages and disadvantages and which risks –at equivalent use- are to be expected from the application of HFC in comparison to alternative substances over the lifetime?

The study first identifies these environmental and health-related risks in section 2 on which the priority attention shall be focussed in the framework of the assessment. In order to enable an evaluation of advantages and disadvantages in the assessment in different effect categories, criteria for a weighting of relevant effect categories shall be drawn up.

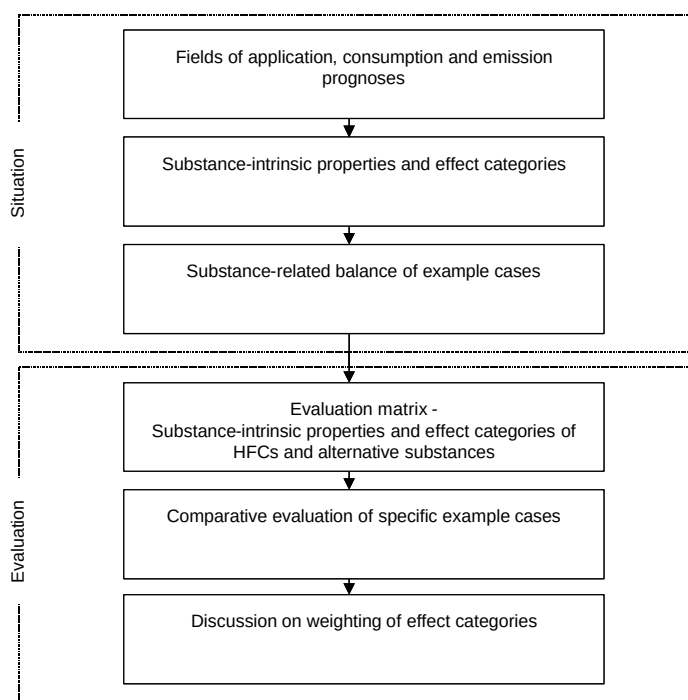


Figure 1: Procedure diagram for risk assessment

The assessment of HFC is based on the description of the state of affairs on the properties intrinsic to the substance of HFC and on the results of the environmental balance of facts of selected applications. The procedure diagram of the assessment is represented in Fig. 1.

After an explanation on the assessment approach the application fields of HFC as well as the current estimates and forecasts on the amounts applied and emissions worldwide are explained in the following section 3. Furthermore, the production and disposal of HFC is characterized. Section 4 summarizes the state of knowledge on properties intrinsic to the substance.

In sections 5 and 6, a comparative balancing of common HFC applications is done. The balancing is limited to the effect category climate, of which the primary relevance is concluded in section 4. As applications polyurethane (PU) rigid foams for insulation of roofs and refrigerated vehicles as well as supermarket refrigeration were selected. In PU rigid foams, HFC-365mfc served as blowing agent (alternatives: n-pentane and c-pentane). In supermarket refrigeration HFC-404A was utilized as refrigerant and carrier (alternatives. Propane, ammonia and CO₂).

The evaluation as such is conducted in section 7. To support a systematic comprehension, the properties intrinsic to the substance and effect categories of the HFCs treated here and of the alternative substances treated in the application examples were categorized in an evaluation

matrix. The relevance of the properties and effect categories of the single substances was categorized as ‘very high’, ‘high’, ‘medium’, ‘low’ and ‘negligible’. The evaluation matrix allows an overview the essential risks and allows a limitation of the comparative assessment on the relevant criteria.

3 Production, Application, Disposal

HFCs are released over the whole lifetime of products:

- During the production of HFC
- During production processes and manufacture of products in which HFC are used
- During the use of products
- In the framework of disposal of products

In the potential release over the whole lifetime of products containing HFC a retarded emission relative to the production time needs to be taken into consideration. This is especially valid for products with a long life span (e.g. industrial refrigeration) and high emissions in the disposal (e.g. mobile air conditioning). Figure 2 displays how HFC can be released over the lifetime of a product (e.g. a household refrigerator).

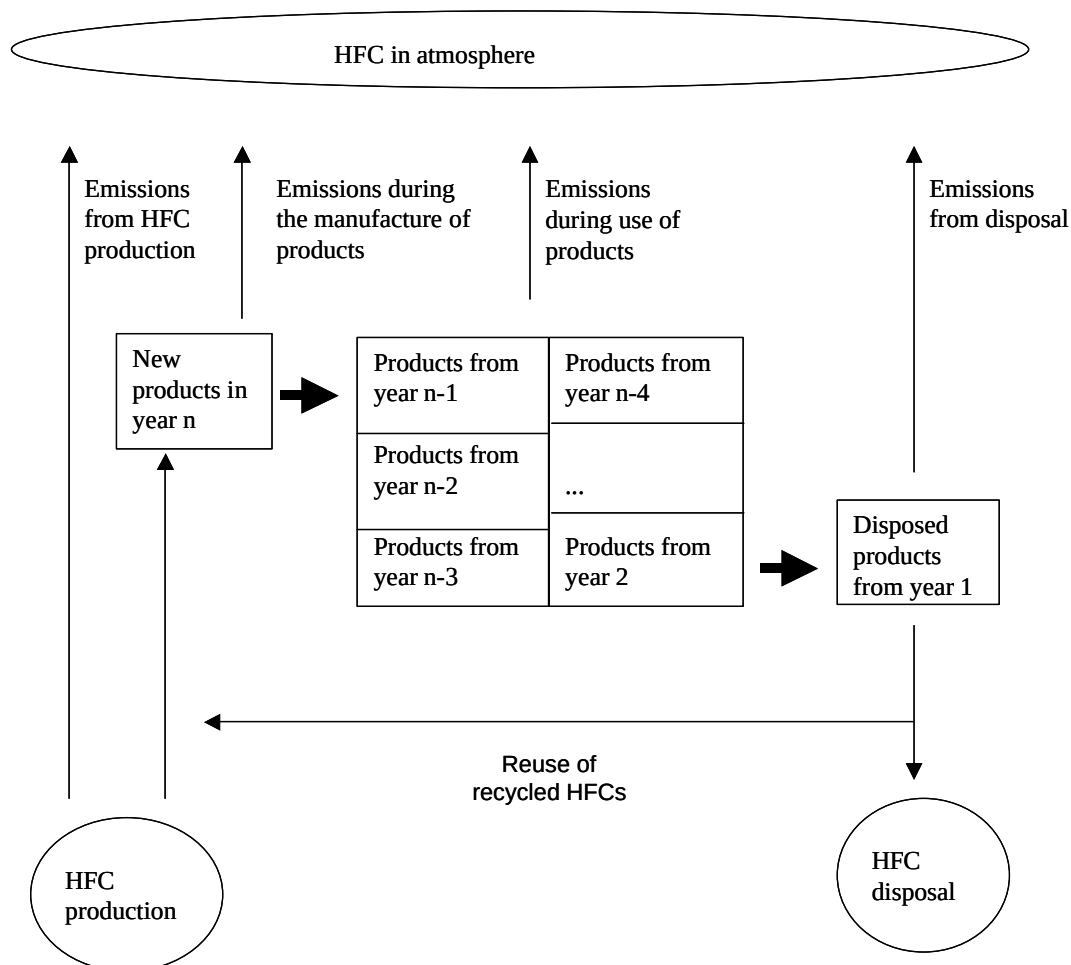


Figure 2: HFC emissions along the lifetime of products containing HFC. Year 1 marks the first year of usage, year n the time today.

Fluorinated GHG in the EU are mainly used in the following application fields:

- Refrigeration and air conditioning
- Blowing agent for rigid foam
- Solvent
- Fire extinguisher
- Aerosol propellant

Presently, the highest share of total emissions is covered by refrigeration, air conditioning and rigid foam. HFC banks in these systems and products will increase from almost 200,000 tons in 1996 to nearly 2 million tons in 2010 and will further rise to approx. 4 million tons in 2020.

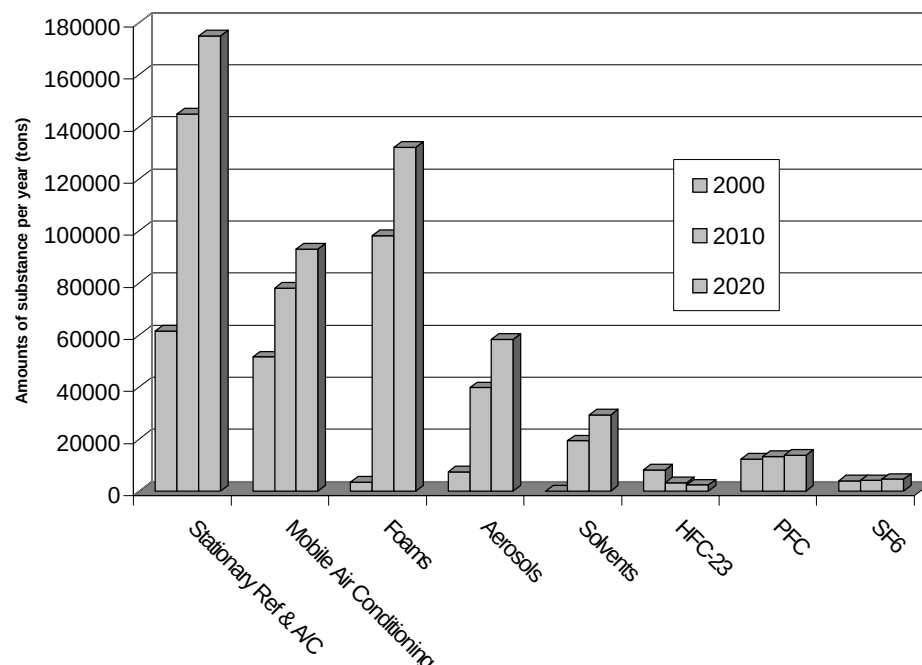
Applications and emissions:

For 2020 a worldwide annual market volume of up to 500,000 t fluorinated GHG can be assumed (s. Figure 3). A maximum of 100,000 t of this can be attributed to Europe. Annual emissions of different fluorinated GHG into the environment may add up to 330,000 tons worldwide and 60,000 tons in Europe. Out of this, fluorinated carbon and SF₆ would cover 5%. In the application as well as in the emissions, HFC would hence dominate the picture. Therefore this study will focus mainly on HFC in the further course.

As a substitute for ozone depleting substances, fluorinated GHG are utilized in a multitude of applications. The most important applications by volume of perfluorocarbons and sulphur hexafluoride are semiconductor manufacture as well as switchgear and as protective sheet gas in the production and processing of magnesium.

In estimates for the amounts of HFC, PFC and SF₆ used European- and worldwide (differentiated in single applications for the years 2000, 2010 and 2020), the applications in refrigeration and air conditioning (including mobile air conditioning) as well as insulation foams represent the greatest share. European-wide, the highest increase until 2020 is anticipated for the field of insulation foams, worldwide in the field of refrigeration and air conditioning. This difference can be attributed to the fact that worldwide insulation foams have less importance to the market compared to refrigeration and air conditioning than in the comparably cool climate in Europe.

Figure 3: Estimated worldwide use of HFC, PFC and SF₆ acc. to application fields. For process emissions, HFC-23 and PFC, the use is set equal to the emissions.



Production:

Fluorinated GHG are commonly produced in synthesis paths based on chlorinated precursor substances. Their respective ‘environmental footprint’ (key word chlorine chemistry) including diffuse emissions of halogenated intermediate and by-products (including their mixing to the product) needs to be considered. All of these are characterized insufficiently. The specific energy consumption and the GHG emissions resulting from the production of fluorinated GHG are considerably greater than those of alternative (halogen-free) substances.

Disposal:

The environmental profile in the disposal of HFC strongly depends on the respective application. The following basic disposal paths are possible:

- Release into the environment
- Extraction with following reuse, processing or destruction
- Disposal together with the product.

The environmentally worst version is the release into the environment. Even in the two other versions, the danger remains the HFC is emitted into the atmosphere in the framework of disposal. In any case, the release into the atmosphere e.g. during the crushing of significant amounts of the product needs to be avoided. In a thermal treatment of waste containing HFC an orderly treatment of the flue gas needs to be ensured to avoid increased emissions of fluoride into the atmosphere. In the most cases, these disposal paths do not exist at present.

Emission prognosis:

In the consideration of the life paths of different applications it can be observed that emissions during the production, use and the disposal are considerably different depending on the application.. The most important share is the emission during the usage phase.

Prognosis data for the worldwide HFC emissions in the years 2010 and 2020 can be found in Figure 4. While emission forecasts for Germany and Europe (not represented here) show that for the single applications a maximum of emissions can be expected for 2020 because the substitution of ozone depleting substances will then be completed, the specific emission rates will be reduced due to improved technology and the growth of applications is so slow that these gains are not offset, the picture is different for the worldwide perspective: a stronger growth of HFC banks in the main application fields and an increased in emissions far beyond the year 2020 are anticipated.

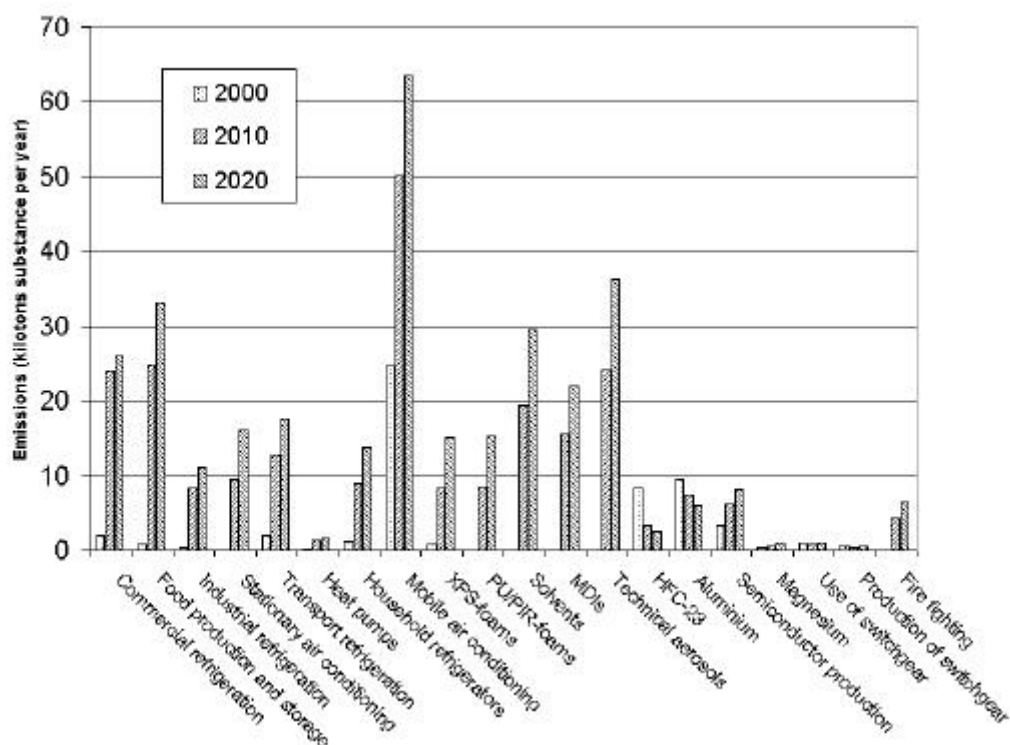


Figure 4: Emission prognosis worldwide for HFC, FC and SF₆ for different applications

4 Fluorinated GHG in the environment

The effect categories GHG effect, ozone depletion, ozone formation, environmental and human toxicity, acidification and eutrophication were examined closely in view of the identification of particularly expressive effect categories. In general, the high GHG potential (because of their significant ability to absorb radiation and their longevity in the atmosphere) as well as their persistence and great range were emphasized as especially problematic properties intrinsic to the substance. In this the contribution to climate change dominates. Therefore, selected application examples are examined on their contribution to the greenhouse effect the following sections 5 and 6. This procedure is oriented towards the ‘lifecycle climate performance’ (LCCP) in international literature, which is focussed on climate protection and compares different technology alternatives under consideration of their emissions over the lifetime (production, operation and disposal). The application examples were selected in such a way that they represent an important application with respect to emissions in Europe with salient technical properties.

5 Application examples

Application A – PU rigid foam: roof insulation

Building insulation panels from PU rigid foam are increasingly used in the insulation of tilted roofs of residential buildings (new and retrofit). For the blowing process, mainly n-pentane is used which substituted the blowing agent HCFC-11 since 1995. In this application example,

the effects of a substitution of HFC-365mfc in place of the hydrocarbon n-pentane is examined.

Fundamentally, this deals with an environmental comparison between lower heat losses from a PU-insulated roof and higher emissions of the blowing agent used for foam production. For this, the emissions of blowing agent over the lifetime of the foam panels i.e. from feedstock products of PU production, during the blowing process, installation, during the usage phase and in the disposal for a standard case with respect to foam thickness, heating energy demand etc. were investigated. The essential losses in this occurred in the framework of disposal. Losses in installation and during the usage phase were negligible. In addition to the losses of blowing agent, the energy-related emissions in the covering of the heating energy demand were considered. This varies at the same thickness of insulation panel because of the different insulation properties of the blowing agents (HFC vs. n-pentane) used. Furthermore, the annual total costs for insulation panel and heating energy demand were calculated.

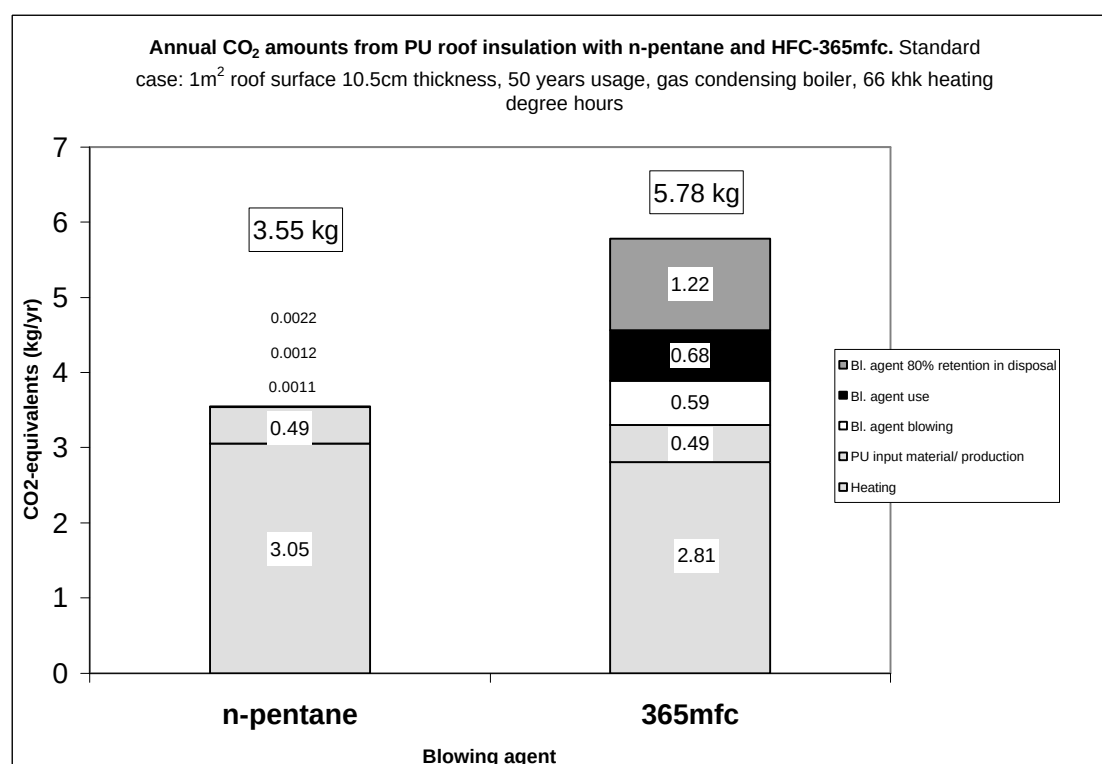


Figure 5: Comparison of annual CO₂ equivalent amounts for PU roof insulation with blowing agent n-pentane and HFC-365mfc.¹

As can be seen in Fig. 5, the insulation with HFC-365mfc results in lower CO₂ emissions from heating. The emission of blowing agent however overcompensates by far the purely energy-related CO₂ benefits. The greenhouse-effective pentane emissions (the global GHG potential of n-pentane is 4, that of HFC-365mfc is 890) are almost negligible.

If only the cost for annual heating energy demand per m² of roof surface and the purchase price apportioned for a year of usage (without interest) are considered for insulation panels with 10.5 cm thickness, the annual operation costs for n-pentane were 1.03 Euro, for HFC-365 these were one cent more at 1.04 Euro. The lower energy cost (0.04 Euro) were slightly overcompensated by the additional cost for the blowing agent HFC-365mfc

¹ In the framework of disposal, an 80% recovery of blowing agent is assumed

In contrast to the PU insulation panel with HFC, the pentane-blown panel features a clearly better GHG balance. This is also valid for the increase of insulation thickness for pentane foam as well as for the slightly higher heating energy demand at constant insulation thickness.

Application A – PU rigid foam: insulation of refrigerated vehicles

In refrigerated vehicles for the transport of perishable goods PU foam is generally used for the insulation of the walls of the cargo hold. In contrary to roof insulation, this is not an even but a three-dimensional insulation structure due to thermal bridges in the vehicle (corners, seals, bolts etc.). In addition to this, the thickness of the insulation panels cannot be increased since this would entail a reduction of payload volume. Commonly, a blend of 70 % c-pentane and 30 % n-pentane is applied. In the application example, the effects of the use of HFC-365mfc instead of c/i-pentane is examined. For this, the losses of blowing agent over the lifetime i.e. in the blowing process, in installation, use and disposal as well as the energy-related emissions for refrigeration were identified.

Before the transport, a pre-cooling with electricity is commonly done, during the transport the refrigeration is covered by a diesel-powered system. Since the vehicles are being sold abroad after half their lifetime, it was assumed that there is no ordered disposal and hence a complete loss of blowing agent at the end of the usage phase. Figure 6 shows the aggregated GHG emissions for the two insulation methods. The largest share of GHG emissions does not stem from blowing agent but from energy consumption for refrigeration.

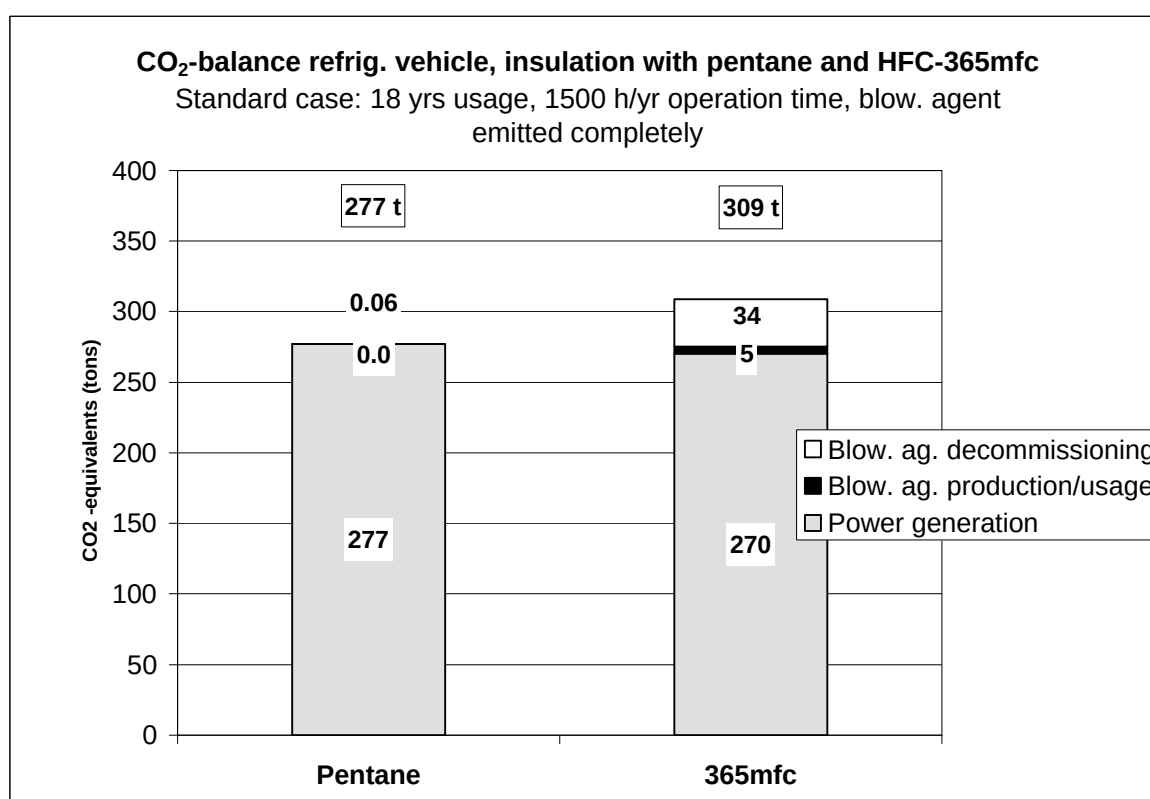


Figure 6: GHG balance for refrigerated vehicles insulated with pentane and HFC-365mfc blown foam.

The total sum of CO₂ and CO₂-equivalent emissions over the whole lifetime was 277t for pentane and 309t for HFC-365mfc. The slightly lower energy-related CO₂-emissions in the HFC-365mfc case were overcompensated by the climate effect of HFC blowing agent which was assumed to be emitted completely due to the lack of disposal facilities.

The annual operation costs for refrigeration of the vehicle over 18 years is always higher for pentane than for HFC foam. For HFC, 2.5% less has to be spent on diesel and electricity. On the other hand there are additional costs from the expenditure for 43.1 kg HFC-365mfc which have to be allocated to the individual usage years (without interest). On the side of pentane, costs for blowing agent hardly carry any weight.

In the application example refrigerated vehicle, it was shown that:

- At the given disposal conditions for refrigerated vehicles (semi-trailer), namely no recovery of blowing agent in the scrapping at the end of lifetime, the HFC-free alternative displays a better GHG balance than HFC-blown insulation even if strict thickness limitations are imposed.
- The GHG balance for the examined refrigerated semi-trailer is generally in favour of the n-pentane version but that this advantage is relatively narrow and can be reduced to equal level with extremely long annual operation times of the refrigeration system.

Application B – supermarket refrigeration (interconnected systems)

For the refrigeration of groceries at approx. 4°C (normal refrigeration, NR) and approx. –18°C (deep freezing, DF) in Germany, refrigeration systems with HFC-404a as refrigerant are used almost exclusively. Basically, three types of systems are applied: plug-in systems, single refrigerated appliances with a dedicated condenser system and interconnected systems with a centralized compressor room and refrigerant ducts to the refrigerated appliances. The energy consumption of these system depends on different factors, among others the size of retail area, the refrigeration demand of the product range the used refrigeration system technologies, the special design of the refrigeration system and its control system but also the maintenance state and the external and internal temperature.

The reference technology (direct evaporation with HFC-404a as refrigerant) were compared to seven alternative technologies. Hence the following were examined:

1. direct evaporation of HFC-404a (reference)
2. secondary sole system with HFC-404a
3. secondary CO₂ system with HFC-404a
4. secondary CO₂ system with propane
5. secondary sole system with ammonia
6. direct evaporation system CO₂ (DF) and secondary sole system with HFC-404a (NR)
7. direct evaporation CO₂ (DF) and direct evaporation HFC-404a (NR)
8. direct evaporation CO₂ (DF and NR(supercritical))

Four of the alternative technologies separate cooling production and cooling distribution. In the primary cycle where cooling is generated HFC-404a, propane and ammonia are applied, in the secondary loop for distribution of cold, CO₂ and sole is used as carrier. Three further systems distinguish between deep freezing and normal refrigeration. All systems have reached market maturity while in Europe presently the technologies 1, 2 and 5 cover significant market shares. The technologies were compared for a fictitious standard case supermarket representative for Germany.

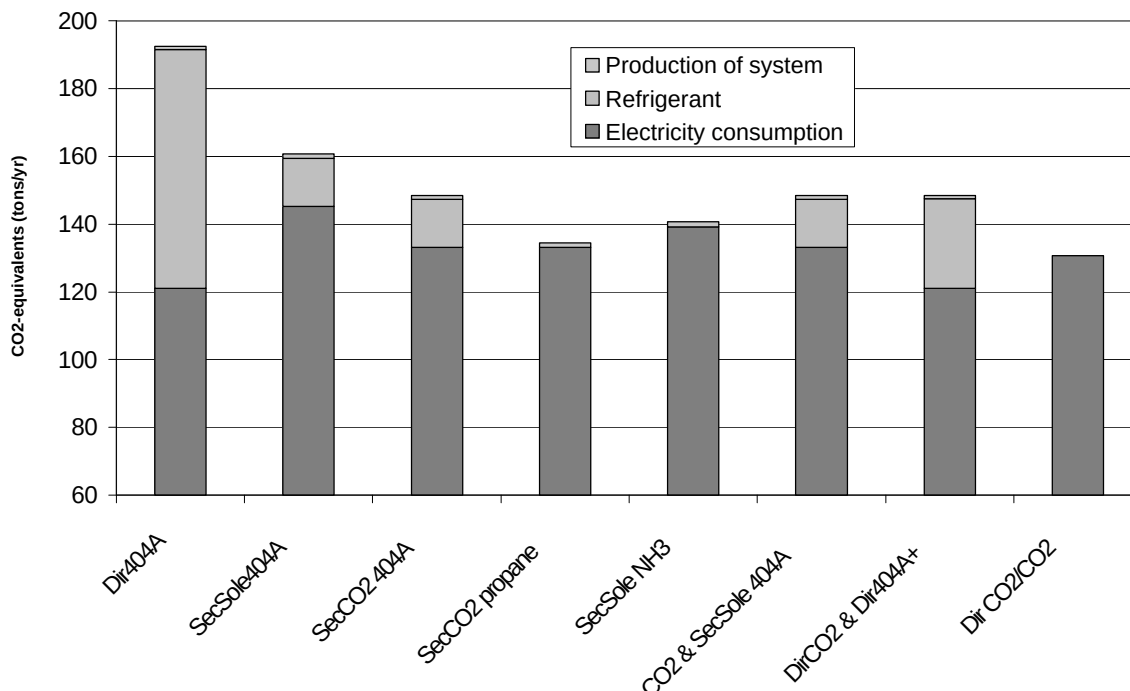


Figure 7: Annual GHG emissions for different technologies under integration of electricity generation, refrigerant losses and manufacture of the system.

As can be seen in Figure 7, the reference technology caused the lowest GHG emissions from electricity generation but the highest refrigerant loss and therefore the highest GHG emissions. The lowest total emissions result from the system with only CO₂ as well as for the systems with ammonia and propane in the primary cycle. The latter however also had the highest hazard potential due to their flammability and toxicity. The annual operation costs are generally inverse to the GHG emissions. On the cost side, the classic HFC-404a direct evaporation system is 10-25 % cheaper than the examined alternative technologies.

The application example shows among other that

- the usage phase and the disposal dominate the emission balance with together 99.5% while the emissions related to energy consumption during the production of components and fluids remain negligible
- the GHG balance of HFC solutions in comparison to alternative technologies deteriorate with lower carbon intensity of the German electricity production in the long range
- the emission potentials of the alternative technologies to direct evaporator HFC solutions examined above are in a range between 10-30% (0.3-1.0 Mt CO₂ equivalent per annum) of the whole direct and indirect emissions of interconnected refrigeration in the commercial sector in Germany
- the costs for the mitigation of one tonne of CO₂ equivalent start at 20€ for a combined CO₂/404A direct evaporation system and rise to more than 200€ for e.g. 404A secondary sole systems.

6 Summary and Outlook

This study comes to the conclusion that as properties intrinsic to the substance of the examined fluorinated substances especially climate effect and persistence stand out negatively. On the positive side their generally low human toxicity and low flammability are identified.

In the framework of two application examples examined in this study (PU roof insulation panels and PU insulation for refrigerated semi-trailers), but also other corresponding analyses it was shown that that even today the application of fluorinated GHG instead of alternative technologies in fields which previously were a domain of HCFC is not or only marginally economical. It has however been demonstrated with the example of supermarket interconnected refrigeration system that there are however application fields in which fluorinated GHG have clear economic benefits over alternative substances.

Up to a certain degree macroeconomic cost disadvantages in the application of alternative substances today are compensated with their low specific mitigation costs. The reductions then contribute a comparably cost-efficiently to climate protection. In singular cases the alternative technologies with higher mitigation costs are too costly even under consideration of this criterion to justify their application today only for economic reasons of climate protection. Other environmental considerations such as the mitigation of risks resulting from persistent substances may tip the scales towards a substitution initiated by legislation in marginal cases.

Beyond the necessary cost-efficiency of climate protection measures it should not be forgotten in the view of the authors that by a system change induced today considerable costs may avoided later if the costs for development, later adaptation and finally the following substitution of a technology not applicable in the long term can be evaded from the start.

The authors of this study find it advisable that the legislator providently supports the development, testing and distribution of new climate-friendly technologies in this situation by appropriate packets of measures without burdening users and consumers with non-justifiable additional risks and costs. This could e.g. be done within the framework of the recommendations made for the support of the application of alternative substances in the final report of the European Climate Protection Programme of 2001. Because of the fundamental problems in the installation-specific and timely monitoring of emissions of fluorinated GHG, market-based instruments such as emission trading will remain unsuitable for fluorinated GHG in the opinion of the authors.

For these reasons, regulation appears as most suitable in the view of the authors to achieve and accelerate the necessary stepwise substitution advisable for the reason of climate protection but also for substance-political sustainability and precaution. These would last but not least in the international context contribute to provide a clear orientation on the direction of further technological development often demanded by industry.

1 Introduction

Today, a number of fluorinated greenhouse gases (GHG) are used in a multitude of technical applications. Next to perfluorinated compounds such as CF_4 , C_2F_6 or SF_6 for special applications, especially fluorinated hydrocarbons (HFC) are of relevance in terms of volume in this group of substances. HFCs, which represent the special emphasis of this study are used as substitutes for Chlorofluorocarbons (CFC) which are depleting stratospheric ozone and became thus internationally banned under the Montreal protocol. Following the phase-out schedule of different applications, different HFC were introduced into the market step by step since 1993. Since the start, the use of fluorinated GHG was under controversial discussion among the expert public. A particular concern was the replacement of one environmentally problematic class of substance by another without being able to evaluate the specific problems of their environmental behaviour.

Fluorinated compounds examined in this study are all effective GHG, which have been included in the basket of GHG that need to be reduced together with carbon dioxide (CO_2) methane (CH_4) and laughing gas (N_2O). Within the European Union, the Commission as well as several Member States including Germany have begun to compile bundles of measures for the limitation of the emission of fluorinated GHG. Under the pressure of environmental organisations, some companies have abandoned the use of fluorinated GHG completely. In addition to the climate protection targets, which are the basis for all these efforts, all acting parties imply inherent environmental risks for HCFC as well as fluorinated GHG mainly because of their persistence in the environment.

It was the objective of this research project to characterise the risk emanating from the application of fluorinated GHG in greater detail and to weigh this against the benefit of the substances in example applications. With this, the research project provides assistance in shaping of a long-term product policy to decision makers in administration and economy. The conventional approach of avoidance of risks as well as precautionary strategies of risk assessment and risk management were utilized for this.

The project consisted of the following sections:

- Development of an application-specific evaluation methodology on the basis of a criteria catalogue
- Overview over actual and predicted future application patterns for fluorinated greenhouse gases
- Summarizing discussion of current state of science on environmental behaviour of fluorinated GHG
- Examination of selected application examples (blowing agent in poly-urethane rigid foam as well as refrigerants in supermarket refrigeration)
- Conclusions for a precautionary environmental policy

The selected application examples are examined in great detail within the framework of this study in order to find opportunities and limitations close to practice for the application of alternative technologies in applications regarded as ideal for fluorinated GHG. The respective results were discussed and validated with experts, among others in an expert meeting. Of course, the examined application examples cannot represent the situation in all application fields of fluorinated GHG. They were however chosen in such a way that a transfer of core statements to other fields of application is possible.

With this study, a summary and discussion of scientific and technical knowledge on environmental evaluation accumulated in the course of the first decade after broad commercial introduction of fluorinated GHG is made available to decision makers in the private and public sector. For the evaluation, a pragmatic approach was selected accommodating the complexity of application fields while at the same time providing assistance in decision situations.

2 Deduction of evaluation approach

2.1 Problem

The use of HFCs is attached to potential emissions into the atmosphere due to their high volatility. With increasing sensitivity towards risks and hazards related to this in society, this study aims to bring light to the following questions:

- Which are the environmental and health risks resulting from the use of HFC under consideration of their intrinsic substance properties?
- Which environmental and health benefits and disadvantages and which risks can be expected from the application of HFC in comparison to alternative substances at equivalent use?

Such criteria relevant to environment and health will be identified that shall be treated with priority attention in the framework of evaluation. In order to enable a comparative evaluation of advantages and disadvantages of different categories of effects, criteria for a weighting for the categories of effects should be implemented.

2.2 Background

The evaluation of substances in view of their properties related to environment and health is conducted in different contexts and with different objectives. Voluntary approaches by companies and economic sectors add to the legally prescribed methods to achieve the optimisation of market chances of products in conjunction with technical and economic audits. Evaluations by environmental and consumer associations however focus mainly on the damaging effects on environment and health, occupational safety and health organisations mainly on health and safety at the work place. Integral evaluation schemes as e.g. environmental balances consider primary and secondary effects in all phases of life.

In order to limit the normative framework for the evaluation in this study, the national guidelines for a sustainable substance policy are summarized in section 2.3. Section 2.3.1 explains how the crucial element of a sustainable substance policy, the provisional principle is anchored in the international, European and German context. Section 2.3.2 discusses considerations on risk and uncertainty of the evaluation of chemicals.

In section 2.4 an evaluation method suited for the objective of this study is proposed based on the approaches presently available.

In the annex to this study (section 11) an outlook to different evaluation approaches oriented towards provision is given to enable an orientation in the context of the discussions on risk policy.

2.3 Models of a sustainable substance policy

The model of a sustainable substance policy designed by the Brundtland commission has been worded with the Agenda 21 of the conference of the United Nations for Environment and Development of June 1992 in Rio de Janeiro. Responding to an assignment of the United Nations General Assembly in 1997 in the *OECD Environmental Strategy for the First Decade of the 21st Century*, the OECD defined four specific criteria for a sustainable environment. Criterion III signifies the following:

Releases of hazardous or polluting substances to the environment shall not exceed its assimilative capacity; concentrations shall be kept below established critical levels necessary for the protection of human health and the environment. When assimilative capacity is effectively zero (e.g. for hazardous substances that are persistent and/or bio-accumulative), effectively a zero release of such substances is required to avoid their accumulation in the environment (OECD 2001).

In the 6th environmental action programme of the European commission (COM 2001a), the aim for environment and health is:

Achievement of a quality of the environment in which anthropogenic pollutants including different types of radiation do not give rise to significant impacts on, or risks to, human health. This is to be achieved by integral and comprehensive approaches with emphasis on precaution and prevention and under special consideration of vulnerable groups such as children and elderly.

The sustainability strategy of the European Union phrases this similarly (COM 2001b):

By 2020, it shall be ensured that chemicals are only produced and used in ways that do not pose significant threats to human health and the environment. In addition to this, the EU should aim to reduce atmospheric greenhouse gas emissions by an average of 1% per year over 1990 levels up to 2020.

In the white paper ‘Strategy for a future Chemicals Policy’ (COM 2001c) the substance policy aim of the protection of human health and support of an environment free of toxins is complemented with some substantiating elements:

Next to a demand to secure economic competitiveness of the chemical industry, especially knowledge gaps which exist for 99% of the chemicals applied in Europe shall be closed. For the future, more consideration of the lifetime impacts of chemicals shall be taken and the principle of precaution shall be applied in cases where there are uncertainties about the exact type and severity of potential damages from chemicals. Substances which give rise to particular apprehension² shall only be applied after special approval. Substitution of dangerous substances by less dangerous substances shall be supported.

While substantiation of substance policy objectives and models on European level are under discussion and development, there are practical approaches on Member State level already: The Swedish ‘New guidelines for chemical policy’ (SOU 2000) propose to terminate the production and application of persistent, bio-accumulating, carcinogenic, mutagenic substances and such which are toxic on reproduction or work as endocrine disruptors in order to achieve the aim of a ‘chemical-free environment’.

In Germany, the Federal Environmental Agency substantiated basic demands for a sustainable development in conjunction with the recommendations of the Enquête-commission of the 13th German Bundestag ‘Protection of man and environment’ already in 1997. In the study ‘Workfields for a precautionary and sustainable substance policy for the example of PVC’ (UBA 1999a), the Federal Environmental Agency of Germany compiled the concepts and ideas of the council of

² According to the white paper, such materials are covered that fulfil the criteria of Annex D of the future Stockholm POP accord as well as such materials with carcinogenic, mutagenic, or toxic effects on reproduction (category 1 and 2); further research demand has been expressed in view of persistent, bio-accumulating and toxic materials as well as of highly persistent and highly accumulating substances.

experts for environmental questions, the Enquête-commission and the ‘guidelines for environmental precautions’ of the German federal government in 1986.

Here it is emphasized that the principles of sustainability and precaution are overlapping and therefore not only defence of hazards but also precaution of risks by avoidance and reduction of risks in the preliminary stages of potential dangers is required.

With the guidelines, substance-related environmental quality objectives are proposed. Five long-term objectives for substance-related environmental action objectives are deduced and justified. Table 1 shows the allocation of these into the eight combinations of substances and properties.

Table 1: Environmental targets related to substance policy of the German Federal Environmental Agency (according to UBA 1999, UBA 2001)

Substance group	Properties			
	persistent and/or bio-accumulating	carcinogenic, mutagenic, toxic on reproduction	Toxic in other respective/ on environment	irreversible
Xenobiotics and their metabolites	Irreversible introduction needs to be avoided completely	Introduction has to be avoided completely	Reduction of the introduction into the environment to the technically unavoidable minimum	Increase of the substance introduction needs to be avoided
Natural substances	No increase over the geogenic/ biogenic background contamination	No increase over the geogenic/ biogenic background contamination	Reduction of the introduction into the environment to the technically unavoidable minimum	Increase of the substance introduction needs to be avoided

2.3.1 The precautionary principle

Under the terms of the founding contract of the European Community, the axiom of the originator principle and of the precautionary principle have to be observed (EGV 1999). The precautionary principle shall be considered in the framework of risk assessment, risk management and risk communication in those cases in which dangerous consequences for a phenomenon, product or method may arise and for which the risk cannot be assessed by means of a scientific assessment (COM 2002). While the precautionary principle in the future chemicals policy of the European Union is not substantiated completely, it has already found its way into substance policy conventions and has been transferred into different national and European regulations.

In such a way, Article 3 of the framework convention on climate change (UNFCCC, 1992) expresses the following on the role of precautionary policies and measures on climate protection:

„The Parties should take precautionary measures to anticipate, prevent or minimize the causes of climate change and mitigate its adverse effects. Where there are threats of serious or irreversible damage, lack of full scientific certainty should not be used as a reason for postponing such measures, taking into account that policies and measures to deal with climate change should be cost-effective so as to ensure global benefits at the lowest possible cost.’

A further example is the OSPAR convention (OSPAR 2001) defining the protection of the seas with instruments based upon the originator principle and best practice technology.

With the directive on the integrated reduction and avoidance of environmental pollution, the originator principle has been put into practice on European regulation for the first time. All suitable precautions against environmental pollution shall be applied, especially by use of best practice technology; among others, Appendix IV states the 'substitution of dangerous substances by less dangerous' (IPCC 1996) as suitable measure.

The three-sector security concept in Germany evolved from legislation for police and public order distinguishing between danger, risk and residual risk.

The danger at which damage is expected with sufficient probability must be counteracted by the state, no matter if cost and use are in an adequate ratio.

Risks, i.e. situations that potentially lead to damage shall be minimized beforehand with consideration of commensurability between cost and use under the reservation of the technically feasible.

Remaining residual risk, i.e. the impossibility to achieve situations free of risk (zero risk) is defined in the category of the risk permitted by legislation and therefore has to be accepted by society (Öko-Institut 2001)

This approach to avoidance of risks in a precaution-oriented chemical policy found its way into several German environmental laws, e.g. into the Federal Law on Exposure Protection and the legislations on water or chemical substances.

One of the instruments for the implementation of a precaution-oriented chemical substance policy is the principle of substitution i.e. the replacement of dangerous substances with less harmful ones. Such a requirement for substitution and minimization is a legal prerequisite in view of the health risks connected to handling of substances in the occupational environment. In the white paper on chemical policy, the support of substitution is mentioned as one of the essential targets (COM 2001).

Prerequisite for the application of the precautionary and substitution principle is however the availability of sufficient information on the properties of substances as a basis for a differentiated risk assessment (e.g. Ahlers 2001).

2.3.2 Risk and Uncertainty

Risk in the sense of natural science is the product of damage extent and probability of occurrence. The more empirical data on potential damages and about the number of occurrences of damages is available and the clearer the cause-effect relations are, the better the conditions for a high certainty in the estimation. The further cause and effect are apart in space and time, and the more risk assessment is based on model assumptions or on results of simplified lab examinations, the higher the uncertainty of the estimation. The uncertainty in the field of chemical assessment is based on the one hand on the insufficient evaluation of the larger part of the substances. A high measure of uncertainty remains even for substances which have been through the process of substance assessment under investment of great efforts, since the cause-effect relations in complex reality in

humans and environment cannot be assessed completely but allows only examination of facts already known.

The Federal Environmental Agency therefore elaborated the limits of chemical assessment in view of a precautionary substance policy in (UBA 1999) in great detail. The use of chemical substances is going to be connected to certain residual risks in a future oriented towards precaution. Which criteria can be observed in order to develop a sense of proportion for the bandwidth between acceptable and controllable residual risk and perilous test runs on global scale is discussed e.g. in the report of the scientific committee of the Federal Government of Germany on global environmental changes (WBGU 1998), in the first report of the risk commission (Risikokommission 2002) or in the report of the European Environmental Agency on precaution (EEA 2001). In this, an estimation was conducted on the application of HFC and the associated risks based on the standard for precaution-oriented assessment of risks and uncertainties mentioned there.

2.4 Procedure for the risk assessment in this study

Evaluation of HFC is based on the demonstration of the status of the intrinsic substance properties of HFC and on the results of the ecological balance on selected applications. The procedure for the assessment is represented in the diagram of Figure 1.

In section 3 following this section, the fields of application of HFC, the current estimates and prognoses of the amounts and emissions worldwide and the characterization of manufacturing and disposal is presented. Section 4 summarizes the state of knowledge on the substance-intrinsic properties³. In sections 5 and 6 a comparative analysis of common applications is conducted. The balance is limited on the effect category climate of which the primary relevance is concluded in section 4. Polyurethane (PU) rigid foams for roof insulation and for the insulation of refrigerated vehicles as well as supermarket refrigeration were chosen as applications. In PU rigid foams, HFC-365mfc serves as the blowing agent alternative to n- and c-pentane. In supermarket refrigeration systems HFC-404A is applied as refrigerant and carrier alternative to propane, ammonia and CO₂.

³ In the context of evaluation of dangerous substances, the term 'substance-intrinsic properties' names the effective potentials of substances. In the context of ecological analysis the effective potentials are summarized in categories of effects. Since this study takes into account and applies both fields, this will be referred to as 'substance-intrinsic properties' from here on. The choice of categories of effects in this is borrowed from the quantifiable and output-related categories of the SETAC-procedure (s. UBA 1999d)

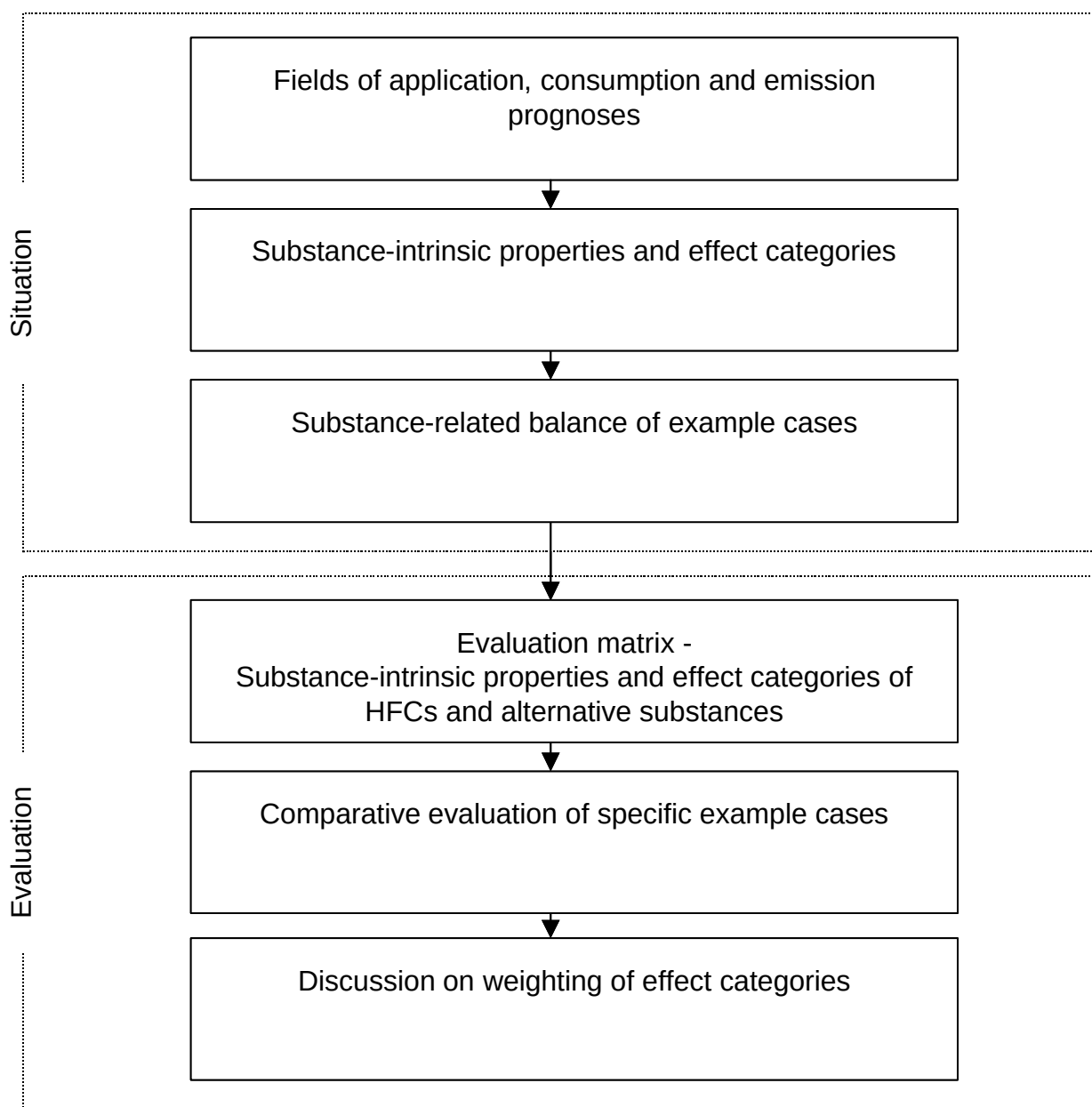


Figure 1: Procedure risk assessment

The evaluation as such will be covered in section 7. To alleviate a systematic comprehension, the substance-intrinsic properties and effect categories of the HFCs treated herein and the alternative substances examined in the example cases are classified into an evaluation matrix. The methodology chosen for this examination on the basis of its semi-quantitative classification system established among experts is similar to the ‘column model’ of the German technical guidelines on dangerous substances (TRGS 440) within the legislation on dangerous substances: the relevance of the properties and effect categories of singular substances are rated in a five-step system as ‘very high’, ‘high’, ‘medium’, ‘low’ and ‘negligible’. For this, the properties toxicity on humans, toxicity on ecology as well as fire and explosion risks based on the R-sentences in the classification suggestions in TRGS 440 are applied. For properties and effect categories not contained in these, an own rating system will be utilized. In this, the lowest known values are taken as the threshold for the rating ‘negligible’ and the highest known value defined as the threshold for ‘very high’ thus giving a framework to establish the ratings ‘low’ ‘medium’ and ‘high’.

This evaluation matrix allows an overview over the fundamental risks and enables the limitation of the comparative evaluation on the relevant criteria. The decision which substance in a specific application would be better from the point of view of health and environmental protection becomes simple if the consideration of the substance-intrinsic properties and effect categories produces an unambiguous impression. If advantages and disadvantages are juxtaposed in different categories, this requires a differentiated consideration of the risks entailed with this application. This also includes considerations on application of risk management measures, which contribute or may contribute to a minimization of these risks.

For each application example in this study, the method for establishment of the evaluation matrix is equal i.e. a classification in levels 'negligible', 'low' 'medium' 'high' and 'very high' is formed. The classification is based on the classification in the evaluation matrix under qualitative consideration of the application pattern and the introduced and applied risk management measures. A property classified as 'medium' may therefore be up- or downgraded depending if the application pattern indicates a reduction or an increase of the risk potentials.

The following criteria and aspects are considered in the application-specific classification:

- Results of analysis in sections 5 and 6
- Application pattern⁴: hermetic, mainly hermetic, semi-hermetic, open
- Distribution of applications: concentrated, punctual, semi-diffuse, diffuse
- Risk management measures: e.g. common and well-established; possible, but not tried or accepted in practice; technically feasible, but only with very high effort; cannot be realized in technology; responsibilities unambiguous etc.
- Unknown risks and uncertainties are estimated to be graver
- Limitation to relative comparison of alternative substances in application case

2.4.1 Weighting

A direct analysis of advantages and disadvantages in single evaluation categories is not considered as adequate. On the one hand, an aggregation of different effect categories e.g. in the framework of ecological balances is generally seen with scepticism from the scientific side (e.g. UBA 1999d). The qualitative and discursive method utilized in the frame of this application-specific evaluation on the other hand excludes the option to offset advantages and disadvantages.

In order to give justice to the potentially significantly different risk dimensions of the evaluation criteria, we hold the opinion that it is essential to elaborate the varying relevance of the effect categories on the basis of a criteria set in a discursive way for the formation of a final verdict. The criteria listed in the following were taken on the basis of the discussion on evaluation of ecological balances (e.g. UBA 1999), the risk discussion (WBGU 2000), the first report on the work on risk dimension and the discussion of a precautionary chemical policy (EEA 2000) and are integrated into a final qualitative weighting of the effect categories.

⁴ Following (UBA 1999b), a distinction of usage patterns in four risk categories is made: The industrial application of a substance in a closed system with the lowest risk and with loss rates <0.01% is considered as hermetic. Industrial applications including open systems within the plant where sufficient environmental management and technology can be assumed are considered as a mainly hermetic usage pattern with related higher risk. The next higher risk level includes semi-hermetic usage patterns where emissions from numerous, widely distributed sources occur at commercial or private users. The highest risk is attributed to open usage patterns causing direct and untreated release of substances into the environment (s. also Appendix 11.1.3.4).

Table 2: Criteria for the weighting of effect categories

Criterion	Lower risk	Higher risk
Spatial range	Local range	Global range
Time range	Short term	Long term
Reversibility of damages	Reversible, acute	Irreversible, chronic
Proximity to originator	Damage close to originator responsibility or liability of originator	Damage far from originator; no responsibility or liability of originator
Damage level	One level affected (e.g. one tropical aquatic level)	Many (all) levels affected (man, flora, tropical levels of fauna)
Relation between cause and effect	Unambiguous, known	Complex, unknown
Experience horizon	Long term experience in diverse context	No or limited experience
Achievement of targets (environmental, traffic)	Target reached, positive trend	Target not reached, negative trend

3 Manufacture, Application and Disposal

3.1 Lifecycle

3.1.1 Overview:

HFC are released over the whole life cycle of products:

- During the production of HFC
- During manufacture in which HFC are applied
- During the use of products
- At the disposal of products

Due to the emission over the whole life span of products containing HFCs, a retarded emission relative to the production time needs to be taken into consideration. This is especially valid for products with long life spans e.g. industrial refrigeration or high emissions at disposal (e.g. mobile air conditioning).

Figure 2 displays how emissions can occur over the life span of a product containing HFC (e.g. household refrigerator).

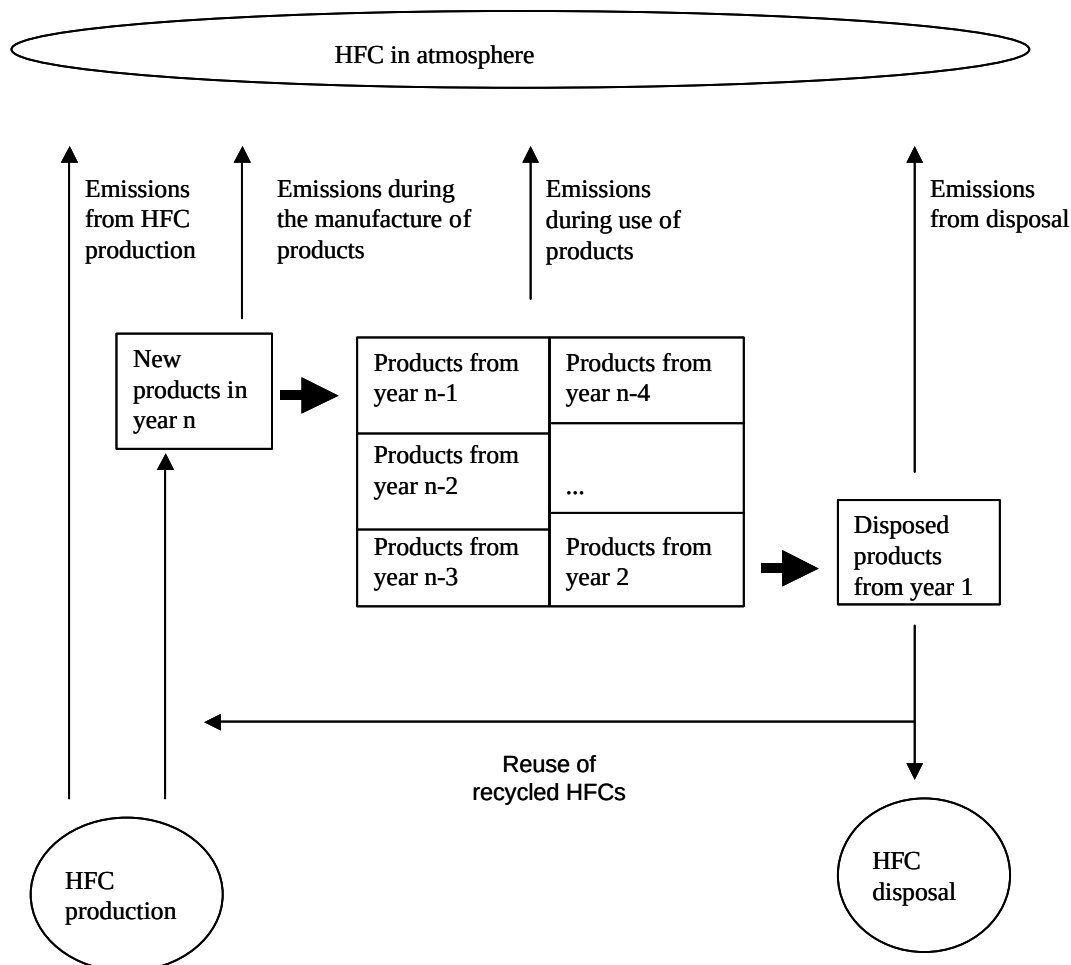


Figure 2: Emissions of HFC during the lifetime of products containing HFC

3.1.2 Application

Fluorinated greenhouse gases can be used for numerous applications in which ozone depleting substances need to be replaced. Table 3 gives an overview over the most important applications (by volume) and the substances used in the respective case (ozone depleting substances, HFC and alternative fluids). The most relevant application cases by volume of per-fluorinated carbon and sulphur hexafluoride are semiconductor manufacture and switchgear as well as blanketing gas in the production and processing of magnesium. In practice, blends of two or three different substances (s. Table 4) are applied to achieve the desired thermo dynamical properties.

Table 3 Substitution of applied substances in different applications⁵

Sector	Base substance		Alternatives	
	CFC etc.	HCFC	fluorinated	Halogen-free
Refrigeration and Air conditioning	12	22	134a	Propane
	11	123	143a	Butane
	115	141b	125	CO ₂
	114	142b	32	Ammonia
Blowing agent for Rigid foam				Water
				"not-in-kind"
	11	141b	134a	i-Pentane
	12	142b	152a	n-Pentane
		22	365mfc	c-Pentane
Solvent			245fa	CO ₂
				"not-in-kind"
Fire fighting	113	141b	43-10mee	Water
			Hydrofluorether	Div. carbohydrates and -derivatives
Propellant for sprays	Halon-1201		227ea	Water, CO ₂ , Powder, Argon
	Halon-1301			
Propellant for sprays	11	141b	134a	Ether
	12	142b	152a	Butane
			227ea	"not-in-kind"

In Figure 3 and in Figure 4 estimates for the European- and worldwide application amounts of HFC, PFC and SF₆, distinguished by single applications can be found for the years 2000, 2010 and 2020. Application in refrigeration and air-conditioning (including mobile air conditioning) as well as production of insulation foams have by far the greatest weight. For the whole of Europe, the highest increase until 2020 can be attributed to insulation foams, worldwide, the highest increase is anticipated in air conditioning. This difference can be explained with the lower worldwide market relevance of insulation foams compared to refrigeration and air conditioning in contrast to the cooler climate in Europe.

⁵ The number code for the fluorinated (and chlorinated) carbohydrates is based on the following scheme: 1st digit (0 suppressed): number of C atoms in the molecule minus one; 2nd digit: number of hydrogen atoms plus one; 3rd digit: number of fluor atoms. Letters behind the number code signify the position place of substitution. Example: 134a = C₂H₂F₄ or CF₃-CH₂F.

The model (Harnisch et al. 2001) represents the application of fluorinated greenhouse gases in over 20 technical applications and takes into account the specific time lag in the transition from ozone depleting substances like HFC and HFC to alternative substances for the four world regions 'Europe', 'North America', 'Japan' and 'Rest of the world'. The original objective of the model was the emission prediction on the basis of given banks of substances. From the change in banks estimates for the respective used substance can be made. The model is operated with adapted input data of August 2003 other than the original version of 2001.

Table 4: Selection of commercially relevant HFC blends

Name	HFC components	Blend ratio [%]
404A	125/143a/134a	44-52-4
407A	32/125/134a	20-40-40
407B	32/125/134a	10-70-20
407C	32/125/134a	23-25-52
410A	32/125	50-50
410B	32/125	45-55
507	125/143a	50-50

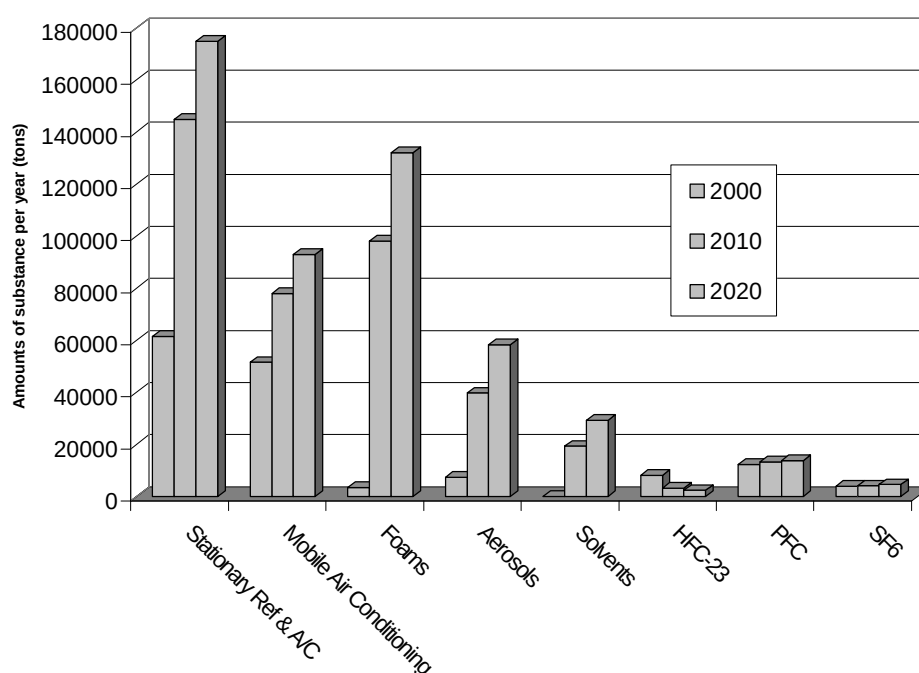


Figure 3: Estimated European amounts of HFC, PFC and SF₆ from different applications – for the process emissions ,HFC-23' and ,PFC' emissions and application are assumed to be equal (Model: Harnisch et al. 2001 – Version: Energy Modeling Forum AUG 2003)

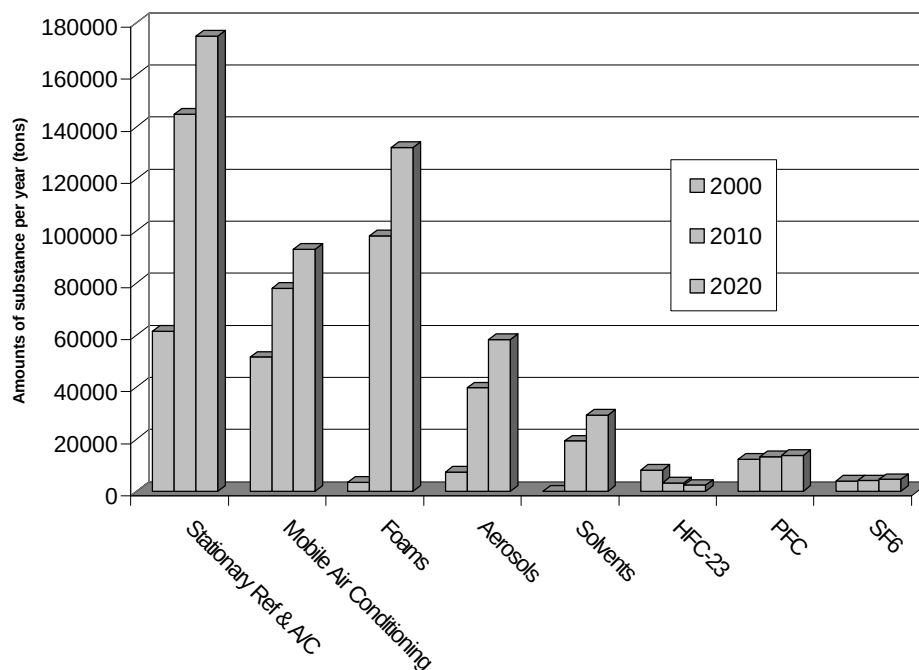


Figure 4: Estimated worldwide amounts of HFC, PFC and SF₆ amounts in several applications- for the process emissions ‘HFC-23’ and ‘PFC’, the application is assumed to be equal to emissions (Model: Harnisch et al. 2001 – Version: Energy Modeling Forum AUG2003)

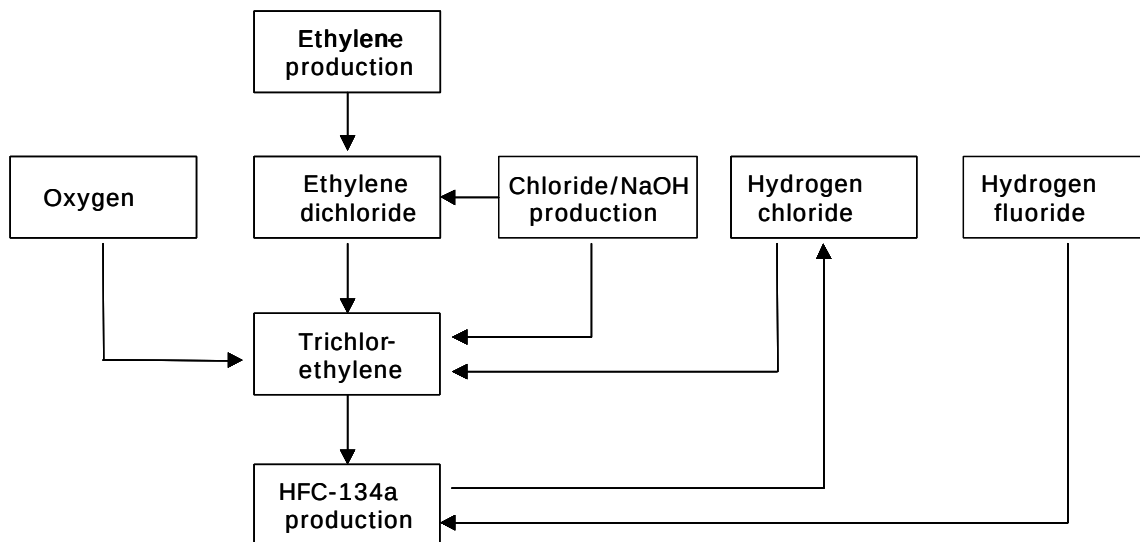
3.1.3 Production

Several examinations on the energy consumption and emission of harmful substances in connection with the production of HFCs are available. Of central importance are the studies of Banks and Sharrat (1996), Campbell and McCulloch (1998), Banks et al. (1996) as well as of Papasavva and Moomaw (1998). Table 5 lists how different HFCs are produced from chlorinated or fluorinated feedstock. In addition to energy consumption and emission of greenhouse gases the emission of byproducts and intermediate products needs to be observed in the characterization of the synthesis path. As far as these contribute to depletion of ozone, the Montreal protocol is not valid since this only covers the manufacture and the trade of ozone depleting substances for end use, not for further processing.

From the reaction of trichloroethylene and hydrofluoride HFC-133a is formed and only in a second processing step HFC-134a is produced. In this process, the toxic and non-saturated HCFC-1122 ($\text{CF}_2=\text{CHCl}$) can be generated as by-product. In Figure 5, the first production path for HFC-134a described in Table 5, which is frequently applied as blowing agent for foams and propelling agent for sprays and as fluid in refrigeration and air conditioning is shown.

Table 5: Production paths for different HFCs

Substance	Production path	Source
HFC-134a	1. hydrofluorination of trichloroethen via HFC-133a 2. Isomerisation / hydrofluorisation of CFC 113 to CFC 114a with appended dechlorination 3. hydrofluorination of tetrachloroethen via HCFC-124 4. hydrofluorination of tetrachloroethen via HCFC-114a	Frischknecht (1999b)
HFC-32	1. hydrofluorination of dichloromethane 2. hydrodechlorination of HCFC-22	Frischknecht (1999b)
HFC-143a	1. hydrofluorination of trichloroethen 2. hydrofluorination of tetrachloroethen	Frischknecht (1999b)
HFC-125	1. hydrofluorination of tetrachloroethen	Frischknecht (1999b)

**Figure 5: Production path for HFC-134a**

The figures in Table 6 show rather clearly that the CO₂ emission related to the energy demand of the production of HFC are low in comparison to the contribution to the greenhouse effect in release of the substances. In comparison to the non-halogenated alternatives, the HFC are clearly inferior with respect to the energy intensity of the production. The energy turnover of the systems in which these fluids are applied during their life cycle (e.g. in refrigeration and air conditioning systems) may however be substantially greater than the energy input in the production of the substances themselves (e.g. Campbell and McCulloch (1998), Papasavva and Moomaw (1998) and Frischknecht (1999b)). Therefore, an energy related assessment should be conducted on the basis of the complete life cycle.

Table 6: Specific energy consumption and greenhouse gas emissions for the production^a of different HFC-134a and comparable substances

	Spec. energy consumption along the process chain [GJ / t]	GHG emissions [T CO ₂ / t]	Direct GHG potential (100 years)	Source
HFC-134a	64-105	6-9	1300	Campbell & McCulloch (1998)
Ammonia	37	2	0	Campbell & McCulloch (1998)
i-Butane	10	0.5	3	Campbell & McCulloch (1998)
c-Pentane	24	1	4	Campbell & McCulloch (1998)

^a the calorific value of the raw materials used and the GWP of potential emissions of intermediate, by- and final products are not considered

In the expert discussion, other environmentally important aspects than energy demand for the production have been neglected so far. This is especially valid for the emissions of intermediate, by- and final products during the production process for which reliable data are unfortunately missing at present. Technical options for a minimisation of such emissions (e.g. by means of a central emission gas capture and –combustion) are probably not exploited so far. Banks et al. (1998) estimate that in the production of HFC-227ea from the different process steps 10 to 40% of fluorinated and chlorinated organic byproducts are emitted in comparison to the yield (Table 7). For the production of HFC-134a, the same group of researchers presents systematically lower figures (Table 8). In general, it can be said that the data situation for this subject is very sparse. For the parameters decisive to the emission situation knowledge is inadequate.

Table 7: Estimated emissions (in kg per t yield product) of by- and intermediate products in the production steps for HFC-227ea (Banks et al. 1998)

Emission	CHCl ₃	CHF ₂ Cl	CHF ₃	CF ₂ =CF ₂	CF ₃ CF=CF ₂	CF ₃ CHF ₂ CF ₃
Production step						
HF	-	-	-	-	-	-
Cl₂	-	-	-	-	-	-
CHCl₃	4-39	-	-	-	-	-
CHF₂Cl	4-39	21-63	34-100	-	-	-
CF₃CF=CF₂	-	8-35	-	23-54	18-28	-
CF₃CHF₂CF₃	-	-	-	-	5-10	5-10

Table 8: Estimated emissions (in kg per t of yield product) of by-products in the production steps for HFC-134a (Banks and Sharratt 1996)

	Emission
Trichlorethylene	1.5
Dichloroethylene	22
Tetrachloroethylene	0.4
Vinyl chloride	10
Ethylenedichloride	6
Vinylidenchloride	0.5
HCFC-1122	0.0006
Other chlorinated carbohydrates	4.0
HCFC -133a	5.0
HFC -134a	1.9
HFC-143a	8.0
HFC-125	0.5
TOTAL	60

3.1.4 Disposal

The discussion of the environmental profile of the disposal of HFC independent from the application is only of limited expedience due to the varying usage conditions in practice. Basically, the following paths of disposal are conceivable:

- a) Release into the atmosphere- in many applications still the rule
- b) Extraction and capture of the HFC and HFC containing blend
 - Direct reuse by installer or user
 - Central reprocessing (manufacturer or recycler)
 - Central destruction (manufacturer or toxic waste incinerator)
- c) HFC are disposed of with the product (e.g. insulation foams)
 - Disposal of the product in landfills
 - Thermal disposal of the product
 - Substantial reuse (s. option b))

Within the framework of this study, an evaluation of the respective disposal paths cannot be covered. It is obvious that a) represents the environmentally worst option, but the losses of HFC into the atmosphere in b) and c) e.g. in the crushing of insulation foams (as far as eventually possible) also need to be avoided to a large extent. The additional costs incurred from recapture and treatment of the substances at the end of the lifetime need to be considered in a general comparison of system cost.

3.2 Emission prognosis

Table 9 shows the emission factors for the release of fluorinated GHG during the manufacture, use and disposal. It can be observed that the emissions during the three phases in the life cycle of the application can differ substantially. In most cases, the most significant emission occurs in the usage phase. Because of refills during the operation phase or recovery at disposal, the total emissions over the life cycle may be greater or smaller than 100%.

Table 9: Emission factors for the use of HFC in different applications for 2010 (March(1999))

Applications	Emission factor production [% mass]	Emission factor application [% Mass p.a.]	Emission factor disposal [% Mass]	lifetime [years]
Refrigeration and air conditioning				
Household refrigerators	1	1	20	13
Commercial refrigeration	2	10	5	13
Industrial refrigeration	2	6	5	25
Mobile air conditioning	1	8	25	12
Blowing agent for rigid foams				
PU-foam in household appliances	3	0.25	60	12
PU-foam in discontinuous panels	10	0.5	25	50
PU-foam in continuous panels	5	0.5	20	50
XPS-foam	25	4	0	50
Spray propellant				
General aerosols	1	96	3	
Dosing aerosols	1	96	3	

Emission prognoses for the years 2010 and 2020 in Germany , Europe and the whole world can be found in Figure 6,

Figure 7 and Figure 8. Data for Germany is consistent with the data sets for the national reports [Öko-Recherche, 2003]. Data for Europe was generated with the emission model described by Harnisch et. al. [2001] and based on actual input figures and assumptions updated 2003.

The prognoses show that in single applications for 2020 in Germany and Europe a maximum of emissions is expected because the transition away from ozone-depleting substances will then be completed. In addition to this, the specific emission rates will decrease due to improved technology, which will not be offset by the slow growth of application. The worldwide picture is different though: an increase beyond the year 2020 can be anticipated, impressively documented in the growth of HFC banks in main application fields (Figure 9). Industrial nations and especially Europe will need to take a precursor role for the responsible handling of this technology.

The example of car air condition system illustrates how the annual use of HFC-134a in this application leads to the accumulation of comparably large refrigerant banks with subsequent emissions of refrigerant during the use phase and –with a certain time lag- in the disposal (Figure 10). An analogue development can also be observed in other air-conditioning and refrigeration applications as well as for rigid foams.

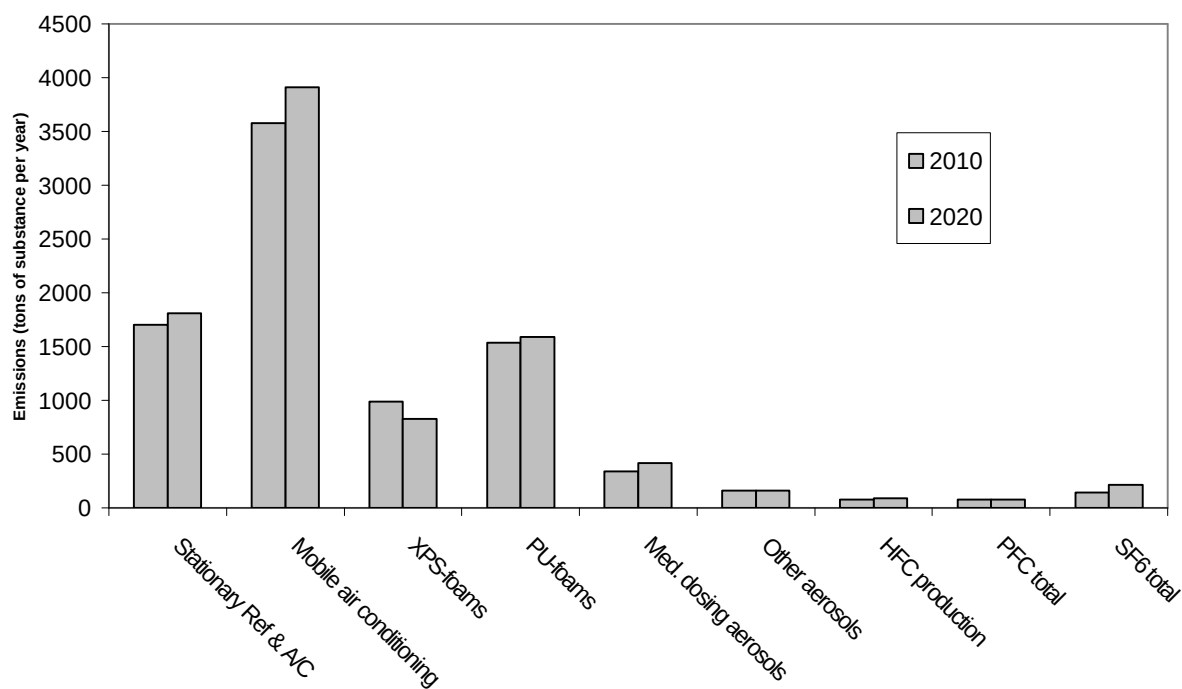


Figure 6 Emission projection (,with measures') for Germany for HFC, PFC and SF₆ (Öko-Recherche (2003))

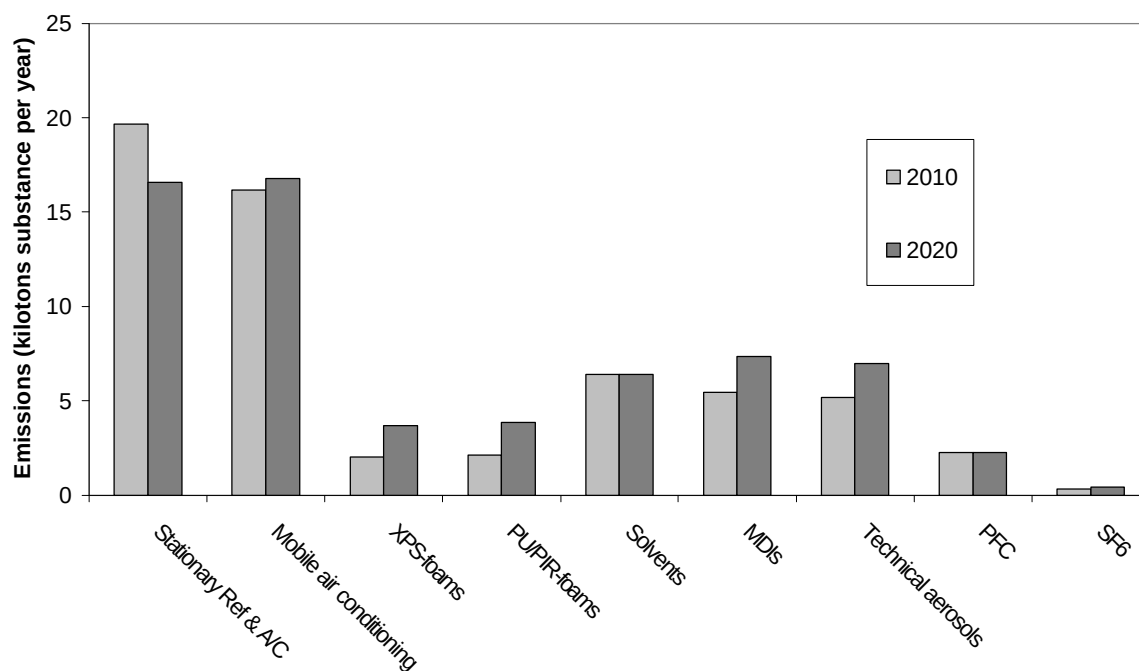


Figure 7: Emission projection for Europe for HFC, PFC and SF₆ (Model: Harnisch et al, 2001 – Version: Energy Modeling Forum AUG2003)

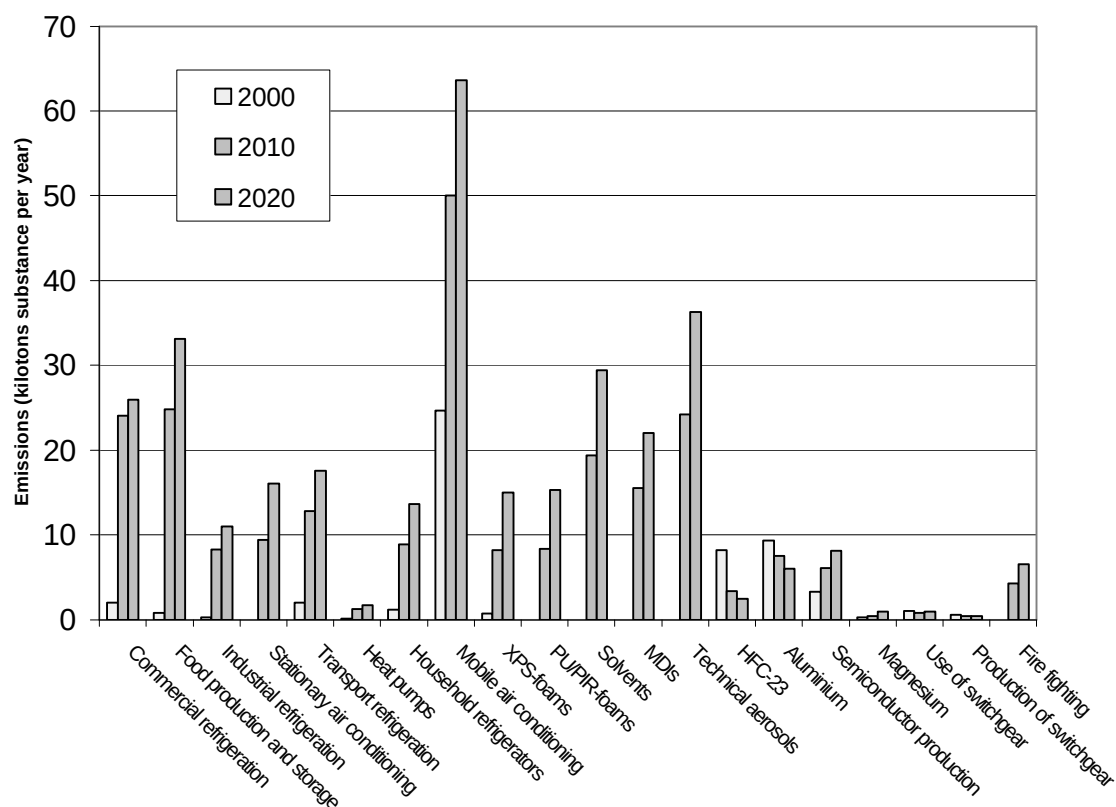


Figure 8: Emission projection worldwide for HFC, PFC and SF₆ (Model: Harnisch et al, 2001 – Version: Energy Modeling Forum AUG2003)

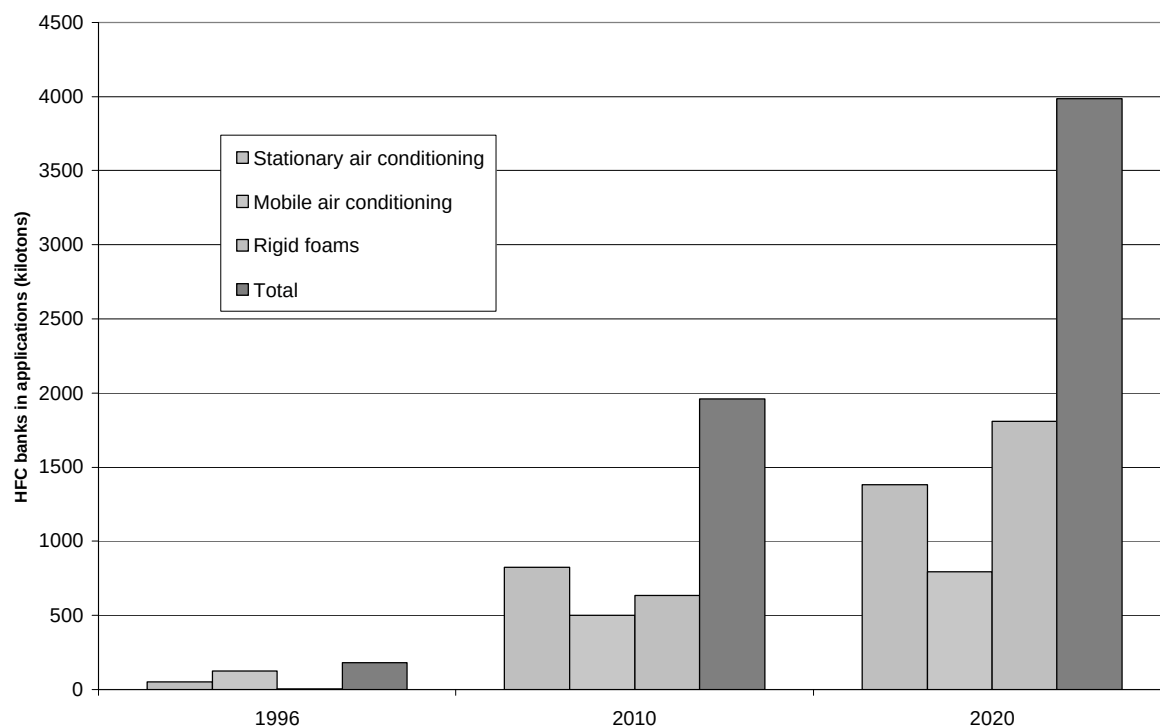


Figure 9: Worldwide development of the HFC banks in the main applications (Model: Harnisch et al, 2001 – Version: Energy Modeling Forum AUG2003)

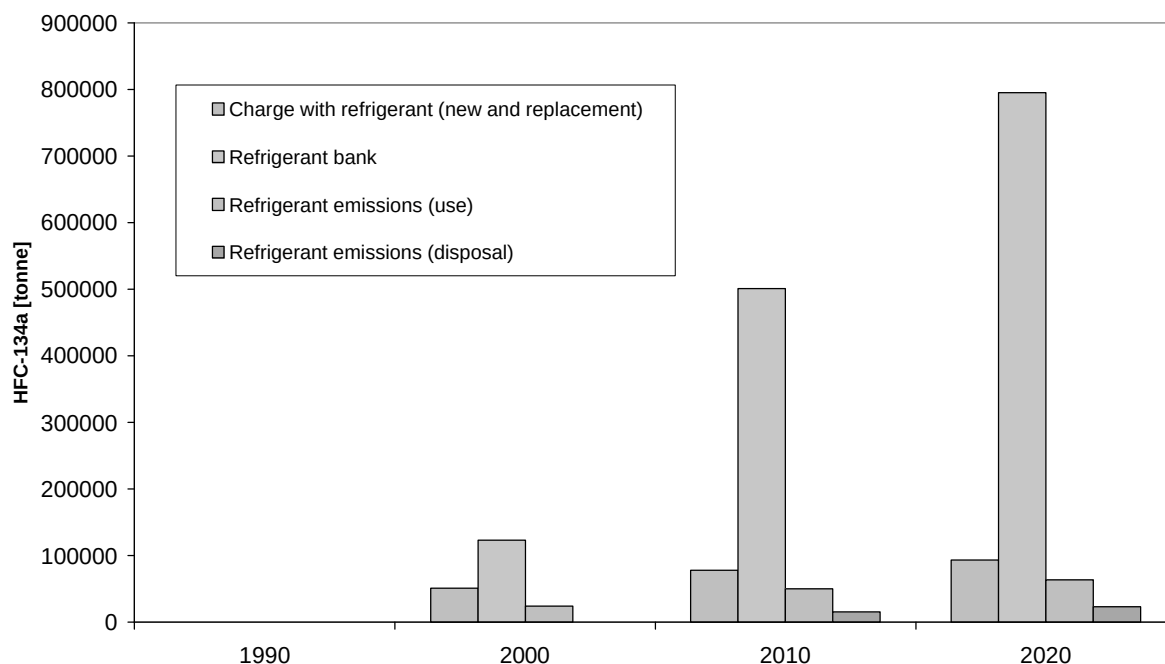


Figure 10: The expanding application of HFC-134a in mobile air conditioning systems (worldwide): comparison of charge with refrigerant HFC-134a (new and replacement), the development of the refrigerant bank and the refrigerant emissions during the use and from disposal (Model: Harnisch et al, 2001 – Version: Energy Modeling Forum AUG2003).

3.3 Summary

Production: Fluorinated GHG are generally produced on synthesis paths based on chlorinated feedstock with an environmental ‘footprint’ (chlorine chemistry) including diffuse emissions of halogenated intermediate and byproducts (including their blending to the product) which needs to be considered. The latter are altogether characterized inadequately. The specific energy consumption and the related GHG emissions for the production of fluorinated GHG are substantially greater than those of alternative refrigerants.

Applications:

Fluorinated GHG are mainly applied in the following fields:

- Refrigeration and air conditioning
- Blowing agent for rigid foam
- Solvent
- Fire fighting agent
- Spray propellant

Air conditioning and refrigeration have the greatest share in the total emissions followed by blowing agents for rigid foam. The refrigerant bank in these main applications is to grow from almost 200,000 t in 1996 to almost 2 million tons in 2010 and further to 4 million tons in 2020.

Disposal: In the disposal of products containing HFC there is the option of extraction and separate treatment prior to disposal or the disposal of the product as a whole next to reckless release. It should be avoided in any case that substantial amounts of HFC is released e.g. in shredding of the product. In thermal processing of waste containing HFC, a sufficient flue gas treatment needs to be ensured in order to avoid increased emissions of fluoride into the ambient air. In most cases, these disposal paths are nonexistent at present.

Use and emissions: A market volume of 500,000 t fluorinated GHG can be assumed for the year 2020. A maximum of 100,000 t of this is accountable for Europe. The resulting annual emissions into the environment might grow to 330,000t of different fluorinated GHG worldwide and approx. 60,000 tons in Europe. Out of this, ca. 5% are CF or SF₆. Therefore HFCs dominate the general impression for use and emission. Therefore a clear emphasis is laid on HFC in the further conduct of this study.

4 Fluorinated GHG in the environment

A multitude of studies on the behaviour of fluorinated chemicals in the environment were conducted during the 90s. A major share of these were prepared by a consortium of large manufacturers of CFC and HFC under the project title AFEAS (Alternative Fluorocarbon Environmental Acceptability Study). In addition to this, there was a considerable number of governmentally funded research projects on single aspects of the environmental behaviour of fluorinated GHG (mostly HFC) in special applications. This section will substantiate the relevant aspects one by one. The environmental behaviour of perfluorinated carbon and sulphur hexafluoride, which are much more stable and have been on the market partly for decades in rather small volumes, is in contrast not characterized so well.

In the past, selected aspects of the environmental behaviour of fluorinated GHG and their substitutes were examined with priority which can mainly be attributed to the emphasis within the AFEAS initiative as well as the demands within the frame of the approval procedure. Published examinations therefore mainly deal with the selection from the effect categories of the Society of Toxicology and Environmental Chemistry (SETAC) (s. also UBA 1999d): greenhouse effect, ozone depletion, ozone formation, toxicity to environment and humans. The effect categories acidification, eutrophication, noise emission, emission of radioactive isotopes or stress on nature and resources were not treated in depth for fluorinated chemicals and their substitutes due to a lack of specific relevance. This can be seen in the comprehensive examination of Frischknecht (1999a and 1999b). With this background, the effect categories greenhouse effect, ozone depletion, ozone formation, toxicity to environment and humans, acidification and eutrophication are examined in order to identify specific effect categories of special relevance.

4.1 *Decomposition in the atmosphere*

With the background of the ozone hole as a result of the emission of halogenated substances, studies mainly focused on the homogenous air chemistry of substitute substances. As main paths of decomposition, reactions with tropospheric hydroxyl radicals as well as under sufficient stability also reactions with oxygen radicals ($O(^1D)$) and the photolysis in stratosphere were identified (WMO 1995, WMO 1999). In contrast to this, the decomposition of extremely persistent fluorinated substances such as CF_4 and SF_6 takes place in mesospheric regions e.g. by capture of electrons (Ravishankara et al. 1993). In detail, these mechanisms and their kinetics are highly inadequately known.

4.1.1 Main decomposition paths

It is assumed in literature that the decomposition of the less stable fluorinated GHG independent from the substance in troposphere occurs following a consistent scheme (Figure 11) differing significantly only in the distinction in end products after formation of the haloalkyl radical. As examples, the atmospheric oxidation of HFC-32 (Figure 12), HFC-134a (Figure 13) and HFC-125 (Figure 14) are discussed because the decomposition path of HFC-32 is comparably simple, because that of HFC-134a contains the branching into trifluoro acetic acid which is missing for HFC-125 despite the great similarity.

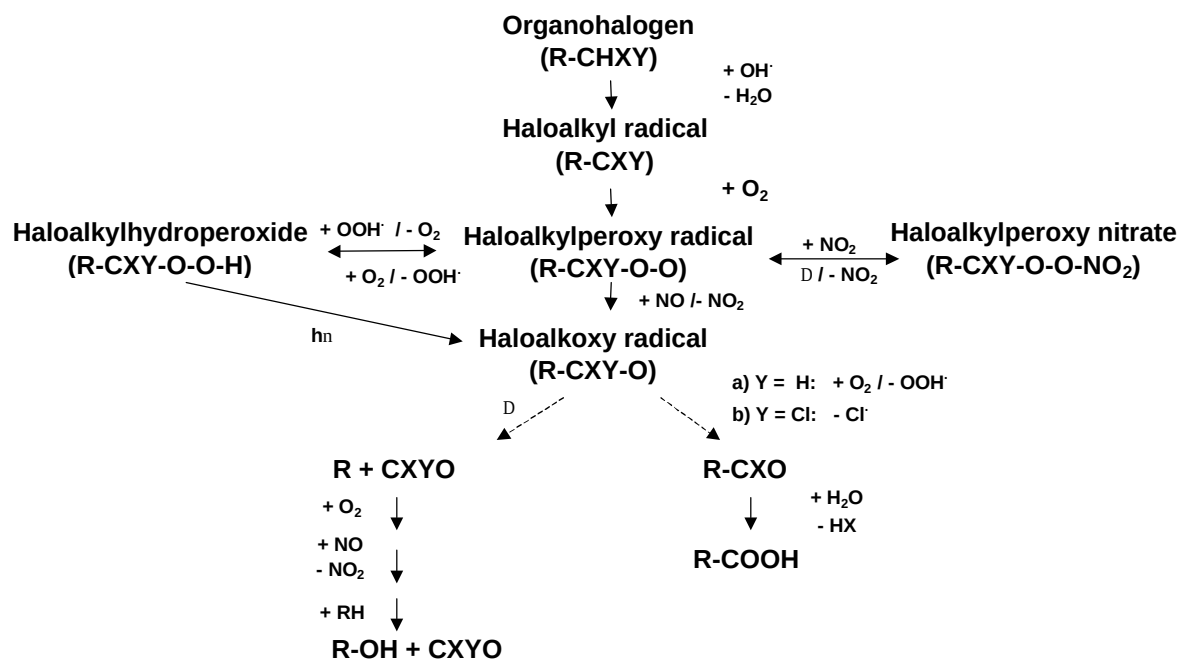


Figure 11: Schematic diagram of the decomposition path of halogenated carbohydrates in troposphere. The respective reaction partners were omitted for better clarity.

For all three reaction paths the first reaction step is similar: After a reaction of HFC with the hydroxyl radical (H-abstraction) (in the figures from first to second level), the respective alkyl radical is formed which immediately reacts with molecular oxygen further to a peroxy radical (in the figures the step from level 2 to level 3). Further decomposition can only proceed in three ways: with HO_2 (3rd level left) or NO_2 (3rd level right) to hydroperoxyde or peroxyxynitrate or by NO (from 3rd to 4th level) which can be reduced to an alkoxy radical. This is also formed in the decomposition of hydroperoxyde or peroxyxynitrate if the reverse reaction to a peroxy radical fails. This radical is highly unstable with a lifetime of <1ms. From its decomposition path results the distribution of end products. Compounds in which further hydrogen atoms are linked to the carbon atom next to an oxygen atom can stabilise by the transfer of a hydrogen atom to an oxygen molecule. If no hydrogen but a chlorine or bromine atom is linked to the carbon atom neighbouring the oxygen radical, the chlorine or bromine atoms can be split off as radicals. In this process, carbonyl compounds (aldehyde or acid halogenides) are formed. If at least a C_2 body is existent, there is a further channel towards stable decomposition products by splitting of the C-C link which competes with the reaction with oxygen or the separation of halogen radicals. In this, compounds such as CF_3OH and CF_2O in the presence of liquid water decompose into HF and CO_2 .

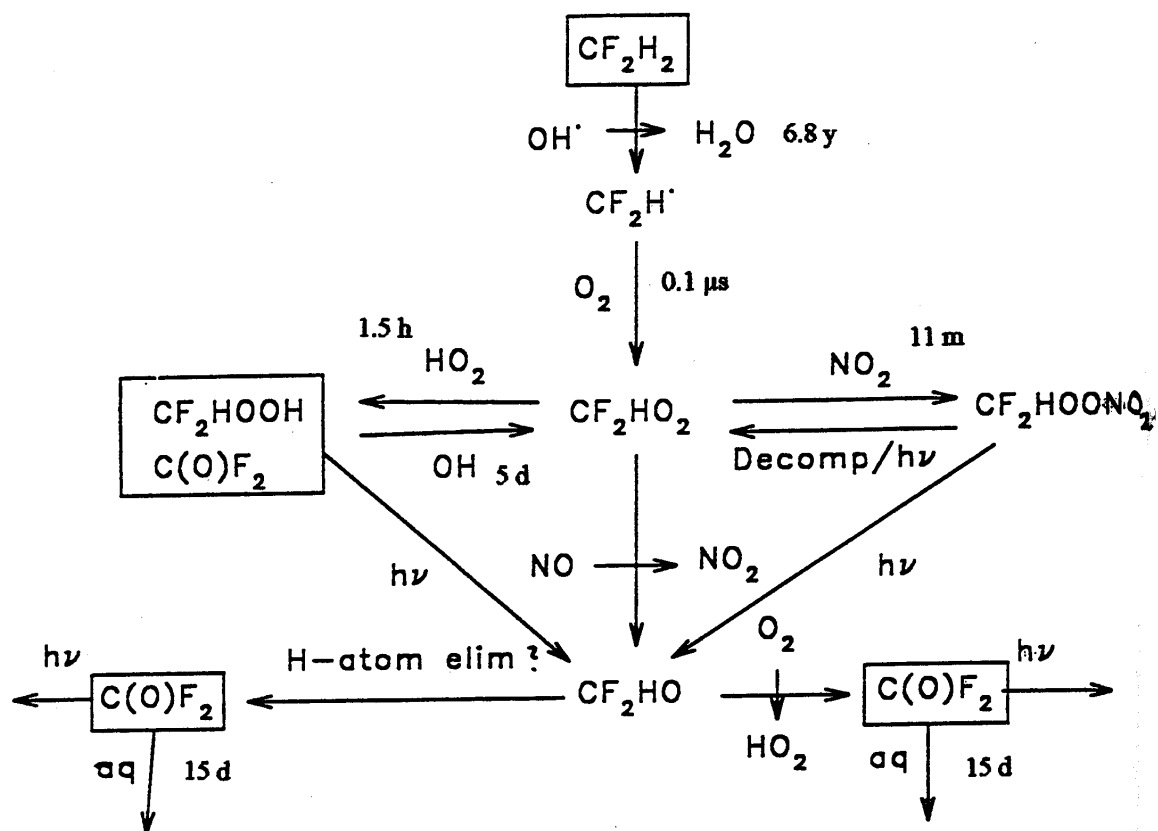


Figure 12: Overview of the decomposition paths of HFC-32 (NASA/NOAA/AFEAS 1993)

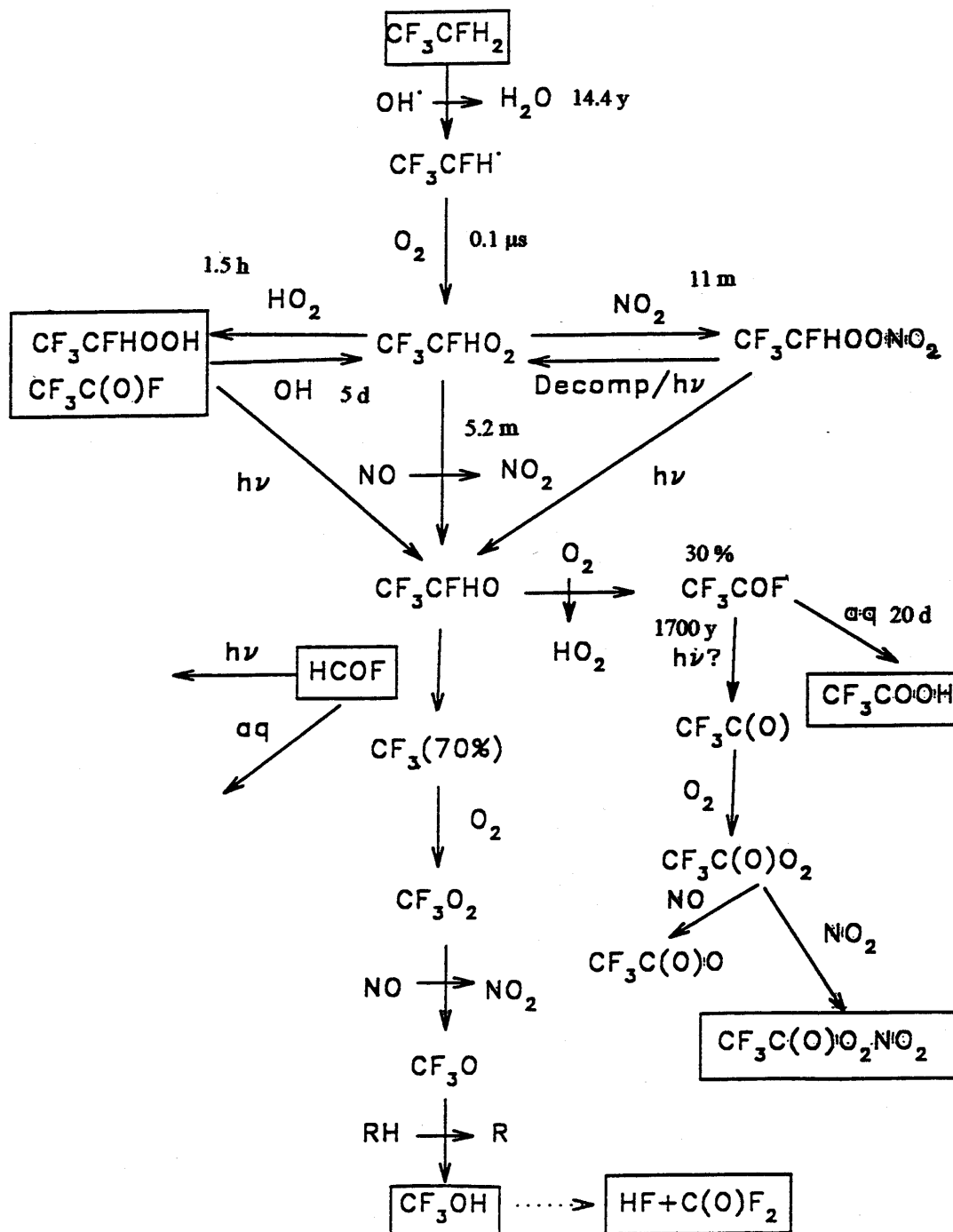


Figure 13: Overview of the decomposition paths of HFC-134a (NASA/NOAA/AFEAS 1993)

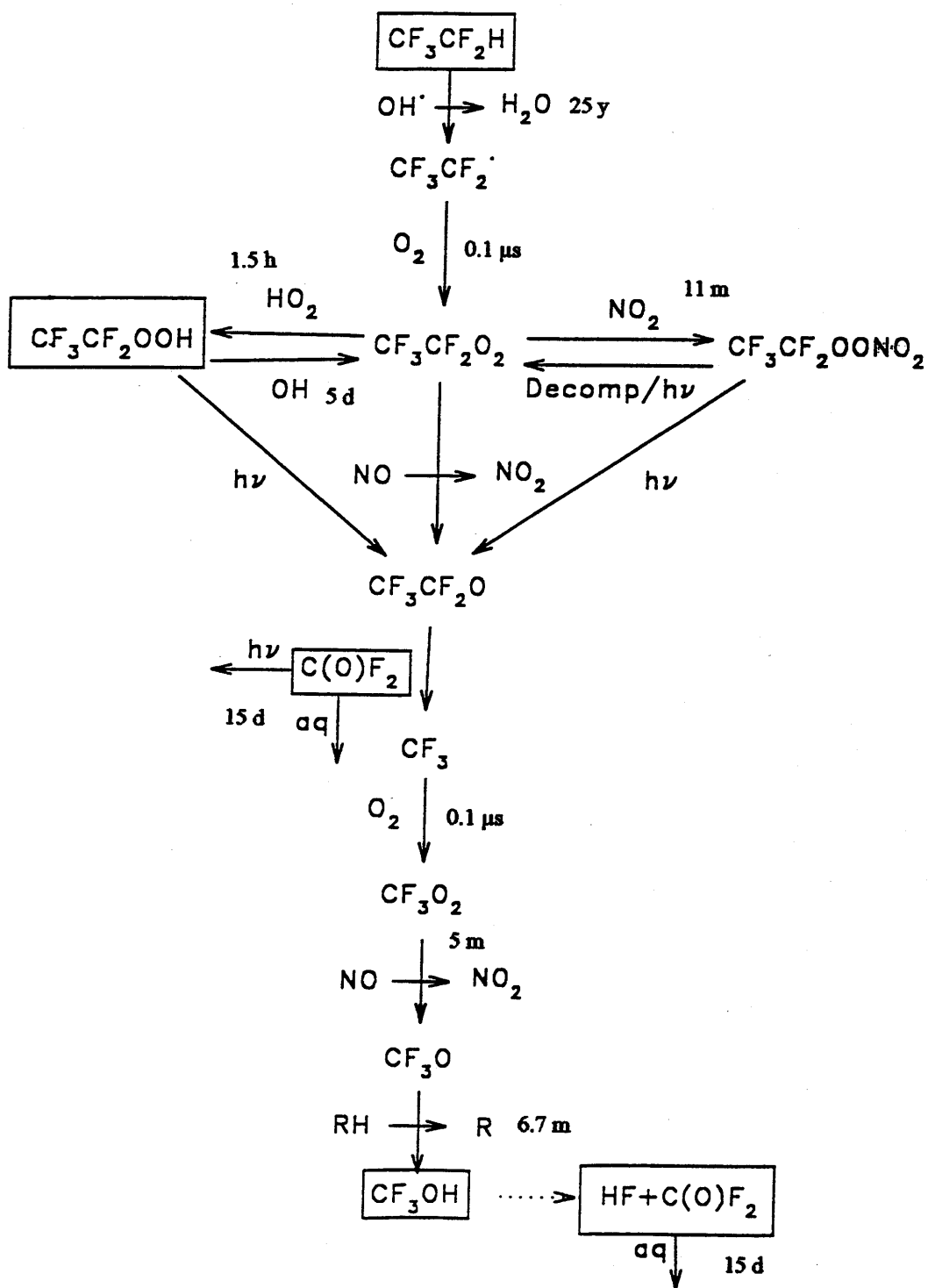


Figure 14: Overview of the decomposition paths of HFC-125 (NASA/NOAA/AFEAS 1993)

Table 10 Decomposition products of different fluorinated GHG in the atmosphere

Substance	Formula	Fluorinated decomposition products
HFC-134a	$\text{CF}_3\text{CH}_2\text{F}$	HF, CF_3COOH
HFC-365mfc	$\text{CF}_3\text{CH}_2\text{CF}_2\text{CH}_3$	HF, CF_3COOH
HFC-245fa	$\text{CF}_3\text{CH}_2\text{CHF}_2$	HF, CF_3COOH
HFC-245ca	$\text{CH}_2\text{FCF}_2\text{CHF}_2$	HF
HFC-143a	CF_3CH_3	CF_3COOH
HFC-227ea	$\text{CF}_3\text{CHF}_2\text{CF}_3$	HF, CF_3COOH
HFC-152a	CHF_2CH_3	HF
HFC-32	CH_2F_2	HF
HFC-125	CF_3CHF_2	HF
HFC-43-10mee	$\text{CF}_3\text{CHFCHFC}_2\text{F}_5$	HF, CF_3COOH
	CF_4	HF
	SF_6	HF

An overview over the main decomposition products of fluorinated GHG is given Table 10. It needs to be stressed that the reaction paths described in this section follow the main decomposition paths in the gas phase (homogenous chemistry). It can be assumed that with a low yield in the most complicated feedstock substances other products may be formed.

4.1.2 Destination of decomposition products

Assuming that the common models of atmospheric chemistry of HFC represents the decomposition of HFC essentially completely and qualitatively correctly, the only question remaining is that of the destination of the two fluorinated decomposition products hydrogen fluoride and trifluoro acetic acid (TFA).

4.1.2.1 Hydrogen fluoride and fluorides

Hydrogen fluoride and fluoride are the main decomposition products of HFC. These belong to the classical air pollutants which resulted in major damage of plants and grazing domestic animals in Germany in the past. Strict conditions for emission from the respective factories have virtually obliterated this problem in Germany. In several other countries, fluoride emissions from the combustion of inferior coal are of grave human-toxicological relevance. The global amounts of HF/F fallout which derive from HFC result in concentrations in precipitation which is five orders of magnitude below the respective thresholds for damage for plants (s. Figure 15).

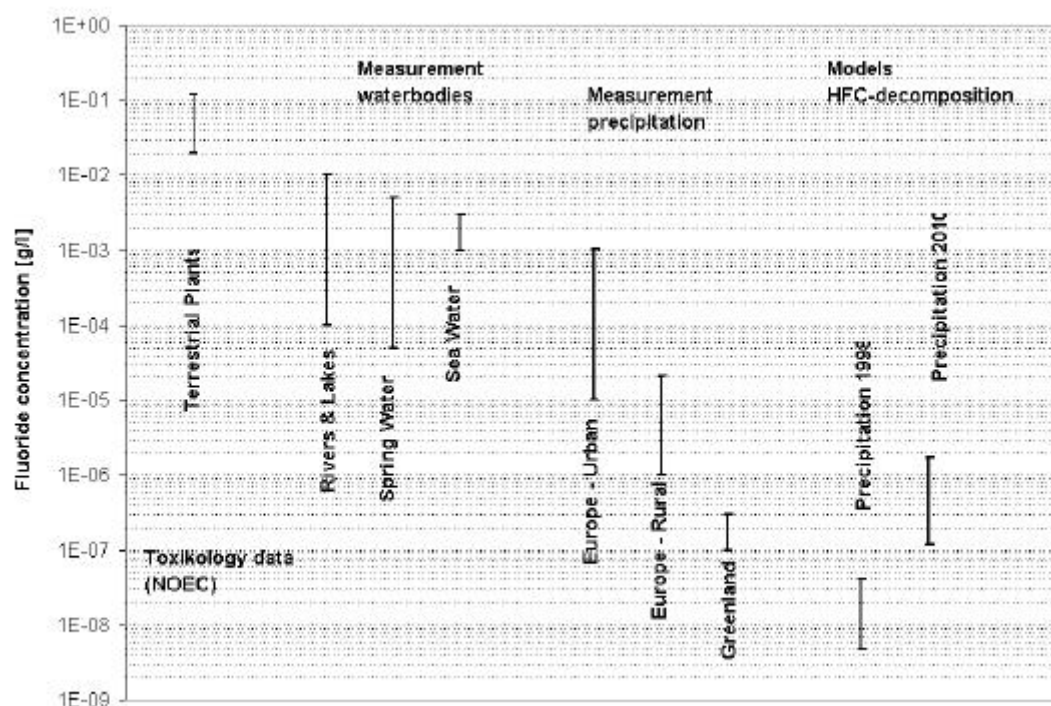


Figure 15: Schematic overview over environmental toxic effect thresholds of fluoride ions, fluoride concentrations in precipitation from the decomposition of HCFC and HFC measured in the environment and of concentrations predicted by models. Source: Allmann and Koritnig (1978); Smith and Hodge (1979)

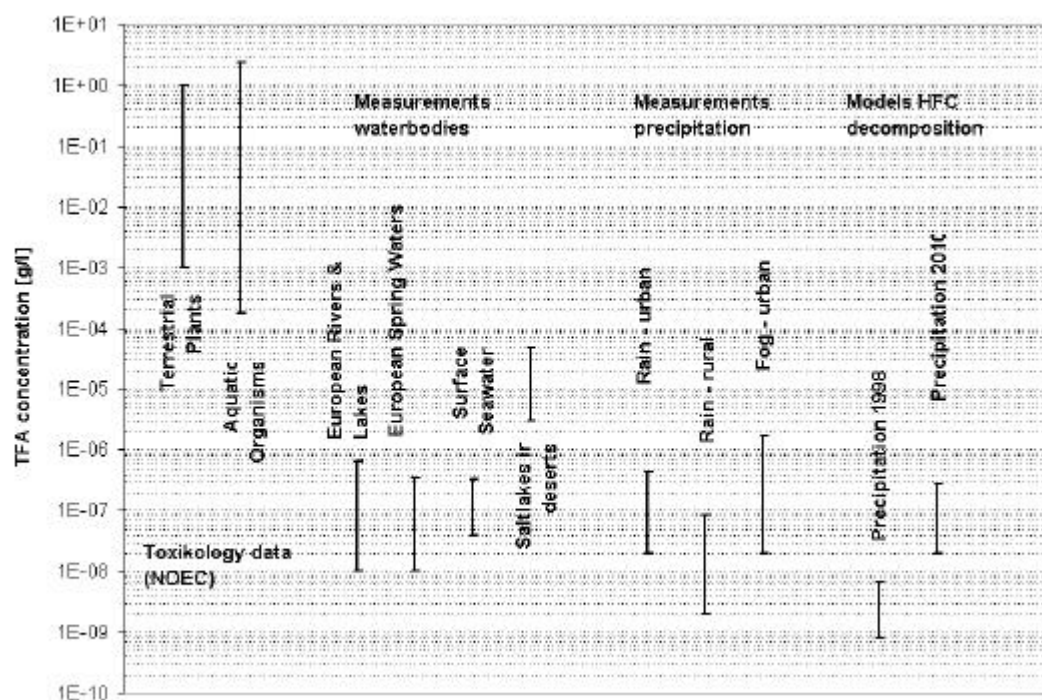


Figure 16: Schematic overview over environmental toxic effect thresholds of TFA, TFA concentrations from the decomposition of HCFC and HCFC measured in the environment in the years 1995-1998 and of concentrations predicted by models.

4.1.2.2 TFA

While geochemistry of fluorides is understood rather well for a considerable time, there are still great uncertainties with respect to the appearance and the sinks and sources of TFA. (Tromp et al. (1995), Frank et al. (1996)).

Therefore it remained controversial in literature if TFA is decomposed in organic processes or if it accumulates in the environment (e.g. Visscher et al. (1994), Emptage et al. (1997), Kim et al. (2000)). The effect of TFA on different types of organisms is rather well characterized by several studies of the 90s (e.g. Boutonnet et al. (1999)). It remains however unclear from which sources TFA that is found in precipitation and surface waters derives today. The main source of TFA according to present knowledge is the decomposition of HFC-134a with a molar yield of approx. 33%. Further TFA sources can be attributed to the decomposition of other molecules containing the CF_3 group e.g. HCFC-123 and HCFC-124 with a respective yield of 100% (Kotamathi et al., 1998). In total, the amounts of HFC and HCFC emitted so far are not sufficient to explain the TFA concentrations in precipitation and surface waters. (e.g. Frank et al. (1996), Wujcik et al. (1999), Berg et al. (2000); Römpf et al. (2001)). In Figure 16, an overview is given for the concentrations of TFA measured in aquatic samples in the years 1995 to 1998. These are compared to results of model calculations for the decomposition of HFC and HCFC and to concentrations seen as ecotoxicological harmless to different species (NOEC). It can be observed that TFA concentrations measured in the environment are several orders of magnitude below the harmless threshold of yet the most sensitive algae. However, most tested species showed resistance to high TFA exposition. (AFEAS, 1999; Wiegand et al. (2000), Benesch und Gustin (2002), Benesch et al. (2002)). High concentrations found in salt lakes are an exception- microorganisms and algae home to this environment would anyway have adaptation strategies towards higher saline concentrations.

Different anthropogenic (Jordan and Frank (1999); Ellis et al. (2001); Ellis et al. (2003)) as well as natural (Harnisch et al. (1999)) sources were suggested to explain the excess of TFA found in the environment. The findings on potential natural deposits of TFA in old firn, glacial ice and artesian water so far remained ambiguous (Sydow et al. (2000) und Nielsen et al. (2001)).

The aptitude of plants to accumulate TFA in their cells depends on a number of factors without concluding explanation (Boutonnet et al. (1999)). In experiments on agricultural plants, enrichment factors exceeding 30 were seldom found. (Boutonnet et al., 1999). Field experiments confirm these values for broad-leafed and conifer trees (Likens et al. (1997) while (Benesch und Gustin (2002)). Klein (1997) und Christof (2002) found concentrations in fir needles at several Bavarian locations showing concentrations which allow a conclusion of enrichment factors of approx. 1000. Enrichment factors in the order of 10,000-100,000 and beyond can be found for 4,4'-DDE, several PCB congeners or some toxaphenes and other so-called persistent organic pollutants (POPs) (Ballschmiter, 1996).

4.1.2.3 Other decomposition products

Comparably little information can be found on other decomposition products of HFC, such as e.g. mono- or difluoro acetic acid (Martin et al. (2000)). The same applies to reaction products with carbohydrates especially in the contaminated troposphere. It is however probable that the total yield for these products from decomposition of common HFC is rather small and that they also derive from the decomposition of other fluor-organic compounds.

It is also not clarified which products result from biogenic decomposition of TFA. If indeed CHF_3 (HFC-23) (Visscher et al., 1994) is generated, then this would deteriorate the total balance of greenhouse gas effect of the feedstock substances by its high GWP.

4.2 Effect category ,environment'

4.2.1 Greenhouse effect

A known property of many volatile fluorinated substances is their substantial ability to absorb radiation in the spectral range of the so-called ,atmospheric window' (WMO, 1995). With this, they become powerful GHG. Different measurement figures are employed today in order to compare the specific greenhouse effect of substances. The most common are radiative forcing and the global warming potential (GWP). While the first dimension relates to the change of radiation balance of the earth after increase of the atmospheric proportion of mixture by one part per billion (ppb) of a substance, the GWP needs to be calculated as a measure relative to CO₂ in view of different time horizons. With this, it considers the decomposition of a substance in the atmosphere. Equation 1 represents the related calculation rule⁶:

$$GWP_{i,n} = \frac{\int_0^n a_i \cdot c_i(t) \cdot dt}{\int_0^n a_{CO_2} \cdot c_{CO_2}(t) \cdot dt} \quad \text{Equation 1}$$

The figures for fluorinated GHG and comparison substances are summarized in Table 11. Values for the atmospheric lifetime of substances are also given there which represent the time after which their initial concentration decreased to 37% (1/e). The United Nations agreed to the use of the GWP values set by IPCC (1996) for the time horizon of 100 years within the context of the United Nation Framework Convention on Climate Change and the Kyoto protocol.

⁶ In this a_i is radiative forcing after increasing the mixing ratio of the substance i by 1 ppb, $c_i(t)$ is the remaining mixing ratio of i after the time t after the release and n is the number of years for which the integration is conducted. The denominator of the fraction contains the reference expression for CO₂ [IPCC, 1990] with a GWP value of 1 for all time horizons by definition

Table 11: Radiative forcing and global warming potential (GWP) for fluorinated GHG and comparison substances (IPCC. 2001; values for NF₃: WMO, 1999). Values valid for the Kyoto protocol are in the column ‘GWP 100 years Kyoto’ and come from IPCC (1996)⁷

	GWP 100 years KYOTO	GWP 20 years	GWP 100 years	GWP 500 years	Radiative Forcing [W/m²]	Atmospheric lifetime [a]
HFC-134a	1300	3300	1300	400	0.15	13.8
HFC-365mfc		2600	890	280	0.21	9.9
HFC-245fa		3000	950	300	0.28	7.2
HFC-227ea		5600	3500	1100	0.30	33
HFC-143a	3800	5500	4300	1600	0.13	52
HFC-152a	140	410	120	37	0.09	1.4
HFC-125	2800	5900	3400	1100	0.23	29
HFC-32	650	1800	550	170	0.09	5.0
HFC-43-10mee	1300	3700	1500	470	0.40	17.1
HFC-23	11700	9400	12000	10000	0.16	260
CF₄	6500	3900	5700	8900	0.08	50000
C₂F₆	9200	8000	11900	18000	0.26	10000
SF₆	23900	15100	22200	32400	0.52	3200
NF₃		7700	10800	13100	0.13	740
For comparison						
HFE-7100^â		1300	390	120	0.31	5
HFE-7200^â		190	55	17	0.30	0.77
N₂O	310	275	296	156	0.0031	114
CH₄	21	62	23	7	0.00037	12.0
CO₂	1	1	1	1	0.000015	

4.2.2 Stratospheric decomposition of ozone

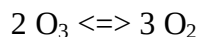
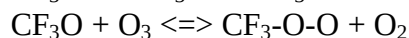
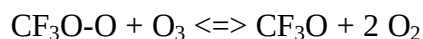
The importance of halogens for ozone chemistry drops with increasing reactivity and electronegativity from iodine, via bromine to chlorine and fluorine, i.e. it becomes increasingly difficult to crack the element from the respective compound. With the understanding of the basic mechanisms of stratospheric ozone depletion it became clear that for the protection of the ozone layer only such substances should be applied that have the following properties: On the one hand, they should mainly decompose in the troposphere already so that they would not reach stratosphere. On the other hand the use of elements iodine and bromine should be avoided completely and a carbohydrate solely with substitutes of fluorine should be preferred over mixed-halogenic compounds if in doubt. The remaining effect of such fluorinated compounds have been examined by Ko et al. (1994) and Ravishankara et al. (1994). A wider overview can be found in WMO (1995, 1999).

Focus of the examinations was the chemistry of the decomposition product of HFC CF₃ radical because of the higher stability of HF in comparison to HCl, HI, HBr.

The main elements of the reaction path of the CF₃ radical to the formation of CF₂O which decomposes to HF and CO₂ in aquatic environment are shown in Figure 17. Analogue to the decomposition path of HFC, the peroxide radical, the hydro peroxide, the peroxy nitrate of CF₃ is formed until finally resulting in an oxide radical.

⁷ The difference between the values in the Kyoto protocol and the newer data result from improved spectroscopic measurements for the atmospheric lifetimes.

In an incomplete transformation to HF and CO₂ and if CF₃ reaches the stratosphere, the following reaction cycle is critical for a decomposition of stratospheric ozone:



Equation 2

Kinetic examinations of this reaction however suggest that this catalytical ozone decomposition reaction is not of significance. (Ko et al., 1994).

The oxyde radical may again react with NO₂ to oxynitrate, with H₂O or CH₄ to alcohol. In addition to this, it can directly form FNO and COF₂, two compounds which can directly be hydrolysed, in a reaction with NO. Huey et al. (1995) as well as Lovejoy et al. (1995) have examined the destination of CF₃OH in the atmosphere with respect to the atmosphere and particles respectively.

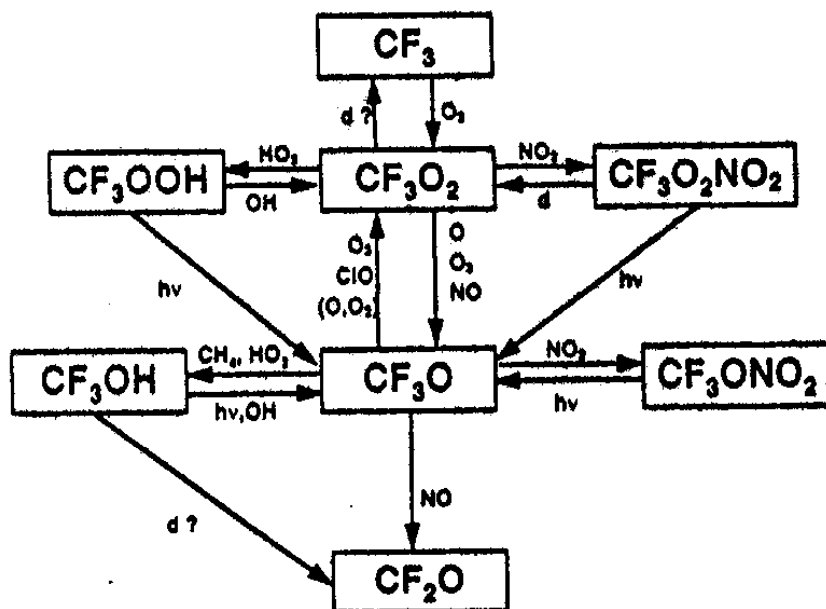


Figure 17: Overview: CF₃-chemistry according to Ko et al. (1994)

Ozone depletion potentials⁸ (ODP) of different HFC in addition to some comparison substances are given in Table 12. It becomes clear that HFCs show comparatively low ODP values.

⁸ The ODP is a value derived from model calculations representing the contribution of decomposition of stratospheric ozone caused by the emission of a substance into the atmosphere in comparison to CFC-11 (s. WMO [1995]).

Table 12: Ozone depletion potential of different HFC and comparison substances

Substance	ODP	Source
HFC-134a	<0.0005	Ravishankara et al. (1994)
HFC-23	<0.0004	Ravishankara et al. (1994)
HFC-125	<0.00003	Ravishankara et al. (1994)
For comparison		
HCFC-22	0.04-0.05	WMO (1995)
HCFC-141b	0.1	WMO (1995)
CFC-11	1.0	WMO (1995)

4.2.3 Photo-chemical formation of ozone

As described above, the most fluorinated GHG and their decomposition products participate intensively in the aero-chemical processes in the troposphere, e.g. via OH, HO₂, NO and NO₂. In situations in which NO_x is available and hydrocarbons are the limiting factor (i.e. in urban air chemistry), these contribute to the formation of tropospheric ozone. In their effect to the total system, these have a similar effect as hydrocarbons.

Table 13: Ozone formation potential (urban air chemistry) of different HFC and comparison substances

Substance	Ozone formation potential	Source
HFC-134a	0.1	Hayman & Derwent, 1997
HFC-365mfc	nicht verfügbar ⁹	-
HFC-245fa	nicht verfügbar ⁹	-
HFC-143a	<0.1	Hayman & Derwent, 1997
HFC-227ea	<0.1	Hayman & Derwent, 1997
HFC-152a	1.0	Hayman & Derwent, 1997
HFC-32	0.2	Hayman & Derwent, 1997
HFC-125	<0.1	Hayman & Derwent, 1997
For comparison:		
Ethylene	100	Hayman & Derwent, 1997
NMVOC	42	UN-ECE (1994)
Trichloroethylene	9	Hayman & Derwent, 1997
HCFC-123	0.3	Hayman & Derwent, 1997

This was quantified by Hayman and Derwent (1997) in a chemistry model for 5-day trajectories. The calculated ozone formation potentials relative to ethylene (defined as 100) are summarized in Table 13.

⁹ For further calculations, a value of 0.1 is assumed

4.2.4 Environmental toxicity

4.2.4.1 Direct toxicity

Those fluorinated GHG of commercial significance are generally rated as not harmful to the environment. This is also the case for the substitutes CO₂ and propane, but not for ammonia, n- and cyclo pentane (Table 14) which are rated as hazardous to water.

Table 14: Rating according to environmental risk (R-sentences)- claims of the manufacturers

Substance	Environmental risk
CF ₄	-
C ₂ F ₆	-
SF ₆	-
NF ₃	-
HFC-134a	-
HFC-365mfc	-
HFC-245fa	-
HFC-143a	-
HFC-227ea	-
HFC-152a	-
HFC-32	-
HFC-125	-
HFC-43-10mee	-
CO ₂	-
Ammonia	Highly poisonous to aquatic organisms (R50)
n-Pentane	Poisonous to aquatic organisms, can have adverse effects in bodies of water on long term (R51 / R53)
cyclo-Pentane	Hazardous to aquatic organisms, can have adverse effects in bodies of water on long term (R51 / R53) (R52 / R53)
Propane	-

The direct effect of HFC-134a on aquatic organisms has been studied comparably extensively (IPCS, 1998). Here it was found that the EC₅₀ thresholds for the bacteria *Pseudomonas Putida* are at 730 mg/l (48h), for *Daphnia Magna* at 980 mg/Liter (48h) and for the rainbow trout at 450 mg/l (LC₅₀: 96h). The occurrence of such high concentrations can be excluded safely under normal environmental conditions. Similar data is available from Solvay for HFC-365mfc and HFC-227ea. For the 'old substance' HFC it remains partly unclear in how far categorization for environmental toxicity is based on tests, modeling and analogue deduction of related substances.

4.2.4.2 Bio-accumulation

The potential for bio-accumulation is only of minor significance for HFC. The logarithm of the distribution coefficient between n-octanol and water as indicators for potential bio-accumulation is represented in Table 15 for a number of key substances. A value of 3 is accepted as the lower threshold for a relevant bio accumulation potential (Streit, 1991). This value is only surpassed by HFC-32.

Table 15: Logarithm of the distribution coefficient between n-octanol and water

Substance	Log Kow	Source
HFC-134a	1.06	Product data sheet Solvay
HFC-245fa	1.35	Several sources- Öko-Recherche
HFC-365mfc	1.6	Product data sheet Solvay
HFC-227ea	2.5	Several sources- Öko-Recherche
HFC-125	1.55	Several sources- Öko-Recherche
HFC-32	3.89	Several sources- Öko-Recherche
HFC-152a	1.13	Several sources- Öko-Recherche
CF ₄	2.7	Several sources- Öko-Recherche
C ₂ F ₆	2.15	Several sources- Öko-Recherche
SF ₆	0.23	Several sources- Öko-Recherche
n-Pentane	2.9	Several sources- Öko-Recherche
Propane	2.4	Several sources- Öko-Recherche
n-Butane	2.9	Several sources- Öko-Recherche

4.2.4.3 Persistence and long distance transport potential

For a characterization of the time- and space- related destination of substances independent from their effect, concepts of persistence and range (expressed as τ [years] and R [e.g. % of earth radius]) were established [Scheringer, 1999]. These model-based dimensions serve as a supplement for conventional evaluation methods in the exposition- and effect analysis.

Persistence τ here is defined as:

$$t = \frac{1}{M_0} \int_0^{\infty} M(t) dt \quad \text{Equation 3}$$

with M_0 as the released amount of substance at the time $t=0$ and $M(t)$ as the amount of substance remaining in the environment at the time t .

The range R is however a measure for the scope of the spatial distribution of a substance in the environment. The calculation method for this is presently determined depending on the fundamental characteristics of the distribution [Schlesinger, 1999]. A definition adaptable to several situations is the distance to the source within which 95 % of the substance can be found in a state of equilibrium. Further sources, asymmetrical distribution as well as multiple dimensions require adaptation of the concept.

There are equivalent transitions from one definition of persistence and atmospheric lifetime into another as soon as the decomposition of a substance –as in the case of fluorinated GHG- occurs almost exclusively in air as fluid. Hence, the figures shown in Table 11 are valid for persistence.

The range as a measure for remote transport potential of a substance can in this case be estimated without modeling as 0,95 earth radius for all HFC (including HFC-152a) since an almost homogenous mixing in the lower atmosphere can be assumed under persistence and at a lifetime greater 1.5 years.

With these figures the property couple persistence and range of fluorinated GHG is strong in comparison to most other environmental chemicals- similar to perfluorosulfonates proven in marine food chains (s. Kennan et al. [2001a, 2001b]).

4.2.5 Acidification

In Table 16 an overview of the acidification potential of common HFC (via the decomposition products HF and TFA) as well as for ammonia and NO₂ is given. The key figures for the chemicals examined are near the reference value 1 for SO₂. HFC contribute to acidification worldwide comparably evenly and therefore differ from classical air pollutants such as SO₂ and NO_x with regional effect.

Table 16: Acidification potential (as kg SO₂-equivalent per kg of substance) (Frischknecht, 1999b)

Substance	Acidification potential as kg SO ₂ -equivalent per kg of substance
HFC-134a	0.96
HFC-152a	0.97
HFC-32	1.21
HFC-125	1.35
HFC-365mfc	Not available ¹⁰
HFC-245fa	Not available ¹⁰
HCFC-22	1.11
HCFC-141b	0.82
HCFC-142b	0.95
Ammonia	1.88
Nitrous oxide as NO ₂	0.77

4.2.6 Eutrophication

Fluorinated GHG do not contribute directly to eutrophication of waters and soil. This is valid also for carbohydrates and CO₂. Only ammonia as a substitute for fluorinated GHG displays a significant eutrophication potential of 0.33 phosphate equivalents.

4.2.7 Use of nature space, noise and emission of radioactive isotopes

In concerned literature (Frischknecht, 1999a und 1999b), there are no signs that the production of fluorinated GHG (e.g. by decomposition of fluoride or rock salt or for the mining of fuels for electricity generation) or of their substitutes contribute to the use of nature space, noise generation and emission of radioactive isotopes more than the level common to chemical industry. For this reason and also because of lacking data on these effect categories and missing measuring dimensions, we refrain from an in-depth treatment.

4.3 Effect categories ,man'

Main reason for the widespread application of fluorinated substances on the one hand is their inflammability or greatly reduced flammability in comparison to the homologue hydrocarbons as well as their generally low human toxicity on the other hand. Both properties were naturally

¹⁰ For calculations further below, a value of 1.1 is assumed.

stronger in completely halogenated CFC than in the partly halogenated HFC. Both aspects are discussed in the following.

4.3.1 Toxicity to humans

As can be seen from Table 17, commercially relevant fluorinated carbohydrates display significant human toxicity only in very high concentrations resulting in the fact that classifications into R-sentences were made for no fluorinated GHG except for NF₃ (s. Table 18). This applies also to the substitutes CO₂, propane, cyclo-propane, but not to ammonia and n-pentane.

Table 17: Data on acute inhalation toxicity¹¹ of HFC, HCFC and alternative substances

	Acute toxicity ¹²	Inhalation Source
HFC-134a	>50 %	Daikin / Honeywell
HFC-365mfc	>10 %	Solvay
HFC-245fa	>20 %	Honeywell
HFC-143a	>54 %	Daikin
HFC-227ea	>11 %	Solvay
HFC-152a	>6.4 %	Daikin
HFC-32	> 76 %	Daikin
HFC-125	> 80 %	Daikin
HFC-43-10mee	>11.1%	3M
C ₅ F ₁₂	>30 %	3M
NF ₃	>0.7%	Air Liquide
For comparison:		
HCFC-123	3.2%	Daikin
HCFC-141b	6.2 %	Daikin / Honeywell
HFE-7100®	>10%	3M
HFE-7200®	>9.2%	3M
CO ₂	>12% ¹³	Unister
n-pentane	>8.8%	BOC
Ammonia	>0.5%	Potash Corporation

In-depth examinations of toxicological behavior are available mainly for HCFC 123 (Dekant, 1996) and HFC-134a (Dekant, 1996; IPCS, 1998). While most of the toxicological tests for HFC-134a had negative results, an increase of benign testicle tumors in rats under chronical exposition with 50 000 ppm was observed, which may be attributable to an interaction of the substance or its metabolites with the hormonal disposition (Collins et al., 1995; Dekant, 1996). A directly toxic effect on such tissue has been proven for trifluoro-acetaldehyde (CF₃CHO), which may possibly be a metabolite of HFC-134a (Lloyd et al., 1988; Dekant, 1996). An increased sensitivity of the heart was only established under very high concentrations of HFC-134a in respiratory air (IPCS, 1998).

¹¹ No liability for correctness and completeness of this data is accepted

¹² The acute inhalation toxicity is determined with a rat population. The threshold value represents concentrations in respiratory air under which 50% of the population die within 24 hrs after 4 hrs of exposition. For LC50 values greater 50%, the oxygen content of the air is increased to avoid suffocation of the test animals which normally occurs below oxygen concentrations of 10%.

¹³ Different: fatal concentration for humans

The limitations of standard tests on different acute and chronic dimensions of human toxicity normally based on animal tests will not be treated here. Many long-term risks from chemicals such as mutagenity and carcinogenity (especially in conjunction with other chemicals or factors) are frequently identified long after successful testing of the substance evaluation. Although these risks cannot be excluded for newly tested HFCs, these show a benign profile in comparison to many chemicals applied in the occupational environment.

Table 18: Classification¹⁴ according to human toxicity into R-sentences for work protection-manufacturer claims

Substance	Human toxicity
CF ₄	-
C ₂ F ₆	-
SF ₆	-
NF ₃	Health risk if inhaled (R20)
HFC-134a	-
HFC-365mfc	-
HFC-245fa	-
HFC-143a	-
HFC-227ea	-
HFC-152a	-
HFC-32	-
HFC-125	-
HFC-43-10mee	-
For comparison:	
CO ₂	-
Ammonia	Poisonous if inhaled (R23)
n-pentane	Health risk: may cause lung injuries if swallowed (R65)
cyclo-pentane	-
Propane	-

4.3.2 Flammability

Table 19 gives an overview over the explosion concentration threshold of different chemicals in air. According to this, four of the eight commercially relevant HFC are flammable. They can nevertheless be used in blends with other HFCs which would then be inflammable. Manufacturers emphasize the much higher ignition energy at similar flammability thresholds than common for carbohydrates.

¹⁴ No liability for correctness and completeness of this data is accepted

Table 19: Overview over flammability data¹⁵ for different fluids

	Lower explosion threshold in air [%]	High explosion threshold in air [%]	Source
HFC-134a	-	-	Solvay
HFC-365mfc	3.5	9	Solvay
HFC-245fa	-	-	Honeywell
HFC-143a	7.1	16.1	Solvay
HFC-227ea	-	-	Solvay
HFC-152a	3.8	21.5	Solvay
HFC-32	13.6	28.4	Daikin
HFC-125	-	-	Solvay
HFC-43-10mee	-	-	3M
For comparison:			
HCFC-141b	7.6	17.7	Honeywell
HFE-7100®	-	-	3M
HFE-7200®	2.4	12.8	3M
c-Pentane	1.4	9.4	Honeywell
n-Pentane	1.3	8.0	Honeywell
Ammonia	15	30	Praxair

4.4 Data availability

Part of the fluorinated GHG treated here (e.g.. HFC-365mfc, 245fa, 43-10mee) passed the extensive risk assessment procedure within the framework of the EU-directive 93/67/EC. Despite the thresholds given in section 2 derived from a comprehensive substance evaluation, HFCs can be characterized as well-examined. The other part of HFC fall into the category ‘old substances’ which were on the market before the directive came into force and therefore never passed a standardized risk assessment process. Because of high sensitivity in view of danger for man and environment, these substances were considered in different examinations and evaluations in view of their intrinsic properties. A well-founded evaluation on how reliable and robust these examinations are in all detail aspects would exceed the objective of this study. Since no evident contradictions and gaps in the examinations can be determined between the sources used, it appears permissible to assume a generally sufficient state of knowledge for the most important intrinsic substance properties. Until old substances have passed a comprehensive and standardized evaluation procedure, a certain uncertainty factor should be considered. This is especially valid if analogue conclusions are drawn for related substances since there are partly significant deviations within the group.

4.5 Specific contributions

The concept of specific contributions [UBA, 1999d] may assist in the establishment of a focal point in the examination of environmental impacts of applications in the different effect categories. In these, the dimension of the quantitative contribution of the application measured in a suitable metric and related to a certain region to the total environmental effect caused by other anthropogenic sources. Within the framework of this study, this estimation was made in summary for all applications of fluorinated GHG (s. section 3) in relation to Germany and with a worldwide perspective. It was assumed that alternatives in a complete substitution cover 50% of emitted mass

¹⁵ No liability for correctness and completeness of this data is accepted

of fluorinated GHG due to their low density and that carbohydrates dominate with 70%, followed by 10% CO₂, 10% ammonia and 10% water and air. The annual reference amounts on the emissions of fluorinated GHG as well as their substitutes are estimated weighted amounts based on statistical data from IPCC, UNEP as well as from the Federal Ministry for Environment and the Federal Environmental Agency of Germany.

Table 20: Estimated specific contribution of emissions 2010 in different effect categories

	Reference unit	Reference region	HFC	Alternatives (at 100% substitution)	Assumed annual reference amount
GWP	GWP100 [CO ₂ eq.]	World	2 %	0.003 %	33 GT CO ₂ – equivalent
ODP	ODP [CFC-11 eq.]	World	0.1%	< 0.02%	0.13 MT FCKW-11-equivalent
Ozone formation potential	Ozone formation potential [Ethylene-eq]	Germany	0.002%	0.3%	0.84 MT Ethylene-equivalent
Acidification potential	SO ₂ -equivalent	Germany	0.3 %	0.03%	4.6 MT SO ₂ -equivalent (SO ₂ & NO _x)
Eutrophication (atmospheric route)	Phosphate-equivalent	Germany	<0.01 %	0.1 %	0.2 MT Phosphate-equivalent

The results are represented in Table 20. It can be observed that the specific contribution of fluorinated GHG in the category GWP at 2% is notably higher than all other effect categories. Next to follow are fluorinated GHG with 0.3% contribution to acidification and substitutes with 0.3% contribution to ozone formation.

For the other effect categories, which cannot be quantified for their specific contribution due to methodological gaps, the following can be concluded:

Environmental toxicity: A direct toxic effect on aquatic indicator organisms of examined fluorinated GHG has been established only for very high concentrations. Bioaccumulation potential is only moderate. According to present state of knowledge, fluorinated GHG can be categorized as minor problematic substances with respect to environmental toxicity.

Persistence: Fluorinated substances examined here are very persistent. Several of the substances display lifetimes in the environment of several thousands of years. This finding needs to be classified as problematic in view of a precautionary chemical policy.

Decomposition products: Only two stable fluorinated decomposition products of fluorinated GHG are mentioned in literature: tri-fluoride acetic acid (TFA) and hydrofluoride (HF) (with their respective anions (TFA⁻ und F⁻). Concentrations in precipitation expected for 2010 from decomposition of HFC are however several orders of magnitude smaller than potential damage

thresholds even for more sensitive organisms. As a matter of fact, concentrations in precipitation in urban regions already are comparably high.

Flammability: A part of the commercially relevant fluorinated GHG is flammable. In blends of several substances (mostly HFC), this property may be eliminated while producing the desired thermodynamical properties.

Human toxicity: HFC can be considered as substances with little human toxicological concern according to present state of knowledge. Acute toxicity exists only for very high concentrations. Under continuously very high concentrations of HFC-134a, rats developed an increased rate of testicle tumour, which is assumed to be a result of a change in hormonal disposition. The relevance of this finding is presently under debate.

In conclusion, the high GWP as well as their persistence and great range should be emphasized as problematic intrinsic substance properties of the fluorinated substances treated here.

4.6 Outlook to application examples

This section showed that the specific contribution of fluorinated GHG to the greenhouse effect clearly dominates the spectrum of ecological effect categories. Therefore, the following two sections will treat selected application examples in view of their contribution to the greenhouse effect. This procedure relates to the method of Lifecycle Climate Performance (LCCP) commonly applied in international literature focused on the comparative evaluation of different technological alternatives under consideration of their emissions during their life cycle (production, use and disposal). Application examples were chosen in such a way that they cover an example relevant for Europe and emissions with unique technical properties. Transfer to neighbouring applications was not a primary criterion for this, but will be discussed in the sections.

5 Application A- PU rigid foam

5.1 Introduction on the insulation properties of different blowing agents

Two typical applications for PU rigid foam are roof insulation panels (nailed onto beams under tilted roofs) as well as for the insulation of refrigerated vehicles. In the first application, differences of foam thickness in the range of millimetres for the compensation of higher thermal conductivity (λ -values) are not problematic. This is different for the application in refrigerated vehicles, where the foam is normally blown with c-pentane (frequently in blends with n-pentane) in Germany. In refrigerated vehicles there is only little play to compensate increased thermal conductivity with thicker insulation walls.

In both cases the effects of a substitution of the hydrocarbons n-pentane/i-pentane with HFC-365mfc is examined.

The insulation effect of PU rigid foam at a given thickness is higher with lower thermal conductivity λ of the blowing agent encapsulated in the foam cells. The λ -values of gases rise in steps of 1.5 mW/mK following the order CFC-11, HCFC-141b, c-pentane, n-pentane: From 8.5 via 10.1 to 12.4 and finally to 14 (at 25°C, Source: Bayer 2000). The λ -value of the foam product is not only determined by the physical blowing agent but also by the higher λ of CO₂ formed in the reaction of polyol with isocyanate, heat transfer through the foam matrix and IR-radiation exchange between the cell walls. In all these processes, the influence of aging of the foam also needs to be taken into consideration, which is normally done in form of a calculation factor.

Typical λ values of such rigid foam in so far as it is laminated diffusion-proof are 21 mW/mK for HCFC-141b, 23 for c-pentane and 24 for n-pentane.

According to the manufacturer Solvay, the λ -value of the new blowing agent HFC-365mfc in gaseous state of 10.6 mW/mK ranges between HCFC-141b and c-pentane. This applies also to HFC-245fa. The foam product then typically displays a λ of approx. 22 mW/mK. Several users and producers of raw materials were able to find differences between the λ values of foam products with n-pentane(λ : 14), but not with c-pentane.

In the following table (Table 21) compares PU foam with HFC-365mfc (λ =22) as blowing agent with PU foam produced with the blowing agents c-pentane (λ =23) and n-pentane(λ =24)¹⁶. There will be no further comparisons with HCFC-141b since this substance is banned in the EU as of 2003.

Table 21: Applied λ -values for different blowing agents in PU rigid foam (mW/mK)

HCFC-141b	HFC-365mfc	c-pentane	c-/i-pentane	n-pentane
21	22	23	>23	24

¹⁶ In the categorisation according to German as well as future EU standard, (s. Bayer 2001), measurement values as far as they are between two integers are rounded up to the next integer. 23.15 of foam with c/i-pentane used in this study would then become 24.

5.2 PU foam roof insulation panels with n-pentane and HFC-365mfc

5.2.1 A remark on the disposal

Insulation foams are presently of minor importance in the disposal industry. In the future however, more and more insulation materials from the building sector will need to be disposed of in large quantities. A typical density for insulation material is approx. 30 kg/m³ thus having only a very small mass component. The volume is of greater importance to the disposal industry. Starting on the basis of the German energy saving ordinance (Energieeinsparverordnung (EnEV, 2001)) approx. 30 million m³ of insulation material will be used per annum in the building sector which will need to be disposed of some 50 years later. Comparing these amounts with the present waste flow of 30-45 million t/a from the building sector, such amounts are of minor importance. But in terms of volume, this amount will represent 50% of future waste flows.

Insulation materials may be disposed of in any of the following ways:

- land filling
- combustion in waste incinerators
- recycling

According to the new German ,ordinance on the environmentally adequate disposal of municipal waste and biological treatment systems' (TA Siedlungsabfall), the land filling of organic material will not be possible in future. Since insulation material is difficult to compress, a future deposition would also compromise a minimisation of landfill volume.

A disposal in waste incinerators is possible, but there are no experiences with the incineration of large shares of insulation materials so far. On the one hand, organic insulation materials do have a high calorific value, on the other hand the low density makes handling on incineration grates difficult. The incineration behaviour is significantly different from all other waste fractions presently dominating and the effect of flame retardant agents is yet unclear.

The following points need to be considered in the analysis of the disposal of insulation materials:

1. Recycling of organic insulation materials is technically possible in different forms. It remains however debatable if this can be applied to insulation materials with long circulation time from the building sector: the great innovation dynamics in insulation materials make re-application of old material questionable. A closed loop recycling cannot be imagined.
2. There are no applications for recycling products from open loop recycling of insulation material.
3. Several different insulation materials are being applied in parallel.
4. Old insulation materials are highly contaminated. Insulation materials are stuck together with (mineral) adhesive. Cleaning can only be realised under high specific cost in relation to volume.
5. The low density leads to high specific transportation cost so that centralised recycling systems are uneconomical

The application of insulation materials in the building sector makes sense but will create a large waste volume in the future. Deposition and recycling do not seem sensible. Due to the high waste volume of insulation material, volumetric input to waste incinerators will change. It can be anticipated that the high transportation cost will be compensated by prior compression of the

foams with subsequent release of blowing agent. This would need to be considered in model calculations.

5.2.2 Modelling of the system: Aluminium-coated PU insulation panel as a reference system

Approx. 35% of the German inland consumption of 65 000 t PU rigid foam for insulation purpose (excluding foam for electrical appliances and installation) ends in foam panels. According to the two market leaders Puren and Bauder (together ca. 2/3 of the German inland market share), the most important application is the insulation of tilted roofs followed by insulation of walls, ceilings or floors etc.

Therefore, a comparison of heat losses through a roof insulated with PU foam and emissions of the foam production have been chosen as the basis for this application example. Only the heat flux through a tilted roof insulated with PU insulation panels will be balanced, not a complete building. Next to the PU foam as decisive component of the insulation, other roof components will be considered. The reference unit is always 1 m² of roof.

For insulation of tilted roofs in (new and existing) residential buildings, PU rigid foam panels are increasingly applied. In the total of the German insulation material market, PU-insulation only has a share of 6% far behind mineral wool and expanded polystyrene (XPS) (Leisewitz/Schwarz 2000). In contrast to this, PU rigid foam has an over proportional share in high performance insulation on rafters (almost without thermal bridges), especially since the desired insulation effect can be achieved with panels of a thickness below 14cm which can be nailed onto common rafters without complication. (Insulation between rafters is dominated by mineral wool)

In terms of most applied, the standard for PU roof panels is marked by panels coated with aluminum foil on both sides and with a raw density of 32 kg/m³ (30 kg/m³ is the required minimum) and a thickness of 105 mm. Other than in the application for refrigerated vehicles, the panels need to be treated with flame retardant agent with in the application for residential buildings (fire protection class B2).

The conversion to n-pentane started in 1995 already, directly from CFC-11 to the flammable hydrocarbon without the transition via HCFC-141b. Because of the heat transfer capability groups (WLG) for λ in steps of five valid in Germany, the common WLG 25 classification (ranging from $\lambda=0.019$ to 0.024 W/mK) could be kept without having to increase the thickness of the panel (105 mm). The insulation effect per square meter (u-value) has however theoretically decreased by 14% under the use of n-pentane. The forthcoming EU-standardization (s. Bayer, 2001) classifying the heat transfer value λ in steps of one will terminate the common classification. By the time the standard will come into effect, the blowing agent HCFC-141b will not be allowed any longer. On the other hand, there would only be HFC-365mfc available on the market with a λ which is 1 mW/mK higher.

5.2.3 Start data for analysis of the roof insulation panel

1. Formulation: Blowing agent and flame retardant

Typical formulations for the production of standard building insulation panels are presented in Table 22. Those for n-pentane are empirically better tried and proven. The formulation with HFC-365mfc is similar to that with HCFC-141b but the lower polarity and resulting lower matrix solubility of 365mfc compared to 141b important for the determination of amounts (Solvay 2001) needs to be taken into consideration.

Table 22: Average values of the framework formulations for PU panel foam with a density of 30-33 kg/m³ for the insulation of tilted roofs in weight proportions

	Formulation with n-pentane	Formulation with 365mfc
Isocyanate	240	240
Polyol	100	100
Water	1	1
Additives	5	5
Flame retardants	12	11
Blowing agent	19	50 ¹⁷
Total	377	407

The amount of blowing agent in common foams with n-pentane comes to 5% while the weight proportion of HFC-365mfc is considerably higher with 12%.

One: For blowing of the reactive PU formulation the same amount of blowing agent in gaseous form per m³ of foam is needed in both cases. Since weights of gas volumes relate equivalent to their molar masses, twice the mass of HFC-365mfc (MG: 148) than of n-pentane (MG: 72) needs to be used. Second: With the higher polarity of HFC-365mfc compared to (non-polar) n-pentane approx. 20 to 30% of the blowing agent dissolve in the foam matrix. To supply sufficient gas for formation of cells, an additional dose is required to compensate this effect.

An important issue for insulation foam for the building sector is the fact that it needs to contain flame retardant to comply with the criteria of building material class 2. Addition of flame retardants (tris(chlorisopropyl)phosphate and/or triethylphosphate) needs to be slightly higher in the case of n-pentane than in the case of the use of less flammable HFC-365mfc as blowing agent: 12 parts compared to 11 parts. Quantities of flame retardants are generally related to the amount of flammable substance (fire load) (Demharter 2002). In case of HFC-365mfc these are isocyanate, polyol, additives (cell stabilizers, activators), For n-pentane, the blowing agent needs to be added to the amount of flammable substance so that the addition of flame retardant needs to be increased slightly.

Since HFC-365mfc is not inflammable but only less flammable than pentane, it is not clear whether the content of flame retardant in the foam can be reduced at all. This study will not treat the subject of flame retardants further.

¹⁷ Potentially formulations with lower HFC-365mfc content may achieve greater importance in practice due to the higher price for the blowing agent (R. Albach (Bayer Polymers, August 2003). Insulation values would then develop towards systems with pentane as blowing agent.

2. Production of foam panels and loss of blowing agent

PU insulation panels coated with flexible aluminium foil are produced in a continuous process on double transport systems. These consist of two conveyor belts installed facing each other vertically with a distance that is adjusted to the thickness of the foam panels.

Blowing process

Aluminium foil is spun off bobbins and conducted into the gap between the conveyor belts. The reactive formula is applied to the lower foil and directed between the two approx. 10 m long belts during the blowing process. At the end of the belts, the panel comes out cured and coated and is cut into desired length after passing the cooling section. A side partition avoids the escape of foam. Manufacturers estimate losses of blowing agent to be 3-4% of the applied amount. For further calculations in this study, an average of 3.5% is assumed.

Processing

The resulting panels are straightened along the edges and tongue and groove are cut. This results in loss of gaseous blowing agent from opening of cells. Cut fragments and sawdust also emit blowing agent. Fragments are ground at the manufacturer and used with the sawdust-containing waste to produce pressed panels. The loss caused by processing is estimated to be between 3 and 4% (average 3.5%).

Installation

Optimised cutting of the panels in the installation on the roof may reduce waste, but will not bring waste to zero since certain waste cuttings always arise at the edges or around the chimney. Waste cuttings are estimated to be in the order of 1% by the manufacturer. This waste is normally disposed of in building or household waste at the building site.

Use phase

Annual diffusion losses of blowing agent are assumed to be 0.2% according to claims of manufacturers (Demharter, 2002; Ehret, 2002) although higher values are mentioned in specialised literature (AFEAS 2000: 0.5 %/a; IPCC 1999: 0.5 %/a).

3. Disposal of insulation panel at end of life: 80% retention of blowing agent

On the fundamental problem of disposal of insulation materials, please refer to section 5.2.1 above. In particular, the following is valid: As long as buildings erected today are planned to be destroyed with a wrecking ball instead of being dismantled, it is technically very complex to dispose of old insulation foam separately and bring it to incineration (and is therefore not applied in practice). In a residential building of average dimensions, the PU foam insulation of a tilted roof sums up to approx. 10 to 15 m³ or 300 to 450 kg. Compared to the total amount of construction waste, this is a comparably small amount- equivalent to e.g. an organic flooring.

Substance recycling of dismantled old roof insulation panels is hardly possible because of dampness. Dry foam can be recycled to pressed panels as described above for homogenous dry new production waste. Such panels only recycle the PU material, but not the blowing agent (Demharter 2002).

The disposal path of old roof insulation panels so far is the building waste landfill. With the new German 'ordinance on the environmentally adequate disposal of municipal waste and biological treatment systems' (TA Siedlungsabfall), this option to landfill the untreated organic waste disappears. PU insulation panels are likely to become part of the 'mixed building waste' which needs to be separated from inorganic building waste. This organic component is then burned in waste incinerators thus destroying residual blowing agent contained in the old foam.

However, it needs to be taken into account that a share of the blowing agent in roof insulation panels is released in the process of building demolition. In the following analysis, it is assumed that 20% is released during demolition and 80% (equivalent to 82% of the initial amount) are destroyed by incineration of the old foam. 80% can be seen as an optimistic figure.

4. Loss of blowing agent over the lifetime

Table 23 gives the values applied for the calculation of the GHG balance for PU insulation panels used in tilted roofs. Under favourable conditions, one third (calculated 34.4%) of the originally used blowing agent is released into the atmosphere untreatedly.

Table 23: PU roof insulation panel: loss of blowing agent in different phases of the life cycle in % on the amount used for production

Loss in 1st year		Use phase emission		Disposal losses 20% of remains	
Blowing	3.5	Diffusion per year	0.2	Loss in demolition	16.4
Processing	3.5				
Installation	1.0				
Total	8.0	Total*	10.0	Total	16.4

Total loss over the whole life cycle: 34.4

* A use phase of 50 years was assumed.

Sources: Puren 2002, Bauder 2002.

5. Insulation properties: heat transfer coefficient (u-value):

The u-value, decisive for the compensation heating energy demand of a square meter of roof surface insulated with 10.5 cm PU foam is in the case of n-pentane ($\lambda=24$ mW/mK) 0,214 W/m²K and in the case of HFC-365mfc ($\lambda=22$ mW/mK) 0,197 W/m²K.

$$u - value = \frac{1}{\left(\sum_{n=1}^n \frac{d_n}{l_n}\right)} \quad \text{Equation 4}$$

u-value: heat conductivity coefficient

d_n : thickness of layer n

λ_n : λ -value of layer n

For the insulated tilted roof examined here, the u-value is calculated to:

$$u - value_{roof} = \frac{1}{\left(0,17 \frac{m^2 K}{W} + \frac{d_{roof}}{l_{roof}} + \frac{d_{insulation}}{l_{insulation}} + \frac{0,02}{0,7} \frac{m^2 K}{W}\right)} \quad \text{Equation 5}$$

The following components are taken into account:

Addend 1: heat transfer coefficient

Addend 2: tilted roof with a wood layer of 2cm thickness with $d_{\text{roof}} = 2 \text{ cm}$, $\lambda_{\text{roof}} = 0,2 \text{ W/(m}\cdot\text{K)}$

Addend 3: Insulation with a standard thickness of 10.5 cm and λ -values of 24 W/(m·K) for insulation panels with n-pentane and 22 W/(m·K) for insulation panels with 365mfc

Addend 4: plaster

6. Heating system: transmission losses, system efficiencies and degree-hours

The heating system compensates the transmission and heat losses through the tilted roof. For this, basic assumptions for the fuel used, the heating system and the number of heating hours were made. For the heating degree hours, 66 khK/a are assumed in the standard case. The heating system consists of a gas-condensing boiler with window ventilation based on DIN-V 4701-10 and DIN-V 4108-6 with a reduced value for heating degree days.

The end energy demand can be derived as follows:

$$q_{\text{roof}} = \text{HzSt} \times \text{u-value}_{\text{roof}}$$

q_{roof} : Energy demand to compensate transmission losses through the roof in kWh/m² roof surface/a

HzSt: heating degree hours in khK/a

$\text{u-value}_{\text{roof}}$: heat transmission coefficient of the roof

End energy demand q_E is calculated as follows:

$$q_E = (q_H + q_V) \times e_g$$

q_E : end energy demand for compensation of heat losses through the insulated roof kWh/m² roof surface area/a

q_H : heating energy demand, limited to transmission losses (here: $q_H = q_{\text{roof}}$)

q_V : energy losses from storage, distribution and transfer

e_g : efficiency for generation of heating energy

Since energy losses from storage, distribution and transfer are mainly independent from thermal insulation or thickness of insulation, q_V is set to be zero for comparison.

CO₂ emissions from the compensation of thermal losses through the insulated roof are then calculated as follows:

$$E_{\text{CO}_2} = EF_{\text{CO}_2} \times q_E$$

Equation 6

E_{CO_2} : CO₂-emissions from compensation of thermal losses through the insulated roof

EF_{CO_2} : emission factors specific to fuel and generation

q_E : end energy demand

In order to determine the end energy demand for a standard case, the system efficiency is set at 1.08 for a gas condensing boiler (70/55°C). Per kWh, 0,2 kg CO₂ are emitted.

7. Energy-related CO₂ emissions in production of the insulation panel

For energy required to manufacture the insulation panel including all feedstock substances and product chains (without blowing agent), also referred to as grey energy, the following assumptions are made: For the feedstock substances including production of 1 m² of PU insulation foam panel of a thickness of 10.5 cm, approx. 23 kg CO₂ (23421g) are emitted (own calculations based on Krähling/Krömer 2000). This value will not be varied for the type of refrigerant in the following.

5.2.4 Balance of the standard case for n-pentane and HFC-365 mfc

1. CO₂ balance for n-pentane and HFC-365mfc

In the standard case (1m² of roof surface, 10.5 cm PU foam thickness, 50 years usage, 80% retention of blowing agent in disposal, 66khK annual heating degree hours and use of a gas condensing boiler, the equivalent annual CO₂ emission for n-pentane comes to 3.55 kg. In the case of HFC-365mfc, the amount (CO₂ and CO₂ equivalents) of 5.78 kg is clearly higher.

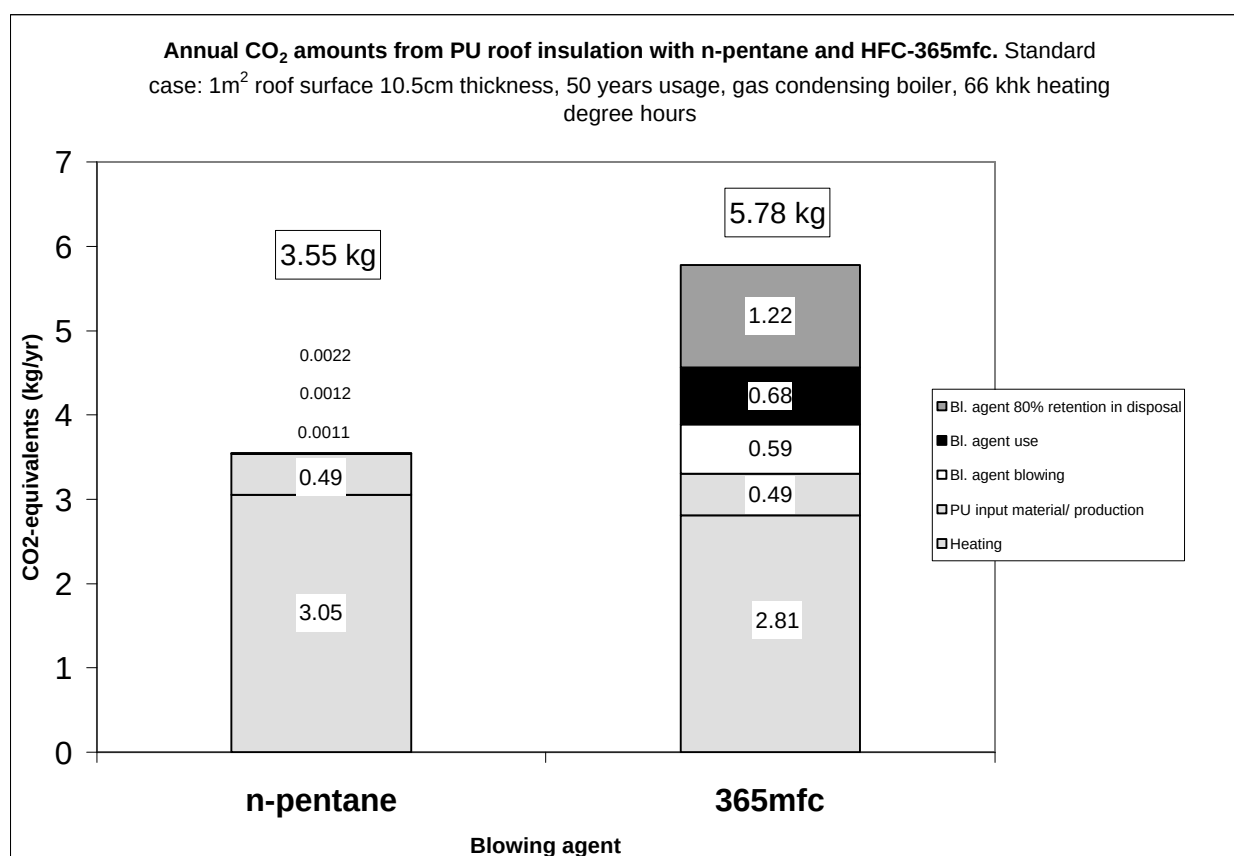


Figure 18: Comparison of annual emissions as CO₂-equivalents for PU roof insulation with blowing agent n-pentane and HFC-365. Standard case (1m² roof surface, 10.5 cm thickness, 50 years usage, gas condensing boiler, 66khK heating degree hours). For n-pentane a total of 3.55 kg and for HFC-365mfc 5.78 kg CO₂-equivalent emissions are generated.

As can be seen in Figure 18, heating-related CO₂ emissions (2.81 over 3.05 kg) are caused in the HFC-365mfc case, but this is overcompensated by far by the CO₂-equivalent emission of blowing agent with 2.49 kg (0.59 + 0.68 + 1.22) (The 0.49 kg CO₂ from panel production are at equal level

for both cases) The pentane emissions with GWP (GWP of pentane: 4) are almost negligible with <0.01 kg. (In future figures, these will not be displayed separately.)

2. Partial cost balance for n-pentane and HFC-365mfc (10.5 cm thickness)

If only annual heating costs per m² roof surface and the investment cost broken down to one year of usage (excluding interest) for insulation panels with 10.5 cm thickness are evaluated, the annual running cost for the n-pentane case total to 1.03 € and to one cent more to 1.04 € for HFC-365mfc. Lower energy costs (0.04 €) are slightly overcompensated by the higher cost of the blowing agent (0.05 €). The price for pentane as blowing agent is hardly discernible at 0.003€ per panel and year, which can also be seen in Figure 19.

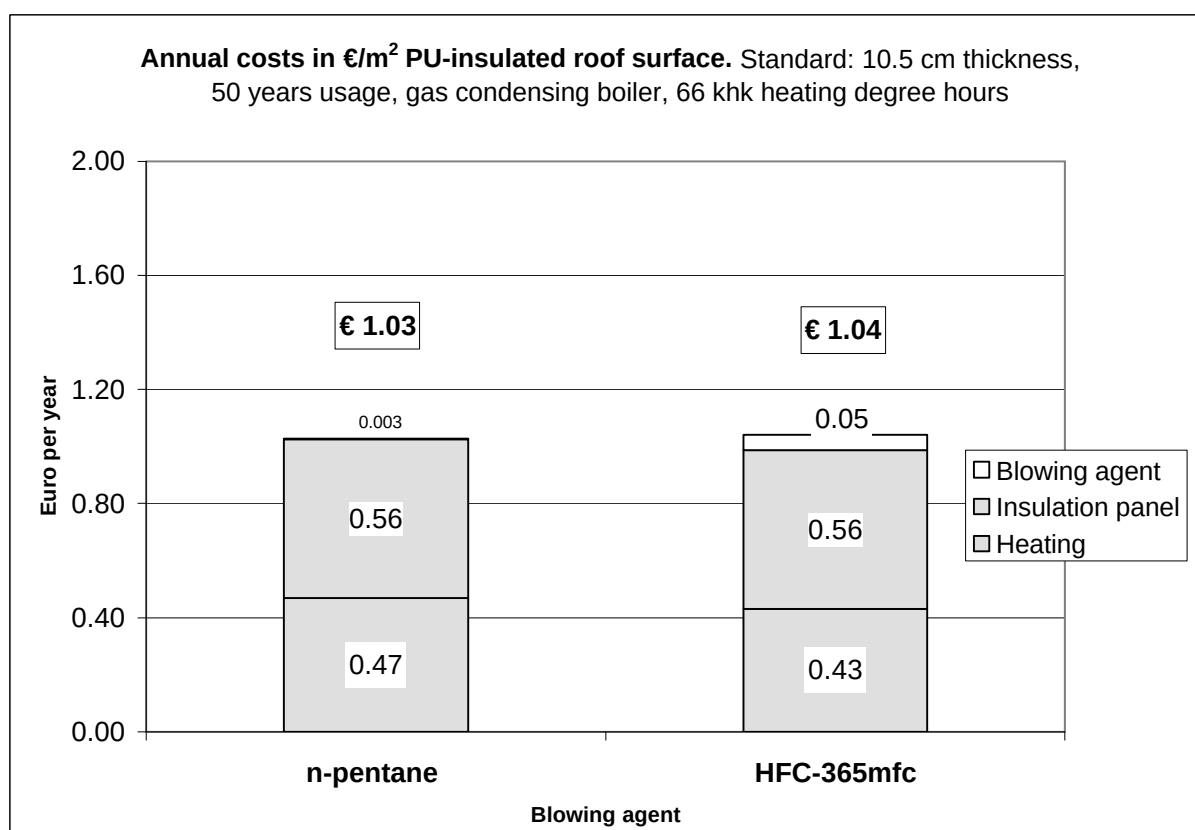


Figure 19: Annual cost in €/m² PU-insulated roof surface. Standard case: 1m² roof surface, 10.5 cm thickness, 50 years usage, gas condensing boiler, 66khK heating degree hours. Summarized partial costs for n-pentane are 1.03€, for HFC-365mfc 1.04€. The reason for slightly higher additional costs for HFC-365mfc is the higher cost of 6.50€/kg for the blowing agent of which more is required than of n-pentane.

Table 24: Prices applied for the operation cost model

1 kWh natural gas	0.031 € (0.306 €/m ³)
1 m ² PU-insulation foam panel, thickness 10.5 cm (RG32)	27.82 €
1 kg HFC-365mfc (pure)	6.50 €
Amount HFC-365 used in 1 insulation panel 10.5 cm	413 g
1 kg n-pentane	1.00 €
Amount n-pentane for 1 insulation panel 10.5 cm	170 g

5.2.5 Sensitivity analysis : CO₂ balance under variation of different parameters

Within the framework of the sensitivity analysis, the type of heating system, usage duration of the insulation, heating hours and the thickness of the insulation layer will be varied. The comparison between n-pentane and HFC-365mfc insulation panel is done in two steps: Firstly, the thickness of the insulation layer will be kept constant at 10.5 cm in order to compare the losses of blowing agent HFC-365mfc with the increased heat losses of n-pentane insulation panels with lower thermal performance. Secondly, the thickness of the n-pentane insulation panel is increased to achieve the insulation effect of the HFC-365mfc insulation panel. Here, the additional material input to the n-pentane insulation panel needs to be balanced.

1. Variation of the heating systems and CO₂ balance

In Figure 20 the effect of three different heating system types on the life cycle emissions is examined. First: gas-fired condensing boiler (standard case so far), second: low-temperature oil boiler with window ventilation, third: direct electric resistance heater with window ventilation.

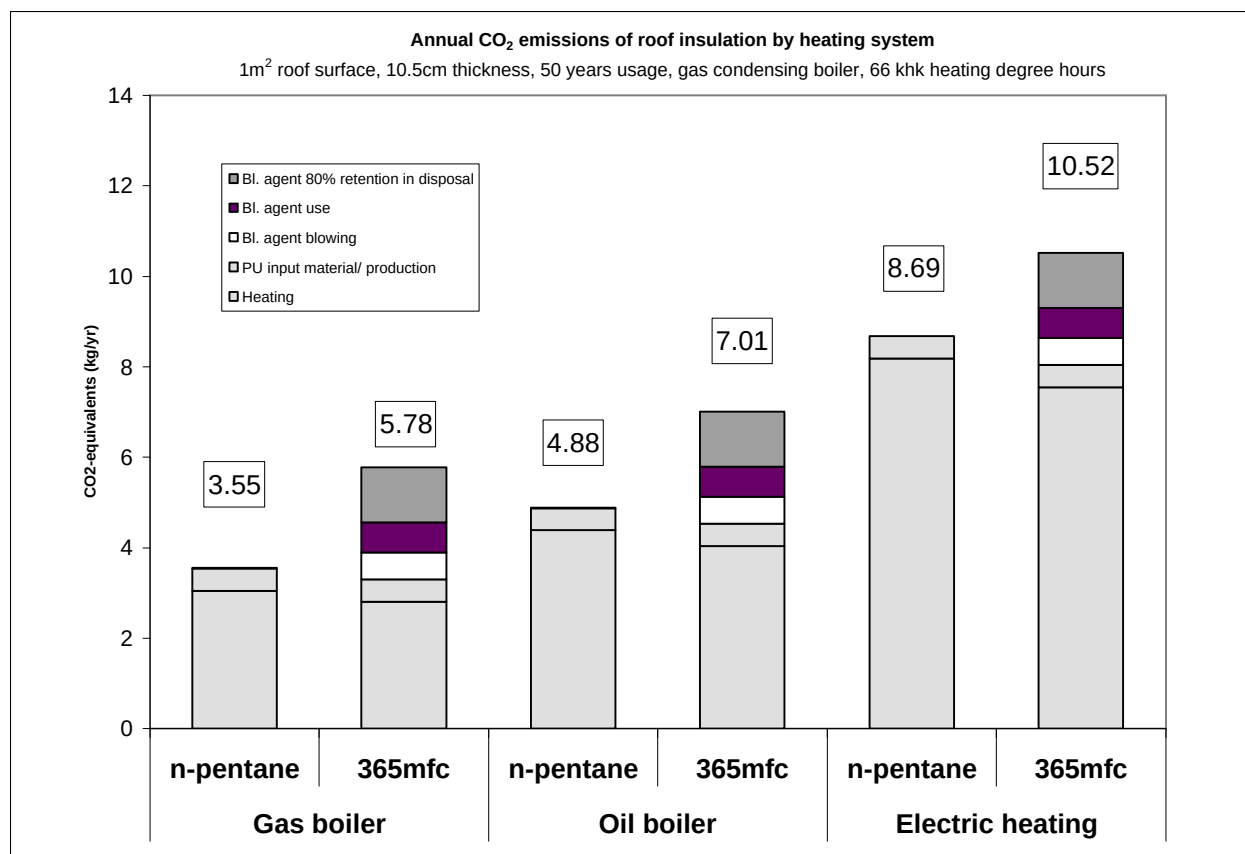


Figure 20: Effect of heating systems on the CO₂-balance of PU insulation. 1m² roof surface, 10.5 cm thickness, 50 years usage, 66khK heating degree hours. The gas-fired condensing boiler (left) generates the lowest total CO₂-emissions, the most are emitted under the use of a direct electric heating system (right). Due to the losses of blowing agent, the HFC-systems (right column) always perform worse than the pentane systems (left columns)

As can be expected, the heating-related CO₂-emissions are lowest for the gas-fired condensing boiler. (3.55/5.78 kg CO₂/a). The highest values occur for the direct electric resistance heating system with 8.69/10.52 kg. In between there is the oil heating system with 4.88 and 7.01 kg. Since only the heating system is varied, but not the operation time of the heating system (usage time,

heating degree hours), the CO₂-equivalent emissions from the blowing agents are equal for all three cases and lead to the generally poor CO₂ balance of HFC cases. The relative difference of the total CO₂ emission to the respective pentane system is highest (+63%) for the gas condensing boiler and lowest for the electrical heating system (+21%) although still very high.

2. Variation of usage time and CO₂ balance

If the usage phase of the insulation foam is varied from the standard case (gas condensing boiler heating system, 1m² roof surface, 10.5 cm thickness, 50 years usage, gas condensing boiler, 66khK heating degree hours), basically the same pattern for the difference in columns of pentane and the HFC can be observed. It needs to be noted that with shorter usage phase of the insulation panel, the higher the emission amounts attributed to every year resulting from the use of this insulation panel. The one-time losses of HFC blowing agent in production and disposal have a stronger effect with less years of usage on which they are spread. This is equally valid for the one-time production of the panel (feedstock substances etc.). Only the annual losses of blowing agent in the usage phase remain equal at 0.2%/a in all three cases.

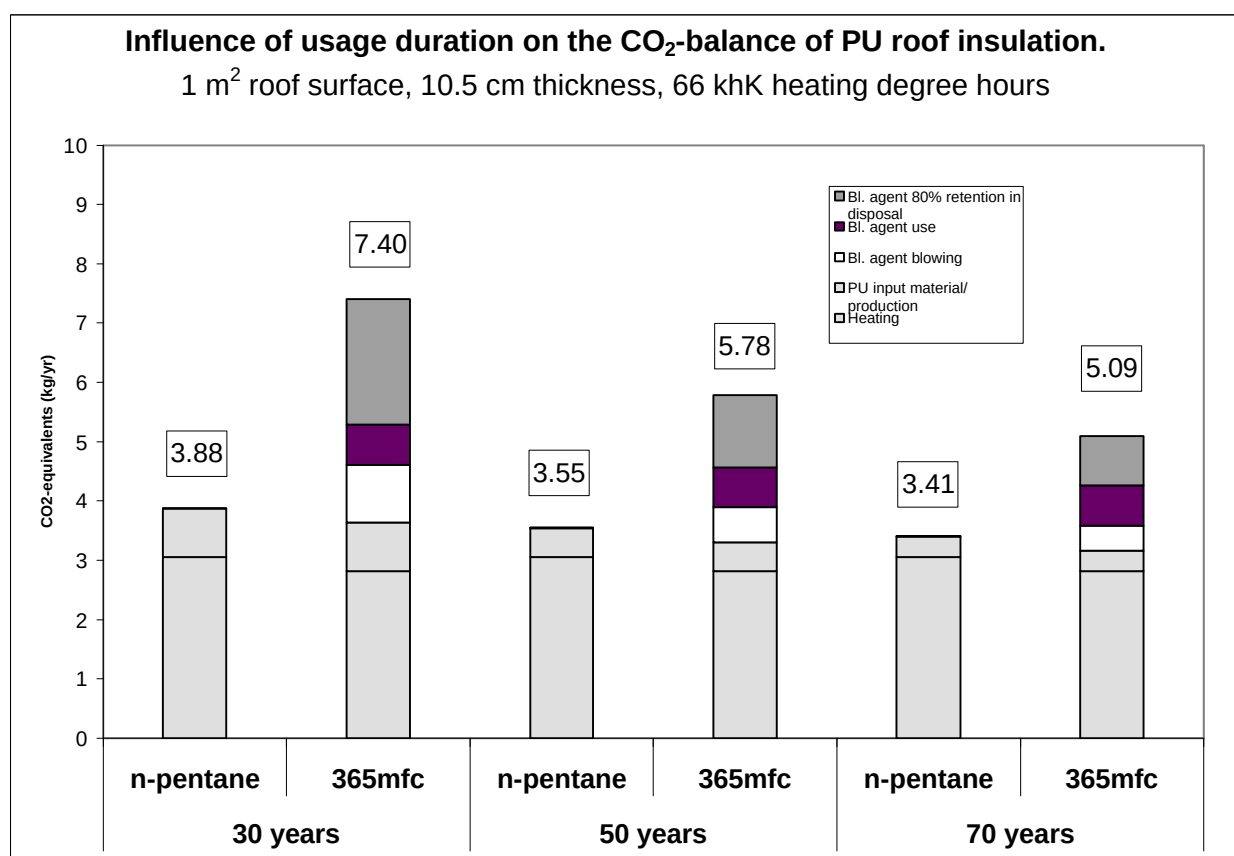


Figure 21: Influence of variation in usage duration (standard case: 50 years) on the CO₂-balance of PU insulation 1m² roof surface, 10.5 cm thickness, gas condensing boiler, 66khK heating degree hours. The shorter usage phase of the insulation panel, the higher the annual losses of blowing agent in production and disposal. CO₂ emissions from production of feedstock substances also increases in effect.

3. Variation of heating degree hours and CO₂ balance

From Figure 22 can be seen that the number of degree hours increases CO₂ emissions from the building heating system notably. In the case of pentane, this increases from 2.94 kg/a (at 53khK/a) to 4.16 kg/a (at 79 khK/a). Equivalent CO₂ emissions resulting from the blowing agent are not affected by the annual duration of the heating period.

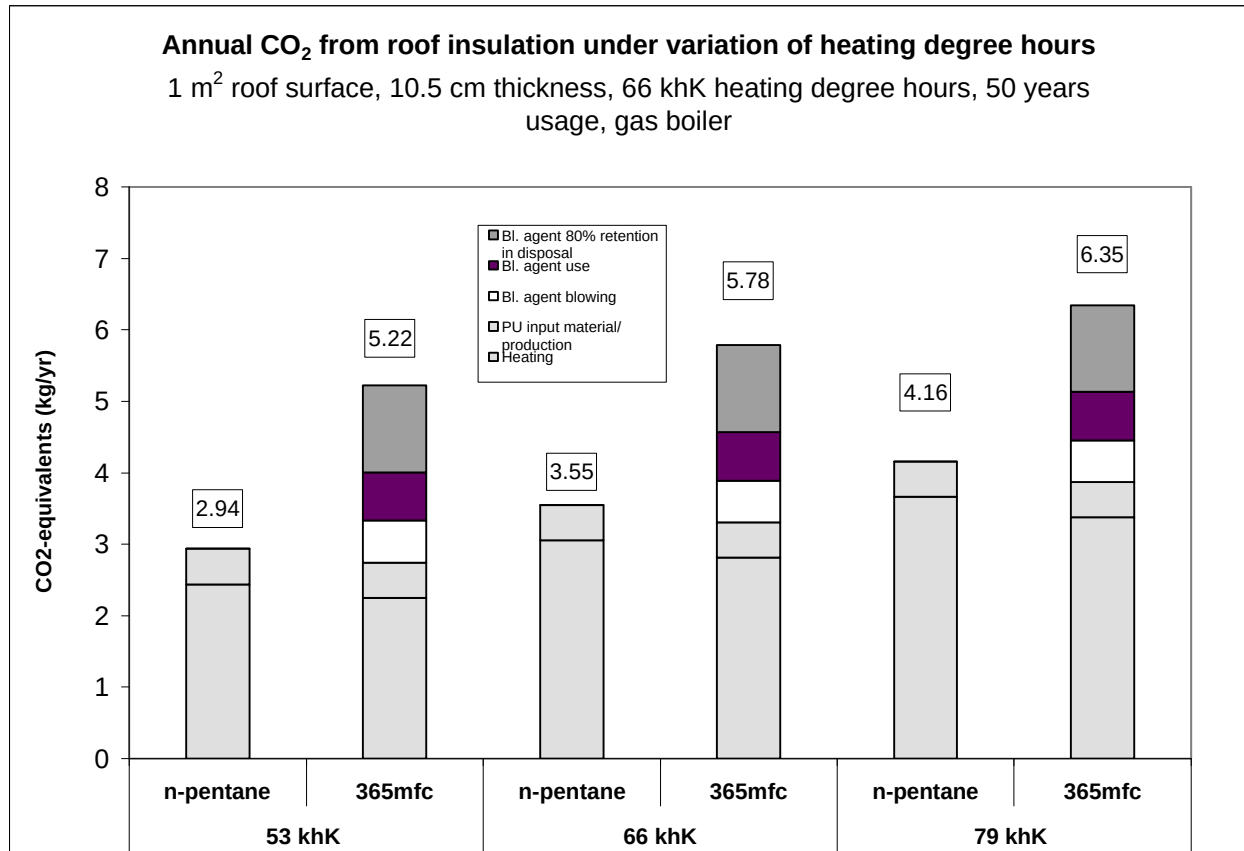


Figure 22: Annual CO₂-equivalent emissions of roof insulation under variation of heating degree hours (standard case 66khK heating degree hours): 1m² roof surface, 10.5 cm thickness, 50 years usage, gas condensing boiler. With longer heating periods per year, the smaller the specific difference between the total CO₂-amounts from pentane and HFC-365mfc without really decreasing.

4. Increased thickness of the insulation layer to maintain equal u-value

In order to achieve equal insulation performance per m² of roof surface for both HFC-365mfc and n-pentane, more foam needs to be applied for n-pentane. Room problems (like in refrigerated vehicle manufacture) are not to be expected for an increase of material thickness by not more than 1 cm. The thickness of the pentane-blown foam panel needs to be increased by 9% to 11.455 cm in order to lower the u-value at standard thickness (10.5 cm) from 0.214 W/m²K to 0.197 W/m²K (for HFC-365mfc at 10.5cm thickness). This is an increase by almost 1 cm.

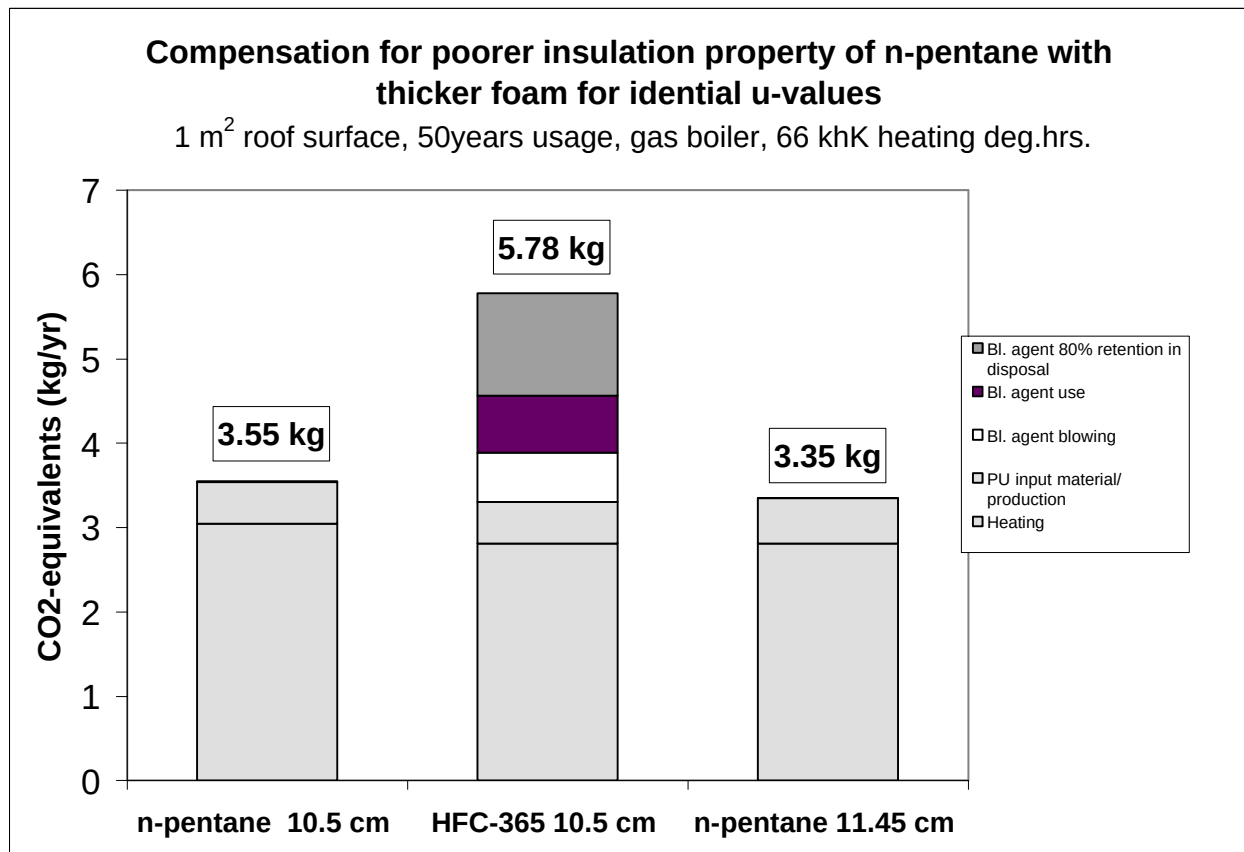


Figure 23: Compensation for poorer insulation property of n-pentane with thicker foam to achieve identical u-values: 66khK heating degree hours, 1m² roof surface, 11.45 instead of 10.5 cm thickness, 50 years usage, gas condensing boiler. The comparison with the right column (pentane, 11.45 cm) with the middle column (HFC) shows that CO₂ emissions from heating are equal at 2,81 kg/a for both cases. CO₂ equivalent emissions from the production of the foam panel (feedstock/manufacture) are slightly increased slightly with 0.54 instead of 0.49 kg CO₂/a. The total equivalent CO₂ emission is by far lowest at 3.35 kg CO₂/a for the pentane insulation panel.

From environmental point of view, the increase in thickness from 10.5 to 11.45 cm of the pentane-blown insulation panel is a good solution. The respective equivalent CO₂ emission of 3.35 kg per annum is much lower than the 5.78 kg CO₂ equivalent resulting from insulation with 10.5 cm of HFC-blown insulation foam and still clearly lower than the 3.55 kg CO₂ emission from the pentane insulation panel of only 10.5 cm thickness. Therefore, a final outlook shall be given on the cost side.

5. Partial comparison of operation cost of the three insulation panels

Figure 24 indicates that the additional cost for almost 1 cm greater thickness in PU insulation foam blown with n-pentane is less than 1.5 cent per annum. Instead of 1.026 €/a, the cost is 1.04 €/a in case of the panel with 11.45 cm thickness- as much as the cost for the HFC-blown panel of 10.5 cm thickness. The direct heating costs are reduced by 3.7 cent/a while the production of the thicker panel costs 5 cent/a more.

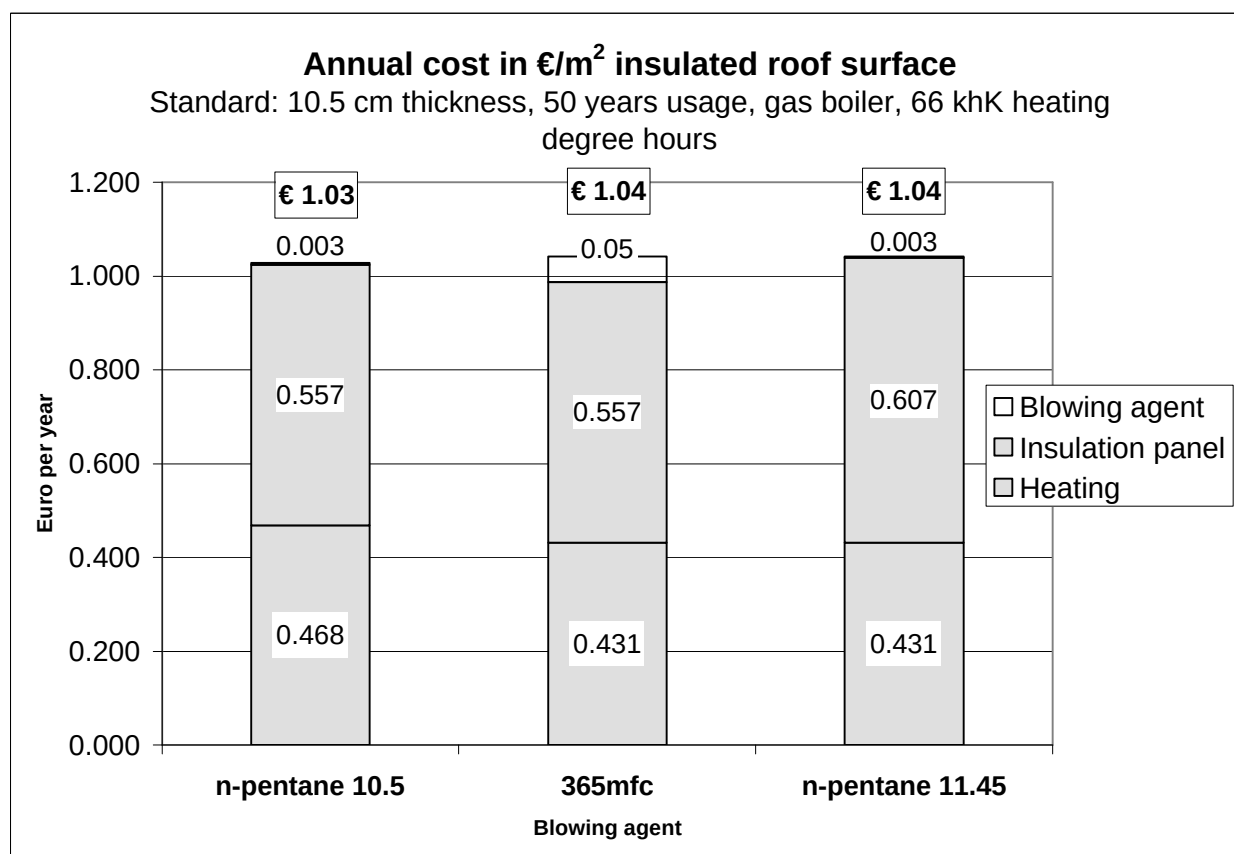


Figure 24: Annual cost in €/m² PU insulated roof surface. Standard: 66khK heating degree hours, 10.5/11.45 cm thickness, 50 years usage, gas condensing boiler. Due to the increase in thickness from 10.5 to 11.45 cm (right column), the total price for insulation increases from 1.03 €/a to 1.04 €/a to the price level of HFC-blown panels. The additional cost consist of approx. 3.7 cent less energy costs and 5 cent additional costs for the panel itself.

5.2.6 Summary

In the framework of this section it was shown that for the application example of PU roof insulation panels the pentane panel displays a clearly better GHG balance than the alternative blown with HFC (With increased insulation foam thickness for pentane as well as for slightly higher heating energy demand at constant insulation thickness).

The sensitivity analysis in which (1) the heating system, (2) the usage phase of the insulation material, (3) the number of heating degree days and (4) the thickness of the insulation 'layer were varied respectively, confirmed this finding in favour of the pentane-blown panel for all parameters.

- With a change of heating system type, the overall CO₂-emissions rise in the sequence of gas condensing boiler, oil heating system and direct electric resistance heater. But due to the losses of blowing agent, the HFC case contributes always exactly the identical amount more to the CO₂-equivalent emissions than the pentane-blown insulation (under otherwise equal conditions)
- If the usage phase of the insulation is varied from 50 years to 30 or 70 years, the additional contribution to the greenhouse effect from HFC blown insulation foam drops with increasing usage phase relative to pentane; losses of blowing agent are then spread over more years. In absolute terms the CO₂-equivalent total emissions from HFC always remain above those from the pentane case.
- A similar result can be stated for the variation of heating degree hours. The longer the heating phase per year, the smaller the difference between equivalent CO₂ emissions from HFC- and pentane-blown insulation panel. However, the additional contribution from application of HFC is not reduced significantly.
- Adaptation of the foam thickness to compensate the lower insulation performance of n-pentane to the same u-value as in foam blown with HFC-365mfc requires an additional input of 9% PU. From the ecological point of view, this seems to be the best option, because the reference case (gas boiler, 50 years usage, 66 kWh/a heating degree hours) the total equivalent CO₂-emission is 5-6% lower than under application of the n-pentane insulation panel of original 10.5 cm thickness.

In terms of costs, the pentane-blown panel is positioned even with the HFC panel. Even as a result of an increase in thickness by 9%, the total price of the insulation caused by additional input of PU comes only just to the slightly higher price level of the HFC blown panel. Mitigation costs here are 0 €/t CO₂ eq.

The disposal path is of significant quantitative relevance for the total result. In the reference case, a rate of 80% substance decomposition of the HFC contained in the panels to dispose. This rate seems very optimistic in view of the present conditions and the medium-term perspectives. However, even this favourable rate still leads to disadvantages of the HFC solution.

It needs to be noted that even at a retention and complete decomposition (incineration, cracking) of 100% of the HFC blowing agent, the ecological bonus of the n-pentane blown panel would be reduced, but it would still remain existent.

5.3 *Insulation of refrigerated vehicles with cyclopentane and HFC-365mfc*

5.3.1 Introduction

PU foam is used in the cargo hold walls of virtually all refrigerated vehicles for the transport of perishable goods. High insulation performance and thus low material thickness allow maximisation of interior space while minimising the introduction of ambient heat.

Basically, the total performance of an insulation system (expressed as the u-value in W/m²K) despite higher heat transmission properties λ of the blowing agent may be maintained with greater foam thickness. However, the dimensions of exterior walls of refrigerated vehicles can only be varied within limits. Extension to the outside can be ruled out since the maximum permitted vehicle width is already utilised. Extension towards the interior is limited by the width of the cargo hold, which has to allow transportation of standardised freight units.

For insulation of refrigerated vehicles, 3000 t PU foam, approx. 4% of the total inland use excluding electronics and installation foam are used per annum. Therefore, the refrigerated vehicle insulation is a suitable reference case to examine the necessity to use halogenated blowing agents, since the λ value of HFC and HCFC is considerably lower than that of pentane or cyclopentane. In the following, it will be assumed that foam with HFC-365mfc features favourable insulation property over foam with c-pentane.

Reference refrigeration vehicle: semi mounted trailer for 33 standard euro pallets

According to statistics of the German Federal Office for Motor Vehicles, 8728 refrigerated road vehicles were registered in 2001. In the range below 26 t, 5079 of these were motorized and 1250 trailers mainly used in local and regional distribution traffic. With regard to transportation capacity (distance, payload), semi mounted trailers towed by trucks are of greater importance. In 2001, 2399 trailers with insulated cargo hold, refrigeration unit and gross weight exceeding 26 t were newly registered and shall therefore serve as a reference vehicle.

A typical semi mounted trailer utilises the legal limits of the road vehicle regulations to the maximum. Hence, the external dimensions of the cargo hold are identical for all leading European manufacturers (e.g. Schmitz, Lamberet, Kögel, Chereau). Maximum width: 2.6 m, maximum height: 4 m (allowing a vertical clearance of 2.65 m), maximum length 13.6 m. On the outside of the front side, the refrigeration unit with a depth of 0.43 m is mounted. This refrigeration unit is typically driven by an own diesel engine independent of the engine of the towing vehicle to enable stand-alone operation. In Germany, the refrigeration unit may commonly be operated with electricity from a mains connection to utilize low-tariff electricity at night for refrigeration outside driving hours.

The refrigerated vehicle as described before can only obtain the highest FRC ATP¹⁸-certification (F=refrigerated; R=reinforced insulation; C=temperature down to -20°C), by the certification authority TÜV Bayern Sachsen if it can maintain the interior temperature of -20°C at ambient temperatures of $+30^{\circ}\text{C}$. For this, the u-value of the total envelope (150m²) must be lower than 0.4 W/m²K. This is checked after six years for the first time and repeated in 3 year intervals thereafter.

Critical for the size of the cargo hold is the horizontal clearance defined by maximum exterior dimensions of 2600mm minus at least two times the insulation thickness of 40mm. The reason for this is the necessity to allow storage of at least 3 rows of 11 European standard pallets (800 mm x 1200 mm) side by side with little room for manoeuvring.

The selected reference vehicle is typical for long distance traffic. The refrigeration capacity and therefore the energy demand depends decisively on the u-value of the walls of the cargo hold. For smaller vehicles which are operated in short distance transport and distribution, door openings for loading and unloading are of greater importance to the cooling capacity than the heat transfer through the walls. The wall thickness offers more options for variation. Semi mounted trailers are therefore not representative for all refrigerated road vehicles. They are however a good example for cases in which insulation properties as well as thickness are of equal importance.

¹⁸ ATP = Accord relatif aux Transports internationaux de denrées Périssables et aux engins spéciaux à utiliser pour ces transports. Or in English: Approved for Transport of Perishable Foodstuffs.

Thicker side walls caused by shift from HCFC-141b to c-pentane

Insulation foam blown with HCFC-141b and of a thickness of 45 mm had a market share of over 50% for the most common type of semi mounted trailer. Included in this wall thickness are two diffusion-proof steel sheets of 0.6 mm thickness respectively. Two profiled 3.5mm aluminium sheets add to the total wall thickness resulting in a total thickness of 52mm with a PU foam thickness of 43.8 mm. The thickness of the roof and rear doors was 80mm including the steel sheets, the front had a thickness of 50 mm. The floor consisted of a 100mm layer of XPS covered by wood panels.

In the course of the shift to c-pentane as the blowing agent at the leading manufacturer (investment cost of 3 MDM), the foam thickness of the side walls (39m² or 49% of the envelope surface of the trailer) was increased from 45 to 60 mm. The sheer PU thickness was increased by 15 mm- from 43.8 to 58.8 mm. The thickness of the roof, front side and rear doors as well as the XPS floor were kept at the same thickness in order to maintain the vertical clearance of 2.65 m and a length of 13.33 m. The PU density was also kept at the same level with 65 kg/m³ on average.

The horizontal clearance of the cargo hold was reduced by 30 mm from almost 2.5 m to 2.46 m. in total by these measures thus keeping the vehicle dimensions sufficient for standard pallets. Three rows of pallets with a width of 0.8 m can be loaded although the space between these rows decreased somewhat.

Dividing the additional volume of the side walls of 1.17 m³ or 34% over the total amount of foam used on the vehicle including the floor, the foam volume increases to 8.1 m³ or by 10.2% over the total vehicle. This increase is in the same order of magnitude as the decrease of the λ value of the foam by some 10.5 %. The new blowing agent is a blend of 70% c-pentane and (for reduction of the boiling point) 30% i-pentane. In the future, this will be addressed simply as pentane.

The vehicle manufacturer claims that the most important indicator for the performance of the insulation, the average u-value of the cargo hold is at least maintained at the same level. The reason for this are partly construction details e.g. the door seal with five seal flaps instead of four, sealing of edges and seamless installation of the PU sandwich panels. All in all, the details focus on minimisation of thermal bridges.

5.3.2 Basic data for analysis refrigerated vehicles

1. Identical technological basis for pentane and HFC

In the comparison of HFC-365mfc and c-pentane as a substituting agent of HCFC-141b, the modifications to the cargo hold –mainly the increasing thickness of the walls- serve as the common technical basis. Table 24 summarizes the common data for the insulated trailer as well as the technical data of the two most commonly applied refrigeration units.

Table 25: Technical basis data for the analysis of refrigerated vehicles

Refrigerated trailer		
Volume PU-foam per vehicle	8.1 m ³	
Raw density of the foam	65 kg/m ³	
PU-weight per vehicle	527 kg	
u-value of the envelope with c-/i-pentane	0.370	
u-value of the envelope with 365mfc	0.361	
Average use in inland	9 years	
Additional usage abroad	9 years	
Refrigeration unit		
Model	Thermo King SL 400	Carrier Vector 1800
Refrigeration capacity at -20° C	9200 W	9000 W
Refrigerant	7.5 kg R 404 A	6.5 kg R 404A
Diesel consumption of ref unit at full load	4 l p. h.	4 l p. h.
Electricity consumption at full load	8.7 kW	8.7 kW
Average run-time of the ref unit	1500 h/a	1500 h/a

Source: Survey on refrigerated vehicles (2002/2003)

The basic question is: which ecological consequences would the production of PU rigid foams with HFC-365 mfc ($\lambda = 22 \text{ mW/mK}$) instead of pentane blend ($\lambda = 23.15 \text{ mW/mK}$) have?

2. Formulas for foams in refrigerated vehicles

Unlike roof insulation foams for buildings, there are experiences with HFC-365mfc as a blowing agent for foams used in refrigerated vehicles from numerous experiments. The formulas are summarized in Table 26.

Table 26: Averages for the formulas applied in the production of foams for refrigerated vehicles (density: 65 kg/m³) in % Vol.

	c-/i-pentan formula	365mfc formula
Isocyanate	100	100
Polyol	100	100
Water	2	1
Additives	1	1
Fire inhibitors	none	none
Blowing agents	7	18 ¹⁹
Total of components	210	220

Source: Survey on refrigerated vehicles (2002/2003)

¹⁹ In practice, formulas with a lower content of HFC-365mfc may become more important because of the increasing cost of blowing agents. (R. Albach (Bayer Polymers, August 2003). The insulation properties for such formulas are likely to develop towards those with pentane.

Different to foams for building materials, no fire inhibitors are required. The relation between isocyanate and polyol components is almost equal and the share of blowing agent with 3.3% for pentane and 8.2% for HFC is lower than in comparable building material foam. The quantitative relation between the two blowing agents is however almost identical. Striking is the high raw density of the foam (65 kg/m³) resulting from the fact that the foam has to display high mechanical stability to complement the steel in the sandwich panel construction.

3. Production method of sandwich panels and loss of blowing agent

PU sandwich panels with the exception of the doors are manufactured in a discontinuous coating process. The rear door is produced with the injection method. Emission rates of blowing agents relevant for practical use are represented in Table 27.

Blowing process

A mixing head is used to apply the reactive mixture on a steel panel with the dimensions 13.6 x 2.86 m. During the reaction, a second steel sheet is lowered onto the foam to the desired foam thickness. The raising foam sticks to both panels thus creating a unit. Loss of foam to the sides is avoided by aluminium frames. For the front side the same procedure is repeated with sheets cut into several shorter segments.

Ventilation holes (2-5 mm diameter) in steel sheets and aluminium frame enable the extraction of excess gases (air, CO₂, blowing agent). Evaporating pentane has to be collected in order to avoid creation of combustible mixtures of flammable blowing agent with air.

Prefabricated door elements (1.25m x 2.7m height) are insulated by injection of foam into the 80mm gap. Surplus gases escape through ventilation holes.

According to a manufacturer, the pentane losses in the blowing process are between 8 and 12% of the uses amount. The same value (average 10%) applies to the use of HFC-365mfc.

Assembly

Completed sandwich panels are assembled to cargo hold structures and mounted on the chassis. Approx. 1% loss of the total of 527 kg of PU foam results from cutting or drilling for e.g. lights, refrigeration unit etc. Presently, the waste containing blowing agent is dumped on landfills.

Usage phase

During the usage phase of a semi mounted trailer of approx. 18 years, there are virtually no diffusion losses of blowing agent. The steel panels on the PU foam are considered to be diffusion-proof. Their main objective is to avoid the introduction of water into the foam which used to be the main cause for deterioration of the u-value during the usage phase of trailers (and easily identified by a distinct net weight increase of the trailer). There are however, some losses: Firstly the sandwich panels are not covered by steel sheets on all sides, but sealing material covers the connecting edges. Secondly, the operation of the vehicle leads to damages from wear or collisions in accidents or improper loading. A conservative estimate is the annual emission of 0.1% of the blowing agent contained in the foam (or 0.1% of the blowing agent used in the production process). Panels replaced in the repair facilities of the manufacturers are currently disposed of in landfills. At least one of the manufacturers active on the German market already disposes of

damaged panels in waste incinerators. This behaviour is assumed to be commonly applied since this will be legally required as of 2005.

Table 27: Refrigerated vehicle: loss of blowing agent during the manufacturing process and lifetime (source: survey on refrigerated vehicles)

Usage	blowing	assembly	Diffusion p.a.	Remaining at decommissioning
9 years	10%	1.0%	0.1%	88.1%
18 years	10%	1.0%	0.1%	87.2%

4. Disposal of insulation foam from old refrigerated vehicles

At present, there is no infrastructure dedicated to the disposal of foam from refrigerated vehicles. The background for this can be identified by the sheer lack of vehicles which need to be decommissioned. For all four manufacturers serving the German market, the used vehicle trade departments, managing directors and workshop administrations report unison that more than 95% of the refrigerated vehicles are sold abroad long before the end of their estimated lifetime of 18 years. The use phase in Germany ranges from less than six to a little over ten years.

This is confirmed by the ATP-certification authority in Munich (interview of March 6th 2003), where vehicles have to undergo testing of their thermal performance 6 years after first registration and every 3 years after that. Only on rare occasions vehicles appear for the second 3-year test i.e. after 12 years of use.

The main markets for used refrigerated vehicles are Eastern and Southern Europe, Middle East and Central Asia. A semi-mounted trailer with a new retail price of 60 000€ still has a value of 10 – 13 000€ after ten years. In the buyer countries, where thermal performance testing is not as strict as in Germany, trailers are operated for about the same period of time they have been used in Germany. Before export, the refrigeration unit, which is not designed for such a long lifetime, is overhauled (Survey on refrigerated vehicle, 2001/2003).

An orderly decommissioning and disposal of the exported refrigerated vehicles in view of the blowing agents contained in the insulation material cannot be assumed for the buyer countries. Such ‘exported’ blowing agents are therefore considered as emitted. A legal influence on this is virtually impossible since the flow of vehicles abroad does not occur because of environmental standards but because of economic imbalance.

So far, there is only a minor share of cargo holds that remains in Germany. These are decommissioned cargo containers, which are transformed into stationary storage containers, mainly in agriculture. For these storage facilities analysis of the blowing agent loss against energy consumption as for vehicles is impossible.

If the flow of used refrigerated vehicles abroad recedes, the disposal of insulated containers will have to take place in Germany. The technical guidelines for household waste does not allow the disposal on landfills after 2005. This implies the incineration of the disassembled and crushed foam walls which have been stripped of their steel sheets. This also guarantees the destruction of the blowing agent remaining in the foam.

5. Relation between λ -value and u-value of the insulated container

An even roof element displays a linear relation between λ - and u-value of the PU foam that can be expressed in the thickness of the foam (s. also the section on PU foam insulation element). In contrast to this, it is far more complex to determine this relation for a three-dimensional container structure with gaps and thermal bridges (edges, seals, bolts etc.). This is the main reason that the thermal performance of the cargo hold is generally tested (i.e. empirically determined in the so-called tunnel test) on a prototype of a refrigerated vehicle at the ATP testing facility of the TÜV in Munich.

According to experiments of Bayer AG, (Welte 2002), lowering the λ -value results in lower u-values of the refrigerated vehicle. But the relation is below proportional: a λ reduction by x% leads to a max. decrease of the u-value of half of x%²⁰.

For conservative analysis, it is assumed that the λ value of HFC-365mfc (22) which is approx. 5% lower than a 70/30 blend of c- and i-pentane (23, 15) leads to a u-value of the insulated container that is 2.5% lower. In our model, the u-value is lowered from 0.37 to 0.36 so that the refrigeration unit consumes 2.5% less energy to maintain the interior temperature. In other words: In case HFC-365mfc is used as the blowing agent, the refrigeration unit has to run 2.5% less time than on a cargo hold insulated with pentane-blown foam to keep the interior temperature. Table 28 shows the most important values of the blowing agents for used for the analysis.

Table 28: Basic data for the blowing agents HFC-365mfc and pentane (70% c-pentane/30% i-pentane) and used in the insulation foam of refrigerated vehicle

Blowing agent	HFC-365mfc	c-pentane/i-pentane
λ -value	0.02200	0.02315
u-value of the cargo hold	0.361	0.370
Amount per vehicle	43.1 kg	17.6 kg
Price per kg	6.50 Euro	1 Euro
GWP	890	4

5.3.3 Balance standard case

1. CO₂-balance for c-pentane und HFC-365mfc

Refrigerated vehicles are normally used by shipping companies for the transportation of deep-frozen (one third) or refrigerated (two thirds) goods over long distances. Depending on the interior and ambient temperature, the refrigeration unit runs between 1000 and 1500 hours per year on average, but actually ranges from 600 to 3000 h/a. For one hour of operation, the refrigeration unit consumes 4 l diesel fuel or 8.7 kWh electricity. In the first 9 years of operation in Germany the

²⁰ Bayer AG compared calculated values to those measured during the ATP tunnel test and came to much lower relations than 50% between λ and u values for refrigerated semi-mounted trailers. The trailers were of the same conceptual lay-out as the 'typical' refrigerated semi-mounted trailers (Welte 2002). The underproportional influence of the λ -value on the u-value is also one of the reasons why the u-value did not experience the expected deterioration during the shift from CFC-11 to HCFC-141 and further to c-pentane (Demharter 2002).

refrigeration unit is operated with electricity for 25% of the operation time, the following 9 years abroad, the unit runs only on diesel fuel (survey on refrigerated vehicles, 2002/2003).

The result of the CO₂ balance calculation of 18 years of usage and 1500 hrs of annual operation (including 375 hrs on the electricity grid) is displayed in Figure 25 for refrigerated vehicles insulated with pentane and HFC-365mfc-blown foam (standard case).

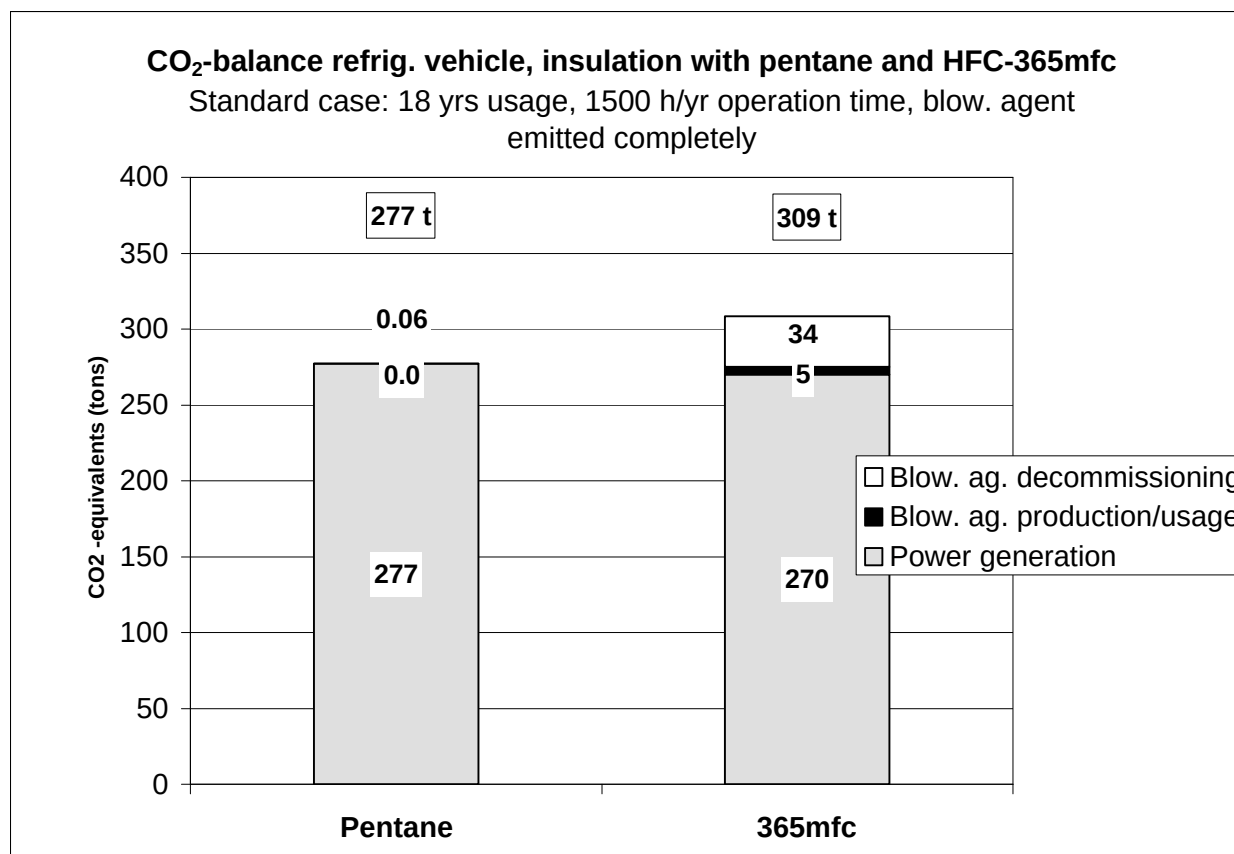


Figure 25: GHG balance for refrigerated vehicle insulated with pentane and HFC-365mfc blown foam, standard case. 18 years of usage, 9 in Germany, 9 in other countries. 1500h/a operation time of refrigeration unit (in Germany, 25% grid operation at 8.7 kWh/h). Blowing agents are emitted completely, 87% at the point of decommissioning. GHG emissions from pentane add up to 277t, HFC-365mfc to 309t.

Over the lifetime of the vehicle, the GHG emissions add up to 277t in the case of foam blown with pentane and to 309t in the case of foam blown with HFC-365mfc. The lower CO₂ emissions which result from lower energy consumption are overcompensated by the 34t CO₂-equivalent of the emitted HFC blowing agent. The reduction of CO₂ emissions from energy demand for cooling in the case of HFC-365mfc results from the lower annual operation time of 1436 h/a at the same energy consumption of 4 l diesel per hour and 8.7 kWh respectively.

2. (Partial) Balance of annual running cost in the standard case

Annual running cost for cooling of the vehicle in 18 years of usage differ in two (or three) points for the blowing agents pentane and HFC used for the foam insulation of refrigerated vehicles:

In the case of HFC, the cost for fuel and electricity are reduced by 2.5%. In this study, standard prices for diesel of 0.85€/l and 0.1 €/kWh are assumed.

On the other hand, the investment cost of the blowing agent is broken down into the years of operation without taking into account interest. For HFC-365mfc, and c-pentane, prices of 6.50 €/kg and 1 €/kg are assumed.

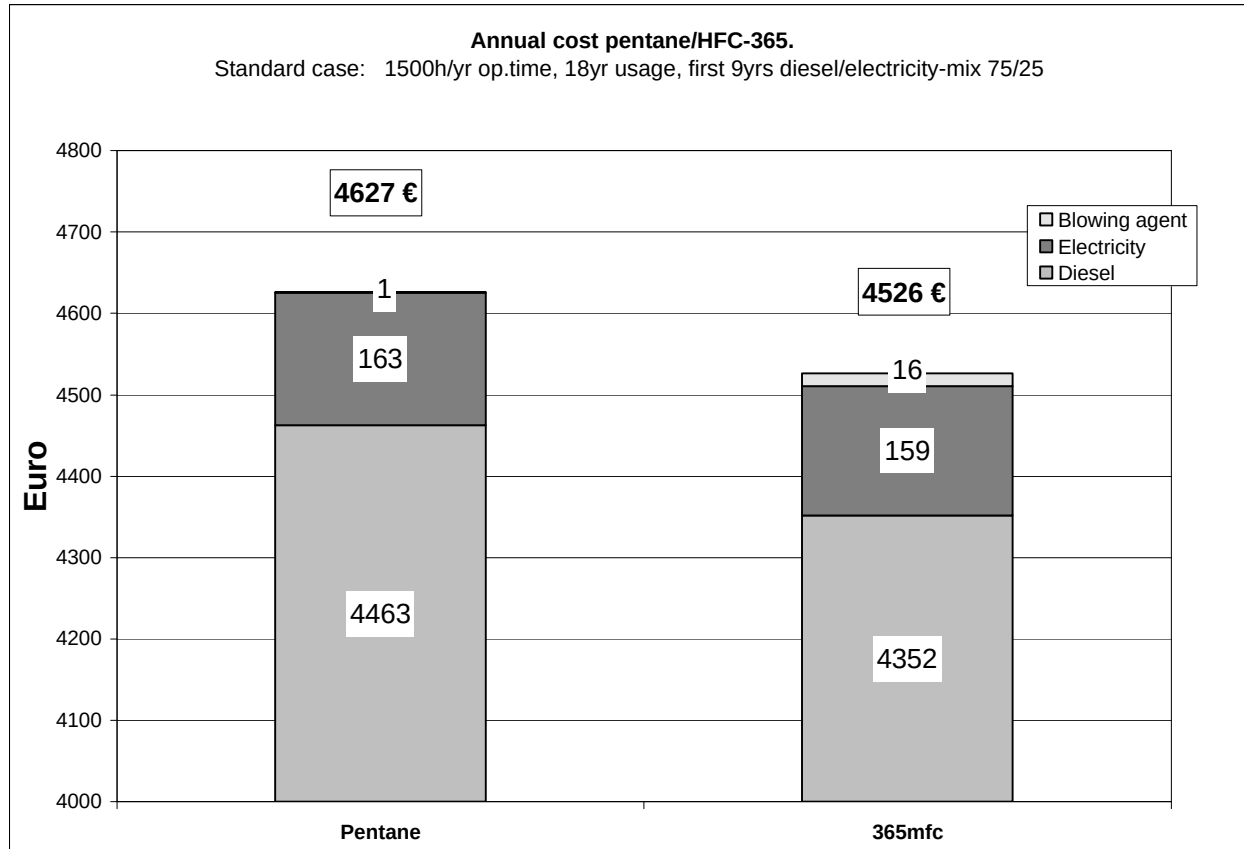


Figure 26: Balance of annual running cost of a refrigerated vehicle with insulation foam blown with pentane and HFC-365mfc. Standard case: 1500 h/a run-time of refrigeration unit, 18 years of usage of which the first 9 years in Germany at an operation mode of 25% on electricity, 75% on diesel. The total of the annual running cost is 4627 € for pentane and 4526 € for HFC. Attention: the diagram starts at a low threshold of 4000 €.

Due to the lower energy consumption of the refrigeration system, the annual energy cost of the refrigerated vehicle insulated with HFC-365mfc blown foam is 2.5% or 111 € lower than for insulation foam blown with pentane.

The difference in energy cost is slightly offset by the cost for the blowing agent (16€ as compared to 1 € p.a.). In total, the cost difference remains at 101€ or 2.2% in favour of the HFC application.

Effect of lower diesel prices

Equal annual operation cost would only occur if diesel prices would drop below 0.34 €/l resulting in total annual operation costs of 1948€. Such low diesel prices are not plain theory but the main reason that refrigeration units are hardly ever operated with electricity in the U.S. Even though 80% of the combined diesel/electricity refrigeration units are supplied by US manufacturers, these are only tailored to serve the European market.

5.3.4 Sensitivity analysis: CO₂-balance at variation of different parameters

1. Annual operation time of the refrigeration unit and CO₂-balance

In the same rate the operation time of the refrigeration unit is increased from 600 to 3000 h/a for the pentane case (or 585 to 2926 h/a for the HFC-365mfc case), the total and relative difference between the respective emissions of CO₂ and CO₂ equivalents drops (s. Figure 27).

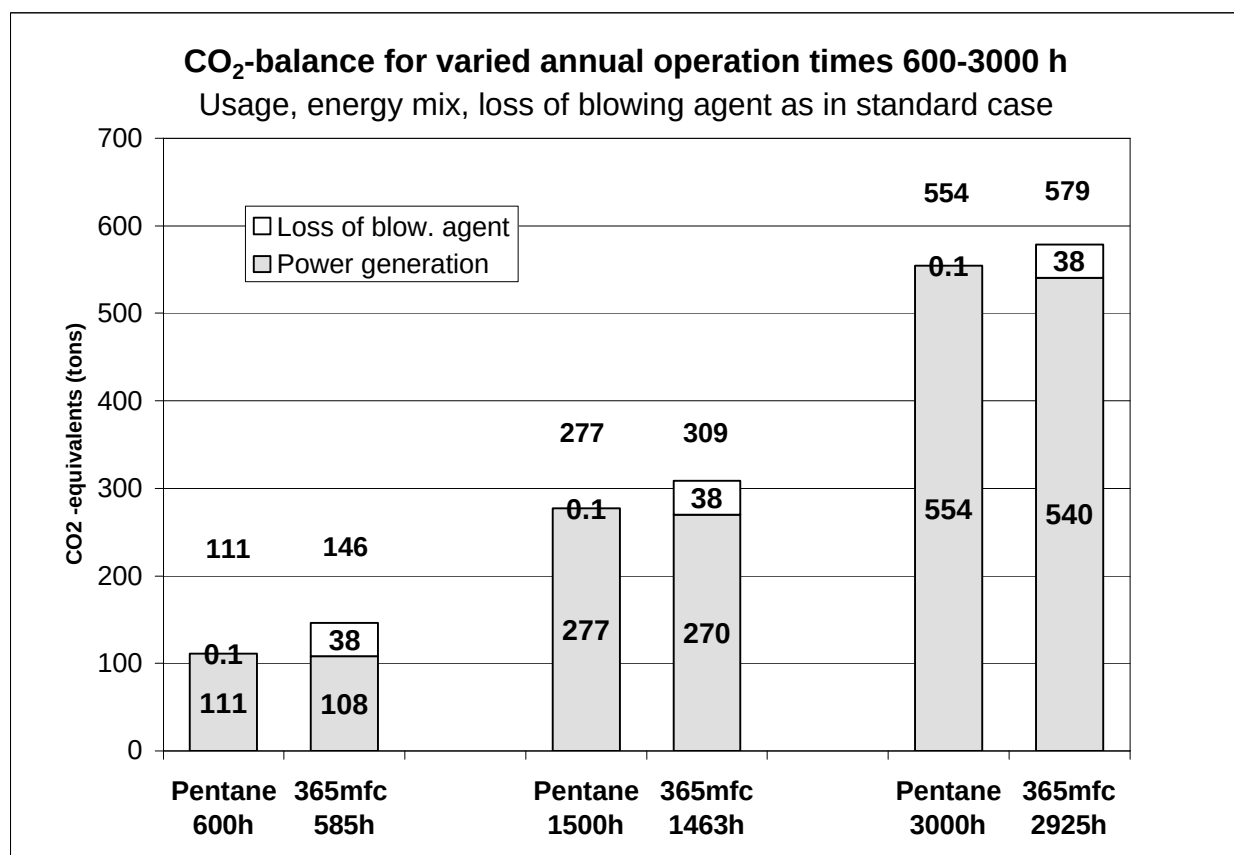


Figure 27: CO₂-balance under variation of the annual operation time of the refrigeration unit between 600 and 3000 hrs, lifetime (18a), energy mix (9a, diesel/electricity 75/25), total loss of blowing agent as in the standard case. The difference between HFC-365mfc and pentane decreases with operation time, but the HFC case never drops below the pentane case.

From Figure 27 can be observed that the difference between the HFC case and the pentane case are considerably greater for short operation times than with very long operation times. At 600 h/a operation of the refrigeration unit in the pentane case, the equivalent CO₂-emissions for the HFC alternative are 35 t or 30% higher. If the run-time is increased to 3000 h/a with pentane, the HFC case is only 25 t or 4 % higher. Even in the case of very long operation times and with the given boundary conditions, the equivalent CO₂ emissions in the HFC case remain higher than in the pentane case. This can be attributed to the fact that the blowing agent is emitted completely into the atmosphere in the process of disposal.

Equal equivalent CO₂-emissions for both cases would only occur if operation times would exceed 7500 h/a. For this, the refrigeration would have to operate almost all year round with diesel.

2. Diesel-only operation and CO₂-balance

During the second half of the vehicle lifetime outside Germany, the refrigeration unit is only operated with diesel. There are however vehicles within Germany which do not feature the bimodal cooling with the additional option of electric driven compressors. The electric drive for the compressor does not entail additional cost, but increases the weight of the refrigeration unit by 100 kg. In this case, the vehicle operator cannot use the much cheaper electricity option which also has the benefit of reduced CO₂-emissions.

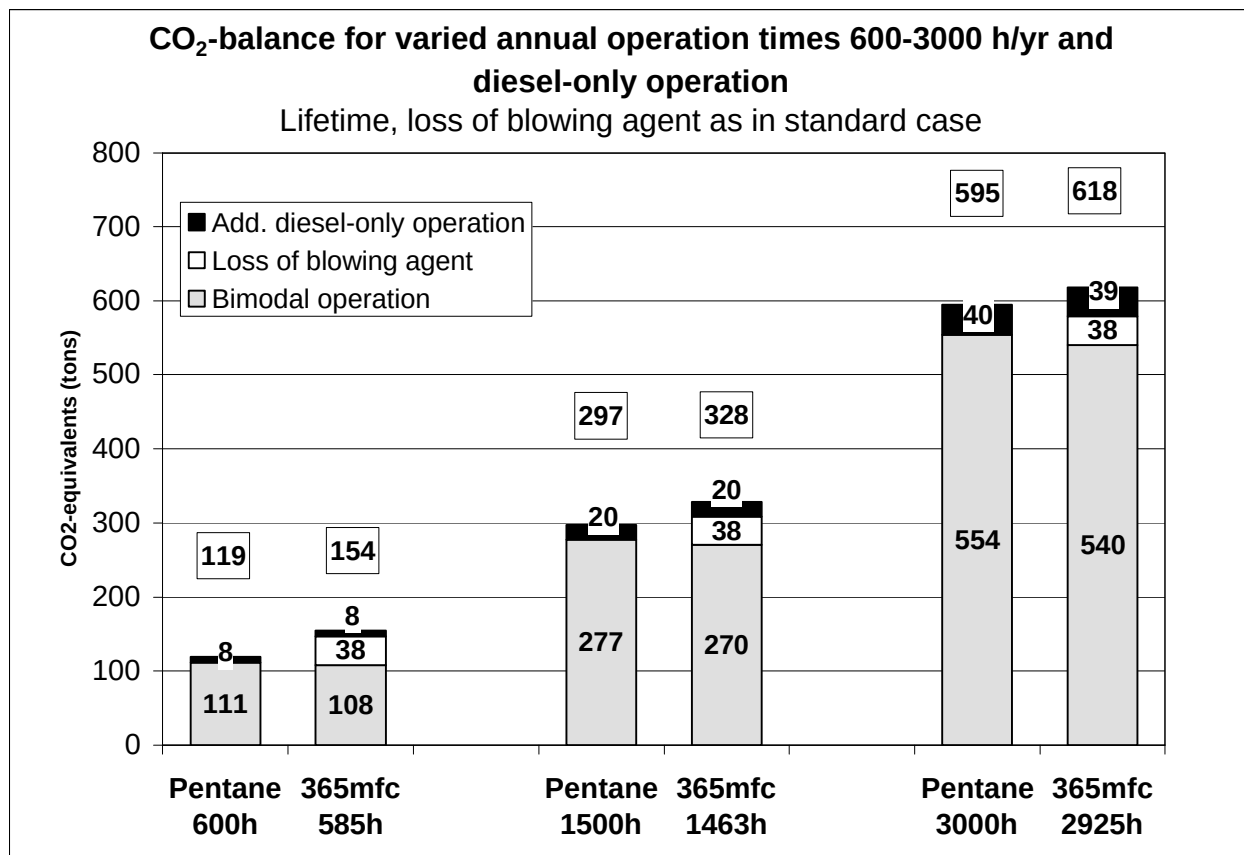


Figure 28: CO₂-balance (blowing agent plus emissions from operation of the refrigeration unit) for varied annual operation times (600, 1500, 3000 h/a) under bimodal operation or diesel-only operation. Lifetime (18 yrs) and loss of blowing agent as in the standard case. The CO₂-emission from bimodal (diesel and electricity) operation is represented by the lower element of the column, the top element shows the additional CO₂ emissions if the option of electric operation is not used. In all three categories of operation times, the value for the HFC case increases slower than the pentane case, but always remains above the pentane case.

Compared to the partial use of electricity for refrigeration, the sole operation with diesel during the 18 years of operation leads to higher equivalent CO₂ emissions in all three operation time cases (600 h/a, 1500 h/a, 3000 h/a). The additional emissions of the diesel-only operation of 8t, 20t and 39/40t respectively is represented by the higher element of the column. (Of course the lower value only applies under the precondition that the electricity originates from the specific

mix of power plants in Germany which results in a CO₂ emission factor of 0.58 kg CO₂/kWh and under the assumption that the refrigeration units use only 8.7 kW of electricity)

The CO₂ growth is slightly higher for the pentane case than for the HFC case, but the diesel-only operation during the 18 years of usage does not change the fact that the equivalent emissions from the HFC case are always higher than in the pentane case.

3. Reduced lifetime and CO₂-balance

Figure 29 shows a lower equivalent CO₂ emission for the refrigerated vehicle with pentane-blown insulation foam than for the one with HFC-365mfc blown foam in the standard case (18 years lifetime, 1500 h/a, bimodal energy mix 87,5/12,5 diesel/electricity). A variation of the operation time (Figure 27) maintained the CO₂ bonus of the pentane case. Figure 29 displays that this is also valid for a reduction of the lifetime from 18 to 12 years.

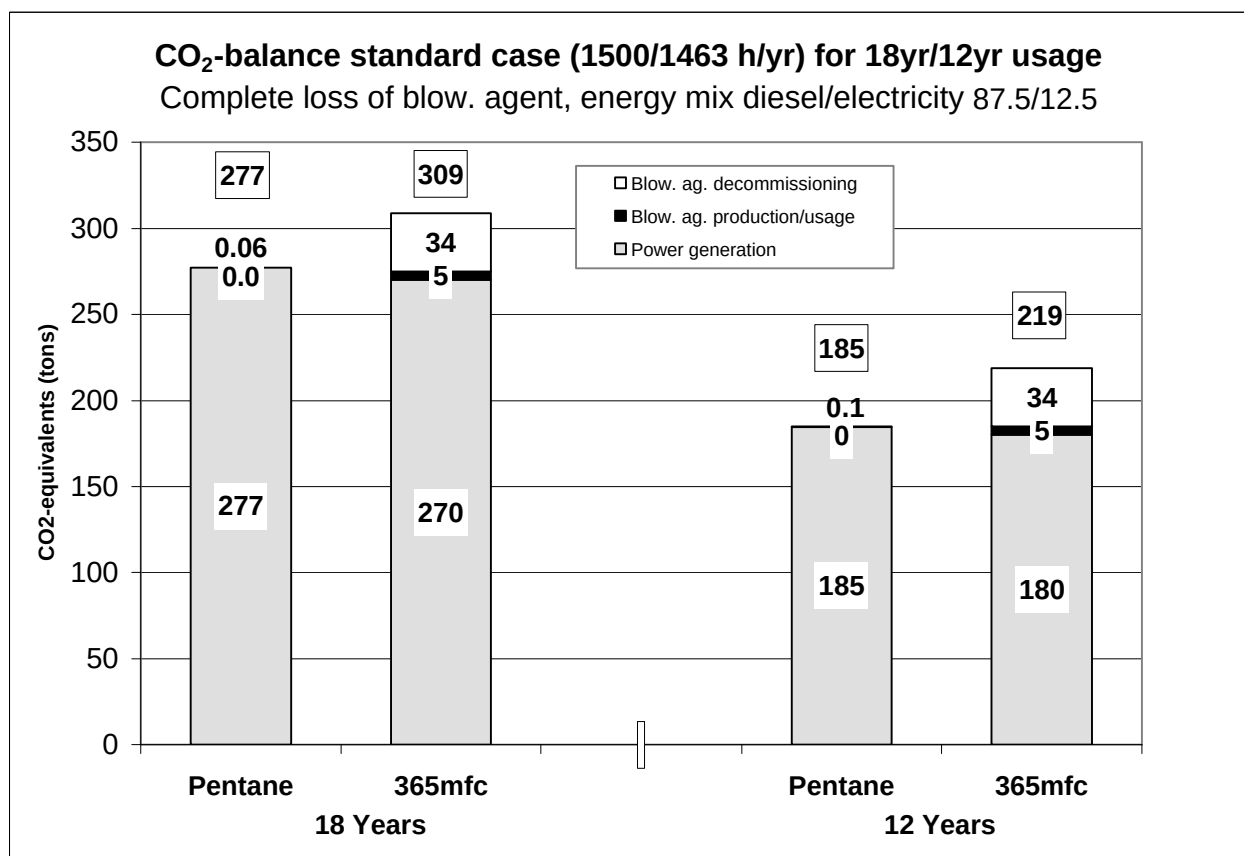


Figure 29: CO₂ balance for the standard case (1500 h/a) at a lifetime of 18 years (left columns) and 12 years (right columns). Energy mix diesel/electricity of 87.5/12.5. Complete loss of blowing agent. If lifetime is reduced by one third, the equivalent CO₂ emissions drop by one third for pentane in the standard case (from 277 to 185 t). In the case of HFC, the equivalent lifetime emissions drop by only 29% from 309 to 219 t because of the constant emission of blowing agent.

It can be said that the shorter the total compressor run-time (by shorter lifetime or lower operation time per year), the less the high equivalent CO₂ emissions of the HFC blowing agent can be compensated with the lower energy-related emissions. (A distinction between different annual operation times is not necessary since this would inevitably emphasize the beneficial properties of the pentane case over the relation shown in Figure 27.) It needs to be kept in mind that most of the

emissions occur at the end of the lifetime due to disposal of the foam without containment of the blowing agent while the emissions from production and operation are comparably low. Without emissions from the disposal, equivalent CO₂ emissions of the pentane and the HFC case would be equal.

4. Lower u-value of the HFC case and CO₂ balance

Despite the fact that PU insulation foam blown with HFC-365mfc has a λ value that is some 5 % lower than PU foam blown with c-/i-pentane, all previous calculations were based on a u-value for the refrigerated value that is 2.5% lower. Other than with foam panels, the u-value of the 3-dimensional construction of the refrigerated trailer is not proportional to the λ value of the foam but max. half of that.

The following examines what the effect of a u-value that is 5% lower and which results in a reduction of energy consumption by 5% would be on the total equivalent CO₂-emission of the HFC case.

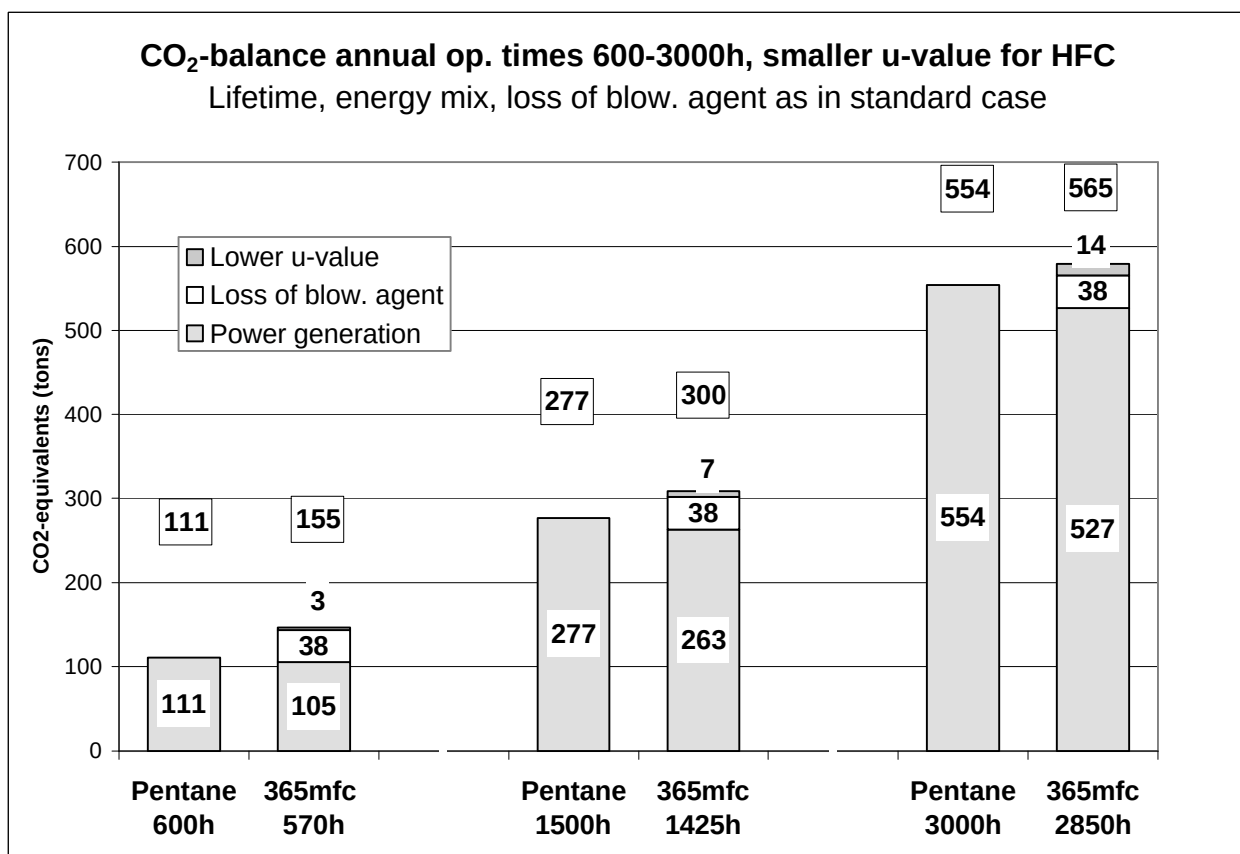


Figure 30: CO₂ balance of the annual operation time 600-3000 h in case of 5% lower u value (instead of 2.5% lower u-value) of the refrigerated vehicle insulated with HFC blown foam (lifetime, energy mix, loss of blowing agent as in the standard case). The equivalent CO₂ emission reduction from the lower u-value are represented as the upper element of the column. The numbers 3, 7 and 14 show the saved amount of CO₂ in tons.

From Figure 25 can be seen that neither in the standard case with 1500/1425 h/a operation time nor in the alternative cases with operation time of 600/570 h/a or 3000/2850 h/a, the accumulated equivalent CO₂ emission of the HFC vehicle drops below that of the pentane vehicle. In case of the extreme operation time of 3000/2850 h/a, the equivalent CO₂ reduction adds up to 14 tons, still

11 tons higher than in the pentane case. Only for operation times of more than 5000 h/a over a lifetime of 18 years, the emissions would be equal.

5. Division of CO₂- and CO₂-equivalent emissions between Germany and other countries

All calculations and diagrams so far were based on the real emission behaviour of typical refrigerated vehicles, which are operated in Germany for the first half of their lifetime and outside Germany for the remainder of the lifetime.

While emissions from operation of the refrigeration units occur inside as well as outside Germany, the losses of blowing agent are highly unequal. The production emissions of some 11 % are only caused in Germany, but the much larger share of 87% from disposal of the vehicle is emitted outside Germany. It is assumed that there are no methods for the containment or recapture of the blowing agent in the countries of disposal leading to slow dissipation of the blowing agent over decades from landfill sites.

For Germany, this division of emissions is a very practical solution, to put it cynical. The current interpretation of the Kyoto protocol supports this position by attacking the global climate problem with local (national) emission attribution and emission reductions. The 'advantage' for Germany is displayed in Figure 31.

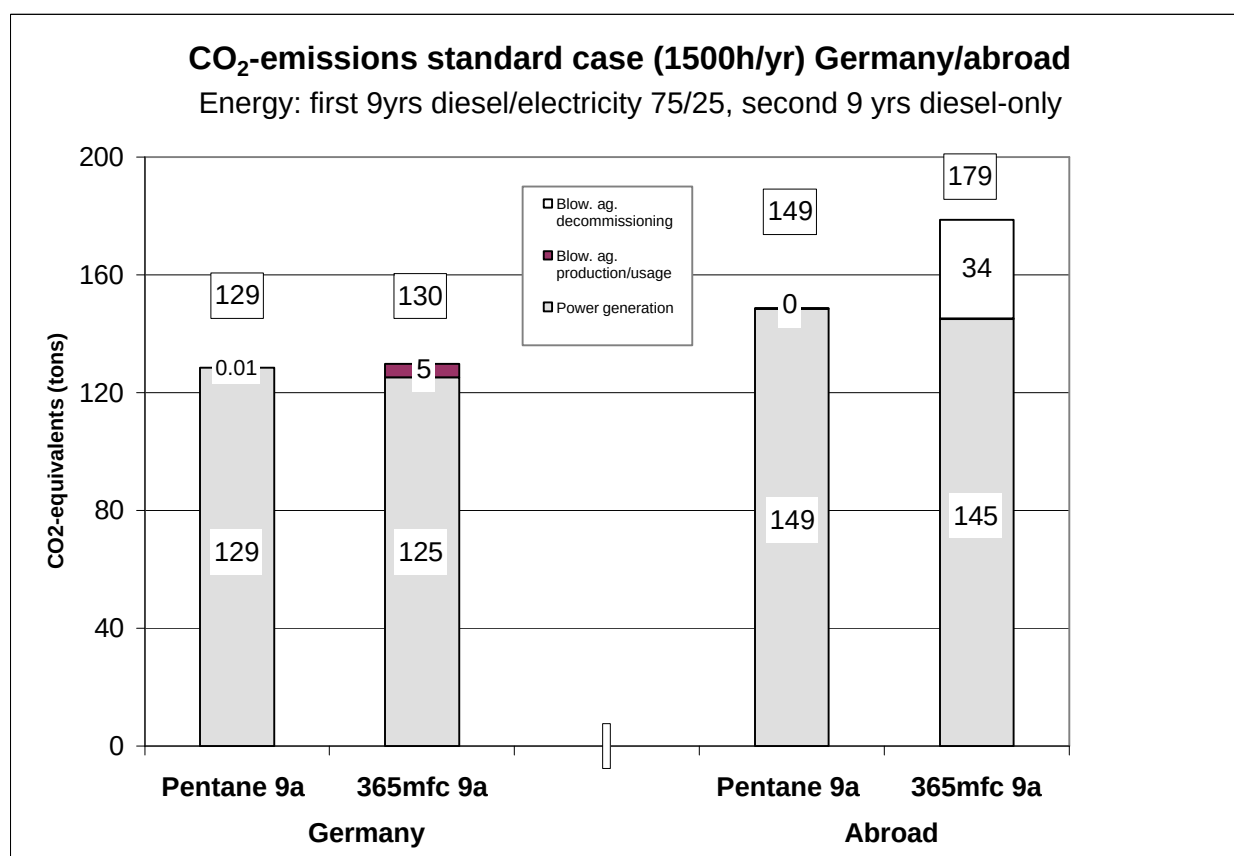


Figure 31: CO₂ emissions in Germany and abroad for the standard case (1500 h/yr). Energy mix in Germany in the first 9 years diesel/electricity 75/25, 10-18 year only diesel abroad. In Germany (left column) the CO₂ emissions from the HFC case are almost equivalent to those of the pentane case (130 to 129 t). Outside Germany (right columns), the CO₂ emissions in the HFC case exceed those of the pentane case by 20% (179 to 149 t). Reason: high emissions of blowing agent at disposal.

In Germany, the CO₂ and CO₂-equivalent emissions in the standard case (1500h/1425h annual operation time) of the refrigerated vehicle insulated with HFC blown foam are not much higher than of the vehicle insulated with pentane-blown foam. The production emissions of the HFC vehicle are not negligible, but they are almost overcompensated with the lower energy consumption of the refrigeration unit in the standard case.

Were HFC-365mfc introduced as blowing agent for the insulation foam of refrigerated vehicles on short notice, the situation represented in Figure 31 would apply. The regular flow of refrigerated vehicles out of Germany leads to almost the same inland CO₂ emission as for vehicles insulated with pentane blown foam. In addition to this, it avoids the need for reclaim and disposal facilities for such vehicles inside Germany.

6. CO₂-balances for disposal inside Germany with variations of the containment and recovery of the remaining blowing agent

What if the used vehicle sales into countries outside Germany would not continue in the present form or even come to a standstill?

In this case, all vehicles would need to be disposed of inside Germany. For chassis and refrigeration unit, this will not be a problem, since these consist of metals that can be easily recovered and recycled. More complex is the sandwich composite of steel sheets and PU foam that the cargo hold consists of.

With the technical guidelines for disposal of municipal (TA Siedlungsabfall), directions for the treatment of such waste already exist. Because of their high content of organic matter, the PU panels must not be disposed of in landfills. This can be solved by incineration of the foam. This is assumed for the future although the material recycling so far did not practice this.

It is not of secondary importance to this examination whether the incineration takes place in municipal waste treatment incinerators or in industrial furnaces. Only the amount of loss of blowing agent during the dismantling of the sandwich panels and the preparation for the incineration (removal of steel sheets, mechanical shredding of the pieces, transport etc.) of the foam is of relevance.

For the foam reaching the incinerator it can be assumed that 100% of the blowing agent in the foam is destroyed. In the process of dismantling and separation of steel and foam a loss of at least 10 % of the blowing agent occurs. Next to this optimal case, more realistic values of 20 and 30 % loss during the dismantling are taken into account. In other words, destruction rates of 90, 80 and 70% of the remaining blowing agent are used for further calculations.

The limited export of used refrigerated vehicles out of Germany entails a longer used period within Germany, but certainly not up to a total lifetime of 18 years. An assumption of a total lifetime 12 years for this case is more likely.

Figure 32 compares the equivalent CO₂ emissions of refrigerated vehicles over their lifetime of 12 years inside Germany and with a constant energy mix for the refrigeration unit of 75/25% relative to annual operation time of the refrigeration unit and various rates (70, 80 90%) of capture of the blowing agent at the disposal of the vehicle. Values given are normalised with emissions from

cooling/operation as well as total loss of blowing agent for the alternative case of a vehicle insulated with pentane blown foam.

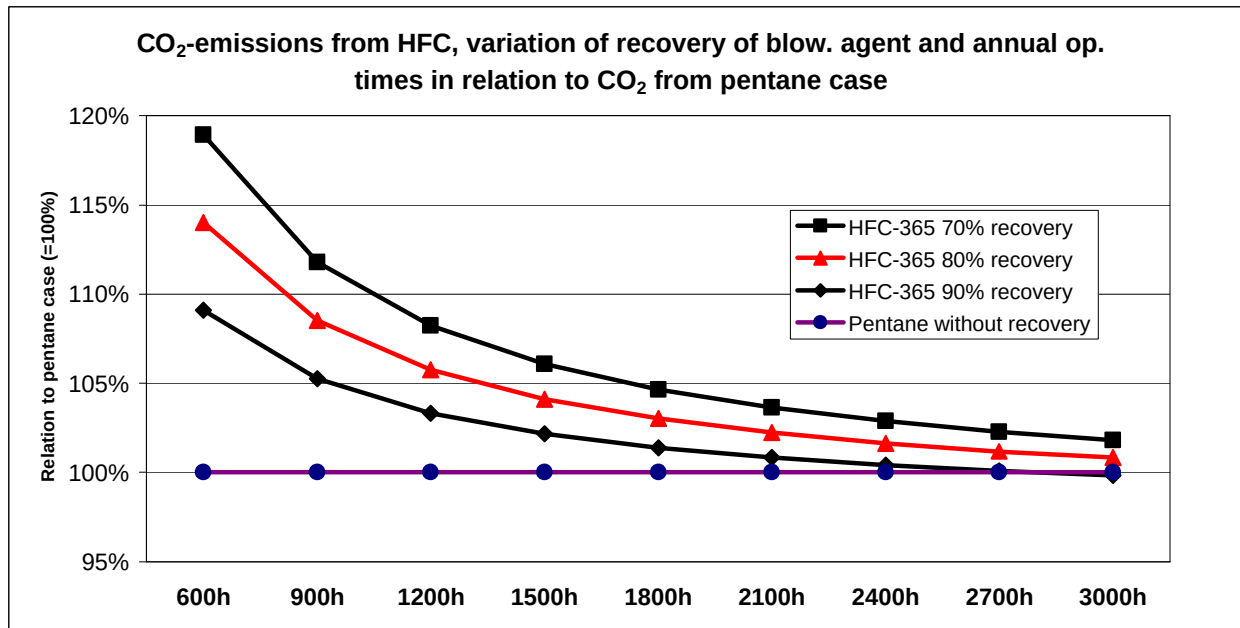


Figure 32: CO₂ equivalent emissions from HFC blown insulation foam in refrigerated vehicles under variation of recovery of the blowing agent and annual operation time of the refrigeration unit relative to CO₂ equivalent emissions from the pentane case. Lifetime (only in Germany) 12 years. Energy mix diesel/electricity 75/25. The HFC case can only underpass the CO₂ equivalent emissions from the pentane case if 90% of the blowing agent is captured and the refrigeration unit is operated for more than 2633 h/a.

It becomes clear that the equivalent lifetime emissions of refrigerated vehicles insulated with HFC blown foam are always higher than those with pentane blown foam as long as the annual operation time of the refrigeration system is lower than 2700 hours. Only beyond 2700 h/a and 2633 h/a operation time for pentane and HFC respectively, the total equivalent CO₂ emissions from the HFC case underpass those of the pentane case if a very optimistic destruction rate of the blowing agent of 90% is assumed.

7. Optimized CO₂ emissions for a HFC application in the model

A better CO₂-balance over the lifetime of the refrigerated vehicle can be demonstrated in the case of disposal in Germany if the difference between the u-value of the cargo hold insulated with HFC blown foam is 5% instead of 2.5% higher than with pentane blown foam. In such a hypothetical case, advantages of the HFC case would appear below an annual operation time of the refrigeration unit of 2700 h/a and below capture/destruction rates of 70% of the blowing agent (s. Figure 33)

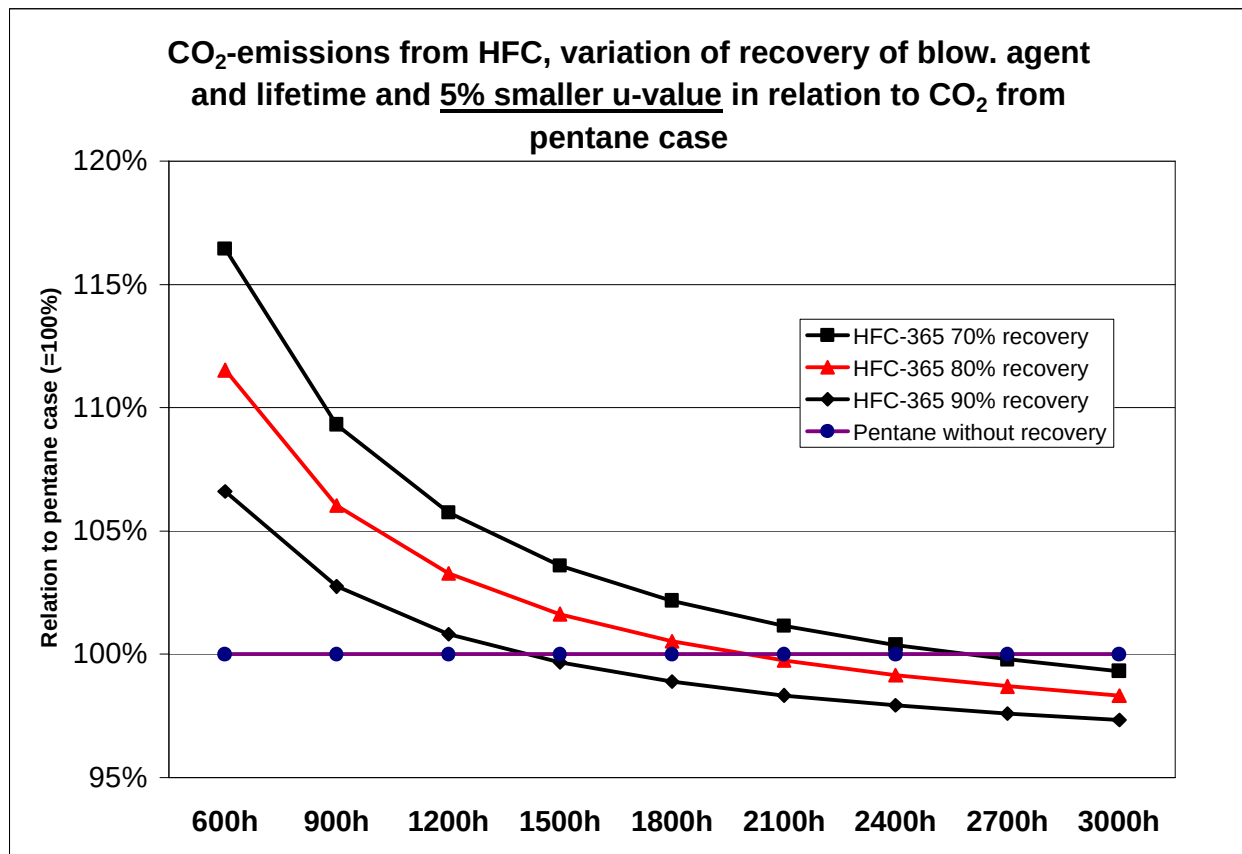


Figure 33: Equivalent CO₂ emissions over the lifetime of a refrigerated vehicle insulated with HFC blown foam normalized with the alternative of pentane as the blowing agent. In case of decreased u-value of the envelope of the cargo hold of 2.5% below the previous calculations, the total equivalent emissions of the HFC case drop below the pentane case at a capture rate of 70% already (high curve). At a capture rate of 90%, the equivalent CO₂ emissions drop below the pentane case at operation times of the refrigeration unit of approx. 1500 h/a (lower curve)

It needs to be noted that the last two cases displayed in Figure 32 and Figure 33 are only hypothetical model calculations as the underlying decommissioning of refrigerated vehicles does not and will for the foreseeable future not occur in Germany.

5.3.5 Summary

In the application example of refrigerated vehicles it was shown that

- even in case of rigorous limitation of thickness, HFC-free alternatives show a better GHG balance than insulation blown with HFC if the present disposal conditions for refrigerated vehicles (semi-mounted trailers) of virtually no recovery of blowing agent at the end of the life cycle remain;
- the GHG balance for the examined refrigerated trailers is basically in favour of the pentane-blown version. This advantage is however rather small in contrast to the previous comparison of insulation panels and can be reduced to an equal level with an increase of annual operation time of the refrigeration unit. The much lower environmental benefit of the c-pentane system is based on technology: it is a result of the very high weight of CO₂

from combustion (here of fuel) in comparison to the CO₂-equivalent contribution of the blowing agent. This great role of the fuel consumption is also represented in the dominance in the cost balance. Not only in the reference case but also in general, the operation costs for HFC systems are lower because the u-value and subsequently the energy demand of the refrigeration system is lower.

- As long as the sensitivity analysis is based on presently realistic conditions of total loss of blowing agent at the end of lifetime and sensible operation times of the refrigeration system, the ecological advantage of a cargo hold insulated with cyclo-pentane-blown PU foam remains.
- If the refrigeration system operates for less than the typical 1500 h/a, the GHG balance improves in favour of the c-pentane case in absolute and relative terms. With a doubling of operation time to 3000 h/a, the relative additional emissions of CO₂ equivalent in the HFC case recede relatively and absolutely compared to the pentane case without dropping as far as the latter (equal level would only be achieved with almost continuous operation)
- If the refrigeration system is operated with diesel only i.e. without the use of electrical power at standstill times, the CO₂-emissions from combustion increase. This leads to an even lower weighting of the climate-relevant HFC blowing agent in the total GHG balance. This means – under otherwise unchanged boundary conditions- that the advantage of c-pentane diminishes without getting lost completely.
- Even at a hypothetical improvement of the u-value of the refrigerated vehicle insulated with HFC-blown foam of additional 2.5% to 5% compared to pentane, the pentane case would still result in less total CO₂-equivalent emissions. Only in case of operation times for the refrigeration system of more than 5000 hours over 18 years an equal level would be reached.
- The environmental benefit of insulation systems with pentane-blown foam in comparison to HFC blown foam will only become smaller or negligible if the present disposal conditions for old refrigerated vehicles are changed or if the perspective on refrigerated vehicles is changed.

From the last point results the demand to see the vehicle not in the unity of the total life cycle but separately for the first (German inland) and the second section abroad. As a matter of fact, refrigerated vehicles are sold abroad after approx. 9 years so that no disposal losses of blowing agent occur within Germany. If the first German inland life phase is considered independently, the environmental equal status of pentane and HFC can be achieved in the standard case (1500 h/a) already –of course with increased disadvantages of the HFC system abroad.

If the life cycle of the refrigerated vehicle is not split but if it is assumed that the disposal of insulation foam improves fundamentally in the German inland, then the GHG balance between HFC and pentane blown insulation foam would change considerably. If a 70% decomposition of the insulation foam to be disposed is implied, (i.e. 30% loss of the remaining blowing agent at dismantling of the refrigerated cargo hold), an equal status in terms of CO₂ equivalent emissions can be achieved at an annual operation time of the refrigeration unit of 2700 h, a value that may be high but not completely unrealistic.

5.4 Outlook

In this chapter, it was shown that

- PU rigid foams blown with pentane display a better GHG balance than products with HFC-365mfc as blowing agent because higher energy consumption of pentane systems is compensated with emissions of blowing agent with high GWP in the HFC case.
- the special design of future disposal paths (incineration, deposition, material recycling) of PU rigid foams and subsequent emissions of blowing agent is of central importance for the result of the analysis while the paths are generally not defined so far.

The question arises in how far the results for the two cases treated in this section could be transferred to other related applications. According to Öko-Recherche (1999), HFC (134a, 245fa and 365mfc) are potentially used in the following processes for the production of PU rigid foam:

- PU – continuous insulation panels
- PU – discontinuous insulation panels
- PU – block foam
- PU – foam spray
- PU – cast foam

Roof insulation panels are produced as continuous panels while sandwich elements e.g. for refrigerated vehicles are produced in a discontinuous process.

While spray and cast foam are applied locally by the end user, e.g. at building sites inevitably need to comply with stricter safety requirements in terms of flammable blowing agent. While this puts pentane as blowing agent in question for such applications, the results of this section are likely to be transferable to almost all industrial production processes of PU insulation panels and block foam. In discontinuous processes, there are virtually no technical objections prohibiting the application of pentane. At small throughput of PU foam in small enterprises (Albach 2002), the situation may occur that the additional investments for fire and explosion protection of facilities for the use of pentane may render the operation uneconomical since the savings for the cheaper blowing agent per facility are small in comparison to the additional investments

6 Application B: supermarket refrigeration (interconnected system)

6.1 Introduction

In the course of this chapter GHG emission levels for different technologies used for cooling applications in supermarkets are compared including a number of sensitivity analyses. In its beginning some background information on the German grocery sector and its most common refrigeration sectors is presented.

6.1.1 Grocery

Modern groceries cover the market in a great variety of shop formats. Depending on the location (city centre, suburb, residential area, village), customer structure and competition situation, the known German chains (e.g. Rewe, Edeka, Spar, Metro, Aldi, Tengelmann, Lidl) and shop owners use standardised shop concepts which are adapted if necessary.

Table 29 and Table 30 give an overview over the most important shop formats and market shares in Germany. Compared to the European neighbours, the German grocery trade has a special structure. Since approx. 2 decades, the market is dominated by price-aggressive grocery discounters (e.g. Aldi, Lidl and Penny). The number of small self-service markets is still relatively large, but suffers from a dramatic decline for some time already. Really large self-service food and non-food stores are still rather rare which can be explained with the restrictive policy on building permits in the periphery of cities.

Table 29: Definition of different German grocery stores (EHI, 2001)

Store type	Definition	Size [m²]
Superstores	Self service store with groceries and a broad range of durable goods and consumer goods	> 4000
Consumer markets	Self service store with mainly groceries and a small range of durable goods and consumer goods	> 1500
Supermarkets	Self service grocery retailer with fresh goods and less than 25% of the shop for non-food articles	> 400
Grocery discounter	Self-service retailer with focus on fast moving articles	400 – 800
Grocery market	Self-service grocery retailer	< 400

Table 30: Market shares and important characteristic figures for shop formats of German grocery stores (EHI, 2001) (only fraction of grocery departments for 1 and 2)

Retailer type	Number	turnover [10 ⁹ €]	Retail area in Mio m ²	Average retail area [m ²]	Turnover per retail area [€ / m ² a]
1. Superstores	681	13.7 ²¹	2.3	3392	6000 ²¹
2. Consumer markets	1682	16.1 ²¹	2.6	1552	6000 ²¹
3. Supermarkets	9230	30.1	6.9	746	4400
4. Grocery discounter	12770	37.7	6.9	543	5500
Subtotal	24363	97.6	18.7	768	5200
5. Self-service stores below 400m ²	45900	17.1	7.4	161	2300
GESAMT	70263	114.7	26.1	372	4400

6.1.2 Refrigeration systems in grocery stores

The demand for refrigeration in grocery stores is diverse and ranges from deep-frozen goods over dairy products, meat and cheese to fruit and vegetables. In addition to this, there is the demand for refrigeration of goods for immediate consumption e.g. ice cream and beverages and temporary storage. Shop format and customer structure is hence decisive for the distribution of demand fields for refrigeration.

It is therefore not surprising that the technical solutions for these refrigeration applications are not uniform but rather adapted to format and location of a shop. Three basic types of refrigeration systems are commonly used in groceries:

1. plug-in refrigeration appliances with low investment cost and great flexibility in placing but relatively high energy consumption
2. single refrigeration appliances with external condenser (also comparably flexible in the choice of location)
3. refrigeration systems with central refrigeration unit and refrigerant tubes to the separate appliances (higher investment cost and lower energy consumption)

Beyond this, there is also demand for the air-conditioning of the retail area, especially if a large number of plug-in refrigeration appliances produces high heat loads inside the building. Air-conditioning of the retail area will however not be examined in this study.

In comparison to central refrigeration systems (3), the average energy consumption of appliances with external condenser (2) is 20-40% lower [BEWAG, 1996]. Plug-in refrigeration appliances (1) consume some 10% more energy than those with external condenser (2) [Eurovent-Certification, 2001]. In practice, shops are frequently equipped with two or three of the technologies. Generally, the trend for larger shops is towards centralised refrigeration systems.

²¹ Own estimates of the division within the group superstores/consumer markets

Energy consumption for refrigeration in grocery is subject to a variety of influence parameters. Figure 34 represents the electricity consumption for the shop format “Penny Market” of the REWE group which has kindly given the permission to use the remotely collected electricity consumption values of the refrigeration appliances in some of their shops in 2001 for this examination. It has become common practice to give the energy consumption per meter of refrigerated appliance to level out effects of different retail areas and different densities of refrigeration applications in the data sets. It can be observed that the top decile exceeds the low decile by more than 100%. Normalising the annual electricity consumption values for retail area of the same group of stores results in a similar picture (Figure 35). These differences exist despite the uniform format of the German “Penny” markets.

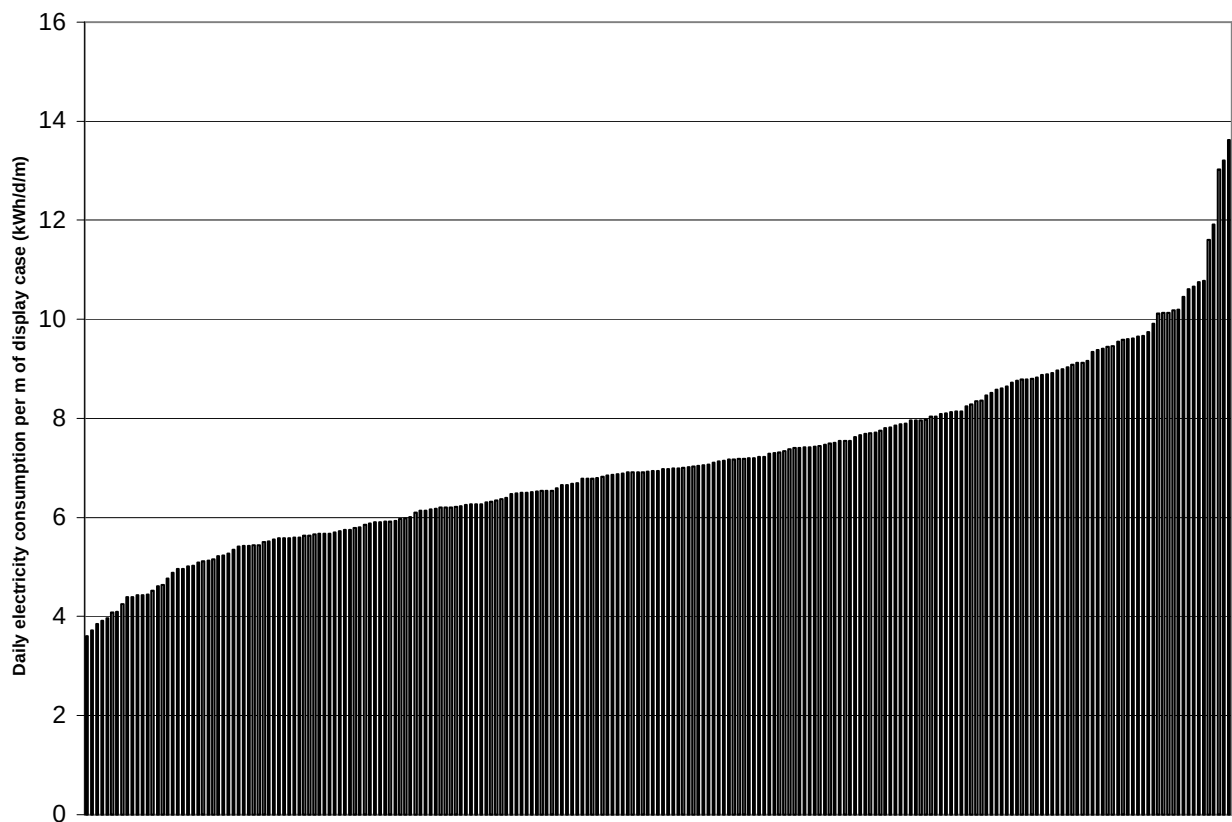


Figure 34: Daily electricity consumption for refrigeration in 226 “Penny” discount markets normalised per meter of refrigerated appliance in the year 2001

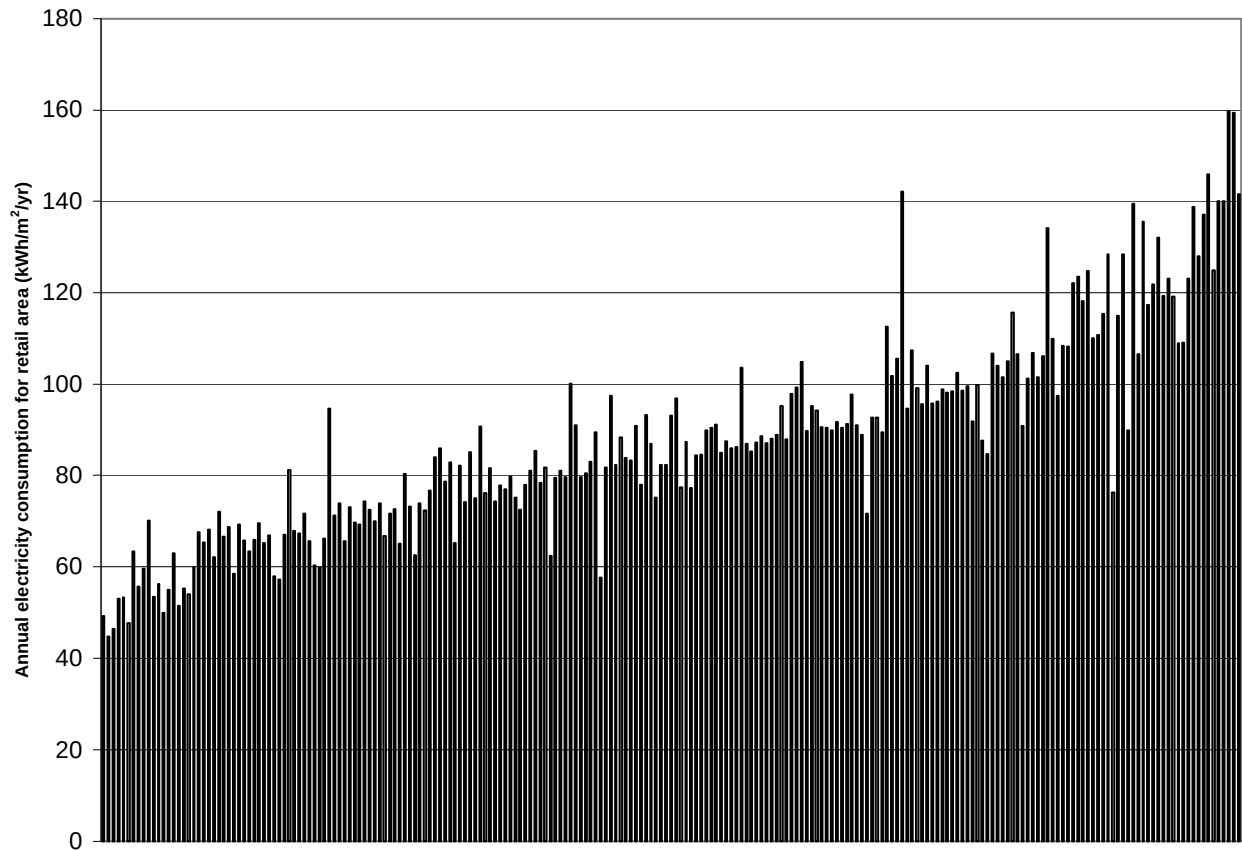


Figure 35: Annual electricity consumption for refrigeration in 226 “Penny” markets in 2001 (same order as in Figure 34) normalised for retail area.

Typically, refrigeration consumes between 45 and 70% of the electricity of a grocery store [BEWAG, 1996]. Relative to the turnover per retail area (5000-6000 €/m²), the annual electricity costs for refrigeration of 4-7 €/m² (in the data of REWE) are in the order of a few per mil. Investment costs for refrigeration appliances takes a share of approx. 40% of the costs for the outfit of a new store (300-700 €/m² [EHI, 2002]) and generate between 0.5 and 1% of the turnover per retail area over the lifetime, depending on the accounting method and lifetime of the appliance. These figures emphasize that the cost of refrigeration is of minor importance to the cost calculation on groceries next to other expenses for goods purchase, staff and rent. On the other hand it has to be recognised that the margins in the German retail trade are in the order of a few per cent which means that savings even in the order of per mil which may be realised with simple measures on refrigeration equipment are interesting as long as these do not lead to decreased shelf life, appearance and accessibility to the goods thus compromising the economic result of the store.

Which influence factors are decisive for the energy consumption for refrigeration in the retail sector? The following items need to be mentioned:

- Demand for refrigerated appliances for different products in the categories refrigeration of fresh goods between –1 and +12°C and freezing for deep frozen goods below –18°C as well as refrigerated storage space.
- Chosen mix of basic technologies (plug-in, external condenser units, refrigeration systems)
- Special design of refrigeration appliances (e.g. horizontal chest freezer with/without day cover, vertical with/without doors, lighting)

- Design and lay-out of the system (e.g. dimensioning, average temperature of condenser and evaporator)
- Choice and adjustment of control system (e.g. temperature of intake / exhaust air of the refrigeration appliance, defrost cycles)
- Choice of technical detail aspects (electrical or gas defrost cycle, direct refrigerant evaporation or secondary carrier loops)
- Maintenance state
- Ambient climate and average internal temperature of store

Such distinct fluctuations in the specific energy consumption as can be observed in the data set from REWE are certainly a result of a combination of the factors enumerated above. Within the framework of this study these figures cannot be analysed in depth, but the fact that even in a relatively homogenous and well-monitored group of grocery markets, deviations of the specific energy consumption of more than 100% occur needs to be kept in mind for the following consideration on the influence of refrigerant on the energy consumption.

6.2 Refrigeration technology

6.2.1 Choice of refrigerant

Refrigeration applications in the grocery sector require a refrigerant for a thermo-dynamical cycle of evaporation and condensation to effect a temperature reduction in a refrigerated appliance. For this, the non-toxic and non-flammable CFC-12 and HCFC-22 as well as the blend of CFC and HCFC in R-502 used to be applied. Due to their ozone-depleting effect, these have been banned for application in new installations. Today, conventional replacements such as HFC-134a and the HFC blends R-404A and R-507 are commonly used.

In addition to this, ammonia, CO₂ and hydrocarbons (HC) such as propylene, propane, butane are available as alternative fluids which would completely avoid emissions of HFC. HC and ammonia require a secondary carrier loop instead of direct evaporation due to their toxic and flammable properties. This carrier loop connects the refrigeration unit with the refrigerated appliance with a fluid, e.g. sole or ice slurry. The refrigerant then remains in the primary loop of the refrigeration unit that is installed safely away from the retail rooms. The additional heat exchanger and pump in the secondary loop increase the investment cost as well as the energy consumption of the system. This technology may also be applied to HFC systems in order to reduce the total refrigerant charge of the system to some 10-20%.

In practice, new systems in Germany commissioned in the last few years were mostly direct-evaporator systems with HFC-404A as the refrigerant. Under the regulations of Switzerland, Luxemburg and Scandinavia, where the use of HFC-404A is strictly limited, this is completely different. New systems in these countries are preferably built with ammonia, small amounts of HFC or to a lesser extent HC as the refrigerant with a secondary carrier loop.

Even without ozone depleting properties, HFCs are relevant to the environment due to their greenhouse gas potential (s. section 4) Especially in the rough environment of everyday use in highly complex tubing systems, it is a significant technical challenge to maintain leakage rates under a few per cent per year. Typical refrigerant leakage rates are 10% per year [ILT, 1999] in addition to the loss of refrigerant at the end of the lifetime.

6.2.2 Model technologies

Within the framework of this study, eight different technologies for supermarket refrigeration systems are examined, all of which have reached a state of market maturity. Especially the technologies 1, 2 and 5 have a significant market share in Europe. In Germany, almost all new systems are based on technology 1. Experiences with secondary carrier loop systems in Germany are virtually all from the time of market introduction of sole systems when considerable problems with reliability of the sole circuit existed. In systems which were realised in other countries since, these problems were solved and do not occur any more.

9. Direct evaporation HFC-404A (reference case)
10. Secondary carrier loop system with sole and HFC-404A in the primary cycle
11. Secondary carrier loop with CO₂ and HFC as the primary refrigerant
12. Secondary carrier loop system with CO₂ and propane as primary refrigerant
13. Secondary carrier loop system with sole and ammonia as primary refrigerant
14. Direct evaporation system with CO₂ for freezers and a HFC-404A secondary carrier loop system with HFC-404A as primary refrigerant for refrigeration
15. Direct evaporation of CO₂ for freezers and direct evaporation HFC-404A for refrigeration
16. Direct evaporation of CO₂ for both freezers and refrigerators (supercritical)

1. Direct evaporation HFC-404A (reference case)

Refrigeration systems with direct evaporation of HFC-404A are the standard technology applied in German supermarkets at present. They combine low investment cost with comparably low energy consumption. Main drawback from the environmental point of view are the large charges of refrigerant in combination with rather large leakage rates resulting from long pipes and numerous connectors leading to high annual losses of refrigerant.

2. Secondary carrier loop system with sole and HFC- 404A in the primary cycle

In secondary carrier loop systems, the amount of refrigerant is reduced by some 80% by using a carrier fluid to transport the cooling energy from the refrigeration unit to the appliance. The carrier fluid is cooled down to the desired temperature in a heat exchanger connecting the secondary loop to the conventional thermodynamical primary cycle with HFC-404A as the refrigerant. Investment costs rise by 15-25% over the reference case because of the additional heat exchanger and the increased tube diameters. As a consequence of the reduced efficiency (heat exchanger) and increased energy demand for pumping of the secondary fluid, the energy consumption increases by 15-25% (figures from: [Linde 1997])

3. Secondary carrier loop with CO₂ and HFC as the primary refrigerant

If the sole in the secondary loop is replaced with CO₂, the following advantage can be realised: investment and energy consumption costs remain below option 2 with +15 and +10% respectively. This is mainly due to smaller diameters of the piping in the secondary loop and smaller pump loads (figures taken from [Kauffeld et al. 2002]; personal communication with [Haaf 2003])

4. Secondary carrier loop system with CO₂ and propane as primary refrigerant

Propane in the primary cycle of supermarket refrigeration systems displays equivalent characteristics in view of investment cost (+20%) and energy consumption (+10%) as option 3. The disadvantage of the flammable refrigerant propane is opposed to the low GHG potential (figures taken from: [Kauffeld et al. 2002], personal communication with [Haaf 2003])

5. Secondary carrier loop system with sole and ammonia as primary refrigerant

An additional technology applied in practice is a primary cycle with ammonia and a secondary carrier loop. In comparison to propane ammonia has a higher COP. Certain materials such as copper have to be avoided in the installation. Because of the toxic properties of ammonia, an additional cycle is normally used for the energy transfer on the condenser-side of the system thus entailing increased investment (+20-35%) and energy costs (10-20%) over the reference case (figures taken from: [Linde 1997], [Haaf 1998]).

6. Direct evaporation system with CO₂ for freezers and a HFC-404A secondary carrier loop system with HFC-404A as primary refrigerant for refrigeration

Only recently supermarket refrigeration systems with CO₂ as the directly evaporating refrigerant have become available. These are based on a special cascade heat exchanger. The refrigeration system uses HFC-404A and a secondary sole carrier system. Investment costs and specific energy consumption are approx. 10% higher than in the reference case (figures taken from Hienbokel [2001] and personal communication with Haaf [2003]).

7. Direct evaporation of CO₂ for freezers and direct evaporation HFC-404A for refrigeration

In this system, CO₂ also evaporates directly in the freezer via a cascade heat exchanger. Refrigeration is provided with direct evaporation from a HFC-404A cycle. The electricity consumption is the same as in the reference case and the investment cost increases by some 2% (figures taken from [Heinbokel 2001] and personal communication with [Haaf 2003]) The charge of the HFC-404A cycle is reduced by 50% and the leakage rate is 25% lower than in the reference case.

8. Direct evaporation of CO₂ for both freezers and refrigerators (supercritical)

This system is based on a description from [Girotto et al. 2003], in which refrigeration is provided from a supercritical CO₂ cycle while low freezer temperatures are provided with a 2 step cascade with CO₂ as refrigerant. Electricity consumption is stated to be 8% higher than the reference system, investment costs increase by 10%.

6.3 Reference market

As a reference, a supermarket refrigeration system for a retail area of 1000 m² of a representative supermarket in Germany is defined and examined. The design of the refrigeration system depends on a number of factors, which are difficult to represent in a model calculation. The best approach is to use a large data set derived from real supermarkets that best cover the whole range of factors. For this, the data from the REWE group (many small markets and a high share of plug-in freezers) and another large German retailer (with larger store formats and generally central refrigeration systems for both freezers and refrigerators) is weighted for the retail area. Table 31 presents an overview of the determined figures for different store formats. In the weighting process, the store formats were weighted for their importance on the German market. These figures form the basis for the definition of the hypothetical reference system, which serves as a reference for the comparison between the different alternatives (Table 31).

Table 31: Overview over averaged raw data for different shop formats of the REWE group and an additional large German retailer

Shop format No.	Retail area [m ²] (Food)	HFC system charge [kg]	HFC-density [kg/m ²] (food area only)	Electricity for refrigeration system [kWh/m ² a] (food area only)
1	504	125	0.248	155
2	574	63	0.110	93
3	813	139	0.171	111
4	555	130	0.234	166
5	1295	161	0.124	239
6	8000	1400	0.175	188
7	3604	950	0.264	223
8	1156	270	0.234	235
Weighted average	1385	265	0.188	150
For comparison: average	2063	405	0.195	176

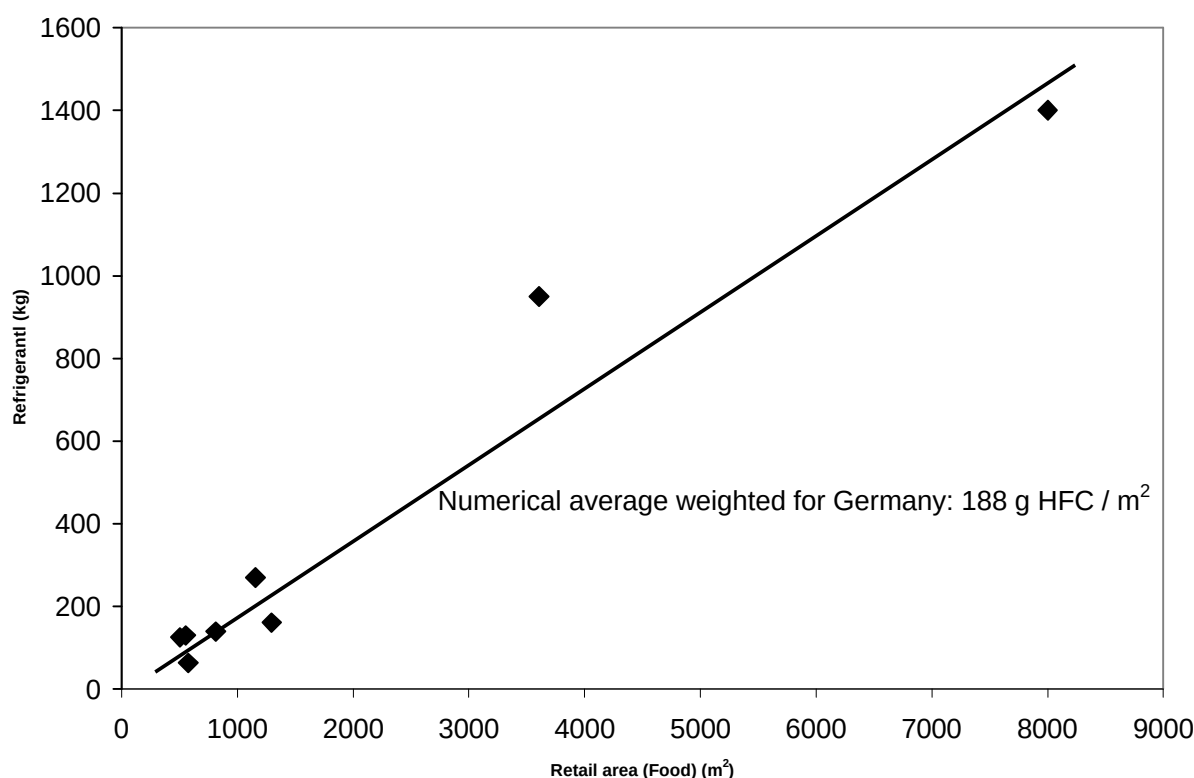


Figure 36: Relation between the food retail area and installed HFC refrigerant in centralised refrigeration units for different store formats of the REWE group and another large German retailer

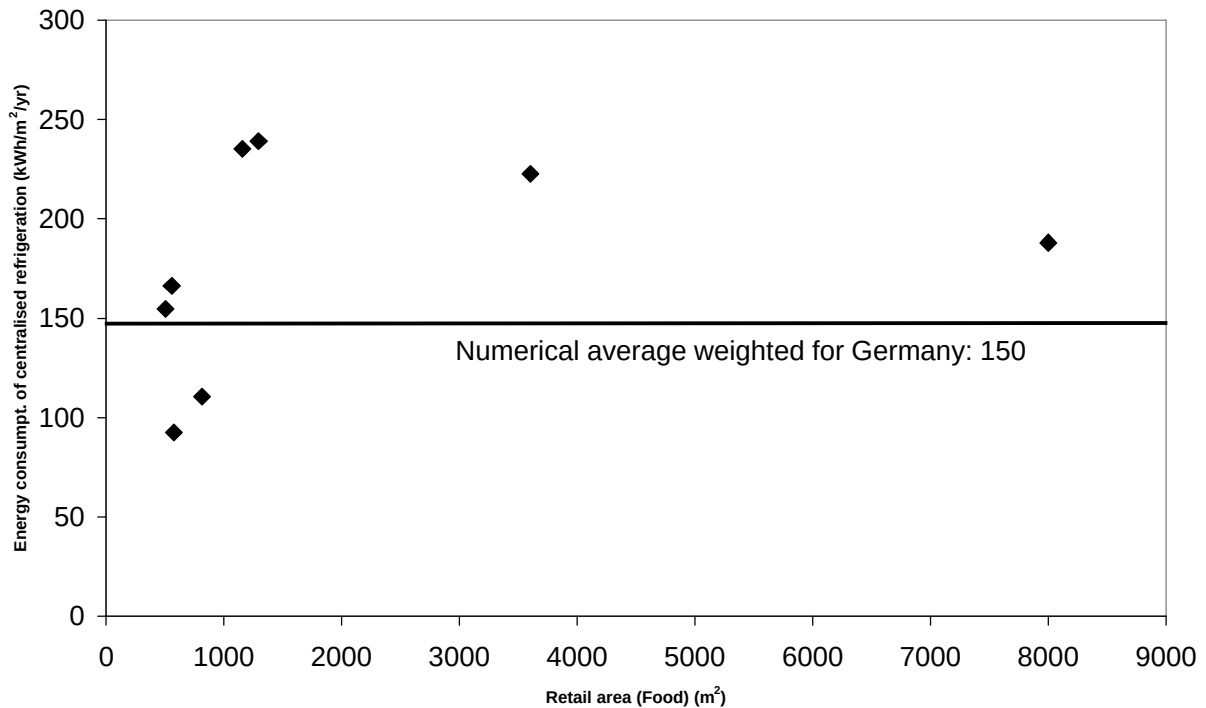


Figure 37: Relation between the retail area and the annual energy consumption of centralised refrigeration units for different store formats of the REWE group and another large German retailer

For a comparison, the numerical averages of the store formats examined are given. These result in a shift from the real grocery store structure towards larger formats and more central refrigeration systems without significant impact on other key parameters such as the specific refrigerant charge or electricity consumption. These values are displayed in the diagrams of Figure 36 and Figure 37.

6.4 Relevance of emissions for Germany

The relevance of direct (refrigerant) and indirect (CO_2 from electricity production) emissions from centralised refrigeration units in German supermarkets can be expressed via the total retail area of 18,7 Mio m^2 of supermarkets with centralised refrigeration units ($>400\text{m}^2$) and the respective area index. For the data of this sector, the share of the food retail area can be assumed to be 95%. Transferring the specific weighted electricity consumption of 150 $\text{kWh/m}^2\text{a}$ (food, Table 31) to the respective sector of the grocery retailers, the total consumption of 2.7 TWh/a for centralised refrigeration units can be calculated. [DKV 2002] estimates a total of 6.3 TWh for all commercial refrigeration, which leads to annual CO_2 emissions of 1.6 Mt if the average emission factor for electricity generated in Germany of 0,58 $\text{kg CO}_2/\text{kWh}$ is assumed. In a hypothetical park with only HFC as refrigerant in the centralised refrigeration units, 10% annual leakage losses, a weighted refrigerant charge density of 188 g/m^2 (representing a total charge of 3300 tons), the annual emissions can be calculated to be 330 t HFC. At a GWP pf 3260 for HFC-404A, the emissions come to 1.1 Mt CO_2 equivalent in Germany and is therefore of the same order of magnitude as the indirect emissions. A more detailed examination of the energy and GHG balances will be conducted in the following.

6.5 Modelling

The systems are characterised by a combination of relative properties and absolute data for a reference system (1) of a representative German reference supermarket. The relative properties are summarised in Table 32 and are based on information from Linde AG [Linde 1997, Heinbokel 2001, personal communication S. Haaf 2002, 2003], for the material density (mass of refrigeration installations incl. refrigerated appliances per m² of retail area) from [Frischknecht 1999b] and on own estimates. Absolute data for the hypothetical reference system are represented with the respective source in Table 33. The emission rate of 11.5% includes losses during charge, operation (incl. maintenance and repair) and at disposal and lies towards the lower limit of the values given by the IPCC in its Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories (2000) of 10-30% for this sector.

Table 32: Relative properties of the different options for centralised refrigeration systems in supermarkets

	Direct evaporation HFC-404A (reference case)	Secondary carrier loop system with sole and HFC-404A in the primary cycle	Secondary carrier loop with CO2 and HFC as the primary refrigerant	Secondary carrier loop system with CO2 and propane as primary refrigerant	Secondary carrier loop system with sole and ammonia as primary refrigerant	Direct evaporation system with CO2 for freezers and a HFC-404A secondary carrier loop system with HFC-404A as primary refrigerant for refrigeration	Direct evaporation of CO2 for freezers and direct evaporation HFC-404A for refrigeration	Direct evaporation of CO2 for both freezers and refrigerators (supercritical)
Electricity consumption	100	120	110	110	115	110	100	108
Investment cost	100	120	115	120	127,5	110	102	110
Maintenance cost	100	200	200	200	200	150	125	125
Leakage rate of refrigerant	100	100	100	20	20	100	75	100
Refrigerant density	100	20	20	10	10	20	50	50
Material density	100	150	140	150	160	120	100	100

Table 33: Absolute properties of the hypothetical reference system

	Value	Source
Electricity consumption	150 kWh/m ² a	Weighted average of the formats at Rewe and a second large German retailer
Investment cost	100 €/m ²	Rewe
Maintenance cost	2 €/m ² a	Rewe
Leakage rate of refrigerant in service, operation and dismantling	11.5 %/a	ILT (1999) + 15% disposal losses spread over the lifetime
Refrigerant density	188 g/m ²	Weighted average of the formats at Rewe and a second large German retailer
Material density	2.3 kg/m ²	Frisknecht (1999a/b)
Lifetime	10 years	Rewe

6.6 Standard case

CO₂ emissions

For the standard case described above, the GHG emissions of the separate technologies are summarized in Figure 38. It can be seen clearly that the reference technology (direct evaporator HFC-404A) causes greater GHG emissions under the standard assumptions of the comparison. The comparably high emissions of refrigerant from the direct evaporator system overcompensate the emissions for higher electricity consumption in the alternative cases. Emissions from production are of minor relevance as they only cause 0.3-0.5% of the total lifetime emissions.

The centralised refrigeration system with primary refrigerant HFC-404A and secondary carrier loop reduces overall lifetime emissions by 13% compared to the reference case. Improvements between 17 and 20% of the emissions can be achieved with the HFC-404A system and CO₂ as fluid in the secondary carrier loop, with the CO₂ system for freezing combined with a HFC-404A and sole as secondary carrier loop for refrigeration and with the CO₂ system for freezing in combination with the HFC-404A direct evaporation system for refrigeration. At 30% below the reference case, the lowest lifetime emissions are caused by systems using propane or ammonia as primary refrigerant in combination with a secondary carrier loop with sole and systems using direct evaporation of CO₂ for both freezing and refrigeration.

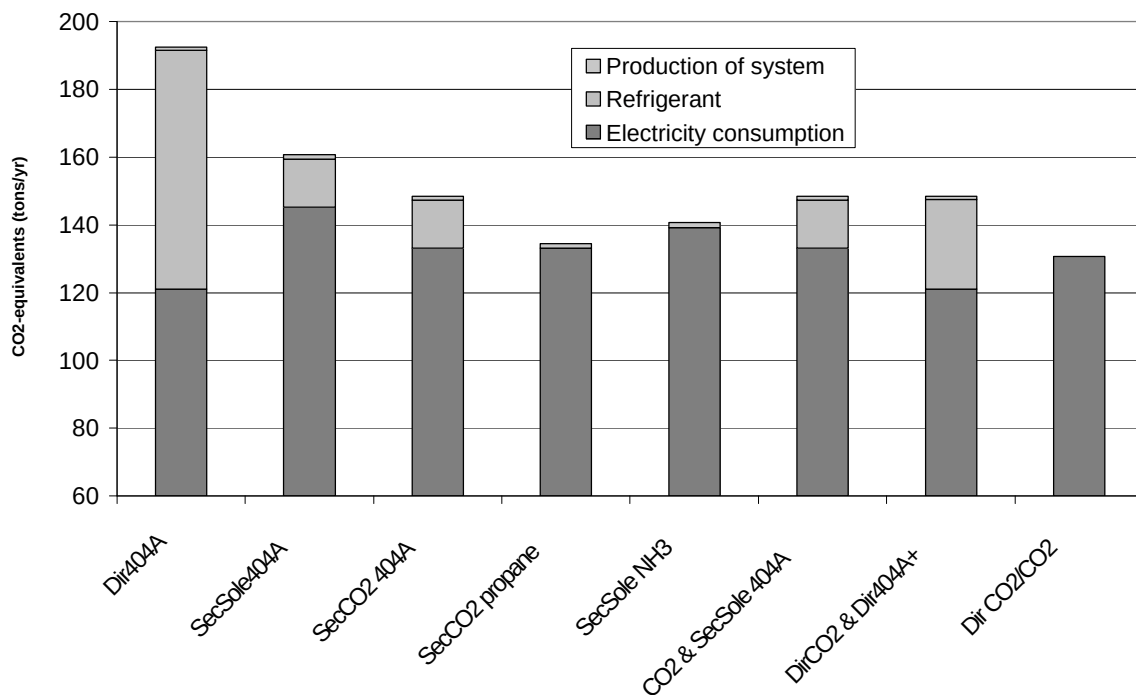


Figure 38: Annual GHG emissions for different technologies under consideration of the electricity production, refrigerant losses and production of the system (Beware: stretched vertical axis)

Costs

The results of the cost calculation for the systems differ significantly from the result of the emission calculation (Figure 39). Here, the reference case is between 10 and 25% more cost-efficient than most of the examined alternatives which represents the German market preference well. Second ranks the system with CO₂ direct evaporator for freezing and HFC-404A for refrigeration with only 3% higher costs than the reference case.

Investment costs were annualised over the lifetime of the system of 10 years applying an interest rate of 10 % per year in order to be in line with economic criteria of commercial decision makers. The resulting reduction cost per ton of CO₂ equivalent are €20 for the best case (CO₂ as refrigerant for freezing and HFC-404A direct evaporation for refrigeration). For other examined technologies, this index is higher (s. Table 34).

As a comparison: According to figures given by the EU commission in KOM(2003) 492 „Proposal for a regulation of the European Parliament and of the Council on certain fluorinated greenhouse gases” emission mitigation costs of HFC-152a or CO₂ instead of HFC-134a in automobile air condition lie between 7 and 26€/t CO₂ equivalent for HFC-152 or 18 – 88 €/t for supercritical CO₂ systems.

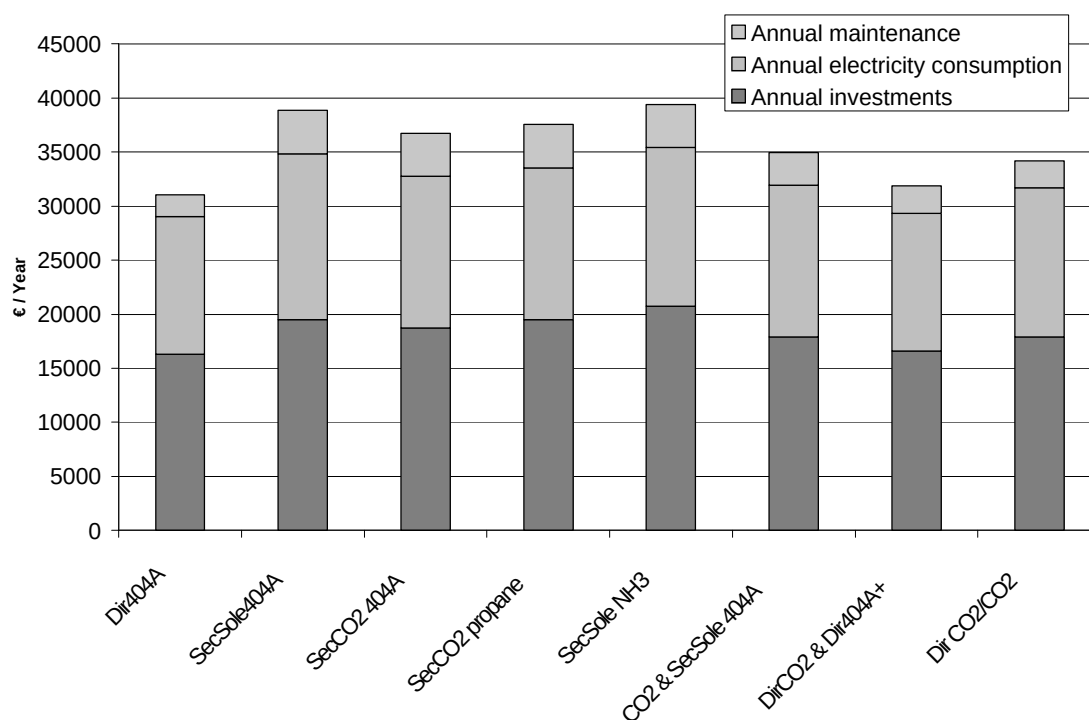


Figure 39: Comparison of total annual costs of different technologies

Table 34: Emission reduction potentials for alternative technologies with related costs per avoided ton of CO₂ equivalent compared to the reference system

	Emission reduction in comparison to reference [%]	Specific mitigation cost [€ / t CO₂]
Direct evaporation HFC-404A (reference)	0	reference
Secondary sole system with HFC-404A	16	246
Secondary CO ₂ system with HFC-404A	23	130
Secondary CO ₂ system with propane	30	113
Secondary sole system with ammonia	27	162
Direct CO ₂ evaporation system for freezing and secondary sole loop for HFC-404 a in refrigeration	23	88
Direct CO ₂ evaporation system for freezing and direct evaporation HFC-404A for refrigeration	23	19
Supercritical CO ₂ direct evaporation for refrigeration and freezing	32	52

6.7 Sensitivity analysis

In order to examine the robustness of the results, the following parameters were varied:

1. 50% lower and 50% higher refrigerant leakage losses
2. 50% lower and 50% higher energy consumption of the reference system
3. variation of mix in electricity production (100% renewable, 100% lignite)

The respective results are summarised in Figure 41, 42 and 43. As a result of the first sensitivity analysis (Figure 40) it can be observed that a reduction of 50% of the energy consumption maintains the ranking of technologies. The relative advantage of using the alternative technologies increases. As a consequence of an increase in energy consumption by 50%, the difference in emissions of the technologies becomes smaller. Advantages of secondary systems are partly lost.

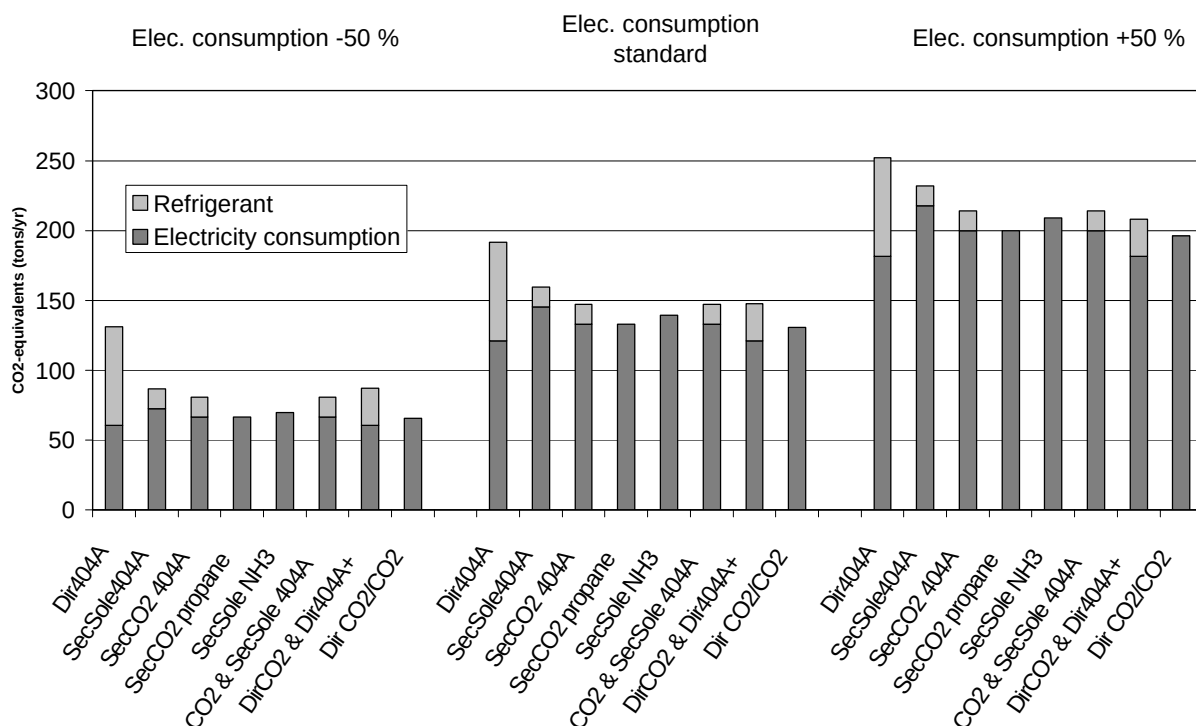


Figure 40: Influence of specific electricity consumption

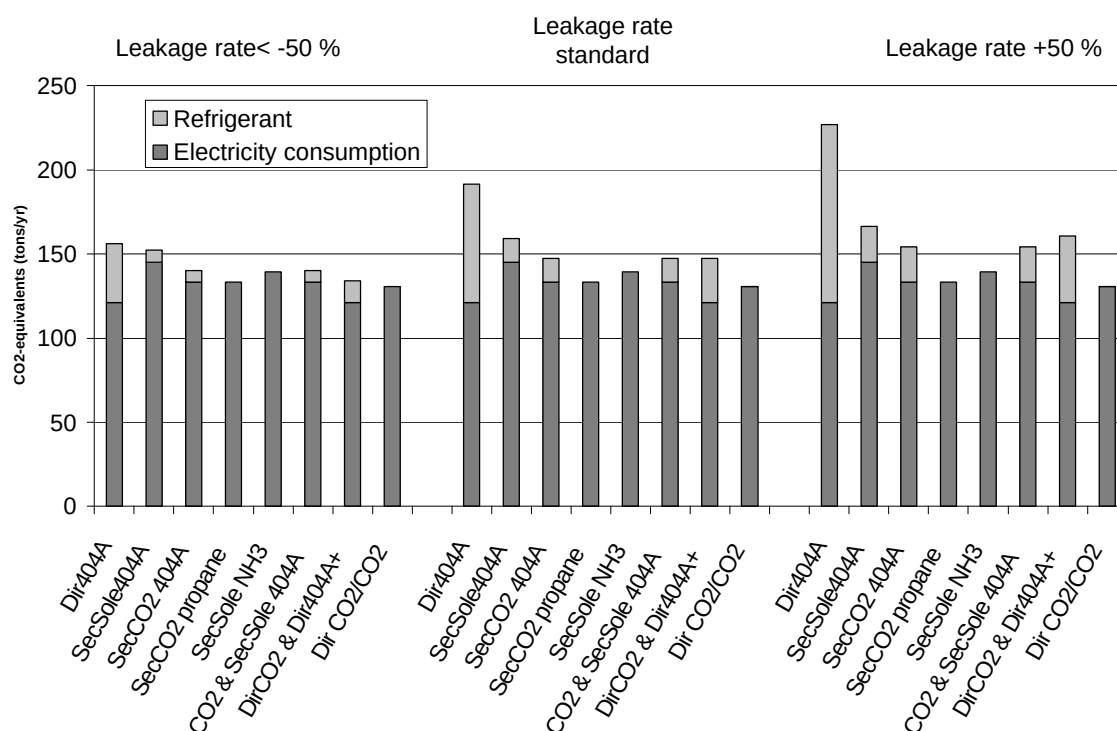


Figure 41: Influence of the assumed refrigerant leakage rate

The second sensitivity analysis (Figure 41) examines the effects of a variation in the refrigerant leakage rates on the ranking of the technologies. It becomes clear that a reduction of leakage rates has a noticeable levelling effect. Systems with direct evaporation of HFC-404A are ranking better than those with secondary HFC-404A systems and almost even with secondary systems based on

ammonia. Systems with CO₂ as refrigerant or as secondary loop carrier still have a 10-15% advantage over the reference technology.

With leakage rates 50% above the standard case, the relative reduction potentials of the alternative technologies rise to between 15 to 40% compared to a reference system with HFC-404A direct evaporation while keeping the same ranking of alternative technologies.

Only at leakage rates below 2%, which is way lower than present state of the art, the reference system causes less emissions than the CO₂ only systems

The third sensitivity analysis examines the influence of the type of electricity production on the emission profile of the different technologies (Figure 42). Increased CO₂ emission in electricity production results in a levelling effect on higher level, but without changing the order of the ranking of the emissions of different alternatives. This behaviour is analogue to the first sensitivity analysis with higher electricity consumption.

In the case of electricity production purely from renewable energy sources (such as is almost the case e.g. in Switzerland and Norway) the emissions for all technologies are however lower but differences are emphasized. It should be kept in mind that a change towards electricity production from renewable energies requires strong incentives to reduce energy consumption and therefore puts additional pressure on the least energy efficient alternatives.

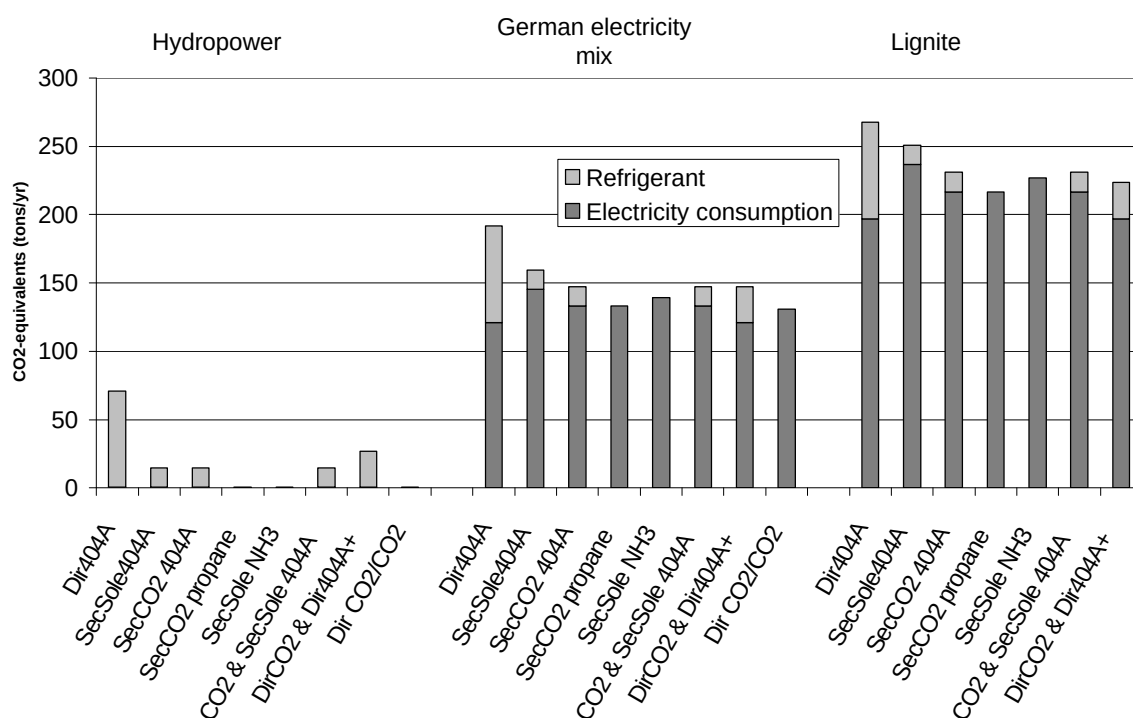


Figure 42: Influence of the electricity production on the emission of the different technologies

6.8 Summary

It has been shown that

- there is a number of technology alternatives with significant advantages over the reference systems with HFC-404A as refrigerant with respect to climate issues
- from the economic and emissions point of view CO₂ as refrigerant of secondary carrier loop is the most attractive alternative to reference systems with HFC-404A direct evaporation at present
- only at refrigerant leakage rates of a few per cent -which is not realized at present- the GHG emission balance of the HFC-404A direct evaporation reference system becomes comparable to HFC-free alternatives
- next to technical reliability, the energy efficiency of the secondary carrier loop is of great importance to the application of alternatives
- usage phase and disposal dominate more than 99.5 % of the emission balance while the emissions related to production of components and fluids are negligible
- the GHG balance of HFC solutions deteriorates with receding carbon intensity of the German electricity production sector in the long term
- emission reduction potentials of the alternatives examined above lie in a range between 10 and 30% of the total direct and indirect emissions from centralised commercial refrigeration in Germany, corresponding to 0.3 to 1.0 Mt CO₂ equivalent/a.
- the resulting costs for mitigation start at 20 €/t CO₂ equivalent for combined CO₂/HFC-404A direct evaporation systems and may rise to well over 200€/t CO₂ equivalent e.g. for HFC404A systems with a secondary carrier loop with sole
- inspections and reduction of investment and operation cost are key factors for the acceptance of alternative technologies in the market
- even within relatively homogenous and well-inspected groups of grocery stores, the deviations of energy consumption exceed 100%, partly because the energy consumption of refrigeration in supermarkets depends on several technical and economical factors so that the choice of refrigerant is not of decisive importance.
- energy consumption and refrigerant loss in contrast to the investment cost in commercial refrigeration in the retail sector often play only a minor role in the decision making process on investments which should be kept in mind for the development of political instruments to influence such decisions

According to Öko-Recherche (1999) HFC (mainly 404A and 134a) can be found mainly in the following applications:

- heat pumps in the residential sector
- commercial refrigeration
- industrial refrigeration and air conditioning
- mid-sized industrial refrigeration
- mid-sized air condition
- room air conditioners and chillers
- systems for small industrial and commercial applications
- mobile refrigeration
- mobile air conditioning

Transfer of results from the examination for supermarket refrigeration to other sectors is only possible to a limited extent since the specific conditions on required cooling capacity,

decentralised cooling demand, energy consumption, dimensions, leakage rates and safety requirements vary strongly between the different applications. A decided consideration of the respective application analogue to the examinations in this chapter is advisable. Centralised supermarket refrigeration systems are however technologically demanding in view of the use of alternative refrigerants because of their size, widespread occurrence and proximity to the end user.

7 Summarizing evaluation and discussion

This section will evaluate the intrinsic properties of fluorinated GHG and their alternatives in summary based upon the information compiled and discussed in the previous section and under application of the evaluation methodology deduced in section 2. This will be followed by a comparative evaluation of the application of fluorinated GHG and their alternatives in the application examples previously examined in view of their relevant effect categories. After a summarizing discussion of findings and their transferability, central open questions will be listed and discussed for their importance. The section will end with a paragraph ‘summary and outlook’ in which the political implications of the study are discussed.

7.1 Evaluation matrix for intrinsic substance properties

In the categorisation of substances into the respective categories a classification according to the criteria in section 2.4 was utilized. This is based upon the ‘column model’ of the technical directive on hazardous substances in the framework of the substitution requirement of the German legislation on hazardous substances (s. also section 2 and 11.1.3.3) and a quantitative spread covering the span of the extreme values as represented in Table 35.

Table 35: Overview over the categorisation criteria for the different categories

Category	Input data	Unit	Lower threshold ‘medium’	Lower threshold ‘high’	Lower threshold ‘very high’
Fire and explosion risk	R-sentences	-	According to column model		
acute human toxicity	R-sentences	-	According to column model		
chronic human toxicity	R-sentences	-	According to column model		
Environmental toxicity	R-sentences	-	According to column model		
Persistence	Atmospheric lifetime	days	100	1000	10000
Bioaccumulability	Distribution coefficient octanol/water	Log K _{ow}	1	3	5
Climate	Global Warming Potential (100 Jahre)	Kg CO ₂ equiv.	1	33	1000
Eutrophication	Eutrophication potential	Kg phosphate equiv.	0.005	0.05	0.5
Acidification	Acidification potential	Kg SO ₂ equiv.	0.01	0.1	1
Ozone formation	Ozone formation potential	Kg ethylene equiv.	0.1	1	10
Ozone depletion	Ozone depletion potential	Kg CFC-11 equiv.	0.01	0.1	1.0

From this, the so-called evaluation matrices as shown in Table 36 and Table 37 result. These concentrate the information compiled in this report into a classification system with five categories for 15 substance-specific categories. This enables the straightforward recognition of profiles of substances and substance classes. Below the main results are summarised:

1. In the category 'fire and explosion risk' there is no clear picture. Several fluorinated substances are ranked 'low' while others are considered 'high'. Within the alternative substances, only CO₂ achieves a 'low' classification.
2. In view of the well-examined fluorinated GHG, we assume that these display only low human and environmental toxicity effect potentials according to present state of knowledge²². An exception is NF₃ with a medium acute human toxicity. Among the alternative substances, especially ammonia and n-pentane are outstanding with their ranking in acute human toxicity and environmental toxicity.
3. With respect to the abiotic effect potentials, the fluorinated GHG can be estimated to be little problematic in view of eutrophication and ozone depletion potential. This also applies to ozone-formation potential – except for HFC-152a which is ranked as 'high'. In the later category the alternative substances stand out with their 'very high' rating with the exception of ammonia and CO₂. In the category acidification, all fluorinated GHG are rated as 'high' and 'very high' due to the high acidity of their decomposition products. Only ammonia gets the same ranking among the alternative substances.
4. The fluorinated GHG receive a rating in respect to their specific contribution to climate change as 'high' to 'very high' while all alternatives fall into the 'low' to 'medium' categories.
5. According to present state of knowledge, fluorinated GHG show a medium bioaccumulation potential and therefore can be regarded as non-problematic in this respect.
6. Fluorinated GHG display a consistently high and very high persistence which is not seen as sufficiently relevant from the point of view of classical avoidance of hazards, as long as it does not occur in conjunction with bioaccumulability and toxic properties. In the case of the fluorinated substances examined here, this is not the case. The emission of persistent substances into the environment contradicts the principles of precaution and sustainability, especially in combination with bioaccumulability and high mobility. The substance class of fluorinated carbons and sulphur hexafluoride with a lifetime of several thousands or tens of thousands of years require a separate assessment in a different framework.

²² An evaluation of the effect as endocrine disruptor is not made within the legal categorisation of chemicals since no test method is defined so far.

Table 36: Evaluation matrix – Part I

effect categories	flammability and explosion risk	human toxicity		environmental risks		
sub-categories:		acute toxicity	chronic toxicity	environmental toxicity	persistence	bioaccumul-ability
CF ₄	low	low	low	low*	very high	medium*
C ₂ F ₆	low	low	low	low*	very high	medium*
SF ₆	low	low	low	low*	very high	medium
NF ₃	high	medium	low	low	very high	medium*
HFC-134a	low	low	low	low	high	medium
HFC-365mfc	high	low	low	low	high	medium
HFC-245fa	low	low	low	low	high	medium
HFC-143a	high	low	low	low	high	medium
HFC-227ea	low	low	low	low	high	medium
HFC-152a	high	low	low	low	mitttel	medium
HFC-32	high	low	low	low	high	high
HFC-125	low	low	low	low	high	medium
HFC-43-10mee	low	low	low	low	high	medium*
CO ₂	low	low	low	low	very high	medium*
Ammonia	medium	high	low	very high	low	low*
n-pentane	very high	low	low	high	low	medium*
cyclo-pentane	high	low	low	medium	low	medium*
propane	very high	low	low	low	low	medium
n-butane	very high	low	low	low	low	medium

* For this substance, no explicit data was available- derived by analogue deduction from related substances

Table 37: Evaluation matrix – Part II

effect categories	climate	eutrophication	acidification	ozone formation	ozone depletion
CF ₄	very high	low*	very high*	low*	low*
C ₂ F ₆	very high	low*	very high*	low*	low*
SF ₆	very high	low*	very high*	low*	low*
NF ₃	very high	low*	very high*	low*	low*
HFC-134a	very high	low*	high	medium	low
HFC-365mfc	very high	low*	very high*	medium*	low
HFC-245fa	very high	low*	very high*	medium*	low
HFC-143a	very high	low*	very high*	low	low
HFC-227ea	very high	low*	very high*	low	low
HFC-152a	high	low*	high	high	low
HFC-32	very high	low*	very high	medium	low
HFC-125	very high	low*	very high	low*	low
HFC-43-10mee	very high	low*	very high*	medium*	low
CO ₂	medium	low*	low*	low*	low*
Ammonia	low	high	very high	low*	low*
n-pentane	medium	low*	low*	very high	low*
cyclo-pentane	medium	low*	low*	very high	low*
Propane	medium	low*	low*	very high	low*
n-butane	medium	low*	low*	very high	low*

* For this substance, no explicit data was available- derived by analogue deduction from related substances

The precedent evaluation is based on the availability of reliable data on substance evaluation. With respect to their risk potentials, most of the HFCs are examined relatively well. If they fall into the requirement of registration of new substances under the German chemical substance legislation (like e.g. HFC-365mfc, -245fa or -43-10mee), they have passed a comprehensive testing of the intrinsic substance properties and could be assessed with respect to their risk potentials on this basis. Effects such as endocrine disruptors were so far not examined in this framework. Part of the HFCs belonging to the group of old substances have been examined in the framework of national or international activities for chemicals assessment and is rated as sufficient for evaluations by the authors. Only a small number of fluorinated GHG with limited commercial relevance is inadequately characterized as old substance.

7.2 Summary: intrinsic substance properties

HFCs as a new substance category for widespread applications with potentially very high production volumes and therefore emissions into the environment are under discussion. Persistence of HFC in conjunction with their volatility and the potentially very large quantities brings the possibility of a long-term and widespread accumulation of large quantities of xenobiotic substances in the sink atmosphere. Reclaim of the substances from the atmosphere is not possible. Experience from the past shows that the discovery of harmful effects and interactions of substances previously unknown cannot be ruled out and that negative influences on complex natural systems may occur.

It can be concluded that HFC give little or no reason for concern with respect to human and environmental toxicity according to the present state of knowledge. Limitations for this are valid for the uncertainties on old substances. It should be noted especially that toxicological and environmental behaviour of single HFC may vary strongly from the sister substances.

This is however opposed by the climate-effect property. It needs to be assessed for every single application in how far a contribution to GHG effect is present. Persistence in combination with high mobility in the atmosphere and the potentially large amounts represents another global risk potential. For precautionary reasons, applications with emissions into the atmosphere should be avoided because of the persistence in combination with high mobility and potentially large amounts used.

7.3 Evaluation in the application examples

Starting from the ratings in the evaluation matrix in Table 36, a categorization of application-specific risk potentials of examined HFC and alternative substances was conducted under consideration of the results from section 5 and 6. For this, only effect categories in which at least one of the examined substances was rated as medium, high or very high were considered. As explained in section 4, an in-depth assessment and evaluation of the effect categories acidification potential and ozone formation potential has been dispensed with.

There is no differentiated examination of the substance-related effects in product chains in this study. Therefore, environmental- human-toxic and safety related risks which may be relevant in the framework of the production of the substances remained unevaluated – keywords for this are chlorine chemistry, petrochemical refineries and ammonia synthesis.

7.3.1 Application examples PU rigid foam

7.3.1.1 Application pattern

With respect to blowing agent, PU insulation panels need to be understood as semi-hermetic applications, which are used in small parts and diffusely in buildings and refrigerated vehicles. As demonstrated in section 5, losses in the order of 8% and 11% occur during production and installation of roof insulation and refrigerated vehicles respectively. During the use phase, annual losses of 0.2% are assumed for roof insulation and 0.1% for refrigerated vehicles. Emissions of the remaining 82% and 87% at the end of the average assumed lifetime of 50 years and 18 years for roof insulation and refrigerated vehicles respectively can be largely mitigated safely in controlled dismantling without crushing and with suitable disposal (thermal utilization). These controlled disposal paths are presently not established for this.

Limitation of emissions in the production and usage phase is mainly reliable, since manufacturers strive to avoid emissions for cost reasons by monitoring of the products. Such monitorings foresee minimum performance in cell impermeability tests for roof insulation panels within the framework of German building regulation requirements (DIBt 2002) and compulsory testing of insulation quality of refrigerated vehicles (s. section 5.3). For the disposal phase, it needs to be assumed that no or only partial retention of blowing agent is realized in practice. In section 5.3 it was shown that for refrigerated vehicles a complete emission of the remaining blowing agent needs to be implied at present. In case of roof insulation there are presently no specific requirements on a non-destructive dismantling of insulation material containing climate-relevant gases and no scenarios dealing with the question of sufficient disposal capacities and differentiated disposal strategies for the quantities of insulation foam accruing in the future. Product responsibilities and liabilities range (indirectly) into the usage phase, but these have no effect on the retention of climate-relevant gases in the disposal phase.

7.3.1.2 Fire and explosion risk

Safety standards concerning fire and explosion risk during the production phase are established and implemented in legislation relating to the system²³. Flame retardants are added to such PU foam panels intended for the use as roof insulation in order to comply with fire protection conditions of the building authorities (s. section 5.2). The safety standard valid in building regulations and system-related legislation in Germany are at a high level, so that a controlled risk for the production phase and a negligible risk for the usage phase can be assumed for pentane-blown as well as for HFC-365mfc- blown foams. In view of fire and explosion risk, HFC-365mfc and c-pentane are therefore rated as low and n-pentane as medium.

7.3.1.3 Acute environmental toxicity

The very high acute environmental toxicity of n-pentane is based on the toxicity for aquatic organisms, the medium rating for c-pentane on the harmfulness on aquatic organisms. In Germany, sufficient measures for the protection of harmful emissions in waters are

²³ Details to the complex regulations in the framework of environmental and work protection regulation can be found in e.g. (TAA 2003):

established and implemented in the framework of system-related and waters legislation so that the risks during the production phase are within acceptable limits if adequate precautions are taken. Acute risks to waters from pentane in the use phase can be ruled out since the diffuse gaseous emissions in conjunction with the medium persistence hardly leads to relevant concentrations in waters. Therefore, the application-related risk is rated as low.

The slightly higher share of flame retardants in pentane-blown roof insulation panels may lead to potentially slightly higher toxic loads in comparison to HFC application. A substitution should be aimed for the flame retardant tri-chloro-propylphosphate still frequently used here because of the unsettled carcinogenic effects of the substance.

7.3.1.4 Persistence

Since none of the substances features a combination of high or very high persistence with high or very high bio-accumulability and toxicity, there is no immediate human- or environmental toxicity risk from persistence in the sense of risk minimisation. In the sense of precaution and sustainability, the emission of persistent substances into the environment is to be avoided, especially if this is connected to a long-term accumulation when introduction rates exceed decomposition rates. Because of the apprehended high emission rates in disposal of insulation materials for roof insulation and refrigerated vehicles in the medium and long term, the risk from persistence is rated as high.

7.3.1.5 Bio-accumulability

HFC-365mfc as well as pentane are characterized with a medium bio-accumulability. Since HFC-365mfc is highly persistent, the application-specific risk of bio-accumulability is rated as medium. Due to the low persistence of pentane, the application-specific bio-accumulation potential of n- and c-pentane is rated as low.

7.3.1.6 Greenhouse effect

In the case of insulation panels, the climate-relevant total emissions of HFC-365mfc-blown insulation materials exceed those of pentane-blown panels in all scenarios. In the standard scenario, the emissions relevant to climate of the HFC-365mfc-blown roof insulation panel are 63% above those of pentane-blown ones. Even under the assumption of a complete retention of climate-relevant blowing agent, which can hardly be realized in practice in the disposal phase by a closed disposal logistic and control, the climate-relevant total emissions of HFC-365mfc-blown roof insulation panels surpass those from pentane-blown ones. It needs to be emphasized that this is even valid if the thickness of the panel is limited for technical reasons.

From the point of view of climate protection, the use of HFC-365mfc-blown roof insulation panels is of serious disadvantage. Therefore, HFC-365mfc will be categorized as very high in the application-specific risk. In the case of refrigerated vehicles balanced in this standard case, the total climate-relevant emissions of the version with HFC-365mfc are 11% greater than in the version with pentane as the blowing agent.

Even in the case of refrigerated vehicles, the application of HFC-365mfc-blown insulation material is of disadvantage for climate protection in comparison to the use of pentane. Because the relative additional contribution is more restrained than for roof insulation, the rating of the application-specific risk is high instead of very high.

7.3.1.7 Summary

Table 38 summarizes the application-specific risk potentials. In the production phase of PU rigid foam, advantages arise from the use of HFC-365mfc as blowing agent due to lower safety requirements on fire protection and water protection. In a consideration of the total life cycle of insulation materials, this is opposed by the disadvantages from poorer rating in the GHG balance and the contribution to persistent xenobiotics in atmosphere.

The use of HFC-365mfc as blowing agent in PU rigid foam for insulation of roofs and refrigerated vehicles is not suitable as a future-oriented solution.

Table 38: Summary of risk potentials in the applications of PU rigid foam

	365mfc	n-pentane	c-pentane
Fire and explosion risk	low	medium	low
Acute environmental toxicity	negligible	low	low
Persistence	High	low	low
Bio-accumulability	medium	low	low
Climate	Very high ¹ , high ²	medium	medium

¹ application PU rigid foam insulation panels

² application refrigerated vehicles

7.3.2 Application example supermarket refrigeration

7.3.2.1 Application pattern

Supermarket refrigeration systems are seen as semi-hermetic applications because they are applied diffusely, but according to regulations for the commercial sector, they are required to be installed, maintained and disposed of by trained personnel and not private consumers²⁴. Refrigeration systems are subject to regulations on tightness, occupational safety, operation safety and disposal. Depending on the intrinsic properties of the refrigerant and the charge weight, different requirements concerning construction, installation, operation and testing need to be complied with. In Germany, the following regulations are valid: The regulation for safety and health at work of the accident prevention and insurance association (Berufsgenossenschaft) on 'Refrigeration Systems, Heat Pumps and Cooling Systems' (BGV D 4 1997) which refers to further relevant regulations and technical rules. Of importance for supermarket refrigeration systems are also the German standards DIN 8975 Part 11 (1999), TRB 801 No. 14 (2002), the ordinance on pressurized containers (2002), the ordinance on occupational safety (2002) and DIN EN 379 Part 1-4 (2003) which is released in a reviewed version in November 2003.

²⁴ On the division of usage patterns, s. section 2.4.

Next to risks from design utilisation according to state of technology and regulations, e.g. from common losses from operation, questions on the status of compliance with regulations or frequency and severity of failure events especially in view of the protection of persons and the immediate environment may be of interest. Data on enforcement deficits or on failure events of refrigeration systems in supermarkets are not available since there is not reporting obligation for this type of systems and since part of the systems described here is not of relevance to the market. The Swiss Federal Energy Agency (BfE) published a risk analysis on refrigeration systems supermarkets with the refrigerants ammonia and propane (Wolfer et al. 1999), which includes possible failure incidents. The results of this analysis have been considered here. An in-depth elaboration of aspects of operational safety has not been conducted in this study since this exceeds the problem specifications in this case. For the evaluation conducted here, it is assumed that the comprehensive system of regulations guarantees a sufficient level of safety.

7.3.2.2 Fire and explosion risk

With HFC-404A and CO₂ are categorised as inflammable, fire and explosion risks can be categorised as negligible.

Risks from the operation of refrigeration systems with flammable refrigerants are considered in the technical regulations stated above. Next to the high technical requirements on construction, maintenance and disposal of refrigeration systems, additional safety is provided by the limitation of the permissible refrigerant charge amount depending on flammability and the installation location. Therefore a sufficient safety standard for the application of ammonia and propane as refrigerant can be assumed.

In view of the risk potential under consideration of other possible failure incidents, the BfE comes to the conclusion that the risk potential for centralized²⁵ refrigeration systems with ammonia and propane are within acceptable limits. For decentralised²⁶ systems with propane refrigerant, a potential injury risk from fire is seen as possible which therefore are bordering to non-acceptable risks. It is however observed that a risk analysis is required enable a transferability of different types of systems and installation environments and to enhance the significance of the analyses (Wolfer et al., 1999). It remains to be stated that for the achievement of a safety standard comparable with inflammable refrigerants, a higher effort for safety is required.

Starting at the safety level given by the existing regulation, both ammonia with medium flammability and propane with high flammability can be categorized into 'low risk potential'. The fact that the highly flammable propane is not categorized in a higher risk level can be justified also with the fact that the decentralised refrigeration system operated with propane assumed by the BfE has no market relevance at present.

It needs to be added that the categorisation of the usage patterns of the highly flammable propane is related to some uncertainty as long as no in-depth risk analyses are available.

²⁵ Wolfer et al. have defined a refrigeration system in a detached engine compartment with a charge of 20 kg propane or ammonia as centralized application.

²⁶ Wolfer et al. have defined a system with a charge of 0.2 kg propane or ammonia placed in the public area as decentralised system.

7.3.2.3 Acute toxicity

Because of the low acute human toxicity of HFC-404A, propane and CO₂ intrinsic to the substance described in section 4.3, the risks in the application described here can be regarded as negligible.

For systems operated with ammonia, the explanations of section 7.3.2.2 on fire and explosion risks are valid analogue. The high acute toxicity of ammonia is considered by the regulations above. A sufficient safety level in view of toxic effects can be assumed. A risk level comparable to non-toxic refrigerants however requires a higher safety effort.

The BfE estimates the risks for decentralised systems to be acceptable, but also sees a risk of injury from release of ammonia for decentralised refrigeration systems operated with ammonia thus a risk bordering to non-acceptable levels.

Since it is assumed that the existing regulation system considers these risk, no higher risk level will be assumed here without founded justification and without consideration of system types and installation conditions close to practice. Therefore, refrigeration systems operated with ammonia are categorised as 'low risk potential'.

It needs to be emphasized again that there is a demand for the reduction of uncertainties by in-depth risk analyses. It is assessed as an indicator for the requirement of such an in-depth risk analysis that incidents with a requirement to be reported under §19 of the German failure ordinance (Störfall-Verordnung) from the sector of refrigeration systems operated with ammonia are in the order of 10% (UBA 2003).

7.3.2.4 Acute environmental toxicity

For HFC-404A, propane and CO₂ the risks from environmental toxicity are negligible since there are not environmental toxic properties.

For the environmental toxic ammonia, emissions into waters during failure incidents in production and transport cannot be ruled out. In the usage phase, this should not be of relevance for the small charges in supermarket applications since leakages occur in the gaseous state. Even the possibility that ammonia cools the immediate environment to such a degree that it remains in a liquid phase for some time after the release should not lead to introduction into waters due to the remoteness from waters and separation from the sewage system.

Since the emphasis of this examination is on the usage phase, the risk of acute environmental toxicity can be categorised as low despite the intrinsic potential.

7.3.2.5 Persistence

Since there is no combination of high or very high persistence and high or very high bio-accumulability and toxicity, there is no risk of toxic effect from any of the substances in the sense of risk minimisation. In the sense of precaution and sustainability however, the emission of persistent substances into the environment is to be avoided. Relevant for this are the volume of substances emitted and the amounts to be expected for accumulation due to lifetime of the substances. For substances occurring naturally such as CO₂, it is of relevance if

the emissions contribute to an increase of natural concentrations and if the substance does not result as waste product from an combustion process anyway.

Because of the atmospheric lifetime of the components of the HFC-404A blend being HFC-125 with 29 years, HFC-134a with 14 years and HFC with 52 years, the application-specific rating of the risk potential is high. It needs however to be distinguished that the HFC-404A systems with secondary loop examined in section 6 are considerably better in view of the introduction of xenobiotics with only approx. 1/5 of refrigerant emission compared to direct evaporation systems.

Emissions of CO₂ as refrigerant are dominated by emissions from combustion processes for electricity generation. Since systems here with CO₂ as refrigerant contribute to a reduction of CO₂ emissions in comparison to other systems, a low application-specific risk is assumed.

7.3.2.6 Bio-accumulability

HFC-404A and propane distinguish themselves by a medium bio-accumulability. Since propane has only a short lifetime, the application-specific risk is set low. For HFC-404A, the risk is medium because of the high persistence. It needs to be distinguished between direct evaporation systems with higher emissions and secondary loop systems with lower refrigerant emissions which need to be rated as favourable in view of bio-accumulability. The risk associated to the ability to bio-accumulate for ammonia and CO₂ is classified as negligible because of their solubility properties and role in the carbon cycle, respectively.

7.3.2.7 Greenhouse effect

The operation of refrigeration systems is generally relevant to climate because of the high electricity consumption, as long as the electricity is not exclusively generated from renewable energy sources. A rating can only be made relative. Therefore, a rating will be made based on a medium rating for the technology with the relatively lowest contribution (ca. 0-10%). Such technologies with higher relative contributions (10-10%) as high and such with emissions of more than 20% as very high. On the basis of the results displayed in Figure 38, the rating is summarized in Table 39.

Table 39: Relative emissions as CO₂ equivalents

System	Relative emissions CO ₂ -equivalents	Rating of application-specific risks
CO ₂ & CO ₂ supercritical.	100%	medium
Propan + sec. CO ₂	102 %	medium
NH ₃ + sec. sole	107 %	medium
CO ₂ + sec. sole 404A	113 %	high
404A + sec.CO ₂	113 %	high
CO ₂ + 404A direct	120%	high
404A sec. sole	122 %	very high
404A direct evaporation	146 %	very high

7.3.2.8 Summary

Systems operated with HFC-404A as refrigerant do have advantages because of a lower required safety standard for fire and explosion protection, water and occupational safety especially during the manufacturing phase but to a lesser extent also during the use phase. In the consideration of the total life cycle, the disadvantages from higher climate effect and the contribution to accumulation of xenobiotics are opposed to this. The application-specific risk potentials for supermarket refrigeration are summarized in Table 40. In respect to economic aspects please refer to the summary of chapter 6 and the concluding section in 7.5.

Table 40: Summary of the application-specific risk potentials for supermarket refrigeration

	404A	C₃H₈	NH₃	CO₂
Fire and explosion risk	low	low	low	negligible
Acute toxicity	negligible	negligible	low	negligible
Acute environmental toxicity	low	low	low	low
Persistence	high	low	low	low
Bio-accumulability	medium	medium	low	low
Climate	very high (high) ¹	medium	low	medium

¹ Depending on the different emission rates of the examined systems

7.3.3 Application examples: weighting of effect categories

The evaluations in the application examples described in the previous sections show that HFCs have advantages in flammability and toxicity but also disadvantages if the whole life cycle is considered because of the greenhouse effect and contribution to accumulation of persistent substances in the atmosphere.

If and how the risks relevant here can be appraised as grave and if and how far the respective potential risks can be minimized with suitable risk management measures will be discussed in the following on the basis of the criteria developed in section 2.

7.3.3.1 Fire and explosion risk

Fires and explosions are exclusively of local relevance, damages occur without time lag. Cause and effect are in close chronological and spatial proximity and can be determined unambiguously. Originators are directly affected by the effects. Knowledge on effects and effective risk management measures is developed over centuries and deeply anchored in society. In addition to this, there is a tight network of regulations which are advanced continuously reducing irreversible damages and casualties and injuries to a small occurrence probability, material damages are reversible.

7.3.3.2 Acute toxicity

Human-toxic risks are given here by failures in central or decentralised refrigeration systems operated with ammonia. Risks are limited locally. Cause and effect can be determined unambiguously. Light injuries are reversible. Irreversible damages by severe injuries and casualties can be reduced to a small number of cases with a regulation system developed over decades and adequate handling of systems.

7.3.3.3 Acute environmental toxicity

Here, acute toxic effects on aquatic organisms in case of local failures with emissions into sewage or surface waters are discussed. The range of such failures is local to regional since decomposition and dilution occurs. The correlation between cause and effect is well known. The effect after abatement of the discharge is reversible since aquatic populations generally have the ability to recover. The originator is not affected directly but liable in case of damage to others and at least identifiable because of the local character of the failure.

7.3.3.4 Greenhouse effect

Climate effects are of global relevance. Damages occur with a time lag. A catastrophic dimension of effects on all levels is assumed. The total world population is affected for generations, no matter how large their contribution to the cause has been. Damages i.e. concentrations are not reversible or only over long time periods. The only possible risk management measure is the precautionary mitigation of emission of gases relevant to climate. The achievement of national and international targets for this is not secured so far and is connected to high efforts for the whole of the society.

7.3.3.5 Persistence

Persistence in connection with the great range results in a great global relevance. The extent of damages is unknown. It may range from zero to severe dimensions. As little as negative effects are proven according to present state of knowledge, the little such effects can be excluded. Emissions of large quantities of HFC into the atmosphere is therefore comparable to a large experiment with uncertain result on a global scale. A recovery of substances from the atmosphere is not possible. If negative effects become discernible, substitution efforts need to be made which are connected to high efforts for all parties concerned. According to present state of knowledge, technical solutions leading to accumulation of persistent substances in the environment cannot be regarded as trendsetting.

7.3.3.6 Summary of the evaluation

In summary it can be asserted that in the risk categories fire and explosion risk and toxicity there are risks for acute risks to humans (workers and users) and aquatic environment. The type of risk and the unambiguous correlation of cause and effect allow effective risk management measures. Despite these risk management measures, residual risks may remain which make the substitution with substances a priori not having such risks desirable and worthwhile. A shift to risks in the field of climate effect and persistence cannot be justified

since these risks are graver in their potential total extent and the difficulty to implement effective risk management measures. De facto, the application of HFC in place of pentane, ammonia and CO₂ brings a relief especially for manufacturers from risk management measures in view of fire and explosion risk and system safety for the mitigation of toxic emission into waters and exposure of persons. This is opposed by a shift to chronological and spatial far-reaching risks and severe effects occurring diffuse and remote from the originator and which must be borne by the whole society.

In comparison to the alternatives discussed here, the application of HFC-365mfc as blowing agent for insulation material for the insulation of roofs and refrigerated vehicles, and of HFC-404A as refrigerant for supermarket refrigeration not only the more unfavourable option in view of the environmental burdens occurring over the total life cycle, it also contradicts the just distribution of use and burden and the originator principle.

7.3.4 Transferability

Within the framework of the three application examples examined in this study, it could be shown that an unconstricted handling of fluorinated GHG would lead to adverse environmental situations. It became however clear that the specifics of the respective applications may partly differ significantly even in case of related applications. The transfer of the results on other application cases should only be done with great cautiousness.

7.4 Open questions

Past examinations on the environmental behaviour of fluorinated GHG formed a comparably sound starting position for this research project. There are however a number of relevant open questions for further research activities which are recommended for further research activities

In addition to the effects hazardous to the environment caused by the emission of all GHG, there is a call for action on HFC because of the combination of the properties persistence and high mobility of HFC as well as on persistence, mobility and bio accumulation ability of the decomposition product trifluoro acetic acid (TFA) within the framework of environmental calls for action of a precautionary substance policy.

It became also very clear that the toxicological and environmental behaviour of single HFC may differ greatly from the sister substances. In the introduction of new HFC, a wide similarity of properties must not be assumed. The comparably comprehensive testing of some new substances of commercially large relevance should be extended to less well examined fluorinated old substances. This should of course also and especially apply to fluorinated organic substances new to the mass market such as hydro- and perfluoro- ether, -amine, -ketone or -nitrate (see e.g. Tapscott et al. (1996), WMO (1999))

The destination of HFC at the end of the lifetime of the examined products was found to be a key factor in the GHG balance. Only as a result of a radical increase of disposal safety, HFC will become competitive with halogen-free alternatives in this regard.

Emission of by-products and intermediate products from production of fluorinated GHG could only be examined and evaluated rudimentary within the framework of this study due to

lack of trustworthy data. It seems however to substantiate that with the emission of diverse chlorinated and fluorinated substances there is further demand for research.

7.5 Summary and Outlook

Fluorinated GHG (especially HFC) mainly produced as substitutes for the ozone-depleting CFC and HCFC will develop to an annual market volume of 500.000 tons worldwide in the next 20 years if present trends are extrapolated. Main applications for this will be stationary refrigeration and air conditioning, mobile air conditioning and the production of rigid foams adding up to a bank of approx. 4 million tons of fluorinated GHG in the coming two decades. For the year 2020 an annual emission level of approx. 300.000 tons is predicted. Because of their high volatility and water-insolubility, fluorinated GHG once emitted almost entirely remain in the atmosphere until their decomposition.

This study comes to the conclusion that especially effects on climate and persistence stand out as negative properties intrinsic to the examined fluorinated substances. On the positive side, their generally low direct toxicity and their very low specific contribution to the formation of photosmog were identified.

The fact that toxic trifluoroacetic acid (TFA) as decomposition product of some important HFCs may accumulate in waters and therefore become an ecological problem did play an important role in the discussion on HFC. In this study it was shown that later research results indicate that other industrial but also natural sources of TFA have already built up concentrations in the environment by far exceeding values resulting from future decomposition of HFC.

Under the assistance of a differentiated consideration of the properties intrinsic to the substance in conjunction with the weighting of effect categories related to application and the establishment of a climate balance under consideration of the life path it could be shown that a case by case approach is best suited to find a decision for or against the application of fluorinated GHG. In the examined application examples, it could be shown that the application of fluorinated GHG leads to a clearly unfavourable situation for the climate.

Within the framework of two application examples examined in this study (PU roof insulation panel and PU insulation in refrigerated transport) but also in other relevant analyses (e.g. Harnisch and Schwarz, 2003) it became clear that already today the use of fluorinated GHG in applications earlier being the domain of CFC is not or only marginally economical in comparison to new alternative technologies. But with the example of an interconnected supermarket refrigeration system, it becomes clear that there are further applications in which fluorinated GHG have economic benefits in comparison to alternative substances. Further, more detailed results of the analyses of the application examples can be found in the respective summaries in sections 5.2.6, 5.3.5 und 6.8.

In the comparison and evaluation of technical systems in which fluorinated GHG and relevant alternative substances are applied, a significant dynamic can be observed in the changes of technical properties and cost data as well as in the widening of the portfolio of technologies available.

To a certain degree total economic cost disadvantages in the application of alternative substances today are compensated by their low specific mitigation cost. These reductions then

offer a rather cost-efficient contribution to climate protection (a frequently used criterion is <20€ per ton of avoided CO₂ equivalent emission). Even if this macro-economic criterion is applied, many alternative technologies with higher specific mitigation cost will remain too expensive to justify their application only for the reason of climate protection. Other ecological considerations such as e.g. the mitigation of risks from persistent substances may tip the scales in marginal cases towards a substitution initiated by legislation.

Beyond the necessary cost efficiency of climate protection measures, it should be taken into consideration according to the opinion of the authors that system changes induced today may avoid considerable cost later if the cost for development, later adaptation and finally the following substitution of a technology not applicable on the long term can be avoided from the start.

The authors of the study propose in this situation that the legislator providently supports the development, testing and dissemination of new technologies benign to climate by suitable measures without burdening consumers and appliers with excessive additional risks and costs. This could take place within the mandate of the recommendations on the promotion of alternative fluids made by the respective group of the European Climate Change Programme (EC, 2001). Because of the fundamental problems in the installation-specific and timely monitoring of emissions of fluorinated GHG (s. e.g. Schwarz and Harnisch (2003) in case of mobile air conditioning), market-based instruments such as emission trade will remain unsuitable according to the view of the authors.

For these reasons, regulation appears as most suitable in the view of the authors to achieve and accelerate the necessary stepwise substitution advisable for the reason of climate protection but also for substance-political sustainability and precaution. These would last but not least in the international context contribute to provide a clear orientation on the direction of further technological development often demanded by industry.

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9 Abbreviations

AFEAS	Alternative Fluorocarbon Environmental Acceptability Study
CFC	Chlorofluorocarbon
DKV	Deutscher Kälte- und Klimatechnischen Verein (German Refrigeration and Air Conditioning Association)
DifB	Deutsches Institut für Bautechnik (German Institute for Building Technology)
GHG	Greenhouse Gas
GWP	Global Warming Potential
HFC	Hydrofluorocarbon
HCFC	Hydrochloroflourocarbon
IPCC	Intergovernmental Panel on Climate Change
ODP	Ozone Depletion Potential
PU	Polyurethane
SETAC	Society of Environmental Toxicology and Chemistry
TFA	trifluoroacetic acid
TRGS	Technische Richtlinie für Gefahrstoffe (Technical Directive for Hazardous Substances)
VOC	Volatile Organic Compounds
WLG	Heat Transfer Coefficient Group (Wärmeleitfähigkeitsgruppe)

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11 Appendix: Background on evaluation approach

11.1 Risk assessment

11.1.1 Risk assessment within the framework of EU chemical substance legislation

A risk assessment for new substances according to directive 93/76/EU and for old substances according to EU ordinance 1488/94 consists of the following steps:

Information collection	
Effect assessment Risk potential (R-sentences) Dosis- (concentration-)/ effect assessment	Exposition assessment Exposition assessment of population (workers, consumers, population exposed via the environment) Exposition environment (water, ground, air)
Description of risk	
Human health	environment
Evaluation of effect data and comparison with exposition data	

Figure 43: Steps of the EU risk assessment for old and new chemical substances

Methods for the determination of physical and chemical properties of substances and compounds as well as their toxicity and environmental toxicity are described in Appendix V of the EU directive 67/548/EC. On the respective categorization methods, (e.g. as ‘very poisonous for water organisms’) quantitative thresholds are defined (example: ‘96h LC₅₀(Fisch)²⁷, 48h EC₅₀ (Daphina)²⁸ or 72h IC₅₀(Algae) ≤ 1 mg/l²⁹) The detailed procedure is described in the technical guidance document (TGD) of the European Commission (KOM 1996):

Starting with the data acquired on the risk potential and effect boundaries, a risk description is made under combination of measured, modelled and exposition data fixed by convention. For the description of the health risks, the expected expositions are put into correlation with NOAEL (No observed adverse effect level) or LOAEL (Lowest observed adverse effect level). Analogue to this, potential environmental concentrations (Predicted Environmental Concentration PEC) are correlated to concentrations for which no damage is expected. In the final step of the risk assessment the necessary further examinations or measures are proposed.

²⁷ concentration in water leading to the death of 50% of the fish population after 96h of exposition in laboratory

²⁸ Concentration in water leading to the immobilisation of 50% of a daphine population after 48h of exposition in laboratory

²⁹ concentration in water leading to a reduction in growth rate of 50% of the algae population after 72h of exposition in laboratory

The German Federal Environmental Agency summarized the criticism, especially with regard to the evaluation of environmental risks in UBA (1999a). The EU risk assessment is recognized as an important assisting factor for the substance and product assessment, but criticized as insufficient with respect to a precautionary and sustainable substance policy. Next to criticism on the methods for determination of risk potentials generally leading to an underestimation of emissions of harmful substances because e.g. the by- and decomposition products and real conditions are not considered sufficiently, the missing consideration of long time lapses, of comparative evaluations, of potential interactions, of data gaps and nescience is criticized. In UBA (2001), the closing of gaps in the protection of sea and artesian water and air is demanded with regard of the updating of the Technical Guidance Documents (TGD). Especially the PEC/PNEC concept implying that local and global sinks may be filled up to the PNEC concentration with the individual substances is criticized as contradictory to the ban of deterioration.

Application of the minimization and substitution principle as well as the inclusion of substance-inherent risk potentials as additional independent evaluation criteria are elements which are demanded to be applied within the framework of precaution-oriented substance evaluation by the Federal Environmental Agency.

11.1.2 Terms: Risk, Uncertainty and Nescience

Risk in the sense of natural sciences is the product of damage extent and occurrence probability. With increased availability of empirical data on potential damages and on the number of occurred damages, the preconditions for the determination of a high assessment certainty improve. Strictly speaking, complete assessment certainty describes a danger and not a risk. Uncertainties considered in the description of a risk are differentiated in terms and in methodology: fluctuations in margin resulting from statistical calculation methods are referred to as statistical uncertainties. Indefiniteness describes the status if the damage potential is known but knowledge on the occurrence probability is missing. If damage extent as well as occurrence probability are unknown, the situation is called nescience. Nescience and Indefiniteness are summarized under the term uncertainty. A historical example for risks resulting from nescience is the destruction of the stratospheric ozone layer by CFC (WBGU 1998). An example for Indefiniteness would be a substance with high danger potential intrinsic to the substance but for which the effects cannot be determined because of missing knowledge on distribution and exposition.

The Scientific Council for Global Environmental Changes of the Federal Government of Germany (WBGU) introduced further criteria enabling a typing of risks in their survey. For consideration of uncertainties and indefiniteness the criteria assessment certainty of occurrence probability and assessment certainty of the extent of damages as well as the criteria ubiquity, persistence, irreversibility, lag effect and social mobilization potential are introduced.

With these criteria the risks can be categorized in six types grouped in different risk areas: normal area, marginal area and prohibition area (WBGU 1999). In this, the normal area does not mark situations with zero risk but such that can be identified well with the 'classical' risk equation [damage extent x occurrence probability] and which can be controlled sufficiently by the existing risk management measures (Renn 1999). Table 41 shows the deduction of risk types by means of risk criteria.

Table 41: Deduction of risk types by means of risk factors

Risk type	Occurrence probability	Assessment certainty	Extent of damage	Assessment certainty	Ubiquity	Persistence	Irreversibility	Delay effect	Mobilisation effect	Example
Damokles	-	++	++	++						Nuclear energy
Zyklop	?	-, ?	++	+						Flooding
Pythia	?	--, ?	?	--, ?						BSE
Pandora	?	?	?	?	++	++	++			Persistent organic compounds
Kassandra	+, ++	-	+, ++	+				++		Climate change
Medusa	-	-	-	+					++	Electromagnetic fields

-- low

- rather low

+ rather high

++ high

? unknown

Source: according to WBGU 1999

Figure 44 shows the risk types deduced by (WBGU 1999) and their attribution to the risk areas.

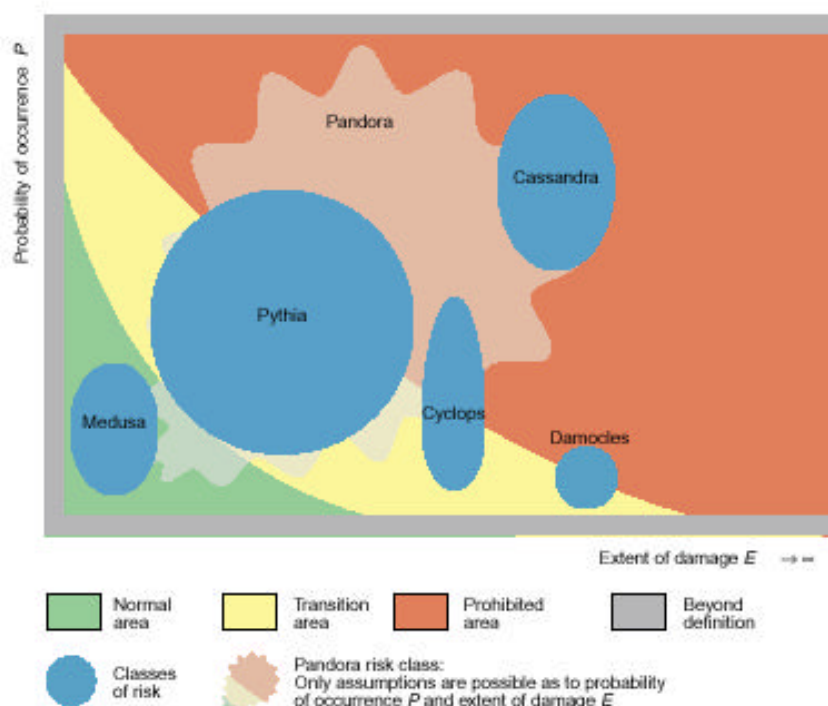


Figure 44: Classes of risk and their location in the normal-, marginal and prohibition area (WBGU 1999)

From the attribution to the risk areas action maxims for risk management can be deduced. Measures should aim at the shift from the prohibition and marginal area into the normal area.

An example from the area of chemicals for a risk in the normal area would be the diffuse application of lightly flammable petrol. According to (WBGU 1999), the risks from release of persistent organic pollutants (POP) and substances with an endocrine effect belong to the risk type Pandora. Effective measures for this risk type include the research and support of substitutes, limitations on amounts and spreading up to bans and damage management such as e.g. technical protection measures.

Risks from chemicals are generally marked by a high degree of nescience due to lack of knowledge on the basis data in 99% of the cases. Basically, this deficit can be reduced by the systematic elaboration of basis data as recommended in the white paper on chemical policy. Especially with regard to long term and widespread effects, complex effect patterns and so far unknown or unexplained effects, evaluation approaches are necessary reaching beyond the paradigm 'Safe are all substances as long as the opposite is not proven' (e.g. Tickner 2001). The question is therefore which systematic and founded evaluation mechanisms in uncertainty and indefiniteness as well as different risk dimensions can do justice to the evaluation of substances.

11.1.3 Approaches to a precaution-oriented risk assessment of substances

11.1.3.1 Late Lessons from Early Warnings

The European Environmental Agency examined which precaution-oriented decision mechanisms need to be observed to prevent damages and cost to society of such dimensions

in the future in the study „Late lessons from early warnings“ (EEA 2001). Case studies for this were historic environment and health related damage events such as asbestos, PCB, CFC or MTBE.

Of the 12 lessons of the EEA which can be assessed within the framework of a risk assessment³⁰, the following need to be mentioned:

- Awareness and differentiation of uncertainty, indefiniteness and nescience
- Observation of early warning criteria such as persistence and bio accumulation ability
- Identification of blind spots by consideration of different parameters such as the produced amount of a substance
- Ensure that the actual conditions in practice of the application are taken into consideration
- Identification of substitution options with lower risk potential

11.1.3.2 Strategy on Management of Substances

In the Netherlands, a comprehensive strategy „Strategy on Management of Substances“ (SOMS 2001) was elaborated under participation of all interested circles which was accepted by the Dutch council of ministers in December 2001. As a basis for a precaution-oriented management of chemicals, criteria for the classification of substances in five classes from low to very high apprehension were constituted. This ‘Quick-Scan’ is done with a basis set of substance-intrinsic properties³¹ under consideration of the data situation for categorisation in classes with higher apprehension. In a next step the substances are attributed to certain risk management categories depending on the usage pattern.

11.1.3.3 TRGS 440 – Column model

The German technical guidelines for hazardous substances 440 (TRGS 440) of the federal work safety and workers protection authority explains the investigation requirements according to paragraphs 16 and 36 of the ordinance on hazardous substances (GefStoffV) for testing and substitution methods and substitution substances with a lower health risk. The column model of the TRGS 440 attributes R- sentences to five levels of risk from very high to negligible. Risk classes are determined in six evaluation categories (columns) e.g. acute health risk, chronic health risk etc. The column model is based on a rather complete database. A consideration of the data quality is done in the comparative evaluation. The emphasis of the TRGS 440 is by design the assessment of risks related to the work environment, a differentiated consideration of the life cycle before and after production is not conducted.

11.1.3.4 Guideline for formulators and other commercial users of chemical substances

In the framework of the study ‘Requirements on substance introduction in waters’ (UBA 1999b), Ökopol examined ten assessment methods evaluation the effect of substances on waters under different contexts and with different weighting and objectives. On the basis of

³⁰ A successful risk minimisation requires a sufficient risk management and respective risk communication after the step of risk assessment. The emphasis of this study is on risk evaluation. Fundamentally, aspects of risk management cannot be excluded from a comprehensive evaluation.

³¹ Reduced data set according to appendix VII A of the guideline 67/548/EU on persistence, bio accumulation ability, toxicity, human toxicity, carcinogenic, mutagenic and reproduction-toxic potential, effectiveness as endocrine disruptor

the results, the ‘guideline for formulators and other commercial users of chemical substances’ (UBA 1999c) was established. Substances are attributed to five risk categories on the basis of selected substance properties and usage patterns. Lack of data leads to classification in a high risk class. The guideline is directed at the effects on waters, but the demonstrated risk profile basically allows the extension to other problems.

Table 42: Risk profile according to (UBA 1999c)

Substance property	Increasing risk				
	I	II	III	IV	IVa
CMR ³²	No indication		suspicion CM	proven	unknown
...					
Usage pattern					
Amount	Very small	small	medium	high	unknown
Usage pattern at the customer	Hermetic application	Industrial use	Distributed use	Application open to environment	unknown
...					

11.1.3.5 Persistence, range and bioaccumulability

(Scheringer 1999) developed an exposition-based approach with the concept of persistence and range for the extension of the effect-based assessment. The concept is presently further developed in the framework of the EU research project ‘Precautionary Screening of New Organic Chemicals with Respect to Global Threat Potentials’. In this, the so-called ‘Pandora filter’ classifies substances on the basis of the parameters half life period, range and bioaccumulability. A test with 33 organic mass chemicals and 23 substances falling under the Montreal/Kyoto/Stockholm agreements shows that the filter would have enabled the identification of the climate-relevant and ozone-depleting substances if calibrated accordingly (Müller-Herold 2002).

The fact that next to properties intrinsic to the substance such as carcinogenicity also properties such as persistence, range or bioaccumulability are consulted for the evaluation of substances and that high persistence or bioaccumulability may trigger limiting measures is controversial in the scientific and political debate. Persistence or bioaccumulability as such do not mean a risk to human health or the environment. They are however indicators for the global extent, the long term extent and the irreversible nature of risks and for the stress on the assimilation capacity of organisms and environmental compartments. The expert council for environmental questions fears in the report of 1998 however that partial assessments based on the factors persistence and ubiquity may lead to ‘speculative’ precaution. These concerns are probably also borne on the fear that massive limitations of mass chemicals may be justified thus causing economic pressure beyond the limit of economic reasonability (SRU 1998). Even from this conservative view, nothing can be said against the use of persistence, range and bioaccumulability as complementary parameters in the framework of differentiated evaluation and substitution decisions and to employ them as important warning signals in the risk assessment of substances especially if new substances are concerned which are foreseen for application in large amounts.

³² CMR (Carcinogenic, mutagenic and substances toxic to reproduction)

In the framework of a master and exam study supervised by the Öko-Institut (Wursthorn 2001) 25 assessment methods for the evaluation of pollutants with persistence or bioaccumulation ability were examined on the basis of three cases (perfluoro sulfonates, tributyl tin, methylene tertiary butylether) and developed into a practice-oriented evaluation module for the assessment of persistent and bioaccumulative properties.

After determination of the risk by these properties, it needs to be ascertained in the next step how these properties can be weighted in relation to further assessment criteria.

11.2 Weighting of effect categories

In the comparative evaluation of systems (products, substances, methods), advantages and disadvantages in different effect categories have to be weighed against each other. There is presently no acknowledged method to bring e.g. the high greenhouse relevance of one substance and the toxicological relevance of another onto a common denominator and comparative measuring unit. A ranking of different effects relevant to environment and health needs to be done on the basis of scientific facts but may only take place under consideration of values and risk perception of different political actors and socio-political priorities.

The German Federal Environmental Agency developed a method for the establishment of a hierarchy of effect categories in (UBA 1999d). An interdisciplinary assessment board with representatives from industry, science, environmental and consumer associations, unions and governmental environmental protection authorities elaborated a weighting of effect categories on the basis of information on 'ecological risk', 'distance to target' and 'specific contribution'

The evaluation of the assessment fields 'ecological risk' and 'distance to target' takes place according to criteria given in 2.4.

For the standardisation of the 'specific contribution', the system-specific contribution of an effect category is put in relation to the total load of this effect category. It can only be determined specifically for a system.

Table 43: Criteria for ecological risk and distance to target (UBA 1999d)

Ecological risk	Distance-To-Target
Potential damage extent	Distance between existing and design state (environmental quality target, alternatively environmental target of action)
Irreversibility	
Ubiquity	
Uncertainty and indefiniteness	
	Trend of exposure (rising or falling)
	Enforceability and effectivity of measures

The results of the three evaluation fields are divided into five classes respectively (A = very high, E = very low). Table 44 summarizes the regulation of the board on 'ecological contribution' and 'distance to target'.

Table 44: Establishment of a hierarchy of effect categories according to (UBA 1999d)

Effect category	Ecological contribution	Distance-To-Target
Acidification	B	B
Greenhouse effect	A	A
Depletion of stratospheric ozone	A	D
Resource use	C	B
Photochemical formation of oxidants	D	B
Use of nature space	A	B (A,C)
Terrestrial eutrophication	B	B
Aquatic eutrophication	B	C

For the effect categories ‚direct human toxicity’ and ‚direct damage of ecosystems’, there is presently no methodological concept for aggregation. An evaluation can therefore not be made for all categories but only for the evaluation of single toxic effects.

This approach and the relevant regulations were explicitly elaborated for the application in eco-balances and cannot be transferred to other assessment coherences or the setting of focal points for environmental policy. The criteria forming the basis for this (see section 2.4) which are normally deduced from the scientific and social discussion on environmental targets, risks, defence against risks and precaution and the methodology of the finding of consensus in a board staffed with the different interest groups are however transferable to similar problems of the evaluation.