Danish Ministry of the Environment
Environmental Protection Agency

Survey of selected fluorinated greenhouse gasses

Part of the LOUS-review

Consultation draft

Title:

Survey of selected fluorinated greenhouse gasses

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Preface

Background and objectives

The Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) is intended as a guide for enterprises. It indicates substances of concern whose use should be reduced or eliminated completely. The first list was published in 1998 and updated versions have been published in 2000, 2004 and 2009. The latest version, LOUS 2009 [Danish EPA, 2011] includes 40 chemical substances and groups of substances which have been documented as dangerous or which have been identified as problematic using computer models. For inclusion in the list, substances must fulfil several specific criteria. Besides the risk of leading to serious and long-term adverse effects on health or the environment, only substances which are used in an industrial context in large quantities in Denmark, i.e. over 100 tons per year, are included in the list.

Over the period 2012-2015 all 40 substances and substance groups on LOUS will be surveyed. The surveys include collection of available information on the use and occurrence of the substances, internationally and in Denmark, information on environmental and health effects, on alternatives to the substances, on existing regulation, on monitoring and exposure, and information regarding ongoing activities under REACH, among others.

On the basis of the surveys, the Danish EPA will assess the need for any further information, regulation, substitution/phase out, classification and labelling, improved waste management or increased dissemination of information.

This survey concerns fluorinated greenhouse gases (HFCs, PFCs and sulphur hexafluoride). These substances were included in the first list in 1998 and have remained on the list since that time.

The main reason for the inclusion in LOUS is that they are *"Substances with particular focus in Denmark since they are potent greenhouse gases - substances being phased out"*.

The entry in LOUS for these substances is "Fluorinated greenhouse gases" with the following examples from the group: HFC 134a, HFC 125, HFC 143a, HFC 152a, CF_4, C_2F_6, C_3F_8 and Sulphur hexafluoride (SF_6).

The main objective of this study is, as mentioned, to provide background for the Danish EPA's consideration regarding the need for further risk management measures.

The process

The survey has been undertaken by COWI in co-operation with DTI from October 2013 to May 2014. The work has been followed by an advisory group consisting of:

- Mikkel Aaman Sørensen, Danish EPA - Chemicals, (Chairman);
- Jakob Zeuthen, Danish Chamber of Commerce;
- Nikolai Nielsen, Confederation of Danish Industry;
- Ida M.L.D. Storm, Danish Agriculture & Food Council;
- Kim Valbum, Association of Authorised Refrigeration Companies;
- Marianne Ripka, Danish EPA, Enterprises;
- Birgitte Holm Christensen, Danish EPA, Commerce;
- Katrine Smith, Danish EPA, Soil and Waste;

- Erik Hansen, COWI A/S;
- Per Henrik Pedersen, Danish Technological Institute.

Data collection

The survey and review is based on the available literature on the substances, information from databases and direct inquiries to trade organisations and key market actors.

The data search included (but was not limited to) the following:

- Legislation in force from Retsinformation (Danish legal information database) and EUR-Lex (EU legislation database);
- Ongoing regulatory activities under REACH and intentions listed on ECHA's website (incl. Registry of Intentions and Community Rolling Action Plan);
- Relevant documents regarding International agreements from the Kyoto Protocol;
- Data on harmonised classification (CLP) and self-classification from the C&L inventory database on ECHAs website;
- Data on eco-labels from the Danish eco-label secretariat (Nordic Swan and EU Flower);
- Pre-registered and registered substances from ECHA's website;
- Production and external trade statistics from Eurostat's databases (Prodcom and Comext);
- Data on production, import and export of substances in mixtures from the Danish Product Register (confidential data, not searched via the Internet);
- Reports, memorandums, etc. from the Danish EPA and other authorities in Denmark;
- Reports published at the websites of:
  - The Nordic Council of Ministers, ECHA, the EU Commission, OECD;
  - Environmental authorities in Norway (Klif), Sweden (KemI and Naturvårsverket), Germany (UBA), UK (DEFRA and Environment Agency), the Netherlands (VROM, RIVM), Austria (UBA). Information from other EU Member States was retrieved if quoted in identified literature;
  - US EPA, Agency for Toxic Substances and Disease Registry (USA) and Environment Canada.

Besides, information was obtained directly from and European trade organisations and a few key market actors in Denmark.

Summary and conclusions

Fluorinated greenhouse gasses (F-gases) as defined by Danish Environmental Protection Agency's List of Undesirable Substances (LOUS) covers substances classified as HFCs (hydrofluorocarbons) and PFCs (perfluorinatedcarbons) besides sulphur hexafluoride.

This survey covers 14 HFC-substances plus 7 PFC-substances besides sulphur hexafluoride (see Table 0). All substances are identified by the European Fluorocarbon Technical Committee (EF-CTC) as major fluorinated greenhouse gasses. Within the groups of HFCs are included 2 substances also named as HFOs (HFOs designates hydrofluoroolefins). HFOs differ from other HFCs in having a double bond between a pair of carbon atoms making the substances more exposed to atmospheric decomposition.

The survey is focused on pure substances. Several HFC-products are marketed, however, which are not single substances, but mixtures of substances designed to replace specific substances for certain applications. These HFC-products will always be characterized by acronyms as HFC-4xx or HFC-5xx (e.g. HFC-401a, HFC-507a).

F-gases are used as heat transmission media in air-conditioning, heat pumps and refrigeration systems. They are also used as blowing agents for plastics foams, and as firefighting agent. Minor uses include propellant for medical spray, as solvent, insulation gas for high voltage applications and cleaning agent in semiconductor manufacturing. Generally F-gases are gasses or volatile liquids at room temperature, thermal and chemical stable, with very low toxicity and with favourable environmental profile apart from their global warming potential.

Regulatory framework

F-gases covering HFCs, PFCs and SF_6 is regulated by EU-legislation as well as Danish legislation. The Danish legislation in many ways is the most restrictive. The Danish legislation allows for the use of HFCs in refrigeration systems with refrigerant charges less than 10 kg HFC refrigerant – the so-called "10 kg window". Future changes of the Danish legislation may be focused at this "window".

New EU legislation which will significantly restrict the use of F-gases in the EU is in the process of being approved. The new regulation, however, allows for continued use of HFC-152a.

Few countries worldwide have national policies going beyond existing EU F-gas regulations. A comprehensive ban exists in Switzerland covering refrigeration as well as many other applications of F-gases.

Only one substance - HFC-365mfe - is subject to harmonised classification (Highly flammable liquid and vapour). None of the substances are addressed further by REACH or are in pipeline for further activities under REACH. All of the substances are covered by the Kyoto Protocol on reduction of emission of greenhouse gases.

The use of HFCs, PFCs and SF_6 are only addressed by a few eco-labels (e.g. heat pumps, floor coverings) and eco-labels are not established for cooling and freezing equipment for private and professional use products besides that existing eco-labels for heat pumps do not restrict the use of HFC-134a. In both cases it may be considered to promote the use of natural refrigerants.

TABLE 0 FLUORINATED GREENHOUSE GASSES COVERED BY THE SURVEY

Acronym, Common name	Chemical Formula	CAS No.	Main applications in Denmark	GWP 100*5	Consumption DK – 2012 tons	Emission DK -2012 tons
HFC-23	CHF_3	75-46-7	No data	12,400	*2	2.0
HFC-32	CH_2F_2	75-10-5	Refrigeration, AC	677	20.6	16.9
HFC-125	CHF_2CF_3	354-33-6	Refrigeration, AC	3,170	71.7	20.7
HFC-134a	CH_2FCF_3	811-97-2	Refrigeration, AC, technical sprays	6,940	198.4	226.0
HFC 143a	CH_3CF_3	420-46-2	Refrigeration	4,800	57.7	6.9
HFC 152a	CH_3CHF_2	75-37-6	Thermostats	138	13.0	10.7
HFC 227ea	CF_3CHFCF_3	431-89-0	Not used	3,350	-	-
HFC 236fa	$CF_3CH_2CF_3$	690-39-1	Not used	8,060	-	-
HFC-245fa	$CHF_2CH_2CF_3$	460-73-1	Not used in 2012 *1	858	*2	-
HFC-365mfc	$CH_3CF_2CH_2CF_3$	406-58-6	Not used in 2012 *1	804	*2	-
HFC-43-10mee	$CF_3CHFCHFCF_2CF_3$	138495-42-8	Not used	1,650	-	-
HFO-1234yf	$CF_3CF=CH_2$	754-12-1	Not used	<1	-	-
HFO-1234zeE	Trans-$CF_3CH=CHF$	29118-24-9	Not used	<1	-	-
PFC-14	CF_4	75-73-0	Optical fibre production	6,630	0.2	*3
PFC-116	C_2F_6	76-16-4	Not used	11,100	-	-
PFC-218	C_3F_8	76-19-7	Not used in 2012	8,900	-	0.8
PFC-318	$c\text{-}C_4F_8$	415-25-3	Other purposes	9,540	0.2	*3
PFC-3-1-10	C_4F_{10}	355-25-9	Not used	9,200	-	-
PFC-4-1-12	C_5F_{12}	678-26-2	Not used	8,550	-	-
PFC-5-1-14	C_6F_{14}	355-41-10	Not used	7,910	-	-
SF_6	SF_6	2551-62-4	Power switches, optical fibre production.	23,500	2.6	4.8

- Not relevant
*1 Former use was only for export
*2 Total consumption of HFC-23, HFC-245fa and HFC-365mfc registered as 3.5 tons in 2012.
*3 Total emission of PFC-14 and PFC-318 registered as 0.38 tons in 2012.
*4 Global warming potential over a 100-year period.

Manufacture and uses
F-gases are produced in several countries globally as well as in Europe. The total global production is probably above 300,000 tons/year. HFC-gases are the main gases consumed while SF_6 counts for 2-3% of the total consumption and PFC-gases for less than 1%.

No F-gases are produced in Denmark and the total consumption is based on import. The consumption has been decreasing from about 1000 tons in 2000 to about 360 tons in 2012. Consumption figures for the individual gases are presented in Table 0.

Refrigeration and air-conditioning are by far the dominant application of F-gases and in particular HFCs. Smaller amounts are used for thermostats and aerosols while the consumption as blowing agent for foams ceased in 2002.

PFCs were earlier used in special low temperature refrigeration equipment, but this use seems to have ceased in Denmark, as no consumption of PFCs were recorded in 2012. SF_6 is today mainly used as dielectric gas SF_6 in high voltage installations, while uses as insulation gas in windows and blanket gas in magnesium production today has ceased.

The consumption of F-gases in Denmark has been stable during the last 5-6 years.

Waste management
As F-gases are not produced in Denmark no waste from production of these substances is generated in Denmark. Collection and recovery of F-gases will take place by maintenance and repair of equipment and facilities in which F-gases are used (e.g. refrigerators, freezers, air condition systems, heat pumps, transformer stations) as well as by conversion of equipment and facilities containing F-gases to new refrigerants/heat transmission media and by dismantling of old equipment and facilities. This is also the case for SF_6 used in transformer stations.

The recovered F-gases will be used directly for filling of existing or new equipment and facilities in Denmark or abroad if necessary after cleaning/regeneration, or be directed to destruction.

Scrapped household refrigerators, freezers and heating pumps and similar small units are generally emptied for refrigerant/heat transmission media and the gas collected is directed to destruction. The majority of units are furthermore treated in a special shredder allowing the insulation foam to be separated and collected and directed to destructing together with its content of blowing agent. A minor part of the units collected are exported for treatment in Sweden and Germany.

F-gases present in foam in other constructions will not be collected and destroyed and will therefore be released to the atmosphere. This is also the case for SF_6 used as insulation gas in double glazing windows.

Destruction of F-gases used as refrigerants as well as F-gases contained in insulation foam separated and collected in Denmark for destruction can be assumed to result in virtually 100% destruction.

Environmental effects and exposure
HFCs, PFCs, HFOs and SF_6 are found in the atmosphere where concentrations are on the rise. Concentrations have steadily increased in the atmosphere since at least 1978, and are continuing to do so at a present rate of 5% per year.

Danish emissions have increased significantly from 1990 to about 2007/08. Emissions are now in the process of lowering. The emissions in 2012 counted for approx. 280 tons HFCs, 1 tons PFCs and 5 tons SF_6 corresponding to approximately 780,000 tons CO_2-eq. Emission figures for the individual gases are presented in Table 0.

There is growing concern over the emission and accumulation of very long-lived fluorinated trace gases in the atmosphere. They have a high persistency due to the stability of the C-F chemical bond. For the PFCs and SF_6 atmospheric degradation is extremely slow, and the compounds have atmospheric lifetimes of the order of millennia. They are greenhouse gases associated with a significant global warming potential as they are strong infrared radiation absorbers. These gases are non-reactive and thus pose no toxic threat to the biosphere.

HFCs have effectively replaced ozone depleting substances (ODS) as CFCs and HCFCs which have been phased out under the Montreal Protocol. As a result of this success HFCs are increasing in the atmosphere.

HFCs and HFOs are subject to degradation in the lower atmosphere due to the C-H bonds in the molecules that are reactive to hydroxyl radicals. The atmospheric lifetimes for these compounds differs between 1.5 and 242 years for the main HFCs while the lifetimes for the main HFOs are down to 0.03-0.04 years.

In the future, HFC emissions have the potential to become very large. Without intervention, the increase in HFC emissions is projected to offset much of the climate benefit achieved by the earlier reduction in ODS emissions. The projected HFC emissions would be equivalent to 7 to 19% of the CO_2 global emissions in 2050.

No toxic effects of degradation products have been identified, including trifluoroacetic acid (TFA) which is a degradation product of some HFOs and HFCs. TFA is a highly persistent pollutant that appears to be a naturally occurring chemical present in seawater and significant concentrations have been found in rain, river and lake water and both coastal and deep-ocean sea water. The oceans are thus a large reservoir for TFA and the observed concentrations are far in excess of those that could occur as a result of atmospheric oxidation of man-made fluorocarbons. The cycle of TFA in the atmosphere and hydrosphere is, however, not well understood and is the subject of ongoing research.

Human health

Among the substances addressed only HFC-365mfe is subject to harmonised classification (Highly flammable liquid and vapour). Industry self-classifications indicate that the flammability of the HFCs increase with shorter carbon-chain length and less fluorination. The self-classifications also show that the shorter-chain HFCs, HFO-1234yf, SF_6 and the PFCs are stored under high pressure and may explode if heated.

Regarding toxicity and based on the knowledge available, it can generally be concluded that HFCs, PFCs and SF_6 cause a low human hazard. At very high doses, reversible effects such as reduced breathing rate, salivation, problems with balance, as well as cardiac sensitisation has been reported for some HFCs. In addition, some HFCs and PFCs might have slight irritating properties.

Available mutagenicity/genotoxicity tests (*in vitro* and *in vivo*) and carcinogenicity studies do not suggest that the addressed substances possess a risk for cancer.

The limited information regarding occupational and consumer exposure suggests that exposure to these substances is low during normal operating conditions. Several references deliberately do not address exposure at all given the very low human health hazards. Consequently, no actual toxicological risk assessments have been identified.

Overall, the main risks of the addressed substances seem to be directed to the flammable properties of HFCs and HFOs and to the thermal degradation products, as thermal degradation might lead to formation of highly toxic degradation products as hydrogen fluoride (HF) and carbonyl fluoride (COF_2). Formation of toxic degradation products also applies to SF_6 subject to electrical discharges occurring in gas-insulated equipment.

Further research on thermal degradation products, including HF and COF_2 formation, might be warranted.

Alternatives
Alternatives have been developed and implemented for most sectors where F-gases are used or have been used. This has been successful, and the consumption of F-gases has decreased to one third from 2000 to 2012.

This development was caused by the Danish regulation on F-gases, including taxes and bans for certain purposes combined with the support to R&D projects to ensure rapid development of alternative technology.

However, the consumption of HFC-refrigerants seems to have stabilized at an annual consumption of about 360 tons since 2009. This stagnation is caused mainly by the so-called "10-kg window" in Danish legislation allowing HFCs still to be used in equipment requiring a charge of refrigerant below 10 kg.

The "10-kg window" thus represents an important group of products still using HFCs due to lack of obvious alternatives and legislation requiring the use of alternatives. The products in question include condensing units, heat pumps and small chillers.

Other important challenges identified include:

- The financial barriers for establishing of very large ammonia refrigeration systems with charges above 5 tons, as special and costly planning and precautions are necessary according to the Danish legislation implementing the EU Risk Directive;
- From 1. January 2015 it will be banned to fill HCFC-22 on existing refrigeration systems. It is estimated that more than 5,000 existing systems are still in use, and some hundreds are essential systems with more than 10 kg of HCFC-22. There is some concern that many of the existing systems may not be able to carry out the phase-out of HCFC-22 in time.

Significant data gabs
Significant data gabs identified include:

- Knowledge on thermal degradation products from F-gases and in particular from degradation of HFCs, HFOs as well as SF_6, including HF and COF_2 formation is limited;
- The cycle of TFA in the atmosphere and hydrosphere is not well understood and there is a need for further research;
- No measurements exist of the amount of F-gases actually destroyed in Denmark by treatment at NORD and the power plant treating PU-foam separated and collected from small units;
- It is unclear, whether existing refrigeration systems based on HCFC-22 will be able to carry out the phase-out of HCFC-22 in time and whether there will be a need for special support to ensure the selection of sustainable alternatives.

Sammenfatning og konklusion

Fluorholdige drivhusgasser (F-gasser) omfattet af Miljøstyrelsens liste over uønskede stoffer (LOUS) dækker kemiske forbindelser klassificeret som HFC'er (hydrofluorcarboner) og PFC'er (perfluorcarboner) foruden svovlhexafluorid (SF_6).

Denne kortlægning omfatter 14 HFC-forbindelser, 7 PFC-forbindelser samt svovlhexafluorid (se Tabel 00). Alle forbindelser er angivet af European Fluorocarbon Technical Committee (EFCTC) som vigtige fluorholdige drivhusgasser. Blandt HFC'erne er medregnet 2 forbindelser, som også er klassificeret som HFO'er (HFO står for hydrofluoroolefiner). HFO'erne afviger fra andre HFC'er ved, at de indeholder en dobbeltbinding mellem 2 kulstofatomer, som medfører, at stofferne er mere udsat for nedbrydning i atmosfæren.

Kortlægningen er fokuseret på de rene forbindelser. Adskillige af de HFC-produkter, som markedsføres, er dog ikke rene stoffer, men er blandinger designet til at erstatte specifikke stoffer til bestemte formål. Disse HFC-produkter vil altid være betegnet med akronymer som HFC-4xx eller HFC-5xx (fx. HFC-401a, HFC-507a).

F-gasser bruges som varmetransmissionsmidler i aircondition, varmepumper og køleanlæg. De bruges også som opskumningsmidler i skumplast og til ildslukning. Mindre anvendelser omfatter blandt andet drivgasser i aerosoler (sprays) til medicinske formal, opløsningsmidler, dielektrisk gas i stærkstrømsanlæg og rensemidler anvendt ved fremstilling af halvledere. F-gasser er ved rumtemperatur gasser eller flygtige væsker, og de er både kemisk og temperaturmæssigt stabile. De er stort set ugiftige og miljømæssigt uproblematiske med undtagelse af deres potentiale som drivhusgasser.

Regulering

F-gasser er omfattet af EU-lovgivning såvel som dansk lovgivning. Den Danske lovgivning er på mange måder den mest restriktive. Den danske lovgivning tillader brugen af HFC'er i køleanlæg der rummer mindre end 10 kg HFC kølemiddel per anlæg – det såkaldte "10 kg vindue". Kommende ændringer af den danske lovgivning kan med fordel fokuseres på dette "vindue".

Ny EU regulering, som væsentligt vil begrænse brugen af F-gasser i EU er ved at blive godkendt. Den nye regulering tillader dog forsat brug af HFC-152a.

Der er verden over kun få lande, der har indført lovgivning, som er mere restriktiv end den eksisterende EU-regulering. Et omfattende forbud, som omfatter både køling og mange andre anvendelser af F-gasser, er indført i Schweiz.

HFC-365mfe er den eneste forbindelse, som er optaget på EU's liste over harmoniserede klassificeringer (meget brandbar væske og damp). Ingen af forbindelserne er i øvrigt omfattet af REACH eller genstand for aktivitet under REACH. Alle forbindelser er omfattet af Kyoto Protokollen om reduktion af emission af drivhusgasser.

Brugen af HFC'er, PFC'er og SF_6 er omfattet af enkelte miljømærker (gælder fx. varmepumper og gulvbelægning). Der er dog ikke indført miljømærker for køle- og fryseudstyr for husholdninger og professionelt brug. Hertil kommer at miljømærker for varmepumper ikke begrænser brugen af HFC-134a. I begge tilfælde kan det overvejes at fremme brugen af naturlige kølemidler.

TABEL 00 FLUORHOLDIGE DRIVHUSGASSER OMFATTET AF KORTLÆGNINGEN

Akronym, betegnelse	Kemisk formel	CAS nummer	Vigtigste anvendelser i Danmark	GWP 100 *4	Forbrug DK – 2012 tons	Emission DK -2012 tons
HFC-23	CHF_3	75-46-7	Ingen data	12.400	*2	2,0
HFC-32	CH_2F_2	75-10-5	Køling, aircondition	677	20,6	16,9
HFC-125	CHF_2CF_3	354-33-6	Køling, aircondition	3.170	71,7	20,7
HFC-134a	CH_2FCF_3	811-97-2	Køling, aircondition tekniske sprays	6.940	198,4	226,0
HFC-143a	CH_3CF_3	420-46-2	Køling	4.800	57,7	6,9
HFC-152a	CH_3CHF_2	75-37-6	Termostater	138	13,0	10,7
HFC-227ea	CF_3CHFCF_3	431-89-0	Bruges ikke	3350	-	-
HFC-236fa	$CF_3CH_2CF_3$	690-39-1	Bruges ikke	8.060	-	-
HFC-245fa	$CHF_2CH_2CF_3$	460-73-1	Ikke brugt i2012 *1	858	*2	-
HFC-365mfc	$CH_3CF_2CH_2CF_3$	406-58-6	Ikke brugt i2012 *1	804	*2	-
HFC-43-10mee	$CF_3CHFCHFCF_2CF_3$	138495-42-8	Bruges ikke	1.650	-	-
HFO-1234yf	$CF_3CF=CH_2$	754-12-1	Bruges ikke	<1	-	-
HFO-1234zeE	Trans-$CF_3CH=CHF$	29118-24-9	Bruges ikke	<1	-	-
PFC-14	CF_4	75-73-0	Produktion af optiske fibre	6.630	0,2	*3
PFC-116	C_2F_6	76-16-4	Bruges ikke	11.100	-	-
PFC-218	C_3F_8	76-19-7	Ikke brugt i2012	8.900	-	0,8
PFC-318	$c\text{-}C_4F_8$	415-25-3	Andre formål	9.540	0,2	*3
PFC-3-1-10	C_4F_{10}	355-25-9	Bruges ikke	9.200	-	-
PFC-4-1-12	C_5F_{12}	678-26-2	Bruges ikke	8.550	-	-
PFC-5-1-14	C_6F_{14}	355-41-10	Bruges ikke	7.910	-	-
SF_6	SF_6	2551-62-4	Stærkstrømskontakter. Produktion af optiske fibre.	23.500	2,6	4,8

- Ikke relevant
*1 Tidligere brug var kun til eksport
*2 Samlet forbrug af HFC-23, HFC-245fa og HFC-365mfc registeret til 3.5 tons i 2012.
*3 Samlet emission of PFC-14 og PFC-318 registeret til 0.38 tons i 2012.
*4 Globalt opvarmningspotentiale over en 100-års periode.

Fremstilling og anvendelser
F-gasser producers i adskillige lande både i og uden for Europa. Den globale produktion er givetvis over 300.000 tons/år. HFC-gasserne er de mængdemæssigt vigtigste, mens SF_6 tæller for 2-3 % af det totale forbrug og PFC-gasserne for mindre end 1 %.

F-gasser produceres ikke i Danmark og hele forbruget i Danmark er baseret på import. Forbruget er mindsket fra ca. 1.000 tons in 2000 til ca. 360 tons in 2012. Forbrugstal for enkelte gasser er angivet i Tabel 00.

Køling og aircondition er langt de vigtigste anvendelser for F-gasser og specielt HFC'er. Mindre mængder er anvendt til termostater og aerosoler (sprays), mens brugen som opskumningsmiddel til skumplast ophørte i 2002.

PFC'er blev tidligere brugt i særligt lavtemperatur køleudstyr, men denne anvendelse er tilsyneladende ophørt i Danmark, da der ikke blev registreret forbrug i 2012. SF_6 bruges i dag hovedsageligt som dielektrisk gas i stærkstrøms installationer, mens brugen som isoleringsgas i vinduer og som beskyttelsesgas ved produktion af magnesium i dag er ophørt.

Forbruget af F-gasser i Danmark har været stabilt gennem de seneste 5-6 år.

Affaldsbehandling
Der genereres ikke produktionsaffald i Danmark, da F-gasser som nævnt ikke produceres i Danmark. Indsamling af F-gasser sker ved reparation og vedligeholdelse af udstyr og anlæg som indeholder F-gasser (fx. køleskabe, frysere, airconditionanlæg, varmepumper, transformerstationer) samt ved konvertering af udstyr og anlæg til nye kølemidler/varme transmissionsmidler og ved skrotning af udtjent udstyr og anlæg.

De opsamlede F-gasser anvendes i eksisterende eller nyt udstyr i Denmark eller udlandet - om nødvendigt efter oprensning - eller sendes til destruktion.

Skrottede husholdnings køleskabe, frysere og varmepumper og lignende små enheder vil generelt blive tømt for kølemiddel/varmetransmissionsmiddel, og den opsamlede gas afleveret til destruktion. Størsteparten af enhederne behandles tillige i et særligt fragmenteringsanlæg, hvor isoleringsskummet kan opsamles og føres til destruktion sammen med indholdet af opskumningsmiddel. En mindre del af de indsamlede enheder eksporteres til behandling i Sverige eller Tyskland.

F-gasser, som er til stede i skumplast i andre konstruktioner, vil ikke blive indsamlet og destrueret og vil derfor blive frigivet til atmosfæren. Dette gælder også for SF_6 anvendt som isoleringsgas i vinduer.

F-gasser anvendt som kølemidler eller indeholdt i skumplast - separeret og opsamlet i Danmark med henblik på destruktion - kan påregnes at blive fuldstændigt destrueret.

Miljøpåvirkninger og -effekter
HFC'er, PFC'er, HFO'er og SF_6 er målt i atmosfæren. Koncentrationerne har været konstant stigende siden i hvert fald 1978 og fortsætter med at stige med en rate på ca. 5 % årligt.

Danske emissioner er steget væsentligt fra 1990 til 2007/08, men er nu på vej nedad. Emissionerne i 2012 udgjorde ca. 280 tons HFC, 1 tons PFC and 5 tons SF_6 svarende til ca. 780.000 tons CO_2-eq. Emissioner for de enkelte forbindelser er angivet i Tabel 00.

Der er stigende bekymring over emissionen og akkumuleringen af meget fluorholdige gasser med lang levetid atmosfæren. De er meget persistente på grund af stabiliteten af den kemiske C-F binding. For PFC'er og SF_6 er den atmosfæriske nedbrydning ekstremt langsomt, og forbindelserne har levetider i atmosfæren på mange tusinde år. De er drivhusgasser med et væsentligt potentiale for global opvarmning, da de stærkt absorberer infrarød stråling. Gasserne er generelt ikke-reaktive og udgør ingen trussel mht. giftighed overfor miljøet.

HFC'er har effektivt erstattet CFC og HCFC, som er udfaset som fastlagt under Montreal Protokollen. Denne succes har medført et øget indhold af HFC'er i atmosfæren.

HFC'er og HFO'er nedbrydes i den lavere atmosfære på grund af C-H bindingerne, som reagerer med hydroxyl radikaler. Den atmosfæriske livetid for disse forbindelser er af størrelsen 1,5 til 242 år for de vigtigste HFC'er, mens levetiden for de vigtigste HFO'er er nede på 0,03-0,04 år.

Emissionen af HFC'er har potentiale til at blive meget væsentlig i fremtiden. Uden indgreb vil stigningen i HFC emissioner medføre, at en stor del af den klimagevinst, som blev opnået ved udfasningen af CFC og HCFC, vil gå tabt. Emissionen af HFC'er i 2050 er estimeret at svare til 7 – 19 % af de globale emissioner af CO_2.

Der er ikke identificeret nedbrydningsprodukter med væsentlig giftvirkning i miljøet, herunder medregnet trifluoreddikesyre (TFA), som er et nedbrydningsprodukt af visse HFC'er og HFO'er. TFA er en meget persistent forbindelse, som synes at forekomme naturligt i havvand. Væsentlige koncentrationer af TFA er registreret i regn, søer og floder og i både kystnære havområder og i oceanerne. Havene er derfor et stort lager for TFA, og de observerede koncentrationer overstiger klart hvad der kunne forventes som resultat af atmosfærisk iltning af menneskeskabte fluorcarboner. Kredsløbet for TFA i atmosfæren og hydrosfæren er dog langtfra klarlagt og er genstand for igangværende forskning.

Sundhed

HFC-365mfe er som nævnt den eneste forbindelse optaget på EU's liste over harmoniserede klassifikationer (meget brandfarlig væske og damp). Industriens selv-klassificeringer viser, at brandbarheden af HFC'er stiger med kortere kulstofkæder og mindre fluorindhold. Selv-klassificeringerne viser også, at de kortkædede HFC'er, HFO-1234yf, SF_6 og PFC'er opbevares ved højt tryk og kan eksplodere ved opvarmning.

Hvad angår giftighed og baseret på den tilgængelige viden kan det generelt konkluderes, at HFC'er, PFC'er og SF_6 kun medfører små farer for mennesker. Ved meget kraftig eksponering er der for visse HFC'er rapporteret reversible effekter såsom åndedrætsbesvær, produktion af spyt, balanceproblemer samt påvirkninger af hjertet. Hertil kommer, at visse HFC'er og PFC'er kan give lette irritationer.

Tilgængelige tests for mutagenicitet/genotoksicitet (in vitro og in vivo) og studier om carcinogenicitet peger ikke på, at de pågældende forbindelser har kræftfremkaldende egenskaber.

Den beskedne information om påvirkningen af forbrugere og gennem arbejdsmiljøet peger på, at der under normale forhold kun sker lille eksponering for de pågældende forbindelser. Meget litteratur beskæftiger sig slet ikke med eksponering grundet de meget beskedne farer for menneskers sundhed. I overensstemmelse hermed er der ikke identificeret nogen aktuelle toksikologiske risikovurderinger.

De væsentligste risici knyttet til de pågældende forbindelser synes således at handle om brandbarheden af HFC'er og HFO'er og om termiske nedbrydningsprodukter, idet termisk nedbrydning kan forårsage dannelse af stærkt toksiske nedbrydningsprodukter såsom hydrogen fluorid (HF) og carbonyl fluorid (COF_2). Dannelse af giftige nedbrydningsprodukter er også relevant for SF_6 udsat for elektriske udladninger i gasisoleret udstyr.

Der kan derfor være et berettiget behov for videre studier om termiske nedbrydningsprodukter; herunder dannelse af HF and COF_2.

Alternativer
Alternativer er blevet udviklet og indført for de fleste anvendelser hvor F-gasser anvendes eller er blevet anvendt. Dette har været en succes og forbruget af F-gasser i Danmark er mindsket til en tredjedel i perioden fra 2000 til 2012.

Denne udvikling er skabt af den danske regulering af F-gasser herunder skatter og forbud for bestemte formal kombineret med støtte til forsknings og udviklingsprojekter for at sikre hurtig Udvikling af alternativ teknologi.

Forbruget af HFC-kølemidler har dog tilsyneladende stabiliseret sig på et årligt forbrug på ca. 360 tons siden 2009. Denne stagnation er forårsaget hovedsageligt af det såkaldte "10-kg vindue" i den Danske lovgivning, som tillader, at HFC stadig anvendes i udstyr, der rummer mindre end 10 kg HFC kølemiddel per anlæg.

"10-kg vinduet" repræsenterer således en vigtig gruppe af produkter, hvor der stadig anvendes HFC'er grundet mangel på indlysende alternativer og lovgivning, der fremmer brugen af alternativer. De pågældende produkter omfatter kondenserende enheder, varmepumper og små kølere.

Herudover kan der identificeres følgende vigtige udfordringer:

- De økonomiske barrierer for etablering af meget store ammoniak køleanlæg, som rummer mere end 5 tons ammoniak, da der er behov for særlig og kostbar planlægning og foranstaltninger i overensstemmelse med risikobekendtgørelsen.
- Fra 1. januar 2015 vil det være forbudt at fylde HCFC-22 på eksisterende køleanlæg. Det er estimeret, at der stadig er mere end 5.000 anlæg i brug og et par hundrede stykker er store systemer med mere end 10 kg HCFC-22. Der er bekymring for, at mange af de eksisterende anlæg kan have problemer med at udfase HCFC-22 i tide.

Væsentlige videns mangler
Der er identificeret følgende væsentlige huller i den foreliggende viden:

- Der er begrænset viden om nedbrydningsprodukter ved opvarmning af F-gasser og i særdeleshed fra nedbrydning af HFC'er, HFO'er og SF_6, inklusive viden om dannelse af HF og COF_2.
- Kredsløbet af TFA i atmosfæren og hydrosfæren er langtfra klarlagt, og der er et behov for videre forskning.
- Mængden af F-gasser der faktisk destrueres i Danmark ved behandling hos NORD og det kraftværk der behandler PU-skum separeret og opsamlet fra små enheder kendes ikke med sikkerhed på grund af manglende målinger.
- Det er uklart, om de eksisterende køleanlæg baseret på HCFC-22 vil være i stand til at udfase HCFC-22 i tide, og om der vil være et behov for særlig støtte til at sikre valget af bæredygtige alternativer.

1. Introduction to the substances

1.1 Definition of the substance group

Fluorinated greenhouse gasses as defined by LOUS 2009 [Danish EPA, 2011] covers compounds classified as HFCs (hydrofluorocarbons) and PFCs (perfluorinated carbons) besides sulphur hexafluoride.

HFCs are aliphatic carbons composed of hydrogen, fluor and carbon only. Similarly PFCs are aliphatic carbons composed of fluor and carbon only. The carbon atoms in PFCs are fully fluorinated (= perfluorinated).

It is noted that PFC frequently also are used as abbreviation for substances as perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and related compounds, which in reality should be classified as fluorocarbon derivatives. These compounds are in a LOUS context described separately (reference is made to the report on "Survey of PFOS, PFOA and other perfluoroalkyl and polyfluoroalkyl substances "[Lassen et al. 2013]) and is not addressed by the present report.

In table 1 is listed the fluorinated greenhouse gasses identified by EFCTC (European Fluorocarbon Technical Committee) under CEFIC (European Chemical Industry Council) as major fluorinated greenhouse gasses [EFCTC 2012]. The list includes all gasses registered as used in Denmark (marked as bold). A more comprehensive list of HFC and PFC gasses and their GWP adopted from the newest draft working group (1) report prepared for the coming IPCC Fifth Assessment Report is included as annex 2.

The compounds named as HFO (1234yf and 1234zeE – HFO designates hydrofluoroolefins) consist as HFCs of hydrogen, fluor and carbon only, and is thus classified as HFCs, but differs from other HFCs in having a double bond between a pair of carbon atoms making the compound more reactive and thereby more exposed to atmospheric decomposition, and significantly reducing the atmospheric lifetime of HFOs as compared to HFCs.

Some of the substances listed (HFC-236fa, HFO-1234zeE, PFC-318, PFC-5-1-14) are neither registered nor pre-registered under REACH, and may thus not be manufactured, imported or placed on the market within the European Community for the time being. Some of these substances may, however, have been used in EU historically, or used in a quantity so small (<1 tons/year) that registration is not required. Some substances have been preregistered, but not yet registered (HFC-245fa, HFC-365mfc, PFC-3-1-10 and PFC-4-1-14). These might be imported/produced in volumes below 100 tons/year per manufacturer/importer and would in that case be due for registration in 2018. From the industry self-classifications (see annex 3) for which there is no tonnage threshold, it can indeed be seen these four substances are actually on the EU marked.

TABLE 1 IDENTIFIED MAJOR FLUORINATED GREENHOUSE GASSES *1

Acronym, Common name	Substance name	Chemical Formula	CAS No.	EC No.	Registered tonnage band *2	Pre-registered
HFC-23 *3	Trifluoromethane	CHF_3	75-46-7	200-872-4	100-1,000 tons/year	
HFC-32 *3	Difluoromethane	CH_2F_2	75-10-5	200-839-4	10,000 – 100,000 tons/year	
HFC-125 *3	1,1,1,2,2- pentafluoro ethane	CHF_2CF_3	354-33-6	206-557-8	10,000 – 100,000 tons/year	
HFC-134a *3	1,1,1,2-tetrafluoroethane	CH_2FCF_3	811-97-2	212-377-0	10,000 – 100,000 tons/year	
HFC 143a *3	1,1,1-trifluoroethane	CH_3CF_3	420-46-2	206-996-5	10,000 – 100,000 tons/year	
HFC 152a *3	1,1-difluoroethane	CH_3CHF_2	75-37-6	200-866-1	1,000 – 10,000 tons/year	
HFC 227ea	1,1,1,2,3,3,3- heptafluoropropane	CF_3CHFCF_3	431-89-0	297-079-2	1,000 – 10,000 tons/year	
HFC 236fa	1,1,1,3,3,3-hexafluoropropane	$CF_3CH_2CF_3$	690-39-1	425-320-1	10-100 tons/year	
HFC-245fa *3	1,1,1,3,3-pentafluoropropane	$CHF_2CH_2CF_3$	460-73-1	680-280-1	No	Yes
HFC-365mfc *3	1,1,1,3,3-pentafluorobutane	$CH_3CF_2CH_2CF_3$	406-58-6	430-250-1/ 609-856-5	Confidential	Yes
HFC-43-10mee	1,1,1,2,2,3,4,5,5,5-decafluoropentane	$CF_3CHFCHFCF_2CF_3$	138495-42-8	420-640-8	100+ tons/year	
HFO-1234yf	2,3,3,3-tetrafluoroprop-1-ene	$CF_3CF{=}CH_2$	754-12-1	468-710-7	1,000 – 10,000 tons/year	
HFO-1234zeE	Trans-1,3,3,3-tetrafluoroprop-1-ene	Trans-$CF_3CH{=}CHF$	29118-24-9	n.d.	No	No
PFC-14 *3	Perfluoromethane	CF_4	75-73-0	200-896-5	No	Yes
PFC-116 *3	Perfluoroethane	C_2F_6	76-16-4	200-939-8	100 – 1,000 tons/year	
PFC-218 *3	Perfluoropropane	C_3F_8	76-19-7	200-941-9	100 – 1,000 tons/year	
PFC-318 *3	Perfluorocyclobutane	c-C_4F_8	415-25-3	n.d.	No	No
PFC-3-1-10	Perfluorobutane	C_4F_{10}	355-25-9	206-580-3	No	Yes
PFC-4-1-12	Perfluoropentane	C_5F_{12}	678-26-2	211-647-5	No	Yes
PFC-5-1-14	Perfluorohexane	C_6F_{14}	355-41-10	n.d.	No	No
SF6 *3	Sulphur hexafluoride	SF_6	2551-62-4	219-854-2	1,000 – 10,000 tons/year	

*1 Identified by EFCTC as major fluorinated greenhouse gasses [EFCTC 2012]

*2 All substances for which a tonnage range are stated are registered within REACH

*3 Fluorinated greenhouse gasses registered as used in Denmark [Poulsen & Werge 2012]

Several HFC-products are marketed, which are not single substances, but mixtures of substances designed to replace specific substances for certain applications. These HFC-products will always be characterized by acronyms as HFC-4xx or HFC-5xx. The most important HFC –mixtures used in Denmark and their composition are presented in table 2 below.

TABLE 2 MAIN HFC-MIXTURES USED IN DENMARK AND THEIR COMPOSTION *1

HFC-mixture, Acronym, Common name	COMPOSITION OF MIXTURES							
	HCFC-22	HCFC-124	HFC-32	HFC-125	HFC-134a	HFC-143a	HFC-152a	Other
HFC-401a	53%	34%					13%	
HFC-402a	38%			60%				2% propane
HFC-404a				44%	4%	52%		
HFC-407c			23%	25%	52%			
HFC-408a *2	47%			7%		46%		
HFC-409a *3	60%	25%						15 % HFC-142b
HFC-410a			50%	50%				
HFC-413a *4					88%			9% PFC-218; 3% isobutane
HFC-417a *5				46.6%	50%			3,4% butane
HFC507a				50%		50%		

*1 Composition data adopted from [Poulsen & Werge 2012], unless other reference is stated.

*2 [DuPont 2011a]

*3 [DuPont 2011b]

*4 [Harp 2013]

*5 [National 2008]

For HFC and PFC compounds and other fluorinated alkanes 2 special numbering systems exists that systematically identifies the molecular structure of these substances. The systems have originally been developed for refrigerants made with a single halogenated hydrocarbon. Based on [Neilorme 2014; Wikipedia 2014] the meaning of the codes and other details of the systems can be described as follows:

System 1:
The rightmost value indicates the number of fluorine atoms, the next value to the left is the number of hydrogen atoms plus 1, and the next value to the left is the number of carbon atoms less one (ze-

roes are not stated). Remaining atoms are chlorine. Thus, HFC-23 contains three fluorine atoms, one hydrogen atom (2-1=1) and one carbon atom (0+1=1). It is therefore CHF_3. Similarly PFC 3-1-10 contains 10 fluorine atoms, no hydrogen atom (1-1=0) and four carbon atoms (3+1=4). It is therefore C_4F_{10}.

System 2:
Add 90 to the number. The resulting value will give the number of carbons as the first numeral, the second numeral gives the number of hydrogen atoms, and the third numeral gives the number of fluorine atoms. The rest of the unaccounted carbon bonds are occupied by chlorine atoms.
For HFC-23 the system gives: 90+23 = 113, corresponding to 1 carbon, 1 hydrogen and 3 fluorine atoms, resulting in CHF_3. Similarly PFC 3-1-10 gives: 90 + 31(10) = 40(10), corresponding to 4 carbon, no hydrogens and 10 fluorine atoms, resulting in C_4F_{10}. Please note that in this case the number 3-1-10 should be read as 3 digits, where the first digit is 3, the second digit is 1 and the last digit is 10.

No matter the numbering system adopted a suffix of a lower-case letter a, b, or c indicates increasingly unsymmetrical isomers.

Regarding the 400- and the 500-series the rightmost digit is assigned arbitrarily by ASHRAE, an industry organization.

The systems described above do not cover the numbering of HFO compounds having 4 digits as e.g. HFO-1234yf. According to [Honeywell 2013] the numbers of these compounds shall be understood as follows:

- First Number = Number of double bonds;
- Second Number = Number of carbon atoms minus one;
- Third Number = Number of hydrogen atoms plus one;
- Fourth Number = Number of fluorine atoms;
- yf = Denominates the specific isomer (position of the fluorine atoms).

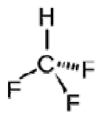
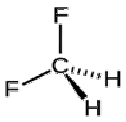
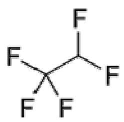
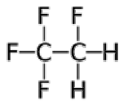
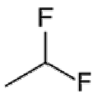
1.2 Physical and chemical properties

Physical and chemical properties of the substances included in this survey are presented in table 3. Preference is given to data presented by ECHA on its homepage on chemicals ([ECHA 2014]). To the extent data is not available with ECHA other sources have been consulted.

As indicated by the data presented most substances are gasses at room temperature and typically low -flammable.

Table 3

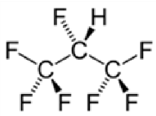
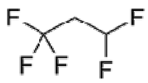
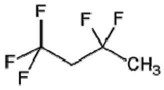
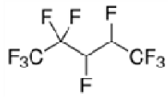
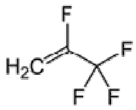
Physical and chemical properties *1

Property	HFC-23	HFC-32	HFC-125	HFC-134a *7	HFC-143a	HFC-152a *2
CAS No.	75-46-7	75-10-5	354-33-6	811-97-2	420-46-2	75-37-6
EC No.	200-872-4	200-839-4	206-557-8	212-377-0	206-996-5	200-866-1
Synonyms	Trifluoro-methane, fluoroform	Difluoro-methane, R 32, Freon 32	1,1,1,2,2- pen-tafluoro-ethane, pen-tafluoro-ethane, F 125, Freon 125	1,1,1,2-tetrafluoro-ethane, norflu-rane, R134a, Freon 134a	1,1,1-trifluoro-ethane, R143a	1,1-difluoroethane
Molecular formula	CHF_3	CH_2F_2	CHF_2-CF_3	CH_2F-CF_3	CH_3-CF_3	CH_3-CHF_2
Structure						
Physical state (20°C, 101.3 kPa)	Colourless gas with a slight ethereal odour	Colourless and odourless gas	Colourless gas with a faint ethereal odour	Colourless gas with a faint ethereal odour	Colourless and odourless gas	Colourless and odourless gas
Flammability	Non-flammable *9	High *9	Non-flammable *9	Non-flammable *9	High *9	Flammable (<50°C, 3.9-16.9 %(v/v)) *2
Melting/freezing point	-155.1/-160 °C	-136°C	-103 °C		-111.3 °C	-117 °C *2
Boiling point	-82.03/-82.1/-84°C.	-51.6/-51,7 °C	-48,5/-68,5 °C	-26 °C (101.3 kPa)	-47.4 °C	-25 °C (101.3 kPa) *2
Relative density	n.d.	Liquid: 0.96 g/cm3 (25°C, liquefied gas, vapour pressure 1690 kPa) Vapours: 2.98 kg/m3 at -51.7°C	5.36 g/L (25°C) 1.53 g/cm³ (Liquid density at -48.5 °C)	1.21 g/cm³ (liquid density, 25 °C)	1.18 g/cm³ (-50 °C)	0.9 g/cc *2
Vapour pressure	4705.4 kPa at (25°C)	1690/1680/ 1701 kPa (25°C),	1203.0 kPa (20°C), 1376/1400 kPa	570/574 kPa (20°C)	1262/1272 kPa (25 °C)	514.6 kPa (25 °C)

Property	HFC-23	HFC-32	HFC-125	HFC-134a *7	HFC-143a	HFC-152a *2
		3140 kPa (50°C).	(25°C)			
Surface tension	2.06 mN/m	n.d.	n.d.	n.d.	n.d.	n.d.
Water solubility (mg/L)	838 mg/L at (25°C, 1 bar (abs) /0.10 wt% at 1 atm and 25°C	1900 mg/L (20°C). 1570 -4400 mg/L (25°C)	430 mg/L (25 °C, atm. pres.) 5970 mg/L (25 °C, saturated vapour pressure)	1 g/L (25 °C)	761 mg/L (25 °C)	2671 mg/L (25 °C) 3200 mg/L (21 °C)
Log P (octanol/water)	0.84 (25 °C)	0.21 (25°C) 0.19-0.71 (20 °C assumed)	1.48/1.55 (20 °C)	1.06 (25 °C)	1.74 (20 °C)	1.13 (25 °C) 0.49/0.75 (20 °C) *2
Molecular weight range	70	52	120.02	102.02	84.02	66.05 *2

Table 3 (continued)

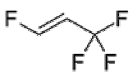
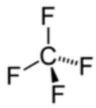
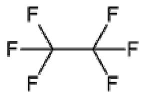
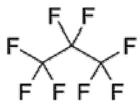
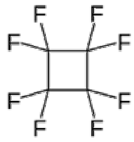
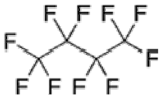
Physical and chemical properties *1

Property	HFC 227ea	HFC 236fa	HFC-245fa *3	HFC-365mfc *8,10	HFC-43-10mee	HFO-1234yf
CAS No.	431-89-0	690-39-1	460-73-1	406-58-6	138495-42-8	754-12-1
EC No.	297-079-2	425-320-1	n.d.	430-250-1	420-640-8	468-710-7
Synonyms	1,1,1,2,3,3,3-heptafluoro-propane	1,1,1,3,3,3-hexafluoro-propane	1,1,1,3,3-pentafluoro-propane	1,1,1,3,3-pentafluoro-butane	1,1,1,2,2,3,4,5,5,5-decafluoro-pentane	2,3,3,3-tetrafluoro-prop-1-ene, polyhaloalkene
Molecular formular	CF_3-CHF-CF_3	CF_3-CH_2-CF_3	CHF_2-CH_2-CF_3	CH_3-CF_2-CH_2-CF_3	CF_3-CHF-CHF-CF_2-CF_3	CF_3-CF=CH_2
Structure						
Physical state (20°C, 101.3 kPa)	Colourless and odourless gas	Colourless gas, slight odour – ether-like	Colourless liquid/gas with faint ethereal odour	n.d.	Clear colourless liquid	Colourless gas
Flammability	Non-flammable	High	Non-flammable	Flammable (Flashpoint: -27 °C)	Likely not (no flashpoint observed)	Flammable
Melting/Freezing point	-129.5 °C	-103 °C	<-160/-160 °C	-35 °C.	-84.0°C.	n.d.
Boiling point	(-18) -(-16)°C	-2 °C (101.3 kPa)	15/15.3°C	40.2°C	53.2-54.2°C	-29°C
Relative density	1.41 g/cm³ (liquid density, 25 °C)	6.18 g/cm3 (22.4 °C).	1.32.	1.264	1.6 (relative density, 25°C)	n.d.
Vapour pressure	54/404/2936 kPa at -30/21/102°C respectively	249 kPa (ambient temperature)	122.7 kPa (20 °C, 101.3 kPa)	46.7 kPa (20 °C)	24.8/31.3 kPa at 20/25°C respectively	314/580/ 1281 kPa at 0/20/50 °C respectively
Surface tension	n.d.	73 mN/m (20 °C, 707 mg/L)	68.5 mN/m	15.6 mN/m (20 °C)	66.7 mN/m at 120 mg/L (below tension of pure water)	n.d.

Property	HFC 227ea	HFC 236fa	HFC-245fa *3	HFC-365mfc *8,10	HFC-43-10mee	HFO-1234yf
Water solubility (mg/L)	0.23 g/L (20-25 °C)	724 mg/L (20 °C)	7.18 g/L (21 °C, 122.7 kPa)	50 % (mass %, 20 °C)	126±33 mg/L (20°C).	198.2 mg/L (24 °C)
Log P (octanol/water)	2.29 (25°C)	1.12 (20 °C)	1.35) (21.5°C)	n.d.	2.7	2.0/2.15 at 25/20°C respectively
Molecular weight range	170.02	152.04	134.05	148.07	252.04	114.03

Table 3 (continued)

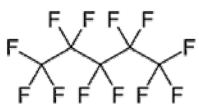
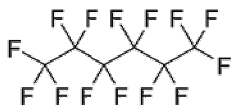
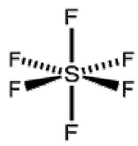
Physical and chemical properties *1

Property	HFO-1234zeE	PFC-14 *4,8	PFC-116 *4,8	PFC-218 *4	PFC-318 *4, 5, 11	PFC-3-1-10 *4,8, 12
CAS No.	29118-24-9	75-73-0	76-16-4	76-19-7	415-25-3	355-25-9
EC No.	n.d.	200-896-5	200-939-8	200-941-9	n.d.	206-580-3
Synonyms	Trans-1,3,3,3-tetrafluoro-prop-1-ene	Perfluoro-methane R14	Perfluoro-ethane R116	Perfluoro-propane, octafluoropro-pane, R218	Perfluoro-cyclobutane, octafluoro-cyclobutane, RC318	Perfluoro-butane, de-cafluoro-butane R610
Molecular formular	Trans-CF_3-CH=CHF	CF_4	CF_3-CF_3	CF_3-CF_2-CF_3	c-C_4F_8 : CF_2-CF_2 | | CF_2-CF_2	CF_3-CF_2-CF_2-CF_3
Structure						
Physical state (20°C, 101.3 kPa)	Colourless gas	Odourless gas	Colourless, odourless gas	Clear colourless gas	Colourless gas	n.d.
Flammability	Non-flammable	Non-flammable	Non-flammable	Non-flammable	Non-flammable	n.d.
Melting/freezing point	n.d.	-183.6°C	-100.6°C	-183°C	−40.1 °C *5	-128.2°C/-84.5°C
Boiling point	-19°C	-128°C	-78°C	-37°C	-5.99 °C *4	- 2/-22°C
Relative density	1.146 g/cm3 (30°C)	1.603 g/cm3 at boiling point and 101.3 kPa	1.607 g/cm3 at boiling point	1.36 g/cm3 (20°C)	Liquid: 1.64 g/cm3 at boiling point 1.48 g/cm3 (20°C) Gas: 0.0088 g/cm3 (101.3 kPa, 15 °C) *4	1.594 g/cm3 at boiling point and 101.3 kPa.
Vapour pressure	~400 kPa (20°C)	3740 kPa at 20°C	2902/2976 kPa (at 18/19°C respectively)	770 kPa (20 °C)	266 kPa (20°C)	2427 kPa (113.3 °C)
Surface tension	n.d.	n.d.	n.d.	4.3 mN/m (25 °C)		n.d.
Water solubility	n.d.	0.0149 g/L	520 mg/L	5.7 µg/L	0.043/0.14	n.d.

Property	HFO-1234zeE	PFC-14 *4,8	PFC-116 *4,8	PFC-218 *4	PFC-318 *4, 5, 11	PFC-3-1-10 *4,8, 12
(mg/L)		(25 °C, 101.3 kpa)	(25°C, 100 kPa)	(25 °C)	g/L (20 °C, 101.3 kPa)	
Log P (oc-tanol/water)	n.d.	n.d.	2.15	2.8	n.d	n.d.
Molecular weight range	114	88.01	138.02	188.03	200.04	283.02

Table 3 (continued)

Physical and chemical properties *1

Property	PFC-4-1-12 *8	PFC-5-1-14 *8	SF_6 *6
CAS No.	678-26-2	355-41-10	2551-62-4
EC No.	211-647-5	n.d.	219-854-2
Synonyms	Perfluoro-pentane, Dodecafluoro-pentane	Perfluoro-hexane	Sulphur hexafluoride
Molecular formular	CF_3-CF_2-CF_2-CF_2-CF_3	CF_3-CF_2-CF_2-CF_2-CF_2-CF_3	SF_6
Structure			
Physical state (20°C, 101.3 kPa)	Liquid	Liquid	colourless, odourless, tasteless gas
Flammability	n.d	n.d	Non-flammable
Melting/Freezing point	-120 °C (pour point)	-90 °C (pour point)	-50.8 °C
Boiling point	29°C	57°C	-63.9 °C (sublimation temperature)
Relative density	1.604	1.682	Liquid: 1.336 g/cm3 Gas: 6.089×10^{-3} g/cm3
Vapour pressure	8.62 kPa (25 °C)	2.94 kPa (25 °C)	2367 kPa
Surface tension	9.4 mN/m	11.1 mN/m	8.02 mN/m (20 °C)
Water solubility (mg/L)	n.d.	n.d.	0.031 g/L (25 °C)
Log P (octanol/water)	n.d.	n.d.	1.68
Molecular weight range	288	338	146.07

n.d.: No data

*1 The data presented is taken from [EFCTC 2014] (name, formula and CAS number for all substances) and [ECHA 2014] (other data to the extent information is available with ECHA). In other cases specific reference has been stated. Data on molecular weight is, however, partly based on own calculations.
Regarding data from ECHA it should be noted that data differ with the approach adopted (calculated or determined by experiments) and the methodology and conditions assumed or adopted (e.g. with respect to pressure and pH). The data presented generally represents minimum and maximum values. For further information reference is made to ECHA. Temperature data stated in Kelvin has been converted to Celsius (x°C = x+273.15°Kelvin). Pressure data stated in bar, atm, and mm Hg has been converted to kPa (1 atm = to 101.325 kPa = 1013.25 millibars = 760 mmHg (torr) or 29.92 in Hg).
*2 [ECETOX 2004a]
*3 [ECETOX 2004b]
*4 [Air Liquide 2014]
*5 [Wikipedia 2014b]
*6 [OECD SIDS 2006c]
*7 [ECETOX 2006]
*8 [Siegemund et al. 2012]
*9 [Environment Canada 2011]
*10 [Solvay 2014]
*11 [Daik1n 2011]
*12 [Chemicalbook 2014]
*13 [Honeywell 2012]

1.3 Function of the substances for main application areas

Fluorocarbons are used as heat transmission media in air-conditioning, heat pumps and refrigeration systems. They are also used as blowing agents for plastics foams, and as firefighting agent. Minor uses include propellant for medical aerosols, as solvent, insulation gas for high voltage applications and cleaning agent in semiconductor manufacturing etc.

Generally fluorocarbons are gasses or volatile liquids at room temperature, low to non- flammable, thermal and chemical stable, with very low toxicity and with favourable environmental profile apart from their global warming potential.

Based primarily on [EFCTC 2014] the function of fluorocarbons can be briefly summarised as follows.

HFC – heat transmission
Heat transmission inclusive of refrigeration and air-conditioning has been the dominant application for HFCs since chlorofluorocarbons (CFCs) were out-phased in Denmark and other countries back in the 1980/90-ties. HFC-134a was developed as a replacement to CFC-12. Apart from appropriate thermodynamic properties also the stability and low toxicity of HFCs are important characteristics.

HFC – blowing agent
As blowing agents for plastic foams it is utilised that several HFCs have good thermal insulating characteristics. These specific properties have made them good candidates as foam-blowing agents for the replacement of HCFC-substances in the production of insulating foam.

This is particularly the case in those applications where there is limited space available for insulation, e.g. appliances such as freezers and refrigerators. The use of HFCs allows manufacturers to fulfil strict energy-consumption standards and still providing appropriate storage capacity.

Apart from their blowing agent and insulation properties also the flammability and low toxicity of HFCs are important characteristics e.g. favouring the use of HFCs as blowing in in-situ insulation.

HFC – fire protection
In fire protection it is utilised that HFCs are heavier than air and displace air. HFCs, furthermore acts, by a chemical process besides having a cooling effect in the process of extinguishing fires [Wickham 2002]. HFCs being utilized are non-flammable and with very low toxicity. They are used at well below toxic levels and can therefore be used in normally occupied spaces.

HFC systems require only a small amount of gas and achieve design concentrations in less than 10 seconds. HFCs, furthermore, are non-conductive, clean agents and therefore leave no residue. HFC fire extinguishing systems are relevant in those cases where speed, space and safety are critical. Typical applications are telecommunication facilities, computer rooms, process control centres, military vehicles, aircraft, etc.

HFC - solvents
HFCs are used as solvents utilizing properties as thermal and chemical stability, good dielectric properties, high material compatibility, low surface tension and viscosity, high liquid density , besides very low toxicity, and favourable environmental profiles apart from their global warming potential . Quite often the HFC is blended with other fluids to obtain tailored properties for specific solvent - uses. Main applications include degreasing, defluxing, particulate removal, drying after aqueous cleaning, dielectric coolant and specialist extraction.

HFC - medical aerosol applications
HFC usage is limited to products where health and safety during use requires a non-flammable and virtually non-toxic propellant. These aerosol products include Metered Dose Inhalers (MDIs) for therapy of asthma and other respiratory problems.

PFC – electronic industry
PFC gases and liquids are traditionally used in several electronics industry processes ranging from semiconductor manufacturing, IC-components quality control testing to direct contact dielectric cooling of e.g. power electronics assembly. Due to the high market prices of PFCs, these substances are typically used in much specialised applications with high requirements of system efficiency and worker safety.

Use by the semiconductor industry is primarily for in-situ chamber cleaning of CVD/PECVD tools and minor volumes for wafer etching.

PFC – medical applications
PFC-3-1-10 is used for medical research. The key feature here is the inert characteristic as well as non-flammability providing good operation conditions and equipment reliability.

PFC – heat transfer
PFC-5-11-14 is mainly used as heat transfer fluid. This highly demanding application require good dielectric characteristic at optimum material compatibility and thermal stability. The use as coolant fluid in very specialized applications ensures a close to zero emission into the environment.

SF_6 – insulating gas in electrical installations
Sulphur hexafluoride (SF_6) is used as a dielectric gas for high voltage applications. It is chemically inert, gaseous even at low temperature, non-flammable, non-toxic and non-corrosive, besides that its dielectric strength and dielectric constant are unchanged from a few Hz up to several GHz. Other relevant properties are high molar heat capacity and low viscosity which enables it to transfer heat very effectively and arc quenching properties to prevent arc from occurring while its molecular fragments rapidly recombine after the source of arc is removed.

SF_6 - uses in the semiconductor industry
To manufacture wafers, the semiconductor industry requires gaseous fluorinated compounds, silanes (e.g. SiH_4) and doping gases (e.g. AsH_3, PH_3). Wafers consist of high-purity silicon and are the basic building blocks for all semiconductor components.

SF_6 or other high-purity gases are used as etching gases for plasma etching of the silicon or as cleaning gases to clean the CVD (Chemical Vapour Deposition) chambers after the etching process to remove the silicon fractions deposited in the chamber.

SF_6 - metal casting:
Magnesium is a highly reactive metal and SF_6 is used in magnesium casting to prevent the surface of the melt to be exposed to ignition, oxidation and the formation of nitrides. Due to the non-toxic and non-corrosive properties of SF_6 it has replaced sulphur dioxide (SO_2) as cover gas used in most magnesium foundries.

SF_6 may also be used in aluminium casting by injecting an SF_6/inert gas mixture as pre-treating of the aluminium melt to remove hydrogen, oxides and solid impurities.

2. Regulatory framework

2.1 Legislation

2.1.1 Existing legislation

The key regulation of fluorinated greenhouse gases in EU is Regulation (EC) No 842/2006 on certain fluorinated greenhouse gases combined with Directive 2006/40/EC of 17 May 2006 (the MAC Directive) relating to emissions from air-conditioning systems in motor vehicles. The content of these regulations can be summarized as follows (see table 4):

The MAC Directive prohibits the use of F-gases (HFCs, PFCs and SF_6) with a global warming potential more than 150 times (mainly HFC 134a) greater than carbon dioxide (CO_2) in new types of cars and vans introduced from 2011 and in all new cars and vans produced from 2017.

The F-gas Regulation contains the following major elements:

- It is promoting good maintenance practices in order to prevent leaks from equipment containing F-gases. The adopted measures comprise containment of gases and proper recovery of equipment together with training and certification of personnel and of companies handling these gases and labeling of equipment containing F-gases. Reporting on imports, exports and production of F-gases is also established;
- It is banning F-gases in some applications where environmentally superior alternatives are cost-effective.

In Denmark regulation establishing a general ban on the use of HFCs, PFCs and SF_6 with certain exemptions was implemented already back in 2002 (see table 4). The Danish regulation is in several ways more restrictive than the EU regulation. The Danish regulation is, however, by Commission Decision of 11 June 2012 (2012/301/EU) approved by the EU commission [EU 2012].

It must be noted that the Danish regulation allows for the use of HFCs in refrigeration systems with refrigerant charges less than 10 kg HFC refrigerant – the so-called "10 kg window". Future changes of the Danish legislation may be focused at this "window".

2.1.2 Proposed new regulation

A revision of the F-gas Regulation has been proposed by the European Commission in November 2012. In December 2013, representatives of the European Parliament and Council agreed on a slightly amended text based on the Commission's proposal. The revision of the Regulation was endorsed by the European Parliament in March 2014 and is now subject to the formal approval of the Council [EU 2014].

The new legislation on fluorinated gases F-gases will [EU 2014; EU2014b]:

- Limit the total amount of the most important F-gases (HFCs) that can be sold in the EU, and reduce this in steps to one-fifth of today's sales in 2030 ("phase-down" measure);
- Prevent emissions of F-gases from existing equipment by requiring controls, proper servicing and recovery of the gases at the end of the equipment's life; and
- Establish new restrictions on the use of F-gases in some equipment for which less harmful alternatives are widely available today.

The new restrictions proposed include [EU2014b]:

- In new fire protection equipment HFC-23 is banned from 1 January 2016.
- In new domestic refrigerators and freezers HFCs (GWP ≥ 150) are banned from 1 January 2015.
- In new refrigerators and freezers for commercial use (sealed systems) HFCs (GWP ≥ 2500) are banned from 1 January 2020 and HFCs (GWP ≥ 150) are banned from 1 January 2022.
- In new stationary refrigeration equipment or equipment designed to cool products to temperatures below - 50°C HFCs (GWP ≥ 2500) are banned from 1 January 2020.
- In new movable room air-conditioning appliances HFCs (GWP ≥ 150) are banned from 1 January 2020.
- For new multipack centralized refrigeration systems for commercial use with a capacity of 40kW or more, fluorinated greenhouse gases (GWP ≥ 150) are banned from 1 January 2022, except in the primary refrigerant circuit of cascade systems where fluorinated greenhouse gases with a GWP of less than 1500 may be used.
- For new single split air-conditioning systems containing less than 3 kg of fluorinated greenhouse gases, fluorinated greenhouse (GWP≥ 750) are banned from 1 January 2025.
- In new foams of extruded polystyrene, HFCs (GWP ≥ 150) are banned from 1 January 2020, and a ban for all new foams is valid from 1 January 2023, except when the use of HFCs is required to meet national safety standards.
- In technical aerosols, HFCs (GWP ≥ 150) are banned from 1 January 2018, except when the use of HFCs is required to meet national safety standards or when the aerosols are used for medical applications.
- The use of SF_6 in magnesium die-casting and in the recycling of magnesium die-casting alloys is banned for all installations from 1 January 2018.
- The use of fluorinated greenhouse gases ((GWP ≥ 2500) to service or maintain refrigeration equipment with a charge size of 40 tons of CO2 equivalent or more, is with some exemptions banned from 1 January 2020.

The proposed exemption of F-gases with GWP<150 allows for use of HFC-152a. HFC-152a is today only used as refrigerant in special equipment, but could be a candidate for more widespread use.

TABLE 4
EXIXTING LEGISLATION ADRESSING HFCS, PFCS AND SF_6

Legal instrument	EU/national	Substances (as indicated in the instrument)	Requirements as concerns substances indicated in the instrument
			Regulation addressing products
Bekendtgørelse om regulering af visse industrielle drivhusgasser BEK nr. 552 af 02/07/2002 Statutory Order no. 552 of 02/07/2002 Regulating Certain Industrial Greenhouse Gasses	National	HFCs, PFCs and SF_6	Import, sale and use of the substances – new and recovered – and of new products containing the substances indicated are prohibited from January 1, 2006. Irrespective of the ban stated above import, sale and use of: - PFCs are banned in all new products from September 1, 2002; and from January 1, 2006 as refrigerant mixtures in which PFCs constitute less than 10 % of the mixture; - SF_6 are banned from September 1, 2002 in new car tyres, from January 1, 2003 in new panes of glass, from July 1, 2003 in new shoes (sale allowed until January 1, 2004), and from September 1, 2002 as tracer gas and as shielding gas in light metal found-

			ries; - HFCs are banned from January 1, 2007 in new cooling plants, heat pumps, air conditioning plants (comfort cooling) and dehumidifiers with charges with or above 10 kg, and from January 1, 2006 in production of flexible polyurethane foam; - all substances indicated are banned from September 1, 2002 in new district heating pipes, jointing foam and spray cans; - SF_6 are exempted from the ban in new high voltage plants (voltage > 1 kV); - HFCs are exempted from the ban in: • Cooling plants, heat pumps, air conditioning systems (comfort cooling) and dehumidifiers with charges between 0.15 kg and 10 kg; • Servicing of cooling plants, air conditioning systems, heat pumps, dehumidifiers, air conditioning in vehicles and planes; • Cooling systems for heat recovery, primarily connected by welding or brazing in a factory assembled compact cabinet and with a charge of or less than 50 kg; • Vaccine coolers, mobile cooling plants, air conditioning in vehicles and planes, low temperature freezers (temperature below −50 °C), medical spray cans, and facilities for testing of cooling equipment. - All the substances indicated are exempted from the ban in new laboratory equipment, new thermostats, valves etc., new products for military use and new products for use on ships.
Regulation (EC) No 842/2006 of the European Parliament and of the Council on certain fluorinated greenhouse gases.	EU	HFC-23 HFC-32 HFC-41 HFC-125 HFC-134 HFC-134a HFC-143 HFC-143a HFC-152a HFC-227ea HFC- 236cb HFC-236ea HFC-236fa HFC-245ca HFC-245fa HFC-365 mfc HFC-43-10mee PFC-14 PFC-116 PFC-218 PFC-318	The Regulation covers the use of HFCs, PFCs and SF_6 (F-gases) in all their applications covered by the Directive, except Mobile Air Conditioning. The regulation set up rules for improving the prevention of leaks from equipment containing F-gases. Measures comprise: - Containment of gases and proper recovery of equipment; - Training and certification of personnel and of companies handling these gases; - Labelling of equipment containing F-gases; - Reporting on imports, exports and production of F-gases. The regulation, also, bans the use of SF_6 or preparations thereof: - in magnesium die-casting from 1 January 2008, except where the quantity of SF_6 used is below 850 kg per year; - For the filling of vehicle tyres from 4 July 2007. The regulation, furthermore, bans the placing on the market of fluorinated greenhouse gases in the following products and equipment:

		PFC-3-1-10 PFC-4-1-12 PFC-5-1-14 SF_6	- HFCs are banned from 4 July 2009 in novelty aerosols; - HFCs and PFCs are banned from 4 July 2007 in non-confined direct-evaporation systems containing refrigerants; - PFCs are banned from 4 July 2007 in fire protection systems and fire extinguishers. - All fluorinated greenhouse gasses indicated are banned : • From 4 July 2006 in footwear; • From 4 July 2007 in non-refillable containers, tyres and windows for domestic use; • From 4 July 2008 in other windows and in one component foams, except when required to meet national safety standards. Unless otherwise stated the Regulation entered into force on 4 July 2006. The Regulation has been supplemented by 10 implementing acts or "Commission Regulations" listed below.
EU F-gas Regulation: Implementing Acts **Commission Regulation (EC) No 1493/2007 of 17 December 2007 establishing the format for the report to be submitted by producers, importers and exporters of certain fluorinated greenhouse gases** **Commission Regulation (EC) No 1494/2007 of 17 December 2007 establishing the form of labels and additional labelling requirements as regards products and equipment containing certain fluorinated greenhouse gases** **Commission Regulation EC) No 1516/2007 of 19 December 2007 establishing standard leakage checking requirements for stationary refrigeration, air conditioning and heat pump equipment containing certain fluorinated greenhouse gases**			Establishes the format for the report to be submitted by producers, importers and exporters of certain fluorinated greenhouse gases to the EU commission Establishing the form of labels be used on products listed in article 7 (2) of Regulation (EC) No 842/2006 and additional labelling requirements that shall apply. The Regulation establishes the standard leakage checking requirements for working and temporarily out of operation stationary refrigeration, air conditioning and heat pump equipment containing 3 kg or more of fluorinated greenhouse gases. The Regulation does not apply to equipment with hermetically sealed systems, which are labelled as such and contain less than 6 kg of fluorinated greenhouse gases.

Commission Regulation (EC) No 1497/2007 of 18 December 2007 establishing standard leakage checking requirements for stationary fire protection systems containing certain fluorinated greenhouse gases			The Regulation establishes the standard leakage checking requirements for working and temporarily out of operation stationary fire protection systems. The Regulation applies to fire protection systems containing 3 kg or more of fluorinated greenhouse gases.
Commission Regulation (EC) No 303/2008 of 2 April 2008 establishing minimum requirements and the conditions for mutual recognition for the certification of companies and personnel as regards stationary refrigeration, air conditioning and heat pump equipment containing certain fluorinated greenhouse gases			The Regulation establishes minimum requirements for the certification referred to in Article 5(1) of Regulation (EC) No 842/2006 in relation to stationary refrigeration, air conditioning and heat pump equipment containing certain fluorinated greenhouse gases as well as the conditions for mutual recognition of certificates issued in accordance with those requirements.
Commission Regulation (EC) No 304/2008 of 2 April 2008 establishing minimum requirements and the conditions for mutual recognition for the certification of companies and personnel as regards stationary fire protection systems and fire extinguishers containing certain fluorinated greenhouse gases			The Regulation establishes minimum requirements for the certification referred to in Article 5(1) of Regulation (EC) No 842/2006 in relation to stationary fire protection systems and fire extinguishers containing certain fluorinated greenhouse gases as well as the conditions for mutual recognition of certificates issued in accordance with those requirements.
Commission Regulation (EC) No 305/2008 of 2 April 2008 establishing minimum requirements and the conditions for mutual recognition for the certification of personnel recovering certain fluorinated greenhouse gases from high-voltage switchgear			The Regulation establishes minimum requirements for the certification of personnel recovering certain fluorinated greenhouse gases from high-voltage switchgear as well as the conditions for mutual recognition of certificates issued in accordance with those requirements.
Commission Regulation (EC) No 306/2008 of 2 April 2008 establishing minimum requirements and the conditions for mutual recognition for the certification of personnel recovering certain fluorinated greenhouse gas-based solvents from equip-			The Regulation establishes minimum requirements for the certification of personnel recovering certain fluorinated greenhouse gas-based solvents from equipment as well as the conditions for mutual recognition of certificates issued in accordance with those requirements.

ment **Commission Regulation (EC) No 307/2008 of 2 April 2008 establishing minimum requirements for training programs and the conditions for mutual recognition of training attestations for personnel as regards air-conditioning systems in certain motor vehicles containing certain fluorinated greenhouse gases** **Commission Regulation (EC) No 308/2008 of 2 April 2008 establishing the format for notification of the training and certification programs of the Member States**			The Regulation establishes minimum requirements for training programmes of personnel recovering certain fluorinated greenhouse gases from air-conditioning systems in motor vehicles falling within the scope of Directive 2006/40/EC as well as the conditions for mutual recognition of training attestations issued in accordance with those requirements. The Regulation establishes the format for notifications of the training and certification programmes of the Member States referred to in Article 5(2) of Regulation (EC) No 842/2006.
Directive 2006/40/EC of the European Parliament and of the Council of 17 May 2006 relating to emissions from air-conditioning systems in motor vehicles and amending Council Directive 70/156/EEC	EU	HFCs, PFCs and SF_6 as referred to in Annex A of the Kyoto Protocol	The Directive covers the use of HFCs in Mobile Air Conditioning for passengers' cars only. This Directive lays down the requirements for the EC type approval or national type-approval of vehicles as regards emissions from, and the safe functioning of, air-conditioning systems fitted to vehicles. It also lays down provisions on retrofitting and refilling of such systems. Restrictions are in the Directive related to fluorinated greenhouse gases with a global warming potential higher than 150(100 years GWP) in the following abbreviated as fluorinated greenhouse gasses (GWP >150). From 4 July 2008 type-approval for new car models shall only be granted if the leakage of fluorinated greenhouse gasses (GWP >150) will be less than either 40 g/year in the case of a simple evaporator system or 60 g/year in the case of a dual evaporator system. Two years later, the same leakage limits is mandatory for all new cars. By 1 January 2011, fluorinated greenhouse gasses (GWP >150) is banned for air conditioning systems for new vehicle models. By 1 January 2017, fluorinated greenhouse gasses (GWP >150) will be banned for all new vehicles. With effect from 1 January 2011, air-conditioning systems designed to contain fluorinated greenhouse gases (GWP >150) shall not be retrofitted to vehicles type-approved from that date. With effect from 1 January 2017, such air-conditioning systems shall not be retrofitted to any vehicles. Air-conditioning systems fitted to vehicles type-approved on or after

			1 January 2011 shall not be filled with fluorinated greenhouse gases (GWP>150). With effect from 1 January 2017 air conditioning systems in all vehicles shall not be filled with fluorinated greenhouse gases (GWP>150), with the exception of refilling of air-conditioning systems containing those gases, which have been fitted to vehicles before that date.
Bekendtgørelse om begrænsning i anvendelse af visse farlige kemiske stoffer og produkter til specielt angivne formål *(Statutory Order of restrictions in the use of certain hazardous chemical compounds for special applications)* **BEK nr 857 af 05/09/2009**			Hydrocarbons containing halogens are not allowed to use in equipment for fire extinguishing. Use of fire extinguishing equipment by Municipal Fire Brigades is exempted from the ban. Use of halons covered by the EU regulation on substances that deplete the ozone layer are exempted from the ban.
Bekendtgørelse af lov om afgift af CFC og visse industrielle drivhusgasser *(Statutory Order on law of fee on CFC and certain industrial greenhouse gasses *1)* **BEK nr 599 af 11/06/2007**	National	HFCs PFCs SF_6 Certain halons or CFC's are also covered by the Order.	Manufacturing and import of the substances indicated requires a fee to the Danish Treasury. The fee differs between substances. The maximum fee required is DKK 400/kg substance corresponding to ca. 53.33 Euro/kg substance. For certain uses the fee may be refunded.
			Regulation addressing design, construction, installation, and maintenance of refrigeration plants
Bekendtgørelse om indretning m.v. af trykbærende udstyr. *(Statutory order on design, and manufacturing of new pressure designed equipment *1)* **BEK nr 694 af 10/06/2013**			The Order establishes rules for design and manufacturing of new pressure designed equipment, inclusive of approval of verification authority. The Order implements EU Directive 97/23/EF in Denmark.
Bekendtgørelse om indretning, ombygning og reparation af trykbærende udstyr inkl. senere ændringer. *(Statutory order on design, reconstruction and repair of pressure designed equipment incl. later amendments *1)* **Bek nr. 99 af 31/01-2007**			The Order establishes rules for design reconstruction and repair of other pressure designed equipment, inclusive of approval of verification authority.
Bekendtgørelse om anvendelse af trykbærende udstyr inkl.			The Order establishes rules for installation, operation and maintenance of refrigeration plants, heat pumps and other pressure de-

senere ændringer *(Statutory Order on use of pressure designed equipment incl. later amendments *1)* **Bek nr. 100 af 31/01-2007**			signed equipment, inclusive of certification of companies and personnel.
Vejledning om Køleanlæg og varmepumper *(Guideline on refrigeration plants and heat pumps *1)* **At-vejledning B.4.4 af oktober 2010**			Guideline issued by the Danish Working Environment Authority. The guideline addresses issues as safety categories, refrigeration substances, installation, monitoring and maintenance.
			Regulation addressing waste
Bekendtgørelse om affald *(Statutory Order on waste *1)* **BEK nr 1309 af 18/12/2012**			HFCs are included in waste category 140601. HFCs are, however, not classified as hazardous substances.
Bekendtgørelse om håndtering af affald i form af motordrevne køretøjer og affaldsfraktioner herfra *(Statutory Order on handling of waste consisting of engine powered vehicles and waste fractions from such vehicles *1)* **BEK nr 1312 af 19/12/2012**	National	Refrigerants	Refrigerants used in air condition systems in vehicles being scrapped must be removed from the vehicles and disposed of according to municipal rules for handling of hazardous waste or by being delivered to companies authorised to receive and treat such types of waste.

*1 Un-official translation of name of Danish legal instrument

2.2 Classification and labelling

2.2.1 Harmonised classification in the EU

Substances and mixtures placed on the market in the EU are to be classified, labelled and packaged according to the CLP regulation (1272/2008/EC).

Table 5 lists the harmonised classification and labelling for HFCs, PFCs and SF_6 according to Annex VI of the CLP Regulation. The table shows that the only substance being classified is HFC-365mfe that is classified as Flammable Liquid 2 with the hazard statement H225 (Highly flammable liquid and vapour).

TABLE 5
HARMONISED CLASSIFICATION ACOORDING TO ANNEX VI OF REGULATION (EC) NO 1272/2008 (CLP REGULATION)

Index No	International chemical identification	CAS No	Classification	
			Hazard Class and Category Code(s)	Hazard statement Code(s)
602-102-00-6	1,1,1,3,3-pentafluorobutane (HFC-365mfc)	406-58-6	Flam. Liq. 2	H225

2.2.2 Self-classification in the EU

Self-Classifications for cadmium compounds provided by companies in their C&L notifications or registration dossiers are summarized in Annex 3. This information is registered in The Classification & Labelling (C&L) Inventory database at the website of the European Chemicals Agency (ECHA). ECHA maintains the Inventory, but does not verify the accuracy of the information (ECHA, 2014).

As stated in Annex 3 most self-classifications are focused on substance characteristics as being flammable gas or gas under pressure that may explode if heated. Many substances are also self-classified as a possible cause for respiratory irritation or irritation of skin or eye. A few substances are self-classified as CMR-substances. It is, however, evident that companies are not able to classify the compounds in question correctly in several cases. These issues are further addressed in Chapter 5 and 6.

2.3 REACH

2.3.1 Authorisation List / REACH Annex XIV

The Authorisation List contains all SVHC substances included in ANNEX XIV under REACH (Appendix 1) requiring uses to be authorised for use. HFCs, PFCs and SF_6 are not included in the Authorisation List as of March 2014.

2.3.2 Ongoing activities - pipeline

2.3.2.1 *Community Rolling Action Plan (CoRAP)*

The Community Rolling Action Plan (CoRAP) is a tool for coordination of substance evaluation between EU Member States, indicating when a given substance is expected to be evaluated and by whom.

HFCs, PFCs and SF_6 are not included in the Community Rolling Action Plan as of March 2013. Next update will take place by the end of March 2014.

2.3.2.2 Registry of Intentions (EU)

The 'registry of intentions' gives an overview of intentions by EU Member States in relation to Annex XV dossiers. Such intentions made include harmonised classification and labelling, identification of a substance as being in the group of Substances of Very High Concern (SVHC) or a restriction related to the substance (Appendix 1).

HFCs, PFCs and SF_6 are not included in the Registry of Intentions as of November 2013.

2.4 Other legislation/initiatives

The Danish Knowledge Centre for HFC-free cooling.

The centre was established in 2005 and is placed with the Danish Technological Institute. The centre objectives is introduction to and dissemination of knowledge on HFC-free cooling systems, cooling equipment etc. to designers, installation personnel, consultants enter, construction enterprises, decision makers etc. in Denmark, inclusive of technical assistance and consulting services to some extent.

The Centre was established by the Danish EPA in co-operation with the Danish Society for Cooling Technics, the Danish Association for Refrigeration, the Association of Authorized Danish Refrigeration Companies and the Association of Danish Manufacturers of Heating Pumps.

The Centre has been and still is a key institution in undertaking research in HFC-free cooling in Denmark. In Table 6 below is listed the research reports published by the Centre as well as by Danish Technological Institute before the Centre was established. It should be noted that several of these rapports are addressing HFCs, PFCs and SF_6 in general.

Other substitution activities

Of other substitution activities in Denmark not covered by Table 6 should be mentioned an effort directed towards replacing the use of SF_6 in in sound-insulating windows [Hoffmeyer (2002)].

TABLE 6
RESEARCH REPORTS PUBLISHED THE DANISH KNOWLEDGE CENTRE FOR HFC-FREE COOLING

All research reports presented here are available at the following homepage: http://www.hfc-fri.dk/19558. Those reports, for which their English title is written in brackets, are only available in Danish.

- Low GWP Alternatives to HFCs in Refrigeration, 2012
- Udvikling af et demonstrations- og testkøleanlæg, der anvender CO2 som kølemiddel **(Development of a demonstration and pilot cooling plant using CO_2 as refrigerant)**, 2009
- Udvikling af demonstrations- og modulopbygget vandkøleaggregat med NH_3 som kølemiddel **(Development of a demonstration and modul based water-cooling unit using NH_3 as refrigerant)**, 2009
- Miljøvenlig iscremefryser med CO2-kølemiddel **(Environmental friendly soft ice freezer with CO_2-refrigerant)**, 2009
- Polymerer i anlæg med CO2 som kølemiddel **(Polymers in equipment using CO_2 as refrigerant)**, 2008
- Kombineret brugsvands- og rumvarmepumpe med CO2 som kølemiddel **(Combined drinking water and room heating pump with CO_2 as refrigerant)**, 2006
- Udvikling af nye generationer fyldestationer, der muliggør påfyldning af CO2 i automobil- og kølebranchen **(Development of new generations of filling stations to allow filling up with CO_2 in the automobile and cooling trade)**, 2005
- Kuldioxid som sekundært kølemiddel i supermarked **(CO_2 as secondary refrigerant in supermarket)**, 2005
- Innovation in small Capacity Ammonia Refrigeration Plants, 2005
- Konvertering af køleanlæg i supermarkeder til anvendelse af CO2 med direkte ekspansion i frost- og

kølemøbler **(Conversion of cooling equipment in supermarkets to CO_2 with direct expansion in freezing and cooling furniture)**.

- Implementering af aircondition splitunit med kulbrinter på det danske marked **(Implementation of air-condition split-unit with hydrocarbons in Denmark),** 2004
- Konvertering af HVAC-unit fra HFC til naturlige kølemidler **(Conversion of HVAC-unit from HFC to natural refrigerants)**, 2003
- Køle- og frostrumsanlæg til køkkener og restauranter - konvertering fra HFC til de naturlige kølemidler propan og CO_2 **(Equipment for cooling- and freezing-room in kitchens and restaurants – conversion from HFC to the natural refrigerants propane and CO_2)**, 2003
- CO_2 som kølemiddel i varmepumper **(CO_2 as refrigerant in heat pumps)**, 2003
- HFC-fri mælkekøling **(HFC-free cooling of milk)**, 2003
- Konvertering af chillerunit på 250 kW med HFC **(Conversion of a chiller-unit on 250 kW with HFC)**, 2003
- **Reefer container unit med CO_2** , 2002
- Individuelle eldrevne varmepumper - Implementering af ny teknologi fase 5-10 **(Individual electricity powered heat pumps – Implementation of new technology phase 5-10)**, 2002
- Anvendelse af naturlige kølemidler i supermarkeder **(Use of natural refrigerants in supermarkets)**.
- Udvikling af køleanlæg med luft som kølemiddel **(Development of cooling plants using air as refrigerant)**, 2001
- Kulbrinter i mellemstore køleanlæg **(Hydrocarbons in medium sized cooling plants)**, 2001
- Vurdering af mulighederne for at erstatte kraftige drivhusgasser (HFC'er, PFC'er og SF_6) **(Assessment of the opportunities for substitution of strong greenhouse gases (HFCs, PFCs and SF_6))**, 2001
- Kombineret solcelle- og varmepumpeanlæg **(Combined solar power and heat pumps)**, 2001
- HFC-fri teknologi til mælketankskøling **(HFC-free technology for cooling of milk containers)**, 2001
- Luft som varmekilde i varmepumper **(Air as the source of heat in heat pumps)**, 2000
- Ejektorbaserede systemer til udnyttelse af spildvarme til køleformål **(Ejector based systems for utilization of excess heat for cooling activities),** 2000
- Demonstration af anvendelse af CO2 og propan i butikker **(Demonstration of the use of CO_2 and propane in shops)**, 2000
- Indførelse af ammoniak i mindre anlæg **(Introduction of ammonia in small cooling plants)**, 1999
- Erstatning af kraftige drivhusgasser (HFC´er, PFC´er og SF_6) **(Substitution of strong greenhouse gases (HFCs, PFCs and SF_6))**, 1998
- Udvikling af små ammoniakanlæg **(Development of small ammonia plants)**, 1995
- **Going towards natural refrigerants**, 1995

2.5 International agreements

The Kyoto Protocol
The Kyoto Protocol [UNFCCC 1998] is an international agreement linked to the United Nations Framework Convention on Climate Change, which commits its Parties by setting internationally binding emission reduction targets. Denmark ratified the Kyoto Protocol in 2002.

The Kyoto Protocol was adopted in Kyoto, Japan, on 11 December 1997 and entered into force on 16 February 2005. The detailed rules for the implementation of the Protocol were adopted at COP 7 in Marrakesh, Morocco, in 2001, and are referred to as the "Marrakesh Accords." Its first commitment period started in 2008 and ended in 2012.

The goal of the Kyoto Protocol is to lower the overall emissions from six greenhouse gases - carbon dioxide, methane, nitrous oxide, sulfur hexafluoride, HFCs, and PFCs - calculated as an average over the five-year period of 2008-12.

The official goal for Denmark was an emission of 92% of the base year (1990 for carbon dioxide, methane, nitrous oxide and 1995 for sulfur hexafluoride, HFCs, and PFCs). This goal was later adjusted to 79% of the base year due to a special "burden-sharing" agreement of the European Community [UNFCCC 2014a].

In Doha, Qatar, on 8 December 2012, the "Doha Amendment to the Kyoto Protocol" was adopted. The amendment includes new commitments for Annex I Parties to the Kyoto Protocol who agreed to take on commitments in a second commitment period from 1 January 2013 to 31 December 2020. Furthermore, the list of greenhouse gases to be reported on by Parties in the second commitment period has been expanded to include also nitrogen trifluoride (NF_3).

The Doha Amendment is, however, not yet in force, as it in accordance with Articles 20 and 21 of the Kyoto Protocol has to be accepted by at least ¾ of the parties to the Kyoto Protocol (corresponding to at least 144 parties). By the end of February 2014 it has been accepted by 7 parties. Neither Denmark nor EU is yet a party to the Doha Amendment [UNFCCC 2014b]. The European Commission by November 2013 proposed the legislation necessary for the European Union to formally ratify the second commitment period (2013-2020) of the Kyoto Protocol [EU 2014c].

The Climate and Clean Air Coalition to Reduce Short-Lived Climate Pollutants
This coalition was established in 2012. The Coalition are focused on short-lived climate pollutants (SLCPs) which are defined as agents that have relatively short lifetime in the atmosphere - a few days to a few decades - and a warming influence on climate. The main short lived climate pollutants are black carbon, methane, tropospheric ozone and hydrofluorocarbons (HFCs). [CCAC 2014]

The Coalition's objectives are to address short-lived climate pollutants by [CCAC 2014]:
- Raising awareness of short-lived climate pollutant impacts and mitigation strategies;
- Enhancing and developing new national and regional actions, including by identifying and overcoming barriers, enhancing capacity, and mobilizing support;
- Promoting best practices and showcasing successful efforts;
- Improving scientific understanding of short-lived climate pollutant impacts and mitigation strategies;
- The Coalition serves as a forum for assessing progress in addressing the challenge of short-lived climate pollutants and for mobilizing resources to accelerate action. It works to catalyze new actions as well as to highlight and bolster existing efforts on near-term climate change and related public health, food and energy security, and environmental issues.

Denmark as well as the European Commission is a partner to the Coalition [CCAC 2014].

2.6 Other relevant national regulation

The majority of EU Member States do not have national policies going beyond existing EU F-gas regulations. According to [SKM Enviros 2012] some important exemptions apart from the Danish exemptions exist:

- Austria has banned the use of HFCs in domestic refrigerators and freezers with refrigerant charge less than 150 g.
- Sweden has a requirement for operators to inform the local authority before installation of a new HFC system over 10 kg.
- Slovenia introduced a tax on sales of F-gases in 2009.
- In Greece national regulations require annual reporting of service records with penalties for non-compliance.
- France is controlling containment of systems above 2 kg of charge compared to 3 kg in EU regulation 842/2006. France is also considering a tax on HFC-sales.
- Hungary has additional legislation covering use of SF_6 for gas insulated switchgears (GIS).
- UK has financial incentives for emission reduction covering gas insulated switchgears (GIS).
- Germany has a maximum leakage limit of 3% for new supermarket refrigeration systems.

Regarding countries outside EU the following regulations are known [Schwarz et al. 2011]:

- In Switzerland a ban on "substances stable in air" exist. "Substances stable in air" includes SF_6, all PFCs, and HFCs with global warming potential in the range of 140-11,700. The ban is organised as a general ban with exemptions. The ban applies e.g. to residential refrigerators, freezers, dehumidifiers, air conditioners and aerosols, while air conditioning systems in motor vehicles are exempt as long as no substitutes are available. The use in foams is forbidden unless insulation is not possible with other materials. Exemptions also exist with respect some uses of solvents etc. Rules has also been established for maintenance, authorisations, registrations and record keeping for refrigeration and air conditioning systems containing charges of "substances stable in air" above 3 kg. For further details reference is made to [Switzerland 2014a].
  For commercial and industrial refrigeration together with air-conditioning and heat pumps a new ban on the use of "substances stable in air" was introduced on 1 December 2013 [Switzerland 2014b]. The ban is based on the cooling capacity of the specific equipment type e.g.:
  a. For air-conditioning equipment use of refrigerants with GWP ≥2000 is not allowed for equipment with cooling capacity above 600 kW while the use of such refrigerants is allowed for equipment with capacity above 80 kW and below 600 kW under certain conditions,
  b. For commercial cooling equipment use of refrigerants with GWP ≥2000 is not allowed for equipment with cooling capacity above 8-40 kW (depending on the specific type of equipment).

  For further details reference is made to [Switzerland 2014b].
- In Japan, current legislation on F-gases focuses on recovery and recycling of refrigerants e.g. from household air conditioners, refrigerators and freezers, and air conditioning systems in vehicles. Also recovery of HFCs from commercial refrigeration and air conditioning systems during servicing and at end of life is required in order to ensure proper destruction.
- In Australia, licensing requirements apply to import, export and manufacture of HFCs and PFCs and equipment containing HFCs. A non-refundable fee of AUD $ 15,000 is payable with the application. License holders are required to maintain records , submit quarterly

reports and pay a levy based on the amount of substances imported. The levy is AUD $ 165/tons HFCs or PFCs.

- In the USA, the Greenhouse Gas Reporting Programme requires e.g. magnesium production to report their greenhouse gas emission to USEPA. Further legislation has been proposed but has so far not been accepted.
  The state of California has implemented several measures to reduce HFC emissions [California 2014]. These include low-GWP requirements for aerosol propellants, a deposit-return recycling program for small cans of motor vehicle air-conditioning (AC) refrigerant, and the Refrigerant Management Program. In addition, beginning with 2017 model year vehicles, the national Clean Cars Initiative is expected to significantly reduce motor vehicle air-conditioning refrigerant emissions. Initiatives for further actions are in process of being developed. [California 2014]
- In Norway, a tax on HFCs and PFCs was introduced in 2003 and amounts to approx. 25 Euro per tons CO_2-eq (2011 figures). This tax is supplemented by a reimbursement scheme for HFCs and PFCs delivered for destruction.

Voluntary programmes and measures addressing F-gases, furthermore, exist in e.g. Australia, USA, Japan and Norway [Schwarz et al. 2011].

2.7 Eco-labels

The use of HFCs, PFCs and SF_6 are only addressed by a few eco-labels. Table 7 below gives an overview of how these substances are addressed by the EU and the Nordic eco-label schemes. The table lists the product types for which the presence of fluorinated greenhouse gases is restricted. It shows that the use of such compounds are not allowed by eco-labels for heat pumps, floor coverings, TV and projectors, windows and exterior doors and labels for furniture and fitments.

It is noted that eco-labels are not established for cooling and freezing equipment for private and professional use. It is also noted that the eco-labels for heat pumps do not restrict the use of HFC-134a. In both cases it may be considered to promote the use of natural refrigerants.

TABLE 7
ECO-LABELS SPECIFICALLY TARGETING HFCS, PFCS OR SF_6.

Eco-label	Articles	Substance	Criteria relevant for HFC, PFC or SF_6 (beyond general EU restrictions)	Document title/number
EU flower	Floor coverings	HFCs	Foam rubber (only for polyurethane) (b) Blowing agents: CFCs, HCFCs, HFCs or methylene chloride shall not be used as blowing agents or as auxiliary blowing agents. Assessment and verification: The applicant shall provide a declaration that these blowing agents have not been used.	Commission Decision of 30 November 2009 on establishing the ecological criteria for the award of the Community eco-label for textile floor coverings

Eco-label	Articles	Substance	Criteria relevant for HFC, PFC or SF_6 (beyond general EU restrictions)	Document title/number
	Heat pumps	Fluorinated refrigerants	The global warming potential (GWP) for the refrigerant must not exceed GWP value > 2000 over a 100 year period. If the refrigerant has a GWP of less than 150 then the minimum requirements of the coefficient of performance and primary energy ratio in heating mode and the energy efficiency ratio in cooling mode, as set out in criteria 1 and 2 of this Annex, shall be reduced by 15 %. GWP values considered will be those set out in Annex 1 of Regulation (EC) No 842/2006 of the European Parliament and of the Council. For fluorinated refrigerants, the GWP values shall be those published in the third assessment report adopted by the Intergovernmental Panel on Climate Change (2001 IPCC GWP values for a 100 year period).	Commission Decision of 9 November 2007 establishing the ecological criteria for the award of the Community eco-label to electrically driven, gas driven or gas absorption heat pumps
Nordic Swan	Floor coverings	HFC	R14 Foam rubber (polyurethane) CFC, HCFC, HFC (hydrofluorocarbons) and methylene chloride must not be used for foaming.	Nordic eco-labelling of Floor coverings Version 5.2 • 12 October 2010 – 31 October 2015
	TV and Projectors	SF_6	The LCD panel must be produced in such a way that the greenhouse gases NF_3 and SF_6, if part of the production process, are abated by a system that is an integrated part of the production process. It is the responsibility of the manufacturing company to ensure that the abatement system is installed, operated and maintained in accordance with the manufacturers (of the abatement system) specifications. The manufacturer of the LCD shall declare the amount of NF_3 and SF_6 purchased in relation to amount of LCD (m2) produced over one year.	Nordic eco-labelling of TV and Projector Version 5.0 20 June 2013 - 30 June 2016
	Windows and Exterior Doors	HFC	Expanding insulation material must not be produced using fluorinated propellants such as hydrofluorocarbons (HFC). Typical materials include expanded polystyrene (EPS) and extruded polystyrene (XPS).	Nordic eco-labelling of Windows and Exterior Doors Version 3.5 • 4 November 2008 – 30 June 2015

Eco-label	Articles	Substance	Criteria relevant for HFC, PFC or SF_6 (beyond general EU restrictions)	Document title/number
	Furniture and fitments	HFC	Blowing agents and isocyanate compounds CFC, HCFC, HFC, methylene chloride and halogenated organic compounds must not be used as blowing agents.	Nordic eco-labelling of Furniture and fitments Version 4.7 • 17 March 2011 – 31 December 2017

2.8 Summary and conclusions

F-gases covering HFCs, PFCs and SF_6 is regulated by EU-legislation as well as Danish legislation. The Danish legislation in many ways is the most restrictive. The Danish legislation allows for the use of HFCs in refrigeration systems with refrigerant charges less than 10 kg HFC refrigerant – the so-called "10 kg window". Future changes of the Danish legislation may be focused at this "window".

New EU legislation which will significantly restrict the use of F-gases in the EU is in the process of being approved. F-gases with GWP<150 are, however, generally exempted from the regulation which allows for use of HFC-152a. HFC-152a is today only used as refrigerant in special equipment, but could be a candidate for more widespread use.

Only one substance - HFC-365mfe - is subject to harmonised classification. This substance is classified as Flammable Liquid 2 with the hazard statement H225 (Highly flammable liquid and vapour). Most other substances are, however, self-classified by companies. Dominant classifications include flammable gas or gas under pressure that may explode if heated.

None of the substances are addressed further by REACH or are in pipeline for further activities under REACH.

All of the substances are covered by the Kyoto Protocol related to climate change and thus subject for the efforts of this Protocol and subsequent amendments to lower the emissions to the atmosphere. HFCs are, furthermore, addressed by The Climate and Clean Air Coalition to Reduce Short-Lived Climate Pollutants.

The majority of EU Member States as well as nations outside EU do not have national policies going beyond existing EU F-gas regulations. Austria, however, has banned the use of HFCs in small domestic refrigerators and freezers while a comprehensive ban exist in Switzerland covering refrigeration as well as many other applications of F-gases.

The use of HFCs, PFCs and SF_6 are only addressed by a few eco-labels inclusive of eco-labels for heat pumps, floor coverings, TV and projectors, windows and exterior doors and labels for furniture and fitments. It is noted that eco-labels are not established for cooling and freezing equipment for private and professional use products and that existing eco-labels for heat pumps do not restrict the use of HFC-134a. In both cases it may be considered to promote the use of natural refrigerants.

3. Manufacture and uses

3.1 Manufacturing

3.1.1 Manufacturing processes

HFCs

Considering HFCs a dominant route of manufacture is hydro-fluorination (reaction with hydrogen fluoride – HF) of chlorinated alkanes. This process has been specifically identified for a number of substances such as:

- HFC-32 (Difluoromethane) is based on hydro-fluorination of dichloromethane. [OECD SIDS 2004];
- HFC-125 (Pentafluoroethane) is based on hydro-fluorination of chlorotetrafluoroethane (HFC-124) and subsequent purification by distillation [OECD SIDS 2005];
- HFC – 134a e.g. is based on hydro-fluorination of trichloroethylene, via 1-chloro-2,2,2-trifluoroethane (HCFC-133a) [ECETOX 2006a] – other routes are, however also relevant, please see below ;
- HFC-152a is produced by catalytic reaction of vinyl chloride with hydrogen fluoride and is purified based on market specification [OECD SIDS 2006];
- HFC-245fa is based on hydro-fluorination of pentachloropropane [ECETOX 2004b].

Other synthetic pathways are:

- Addition of hydrogen fluoride to olefins or alkynes (e.g. HFC 152a) [Siegemund et al. 2005];
- Exchange of chlorine for fluorine using metal fluorides such as antimony fluoride [Siegemund et al. 2005];
- For HFC-134a: Isomerisation/hydro-fluorination of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) to 1,1,-dichloro-1,2,2,2-tetrafluoroethane (CFC-114a) followed by hydro-dechlorination of the latter [ECETOX 2006a];
- For HFC-134a: Hydro-fluorination of tetrachloroethylene to 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124) and subsequent hydro-dechlorination to HFC-134a [ECETOX 2006a];
- Monohydroperfluoroalkanes can be obtained by adding hydrogen fluoride to perfluoroalkenes (e.g. HFC 227ea) or by decarboxylation of perfluorocarboxylates in the presence of proton donors;
- Replacement of chlorine atoms in the starting chlorocompounds by fluorine may also be obtained by liquid phase reactions in the presence of catalysts such as antimony(V) or tin(IV) chlorofluorides or vapour phase reactions using solid-phase catalysts based on chromium. Preferred starting materials are chloroform for HFC 23, dichloromethane for HFC 32 and 1,1,1-trichloroethane for HFC 143a [67]. The conversion of tetrachloroethylene to HFC 125 and trichloroethylene to HFC 134a involves initial HF-addition across the double bond followed by a series of chlorine – fluorine exchange reactions [Siegemund et al. 2005].

HFC-23 is also generated as a by-product during the manufacture of HCFC-22 up to a level of 3%. The HFC-23 may be captured for use or wented to the atmosphere [Schwarz & Wartmann 2005; USEPA 2009].

PFCs

Perfluorocarbons can be produced by a variety of routes. Generally the following processes are utilised [Siegemund et al. 2005]:

- Indirect fluorination of hydrocarbons with cobalt(III) fluoride or silver(II) fluoride carried out in a steel or nickel tube with stirring. The hydrocarbon vapours are passed at 150 – 450 °C over the fluorinating agent, which is regenerated in a fluorine stream;
- Fluoroalkanes can also be produced electrochemically e.g. by the Simons process by which solutions of organic compounds are electrolyzed in anhydrous hydrogen fluoride. Fluorination takes place at a nickel anode.

Identified processes for specific compounds include the following [Siegemund et al. 2005]:

- PFC-14 (tetrafluoromethane, CF_4) can be produced by reaction of CCl_2F_2 or CCl_3F and hydrogen fluoride in the gas phase or by direct fluorination of carbon;
- PFC-116 (hexafluoroethane) is often obtained as a by-product in the production of CFC 115;
- PFC-218 (octafluoropropane) can be produced by direct, electrochemical, or CoF_3-fluorination of hexafluoropropene.;
- PFC-318 (octafluorocyclobutane) is obtained by combination of two molecules of tetrafluoroethylene or by passing 1,2-dichloro- 1,1,2,2-tetrafluoroethane, $CClF_2CClF_2$, over a nickel catalyst at 590 °C.

SF_6

SF_6 is synthesised from the reaction of elemental sulphur with F_2 [OECD SIDS 2006c].

3.1.2 Manufacturing sites

European manufacturers of fluorocarbons are organised under the umbrella of Cefic (European Chemical Industry Council) and include the following companies [EFCTC 2014]:

- Mexichem Fluor (Great Britain);
- Arkema (France) ;
- DuPont;
- Solvay Fluor (Germany);
- Honeywell Fluorine Products (Netherlands)

Together these companies maintain production of fluorocarbons in the following EU countries (2007 –data [Afeas 2013]): Netherlands, France, Spain, Germany, Italy, and UK.

Globally production of fluorocarbons also takes place in Argentina, Japan, Canada, USA, Brazil, Mexico and China [Afeas 2013]. It is likely that production also takes in other countries e.g. Russia and India.

No certain information on location of plants for production of specific compounds is available. It is known that the main countries of production of HFC-32 around 2004 were Spain, USA, Japan and Korea [OECD SIDS 2004], while production of HFC-125 took place e.g. in USA and Italy [OECD SIDS 2005].

3.1.3 Manufacturing volumes

HFCs are the most important category of F-gases. HFCs were introduced as alternatives for ozone depleting substances: CFCs and (later on) HCFCs. The production increased during the 1990s and later on when restrictions on the use of HCFCs went into force.

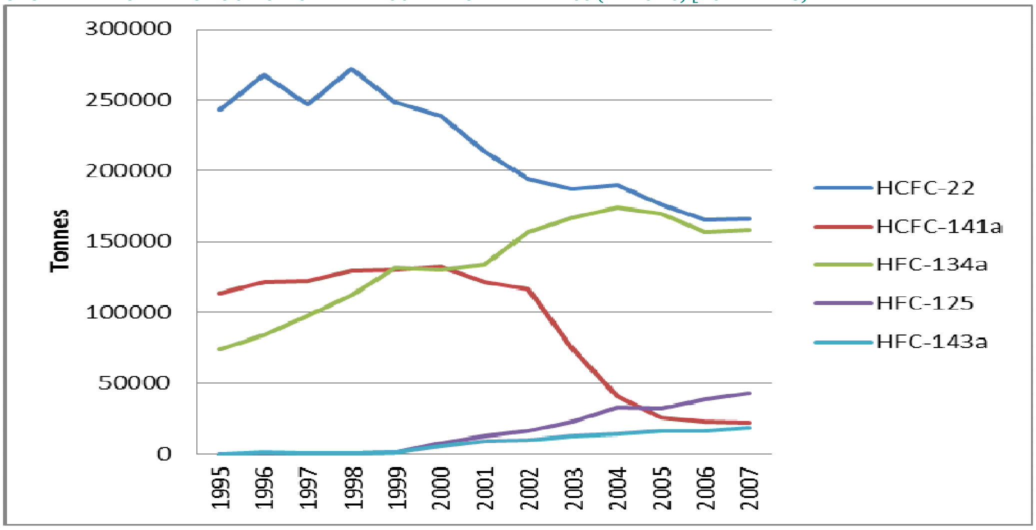
Figures on global production of the most important HCFC and HFC compounds are presented in Table 8 and Figure 1. From the table and figure it can be seen that the global production of HFCs is increasing very fast in counter-phase to the reduction of the production of HCFCs.

TABLE 8
GLOBAL ANNUAL PRODUCTION OF THE MOST IMPORTANT HFCS (IN TONS) [*ÖKO-RECHERCHE ET AL, 2011*]*1

	HCFC-22	HCFC-141b	HFC-134a	HFC-125	HFC-143a
1995	243,468	113,154	73,769		
1996	267,523	121,085	83,674	0	794
1997	246,937	122,356	97,949	296	339
1998	271,980	129,037	112,174	698	557
1999	248,552	130,415	131,710	1,243	750
2000	239,197	132,476	130,056	7,400	5,396
2001	213,328	121,757	133,956	12,583	9,151
2002	193,955	116,673	156,987	16,190	9,656
2003	187,262	74,596	166,899	22,631	12,972
2004	189,545	40,417	173,851	32,734	14,053
2005	176,373	25,619	169,999	31,819	16,321
2006	165,478	22,548	156,573	38,537	16,257
2007	165,862	21,835	158,161	42,573	18,325

*1 The data does not include China and India. The table is from the EU preparatory study for the review of the F-gas regulation. HFC-32 is not included because data is not published. Production trend of HFC-32 will have some similarities to HFC-143a . Note that the table also includes two major HCFCs, and note the decline in production of HCFCs to some degree fits to the increase of production of HFCs.

FIGURE 1
GLOBAL ANNUAL PRODUCTION OF THE MOST IMPORTANT HFCS (IN TONS) [AS TABEL 8)



The data presented does not include production in China and India. In 2004 the production data presented for HFC compounds was thought to represent between 85 and 90% of the global production [Afeas 2013]. China has now increased production of HFCs significantly (production capacity for HFC-134a is estimated to 75,000 tons/year) [Afeas 2013]. Available knowledge regarding global production of other fluorocarbons is as follows:

- Annual worldwide production capacity of HFC-32 was estimated at approximately 15,000 tons by 2004 [OECD SIDS 2004];
- Production capacities for HFC-152a are confidential, but in excess of 5,000 tons/year [OECD SIDS 2006],
- Regarding SF_6 the global sale was reported at 6,435 tons in 2001. The sold volumes are considered to be well descriptive of the produced volumes [OECD SIDS 2006c].

Based on this knowledge it seems fair to anticipate that the total global production of F-gases probably will be above 300,000 tons/year.

The knowledge available regarding production of HFCs, PFCs and SF_6 in the European Union is presented in Table 9. Production in EU may based on these figures be estimated at 50,000 – 60,000 tons/year.

TABLE 9
PRODUCTION OF HFCS, PFCS AND SF_6 IN THE EUROPEAN UNION IN THE PERIOD 2007 TO 2011 (METRIC TONS) [EEA 2012].

Gas	2007	2008	2009	2010	2011
HFC-125	6 553	conf.	conf.	conf.	conf.
HFC-134a	31 246	21 529	18 609	21 476	conf.
HFC-143a	6 159	5 224	conf.	conf.	5 122
SF_6 + other HFCs and PFCs	14 079	14 894	16 514	24 983	38 908
Total	**58 037**	**41 647**	**35 123**	**46 459**	44 039

*1 Figures are based on reporting from companies producing in Europe. When less than 3 companies are providing figures, figures are treated as confidential and "conf." (confidential) is stated instead. In case no data is available n.d. (no data) is stated.

3.2 Import, export and sale

3.2.1 Import and export of HFCs, PFCs and SF_6 in Denmark

Statistical data

HFCs, PFCs and SF_6 are not manufactured in Denmark. Some import and export of such goods takes place. Existing statistical data is presented in Table 10.

The data presented cover import and export of individual HFCs and PFCs (position number 29033010, 29033080, 29037921 and 29037929) together with import and export of mixtures covering HFCs and PFCs partly together with other substances. No statistics have been presented for SF_6, as this substance in the foreign trade statistics is registered together with other fluorides, and in this context is a minor substance for which reason it is thus not possible to obtain data on import and export of SF_6 from the foreign trade statistics [DS 2014].

The dominant position number in the foreign trade statistics is 38247800 that cover mixtures containing PFCs or HFCs without CFCs or HCFCs. The figures registered indicate that import as well as export has been strongly increasing in the years of 2007 to 2012.

As a contrast no import and export of individual substances has been registered (reference is made to position numbers 29033010, 29033080, 29037921 and 29037929). It is possible that individual substances instead are registered together with mixtures under position number 38247800. It is noted that high export figures are registered for position number 38247800 which is consistent with a registered sale of own commodities from Danish companies [DS 2014].

It is found relevant also to present position number 38247100 that covers mixtures with content of CFCs, but also with content of HCFCs, PFCs or HFCs, as some HFCs etc. by mistake may be registered under this position number.

No investigations are available to present an adequate explanation on the figures registered by the Danish foreign trade statistics.

TABLE 10
DANISH IMPORT AND EXPORT OF HFCS, PFCS AND SF_6 AS REGISTERED BY STATISTICS DENMARK (DS, 2014) *1

CN code	Product	Tons/year					
		2007	2008	2009	2010	2011	2012
Import							
38247100	Mixtures containing halogenated derivatives with content of CFCs, also with content of HCFCs, PFCs or HFCs	335.3	278.5	422.5	228.7	118.4	109.1
38247800	Mixtures containing PFCs or HFCs, but without CFCs or HCFCs.	52.4	110.1	13.4	418.7	583.6	590.7
Export							
38247100	Mixtures containing halogenated derivatives with content of CFCs, also with content of HCFCs, PFCs or HFCs	445.4	325.4	346.4	299.1	234.3	117.2
38247800	Mixtures containing PFCs or HFCs, but without CFCs or HCFCs.	0.0	0.1	0.0	206.2	530.7	437.0

*1 SF_6 are in the statistical CN-code system registered together with other fluorides, and it is thus not possible to obtain data on import and export of SF_6 from import7export statistics. Apart from the CN-codes shown the following CN-codes may also be relevant to consider:
29033010 Fluorides of acyclic carbon hydrides.
29033080 Fluor- and iodine derivatives of acyclic carbon hydrides.
2903 7921 Halogenated derivatives of methane, ethane or propane halogenated with fluorine or bromine only.
2903 7929 Halogenated derivatives halogenated with fluorine or bromine only, except derivates of methane, ethane or propane.
For none of these codes, however, is registered any import or export.

Danish investigations

The Danish Environmental Protection Agency publishes an annual report on Danish consumption and emissions of HFCs, PFCs and SF_6. The latest report is describing the import and consumption in 2012 [Poulsen & Museaeus 2103].

As stated above there is no production of HFCs, PFCs and SF_6 in Denmark and all consumed gases have to be imported. The imported bulk (net import minus re-export) corresponds to the Danish consumption of HFCs, PFCs and SF_6. The bulk import is presented in Table 11 as the substances and blends actually registered and in Table 12 recalculated to pure substances to the extent possible based on the composition of blends noted in Table 2.

The figures in the columns for "All HFCs" in Table 11 and 12 do not math exactly because some blends besides HFCs substances also include HCFC-substances (e.g. HCFC-22) or other substances as propane and butane. Furthermore, the consumption of HFCs represented by "Other HFCs" in Table 11 is not included in the figures in Table 12, as the exact bulk import of the individual blends or compounds is not known.

It can be seen from Table 11 that the HFCs is the most important import (and consumption) category. The import in 2012 of HFCs was 365.1 tons. The import of SF_6 was 2.6 tons and the import of PFCs was 0.5 tons.

From Table 12 is it clear that the dominant part of all HFCs imported is represented by the substances HFC-23, HFC-125, HFC-134a, HFC-143a and HFC-152a and that in particular HFC-134a is important.

TABLE 11

DEVELOPMENTS IN BULK IMPORTS OF GREENHOUSE GASES TO DENMARK, TONS [POULSEN & MUSEAEUS, 2013] (IN TONS, PLEASE NOTE THE USE OF DANISH PUNCTUATION)*1

Year / Substance	HFC-134a	HFC-152a	HFC-401A	HFC-402A	HFC-404a	HFC-407C	HFC-507A	HFC-410A	HFC-413A	HFC-417A	Other HFCs¹	All HFCs	SF6	PFCs
1992	20,0	4,0			-						-	24,0	15,0	-
1994	524,0	51,0			36,0						1,0	612,0	21,0	-
1995	565,0	47,0			119,0						14,0	745,0	17,0	1,5
1996	740,0	32,0			110,0						20,0	902,0	11,0	3,0
1997	700,0	15,0			110,0						65,0	890,0	13,0	8,0
1998	884,0	14,0	15,0	10,0	146,0	17,0	10,0				15,0	1.111,0	9,0	
1999	644,6	35,8	15,0	10,0	193,7	40,0	10,0				29,2	978,3	12,1	7,9
2000	711,1	16,4	9,5	4,2	193,1	44,7	23,8				24,1	1.027,0	9,0	6,9
2001	472,8	11,1	4,1	0,8	126,2	40,3	2,2				18,4	675,9	4,7	3,7
2002	401,6	11,9	-	-	188,7	89,1	14,4				7,5	713,2	1,4	2,0
2003	241,2	3,3	0,2	1,7	145,0	96,8	9,2				13,0	510,4	2,2	0,5
2004	306,5	11,0	-	-	252,6	101,3	10,6	2,6	7,2	6,0	4,4	702,2	2,3	0,3
2005	235,4	5,5	-	-	162,4	61,6	5,4	3,1	5,0	1,3	5,1	484,8	3,6	0,5
2006	280,7	11,6	-	-	176,4	70,6	6,1	7,7		0,9	4,8	558,8	4,2	-
2007	160,7	13,0	-	-	129,9	50,5	11,4	12,8	1,0	2,1	21,0	402,4	5,4	0,7
2008	164,5	15,0	-	-	114,1	76,8	1,8	16,9	0,7	0,7	8,9	399,4	5,9	68,9
2009	175,3	12,0	-	-	106,9	49,3	7,0	12,1	-	-	0,6	363,2	4,3	0,9
2010	160,6	15,0	-	-	103,6	42,4	9,1	16,0	-	1,0	5,4	352,9	3,8	0,9
2011	180,5	8,0	-	-	105,0	42,8	6,1	15,5	-	2,0	13,0	372,9	3,1	0,9
2012	171,7	13,0	-	-	99,5	42,7	12,1	21,5	-	1,0	3,5	365,1	2,6	0,5

*1 The category "Other HFCs" includes HFC-408A, HFC-409A, R422, R424A, R426A, RS24, and RS44. Some of the HFCs belonging to the 400-500 series may include HCFC-compounds or other substances as propane and butane – see Table 2.

TABLE 12
DEVELOPMENTS IN BULK IMPORTS OF HFC GREENHOUSE GASES TO DENMARK, TONS – RECALCULATED AS PURE SUBSTANCES [POULSEN & MUSEAEUS, 2013] *1

Gas	HFC-23	HFC-125	HFC-134a	HFC-143a	HFC-152a	All HFCs
1992	0.0	0.0	20.0	0.0	4.0	24.0
1994	0.0	15.8	525.4	18.7	51.0	611.0
1995	0.0	52.4	569.8	61.9	47.0	731.0
1996	0.0	48.4	744.4	57.2	32.0	882.0
1997	0.0	48.4	704.4	57.2	15.0	825.0
1998	3.9	79.5	898.7	80.9	16.0	1079.0
1999	9.2	106.2	673.1	105.7	37.8	932.1
2000	10.3	110.6	742.1	112.3	17.6	992.9
2001	9.3	67.2	498.8	66.7	11.6	653.6
2002	20.5	112.5	455.5	105.3	11.9	705.7
2003	22.3	93.6	297.3	80.0	3.3	496.5
2004	24.6	145.9	378.6	136.7	11.0	696.7
2005	15.7	91.7	279.0	87.1	5.5	479.1
2006	20.1	102.6	324.9	94.8	11.6	554.0
2007	18.0	82.9	194.1	73.2	13.0	381.2
2008	26.1	79.1	210.0	60.2	15.0	390.4
2009	17.4	68.9	205.2	59.1	12.0	362.6
2010	17.8	69.2	187.3	58.4	15.0	347.7
2011	17.6	68.6	208.0	57.7	8.0	359.8
2012	20.6	71.7	198.4	57.8	13.0	361.5

*1 Figures are based on the bulk import presented in Table 11 but recalculated to pure substances to the extent possible based on the composition of blends noted in Table 2. The reasons behind that the figures in the columns for "All HFCs" in Table 11 and 12 do not math exactly sre explained in the text.

3.2.2 Sales of HFCs, PFCs and SF_6 in EU

European investigations

The data available on import, export and sale of HFCs, PFCs and SF_6 in the European Union is presented in Tables 13 to 15. The figures are based on the reporting requirement established by the European Union Regulation (EC) No 842/2006 on certain fluorinated greenhouse gases (the 'F-Gas Regulation'). According to this Regulation all producers, importers and exporters of more than one ton of F-gases (HFCs, PFCs and SF_6) are required to report to the European Commission on the quantities produced, imported and exported in each calendar year, and provide related data such as the main intended applications of the F-gases. Imports and exports of F-gases contained in products or equipment are not covered by the reporting [EEA 2012].

The figures presented in the tables illustrate:

- That HFCs are traded and sold in significant higher quantities than PFCs and SF_6; and

- That most of the substances in question are produced in EU and that both EU production and import to EU are important routes of supply.

TABLE 13
IMPORTS OF HFCS, PFCS AND SF_6 TO EU IN THE PERIOD 2007 TO 2011 (METRIC TONS) [EEA 2012] *1

Gas	2007	2008	2009	2010	2011
HFC-23	129	187	124	144	128
HFC-32	2 302	2 429	1 766	3 010	3 282
HFC-125	10 171	10 816	13 756	15 406	13 653
HFC-134a	34 511	37 799	27 619	33 380	33 223
HFC-143a	4 445	6 510	4 448	5 073	5 597
HFC-152a	4 440	6 401	5 262	6 448	6 622
HFC-227ea	273	1 738	1 634	1 551	1 574
HFC-236fa	49	Conf.	Conf.	34	51
CF_4	13	87	37	61	67
C_2F_6	112	186	77	150	140
C_3F_8	121	Conf.	10	Conf.	Conf.
c-C_4F_8	Conf.	6	5	Conf.	8
SF_6	801	691	671	539	587
Other HFCs and PFCs	2 280	1 869	3 496	4 644	1 564
Total	**59 647**	**68 721**	**58 904**	**70 439**	**66 497**

*1 Figures are based on reporting from companies producing in Europe. When less than 3 companies are providing figures, figures are treated as confidential and "conf." (confidential) is stated instead. In case no data is available n.d. (no data) is stated.

TABLE 14
EXPORTS OF HFCS, PFCS AND SF_6 FROM EU IN THE PERIOD 2007 TO 2011 (METRIC TONS) [EEA 2012].

Gas	2007	2008	2009	2010	2011
HFC-23	Conf.	15	1	4	8
HFC-32	1 245	771	605	1 319	1 335
HFC-125	2 622	2 041	1 420	2 267	3 520
HFC-134a	14 142	11 374	9 780	10 469	11 079
HFC-143a	1 351	1 455	701	984	1 236
HFC-152a	Conf.	158	Conf.	632	262
HFC-227ea	120	135	356	351	433
HFC-245fa	16	Conf.	Conf.	Conf.	1
HFC-365mfc	2 254	2 110	1 932	2 813	3 264
HFC-43-10mee	Conf.	46	16	48	n.d.
CF_4	Conf.	1	Conf.	11	4
C_2F_6	Conf.	28	Conf.	Conf.	Conf.
SF_6	1 659	1 185	1 423	1 697	1 964
Other HFCs and PFCs	245	54	928	1 491	106

Gas	2007	2008	2009	2010	2011
Total	**23 654**	**19 373**	**17 162**	**22 086**	**23 210**

*1 Figures are based on reporting from companies producing in Europe. When less than 3 companies are providing figures, figures are treated as confidential and "conf." (confidential) is stated instead. In case no data is available n.d. (no data) is stated.

TABLE 15
SALES OF HFCS, PFCS AND SF_6 IN EU IN THE PERIOD 2007 TO 2011 (METRIC TONS) [EEA 2012]. *1

Gas	2007	2008	2009	2010	2011
HFC-23	267	194	192	240	182
HFC-32	4 186	5 545	4 328	5 437	4 957
HFC-125	12 933	15 427	13 438	18 345	15 592
HFC-134a	51 693	48 123	42 005	45 580	40 844
HFC-143a	9 605	10 487	8 940	10 118	8 644
HFC-152a	4 301	2 782	5 182	6 213	6 352
HFC-227ea	857	2 336	2 075	2 199	1 566
HFC-245fa	n.d.	n.d.	1248	Conf.	Conf.
HFC-365mfc	Conf.	3 785	3 054	3 554	4 102
HFC-236fa	29	37	25	30	43
HFC-43-10mee	n.d.	n.d.	50	56	Conf.
CF_4	Conf..	88	42	60	57
C_2F_6	87	183	113	154	131
C_3F_8	168	61	18	24	23
c-C_4F_8	n.d.	n.d.	3	6	10
SF_6	2 223	3 011	1 928	1 851	2 174
Other HFCs and PFCs	6 777	1 984	2 590	4 128	1 576
Total	**93 126**	**94 043**	**85 230**	**97 995**	**86 253**

*1 Figures are based on reporting from companies producing in Europe. When less than 3 companies are providing figures, figures are treated as confidential and "conf." (confidential) is stated instead. In case no data is available n.d. (no data) is stated.

Regarding PFCs not specified in table 12-14 above, the following knowledge is available [EFCTC 2014]:

PFC 3-1-10 (C_4F_{10}):
The total European volume for physics research is estimated < 5 tons/year

PFC 5-1-14 (C_6F_{14}):
The total European market is estimated as <200 tons for 1999 with a downward trend.

Statistical data
For comparison the existing statistical data from Eurostat (EU Trade Since 1988 By CN8) on import and export of HFCs and PFCs to and from EU27 have been presented in table 16. No data on production of these substances have been presented as the substances in question cannot be identified in the EU database on industrial production (Prodcom).

As for table 10 (import/export to and from Denmark) the data presented for EU cover import and export of individual HFCs and PFCs (position number 29033010, 29033080, 29037921 and 29037929) together with import and export of mixtures covering HFCs and PFCs partly together with other substances. No statistics have been presented for SF_6, as this substance in the foreign trade statistics is registered together with other fluorides, and in this context is a minor substance for which reason it is thus not possible to obtain data on import and export of SF_6 from the foreign trade statistics [Eurostat 2014]. It is noted that while the position numbers are the same as in table 10 the label text may differ slightly.

The dominant position number in the foreign trade statistics is 38247800 that cover mixtures containing PFCs or HFCs without CFCs or HCFCs. The figures registered indicate that import as well as export has been strongly increasing in the years of 2007 to 2012. Attention should be paid to that position 38247100 in Table 16 seems to address chlorofluorocarbons (CFCs) while the similar position in Table 10 seems to address also mixtures of HFCs and CFCs.

Generally the registered import/export is significantly below the figures presented in Table 13 and 14 above. No effort has been invested to investigate this discrepancy. It must be concluded that in this context the figures registered by Eurostat are likely not reliable.

TABLE 16
IMPORT AND EXPORT OF HFCS, PFCS AND SF_6 BY EU27 AS REGISTERED BY EUROSTAT (EUROSTAT 2014) *1

CN code	Product	Tons/year					
		2007	2008	2009	2010	2011	2012
Import							
2903 7929	Halogenated derivatives of acyclic hydrocarbons containing two or more different halogens, halogenated only with fluorine and bromine, n.e.s.	n.a.	n.a.	n.a.	n.a.	n.a.	37
3824 7100	Mixtures containing acyclic hydrocarbons perhalogenated only with fluorine and chlorine	504	84.9	63.9	29.4	29.1	14.8
3824 7800	Mixtures containing PFCs or HFCs, but not containing CFCs or HCFCs.	658	206	617	1714	2752	6189
Export							
2903 7929	Halogenated derivatives of acyclic hydrocarbons containing two or more different halogens, halogenated only with fluorine and bromine, n.e.s.	n.a.	n.a.	n.a.	n.a.	n.a.	0.7
3824 7100	Mixtures containing acyclic hydrocarbons perhalogenated only with fluorine and chlorine	14337.7	1997.9	948.3	67.3	11.7	28,5
3824 7800	Mixtures containing PFCs or HFCs, but not containing CFCs or HCFCs.	1953	5743	3535	5762	6298	5303

*1 SF_6 are in the statistical CN-code system registered together with other fluorides, and it is thus not possible to obtain data on import and export of SF_6 from import7export statistics. Apart from the CN-codes shown the following CN-codes may also be relevant to consider:
29033010 Fluorides
29033080 Fluorides and iodides derivatives of acyclic hydrocarbons
2903 7921 Halogenated derivatives of acyclic hydrocarbons containing two or more different halogens, halogenated only with fluorine and bromine of methane, ethane or propane, n.e.s.
For the codes **29033010 and 29033080**, however, is not registered any import or export, while for code **2903 7921** figures are registered for 2012 only (import 3 tons/year); export 0 tons/year).

3.3 Use

3.3.1 Registrations by the Danish Product Register

Data on HFCs, PFCs and SF_6 in preparations registered in the Danish Product Register are summarised in Table 17. The data presented indicate the use/function for the different substances placed on the Danish market in 2010-2012. As all substances are registered by less than 3 companies all data on quantities used are confidential.

The registered uses/functions include:

- Heat transferring agents in industrial cooling- and air-conditioning plants;
- Fillers/joints for construction activities;
- Construction material for manufacture of metal constructions;
- Intermediate for manufacture of plastic products; while
- Cleaning/washing and other uses/functions include manufacture of electronic and optical products as well as electrical equipment.

TABLE 17
HFCS, PFCS AND SF_6 IN PREPARATIONS PLACED ON THE DANISH MARKET IN 2010-2012 AS REGISTERED IN THE DANISH PRODUCT REGISTER

Use/function	Substance	Quantity tons/year
Heat transferring agent	HFC-32 HFC-125 HFC-143a HFC-152a HFC-365mfe	Confidential
Fillers	HFC-134a HFC-152a	Confidential
Construction materials	HFC-245fa HFC-365mfe	Confidential
Intermediates	HFC-245fa HFC-365mfe	Confidential
Cleaning/washing agent and other uses/functions	HFC-134a	Confidential

3.3.2 Use of HFCs, PFCs and SF_6 in EU

The reported intended applications of F-gases in the European Union are, based on reports from manufacturers and importers of these gases to EU, listed in Table 18.

Based on [EFCTC 2014; EFCTC 2012] the applications of the substances may be briefly described as follows:

Refrigeration and air-conditioning cover domestic as well as commercial refrigeration besides mobile air-conditioning in vehicles, domestic/commercial air-conditioning for buildings and heat pumps. The substances used are HFC 134a, HFC-143a (blend component), HFC-125 (blend component), HFC-23 (low temperature refrigeration), HFC-32 (blend component), HFO-1234yf and PFC 116 (specialist low temperature refrigerant). To these substances can be added HFO-1234zeE and PFC 5-1-14, which are likely not used in significant quantities (see chapter 1).

Fire protection of sensitive facilities as telecommunication facilities, computer rooms, process control centres, aircrafts etc. is based on substances as HFC 125, HFC-227ea, HFC-236fa andHFC-23.

As propellants in *aerosols* (sprays) for medical and specialized industrial purposes are used HFC-134a, HFC-152a and HFC-227ea.

As solvents is used HFC-365mfc (blend component) and HFC-43-10mee for specialized applications.

TABLE 18
INTENDED APPLICATIONS OF SALES OF F-GASES IN THE EUROPEAN UNION IN THE PERIOD 2007 TO 2011 (TONS/YEAR) [EEA 2012] *1

Intended application	2007	2008	2009	2010	2011
Refrigeration and air-conditioning	64 600	64 176	60 049	69 404	53 571
Fire protection	685	598	735	1 686	1 938
Aerosols	9 545	11 614	8 572	9 922	6 861
Solvents	209	173	162	205	Conf.
Foams	14 578	10 664	11 799	11 893	6 611
Feedstock	9	2	Conf.	1 340	Conf.
Electrical equipment	1 568	2 386	1 384	1 614	1 992
Magnesium die casting operations	31	8	Conf.	Conf.	Conf.
Semiconductor manufacture	129	312	184	269	248
Other or unknown	1 773	4 110	2 278	1 622	2 766
No information available	n.d.	n.d.	n.d.	n.d.	12 268
Total	**93 127**	**94 043**	**85 163**	**97 955**	**86 253**

*1 Figures are based on reporting from companies producing in Europe. When less than 3 companies are providing figures, figures are treated as confidential and "conf." (confidential) is stated instead. In case no data are available n.d. (no data) is stated.

As blowing agent for production of *foam* is HFC-134a and HFC 152a used for production of XPS - extruded polystyrene foam. HFC-245fa and HFC-365mfc is used for production of polyurethane foam, while HFC-365mfc is also used for phenolic foams. To these substances can be added HFO-1234zeE which is likely not used in significant quantities (see Chapter 1).

Regarding feedstock applications no further knowledge is available.

In *electrical equipment,* SF_6 is used as a dielectric gas for high voltage applications, while SF_6 is also used as blanket gas for *magnesium die casting*.

In *semiconductor manufacture* is used PFC-14, PFC-116, PFC-218, PFC-318 as well as SF_6.

Other applications include the use of PFC 3-1-10 for physics research and PFC-4-1-12 for medical research.

3.3.3 Danish investigations

As mentioned earlier the use of HFCs is the far most important category of F-gases, which are used in Denmark. The consumption of HFC and HFC-mixtures in main industrial sectors in Denmark in 2012 is presented in Table 19 as the substances and blends actually registered and in Table 20 recalculated to pure substances based on the composition of blends noted in Table 2. Differences between figures in Table 19 and 20 are due to rounding only.

TABLE 19
CONSUMPTION OF HFC DISTRIBUTED ON APPLICATION AREAS IN 2012, TONS [POULSEN & MUSEAEUS, 2103] (PLEASE NOTE DANISH PUNCTUATION)

Substance / Use	Insulation foam	Foam systems	Soft foam	Other applications	Household fridges/freezers	Commercial refrigerators	Transport refrigeration	Mobile A/C	Stationary A/C	Total
HFC-134a	-	-	-	5,3	9,4	88,1	0,3	58,6	10,0	**171,7**
HFC-152a	-	-	-	13,0	-	-	-	-	-	**13,0**
HFC-401A	-	-	-	-	-	-	-	-	-	**-**
HFC-402A	-	-	-	-	-	-	-	-	-	**-**
HFC-404a	-	-	-	-	1,7	91,0	6,7	-	-	**99,5**
HFC-407C	-	-	-	-	-	-	-	-	42,7	**42,7**
HFC-507A	-	-	-	-	-	12,1	-	-	-	**12,1**
HFC-410A	-	-	-	-	-	21,5	-	-	-	**21,5**
HFC-413A	-	-	-	-	-	-	-	-	-	**-**
HFC-417A	-	-	-	-	-	1,0	-	-	-	**1,0**
Other HFCs[1]	-	-	-	0,5	-	3,0	-	-	-	**3,5**
All HFCs	**-**	**-**	**-**	**18,8**	**11,1**	**216,8**	**7,0**	**58,6**	**52,7**	**365,1**

TABLE 20
CONSUMPTION OF HFC DISTRIBUTED ON APPLICATION AREAS IN 2012, TONS - RECALCULATED AS PURE SUBSTANCES [POULSEN & MUSEAEUS, 2013]]. *1

Substance /Use	Household fridges /freezers	Commercial refrigerators	Transport refrigeration	Mobile A/C	Stationary A/C	Other applications	Total
HFC-32	0.0	10.8	0.0	0.0	9.8	0.0	20.6
HFC-125	0.7	57.3	2.9	0.0	10.7	0.0	71.7
HFC-134a	9.5	92.2	0.6	58.6	32.2	5.3	198.4
HFC-143a	0.9	53.4	3.5	0.0	0.0	0.0	57.7
HFC-152a	0.0	0.0	0.0	0.0	0.0	13.0	13.0
Other HFCs	0.0	3.0	0.0	0.0	0.0	0.5	3.5

Sub-stance /Use	Household fridges /freezers	Commer-cial refri-gerators	Transport refrigera-tion	Mobile A/C	Stationary A/C	Other appli-cations	Total
All HFCs	11.1	216.7	7.0	58,6	52.7	18.8	364.9

*1 Figures are based on the consumption figures presented in Table 19 but recalculated to pure substances to the extent possible based on the composition of blends noted in Table 2.

As shown the consumption in the refrigeration industry is the far most important. The refrigeration industry counts for 346.3 tons (95%) of the total consumption. HFC-134a is the most used refrigerant followed by HFC-404A, HFC-407C, HFC-410A and HFC-507A.

The consumption for special technical sprays was 5.3 tons HFC-134a, while 13 tons of HFC-152a has been used for thermostats (thermostatic control valves). The consumption of HFCs for foam production has ceased.

From Table 19 and 20 it can be seen that the biggest consumption sector is commercial refrigeration with 216.8 tons (59%). This sector includes central supermarket refrigeration systems, condensing units for smaller retail stores, walk-in cold rooms, smaller cold stores and smaller industrial refrigeration systems (for cooling processes). A wide range of HFC-refrigerants is used for this purpose.

The second largest consumption sector is mobile air conditioning in cars, trucks, buses, trains and tractors. This counts for 58.6 tons HFC-134a (16%).

The third consumption sector is stationary air conditioning, and this includes small split-AC-systems for cooling or heating a room (small air-air heat pumps) and smaller chillers producing cold water to cool a building. This sector counts for 52.7 tons (14%). The refrigerant types are HFC-407C and HFC-134a. Some HFC-410A must also be used for small split air conditioners, but this is not reflected in Tabel 19 and 20 and is possible caunted for in the category "Commercial refrigerators" in that table.

Household refrigerators and freezers and professional refrigerators and freezers of plug-in-type (with integrated refrigeration system) counts for only 11.1 tons (3% of total HFC use). The refrigerants used are HFC-134a and HFC-404A. This relative small consumption shall be seen in the light of introduction of natural refrigerants in household appliances 20 years ago and in professional appliances 10 years ago.

7 tons of HFCs were used in refrigerated vans and trucks (2% of total HFC consumption). The refrigerants used are HFC-404A and HFC-134a.

SF_6

The consumption of SF_6 was 2.6 tons in 2012. From Table 21 can be seen that the biggest consumption is for refilling power switchgears in high voltage systems. 0.7 tons was used in optical fibres production and 0.03 tons was used in laboratories (probably as track gas).

TABLE 21
CONSUMPTION OF SF_6 BY APPLICATION AREA, TONS [POULSEN & MUSEAEUS, 2013]

Application area	DK consumption, tonnes
Power switches in high-voltage plants	1,86
Plasma erosion	0,70
Laboratories	0,03
Total	**2,59**

PFCs

The consumption of PFCs was 0.4 tons in 2012. 0.2 tons PFC-14 was in 2011 used in the optical fibres production, and 0.2 tons PFC-318 was used for (other) technical purposes in 2011 [Poulsen & Museaeus, 2013]. Previously some PFC has been used in special refrigerant blends, but for 2012 no consumption has been recorded.

3.4 Historical trends in use

In Table 11 and 12 the historical usage of F-gases for the last 20 years can be seen.

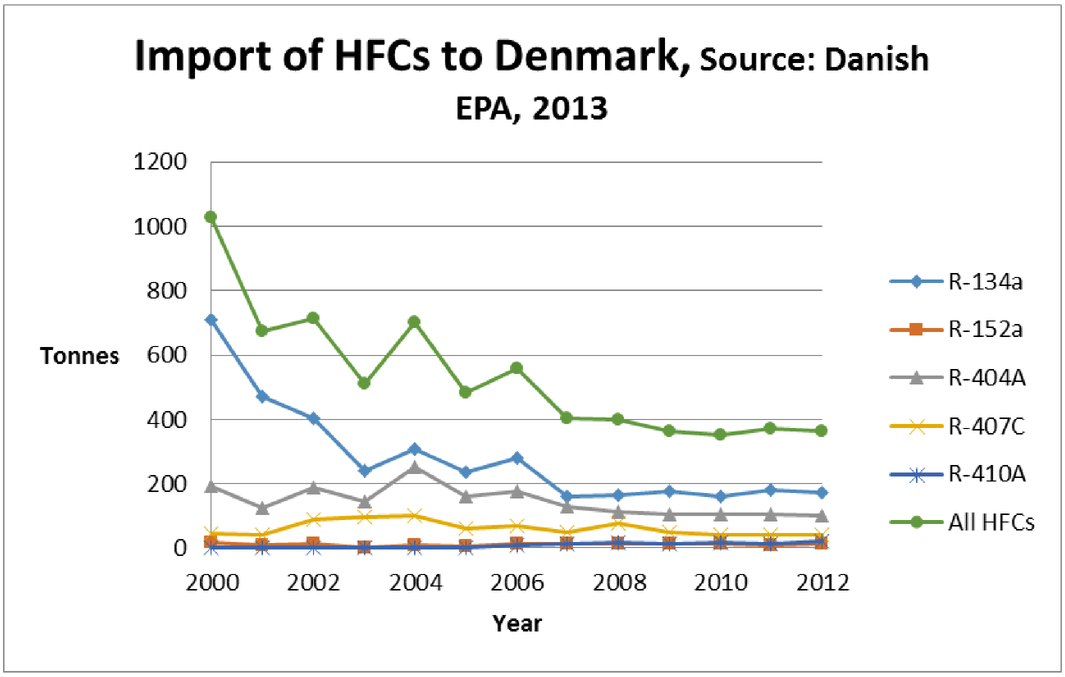
HFCs

The HFC refrigerants were introduced in the market about 1992 as substitutes for ozone depleting CFCs, which were controlled by the Montreal Protocol (from 1987). In Denmark the CFCs were phased out in the 1990'ties and a big part of the CFC usage was substituted by HFCs.

The use of HCFC in new refrigeration systems was banned from January 2000 and the use of new HCFC for service in refrigeration systems was banned from 2002. A big share of the traditionally HCFC consumption was substituted with HFCs, and this process was started in the late 1990s when the schedule of the bans on HCFC was known.

The consumption of HFCs had its maximum in the late 1990s with about 1000 tons per year and has decreased to about one third of this amount. In Figure 2 the historical trend of HFC consumption can be seen in the period 2000 – 2012, while Table 11/12 cover the whole period of 1992-2012.

FIGURE 2
IMPORT OF BULK HFCS INTO DENMARK IN THE YEARS 2000 – 2012. *1



From Figure 1 it can be seen that the import of HFC in total has decreased to about one third in the period from 2000 to 2012. This is a logical trend since the national regulation was introduced in the beginning of this period (the tax was implemented in 2001 and the bans of certain applications was introduced in 2002).

It can also be seen:

- That the consumption in the last part of the period has been stabilized with an amount of about 360 tons per year;
- The consumption of HFC-404A (with high GWP and hence a high tax) is decreasing from more than 200 tons in 2004 to a level of about 100 tons per year in 2012. This can be explained by many commercial refrigeration systems with HFC-404A are replaced with refrigeration systems with CO_2 (e.g. in supermarkets). In addition, the need for HFC-404A for refilling is decreasing because (old) systems with HFC-404A are slowly taken out of duty;
- The consumption of R410a is increasing a little to a level of 21.5 tons in 2012. This refrigerant was introduced as a substitute for HCFC-22 in stationary air conditioning (and air-to air heat pumps), and the amounts of systems is increasing. Hence, the need for refill in connection to service is increasing;
- The consumption of HFC-134a has been quite stable during the last 5 – 6 years; and
- The consumption of HFC-407a topped in 2004 and has been decreasing slowly since that.

HFC in polyurethane insulation foam:
HFC has been used for producing rigid polyurethane foam for insulation purposes. This insulation foam is with closed cells, and the HFC will stay inside the cells and contribute to the good insulation value of the foam. This type of insulation foam has been produced from 1993 to 2002 where the production stopped. Most of the usage was for domestic refrigerators and freezers and for commercial refrigerators and freezers substituting CFC-11.

It was also for a very short period used for pre-insulated district heating pipes, but this was rapidly substituted to cyclopentane around 1993 – 1994. A small usage was seen for insulation in industrial doors (ports) and water heaters. However, the major usage was for refrigerators and freezers.

From the annual reports from the Danish EPA it can be seen that the consumption for rigid insulation foam started with 164 tons HFC-134a in 1993 and had it maximum on 357 tons in 1999 and decreased to 72.3 tons in 2002. There was no consumption in 2003.

In [Poulsen & Museaeus, 2013] it is mentioned that the stock of HFC-134a in rigid polyurethane foam is estimated to be 514 tons in 2012 and this figure falls to 159 tons in 2015.

It is assumed that most of the stock is placed in refrigerators and freezers, and those products will be handled in a proper way by the existing systems to handle scrapped refrigerators and freezers and collect refrigerants and blowing agents (e.g. CFC-11) for destruction.

SF_6

The import and consumption of SF_6 was earlier much higher. The consumption was 21 tons in 1994 and decreased to 9 tons in 2000 and 2.6 tons in 2012.

SF_6 was earlier used in sound reducing thermal windows, but this application was banned in 2003. SF_6 has at an earlier stage also been used as a protecting gas in magnesium production. The main use today is in high voltage switch gears, and the power transmission utilities has done a significant effort to reduce the use and emission of SF_6.

PFCs

The consumption of PFCs has traditionally been quite small. There was an increase in the years 1997 – 2000 (about 8 tons per year), and this is likely because PFCs were used in special refrigerant-mixtures used to substitute CFCs in special low temperature refrigeration equipment. The consumption has been less than 1 tons in the last 4 years, and in 2012 there was no use for refrigeration purposes.

3.5 Summary and conclusions

F-gases are produced in several countries globally as well as in Europe. Precise knowledge on production of F-gases is not available, but existing knowledge and estimates indicates that the total global production will probably be above 300,000 tons/year. Production in EU may be estimated to 50,000 – 60,000 tons/year. The total consumption in EU is about 90,000 tons/year indicating that EU is a significant net-importer of F-gases. HFC-gases and in particular HFC-134a and HFC-125 are the main gases consumed while SF_6 counts for 2-3% of the total consumption and PFC-gases for less than 1%.

The dominant application in EU is refrigeration and air-conditioning which is responsible for more than 60% of the total consumption. Other important applications on EU-level include blowing agent for foams, propellant in aerosols, fire protection, and use as dielectric gas in electrical equipment.

No F-gases are produced in Denmark and the total consumption is based on import. The consumption has been decreasing from about 1000 tons in 2000 to about 360 tons in 2012.
Also in Denmark refrigeration and air-conditioning are by far the dominant application of F-gases and in particular HFCs. Smaller amounts are used for thermostats and aerosols (sprays) while the consumption as blowing agent for foams ceased in 2002.

PFCs were earlier used in special low temperature refrigeration equipment, but this use seems to have ceased in Denmark, as no consumption of PFCs were recorded in 2012.
SF_6 is today mainly used as dielectric gas SF_6 in high voltage installations, while uses as insulation gas in windows and blanket gas in magnesium production today has ceased.

The consumption of F-gases in Denmark has been stable during the last 5-6 years.

4. Waste management

4.1 Waste from manufacture and use of HFCs, PFCs and SF_6

As HFCs, PFCs and SF_6 are not produced in Denmark, no waste from production of these substances is generated in Denmark.

Collection and recovery of F-gases will take place by:

- Maintenance and repair of equipment and facilities (e.g. refrigerators, freezers, air condition systems, heat pumps) in which F-gases are used as refrigerant/heat transmission media;

- Conversion of equipment and facilities containing F-gases to new refrigerants/ heat transmission media; and
- Closing and dismantling of facilities and equipment containing F-gases.

Collection and recovery of refrigerants is in Denmark undertaken by companies authorised by KMO (KølebranchensMiljøOrdning - the Danish Refrigeration Trades Environmental Arrangement). Collected refrigerants will be used for refilling of existing or new systems if necessary after cleaning/regeneration. If cleaning/regeneration is not possible, they will be directed to destruction either in Denmark or abroad. [KMO 2014]

The total quantity of refrigerant reported collected and returned to suppliers in Denmark has for the period 2007-2011 been in the range of 3-8 tons yearly [Høft 2012]. The figure is expected to be about 10 tons for 2012. These figures cover F-gases as well as CFCs/HCFCs and other refrigerants and no data indicating the quantity of F-gases collected is available. F-gases used directly for refilling in Denmark by authorised companies are not included in these figures, but the figures are anticipated to include all refrigerants directed to cleaning/regeneration in Denmark and abroad. [KMO 2014]

It is unclear to what extent F-gases are delivered to destruction in Denmark directly by authorised companies without going through the KMO-system, but the figures on quantities of refrigerants received by NORD (see section 4.3) indicates that this is likely the dominant procedure.

Collection and recycling is also used for SF_6 employed in electric distribution and transmission systems. Recovered SF_6 will be cleaned and reused either in Denmark or abroad. If cleaning/recycling is not possible, they will be directed to destruction either in Denmark or abroad. To the best of knowledge the dominant part of the SF_6 collected will be reused. No figures are, however, available. [Jacobsen 2014]

4.2 Waste products from the use of HFCs, PFCs and SF_6 in mixtures and articles

As described in section 4.1, collection and recovery of F-gases will take place in Denmark by dismantling of old equipment and facilities containing such gases (e.g. refrigerators, freezers, air condition systems, heat pumps). This is also the case for SF_6 in electric distribution and transmission systems.

Household refrigerators, freezers and heating pumps and similar small units are primarily received and treated by one major metal scrap dealer in Denmark. This company assumes to receive approximately 90% of all units being scrapped in Denmark. The units are treated in a separate process flow [Wendel, 2014]:

- First step is to empty the units for refrigerant/heat transmission media. The gas collected is directed to destruction. The gas is a mixture of F-gases used in newer units and CFC-12 used in older units. The content of different substances is not determined.

- Second step is to treat the units in a special refrigerator shredder, thereby separating the isolation foam from other materials. The collected isolation foam is directed to incineration. The gas destroyed is a mixture of F-gases used in newer units and CFC-11 used in older units. The content of different substances is not determined.

Regarding the remaining units (approximately 10%), these units are exported for treatment in Germany and Sweden [Jensen 2014].

Refrigerants in mobile air conditions systems in cars and lorries being disposed of will be removed and collected as part of the environmental treatment process legally required for all vehicles being disposed of in Denmark [Danish Ministry of Environment, 2012].

Metal constructions containing polyurethane insulation foam such as aluminium gates, tubes for district heating etc. will be treated as metal waste and treated in shredders or by similar procedures [Wendel, 2014]. F-gases present in such foam will be released to the atmosphere.

Wood or plastic constructions containing polyurethane insulation foam as well as will be directed to incineration. Also other items based on combustible materials as shoe soles containing F-gases will be directed to incineration [Poulsen & Musaeus, 2013].

Windows containing SF_6 as insulation gas in double glazing will to the best of knowledge by disposal be crushed releasing the remainder of the gas to atmosphere. 66% of the original content of SF_6 is assumed still to be present in the windows at the typical time of disposal [Poulsen & Musaeus, 2013]. The stock of SF_6 in windows is expected to be 16.8 tons in 2015. The emission is estimated to 3.6 tons in 2012, 3.9 tons in 2015 and 1.2 in 2020 (Poulsen, 2013). A scheme for collecting the gas from scrapped windows has been discussed, but such a scheme would be difficult (and expensive) to establish [Pedersen 1998].

4.3 Release of HFCs, PFCs and SF_6 from waste disposal

F-gases collected and not recycled will in Denmark be directed to destruction at NORD (the former Kommunekemi – the Danish facility for treatment and destruction of chemical waste). In 2012 NORD received 132 tons refrigerants. They receive refrigerants (CFCs/HCFCs/HFCs) recovered from refrigerators etc. as well as mixtures of refrigerants with solvents as e.g. methanol and acetone). No figures on the quantity of F-gases received are available. The refrigerants are delivered in special pressure containers and are treated by incineration. NORD does not receive products as refrigerators or waste from shredder operations. [NORD 2014]

Polyurethane foam from refrigerators is directed to incineration at a power plant equipped with facilities for burning of coal, oil, biomass as well as methane gas from landfills [Wendel, 2014].

In both cases it can be assumed that the incineration/destruction process will result in virtually 100% destruction of the F-gases supplied.

4.4 Summary and conclusions

F-gases are not produced in Denmark and no waste from production of these substances is generated in Denmark. Collection and recovery of F-gases will take place by maintenance and repair of equipment and facilities in which F-gases are used (e.g. refrigerators, freezers, air condition systems, heat pumps, transformer stations) as well as by conversion of equipment and facilities containing F-gases to new refrigerants/ heat transmission media and by dismantling of old equipment and facilities. This is also the case for SF_6 used in electric distribution and transmission systems.

The recovered F-gases will be used directly for filling of existing or new equipment and facilities in Denmark or abroad if necessary after cleaning/regeneration, or be directed to destruction.

Scrapped household refrigerators, freezers and heating pumps and similar small units are generally emptied for refrigerant/heat transmission media and the gas collected is directed to destruction. The majority of units are furthermore treated in a special shredder allowing the insulation foam to be separated and collected and directed to destructing together with its content of blowing agent. A minor part of the units collected are exported for treatment in Sweden and Germany.

F-gases present in foam in other constructions will not be collected and destroyed and will therefore be released to the atmosphere. This is also the case for SF_6 used as insulation gas in double glazing windows.

Destruction of F-gases used as refrigerants is in Denmark carried out at NORD while destruction of F-gases contained in insulation foam is undertaken by a power plant. In both cases it can be assumed that the incineration/destruction process will result in virtually 100% destruction of the F-gases supplied.

5. Environmental hazards and exposure

5.1 Environmental Hazards

5.1.1 Classification

Of the substances discussed in this report, no gasses have been given a harmonized classification addressing environmental issues. However from Annex 3, it can be seen that most substances have been subject to industry self-classifications.

Among the substances self-classified by industry only HFC-43-10mee has a classification pertaining to environment, Aquatic Chronic category 3, H412: harmful to aquatic life with long-lasting effects. This classification has been proposed by almost all notifiers.

5.1.2 Global warming potentials

The main environmental concern with the rising emissions of fluorinated greenhouse gases is their contribution to global warming. Global-warming potential (GWP) is a relative measure of how much heat a greenhouse gas traps in the atmosphere. The GWP of a compound depends on its radiative properties, its molecular weight and its lifetime in the atmosphere. Fluorinated gases generally absorb infrared radiation in the 8 to 12 µm range, which is a region transparent in the atmosphere.

The GWP is defined as the warming influence over a set time period (usually 20 or 100 years) of a gas relative to that of carbon dioxide, which is set at 1. For example, the 20 year GWP of methane is 86, which means that if the same mass of methane and carbon dioxide were introduced into the atmosphere, methane will trap 86 times more heat than the carbon dioxide over the next 20 years. [IPCC, 2013]

5.1.2.1 HFCs

Hydrofluorocarbons are organic compounds that contain carbon, fluorine and hydrogen atoms. The carbon-hydrogen bonds in the molecules render them reactive towards atmospheric hydroxyl radicals. This makes the compounds degradable in the lower atmosphere in contrast to perhalogenated compounds which are resistant to atmospheric oxidation. As they contain no bromine or chlorine atoms and are destroyed in the lower atmosphere, they do not contribute to stratospheric ozone depletion.

Short-lived HFCs: HFC-32, HFC-43-10mee, HFC-134a, HFC-152a, HFC-245fa, HFC-365mfc

The short-lived HFCs HFC-32, HFC-43-10mee, HFC-134a, HFC-152a, HFC-245fa and HFC-365mfc are HFCs with atmospheric lifetimes less than 20 years. The major fraction of the removal of these compounds occurs in the troposphere. These compounds are volatile, odourless gases that will be partitioned almost exclusive to the gas phase upon emission.

The global warming potentials (GWP 100) of these compounds are high and range from 138 for HFC-152a, which has the shortest lifetime, to 1,650 for HFC-43-10mee, which has the longest lifetime and the highest number of C-F bonds (see Table 27). The most abundant of these gases is HFC-134a with a global concentration of 63 ppt. With rising concentrations the contribution of these compounds to global warming is a growing concern.

Longer-lived HFCs: HFC-23, HFC-125, HFC-143a, HFC-227a, HFC-236fa
The longer-lived HFCs HFC-23, HFC-125, HFC-143a, HFC-227a, HFC-236fa are HFCs with atmospheric lifetimes of more than 20 years. These compounds are volatile, odourless gases that will be partitioned almost exclusive to the gas phase upon emission. The removal of these compounds occurs by reaction with hydroxyl radicals in the troposphere and with hydroxyl radicals and to a lesser extent with oxygen atoms in the stratosphere.

The compounds are powerful greenhouse gases due to the infrared absorption of the C-F chemical bonds. The global warming potentials (GWP 100) of these compounds are high and range from 3,170 for HFC-125, which has the shortest lifetime, to 12,400 for HFC-23 (see Table 27).

The most abundant of the long-lived HFCs is HFC-143a with a concentration of 12 ppt (see Table 27). With rising concentrations the contribution of these compounds to global warming is a potentially serious concern.

5.1.2.2 PFCs

PFC-14, PFC-116, PFC-218, PFC-318, PFC-3-1-10, PFC-4-1-12, PFC-5-1-14
PFCs are gases or volatile liquids and partition into the gas phase upon release. The PFCs are resistant to reaction with atmospheric radicals in the troposphere and the lower stratosphere and the major loss processes for these compounds is photolysis in the upper stratosphere and mesosphere by high-energy ultraviolet radiation (121.6 nm) [Ravishankara et al. 1993].

The removal processes by chemical reaction and photolysis have, however, not been investigated for all the PCFs included in this survey. As the compounds are chemically analogous they can be expected to have similar removal characteristics [JPL 2011; Atkinson et al. 2008].

The global warming potentials (GWP 100) of these compounds are very high and range from 6630 (PFC-14) to 11100 (PFC-116) (see Table 27). The atmospheric abundance of these compounds is low, of the order of a few ppt, except for PFC-14 which has a concentration of 79 ppt. Rising concentrations of these gases are of serious concern with respect to global warming.

5.1.2.3 HFOs

HFO-1234yf and HFO-1234zeE
HFOs contain hydrogen, fluorine and carbon like the HFCs, but they are distinctly different. They are olefins, which mean that they contain a carbon-carbon double bond. The double bond makes HFOs react two orders of magnitude faster with atmospheric hydroxyl radicals than HFC-134a. This leads to very short atmospheric lifetimes of a few days, which means that these compounds have negligible global warming potentials. As they contain no bromine or chlorine atoms and are destroyed in the lower atmosphere, they do not contribute to stratospheric ozone depletion.

HFOs with their more favorable environmental characteristics are expected to be put to use in the automotive industry as replacements for compounds with high GWPs. A next-generation mobile automobile air-conditioning refrigerant, HFO-1234yf, does break down to trifluoroacetic acid (TFA) in the atmosphere (see section 5.2.2.1).

5.1.2.4 SF_6

Sulphur hexafluororide, SF_6, is an inorganic gas with an octahedral geometry, consisting of six fluorine atoms attached to a central sulphur atom. It is a hypervalent molecule. Typical for a nonpolar gas, it is poorly soluble in water but soluble in nonpolar organic solvents. It is generally transported as a liquefied compressed gas. It has a density of 6.12 g/L at sea level conditions, which is considerably higher than the density of air (1.225 g/L).

According to the Intergovernmental Panel on Climate Change, SF_6 is the most potent greenhouse gas that it has evaluated, with a global warming potential of 23,500 times that of CO_2 when compared over a 100-year period [IPCC 2013]. Measurements of SF_6 show that its global average mixing ratio has increased to over 7 ppt (see Table 27). Sulphur hexafluoride is also extremely long-lived, is inert in the troposphere and stratosphere and has an estimated atmospheric lifetime of 800–3200 years.

5.1.3 Other environmental hazards

The HFCs, PFCs, HFOs and SF_6 discussed in this survey are all gases or volatile liquids and they partition primarily into the gas phase upon release to the environment. The solubility of these compounds ranges from a few µg/L to a few g/L (see table 3) and these compounds do not contain functional groups that can undergo hydrolysis.

The compounds are generally stable in water and biodegradability is assessed as low for the HFCs [OECD, 2005; OECD, 2006b; OECD, 2010]. There is no data for the biodegradability of the PFCs and SF_6. These compounds are, however, less reactive than the HFCs and their level of aqueous phase degradation can be expected to be similar to and lower than the HFCs [OECD, 2006c].

5.2 Environmental Exposure

5.2.1 Sources of release

The F-gases are exclusively man-made and the sources of emissions are from industrial uses exclusively. Estimated emissions in Denmark in 2012are presented in Table 22-24.

The emissions are presented in Table 22 as the substances and blends actually emitted, and in Table 23 recalculated to pure substances to the extent possible based on the composition of blends noted in Table 2.

When the figures in the columns for "All HFCs" in table 22 and 23 do not match exactly it is because some blends besides HFCs substances also include HCFC-substances (e.g. HCFC-22) or other substances as propane and butane. The emission for the category "other HFCs" is assumed distributed equally on the substances HFC-32, HFC-125, HFC-134a and HFC-143a.

As stated in Table 22 and 23 refrigeration and air-conditioning is the dominant source of release of HFCs to the atmosphere in Denmark. Insulation foam is, however, still a significant source although the consumption of HFCs for this application stopped for more than a decade ago.

The dominant HFC-substances being emitted in Denmark is HFC-134a, while other HFCs in this context are of less importance.

TABLE 22
EMISSION OF HFCS DISTRIBUTED ON APPLICATION AREAS IN 2012, TONS [POULSEN & MUSEAEUS, 2013].

Sub-stance/Use	Household fridges/freezer	Commercial refrigerators + stationary AC	Transport refrigeration + mobile AC	Insulation foam	Aerosol sprays	Medical dose inhalers	Optical fibre prod.	Total
HFC-23							2	2
HFC-134a	7.3	67.6	59.3	50.4	5.5	6.8		196.9
HFC-401a		82.5						82.5
HFC-402a		0.6						0.6
HFC-404a	1.0	1.2	5.0					7.2
HFC-407c		42.9						42.9
HFC-507a		6.6						6.6
Other HFCs *1		12.6						12.6
All HFCs	8.3	214	64.3	50.4	5.5	6.8	2	351.3

*1 The category "Other HFCs" includes HFC-408a, -409a -410A, -413a, -417A.

TABLE 23
EMISSION OF HFCS DISTRIBUTED ON APPLICATION AREAS IN 2012, TONS – RECALCULATED AS PURE SUBSTANCES [POULSEN & MUSEAEUS, 2013]]. *1

Sub-stance/Use	Household fridges/freezers	Com. refrigerators + stationary AC	Transport refrigeration + mobile AC	Insulation foam	Aerosol sprays	Medical dose inhalers	Optical fibre prod.	Total
HFC-23							2	2
HFC-32		16.9						16.9
HFC-125	0.4	18.1	2.2					20.7
HFC-134a	7.3	96.4	59.5	50.4	5.5	6.8		226.0
HFC-143a	0.5	3.8	2.6					6.9
HFC-152a		10.7						10.7
All HFCs	8.2	145.9	64.3	50.4	5.5	6.8	2	283.2

*1 Figures are based on the emission figures presented in Table 22 but recalculated to pure substances to the extent possible based on the composition of blends noted in Table 2. The emission for the category "other HFCs" is assumed distributed equally on the substances HFC-32, HFC-125, HFC-134a and HFC-143a.

As stated in Table 24 emission from double glazed windows is the dominant source of SF_6 to the atmosphere in Denmark followed by contributions from power switches in high-voltage plants, refrigeration and laboratory purposes (manufacture of microchips).

Emission of PFCs in Denmark in 2012 was due to use of the blend HFC-413a in commercial refrigerators (the blend contains 9% PFC-218) and use of PFC-14 and PFC-318 in the production of optical fibers.

TABLE 24
EMISSION OF SF_6 AND PFCS IN DENMARK DISTRIBUTED ON APPLICATION AREAS IN 2012, TONS [POULSEN & MUSEAEUS, 2013].

Substance	Windows	Power switches	Lab. purpose	Com. refrigerators	Optical fibre prod.	Total
SF_6	3.6	0.6	0.6			4.8
PFC-14/ PFC-318 *1					0.38	0.38
PFC-218				0.8		0.8

*1 The emission includes PFC-14 as well as PFC-318. The total is known but cannot be divided on substances.

Danish yearly emissions of HFCs, PFCs and SF_6 expressed in CO_2-equivalents are shown in Table 25 below. The figures covers the period of 1990-2012. For comparison also the emissions from EU27 for the period 1990-2011 is shown in Table 26. The emissions are reported in billion metric tons of CO_2 -equivalent ($GtCO_2$-eq) which is the reporting standard of the IPCC. The CO_2-equivalency for a gas is obtained by multiplying the mass of gas released with the 100-year global warming potential of the gas (see table 22).

TABLE 25 F-GAS EMISSION INVENTORY CO_2-EQUIVALENTS DENMARK - 1000 TONS [EIONOT EMISSION INVENTORIES, 2011; POULSEN & MUSEAEUS, 2013].

Year	HFCs	PFCs	SF_6	Total
1990	-	-	44	44
1991	-	-	64	64
1992	-	-	89	89
1993	94	-	101	195
1994	135	0.1	122	257
1995	218	1	107	326
1996	329	2	61	392
1997	324	4	73	401
1998	411	9	59	480
1999	504	12	65	582
2000	607	18	59	684
2001	650	22	30	703
2002	676	22	25	723
2003	701	19	31	751
2004	755	16	33	804
2005	801	14	22	838
2006	823	16	36	875
2007	850	15	30	896
2008	853	13	32	897
2009	799	14	37	850
2010	804	13	38	856
2011	759	11	73	843
2012	656	14	114	784

TABLE 26 F-GAS EMISSION INVENTORY CO_2-EQUIVALENTS EU27 - 1000 TONS [UNFCCC, 2011].

Year	HFCs	PFCs	SF_6	Total
1990	27 882	20 368	10 947	59 197
1991	27 537	18 828	11 385	57 750
1992	29 447	15 763	12 206	57 416
1993	31 880	14 890	13 135	59 905
1994	36 039	14 303	14 220	64 562
1995	40 376	14 028	15 320	69 724
1996	45 693	13 496	15 123	74 312
1997	52 706	12 527	13 497	78 730
1998	54 096	11 871	12 609	78 576
1999	47 539	11 560	10 271	69 370
2000	46 971	9 876	10 270	67 117
2001	46 653	8 904	9 616	65 173
2002	49 349	10 389	8 540	68 278
2003	54 615	8 635	7 988	71 238
2004	56 811	7 327	8 261	72 399
2005	61 352	6 129	8 178	75 659
2006	64 172	5 497	7 561	77 230
2007	68 913	5 083	7 304	81 300
2008	72 321	4 376	6 855	83 552
2009	75 554	2 844	5 463	83 861
2010	79 709	3 329	6 549	89 587
2011	81 285	3 602	6 419	91 306

As shown in table 25, Danish emissions have increased significantly from 1990 to about 2007/08. Since then, emissions have been falling in Denmark. Emissions are on the rise in Europe and globally particularly due to increased emissions of HFC-134a. [Danish EPA, 2012]. Global emission inventories for most of these compounds are likely to be inconsistent and incomplete, particularly from East Asia, where industrial use is widely underreported [Mühle et al, 2010].

5.2.2 Monitoring data

Most of the F-gases being addressed in this report are monitored in the atmosphere. The concentrations of HFCs, PFCs and SF_6 in the atmosphere as registered by IPPC [IPPC, 2013] are stated in table 27 below. The dominant compounds are PFC-14, HFC-134a and HFC-34with concentrations of 79 ppt (part per trillion), 63 ppt and 24 ppt respectively.

5.3 Environmental impact

5.3.1 Global Warming

The main environmental impact of F-gases is their contribution to global warming. The most important greenhouse gas overall is water vapour followed by CO_2 and CH4. These gases have lower global warming potentials than the F-gases but are much more abundant.

F-gases constitute about 2% of total European greenhouse gas emissions in terms of CO_2 equivalents but F-gas emissions have risen by 60% since 1990 – in contrast to all other greenhouse gases, which have been reduced [EU, 2014].

HFCs have effectively replaced ozone depleting substances (ODS) as CFCs and HCFCs which have been phased out under the Montreal Protocol. As a result of this success HFCs are increasing in the atmosphere. For example, CO_2 equivalent emissions of HFCs (excluding HFC-23) increased by approximately 8% per year from 2004 to 2008. As a consequence, the abundances of HFCs in the atmosphere are also increasing. For example, HFC-134a, the most abundant HFC, has increased by about 10% per year from 2006 to 2010. [UNEP 2011]

In the future, HFC emissions have the potential to become very large. Without intervention, the increase in HFC emissions is projected to offset much of the climate benefit achieved by the earlier reduction in ODS emissions. Annual global emissions of HFCs are projected to increase to about 3.5 to 8.8 Gt CO_2-eq in 2050, which is comparable to the drop in ODS annual global emissions of 8.0 Gt CO_2-eq between 1988 and 2010. The projected HFC emissions would be equivalent to 7 to 19% of the CO_2 global emissions in 2050 based on the IPCC's Special Report on Emissions Scenarios (SRES). [UNEP 2011]

If HFC emissions continue to increase, they are likely to have a noticeable influence on the climate system. By 2050, the build-up of HFCs in the atmosphere is projected to increase radiative forcing by up to 0.4 W/m^2 relative to 2000 (the radiative forcing is the difference between the sunlight energy received by the Earth and energy radiated back to space). The increase of 0.4 W/m^2 may be as much as 20 – 25 % of the expected increase in radiative forcing due to the build-up of CO2 since 2000, according to the SRES emission scenarios. [UNEP 2011]

The future radiative forcing by HFCs in 2050 would, however, be relatively small and at the same level as it is today (<1% of CO2), if the current mix of HFCs were replaced with low or non-GWP substances with lifetimes of a few months or less [UNEP 2011].

5.3.2 Degradation Products

The oxidation of HFCs and HFOs by hydroxyl radicals in air lead to the formation of CO_2 and HF. Intermediate degradation products include formic acid, carbonyl fluoride and hydrofluoric acid. Because these compounds do not contain chlorine or bromine atoms they are considered harmless to stratospheric ozone. The potential for formation of photochemical ozone at ground level is low for these compounds since they have fewer or no carbon-hydrogen bonds than their alkyl equivalents and react slowly with atmospheric radicals. CO_2 is a persistent greenhouse gas, however the contribution from this source is insignificant compared with the total CO_2 burden. The amount of HF produced from current and expected future concentrations of hydrofluorocarbons is insignificant with respect to acidification [ECETOX 2008].

PFCs and SF_6 are resistant to atmospheric degradation. As the solubility and aquatic toxicity of these compounds is low, they are not considered to be of concern in aquatic environments [ECETOX 2008; ECETOX 2006; ECETOX 2004a;ECETOX 2004b].

HFC-43-10mee is self-classified by industry as harmful to aquatic life. There is, however, no published conclusive data to support this.

TABLE 27
POTENTIAL FOR TFA-FORMATION, LIFETIME, GLOBAL WARMING POTENTIALS AND GLOBAL ABUNDANCE FOR F.GASES [IPCC, 2013]

Acronym, Common name	TFA*1	Lifetime (years)	GWP 20	GWP 100	Global abundance 2011 (ppt)*2
HFC-23	No	222	10 800	12 400	24
HFC-32	No	5,2	2 430	677	4,9
HFC-125	Yes	28,2	6 090	3 170	9,6
HFC-134a	Yes	13,4	3 710	6 940	63
HFC 143a	Yes	47,1	6 940	4 800	12

HFC 152a	No	1,5	506	138	n.d.
HFC 227ea	Yes	38,9	5 360	3 350	0,65
HFC 236fa	Yes	242	6 940	8 060	n.d.
HFC-245fa	Yes	7,7	2 920	858	1,24
HFC-365mfc	Yes	8,7	2 660	804	n.d.
HFC-43-10mee	Yes	16,1	4 310	1 650	0
HFO-1234yf	Yes	0,03	1	<1	n.d.
HFO-1234zeE	Yes	0,04	4	<1	n.d.
PFC-14	No	50 000	4 880	6 630	79
PFC-116	n.d.	10 000	8 210	11 100	4,2
PFC-218	n.d.	2 600	6 640	8 900	n.d.
PFC-318	No	3 200	7 110	9 540	1,2
PFC-3-1-10	n.d.	2 600	6 870	9 200	n.d.
PFC-4-1-12	n.d.	4 100	6 350	8 550	n.d.
PFC-5-1-14	n.d.	3 100	5 890	7 910	0
SF_6	No	3 200	17 500	23 500	7,3

*1 If the compound contains a CF_3-CX_3 group it could potentially form TFA upon atmospheric breakdown. However, the presence of this structural group is not in itself evidence that the compound is a source of TFA.

*2 The concentrations in parts per trillion of these compounds in the atmosphere.

5.3.2.1 TFA

Atmospheric breakdown of some of the fluorocarbons already in wide use HCFC-123 (CF_3CHCl_2), HCFC-124 (CF_3CHFCl), HFC-134a (CF_3CH_2F) and HFC-227ea (CF_3CHFCF_3) - and some that may be used in the future - HFO-1234yf ($CF_3CF=CH_2$) - may produce traces of trifluoroacetyl halides (CF_3COCl or CF_3COF) in the atmosphere.

The trifluoroacetyl halides will hydrolyse in environmental water to produce trifluoroacetic acid (TFA). Gaseous TFA is washed out of the atmosphere and deposited on land and water as trifluoroacetate. Trifluoroacetate is environmentally stable and has the potential to accumulate in terminal water bodies and in plant material. Based on the relative insensitivity of aquatic organisms to TFA, predicted concentrations of TFA in terminal water bodies are not expected to impair aquatic systems significantly, even considering potential emissions over extended periods [Russell et al, 2012].

The cycle of TFA in the atmosphere and hydrosphere is currently not well understood and is the subject of ongoing research. TFA appears to be a naturally occurring chemical present in seawater and significant concentrations have been found in rain, river and lake water and both coastal and deep-ocean sea water. The measured concentrations in water bodies vary greatly (0 -> 40,000 ng / L), the highest concentrations have been measured in lakes with low drainage. The average concentration of TFA in the oceans has been estimated by certain studies to be about 200 ng/L. There is, however, considerable variation in the reported data. The oceans are thus a large reservoir for TFA and the observed concentrations are far in excess of those that could occur as a result of atmospheric oxidation of man-made fluorocarbons. TFA appears to have been accumulating in the environment prior to the introduction of anthropogenic sources and a suggested natural source is sub-oceanic volcanic activity. This is to some extent contradicted by studies of ice cores containing old sea water as TFA has not been measured in these. There are a few studies that have examined the worst-case scenarios for the current release and projections of future emissions of fluorinated gases that can be converted to TFA. This load will, according to these studies raise the concentration in the oceans by 3.7-7.4 ng /L. [Henne et al, 2012]

The accumulation of TFA in the environment must be regarded as a minor concern overall with the possible exception of closed water bodies where monitoring of concentrations is advisable. European emissions of fluorocarbons may, via the atmosphere, contribute to TFA accumulation in for example Lake Aral, Lake Chad and the Caspian Sea. However no conclusive evidence that this is occurring has been found.

In Table 27 is for all HFCs, PFCs addressed in this report as well as SF_6 stated, whether the compound potentially could form TFA upon atmospheric breakdown.

5.4 Summary and conclusions

HFCs, PFCs, HFOs and SF_6 are found in the atmosphere where concentrations are on the rise. Concentrations have steadily increased in the atmosphere since at least 1978, and are continuing to do so at a present rate of 5% per year.

Danish emissions have increased significantly from 1990 to about 2007/08. Emissions are now in the process of lowering. The emissions in 2012 counted for approx. 280 tons HFCs, 1 tons PFCs and 5 tons SF_6 corresponding to approx. 780,000 tons CO_2-eq.

There is growing concern over the emission and accumulation of very long-lived fluorinated trace gases in the atmosphere. They have a high persistency due to the stability of the C-F chemical bond. For the PFCs and SF_6 atmospheric degradation is extremely slow, and the compounds have atmospheric lifetimes of the order of millennia. They are greenhouse gases associated with a significant global warming potential as they are strong infrared radiation absorbers. These gases are non-reactive and thus pose no toxic threat to the biosphere.

HFCs have effectively replaced ozone depleting substances (ODS) as CFCs and HCFCs which have been phased out under the Montreal Protocol. As a result of this success HFCs are increasing in the atmosphere.

HFCs and HFOs are subject to degradation in the lower atmosphere due to the C-H bonds in the molecules that are reactive to hydroxyl radicals. The atmospheric lifetimes for these compounds differs between 1.5 and 242 years for the main HFCs while the lifetimes for the main HFOs are down to 0.03-0.04 years.

In the future, HFC emissions have the potential to become very large. Without intervention, the increase in HFC emissions is projected to offset much of the climate benefit achieved by the earlier reduction in ODS emissions. The projected HFC emissions would be equivalent to 7 to 19% of the CO_2 global emissions in 2050.

No toxic effects of degradation products have been identified, including trifluoroacetic acid (TFA) which is a degradation product of some HFOs and HFCs. TFA is a highly persistent pollutant, but there is no conclusive evidence of the environmental toxicity of this compound. TFA appears to be a naturally occurring chemical present in seawater and significant concentrations have been found in rain, river and lake water and both coastal and deep-ocean sea water. The oceans are thus a large reservoir for TFA and observed concentrations are far in excess of those that could occur as a result of atmospheric oxidation of man-made fluorocarbons. The cycle of TFA in the atmosphere and hydrosphere is, however, not well understood and is the subject of ongoing research.

6. Human health effects and exposure

Issues related to the addressed substances' ability to trigger photochemical ozone formation and to create trifluoroacetic acid (TFA) as degradation product are addressed in Chapter 5. As Chapter 5 shows that the ozone and TFA contributions from the addressed substances are low as compared to other sources, these reaction/degradation products will not be addressed further in this chapter.

6.1 Human health hazard

6.1.1 Classification

Flammability and explosively

From Section 2.2 it can be seen that among the substances addressed in this project, only HFC-365mfc is subject to a *harmonised classification*: Flammable Liquid category 2, H225: Highly flammable liquid and vapour.

However from Annex 3, it can be seen that among the substances addressed in the project, the other 15 (pre-)registered substances have been subject to industry self-classifications. Among the HFCs there seems to be consensus that the C1-C2 substances are *self-classified* with H280: Contains gas under pressure; may explode if heated. This also applies to one C3 substance (HFC 227ea). The other C3 (HFC245fa) and C4 and C5 substances are not classified with H280.

Among the less fluorinated substances C1 and C2 HFCs (HFC-32, HFC 143a and HFC 152a), there seems to be consensus among notifiers to self-classify with H220: Extremely flammable gas. For one C3 (HFC-245fa) there is general agreement to *self-classify* with H225: Highly flammable liquid and vapour. This classification also applies to HFC 365mfc, subject to harmonised classification as noted above.

The more fluorinated C1-C3 substances (HFC-23, HFC 125 and HFC 227ea) as well as the C5 substance (HFC-43mfc) are not *self-classified* for flammability.

For HFO-1234yf there seems to be consensus to self-classify with H220: Extremely flammable gas, and about half of the self-classifications in addition classify with H 280: Contains gas under pressure; may explode if heated.

Except for the C6 PFC (PFC-4-1-12), there is consensus that the pre-registered PFCs should be classified with H280: Contains gas under pressure; may explode if heated. The PFCs are not classified for flammability.

SF_6 is generally classified with H280: Contains gas under pressure; may explode if heated.

Toxicity

None of the addressed substances are subject to harmonised classification for toxicity.

HFO-1234yf has been self-classified, but not for toxicity.

2/2 notifiers have self-classified the C5 PFC-4-1-12 for skin and eye irritation (Category 2, H315 and H319). The same applies to 1 of 36 notifiers for PFC-3-1-10 (C4), 18/110 notifiers for HFC-43-10mee (C5), 1/122 notifiers for HFC-23 (C1) and 3/117 notifiers for SF_6. 23/87 notifiers have self-classified HFC-245fa (C3) for eye irritation category 2 (H319), but not for skin irritation.

Some notifiers for HFC-32 (37/192) and HFC-152a (35/381) have self-classified with Mutagenic Category 1B (H340) and Carcinogenic Category 1A (H350).

For several of the HFCs, PFCs and for SF_6 there are a few self-classifications for target organ toxicity following single exposure category 3 (STOT SE 3) with H335 (May cause respiratory irritation) and/or H336 (May cause drowsiness and dizziness). This self-classification is most prevalent for HFC-245fa (H336 for 34/87 notifiers) and HFC-43-10mme (H335 for 18/110 notifiers).

Finally, some self-classifications which might be considered as outliers should be mentioned:
- 1/152 (HFC-143a) and 1/122 (HFC-32) have self-classified for acute toxicity category 4, H312: Harmful in contact with skin.
- 5/269 (HFC-134a) and 1/381 (HFC-152a) have self-classified for target organ toxicity following single exposure category 1 (STOT SE1), H370: Causes damage to organs.
- 1/110 (HFC-125) and 1/269 (HFC-134a) have self-classified for target organ toxicity following single exposure category 2 (STOT SE2), H371: May cause damage to organs.
- 1/135 (PFC-218) have self-classified for specific target organ toxicity after repeated exposure category 3 (STOT RE 3), H373: May cause damage to organs.

6.1.2 Hazard assessment

6.1.2.1 HFCs
The hazards of HFCs will be described based on OECD Screening Information Data Sheets (SIDS) for HFC-32, HFC-125, HFC-143a, HFC-152a [OECD, 2006a, 2005, 2010, 2006b] and ECETOC Joint Assessment of Commodity Chemicals (JACC) programme for HFC-32, HFC-134a, HFC-152a and HFC-245fa [ECETOC 2008, 2006, 2004a, 2004b].

Toxicokinetics
Available data on toxicokinetics, mainly for the C2 HFCs indicate that HFCs are poorly absorbed and distributed in the body. The small quantities absorbed are readily excreted [OECD, 2005, 2006a, 2010; ECETOC, 2008].

Acute toxicity
Several HCSs have been tested for acute toxicity via inhalation. Even at very high concentrations – thousands of grams/m^3 (millions of mg/m^3) – no deaths occurred [OECD, 2005, 2006a, 2006b, 2010; ECETOC, 2008]. Thus LC50 is above millions mg/m^3.

At ranges from 183 g/m^3 to 3,927 g/m^3- (183,000 mg/m^3 - 3927,000 mg/m^3) reversible CNS effects such as reduced breathing rate, salivation, ataxic gate (problems with balance) occurs [OECD 2005, 2006a; ECETOC, 2008].

(Pre-)narcosis might occur at even higher concentrations [ECETOC 2006, 2008].

Regarding cardiac sensitisation (to adrenaline), the following is reported:
- HFC-32: No evidence up to 250,000 ppm (approx. 531,000 mg/m^3) [OECD 2006a; ECETOXC 2008];
- HFC-125: Evidence > 368,160 mg/m^3 [OECD 2005];

- HFC-134a: Evidence at 334,000 mg/m³ [ECETOC, 2006];
- HFC-143a: Evidence at 300,000 ppm (approx. 1,030,000 mg/m³) [OECD, 2010];
- HFC-152a: Evidence at 405,000 mg/m³ [ECETOC, 2004a; OECD, 2006b];
- HFC-245fa: Evidence > 241,000 mg/m³ [ECETOC, 2004b].

These references generally conclude that acute toxicity is very low.

Obviously, these acute toxicity effects described here (at very high dose levels) have lead some notifiers to self-classify HFC for acute toxicity or target organ toxicity following single exposure (STOT SE), see Section 6.1.1. It is outside the scope of this project to evaluate whether these self-classifications are reasonable, although it should be noted that effects are seen at very high dose levels only.

Irritation and sensitisation
In general, short term and repeated dose toxicity studies did not indicate potential for dermal or eye irritation. For HFC-152a, considerable effusion of fluid from the respiratory tract, indicative of acute irritation of the lungs, at concentrations ≥ 400,000 ppm (approx. 1,080,000 mg/m³) was seen. Also long-term inhalation studies indicate mild/low irritation of the lung and nose tissues [OECD, 2006b].

Generally, these substances do not seem to cause significant irritation. A more narrow review of the literature would be needed to evaluate whether the self-classifications for irritation reported in Section 6.1.1 are reasonable.

No positive sensitisation studies are reported.

Repeated/long-term toxicity
Repeated inhalation studies (generally 4 and 13 weeks) in rats and/or rabbits are available for all HFCs addressed by OECD SIDS and ECETOX JACCs [OECD, 2006a, 2005, 2010, 2006b; ECETOC 2008, 2006, 2004a, 2004b]. These references indicate that the highest dose tested – generally 40,000 or 50,000 ppm – can be considered as the NOAEC, as no (or very minimal) signs of toxicity attributable to the test substance were found.

HFC-152a showed anaesthetic properties in a 2 week repeated inhalation study in rats at 100,000 ppm.

Developmental toxicity/fertility
Developmental toxicity studies (generally rats with exposure from days 5/6/7 to 15/16/18) are reported for HFC-32 [OECD, 2006a, ECETOC, 2008], HFC-125 [OECD, 2005] and HFC-143a [OECD, 2010]. The NOAEC for maternal toxicity as well as embryofoetal development was in all studies concluded to be the highest dose tested (40,000 or 50,000 ppm) due to absence of significant effects, although ECETOC [2008] would not rule out completely that HFC-32 might cause foetotoxicity.

Fertility studies are generally not available. The available repeated inhalation toxicity studies indicate no adverse effects on reproductive organs attributable to the test substance.

Mutagenicity and carcinogenicity
HFC-32 [OECD, 2006a, ECETOC, 2008], HFC-125 [OECD, 2005], HFC-134a [ECETOC, 2006] and HFC-143a [OECD, 2010] have all been tested for *in vitro* as well as *in vivo* mutagenicity/genotoxicity. All results were negative.

HFC-152a showed negative results in Ames test, but showed weak clastogenicity in an *in vitro* human lymphocytes assay. A follow-up *in vivo* micronucleus test produced negative results [OECD, 2006; ECETOC, 2004a]. ECETOC [204a9 further notes that the *in vitro* clastonegenicity effect was only seen after 19 hours of continuous exposure and therefore considered the findings of marginal biological relevance.

A similar picture was seen for HFC-245fa which was not mutagenic *in vitro* (Ames test), but induced some chromosome aberrations in cultured human lymphocytes. An *in vivo* micronucleus test was negative. Overall a low order of genotoxic potential is assumed by ECETOC [2004fa].

HFC-134a, HFC-143s and HFC-152a have been tested in various carcinogenicity assays. None of the studies report signs of carcinogenicity attributable to the test substance [OECD, 2006b, 2010; ECETOC, 2004a, 2006].

These results might have triggered some notifiers to self-classify HFCs for mutagenicity and carcinogenicity, see Section 6.1.1. It is outside the scope of this study to assess whether the self-classifications are reasonable.

6.1.2.2 HFOs

None of the HFOs addressed by the project have been registered under REACH, although HFO-1234yf is pre-registered and self-classifications have been filled, see Section 6.1.1. The self-classifications do not point to hazardous effects, but to flammability, which will be further addressed in Section 6.4.1.1, including the possibility of creating Hydrogen Fluoride (HF) as thermal degradation product.

6.1.2.3 PFCs

Of the addressed PFCs in the project, PFC-116 and PFC-218 have been registered under REACH and description of their hazard profile will be based on hazard data obtainable from the ECHA dissemination site [ECHA, 2014].

In addition, PFC-14, PFC-3-1-10 and PFC-4-1-12 have been self-classified, see Section 6.1.1.

Toxicokinetics

Acute toxicity

For PFC-116, a LC50 above 500,000 ppm is reported and for PFC-218 it is concluded that the substance is practically non-toxic based on a 1 hour study in which rats were exposure to 80% PFC-218/20% oxygen. The following clinical signs were reported "Initial hyperactivity, later decreased activity, redness of skin, closed eyes".

In a study from 1972, PFC-116 did not show cardiac sensitisation in beagle dogs at exposure levels of 200,000 ppm.

Irritation and sensitisation

Irritation and sensitisation studies are waived in the REACH registrations with the justification that these are not technical feasible. However, note the clinical signs observed for PFC-218 in the acute toxicity study summarised above.

Repeated/long-term toxicity

For PFC-116, a recent OECD Guideline 412 (Repeated Dose Inhalation Toxicity: 28/14-Day) rat study including examination of FOB (Functional Observational Battery) and motor activity endpoints, identifies a NOAEL of 50,000 ppm established based on the absence of effects in all endpoints at the highest concentration tested. It is noted that a 90-days study (OECD 413) is in the pipeline.

For PFC-218, two studies indicated as "not reliable" report "mild adverse symptoms" in control as well as test groups. It is not clear what the tested concentrations/doses were. It is overall concluded that "We see no reason to suppose any chronic effects, but accept that the trial is not conclusive."

Developmental toxicity/fertility
PFC-116 was tested according to OECD Guideline 422 (Combined Repeated Dose Toxicity Study with the Reproduction / Developmental Toxicity Screening Test). A NOAEC for reproductive effects of 50,000 ppm was established based on the absence of effects on reproductive endpoints and offspring at the highest concentration tested. It is noted that a two-generation Reproduction Toxicity Study is in the pipeline (OECD Guideline 416).

For PFC-218 developmental toxicity studies are waived as these are assessed not to be scientifically justified.

Mutagenicity and carcinogenicity
PFC-116 and PFC-218 are negative in *in vitro* tests (Ames and chromosome aberration). PCF-116 was negative in an *in vivo* micronucleus assay.

6.1.2.4 SF_6

An initial Screening Information Data Sheet (SIDS) for SF_6 (OECD, 2006) concludes the following regarding human health:

"SF_6 accumulation, distribution and elimination were studied in rats exposed by inhalation. SF_6 was found to distribute widely in the body with a relatively higher affinity for blood and fatty tissues, and to be rapidly eliminated, likely via the exhaled air, suggesting a low accumulation potential.

No significant adverse effects were recorded in several studies in humans acutely exposed to an atmosphere containing up to 80% SF_6, although a slight anaesthetic effects and slight signs of discomfort, such as coolness in the upper respiratory tract and the occurrence of voice deepening, were observed.

Limited acute inhalation studies were conducted in rats exposed up to 80% SF_6. No deaths or adverse effects clearly attributable to SF_6 were recorded in these studies.

No cardiac sensitisation was observed in dogs previously injected with adrenaline and exposed up to 20% SF_6 in air. A slight anaesthetic potential has been identified for SF_6 in following acute exposure to high SF_6 concentration in rats, dogs and humans. Signs of CNS depression attributable to anaesthetic effects were also observed in rats and Guinea pigs exposed to 12,800 ppm and, with lower severity, 1,600 ppm for 4 consecutive months. No adequate studies are available for the assessment of repeated exposure to SF_6 and for the mutagenicity, carcinogenicity and reprotoxicity endpoints. However, its chemical inertness and its very low accumulation potential support the low concern for the toxicity of this substance.

The possible formation of highly toxic breakdown products may occur when SF_6 is subjected to high stress conditions; in particular electrical discharges occurring in the gas-insulated equipment may promote the formation of highly reactive species of toxicological concern."

6.2 Human exposure

6.2.1 Direct exposure

Generally very little information regarding consumer and occupational exposure has been identified. Focus does not seem to have been on exposure estimation for these substances, which are generally considered low toxic.

6.2.1.1 HFCs

OECD [2006a] notes the following regarding HFC-32: "Difluoromethane is manufactured in closed system. Therefore under normal manufacturing practices, emissions to the atmosphere during production are negligible … There is no direct consumer exposure to difluoromethane due to the fact that domestic air conditioning equipment (<5 kW) are hermetically sealed. Air conditioners of medium size are located in dedicated buildings and only maintained by professionals."

OECD [2005] notes the following for HFC-125: "Occupational exposure to HFC-125 may occur during production and mainly during repair/maintenance operation in refrigeration systems. Since refrigeration units and fire extinguishing systems are hermetically sealed, consumer exposure would occur most likely from slow leaks. However, when used to extinguish fires, there may be some short term exposure to HFC-125 as well as thermal degradation products such as hydrogen fluoride." OECD [2005] however concludes that the substance is of low priority due to low toxicity.

OECD [2010] notes the following for HFC-143a: "Since 1,1,1-trifluoroethane is a gas with a low boiling point (-47.4˚C), it is produced in sealed systems. There is no monitoring data for 1,1,1-trifluoroethane (from effluents, surface water in occupational settings) available from the production and processing sites in the US or France. … During the past 6 years a total of 19 samples were collected at Honeywell's production site. Most samples were below the limit of detection (approximately 0.1 ppm) and the highest level reported was 0.65 ppm. Occupational exposure through inhalation is possible. Consumer exposure is considered to be negligible…"

OECD [2006b] notes the following regarding HFC-152a: "Industrial hygiene monitoring data during manufacture and industrial use show exposure to be well under acceptable exposure limits. The current AIHA WEEL (Workplace Environmental Exposure Limit) and DuPont AEL (Acceptable Exposure Limit) are 1000 ppm, 8-hour TWA (time-weighted average). Though consumer exposure has not been measured directly, modelling based on measurement of similar uses shows consumer exposure to be minimal during intended uses."

6.2.1.2 HFOs

No data regarding occupational or consumer exposure to HFOs have been identified.

6.2.1.3 PFCs

No data regarding occupational or consumer exposure to PFCs have been identified.

6.2.1.4 SF_6

An initial screening SIDS for SF_6 [OECD, 2006c] notes that SF_6 is used in industrial applications and that "Due to the low toxicological concern, occupational exposure to SF_6 is not monitored".

6.2.2 Indirect exposure

No data on indirect exposure has been identified.

Outdoor air concentrations of the fluorinated gases must be assumed to be well below what could be reached in the working environment.

6.3 Bio-monitoring data

No biomonitoring data relevant for human exposure have been identified.

6.4 Human health impact

6.4.1.1 Flammability

Fluorinated carbons are generally supplied and used under pressure, causing in itself a risk for accidents. This is also evident from the self-classifications reported in Section 6.1.1, showing that several of the substances addressed in this study are self-classified with H280: Contains gas under pressure; may explode if heated.

Several HFCs (and HFO, see further down) are in addition highly/extremely flammable.

Whether flammable properties will lead to accidents and thereby effects/impacts is highly dependent on the amount, use situation, handling (instructions), surroundings etc. It is therefore difficult to generally assess risk/impacts caused by these substances.

We have not identified any information sources comprehensively addressing risks/impacts due to the flammable properties of some of fluorinated carbon. However, some identified references addressing the issue will be summarised in the following.

The European Fluorocarbons Technical Committee (EFCTC) has on their web-site recently published a factsheet regarding published refrigerant related accidents. Based on a 2006-2013 Google search 981 injuries and 95 fatalities related to refrigerant accidents could be identified. These statistics were dominated by ammonia. One fatality due to a fluorocarbon accident is reported. [EFCTC, 2013]

In 2009, BAM (Bundesanstalt für Materialforschung und – prüfung) was commissioned by the Federal Environment Agency in Germany (UBA) to examine the reaction behaviour of HFO-1234yf when exposed to ignition sources like sparks or hot surfaces [BAM, 2009]. It is noted that according to the CLP classification criteria, HFO-1234yf should be classified as extremely flammable. The report, among others, concludes that the Lower Explosion Limit (LEL) is higher than for propane or petrol vapours and thereby not as easy to ignite. It is noted that ignition behaviour is strongly dependent on the circumstances at which HFO-1234yf is possibly released. The minimum ignition temperature of HFO-1234yf is 405 °C. This is defined as the lowest temperature at which an ignition can occur when the most ignitable mixture is present. In release scenarios higher surface temperatures are needed for an ignition. BAM [2009] notes that regarding fire and explosion hazards of HFO-1234yf when used in air conditioning system in cars, many other substances like fuels and materials are used, which – depending upon the scenario – can also lead to hazards to humans and the environment, and that the additional hazard regarding fire and explosion caused by the HFO1234yf is comparable low compared to all other fuels and materials.

BAM (2009) concludes that the formation of Hydrogen Fluoride (HF) is critical when HFO1234yf is exposed to ignition sources like open flames and hot surfaces. During the ignition tests performed, critical levels of HF could be formed (levels above 95 ppm), which is the AEGL (Acute Exposure Guideline Level) established by NIOSH, which can lead to irreversible damages to human health. Finally, it was evaluated that HF formation is higher for HFO-1234yf as compared to HFC-134a which it is often substituting.

Building on these finding, in particular the fact that HF can be formed when HFO-1234yf is in contact with hot surfaces (at temperatures of 350ºC, which can occur the exhaust manifold and the catalytic converter during driving), the Federal Environment Agency in Germany (UBA) recommends using CO_2 as cooling agent rather than HFO-1234yf [UBA, 2010].

Lewandowski [2013] in a report prepared for SAE International concludes regarding the use of HFO-1234yf as refrigerant in the automotive industry: "...the estimated overall risk of vehicle fire exposure attributed to use of R-1234yf is conservatively estimated at 3×10^{-12} events per vehicle operating hour. This is nearly six orders of magnitude less than the current risk of vehicle fires due to all causes (approximately 1×10^{-6} per vehicle operating hour) and also well below other risks accepted by the general public."

6.4.1.2 Toxic risks - HFCs

For HFC-32, ECETOC [2008] concludes: "There are no reports of adverse health effects due to HFC-32" and OECD [2006a]: "The chemical is currently of low priority for further work".

For HFC-125, OECD [2005] concludes: "The chemical is currently of low priority for further work due to its low hazard profile for human health..."

For HFC-134a, ECETOC [2006] concludes: "No adverse health effects in humans from exposure to HFC-134a have been reported". This is backed up with results from a human/clinical study with large doses showing no human toxicity.

For HFC-143a, OECD [2010] concludes: "This chemical does not present hazard for human health based on its low hazard profile."

For HFC-152a, OECD [2006b] concludes: "The chemical is currently of low priority for further work, due to its low hazard profile" and ECETOC [2004a]: "There are no reports of adverse health effects associated with the occupational or consumer use of HFC-152a."

For HFC-245fa, ECETOC [2004b] concludes: "Commercial production of HFC-245fa has only recently been initiated, limiting the opportunity for health effects screening. To date no reported adverse health effects have been ascribed to HFC-245fa."

6.4.1.3 Toxic risks – HFOs

New information indicates that besides hydrogen fluoride also carbonyl fluoride (COF2) will be present as thermal degradation product from burning of HFC-1234yf [R744.com 2014]. According to R744.com [2014] carbonyl fluoride should be considered more dangerous than hydrogen fluoride and it is recommended that these effects are taken into consideration in future risk analyses of R1234yf.

6.4.1.4 Toxic risks - PFCs

No information has been identified.

6.4.1.5 Toxic risks - SF_6

For SF_6, OECD [2006c] concludes: "The chemical is currently of low priority for further work due to its low hazard profile for human health".

6.5 Summary and conclusions

Among the substances addressed in this study, only HFC-365mfe is subject to harmonised classification: Flammable Liquid category 2, H225: Highly flammable liquid and vapour.

15 of the other addressed substances are self-classified. There is general consensus among self-classifications for physicochemical properties. The self-classifications indicate that the shorter carbon-chains and the less fluorinated, the more flammable are the HFCs. This is inherently logic as these substances are structurally more prone to oxidation. This also corresponds with the fact that the more fluorinated HFCs (and the PFCs) are used for fire-fighting applications.

The self-classifications also show that the shorter chain HFCs, HFO-1234yf (C3), SF_6 and the PFCs are stored under high pressure and may explode if heated (H280).

Regarding toxicity, some HFCs and PFCs, as well as SF_6 have been self-classified, but there is much less consensus among the notifiers as compared to classifications for physiochemical properties. Most prevalent self-classifications (although still by a minority of the notifiers) for toxicity pertain to skin and eye irritation category 2 (various HFCs and PFCs, as well as SF_6), mutagenicity category 1B and carcinogenicity category 1A (for HFC-32 and HFC-152a) and classification for respiratory irritation and/or ability to cause drowsiness and dizziness (mainly indicated for HFC-245fa and HFC-43-10mme). Except for HFC-245fa self-classification for drowsiness and dizziness, all other self-classifications are suggested by a clear minority of the notifiers.

Based on i) OECD Screening Information Data Sheets (SIDS) and ECETOC Joint Assessment of Commodity Chemicals (JACC) programme dossiers for HFCs and SF_6 and ii) publicly available data from REACH registrations for the two PFCs registered under REACH, it can generally be concluded that HFCs, PFCs and SF_6 cause a low human hazard. Reviewed literature regarding HFO seems to focus on thermal degradation products rather than inherent toxicity of HFO itself.

At very high doses, reversible effects such as reduced breathing rate, salivation, ataxic gate (problems with balance), as well as cardiac sensitisation has been reported for some HFCs.

In addition, some HFCs and PFCs might have slight irritating properties.

Available mutagenicity/genotoxicity tests (in vitro and in vivo) and carcinogenicity studies do not suggest that the addressed substances possess a risk for cancer.

It has not been within the scope of this project to assess whether the suggested self-classifications for toxicity are supported by available hazard data, although it appears that toxic effects are only seen at very high doses.

The limited information regarding occupational and consumer exposure suggests that exposure to these substances is low during normal operating conditions. Several references deliberately do not address exposure at all given the very low human health hazards. Consequently, no actual toxicological risk assessments have been identified.

Overall, the main risks of the addressed substances seem to be directed to the flammable properties of HFCs and HFOs and to thermal degradation products.

A review of refrigerant-related accidents for the period 2006-2013 reports that 1 of 95 fatalities can be attributed to use of fluorocarbons. Most of the others are related to the use of ammonia. Two references find that the risk of using HFO in cooling system in cars is very low and not higher than risks caused by the use of fuels and other materials.

However, no comprehensive analysis of the risk/impacts of fire/explosion has been identified, probably due to the fact that such analyses cannot be generalised but is very site/situation specific.

The main toxic risk identified for the substances addressed in this study seems to stem from the fact that thermal degradation might lead to formation of highly toxic degradation products.

E.g. for SF_6 it is noted that when subjected to electrical discharges occurring in the gas-insulated equipment, highly reactive species of toxicological concern might be generated.

Specifically hydrogen fluoride (HF) might be generated. A study indicates that the risk of HF formation is higher for thermal degradation of HFOs than for HFCs. One of the main foreseen uses of HFO-1234yf is for air conditioning systems in cars. Based on the fact that thermal degradation of HFO-1234yf might occur when in contact with > 350°C hot surfaces (a temperature judged to be reached in relevant parts of a driving car), the Federal Environment Agency in Germany (UBA) recommends using CO_2 as cooling agent rather than HFO-1234yf. New information indicates that by burning of HFO-1234yf also carbonyl fluoride (COF2) will be generated which should be considered more dangerous than hydrogen fluoride.

Further work on thermal degradation products, including HF and COF_2 formation, might be warranted.

7. Information on alternatives

Several reports about alternatives have been prepared for the Danish Environmental Protection Agency and the Nordic Council of Ministers during the last 15 years.

In this period great technological developments with natural refrigerants and other substitutes to F-gases have taken place, often supported by Danish EPA; directly by supporting R&D-projects, or indirectly through the “Center for HFC-free technology”, which is founded in cooperation between the Danish EPA and the Danish Technological Institute.

The latest reports describing the state of developing and implementing alternatives is “Low GWP Alternatives to HFCs in Refrigeration” environmental Project no. 1425, Danish EPA [Pedersen 2012] and HCFC Phase out in the Nordic Countries”, Nordic Council of Ministers, [Pedersen 2014].

The information in the newest Danish and Nordic reports is the basis source for the content of this chapter on alternatives.

7.1 Identification of possible alternatives

In this chapter, all major sectors are treated and a special view is taken on alternative technology using natural refrigerants like hydrocarbons, ammonia and CO_2. The examples are primarily based on technology developed in Denmark and in the Nordic countries.

7.1.1 Domestic refrigerators and freezers

Ozone-depleting substances were once used when manufacturing refrigerators and freezers. CFC-11 was used for blowing polyurethane foam for insulating refrigerators and R12 (CFC-12) was used as the refrigerant in the refrigeration system. In a transitional period, different technologies were used instead of CFC, including HCFCs for blowing polyurethane foam. Companies have pursued different paths in their development work. All the manufacturers used R134a (HFC-134a) as a substitute for R12 in their refrigeration systems. R134a was also used by some manufacturers for blowing polyurethane foam.

In 1993, environmental organisations began questioning the environmental impact of HFCs because the substances (like CFCs and HCFCs) are potent greenhouse gases.

In Germany, a manufacturer together with environmental organisations introduced refrigerators with hydrocarbons. Other manufacturers soon followed suit. One compressor manufacturer was quick off the mark with a complete compressor programme for domestic appliances with isobutane (R600a) as refrigerant.

Within just a few months, the entire German market was forced to use hydrocarbons. This also applied to foreign manufacturers who wanted to sell on that market. Many people feared that explosions might occur in some of the refrigerators because there was a risk of an explosive mixture of hydrocarbons and air developing in the cabinet. The mixture could be ignited by a spark from the thermostat, door contact or other spark generator. The problem was solved by placing potential spark generators outside the cabinet and by preventing leakage of refrigerant inside the cabinet.

In the same period of time (first half of the 1990s) it was experienced that hydrocarbons (including cyclopentane) was useful and competitive for blowing polyurethane foam for insulation purposes including appliances.

At present, several hundred million of appliances have been built and the technology has proven to be safe.

Furthermore, refrigerators and freezers with hydrocarbons have proved to be more efficient than HFC models, and refrigerators with hydrocarbons are less noisy than corresponding HFC models because of lower pressure in the refrigeration system. The manufacturers in most of the world already have invested in production equipment for handling flammable refrigerants. Therefore there will be no (or almost no) additional costs.

The technology has proved to be reliable, energy efficient and safe. In the manufacturing process, safety is ensured when handling flammable refrigerants. The products have also proved to be safe during their lifetime in households.

Today, most of the European production is based on hydrocarbon technology and the development work for compressors and new energy efficient appliances is based on hydrocarbons.

Hydrocarbon technology is also gaining momentum in most countries in Asia, Africa and Latin America and it is expected to be introduced on the US market.

7.1.2 Commercial refrigerators and freezers (plug-in)

A significant number of commercial refrigerators and freezers is manufactured and installed in the Denmark. It is estimated that there are about 200,000 units installed, although the specific figure is unknown. The three largest groups of appliances within commercial refrigerators and freezers (plug-in) are bottle coolers, professional kitchen refrigerators & freezers and ice cream cabinets. Commercial refrigerators and freezers also include vending machines, water coolers, supermarket plug-in display cabinets, minibars, ice machines, wine coolers etc.

Bottle coolers

Glass door bottle coolers can be found in nearly every supermarket, gas station and kiosk. The most common type is the one door 400 litres type, but also bigger (2 or 3 glass doors) and smaller types are on the market. Glass door coolers are often installed by a soft drink company or a beer company and they are labelled with the logo of the company.

It is estimated that about 70,000 bottle coolers are installed in Denmark, where a significant production also takes place.

Previously, R-134a and R-404a were the standard refrigerants in bottle coolers and almost all bottle coolers sold until a few years ago use F-gases.

However, this has changed rapidly during the last years. Already in 2000, a Danish manufacturer marketed a hydrocarbon version using R600a and has delivered several thousand units to the European marked. Later on another Danish manufacturer also started a production with R600a.

In 2006 – 2007, the Danish Technological Institute conducted a field test in Copenhagen. Nine coolers were operated with CO_2, five with R134a and four with R600a. In 2006, they were placed in supermarkets for three months and during this time field tests were carried out.

The hydrocarbon coolers as well as the CO_2 coolers showed good performance; the hydrocarbon coolers showed 27.7% reduced energy consumption compared to the R134a coolers and the CO_2 coolers showed 11.7% reduced energy consumption compared to the R134a coolers. [Pedersen, 2008].

On the basis of these results and other investigations, a Danish based global brewery has decided to go for hydrocarbon coolers where possible and where educated technicians can service the appliances. Hydrocarbon coolers have proved reliable and the brewery is installing bottle coolers in the Nordic countries and has started installation in Germany and Switzerland. Soon, they will be installed in other countries as well [Andersen, 2011].

Status of HFC free technology
HFC free technology with hydrocarbon refrigerant is very rapidly being introduced to the EU market. The manufacturers in Europe already have invested in production equipment for handling flammable refrigerants. Therefore, there will be no (or almost no) additional costs.

The technology has proved to be reliable, energy efficient and safe. In the manufacturing process, safety is ensured when handling flammable refrigerants. The products have also proved to be safe during their lifetime.

CO_2 based coolers are also a possibility, but so far these have only been produced in limited numbers.

Ice cream cabinets
Ice cream cabinets with glass lids can be found in almost every supermarket and kiosk in the Denmark. Most of them have been installed by sizeable ice cream producers.

Many ice cream cabinets were earlier produced in Denmark. However, most of this production has been moved to low income countries. There is still a production at two Danish manufacturers.

HFC refrigerants were standard use (R404A and R134a). However, hydrocarbon cabinets have been available for many years and it seems as if hydrocarbon technology now is the standard within the EU. A global ice cream producer has chosen hydrocarbons for their ice cream cabinets and they are implementing hydrocarbon cabinets worldwide.

The company started the hydrocarbon cabinet rollout in Europe (in Denmark) in 2003 (with 800 cabinets). In 2004, the company introduced about 15,000 cabinets into 17 countries in the EU followed by an additional 40,000 cabinets in 2005. In 2010, the company installed approx. 100,000 cabinets with hydrocarbons and the company has now installed more than a million units worldwide. This figure is going to increase to 1.3 million in 2015 [Refrigerants naturally 2013].

Status of HFC free technology
HFC free technology is available and it is marketed and implemented. Moreover, it is a standard technology using hydrocarbon refrigerant. The manufacturers in most of Europe already have invested in production equipment for handling flammable refrigerants. Therefore there will be no (or almost no) additional costs.

The technology has proved to be reliable, energy efficient and safe. In the manufacturing process, safety is ensured when handling flammable refrigerants. The products have also proved to be safe during their lifetime.

Professional kitchen refrigerators & freezers
It is estimated that about 50,000 professional kitchen refrigerators and freezers are installed in Denmark. Most of them are of the stainless steel upright type, but also counter types are present. One important manufacturer is present in Denmark.

Since 2002 the Danish manufacturer has marketed appliances with R290, and this type is now standard for the company's products in Denmark and other European countries. The company has about 50% of the market in Denmark and 85% of the production is exported to mainly UK, Germany, Austria, Holland, Belgium, Sweden and Norway.

Wine coolers
To some degree wine coolers look like bottle coolers and they have become popular for professional as well as domestic use. There is a great variety of wine coolers and they use different cooling technologies, including thermoelectric cooling for the smallest units. Other units use compression refrigeration.

There is one manufacturer in Denmark, and this manufacturer produces energy efficient coolers and uses compressor cooling technology, which uses R600a as the standard refrigerant in their production.

Walk-in cold rooms
Small cold rooms (WICR, Walk-in cold rooms) less than 10 m^3 are now available with R290 (propane) refrigerant.

A Finnish company has developed and marketed these new products. The refrigerant charge is less than 150 grams and the price is 2 – 5 % higher compared to HFC-systems [Kahrola, 2013].
The new WICR are marketed in the Nordic countries and the EU.

Minibars
Three different refrigeration technologies are available for use in hotel minibars. Absorption minibars have so far been the most common type.

Absorption minibars do not have a compressor. They are quiet but have high energy consumption and a long pull down time. The refrigerant is ammonia and the refrigeration system consists of ammonia, water and hydrogen.

Thermoelectric minibars are also available in smaller numbers. They are quiet but have high energy consumption and a long pull down time. Thermoelectric cooling uses a “Peltiér element” which is a semi-conductor.

Compressor minibars are much more energy efficient but they have a slightly higher sound level, when the compressor is working. The use of compressor minibars is now expanding very quickly in Europe and they represent at least 50 % of the market. This figure is increasing. The driving force is energy efficiency. Compressors for R600a of relevant sizes are available and they are becoming the standard. [J. Christensen, 2013].

There is no production of minibars in Denmark. The energy efficiency, costs and safety issues is very similar to the production of household refrigerators.

Vending machines
R134a is the standard refrigerant in vending machines. Most soft drink vending machines are purchased by large suppliers of soft drinks. The refrigerant policy of a big global supplier of soft drinks focuses on CO_2 as refrigerant and the objective is to be HFC-free in the near future.

There is no production of cold vending machines in Denmark.

Water coolers

A great number of water coolers for both bottled water and tap water are installed in the Nordic countries. They are installed with a small compressor refrigeration system and HFC refrigerants were earlier the standard use. Coolers using hydrocarbon (R600a) are available on the market. The energy efficiency, costs and safety issues is very similar to the production of household refrigerators.

Ice machines

A great number of ice machines are installed in restaurants and bars. So far, HFC refrigerants have been the standard. A Japanese company with production in the UK has developed and marketed ice machines with hydrocarbon technology (R290) and the first units are available on the European market. Another supplier also provides units with R290 and other ice machines prepared for CO_2 refrigerants delivered from external (remote) refrigeration systems.

Supermarket display cabinets

The use of supermarket cabinets of the plug-in type is increasing in Northern Europe. Many small and medium sized supermarkets install such units instead of cabinets for remote cooling machinery.

The plug-in cabinets are cheaper and more flexible. Moreover, with glass lids they are also economic in use.

The condenser heat is submitted into the supermarket sales area where the cabinets are placed. This might cause high room temperatures during summertime.

A company in Austria is a major manufacturer of such cabinets. Since 2007, hydrocarbon cabinets using R290 have been standard. The energy efficiency, costs and safety issues is very similar to the production and use of bottle coolers and ice cream cabinets.

Vaccine coolers

WHO plays an important role in approving vaccine coolers for health stations. A large number of vaccine coolers (several hundred thousands) are installed in health stations around the world and many of them are placed in rural areas in developing countries.

A Danish company has a production of vaccine coolers (for the global market) in Denmark.

R134a has been the standard refrigerant, but WHO has drafted new standards, which also allow hydrocarbon as refrigerant. The Danish manufacturer now offers vaccine coolers (“ice liner”) with R600a.

DC coolers

There is some production of DC refrigerators (Direct Current, 12 V or 24 V) for trucks, small boats etc. and for vaccine chillers which are powered by solar cells (photovoltaic). R134a is the main refrigerant used. New DC compressors for isobutane and propane have, however, been developed and marketed. Up till now, DC compressors have been used in a limited number of solar powered vaccine coolers and solar powered ice cream cabinets.

SolarChill vaccine coolers

A Danish manufacturer was first on the global market with a SolarChill vaccine cooler, approved by WHO. This SolarChill vaccine cooler is powered directly by photovoltaic panels. It uses hydrocarbon refrigerant and has an ice storage which can keep the vaccine cool for up to 5 days without any power. At least 2,000 SolarChill vaccine coolers are now installed at health centres in areas without grid electricity. The SolarChill technology is developed in a partnership between the organizations: WHO, UNICEF, UNEP, PATH, GIZ, Greenpeace International and Danish Technological Institute.

7.1.3 Commercial Refrigeration

This section includes centralized systems in supermarkets and condensing units for special shops, restaurants, professional kitchens, bars, café's etc.

The area of commercial refrigeration covers a wide range of refrigeration applications. Commercial refrigeration is the part of the cold chain comprising equipment used mainly in retail outlets for preparing, storing and displaying of frozen and fresh food as well as beverages. However, equipment for commercial refrigeration can also be used by small producers of food products and smaller refrigerated warehouses for storage. In some cases, there might be some overlap with the industrial segment for these latter applications.

For commercial systems, two levels of temperatures are typically used (medium temperature for preservation of fresh food and low temperature for frozen products). Commercial refrigeration is the refrigeration subsector with the largest refrigerant emissions calculated as CO_2 equivalents. These represent about 40% of the total annual global refrigerant emissions [IPCC/TEAP, 2005]. This is due to high charges of refrigerant (distributed systems) and high leakage rates. For commercial systems, it is typically seen that the direct emissions of greenhouse gases amount to 40% of the total climate impact from the refrigeration system. In countries with a big share of hydropower and/or nuclear power, this figure is even bigger. Taking these considerations into account, it is very important to focus on this segment.

Furthermore, HCFC-22 was widely used before the ban of this substance in new refrigeration systems. HCFC-22 was widely used in both centralised systems in supermarkets and in condensing units in small shops, small walk-in cold rooms etc. HCFC-22 systems have been installed up to 2000, and it has been possible to service those systems since then. This is the reason why there still are some HCFC-22 systems.

After the ban of installation of HCFC systems came into force, R-404A has been the preferred refrigerant for commercial refrigeration. R-404A has a quite low normal boiling point so it can be used at both low and medium temperatures. R-134a has also been used, but mainly for medium temperatures.

Commercial refrigeration comprises of three main types of equipment:

1. Stand-alone equipment (plug-in);
2. Condensing units;
3. Centralised systems.

Stand-alone equipment (plug-in) is described in the previous section of this report.

Condensing units are used with small commercial equipment and they comprise of one or two compressors, a condenser and a receiver which are normally located in the ambient. The evaporator is placed in display cases in the sales area and/or a small cold room for food storage.

Centralised supermarket systems

Centralised systems consist of a compressor unit including valves and receivers placed in a machinery room. The unit is connected with distributed piping to evaporators placed in cabinets, cold stores etc. The condenser is typically placed in the ambient. The centralised systems tend to be more effective than the plug-in systems and condensing units. The centralised system can be subdivided into three groups:

Direct systems; where the primary refrigerant (R404A and now: CO_2) is circulated directly to the evaporators.

Indirect systems; where the primary refrigerant and a heat transfer medium (a secondary refrigerant) exchange heat in an extra heat exchanger and the heat transfer medium is pumped to the cabinets and storage rooms. The heat transfer medium can be single-phase brine, but also two-phase fluids such as volatile CO_2 or ice slurry can be used.

The last group is *hybrid systems;* where two or more different primary refrigerants are combined, e.g. in a cascade system, where the high temperature refrigerant is used in the medium temperature level (chilled food) as well as to cool the low temperature refrigerant in the cascade heat exchanger. The low temperature refrigerant is used at the low temperature level (frozen food). Some cascade systems (increasing in numbers) with CO_2 and a conventional refrigerant use CO_2 even for cooling demand at approx. 0 °C.

So far, a lot of work has been carried out regarding the development and implementation of refrigeration systems working on natural refrigerants.

Legislation
The introduction of HFC taxes in Denmark has indirectly established a situation, where direct cooling with HFC refrigerants is economically less favourable.

Since 1 of January 2007, a total ban on the use of HFC refrigerants in Denmark in new systems with charges exceeding 10 kg has been in force. This ban has had a huge impact on the systems implemented especially in supermarkets, as practically all new supermarkets are built with transcritical CO_2 systems.

Leakage rates
The leakage of HCFC and HFC refrigerant from commercial refrigeration systems is rather high due to distributed piping. The leakage rates have earlier been estimated to be about 15% and even more of the charge per year. However, a great deal has been done in the past to reduce the leakage. Today, all references indicate that the leakage rate is about 10% per year (including accidents, e.g. breaking pipes).

The leakage from more compact systems such as stand-alone and condensing units is smaller. It is estimated to be about 1 - 5% (stand-alone) and 5% (condensing units) per year.

Experience with alternative systems
During the past decade, many different concepts of supermarket refrigeration systems have been designed, built and tested.

These alternative systems can be divided into three main groups:

a) Indirect systems with brine. The refrigerant in the primary system can be R134a, R404A, propane or ammonia;
b) Cascade systems with propane, ammonia, R134a or R404A in the primary system and CO_2 as low temperature refrigerant. Different designs have been tested;
c) CO_2 used as transcritical fluid. Different designs have been developed and transcritical CO_2 systems are now the standard concept for supermarket refrigeration systems in Denmark and other countries.

Transcritical CO_2 systems
A ”transcritical refrigeration system” is using a thermodynamic process, where the refrigerant is passing the critical point of the refrigerant (which is CO_2). The critical point is the condition above which condensation of gas to a liquid is no more possible.

The idea of using CO_2 in a transcritical system is not new. For the past 20 years, research and development has been carried out on smaller systems especially for heat pumps and air-conditioning units. However, the know-how required to build an economic transcritical CO_2 system for the supermarket area was limited. A few test installations were made in Sweden, Denmark and Norway up to about 2005. Later on, an increasing amount of components became available and increasing experience was achieved. Moreover, large installers and supermarket chains chose this technology to be the standard.

The system operates under transcritical conditions during higher ambient temperatures (e.g. 25°C). A transcritical CO_2 system is an attractive option for supermarkets because they are much more simple than cascade systems. The system comprises of a high-pressure compressor that compresses the CO_2 to 120 bar. The compressed gas then enters a gas cooler where it is cooled to a temperature close to the ambient. Subsequently, the cooled, high-pressure gas passes through a high-pressure valve, which allows the gas to expand and reduces pressure to a level below the critical point where saturated liquid can exist (under the critical point). The liquid is circulated towards the low and high temperature refrigeration cabinets where after the liquid is allowed to expand to 25 bar in the high-temperature cabinets and to 15 bar in the low-temperature cabinets by the expansion valves. The liquid evaporates in the cabinets and the resulting gas from the low-temperature cabinets is removed by the low-pressure compressor and mixed with the gas from the high-temperature cabinets after compression. The mixture is then led to the high-pressure compressor and the closed cycle starts again.

Status of supermarket refrigeration systems, 2013
Transcritical CO_2 systems need high pressure components and the availability was very limited until about 2005, where the first mass-produced commercially available compressors and regulation valves were launched on the market.

When this happened, it became clear to a number of people and companies that this technology poses a great potential. The technology has become competitive and superior because of the following issues:

- Only one refrigerant is necessary in supermarkets (CO_2);
- No need for additional heat exchangers (and the related loss caused by temperature differences in the exchangers);
- Environmental properties are very fine;
- Properties for working environment are fine;
- Good thermo physical properties for the refrigerant;
- Good energy efficiency at normal ambient temperatures.

In Denmark (and Norway), the conditions for a quick implementation of this technology became relevant, because of the high taxes on HFC refrigerants and (in Denmark) the introduction of the ban on building new systems with more than 10 kg HFC.

In the years from 2005 to 2009, a total of about 150 systems were installed in Denmark and a similar number in the rest of Europe. In 2010, about 200 systems were installed in Denmark and the total figure for Europe was more than 400 units.

In 2013, more than 1000 systems were installed in Europe. In the first part of 2014, the total amount of transcritical CO_2 systems in supermarkets is going to pass 3000 systems in Europe, approx. 700 of these systems will be installed in Denmark [Christensen, 2013].

Supplier of transcritical CO_2 components and systems
The fast development of this technology has resulted in new business areas.

A Danish company which is supplier of components for the refrigeration industry on global scale has developed a full programme for valves and controls for transcritical (and subcritical) CO_2 systems. The company offers these components worldwide and the business is increasing.

There are a number of suppliers of compressors as well as several manufacturers of heat exchangers, covering evaporators and gas coolers as well as plate heat exchangers for heat recovery and special applications.

New qualities of pipes have been available and can manage the high pressure in the systems as well as the inline components from different manufacturers.

In Denmark, at least three companies are building transcritical CO_2 systems.

One of the companies was founded in 2006 and has achieved great success with developing a "remote refrigeration pack" for transcritical CO_2 refrigeration systems for supermarkets.
The packs are mass-produced at their factory in Aarhus, Denmark, and they are sold to large installers throughout Europe. The packs are sized in modules, and the company has a full programme for all supermarket sites. In 2011, about 300 supermarket refrigeration systems was built and about 80% were being exported [Christensen, 2013].

Now the company is expanding their activities in Europe as well as globally. In Europe, the company is going to establish new production facilities outside Denmark to ensure a larger volume at even more effective conditions. By the end of 2014, the company's production capacity is going to exceed 1000 systems per year.

This company is the world's biggest producer of transcritical CO_2 systems for supermarkets. Since the beginning in 2006, new generations of systems have been developed and produced. This work ensures continuously better energy efficiency as well as lower investment and running cost.

The transcritical CO_2 systems use approx. 10% less energy compared to similar HFC systems and the technology has proved to be reliable.

Economy and energy efficiency
The new generation systems use about 10% less energy in Northern Europe compared to direct DX HFC systems (R404A).

In Central Europe, the figure is around 5% less energy.

In Southern Europe, the systems have to be tailor-made due to higher ambient temperatures and in some cases, cascade systems with subcritical CO_2 systems have to be used. New developments for warmer climate are now available in the market. These systems use more advanced technologies, e.g. parallel compressors or subcooling features, and actually improve energy efficiency for warmer climates. These new developments are going to move CO_2 into southern Europe as well.

In 2011, the price was 4 to 5% higher (for the total refrigeration system) compared to similar HFC systems and the payback time was 1 to 2 years in Denmark (because of the HFC taxes) and 3 to 5 years in other countries [Christensen 2011]. In 2013 these numbers are even lower. In countries with taxes on HFC, the prices are more or less even, whereas prices in countries with no taxes are currently (2013) only 3-6% higher which reduces the payback time to 2-3 years at the most [K. G. Christensen, 2013].

Safety:
The technology is safe. It requires skilled refrigeration technicians to install commercial refrigeration systems, and the technicians must be educated to install CO_2 refrigeration systems.
There has been one accident in UK, when the CO_2 refrigeration system was not been assembled in a correct way. This accident resulted in minor damage. No accidents have (to the knowledge of the DTI) been reported in Denmark, which has the greatest numbers of installations in one country. Hundreds of refrigeration technicians have been educated in Denmark to handle CO_2 systems.

Condensing units
Condensing units with CO_2 are quite new products. There is one Danish producer. This product is quite new and supposed to replace the “old” condensing units with HCFC-22 and HFCs.

It is in fact not correct to name them “Condensing units”, because during transcritical duty there is no condensing taken place due to the special nature of CO_2. “Gas cooler units” might be a more correct term, but this would not be understood by most users. Thus, they are called “Condensing units” in this report.

The new condensing units are more expensive compared to HFC-units. According to the Danish producer, the new product is optimized according to energy efficiency and this might be the driving force for this new technology. So far (ultimo 2013), about 40 units have been installed [Christensen, 2013].

Safety issues are as for centralised CO2 refrigeration systems.

7.1.4 Chillers for Air Conditioning and industrial processes
In many office buildings and hospitals, chillers are installed for distribution of cold water in the buildings. The air in the individual rooms is cooled in heat exchangers by means of the cold water. Moreover, many industrial processes are cooled by cold water generated by chillers, e.g. cooling of plastic moulding machines and fermentation processes in the pharmaceutical industry. Various refrigeration systems are available for this purpose and CFCs and HCFCs were used previously. At present, HFC is the standard in Europe. In the past years, however, a large number of ammonia-based and hydrocarbon based refrigeration systems have been installed for this purpose.

Ammonia
In the first Nordic report [Pedersen, 2000], hundreds of ammonia-based chillers in the Nordic countries were listed. This list includes systems which were installed in the period from 1990 to 1998.

Because of data confidentiality, it has not been possible to update the reference lists in later reports, but according to the largest manufacturer and installer in the Nordic countries, many new ammonia chillers have been installed since then to cool large office buildings, hospitals, airports and other big buildings.

This manufacturer and installer offers a wide range of ammonia chillers, heat pumps and tailor made industrial refrigeration systems (cascade, air and liquid cooled plants) in the range from 300 to 6,500 kW cooling capacity [Pachai, 2013].

The price of ammonia chillers is higher than HFC chillers. The difference depends on the size of the chiller. Ammonia chillers are often competitive with other chillers because of the higher energy efficiency.

Ammonia is toxic and flammable and installation of ammonia chillers must only be made with refrigeration technicians educated and certified to handle ammonia. Chillers are very compact machines placed in rooms and other places (e.g. roofs) without admittance of non-professionals. Chillers are producing cold water (liquids) for cooling rooms and processes.

Hydrocarbon

Two Danish companies have started a production of hydrocarbon chillers in the medium to large range (50-400 kW). Annually, the two competing companies produce about 150 units and most of the produced units are installed in Denmark and some are exported to e.g. Norway, UK and Germany.

The energy efficiency is better than in HFC systems (about 10%), but the price is about 20% higher compared to HFC systems. The payback time for countries without taxes will typically be 1 to 2 years [Pachai, 2013].

Hydrocarbon chillers cool the new University Hospital in Aarhus (Skejby), Denmark. Hydrocarbons are flammable and installation of hydrocarbon chillers must only be made with refrigeration technicians educated and certified to handle hydrocarbon refrigerants. Chillers are very compact machines placed in rooms and other places (e.g. roofs) without admittance of non-professionals. Chillers are producing cold water (liquids) for cooling rooms and processes.

Absorption

There are systems that use absorption refrigeration (often lithium-bromide water absorption refrigeration systems). One example is the use of cooling water from an incineration plant in Trondheim, Norway. This “cooling water” is warm and runs a huge absorption refrigeration plant at the University Hospital in Trondheim.

Absorption chillers are only economically with the accessibility of sufficient cheap waste heat at certain high level temperature.

Water vapour compression

Chillers using water vapour compression is currently being developed and a pilot plant is being developed in Denmark. This work is economically supported by the Danish Energy Agency.

Energy efficiency

Energy efficiency is a very important issue for chillers. As the leakage rate is relatively small, the energy use is the most important factor for the environmental impact. Danish Technological Institute has carried out a small analysis in the Nordic report from 2007 [Pedersen, 2007]. The Analysis compared the energy efficiency of chillers with different refrigerants (HFCs, HCs and ammonia).

A calculation tool “CoolPack”, developed at the Technical University of Denmark, has been used to analyse the energy efficiency. CoolPack is used by thousands of refrigeration engineers around the world and contains thermodynamic properties for different refrigerants as well as algorithms for calculation of refrigeration systems. The calculations have been made for two different situations:

a) Evaporation temperature - 10°C and condensation temperature + 35°C; and
b) Evaporation temperature + 5°C and condensation temperature + 45°C.

The evaporation temperature refers to the temperature to which the liquid is cooled and the condensing temperature refers to the ambient temperature. A small temperature difference will always occur between the heat exchangers.

For the compression cycle, the isentropic efficiency is set to 0.60 and heat loss from the compressor is set to zero.

TABLE 28
COMPARISON OF COP (COEFFICIENT OF PERFORMANCE) FOR REFRIGERATION SYSTEMS WITH DIFFERENT REFRIGERANTS - COP EXPRESSES THE ENERGY EFFICIENCY OF REFRIGERATION SYSTEMS.
THE HIGHER THE VALUE, THE MORE ENERGY EFFICIENT COOLING SYSTEM *1

Refrigerant	COP, Situation a) T_o=-100C, T_C=+350C	COP, Situation b) T_o=+50C, T_C=+450C
R134a	2.78	3.30
R404A	2.53	2.94
R407C	2.71	3.15
R410A	2.65	3.05
R717 (ammonia)	2.82	3.41
R290 (propane)	2.74	3.25
R600a (isobutane)	2.80	3.36
R1270 (propylene)	2.73	3.21

*1 The refrigerants with mixtures (R404A, R407C and R410A) have temperature glides by evaporation. R407C has a significant glide, making an explicit comparison with refrigerants without glide difficult. No pressure drop in condenser and evaporator and no internal heat exchange.

Table 28 shows a variety in the energy efficiency of about 11% in situation a) and 15% in situation b). In both situations, ammonia (R717) shows the best efficiency with isobutane in the second place.

The comparison shows that R410A is inferior in terms of theoretical efficiency. Nevertheless, a great share of the marked has been turned towards R410A in smaller AC applications. The main advantage of R410A is the volumetric efficiency that results in smaller components and better price competitiveness.

Emissions to surrounding environment/accumulation in scrapped products
Chillers are compact, factory-made systems with a relatively small charge and limited emissions. The leakage rate is estimated to be 4 – 5% per annum.

With a lifetime of 15 to 20 years, there is some leakage of refrigerant. A large part of the refrigerant will remain in the system when it is scrapped. It is assumed that this refrigerant will be collected and reused in other systems. However, a small part of it will be emitted when the refrigeration system is opened during the scrapping process.

A few small, very inexpensive HFC chillers are expected to have a shorter lifetime.

Situation with respect to alternative technology
Alternative technology with natural refrigerants already exists. The price of ammonia chillers is higher than HFC chillers. The difference depends on the size of the chiller. Ammonia chillers are often competitive with other chillers because of the higher energy efficiency. This is especially the case for big chillers.

The energy efficiency for hydrocarbon chillers is better than in HFC systems (about 10%), but the price is about 20% higher compared to HFC systems. The payback time for countries without taxes will typically be 1 to 2 years.

Ammonia is toxic and flammable and installation of ammonia chillers must only be made with refrigeration technicians educated and certified to handle ammonia.

Hydrocarbons are flammable and installation of hydrocarbon chillers must only be made with refrigeration technicians educated and certified to handle hydrocarbon refrigerants
Chillers are very compact machines placed in rooms and other places (e.g. roofs) without admittance of non-professionals. Chillers are producing cold water (liquids) for cooling rooms and processes.

Small air-conditioning systems
No production of small air-conditioning systems takes place in the Nordic countries. Although the climate does not necessitate air-conditioning, there is a growing tendency to set up small split systems – in almost each case, the systems are made in Asia. The refrigerant is R410A.

The systems are often reversible systems, which means a combination of AC and heat pump systems (air to air), where it is possible to switch mode. Most of the small air to air heat pumps sold in the Nordic countries can also be switched to AC-mode.

Hydrocarbon-based systems are being developed in Asia with refrigerant charges of 250-300 g R290. A limited production is taken place in India. So far, there is no experience with these systems in Denmark, maybe because nobody has tried to install them.

Japanese based manufacturers have developed new products with HFC-32, and they will be marketed in 2014 on the Japanese market. The products will likely be introduced in the European market a little later. The efficiency is a little better compared to HFC-410A, and the GWP of HFC-32 is about one third compared to HFC-410A.

Moreover, an Italian company offers a small local air conditioner with propane. So far, Danish Technological Institute has not heard about the installation of such an air conditioner in Denmark.

7.1.5 Industrial refrigeration systems
Normally, industrial refrigeration systems are very large systems used for process refrigeration and cold storage within the food industry and the chemical/biochemical industry. Industrial refrigeration systems are built on site, using components suited for ammonia refrigeration systems.

Ammonia
In the Denmark, traditional ammonia refrigeration systems are used for these purposes. Probably all dairies, slaughterhouses, breweries and fishery companies have ammonia refrigeration systems. There is a more than a 100-year-old tradition for this.

There is a growing trend towards the use of indirect refrigeration in order to reduce the refrigerant charge and avoid ammonia in working areas etc.

CO_2
The installation of industrial refrigeration plants with CO_2 for low temperature purposes in cascade system is growing rapidly. Ammonia is used in the high temperature stage and CO_2 in the low temperature stage. A Danish based company has built many such systems including warm climates [Pachai, 2013].

Financial barriers
There are normally no financial barriers related to the use of ammonia as refrigerant in large industrial refrigeration systems. In the case of small systems, the situation corresponds to the situation for commercial refrigeration systems or air-conditioning systems.

There may, however, be financial barriers for very large ammonia refrigeration systems with charges above 5 tons, if the refrigeration system is placed within 200 meters from residential buildings, kindergartens or other buildings with public access. The Danish legislation implementing the EU Risk Directive (EU Directive 96/82/EC of 9 December 1996) requires risk considerations and planning which may significantly add to the costs of the ammonia system. It is for the time being somewhat uncertain, how this problem may be handled.

Situation with respect to alternative technology
Alternative technology using natural refrigerants is available; it has been widely implemented and today, it is the standard for industrial systems.

Ammonia is toxic and flammable and installation of ammonia refrigeration equipment must only be made with refrigeration technicians educated and certified to handle ammonia. Parts of industrial refrigeration systems with ammonia are often placed in working areas, and this can be a problem, especially if a pipe breaks, which is very seldom. There have been such accidents at slaughterhouses in Denmark, but this is for our knowledge without fatal consequences. For small leakages, the powerful odour of ammonia will warn personal before a real dangerous situation appears.

7.1.6 Mobile refrigeration systems
Mobile refrigeration systems are to be understood as the refrigeration systems installed in cars, trains, aircrafts, ships and containers.

Air-conditioning systems in cars
Since the mid-1990s, R134a has been used for mobile air conditioners (MAC).

Great efforts have been made by car manufacturers and sub-suppliers to develop MAC for CO_2. This technology is almost mature.

In the meantime, new low GWP HFCs have been introduced onto the market, and for a couple of years, car manufacturers have been working to implement the new low GWP substances which include HFC-1234yf. It would be easy to change to this substance as the existing refrigeration system can be used with no (or very simple) changes. However, the fluid is more expensive.

Some German manufacturers have declared that HFC-1234yf is dangerous to use and have stopped the development. They now declare that they will continue to develop CO_2-based air conditioning systems. Other manufacturers want to continue with HFC-1234yf, but the situation is unclear.

It should be mentioned that in some countries hydrocarbons are used (by do it yourself enthusiasts) in car air-conditioning systems. This is for instance the case in Australia and USA. The refrigerant is a mixture of propane and butane which can be used as drop-in substitute for CFC-12 in existing systems.

The risk of fire and/or explosion in connection with the use of hydrocarbons in car air-conditioning systems has been debated. Hydrocarbons could be a natural choice as several kilos of hydrocarbons in the form of petrol, diesel oil or gas are already present in the car. However, it is important that the system is designed correctly so an explosive mixture cannot occur inside the car.

The EU directive 2006/40/EF, adopted in May 2006, put a ban on the use of refrigerants in MACs with a GWP higher than 150. From 2011, there was a ban on refrigerants with a GWP higher than 150 in car air-conditioning systems in new types of cars. From 2017, the ban is effective in connection with all new cars.

The typical refrigerant charges in new vehicles are (Öko-Recherche, 2011):

- Cars and light trucks: 400 – 800 grams;
- Heavy trucks: 0.7 – 1.5 kg;
- Busses: 6 – 14 kg;
- Double decker and articulated busses: up to 18 kg and more.

Emission to the surroundings/accumulation in scrapped products
There is a relatively large leakage of refrigerant from mobile air-conditioning systems; in the order of 20-30% of the charge per year. The leakage used to be even bigger. The leakage is due to seals and leaky hoses, but it has been reduced in recent years by means of tighter hoses. The leakage rate for new systems is now 10 - 20% per year.

The relatively large leakage amount means that almost all the refrigerant used will be emitted to the atmosphere during the lifetime of the vehicle. The remainder should be collected when the vehicle is scrapped.

Situation with respect to alternative technology
Alternative technology is being developed by car manufacturers and suppliers.

Air conditioning in trains, trams and metro vehicles
The total number of trains, trams and metro vehicles in the EU is about 160,000 of which about 75.000 are equipped with air conditioning systems. 75% of these are charged with HFC-134a and 25 % with R-407C. HCFCs are no more in use [Öko-Recherche, 2011]. The leakage rate is lower compared to MACs; about 7 % p.a. for rail vehicles. The refrigerant charge is between 5 and 30 kg. For a double decker: up to 50 kg.

The European manufacturers have been working with two different alternatives: air cycle and CO_2.

About 500 individual cars of German ICE-3 high speed trains have been installed with air cycle systems (using the Joule process). They are light systems compared to normal HFC-systems, but they use about 20 to 30 % additional energy.

This technology might be interesting for Nordic countries (and Northern Europe) where air conditioning is needed only for a few days during the year. The additional energy consumption could be compensated by the light weight and the emissions savings of HFCs [Öko-Recherche, 2011].

Some manufacturers have developed prototypes with CO_2 refrigeration systems which have been presented at trade fairs. One leading German manufacturer has tested a prototype in a tram, and the energy efficiency has shown to be about 10 % higher (Öko-Recherche 2011).

Integral reefer containers
A Danish based company is the world's leading carrier of refrigerated goods and has a big fleet of reefer containers in traffic at global level.

Since 1993, all new refrigeration systems have been installed with R134a as refrigerant. The company had a considerable production of integral reefer containers in Denmark, but this production has been moved to low-income countries. CO_2 has been suggested as a refrigerant in reefer containers and Carrier offers refrigeration systems for containers with this refrigerant.

Emissions to the surroundings/accumulation in scrapped products
There is a relatively large leakage from integral reefer containers because of the violent actions they are subject to in ports and at sea. The leakage rate is of the same order of magnitude as for air-conditioning systems in cars - probably 20-30% of the charge per year.

Therefore, most of the refrigerant used for this purpose will be emitted to the atmosphere. When a container is scrapped, the remaining refrigerant will be collected, cleaned and reused in another container.

Ships
HFC refrigerant is the standard use on ships today. There is a large leakage of refrigerant from these ships because of rough physical actions at sea. Experts estimate a substantial annual leakage rate for reefer ships.

Large, new or retrofitted ships are also using ammonia as refrigerant, but ammonia cannot always be used in old ships.

Before 2000, HCFC-22 was the preferred refrigerant on board fishing vessels in the Nordic countries. Some of these ships are still in operation.

During the last 15-20 years, ammonia has become a common alternative to HFCs in new fishing vessels. In Norway, most of the new vessels over a certain size are equipped with ammonia systems.

Air-conditioning in aircrafts
For many years, cold-air refrigeration systems were used to cool passenger cabins in ordinary airplanes. A simple joule process is used, i.e. air is compressed and cooled through heat exchange with the surroundings. Subsequently, the air is expanded in a turbine, whereby it becomes cold. The process is not particularly energy efficient, but it is used in aircrafts because of the lightness of the components.

7.1.7 Heat pumps
The function of heat pumps is similar to that of refrigeration systems as heat is collected from a source (e.g. fresh air, soil, stable air, process water, etc.). At a higher temperature, the heat is rejected to a heat carrier - for example, a hydronic heating system.

The following main types of heat pumps are used: domestic heat pumps, commercial heat pumps, often combined with air conditioning, industrial heat pumps, medium sized heat pumps for heating groups of buildings and large heat pumps for district heating systems. Domestic heat pumps are used for space heating and for heating of water for domestic use in single family homes or in apartment buildings.

Domestic heat pumps
In the Nordic countries, about 1.5 to 2 million domestic heat pumps are installed, more than half of these in Sweden and most of them are air/air heat pumps. The sale in Denmark was about 30,000 in 2012.

The domestic heat pumps can be divided into 5 categories:
- Air to air (Heat source: Outside air / Heat sink: inside air);
- Air to water (Heat source: Outside air/ Heat sink: hydronic system with water);

- Liquid to water (Heat source: heat from ground/ Heat sink: hydronic system with water);
- Exhaust air heat pumps: (Heat source: exhaust air from the house/ Heat sink: hydronic system with water and/or inlet air to the house);
- Tap water heat pump: (Heat source: mostly exhaust air from house/ Heat sink: Tap water for local use in the building).

Liquid to water heat pumps and air to water heat pumps are mostly produced with R407C as refrigerant. A very small number of units are produced with propane (R290). A big production takes place in Sweden at a number of different producers.

Small exhaust air heat pumps and tap water heat pumps are often produced with R134a, even though at least one manufacturer has chosen propane (R290) as refrigerant.

Most (if not all) small heat pumps produced in Denmark do make use of HFC refrigerants.

Almost all air to air heat pumps are imported from Asia and they use R410A. This type of heat pump is normally reversible and can be switched to AC-mode. Japanese based companies plan to introduce products with HFC-32 in the near future.

It is possible to make domestic heat pumps for propane without major additional costs. However, precautions have to be taken to eliminate the risk of fire. When the necessary infrastructure and service is in place, the additional cost of propane heat pumps is expected to be modest.

CO_2 is very interesting in connection with heat pumps, and some manufacturers are committed to offering heat pumps with this refrigerant. The current price for CO_2 heat pumps in the small and medium sized range is significantly higher than for HFC systems. This is due to a lack of mass produced components (compressors) at the moment. In the long term, it should be possible to deliver CO_2 heat pumps with modest additional costs.

A typical liquid/water heat pump is charged with 2.5 kg HFC and a tap water heat pump with 0.8 – 1.0 kg HFC. A typical split type air to air heat pump is charged with about 1 kg R410A.

The leakage from heat pumps has become quite small, a few percentages annually, due to compact refrigeration systems and good quality. When a heat pump is scrapped, the remaining refrigerant should be collected and reused or incinerated.

Some cheap split type air to air heat pumps have been sold from supermarkets. Educated refrigeration technicians are required for the installation of such systems, but it is assumed that many systems have been installed by DIY people resulting in a considerable part of the refrigerant being emitted to the atmosphere. In such cases, the heat pump might not work or it will work with poor efficiency because of the lack of refrigerant. Finally, air might have entered the refrigeration cycle and this will also reduce the efficiency of the appliance.

Medium sized heat pumps
Heat pumps for heating single commercial buildings or groups of buildings, e.g. dwellings, cover a capacity range from approximately 50 kW to a couple of MW. Traditionally, HFCs have been used as refrigerants. In Norway, an increasing number is now using ammonia.

Large heat pumps
At least one Danish manufacturer offers heat pumps using ammonia or hydrocarbons as refrigerant. CO_2 is also interesting for large heat pumps and another Danish company is offering large CO_2 heat pumps. Large heat pumps using water vapour compression is also a possibility and some R&D work is on-going in Denmark.

7.1.8 Foam

The consumption of F-gases (HFCs) for foam production has ceased in Denmark. Insulation foam for appliances (refrigerators and freezers), for pre-insulated district heating pipes and for insulation panels are now produced with hydrocarbons (cyclopentane and other pentanes) as blowing agent.

Flexible polyurethane foam is produced with CO_2 as blowing agent.

7.1.9 SF_6

SF_6 is used as arc-breaker in high voltage power switches. SF_6 has a remarkable high dielectric value, which makes it suitable for this purpose.

There has been some attempt abroad to develop medium voltage switches without SF_6, but in the high voltage end, SF_6 is used as standard. A lot of attempt has been done to minimize emissions and reuse SF_6 when the hermetically sealed switches are dismantled for service.

SF_6 was used in special sound reducing windows, but this was banned in 2003, and the producers developed sound reducing windows by changing the construction of the windows.

7.1.10 PFCs

There is a very small consumption of PFCs (and SF_6) for producing components for the optical fibre industry. The authors of this report are not aware of any alternative technology for this purpose.

7.2 Historical and future trends – recognized gabs and challenges

As described earlier in the chapter a great effort has been done during the last 15 – 20 years to develop products and processes, which do not use F-gases. The consumption has decreased to about one third compared to the consumption in the late 1990s. This process will continue and some R&D work is ongoing to develop new products and processes without F-gases.

However, the consumption of HFC-refrigerants seems to have stabilized at an annual consumption of about 360 tons since 2009. There are two main reasons for this:

1) A great part is caused by the "10 kg window" in the Danish legislation, which means that still many new HFC refrigeration systems are installed with refrigerant charges less than 10 kg HFC refrigerant;

2) In addition to this big amounts of HFC refrigerants are used for service of HFC refrigeration systems installed before the ban of new HFC-systems (>10 kg) went into force in 2006. This amount will slowly decrease, and this tendency can be seen at the trend for consumption of HFC-404A, which was the main refrigerant in the bigger and medium sized commercial refrigeration systems.

7.2.1 The "10-kg window" gab

The "10-kg window" in the Danish legislation represents an important group of products still using HFCs due to lack of obvious alternatives and legislation requiring the use of these alternatives. The products in question include:

Condensing units

Almost 100 % of all condensing units small shops (bakeries, cafés, walk-in cold rooms etc.) use HFC. One Danish company has recently marketed a condensing unit with CO2 refrigerant, and a number of products have been installed in Denmark. The product is very new and expensive due to expensive components, and due to optimizing energy efficiency of the product. The strategy is to market the product for its energy efficiency. Further development to develop condensing units with natural refrigerants could be needed, especially for units that is affordable and in the long turn can compete with the HFC-based units.

Heat Pumps
Almost all small heat pumps for households are using HFCs. The technology for using propane is present, but the manufacturers are reluctant to use this for heat pumps installed inside a house probably because they are afraid of the risk for fire or explosions. It is possible (and legal) to install propane based heat pumps, but this require certain precautions (gas detector, automatic closing the heat pump, ventilation to outside etc.) and this will add to the installation costs. Units installed outside producing warm water for the central heating system in the house could use propane without severe problems.

Small chillers
Most (or all) small chillers for air conditioning of (smaller) buildings and cooling of processes are using HFCs (less than 10 kg). The cooling capacity is up to 50KW. It should be possible to produce such units with propane in the future. Many chillers are placed outside and produce cold water (or brine), which is pumped inside for comfort cooling or for cooling an industrial process. R&D efforts should be focused on these products, which in the end should result in affordable and compatible products.

7.2.2 Replacement of HCFC-22 systems – an important challenge
An actual challenge requiring attention is the fact that from 1. January 2015 it will be banned to fill HCFC-22 on existing refrigeration systems due to EU legislation. This might cause special problems for Danish owners of HCFC-22 refrigeration systems, since it will not be allowed to change to HFC-substitutes if the charge exceeds 10 kg due to the national legislation. It was banned to build new HCFC-22 refrigeration systems in Denmark 1. January 2000, hence the existing systems will be at least 15 years old when the ban goes into force.

It is estimated that more than 5,000 existing systems are still in use, and some hundreds are essential systems with more than 10 kg of HCFC-22. It is envisaged that many of the existing systems may not be able to carry out the phase-out of HCFC-22 in time, despite the fact that the Danish refrigeration trade has done a significant effort to inform owners and users of the systems that they will have a problem, if the systems are not changed or rebuild.

7.3 Summary and conclusions
Alternatives have been developed and implemented for most sectors where F-gases are used or have been used. This has been successful, and the consumption of F-gases has decreased to one third from 2000 to 2012.

This development was caused by the Danish regulation on F-gases, including taxes and bans for certain purposes combined with the support to R&D projects to ensure rapid development of alternative technology.

The Danish Environmental Protection Agency (EPA) conducted the scheme and a number of projects in the refrigeration area were supported financially with app. DKK 20 million. In addition, the “HFC free Centre” was established by the Danish EPA. The Centre offers consultancy services that are free of charge (up to 5 hours of engineering consultancy) for the refrigeration industry and installers to help them implement alternative technologies.

Simultaneously, the capacity for educating installers was increased, and hundreds of refrigeration technicians have now been educated to handle refrigeration systems with CO_2, hydrocarbons and ammonia.

However, the consumption of HFC-refrigerants seems to have stabilized at an annual consumption of about 360 tons since 2009. This development is mainly caused by the so-called "10-kg window" in Danish legislation allowing HFCs still to be used in equipment requiring a charge of refrigerant below 10 kg.

The "10-kg window" thus represents an important group of products still using HFCs due to lack of obvious alternatives and legislation requiring the use of these alternatives. The products in question include condensing units, heat pumps and small chillers.

Other important challenges identified include:

- The financial barriers for very large ammonia refrigeration systems with charges above 5 tons, as special and costly planning and precautions are necessary according to the Danish legislation implementing the EU Risk Directive (EU Directive 96/82/EC of 9. December 1996).
- From 1. January 2015 it will be banned to fill HCFC-22 on existing refrigeration systems. It is estimated that more than 5,000 existing systems are still in use, and some hundreds are essential systems with more than 10 kg of HCFC-22. It is envisaged that many of the existing systems may not be able to carry out the phase-out of HCFC-22 in time.

Abbreviations and acronyms

AC	Air Conditioning
AEL	Acceptable Exposure Limit
AEGL	Acute Exposure Guideline Level
As	Arsene
AsH_3	Arsine (a gas)
ASHRAE	the American Society of Heating, Refrigerating and Air-Conditioning Engineers
AUD	Australian dollars (the currency of Australia)
BAM	Bundesanstalt für Materialforschung und – prüfung
BEK	Bekendtgørelse (Statutory Order)
C	Carbon
CAS	Chemical Abstracts Service
CEFIC	European Chemical Industry Council
CFC	ChloroFluoroCarbon
CLP	Classification, Labelling and Packaging Regulation
CN	Combined Nomenclature
CNS	Central Nervous System
CO_2	Carbon dioxide
CO_2-eq	CO_2-equivalents COP Coefficient of Performance
COP7	7th Conference of the Parties (COP7) to the United Nations Framework Convention on Climate Change Control
CVD	Chemical Vapour Deposition
DKK	Danish kroner (the currency of Denmark)
EC	European Community
ECHA	European Chemicals Agency
EFCTC	European Fluorocarbon Technical Committee
EPA	Environmental Protection Agency
EU	European Union
F	Fluor
F-gas	Fluorinated greenhouse gases (includes HFCs, PFCs and SF_6)
GHz	GigaHertz
GIS	Gas insulated switchgears
GIZ	Die Deutsche Gesellschaft für Internationale Zusammenarbeit
GWP	Global Warming Potential
GWP20	Global Warming Potential over 20 years
GWP100	Global Warming Potential over 100 years
H	Hydrogen
HCFC	HydroChloroFluoroCarbon
HF	Hydrogen Fluoride
HFC	HydroFluoroCarbon
HFO	HydroFluoroOlefin
HVAC	Heating, Ventilation, Air Conditioning
Hz	Hertz (the unit of frequency)
IPCC	Intergovernmental Panel on Climate Change

kPa	kilopascal (measure for pressure)
kV	kilovolt
kW	kilowatt
LOUS	List of Undesirable Substances (of the Danish EPA)
MAC	Mobile Air Conditioning
mN	milli Newton (measure for force)
MW	Megawatt
NF_3	Nitrogen trifluoride
NIOSH	National Institute for Occupational Safety and Health
OECD	Organisation for Economic Co-operation and Development
P	Phosphor
PATH	An international health organization driving transformative innovation to save lives
PH_3	Phosphine (a gas)
PECVD	Plasma-enhanced chemical vapour deposition
PFOA	Perfluorooctanoic acid
PFC	PerFluorinated Carbon
PFOS	Perfluorooctane sulfonic acid
ppm	parts per million
ppt	parts per trillion
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
S	Sulphur
SF_6	Sulphur hexafluoride
Si	Silicium
SiH_4	Silane (a gas)
SIDS	Screening Information Data Sets
SLCPs	Short-lived climate pollutants
SVHC	Substance of Very High Concern
TFA	Trifluoroacetic acid
TWA	Time-weighted average
UBA	Umwelt Bundes Amt (the Federal Environment Agency in Germany)
UNEP	United Nations Environmental Programme
UNICEF	United Nations Children's Fund
WEEL	Workplace Environmental Exposure Limit
WHO	World Health Organisation
WICR	Walk-in cold rooms
XPS	Extruded Polystyrene

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Annex 1: Background information to chapter 3 on legal framework

The following annex provides some background information on subjects addressed in Chapter 3. The intention is that the reader less familiar with the legal context may read this concurrently with chapter 3.

EU and Danish legislation

Chemicals are regulated via EU and national legislations, the latter often being a national transposition of EU directives.

There are four main EU legal instruments:

- Regulations (DK: Forordninger) are binding in their entirety and directly applicable in all EU Member States.
- Directives (DK: Direktiver) are binding for the EU Member States as to the results to be achieved. Directives have to be transposed (DK: gennemført) into the national legal framework within a given timeframe. Directives leave margin for manoeuvering as to the form and means of implementation. However, there are great differences in the space for manoeuvering between directives. For example, several directives regulating chemicals previously were rather specific and often transposed more or less word-by-word into national legislation. Consequently and to further strengthen a level playing field within the internal market, the new chemicals policy (REACH) and the new legislation for classification and labelling (CLP) were implemented as Regulations. In Denmark, Directives are most frequently transposed as laws (DK: love) and statutory orders (DK: bekendtgørelser).
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The European Commission has the right and the duty to suggest new legislation in the form of regulations and directives. New or recast directives and regulations often have transitional periods for the various provisions set-out in the legal text. In the following, we will generally list the latest piece of EU legal text, even if the provisions identified are not yet fully implemented. On the other hand, we will include currently valid Danish legislation, e.g. the implementation of the cosmetics directive) even if this will be replaced with the new Cosmetic Regulation.

- Decisions are fully binding on those to whom they are addressed. Decisions are EU laws relating to specific cases. They can come from the EU Council (sometimes jointly with the European Parliament) or the European Commission. In relation to EU chemicals policy, decisions are e.g. used in relation to inclusion of substances in REACH Annex XVII (restrictions). This takes place via a so-called comitology procedure involving Member State representatives. Decisions are also used under the EU ecolabelling Regulation in relation to establishing ecolabel criteria for specific product groups.
- Recommendations and opinions are non-binding, declaratory instruments.

In conformity with the transposed EU directives, Danish legislation regulate to some extent chemicals via various general or sector specific legislation, most frequently via statutory orders (DK: bekendtgørelser).

Chemicals legislation

REACH and CLP

The REACH Regulation[1] and the CLP Regulation[2] are the overarching pieces of EU chemicals legislation regulating industrial chemicals. The below will briefly summarise the REACH and CLP provisions and give an overview of 'pipeline' procedures, i.e. procedures which may (or may not) result in an eventual inclusion under one of the REACH procedures.

(Pre-)Registration

All manufacturers and importers of chemical substance > 1 ton/year have to register their chemicals with the European Chemicals Agency (ECHA). Pre-registered chemicals benefit from tonnage and property dependent staggered dead-lines:

- 30 November 2010: Registration of substances manufactured or imported at 1000 tons or more per year, carcinogenic, mutagenic or toxic to reproduction substances above 1 ton per year, and substances dangerous to aquatic organisms or the environment above 100 tons per year.
- 31 May 2013: Registration of substances manufactured or imported at 100-1000 tons per year.
- 31 May 2018: Registration of substances manufactured or imported at 1-100 tons per year.

Evaluation

A selected number of registrations will be evaluated by ECHA and the EU Member States. Evaluation covers assessment of the compliance of individual dossiers (dossier evaluation) and substance evaluations involving information from all registrations of a given substance to see if further EU action is needed on that substance, for example as a restriction (substance evaluation).

Authorisation

Authorisation aims at substituting or limiting the manufacturing, import and use of substances of very high concern (SVHC). For substances included in REACH annex XIV, industry has to cease use of those substance within a given deadline (sunset date) or apply for authorisation for certain specified uses within an application date.

Restriction

If the authorities assess that that there is a risks to be addressed at the EU level, limitations of the manufacturing and use of a chemical substance (or substance group) may be implemented. Restrictions are listed in REACH annex XVII, which has also taken over the restrictions from the previous legislation (Directive 76/769/EEC).

Classification and Labelling

The CLP Regulation implements the United Nations Global Harmonised System (GHS) for classification and labelling of substances and mixtures of substances into EU legislation. It further specifies rules for packaging of chemicals.

Two classification and labelling provisions are:

1. **Harmonised classification and labelling** for a number of chemical substances. These classifications are agreed at the EU level and can be found in CLP Annex VI. In addition to newly agreed harmonised classifications, the annex has taken over the harmonised classifications in Annex I of the previous Dangerous Substances Directive (67/548/EEC); classifications which have been 'translated' according to the new classification rules.

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[1] Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

[2] Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures

2. **Classification and labelling inventory**. All manufacturers and importers of chemicals substances are obliged to classify and label their substances. If no harmonised classification is available, a self-classification shall be done based on available information according to the classification criteria in the CLP regulation. As a new requirement, these self-classifications should be notified to ECHA, which in turn publish the classification and labelling inventory based on all notifications received. There is no tonnage trigger for this obligation. For the purpose of this report, self-classifications are summarised in Appendix 2 to the main report.

Ongoing activities - pipeline
In addition to listing substance already addressed by the provisions of REACH (pre-registrations, registrations, substances included in various annexes of REACH and CLP, etc.), the ECHA web-site also provides the opportunity for searching for substances in the pipeline in relation to certain REACH and CLP provisions. These will be briefly summarised below:

Community Rolling Action Plan (CoRAP)
The EU Member States have the right and duty to conduct REACH substance evaluations. In order to coordinate this work among Member States and inform the relevant stakeholders of upcoming substance evaluations, a Community Rolling Action Plan (CoRAP) is developed and published, indicating by who and when a given substance is expected to be evaluated.

Authorisation process; candidate list, Authorisation list, Annex XIV
Before a substance is included in REACH Annex XIV and thus being subject to Authorisation, it has to go through the following steps:

1. It has to be identified as a SVHC leading to inclusion in the candidate list[3];
2. It has to be prioritised and recommended for inclusion in ANNEX XIV (These can be found as Annex XIV recommendation lists on the ECHA web-site);
3. It has to be included in REACH Annex XIV following a comitology procedure decision (substances on Annex XIV appear on the Authorisation list on the ECHA web-site).

The candidate list (substances agreed to possess SVHC properties) and the Authorisation list are published on the ECHA web-site.

Registry of intentions
When EU Member States and ECHA (when required by the European Commission) prepare a proposal for:

- a harmonised classification and labelling,
- an identification of a substance as SVHC, or
- a restriction.

This is done as a REACH Annex XV proposal.

The 'registry of intentions' gives an overview of intensions in relation to Annex XV dossiers divided into:
- current intentions for submitting an Annex XV dossier,
- dossiers submitted, and
- withdrawn intentions and withdrawn submissions

for the three types of Annex XV dossiers.

[3] It should be noted that the candidate list is also used in relation to articles imported to, produced in or distributed in the EU. Certain supply chain information is triggered if the articles contain more than 0.1% (w/w) (REACH Article 7.2 ff).

International agreements

OSPAR Convention

OSPAR is the mechanism by which fifteen Governments of the western coasts and catchments of Europe, together with the European Community, cooperate to protect the marine environment of the North-East Atlantic.

Work to implement the OSPAR Convention and its strategies is taken forward through the adoption of decisions, which are legally binding on the Contracting Parties, recommendations and other agreements. Decisions and recommendations set out actions to be taken by the Contracting Parties. These measures are complemented by other agreements setting out:

- Issues of importance;
- Agreed programmes of monitoring, information collection or other work which the Contracting Parties commit to carry out;
- Guidelines or guidance setting out the way that any programme or measure should be implemented;
- Actions to be taken by the OSPAR Commission on behalf of the Contracting Parties.

HELCOM - Helsinki Convention

The Helsinki Commission, or HELCOM, works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM is the governing body of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area" - more usually known as the Helsinki Convention.

In pursuing this objective and vision the countries have jointly pooled their efforts in HELCOM, which is works as:

- an environmental policy maker for the Baltic Sea area by developing common environmental objectives and actions;
- an environmental focal point providing information about (i) the state of/trends in the marine environment; (ii) the efficiency of measures to protect it and (iii) common initiatives and positions which can form the basis for decision-making in other international fora;
- a body for developing, according to the specific needs of the Baltic Sea, Recommendations of its own and Recommendations supplementary to measures imposed by other international organisations;
- a supervisory body dedicated to ensuring that HELCOM environmental standards are fully implemented by all parties throughout the Baltic Sea and its catchment area; and
- a co-ordinating body, ascertaining multilateral response in case of major maritime incidents.

Stockholm Convention on Persistent Organic Pollutants (POPs)

The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment. The Convention is administered by the United Nations Environment Programme and is based in Geneva, Switzerland.

Rotterdam Convention

The objectives of the Rotterdam Convention are:

- to promote shared responsibility and cooperative efforts among Parties in the international trade of certain hazardous chemicals in order to protect human health and the environment from potential harm;

- to contribute to the environmentally sound use of those hazardous chemicals, by facilitating information exchange about their characteristics, by providing for a national decision-making process on their import and export and by disseminating these decisions to Parties.
- The Convention creates legally binding obligations for the implementation of the Prior Informed Consent (PIC) procedure. It built on the voluntary PIC procedure, initiated by UNEP and FAO in 1989 and ceased on 24 February 2006.

The Convention covers pesticides and industrial chemicals that have been banned or severely restricted for health or environmental reasons by Parties and which have been notified by Parties for inclusion in the PIC procedure. One notification from each of two specified regions triggers consideration of addition of a chemical to Annex III of the Convention. Severely hazardous pesticide formulations that present a risk under conditions of use in developing countries or countries with economies in transition may also be proposed for inclusion in Annex III.

Basel Convention
The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal was adopted on 22 March 1989 by the Conference of Plenipotentiaries in Basel, Switzerland, in response to a public outcry following the discovery, in the 1980s, in Africa and other parts of the developing world of deposits of toxic wastes imported from abroad.

The overarching objective of the Basel Convention is to protect human health and the environment against the adverse effects of hazardous wastes. Its scope of application covers a wide range of wastes defined as “hazardous wastes” based on their origin and/or composition and their characteristics, as well as two types of wastes defined as “other wastes” - household waste and incinerator ash.

The provisions of the Convention center around the following principal aims:

- the reduction of hazardous waste generation and the promotion of environmentally sound management of hazardous wastes, wherever the place of disposal;
- the restriction of transboundary movements of hazardous wastes except where it is perceived to be in accordance with the principles of environmentally sound management; and
- a regulatory system applying to cases where transboundary movements are permissible.

Eco-labels
Eco-label schemes are voluntary schemes where industry can apply for the right to use the eco-label on their products if these fulfil the eco-labelling criteria for that type of product. An EU scheme (the flower) and various national/regional schemes exist. In this project we have focused on the three most common schemes encountered on Danish products.

EU flower
The EU eco-labelling Regulation lays out the general rules and conditions for the EU eco-label; the flower. Criteria for new product groups are gradually added to the scheme via 'decisions'; e.g. the Commission Decision of 21 June 2007 establishing the ecological criteria for the award of the Community eco-label to soaps, shampoos and hair conditioners.

Nordic Swan
The Nordic Swan is a cooperation between Denmark, Iceland, Norway, Sweden and Finland. The Nordic Eco-labelling Board consists of members from each national Eco-labelling Board and decides on Nordic criteria requirements for products and services. In Denmark, the practical implementation of the rules, applications and approval process related to the EU flower and Nordic Swan is hosted by Eco-labelling Denmark "Miljømærkning Danmark" (http://www.ecolabel.dk/). New

criteria are applicable in Denmark when they are published on the Eco-labelling Denmark's website (according to Statutory Order no. 447 of 23/04/2010).

Blue Angel (Blauer Engel)

The Blue Angel is a national German eco-label. More information can be found on: http://www.blauer-engel.de/en.

Annex 2: HFC and PFC gasses and sulphur hexafluoride

Lifetime and GWP for HFC and PFC gasses and sulphur hexafluoride as presented in the newest draft working group (1) report prepared for the coming IPCC Fifth Assessment Report is listed in Table Annex 2/1 below.

TABLE ANNEX2/1 HFC AND PFC GASSES AND SULPHUR HEXAFLUORIDE, THEIR LIFETIME AND GWP

Acromym, common name or chemical name	Chemical formula	Lifetime years	GWP 20-year	GWP 100-year
HFC-gasses				
HFC-23	CHF_3	222	10 800	12 400
HFC-32	CH_2F_2	5.2	2 430	677
HFC-41	CH_3F	2.8	427	116
HFC-125	CHF_2CF_3	28.2	6 090	3 170
HFC-134	CHF_2CHF_2	9.7	3 580	1 120
HFC-134a	CH_2FCF_3	13.4	3 710	1 300
HFC-143	CH_2FCHF_2	3.5	1 200	328
HFC-143a	CH_3CF_3	47.1	6 940	4 800
HFC-152	CH_2FCH_2F	0.1	60	16
HFC-152a	CH_3CHF_2	1.5	506	138
HFC-161	CH_3CH_2F	66 days	13	4
HFC-227ca	$CF_3CF_2CHF_2$	28.2	5 080	2 640
HFC-227ea	CF_3CHFCF_3	38.9	5 360	3 350
HFC-236cb	$CH_2FCF_2CF_3$	13.1	3 480	1 210
HFC-236ea	CHF_2CHFCF_3	11	4 110	1 330
HFC-236fa	$CF_3CH_2CF_3$	241	6 940	8 060
HFC-245ca	$CH_2FCF_2CHF_2$	6.5	2 510	716
HFC-245cb	$CF_3CF_2CH_3$	47.1	6 680	4 620
HFC-245ea	$CHF_2CHFCHF_2$	3.2	863	235
HFC-245eb	$CH_2FCHFCF_3$	3.1	1 070	290
HFC-245fa	$CHF_2CH_2CF_3$	7.7	2 920	858
HFC-263fb	$CH_3CH_2CF_3$	1.2	278	76
HFC-272ca	$CH_3CF_2CH_3$	2.6	530	144
HFC-329p	$CHF_2CF_2CF_2CF_3$	28.4	4 510	2 360
HFC-365mfc	$CH_3CF_2CH_2CF_3$	8.7	2 660	804
HFC-43-10mee	$CF_3CHFCHFCF_2CF_3$	16.1	4 310	1 650
HFC-1132a	$CH_2{=}CF_2$	4 days	0	0
HFC-1141	$CH_2{=}CHF$	2.1 days	0	0

Acromym, common name or chemical name	Chemical formula	Lifetime years	GWP 20-year	GWP 100-year
HFC-1225yeZ	$CF_3CF=CHF$	8.5 days	1	0
HFC-1225yeE	$CF_3CF=CHF$	4.9 days	0	0
HFC-1234zeZ	$CF_3CH=CHF$	10 days	1	0
HFO-1234yf	$CF_3CF=CH_2$	10.5 days	1	0
HFO-1234zeE	trans-$CF_3CH=CHF$	16.4 days	4	1
HFC-1336Z	$CF_3CH=CHCF_3$	22 days	6	2
HFC-1243zf	$CF_3CH=CH_2$	7 days	1	0
HFC-1345zfc	$C_2F_5CH=CH_2$	7.6 days	0	0
3,3,4,4,5,5,6,6,6-Nonafluorohex-1-ene	$C_4F_9CH=CH_2$	7.6 days	0	0
3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooct-1-ene	$C_6F_{13}CH=CH_2$	7.6 days	0	0
3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodec-1-ene	$C_8F_{17}CH=CH_2$	7.6 days	0	0
PFC-gasses				
PFC-14	CF_4	50 000	4 880	6 630
PFC-116	C_2F_6	10 000	8 210	11 100
PFC-c216	c-C_3F_6	3 000	6 850	9 200
PFC-218	C_3F_8	2 600	6 640	8 900
PFC-318	c-C_4F_8	3 200	7 110	9 540
PFC-3-1-10	C_4F_{10}	2 600	6 870	9 200
Perfluorocyclopentene	c-C_5F_8	31 days	7	2
PFC-4-1-12	n-C_5F_{12}	4 100	6 350	8 550
PFC-5-1-14	n-C_6F_{14}	3 100	5 890	7 910
PFC-61-16	n-C_7F_{16}	3 000	5 830	7 820
PFC-71-18	C_8F_{18}	3 000	5 680	7 620
PFC-91-18	$C_{10}F_{18}$	2 000	5 390	7 190
Perfluorodecalin (cis)	Z-$C_{10}F_{18}$	2 000	5 430	7 240
Perfluorodecalin (trans)	E-$C_{10}F_{18}$	2 000	4 720	6 290
PFC-1114	$CF_2=CF_2$	1.1 days	0	0
PFC-1216	$CF_3CF=CF_2$	4.9 days	0	0
Perfluorobuta-1,3-diene	$CF_2=CFCF=CF_2$	1.1 days	0	0
Perfluorobut-1-ene	$CF_3CF2CF=CF_2$	6 days	0	0
Perfluorobut-2-ene	$CF_3CF=CFCF_3$	31 days	6	2
Sulphur hexafluoride				
Sulphur hexafluoride	SF_6	3 200	17 500	23 500

* Source :
IPPC 2013. WORKING GROUP I CONTRIBUTION TO THE IPCC FIFTH ASSESSMENT REPORT CLIMATE CHANGE 2013: THE PHYSICAL SCIENCE BASIS - Final Draft Underlying Scientific-Technical Assessment. http://www.climatechange2013.org/images/uploads/WGIAR5_WGI-12Doc2b_FinalDraft_All.pdf (January 2014).

Annex 3: Self-classifications

The Classification & Labelling (C&L) Inventory database at the website of the European Chemicals Agency (ECHA) contains classification and labelling information on notified and registered substances received from manufacturers and importers. The database includes as well the harmonised classification. Companies have provided this information in their C&L notifications or registration dossiers. ECHA maintains the Inventory, but does not verify the accuracy of the information [ECHA, 2014].

CLASSIFICATION INFORMATION ON NOTIFIED AND REGISTERED SUBSTANCES RECEIVED FROM MANUFACTURERS AND IMPORTERS (C&L LIST)*

CAS No	Common name	Substance name	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
75-46-1	HFC-23	Trifluoromethane	Press. Gas Liq. Gas Skin Irrit. 2 Eye Irrit. 2. STOT SE 3	H280 H280 H315 H319 H335	122 59 1 1 1
75-10-5	HFC-32	Difluoromethane	Flam. Gas Press. Gas Liq. Gas Muta. 1B Carc. 1A	H220 H280 H280 H340 H350 H312	192 11 158 37 37 1
354-33-6	HFC 125	1,1,1,2,2- pentafluoromethane	Press. Gas Liq. Gas STOT SE 2	H280 H280 H371	110 41 1
811-97-2	HFC-134a	1,1,1,2-tetrafluoromethane	Press. Gas Liq. Gas STOT SE 1 STOT SE 2 Not Classified	H280 H280 H370 H371	193 67 5 1 76
420-46-2	HFC 143a	1,1,1-trifluoroethane	Flam. Gas Flam. Liq. Press. Gas Liq. Gas	H220 H224 H280 H280 H312	152 19 11 140 1
75-37-6	HFC 152a	1,1-difluoroethane	Flam. Gas Flam. Liq. Press. Gas Liq. Gas Muta. 1B Carc. 1A	H220 H224 H280 H280 H340 H350	377 24 24 227 35 35

CAS No	Common name	Substance name	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
			STOT SE 1 STOT SE 3 Not Classified	H370 H335	1 10 4
431-89-0	HFC 227ea	1,1,1,2,3,3,3- heptafluoro-propane	Press. Gas Liq. Gas Not Classified	H280 H280	1 111 20
290-39-1	HFC 236fa	1,1,1,3,3,3-hexafluoropropane	n.d	n.d.	n.d.
460-73-1	HFC-245fa	1,1,1,3,3-pentafluoropropane	Flam. Liq. 2 Eye Irrit. 2. STOT SE 3 Not Classified	H225 H319 H336	54 23 34 33
406-58-6	HFC-365mfc	1,1,1,3,3-pentafluorobutane	Flam. Liq. 2	H225	91
138495-42-8	HFC-43-10mee	1,1,1,2,2,3,4,5,5,5-decafluoropentane	Aquatic Chronic 3 Skin Irrit. 2 Eye Irrit. 2. STOT SE 3	H412 H315 H319 H335	110 18 18 18
754-12-1	HFO-1234yf	2,3,3,3-tetrafluoroprop-1-ene	Flam. Gas Press. Gas Liq. Gas	H220 H280 H280	43 23 20
29118-24-9	HFO-1234zeE	Trans-1,3,3,3-tetrafluoroprop-1-ene	n.d.	n.d.	n.d.
75-73-0	PFC-14	Perfluoromethane	Press. Gas Liq. Gas	H280 H280	133 1
76-16-4	PFC-116	Perfluoroethane	Press. Gas Liq. Gas	H280 H280	112 49
76-19-7	PFC-218	Perfluoropropane	Press. Gas Liq. Gas STOT RE 3 Not classified	H280 H280 H373 H336 H281	1 81 1 1 1 54
415-25-3	PFC-318	Perfluorocyclobutane	n.d.	n.d.	n.d.
355-25-9	PFC-3-1-10	Perfluorobutane	Liq. Gas Skin Irrit. 2 Eye Irrit. 2. STOT SE 3	H280 H315 H319 H335	36 1 1 1
678-26-2	PFC-4-1-12	Perfluoropentane	Skin Irrit. 2 Eye Irrit. 2. STOT SE 3	H315 H319 H335	2 2 2
355-41-10	PFC-5-1-14	Perfluorohexane	n.d.	n.d.	n.d.
2551-62-4	SF_6	Sulphur hexafluoride	Press. Gas Liq. Gas	H280 H280	117 39

CAS No	Common name	Substance name	Hazard Class and Category Code(s)	Hazard Statement Codes	Number of notifiers
			Skin Irrit. 2 Eye Irrit. 2. STOT SE 3	H315 H319 H335 H280/H315/ H319/H335	1 1 1 2

n.d. No data

* Source : Search Classification and Labelling Inventory at http://echa.europa.eu/web/guest/information-on-chemicals/cl-inventory-database

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