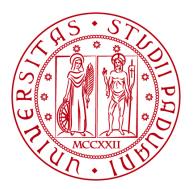
UNIVERSITÀ DEGLI STUDI DI PADOVA

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FINAL THESIS

LIFE CYCLE ENVIRONMENTAL IMPACT OF REFRIGERATION IN SUPERMARKETS: A COMPARATIVE STUDY UNDER DIFFERENT OPERATIONAL CONDITIONS

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Abstract

This thesis investigates the Life Cycle Assessment (LCA) of a commercial refrigeration system, focusing on the environmental impact of refrigerants. The first section provides a technical overview of refrigerant development and regulatory frameworks, particularly highlighting the role of PFAS (Per- and polyfluoroalkyl substances), their associated risks, and the current restrictions in refrigeration systems. It also explores potential alternatives to PFAS-based refrigerants. The core of the study consists of an LCA case study, starting with an inventory analysis that incorporates both real-world data and literature. The assessment covers the entire life cycle of the system, including the manufacturing phase, the use phase—divided into direct and indirect emissions—and the end-of-life phase. Various methodologies are applied to analyze the results, both on a system-wide level and by breaking down the analysis into smaller sections. This multi-faceted approach provides a detailed understanding of the environmental impact across different life cycle stages.

The study specifically analyzes a commercial refrigeration system using three different refrigerants across three distinct cities and two varying leakage rates. Results indicate that the manufacturing phase emissions are quite similar between the different configurations. Indirect emissions during the use phase vary significantly based on geographic location and energy mix, illustrating stark differences between regions. Direct emissions are influenced by leakage rates, with certain refrigerants showing a higher potential for ozone depletion. While the overall differences in emissions among refrigerants are relatively small, the end-of-life phase has a negligible impact, accounting for a minor portion of the total environmental footprint. Overall, this study highlights the sustainability challenges posed by refrigeration systems and the critical role of refrigerant choice and local energy sources in determining environmental impacts.

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List of Abbreviations

AP - Acidification Potential Br - Bromine **BP** - Biocidal Products **CFCs** - Chlorofluorocarbons CH₄ - Methane CCl₄ - Carbon tetrachloride Cd - Degradation Coefficient C₂HCl₃ - Trichloroethylene C₂H₄ - Ethylene Cl - Chlorine CLP - Classification, Labelling and Packaging CO₂ - Carbon dioxide **COP** - Coefficient Of Performance **CR** - Capacity Ratio **DALYs** - Disability Adjusted Life Years **DCM** - Dichloromethane ECHA - European Chemical Agency EoL - End of Life **EPA** - Environmental Protection Agency **GHGs** - Greenhouse gases GWP - Global Warming Potential H - Hydrogen HF - Hydrogen fluoride HCFCs – Hydrochlorofluorocarbons HCl - Hydrochloric acid HFCs - Hydrofluorocarbons HFOs – Hydrofluoroolefins HVACR - Heating, Ventilation and Air Conditioning and Refrigeration I - Iodine LCA - Life Cycle Assesment LCIA - Life Cycle Impact Assesment LT - Low Temperature MAC - Mobile Air-Conditioning **MT** - Medium Temperature MoE - Margin of Exposure **MP** - Medicinal Products N₂O - Nitrous oxide NOEC - No-observed-effect concentration **NOEL** - No-observed-effect level **OECD** - Organization for the Economic Co-operation and Development **ODSs** - Ozone depleting substances **P** - Phosphorus **PFASs** - Per- and polyfluoroalkyl substances PFCAs - Perfluoroalkyl carboxylic acids PFCs - Perfluorinated compound **PFHxS** - Perfluorohexane sulfonate **PFOA -** Perfluorooctanoic acid **PFOS** - Perfluorooctanesulfonic acid

PFPEs - Perfluoropolyethers **PFSAs -** Perfluorosulfonic acids PL - Partial Load **POPs -** Persistent Organic Pollutants **PPP** - Plant Protection Products **R-11** - Trichlorofluoromethane **R-12** - Dichlorodifluoromethane **R-21** - Dichlorofluoromethane **R-22** - Chlorodifluoromethane **R-32** - Difluoromethane R-123 - 2,2-Dichloro-1,1,1-trifluoroethane R-1234yf - 2,3,3,3-Tetrafluoroprop-1-ene R-1234ze - Trans-1,3,3,3-Tetrafluoroprop-1-ene **R-134a -** 1,1,1,2-Tetrafluoroethane R-142b - 1-Chloro-1,2-difluoroethane R-455A - Solstice L40X R-744 - Carbon Dioxide **REACH -** Registration, Evaluation, Authorisation and Restriction of Chemicals **R&D** - Research and Development **RMOs -** Risk management options **SEPR** - Seasonal Energy Performance Ratio SF₆ - Sulfur hexafluoride SO₂ - Sulphur Dioxide SVHCs - Substances of Very High Concern **TEAP** - Technology and Economic Assessment Panel TFA - Trifluoroacetic Acid TULAC - Textile, upholstery, leather, apparel and carpets **UNEP -** United Nations Environment Programme **UNFCCC** - United Nations Framework Convention on Climate Change WEEE - Waste from Electrical and Electronic Equipment WHO - World Health Organization Zn - Zinc

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1. Environmental Impact of Refrigerants

1.1 Technical Progression

Refrigeration, as we know it today, began in the mid-19th century during the Industrial Revolution when the principles of thermodynamics were first understood. The origins of vapor-compression refrigeration date back to Professor William Cullen of Glasgow, who, in 1755, produced ice by evaporating water at low pressure [1]. He also experimented with the evaporation of ethyl ether to achieve cooling. In 1834, Jacob Perkins patented a vapor-compression refrigeration system using ethyl ether in a closed circuit. His patent included all essential components of modern systems: the compressor, condenser, expansion device, and evaporator. This initiated the ongoing quest for the ideal refrigerant, a search that continues to this day [2].

At the dawn of the 20th century, refrigeration had become well-established on an industrial scale, though domestic refrigeration using vapor-compression systems had yet to be developed. In commercial settings, belt-driven ammonia or sulfur dioxide machines were common. Some of these systems were notably reliable, running for long periods with minimal maintenance. However, the use of packed glands for crankshaft seals was problematic due to the strong odors and toxicity of the refrigerants.

Ammonia continued to dominate industrial refrigeration thanks to thermodynamic properties and economy, while air and carbon dioxide were phased out due to their low efficiency [3]. Commercial and domestic refrigeration used a variety of refrigerants, including ammonia, methyl chloride, sulfur dioxide, propane, and isobutane.

Charles F. Kettering of General Motors recognized the potential for mass-producing affordable electric refrigerators and air conditioners if a better refrigerant could be found. He tasked Thomas Midgley, an able engineer, with finding the "ideal" refrigerant, which had to be:

- Stable
- Non-toxic
- Non-flammable
- Miscible with lubricating oil
- Capable of operating in a domestic refrigerator without dropping below atmospheric pressure
- A good electrical insulator
- A substance with a low index of compression to keep the compressor running cool [4].

Midgley and his colleagues observed that flammability and toxicity generally decreased as one moved from left to right and from bottom to top in the periodic table [5]. This insight led them to explore chlorinated and fluorinated hydrocarbons. They noted how variations in chlorination and fluorination affected boiling point, flammability, and toxicity. They identified dichlorofluoromethane R-21 as a promising candidate, synthesized a small quantity, and confirmed its low toxicity. Subsequent investigations into other chlorofluorocarbons followed, leading to the commercial production of dichlorodifluoromethane R-12 in 1931 and trichlorofluoromethane R-11 in 1932.

Chlorofluorocarbons CFCs, as R-11 and R-12, dominated the second generation of refrigerants, followed by hydrochlorofluorocarbons HCFCs, as R21, which became especially prevalent in residential and small commercial air conditioners and heat pumps starting in the 1950s. Ammonia remained the most popular refrigerant for large industrial systems, particularly in food and beverage processing and storage, and continues to be widely used today.

The link between released CFCs, including CFC refrigerants, and the depletion of the protective ozone layer catalyzed the third generation of refrigerants, focusing on stratospheric ozone protection. The Vienna Convention and the resulting Montreal Protocol mandated the abandonment of ozone-depleting substances ODSs. Fluorochemicals remained the primary focus, with HCFCs used for interim purposes and hydrofluorocarbons HFCs for the longer term [6].

The transition from HCFCs is also underway. The Montreal Protocol limits HCFC consumption in steps: a freeze in 1996, followed by reductions to 65% in 2004, 25% in 2010, 10% in 2015, 0.5% in 2020, with full phaseout by 2030 in non-Article 5 countries. Different countries have adopted varied approaches, with many Western and Central European countries accelerating the phaseout, while others focused on phasing out propellant and blowing agent uses early.

The fourth-generation refrigerants feature fluorinated propene (propylene) isomers with low Global Warming Potential (GWP). The most promising replacements are Hydrofluoroolefins (HFOs), a new class of fluorocarbon refrigerants. These HFOs, such as HFO-1234yf, have very low GWP and are anticipated to replace HFCs in many applications [7].

INCREASINGLY STRINGENT REQUIREMENTS

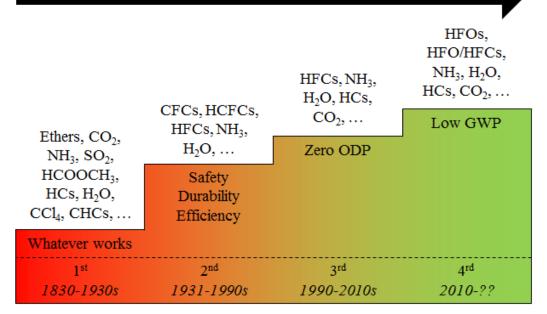


Figure 1-1 Evolution of Refrigerants

1.2 Regulatory Systems

The first significant accord addressing halogenated refrigerants was the Montreal Protocol of 1987, which aimed to outright ban R-12 and initiate a phased reduction of interim substitutes like R-22, R-142b, and R-123 [9]. Known for its role in phasing out ozone-depleting substances such as CFCs and HCFCs, the Montreal Protocol did not include HFCs due to their negligible impact on the ozone layer. Since 2010, 108 nations have committed to the Montreal Protocol, pledging to transition from CFCs and HCFCs to more environmentally friendly alternative refrigerants [10].

The Figure 1-2 illustrates projected radiative forcing from harmful and low-GWP refrigerants. In scenarios without the Montreal Protocol (hatched blue line), ODS production could have increased by 2–3% annually, potentially resulting in a radiative forcing of 0.64 W/m² by 2010. However, the Protocol's measures helped avoid approximately 10 Gt CO₂/year in ODS emissions by that time. Reductions in CFCs and HCFCs commenced in 1989 and 1996, respectively, under the Montreal Protocol. The climate benefits achieved could be compromised if emissions from high-GWP ODS replacements continue to rise [11].

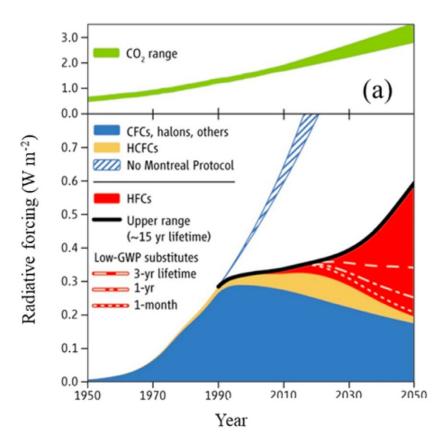


Figure 1-2 Effects and Projections of Montreal Protocol [12]

Following the Montreal Protocol, the Kyoto Protocol was ratified in 1997 by industrialized countries. The Kyoto Protocol aims to reduce emissions of six major greenhouse gases, including CO_2 , CH_4 , N₂O, HFCs, PFCs, SF₆. Key conditions of the Kyoto Protocol included ratification by at least 55 nations and their cumulative CO_2 emissions accounting for at least 55% of global greenhouse gas emissions. These criteria were met with Iceland and Russia's ratifications in 2002 and 2004, respectively.

Criticism of the Kyoto Protocol centered on its differentiation among countries under the UNFCCC principle of "Common but Differentiated Responsibilities" [13]. While ratified by 190 countries, legally binding emission reduction targets were assigned only to Annex B countries (37 industrialized nations, among which Italy). Annex B countries were required to reduce their GHG emissions by 5.2% compared to 1990 levels. Concerns also arose over the first commitment period's timeframe, set for 5 years from 2008 to 2012, which was deemed insufficient given the long-lasting effects of CO₂ and other GHGs in the atmosphere.

Another category of substances, hydrofluorocarbons (HFCs), emerged as ozone-depleting-free alternatives to facilitate the phased-out of CFCs and HCFCs. Widely used today in air conditioners, refrigerators, aerosols, foams, and various other products, HFCs do not harm the stratospheric ozone layer [14]. However, some HFCs possess high Global Warming Potentials (GWPs) ranging from 12000 to 14000. Global emissions of HFCs are increasing at a rate of 8% annually, and projections suggest they could contribute 7-19% of global CO₂ emissions by 2050. Unchecked growth in HFC emissions poses a significant challenge to efforts aimed at limiting global temperature rise to within 2°C this century. Urgent action on HFCs is essential to safeguard the climate system.

At the 28th Meeting of the Parties to the Montreal Protocol held on 15 October 2016 in Kigali, Rwanda, Parties reached an agreement to phase down HFCs. Countries decided to include HFCs in the list of controlled substances and approved a timeline for their gradual reduction, aiming for an 80-85% decrease by the late 2040s [15]. Developed countries are expected to initiate reductions starting in 2019, while developing countries will freeze their HFC consumption levels by 2024, with some nations implementing the freeze by 2028.

The strategy to implement the HFC phase-down involves reducing reliance on high-GWP alternatives and increasing the adoption of low-GWP, energy-efficient technologies, aligning with the HCFC phase-out process under the Montreal Protocol. This "smart approach" not only achieves the Protocol's goal of phasing out HCFCs but also enhances energy efficiency and reduces CO₂ emissions, providing additional climate benefits.

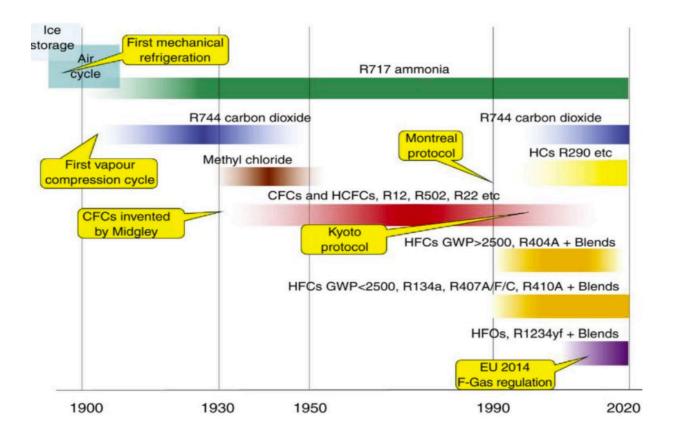


Figure 1-3 Correlation between Technical Evolutions and Regulatory Frameworks

In recent years, there has been a growing awareness and concern regarding the presence of PFAS (per- and polyfluoroalkyl substances) in refrigerant liquids, prompting extensive research and regulatory scrutiny to address their potential environmental and health impacts.

1.3 PFAS

Per- and polyfluoroalkyl substances (PFASs) are a group of thousands of synthetic chemicals used extensively in the EU and worldwide in a variety of applications such as textiles, food packaging, lubricants, refrigerants, and electronics. All PFASs are either highly persistent themselves or degrade into very persistent PFASs in the environment. Consequently, without minimizing PFAS releases, humans and other organisms will be exposed to increasing levels of PFASs, eventually reaching unavoidable and irreversible levels of exposure due to the technical difficulty, if not impossibility, of removing PFASs from the environment [16].

The most thoroughly researched PFASs, such as PFOS and PFOA, are suspected carcinogens, cause harm to developing children through intergenerational exposure, and trigger effects at low concentrations in organs like the liver or the immune system. Some PFASs are identified as hazardous to the aquatic environment. Although data are insufficient for most PFASs to assess their effects on human health and the environment adequately, increasing research has reported similar adverse effects for other PFASs beyond PFOS and PFOA. Thus, there is growing concern about the harmful effects of the entire PFAS family, as similar concerns may apply to the less studied substances. Adverse effects from 'combined exposure' to complex PFAS mixtures are likely for both humans and wildlife but cannot currently be quantitatively assessed with sufficient certainty for regulatory purposes. A group approach to regulating PFASs is effective in addressing this complex interplay of concerns [17].

According to ECHA Annex XV restriction proposal, PFASs are defined as substances containing at least one fully fluorinated methyl (CF₃-) or methylene (-CF₂-) carbon atom, without any H/Cl/Br/I attached to it. This definition aligns with the OECD's 2021 definition, which states: "PFASs are fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it)" [18]. Essentially, any chemical with at least a perfluorinated methyl group (-CF₃) or a perfluorinated methylene group (-CF₂-) is considered a PFAS, with few exceptions.

PFASs, as defined in the restriction proposal, form a broad group of substances, including volatile and non-volatile PFASs, anionic, cationic, zwitterionic, and non-ionic substances, polymers, nonpolymers, and amphoteric liquids (surfactants), with various chain lengths and degrees of fluorination. The group of PFASs cannot be characterized by specific physicochemical properties, but they (or their degradation products) share a common characteristic of very high persistence.

1.3.1 Chemical structure and nomenclature

A study by the OECD/UNEP Global PFC Group identified 4730 CAS numbers associated with individual PFASs or PFAS mixtures [19]. A recent analysis of PFASs registered under REACH and/or notified to the CLP classification and labeling inventory in 2019, compared with the OECD/UNEP list, suggested there may be over 9000 different individual PFASs. The US EPA's master list, which consolidates information from several existing lists, contained 6330 different PFASs in 2019, and this number grew to 12034 by July 2022. Therefore, it is reasonable to estimate that the current number of PFASs is at least 10000.

In perfluoroalkyl substances, all C-H bonds are replaced by C-F bonds, while in polyfluoroalkyl substances, two or more C-H bonds are replaced by C-F bonds, but some C-H bonds remain in the molecular structure. Polyfluoroalkyl substances containing at least one perfluorinated moiety (-CF₂- or -CF₃, not directly attached to -H, -Cl, -Br, or -I) fit within the definition. However, a perfluorinated olefinic carbon atom (=CF₂) or an aromatic ring bound directly to an F-atom (-CF=) does not meet the PFAS definition alone. Consequently, olefins and aromatic substances require additional fluoroalkyl elements to be considered PFASs [20].

PFASs can be divided into functional subgroups in several ways. One method, shown in Figure 1-4, is based on the main chemical moieties present. The non-polymeric PFASs include a diverse range of molecules, such as perfluoroalkyl carboxylic acids (PFCAs, e.g., PFOA), perfluoroalkane sulfonic acids (PFSAs, e.g., PFOS), fluorotelomer-based compounds, per- and polyfluoroalkanes (e.g., perfluorooctane), perfluorotrialkylamines, and per- and polyfluoroalkyl ether compounds.

Within the polymeric PFAS group are fluoropolymers (polymers with a fluorinated carbon backbone), side-chain fluorinated polymers (polymers with non-fluorinated backbones and per- or polyfluoroalkyl/alkyl ether side-chains), and perfluoropolyethers (PFPEs, polymers with an ether backbone and F atoms directly attached).

Some substances contain only a single $-CF_3$ group attached to carbon and are potential precursors to trifluoroacetic acid (TFA). This subgroup includes some fluorinated gases and active ingredients in biocides, plant protection products, and pharmaceuticals containing a $-CF_3$ group bound to an aromatic ring. Fluorinated gases that meet the scope definition contribute the largest production volume to this subgroup.

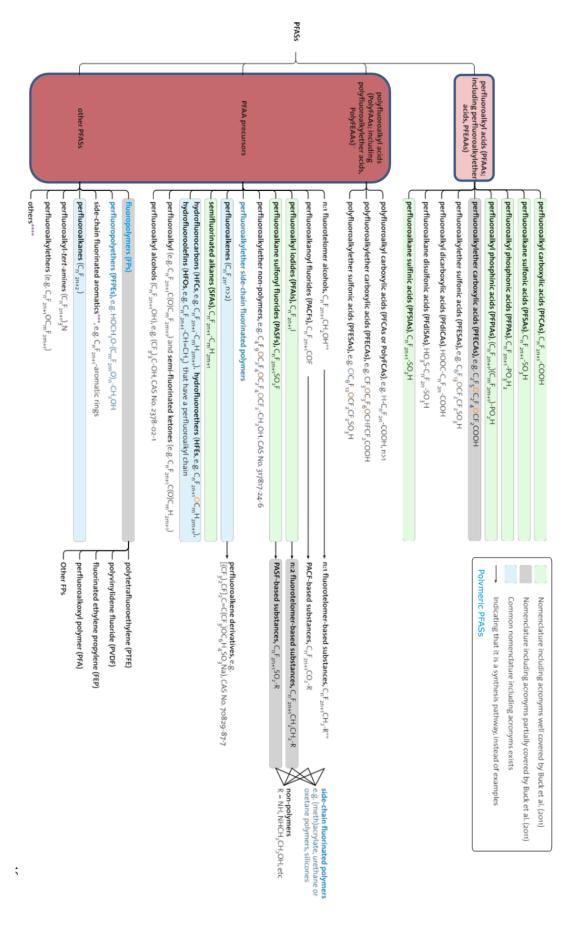


Figure 1-4 Nomenclature of PFAS

1.3.2 Risks and properties of PFAS

All PFASs covered by the restriction proposal are either inherently very persistent or degrade into persistent PFASs in the environment. Additional concerns vary among these substances, including bioaccumulation, mobility, long-range transport potential, plant accumulation, global warming potential, and ecotoxicological effects, along with issues arising from a combination of these properties. Collectively, these characteristics raise significant concerns about environmental contamination of vital resources such as groundwater, with extensive literature supporting these concerns.

A study made by Goldenman et al. in 2019 indicate that PFAS contamination may be poorly reversible or even irreversible, potentially rendering natural resources like soil and water unusable far into the future. This could result in continuous exposure and unavoidable harmful health effects, particularly for vulnerable populations, such as children [21].

Exposure to PFASs has been linked to adverse health effects in humans, primarily through consumption of contaminated food or water. Specifically, long-chain PFASs such as PFOS and PFOA have been shown to cause reproductive, developmental, liver, kidney, and immunological effects in laboratory animals, with both substances also inducing tumors in animal studies. Consequently, PFOS and PFOA are regulated under the Stockholm Convention. Other PFASs, have been identified as Substances of Very High Concern (SVHCs) under REACH, due to their comparable levels of concern to carcinogens, mutagens, and persistent, bioaccumulative, and toxic/very persistent and very bioaccumulative chemicals [22].

Considering the physical properties of PFASs, particularly their mobility and persistence, along with the identified health effects, PFASs pose a significant environmental and human health hazard. They are all considered very persistent, either directly or through their terminal degradation products. Additional hazardous properties depend on the specific structure of each PFAS.

1.3.3 Restriction on PFAS

In response to the risks related to PFAS, this section will provide an analysis of current regulations as well as an examination of future options that could be adopted concerning restrictions on these substances.

1.3.3.1 Stockholm Convention and POP regulation

The Stockholm Convention is an international treaty aimed at eliminating or restricting the production and use of Persistent Organic Pollutants (POPs) to protect human health and the environment from these chemicals. POPs are chemicals that persist in the environment for long periods, become widely distributed geographically, accumulate in humans and wildlife, and have harmful impacts on human health and the environment [23].

The Stockholm Convention is implemented in the EU through the POP Regulation. PFOS and PFOA are restricted under the Stockholm Convention. PFOS has been identified as a POP and included in Annex B of the Convention. PFHxS and long-chain PFCAs are currently being considered for inclusion [24].

In 2019, the PFOS ban under the Stockholm Convention was re-evaluated, and all previously granted exemptions in the EU were removed, except for the use of PFOS as a spray suppressant for non-decorative hard chrome plating (chromium VI) in closed-loop systems.

1.3.3.2 Reach Regulation

Under REACH, PFOA, its salts, and related substances (substances that can degrade to PFOA) have been restricted within the EU with certain derogations since July 4, 2020. In May 2019, PFOA, its salts, and PFOA-related compounds were added to Annex A of the Stockholm Convention, which comprehends the chemicals that must be eliminated. Consequently, the inclusion of PFOA in the EU POP Regulation was prepared and finalized in April 2020, with its incorporation into Annex I of the POP Regulation.

Perfluorohexane sulfonic acid (PFHxS), its salts, and related substances will be included in the Stockholm Convention in autumn 2022. Norway has prepared a proposal for a restriction under REACH for this substance, which has undergone the scientific opinion process at ECHA. This proposal is now awaiting a decision from the European Commission for inclusion in the EU POP Regulation.

1.3.3.3 Regulation of fluorinated gases

In addition to the regulation concerning ODS, there is specific legislation on fluorinated greenhouse gases (F-gases) under Regulation (EU) No 517/2014 [25]. Since the mid-1990s, ODS have been replaced by certain fluorinated greenhouse gases, particularly hydrofluorocarbons (HFCs).

Regulation (EU) No 517/2014 aims to reduce emissions (measured as CO₂ equivalents) from industry by 70% by 2030 compared to 1990 levels. This reduction is to be achieved through three main strategies:

- Gradual phase-down of the quantities of HFCs used, measured as CO₂ equivalents. This phase-down applies only to HFCs and not to perfluorocarbons (PFCs) or sulphur hexafluoride (SF₆).
- Prohibitions on use and placement on the market where technically feasible and more climatefriendly alternatives are available.
- Continuation and expansion of regulations concerning leak tests, certification, disposal, and labelling.

1.3.3.4 MAC Directive

The Mobile Air-Conditioning (MAC) Directive prohibits the use of F-gases with a Global Warming Potential (GWP) of more than 150 in new types of cars and vans introduced from 2011, and in all new cars and vans produced from 2017. The traditionally used refrigerant in MAC systems, R-134a, has a GWP of 1430 and has been phased out for use in air conditioning equipment in new cars in the EU. The Directive does not specify any refrigerant or system, leaving the technical choice to car manufacturers [26].

The MAC Directive is limited to the use of fluorinated gases in air-conditioning systems in cars and vans, and does not apply to buses, trains, ships, etc. Air conditioning equipment is only one of several applications of fluorinated gases.

1.3.4 Environmental impacts of PFAS

Table below summarizes the projected total emissions resulting from the continued use of PFASs over the next 30 years. These emission estimates incorporate assumptions about sector-specific growth rate. The estimates are presented for various use sectors and for the EU, representing the aggregate of all sectors.

PFAS Use Sector	PFAS use [t]	Emissions [t]	Percentage of emissions[%]
TULAC	5 472 040	1 431 511	26
Food contact material and packaging	1 495 936	43 708	3
Metal plating and manufacture of metal products	30 675	183	0,5
Consumer mixture	55	55	100
Cosmetics	995	995	100
Ski wax	22	13	59
Applications of fluorinated gases	25 369 435	1 942 313	8
Medical devices	3 964 549	512 432	13
Transport	3 409 168	49 824	1,5
Electronics and semiconductors	1 419 743	293 248	21
Energy sector	893 520	16 772	1,8
Construction products	550 564	152 555	28
Lubricants	102 072	20 698	20
Petroleum and mining	209 124	77 018	37
Total use	42 917 898	4 540 825	11

Table 1-1 PFAS projection under baseline scenario

In addition to emissions occurring during the use phase, PFASs are also emitted during the production phase and at the end of their life cycle, during the waste phase. Yearly emission estimates for PFAS production were derived from tonnage estimates provided by industry.

Specific applications of fluorinated gases are expected to experience substantial growth over the next 30 years. For instance, in commercial refrigeration, a yearly real growth rate of 3% is projected. Additionally, the EU air conditioning market has shown significant expansion over the past 25 years, initially in the commercial sector and now increasingly in the residential sector. Demand in Europe for both residential and commercial air conditioning is forecasted to approximately double over the next three decades. Despite improved efficiency at data centers, which has mitigated significant growth in cooling demand for the sector, it remains uncertain how long this efficiency trend will continue to offset increased internet traffic [27].

Market data for fire suppression agents indicate robust growth from 2018 to 2025, with a compound annual growth rate of 5.9%, and the fire detection and suppression market valued at USD 3.27 billion in 2018. Growth is expected to be driven by heightened safety measures, including stricter building

codes. However, these figures reflect growth across the entire market and do not specifically differentiate sectors using fluorinated gases from those using other fire suppressants. While projecting sector-level market growth with high reliability is challenging, an annual real growth rate of 2% is assumed, taking into consideration available information on market trends in various sub-sectors.

Regarding emission estimation only considering the application of fluorinated gases there is the following prediction.

	2020	2025	2030	2035	2040	2045	2050	2060	2070
PFAS use [t]	542 194	598 626	660 931	729 722	805 672	889 527	982 109	1 197 186	1 459 363
PFAS emissions [t]	41 51 1	45 841	50 601	55 868	61683	68 103	75 191	91658	111731

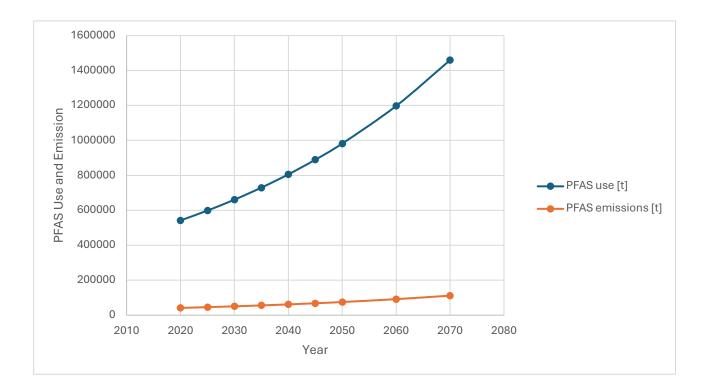


Table 1-2 PFAS use and emissions related to Fluorinated gases

Figure 1-5 PFAS use and emissions related to Fluorinated gases

1.3.5 Restriction Scenario

Based on the conclusions of the risk assessment, the release of PFASs is considered to pose an uncontrolled risk to the environment. In response to this identified risk, various risk management options (RMOs) were analyzed to determine the most appropriate measures. The proposed restriction aims to minimize PFAS releases into the environment as much as possible. Given the chemical

stability of PFASs, it is crucial to address releases during all stages of their life cycle, including the waste stage. The optimal approach to prevent PFAS emissions during manufacture, production, use of PFAS-containing articles, and at the waste stage is to largely prohibit their manufacture and use.

As a starting point, the proportionality of a full ban on all PFASs is analyzed. Restriction Option 1 is proposed to come into force after an 18-month transition period. This most stringent restriction option is then compared to Restriction Option 2, which bans all PFASs except for certain time-limited, use-specific derogations, lasting either five or twelve years after the transition period, based on defined criteria. The details of the transition period and derogations are summarized in Table 1-3.

Restriction option (RO)	Transition period before RO takes effect	Duration of derogation
RO1: Full ban		Not applicable
RO2: Ban with use-specific derogations	18 months	5 years
		12 years
		Time unlimited for specific uses

Table 1-3 Relations between possible Restriction Options

Under RO2, two types of time-limited derogations are considered. The first is a five-year derogation, proposed when strong evidence indicates that:

- Technically and economically feasible alternatives do not yet exist on the market at the entryinto-force date (EiF), but potential alternatives are already identified and in development.
- Known alternatives are unavailable in sufficient quantities at the entry-into-force date or cannot be implemented before the transition period ends.

The second is a 12-year derogation, proposed when strong evidence indicates that:

- Technically and economically feasible alternatives do not exist on the market at the EiF date, with R&D efforts failing to identify possible PFAS-free alternatives likely to become available soon.
- Certification or regulatory approval of PFAS-free alternatives cannot be achieved within a five-year derogation period.

The Dossier Submitters consider these timeframes generally sufficient for the industry to benefit from technical progress and conduct R&D activities to find and deploy feasible alternatives.

For some specific uses, practical reasons may necessitate time-unlimited derogations. At the submission of the restriction proposal, the Dossier Submitters justify such derogations for:

- Use of PFASs in refrigerants in HVACR equipment in buildings where national safety standards and building codes prohibit the use of alternatives.
- Use of PFASs in the calibration of measurement instruments and as analytical reference materials, necessary for the targeted analysis of PFASs in various matrices.
- Use of PFASs as active ingredients in PPP, BP, and human and veterinary MP.

As indicated in the criteria above, a derogation requires a strong evidence base to justify its necessity. Consequently, if the evidence base is weak, a derogation is not supported now, though it could potentially be warranted. Such derogations will be reconsidered for inclusion in the restriction proposal if additional information strengthening the evidence base becomes available during the Annex XV report consultation.

The environmental and socio-economic impacts of the proposed restriction options are assessed per sector, including the manufacturing of PFASs, TULAC, food contact materials and packaging, metal plating and manufacture of metal products, consumer mixtures, cosmetics, ski wax, applications of fluorinated gases, medical devices, transport, electronics and semiconductors, the energy sector, construction products, lubricants, and petroleum and mining.

For RO1, environmental impacts are assessed quantitatively for all sectors based on available emission data at the sector level and information on expected market growth for different sectors. For RO2, environmental impacts are assessed either quantitatively (where emission data is available) or qualitatively (where such data is lacking).

1.4 Alternatives

Identifying alternatives must occur at the specific application level. In some cases, an alternative non-PFAS substance can provide nearly identical performance, or a different technical solution altogether may suffice. Even a slightly different functionality can meet operational needs adequately. The focus should be on exploring possibilities rather than limitations when selecting the optimal refrigerant for a project or product. No single fluorinated gas or non-PFAS alternative can universally address all applications. While parts of the market have shifted away from fluorinated gases to other substances or solutions, finding suitable alternatives can be more challenging in specific cases.

Stakeholder input reveals diverse opinions on the suitability and availability of non-PFAS alternatives for current fluorinated gas applications. Some argue that fluorine-free options are broadly available, while others contend they are generally unsuitable due to properties like high flammability (hydrocarbons), toxicity (ammonia), or the need for high operating pressures (CO₂) [28]. However, many technical and safety challenges can be mitigated through equipment design. The assessment evaluates alternative availability at the sub-application level, emphasizing demonstrated solutions.

Under the Montreal Protocol, the Technology and Economic Assessment Panel (TEAP) regularly evaluates alternative availability to HFCs across various applications. Their latest report provides detailed insights into non-HFC alternatives categorized by uses such as foam blowing agents, fire suppressants, medical and chemical applications, refrigeration, air conditioning, and heat pumps [29]. However, TEAP primarily considers global warming potential and ozone depletion potential, not factors like degradation to persistent TFA in the atmosphere and ensuing environmental impacts, thus differing from this dossier's assessment.

Certain stakeholders highlight the significance of fluorinated gases in military applications like refrigeration, fire suppression, and air conditioning, where alternatives may not be viable due to safety considerations. Military refrigeration in transport equipment (ships, submarines) faces barriers to substitution due to stringent operating and safety conditions. Despite challenges, alternatives are available for many military and civilian applications.

Several stakeholders endorse R-32 (CH_2F_2) as a viable alternative for multiple applications, despite its classification as an F-gas under current regulations rather than a PFAS under this proposal. R-32 has a Global Warming Potential (GWP) of 675 and contributes significantly to climate effects. It has a short atmospheric lifetime and degrades into CO₂ and HF. Notably, R-1234ze has been found to be highly flammable in combustion tests, producing CO₂, HF, and toxic carbonyl fluoride as combustion products [30]. Evaluations of hydrocarbon alternative flammability are crucial.

1.4.1 Commercial and Industrial Refrigeration

There is increasing acceptance of alternatives like CO_2 or hydrocarbons in the commercial sector. However, fluorinated gases still dominate, and assuming the sector is fully prepared to switch to alternatives may be premature. Ongoing research is exploring various aspects. In some cases of commercial refrigeration, a secondary or indirect loop (glycol or water) can mitigate risks with flammable alternatives, albeit at the cost of reduced energy efficiency and higher expense [31]. Isobutane and propane are currently limited to very small equipment due to their high flammability (classified as A3), with safety regulations setting a 150 g limit. However, relaxing safety laws could be feasible with advancements in technology. CO_2 faces challenges in small to mid-size commercial chillers/refrigerators due to high working pressures and suboptimal performance in hot climates, though CO_2 multipack or rack systems are becoming more prevalent [32].

 CO_2 has garnered significant attention as a refrigerant, with the fourth generation of supermarket CO_2 units now emerging. It is also used in cascade systems with other natural refrigerants like ammonia, widely employed in warehouses and industrial refrigeration and heat pump systems. Stakeholders note that drawbacks of CO_2 include high working pressures necessitating robust equipment design and lower energy efficiency in warm climates.

Ammonia-based systems have proven efficient in industrial refrigeration for many years. Other alternatives to fluorinated gases are also viable for certain applications. While fluorinated gases currently dominate the industrial heat pump market in terms of efficiency, natural refrigerant alternatives could easily replace them. However, there may be specific processes or situations where fluorinated gases remain necessary.

It is asserted that a complete shift to natural refrigerants is already underway for new installations in commercial and industrial refrigeration, with training identified as the primary barrier to transitioning to natural alternatives in commercial refrigeration. Similar transitions are anticipated within the air conditioning and heat pump sector over the next decade.

According to stakeholder insights, it is technically feasible to eliminate fluorinated gases from domestic, commercial, and heat pump refrigeration today. Commercial and industrial applications

using CO_2 as a refrigerant are already feasible and in use. However, concerns about flammability with hydrocarbons and cost remain potential barriers to fully substituting fluorinated gases. In commercial and industrial refrigeration, large-scale refrigeration below -50°C is projected to continue relying on fluorinated gases for the next decade, particularly for storing medical (e.g., vaccines) or biochemical materials.

In refrigeration equipment used in industrial, laboratory, medical, and measurement applications, fluorinated gases offer precise temperature control, while non-PFAS alternatives can achieve the entire temperature range, no single non-PFAS refrigerant appears to match the broad operational flexibility of fluorinated gases. Hence, fluorinated gases may hold an advantage in equipment where temperatures frequently vary throughout the range.

1.5 Degradation in TFA and risk assessment

Quantifying emissions of per- and polyfluoroalkyl substances (PFAS) in refrigerant systems presents significant challenges due to a lack of comprehensive data and the complex nature of these substances. Various sources of PFAS emissions, including refrigerants, make it difficult to isolate and measure their specific contributions to atmospheric contamination.

Recent studies have particularly focused on trifluoroacetic acid, a degradation product of hydrofluoroolefins (HFOs) used in modern refrigerants like R1234yf. Despite some progress, data on TFA and its environmental impact remains limited and inconsistent, hindering a full understanding of PFAS emissions from refrigerants [33].

Trifluoroacetic acid meets the definition of PFAS because it has a $-CF_3$ (methyl) radical on the molecule, and it has a high solubility in water, it's very persistent in the environment and it's considered very mobile [34].

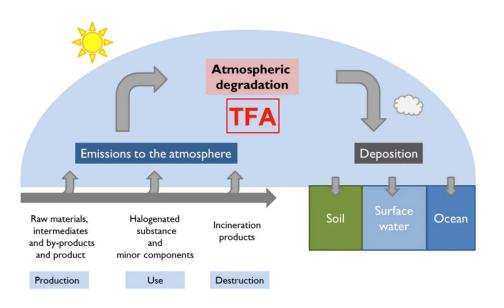


Figure 1-6 Atmospheric degradation of TFA

To derive the yield of trifluoroacetic acid (TFA) from a refrigerant liquid, one would start by examining the specific degradation pathways of the refrigerant in the atmosphere. This involves understanding the photolysis and hydroxyl radical reactions that lead to the formation of intermediate compounds such as trifluoroacetyl fluoride (TFAF), which then hydrolyzes into TFA. Quantifying the yield requires detailed knowledge of the reaction kinetics and atmospheric conditions, as well as accurate measurements of the initial refrigerant concentrations and the resulting TFA levels.

The Table 1-3 provides a comparison of various refrigerants, detailing their Ozone Depletion Potential (ODP), Global Warming Potential (GWP), whether they are classified as per- and polyfluoroalkyl substances (PFAS) according to the OECD and the yield of trifluoroacetic acid (TFA) from their atmospheric degradation [35].

Refrigerant	ODP	GWP	PFAS	TFA Creation
R744	0	1	No	No
R290 (Propane)	0	3	No	No
R717 (Ammonia)	0	0	No	No
R32	0	675	No	No
R134a	0	1430	Yes	10-20%
R448a	0	1386	Yes	20%
R455a	0	146	Yes	100%
R1234yf	0	<1	Yes	100%
R1234ze	0	<1	Yes	10%

Table 1-4 Detailed Analysis of Refrigerants [35]

1.5.1 Concentration of TFA measured in environment

1.5.1.1 Rainfall and snow

The presence of TFA in rain is well-documented, though its concentrations vary significantly across different locations. In California, studies reported TFA concentrations in fog and rain ranging from 31 to 3779 ng/L, with generally lower levels in more remote areas [38]. Observations in Switzerland confirmed this trend, showing TFA concentrations in rain and snow ranging from below the detection limit (3 ng /L in this study) to 1550 ng/L [39]. Notably, TFA concentrations were highest at the beginning of rainfall events, with the first millimeter of rain containing the greatest concentrations. This pattern aligns with TFA's high solubility in water and rapid partitioning from air to water.

1.5.1.2 Soils

Rain, fog, and snow effectively scavenge TFA from the atmosphere. In terrestrial systems, the initial contact point of precipitation, and thus TFA, is vegetation, soil, and surface water. Upon contact with soil or surface water, TFA reacts with minerals to form salts. noted that TFA retention in soils is generally poor but is greater in soils with higher organic matter content.

Measured TFA concentrations in soils are relatively low in Canada, values ranged from <0.0 to 1400 ng/kg dry weight of soil; in the UK, 850 to 5000 ng/kg d.w.; and in Chile, 100 to 9400 ng/kg d.w.

These low concentrations suggest that soils are not a significant repository or terminal sink for TFA salts in the environment, consistent with the known chemical properties of these salts [40].

1.5.1.3 Surface Waters

Concentrations of TFA in surface waters vary widely based on location, season, and type of water body. Recent studies, continue to reflect this variability. Measurements from diverse locations indicate existing TFA concentrations of 100 to 300 ng a.e./L in water, with one site (the Dead Sea) showing a concentration of 6400 ng a.e./L. This high concentration is attributed to the accumulation of TFA-salts over thousands of years [41].

In a modeling study on the projected use of R1234yf in the USA, it is predicted that concentrations of TFA-salts in terminal water bodies in North America could increase to 1000 –15000 ng/L after 50 years of use. In specific locations, such as playas in the Sonoran Desert, concentrations could rise to 40000 to 200000 ng/L over the same period. This is likely due to the proximity of the Sonoran Desert to major sources of TFA, such as California [42].

1.5.1.4 Oceans

TFA concentrations have been measured in various oceanic regions. In the mid-Atlantic and the Southern Ocean off Elephant Island, concentrations were consistently around 200 ng/L at depths ranging from the surface to 4150 meters. Measurements in the Western and Eastern Arctic, the North Atlantic, and the North and South Pacific showed concentrations up to 200 ng/L, with some as low as 1 ng a.e./L. The reasons for the lower concentrations in the Pacific compared to the Atlantic are unclear. Overall, a general value of 200 ng/L is considered representative for TFA concentrations in the oceans.

The projected contribution of TFA from the use of HFC and HFO refrigerants and blowing agents up to 2050 is estimated to be 15.3 ng/L, which would add about 7.5% to the levels measured in the year 2000. The total concentration of TFA, expressed as the sodium salt, is 256 ng/L.

1.5.2 Toxicity

Like other strong acids such as sulfuric or nitric, high concentrations of TFA can damage organisms due to its acidity. This mode of toxicity is relevant only to organisms exposed to TFA in precipitation or through any dry deposition from the atmosphere. However, the amounts of sulfuric and nitric acids in acid rain are significantly greater than those of TFA and are known to increase the acidity of surface waters.

TFA salts are neutral, chemically unreactive, and there is no known specific receptor to which they bind to initiate a biological response. However, effects have been reported at high exposure levels, which are discussed in the following sections.

1.5.2.1 Mammals

Mammals exhibit insensitivity to TFA and its salts. The acute oral no-observed-effect concentration (NOEC) for TFA in rats is 250 mg/kg body weight (b.w). For humans, the threshold concentration for respiratory irritation after a one-minute exposure is 0.25 mg/L of air. The acute NOEC for the sodium salt of TFA in rats is \geq 5000 mg/kg b.w., and the 8-day chronic oral no-observed-effect level (NOEL) for the sodium salt in rats is 114 mg/kg b.w./day.

There have been no published tests on the carcinogenicity or reproductive toxicity of TFA or its salts. While toxicity tests in other terrestrial vertebrates, such as birds, have not been published, it is expected that TFA would not be significantly more toxic to other vertebrates than it is to mammals.

1.5.2.2 Environmental

Due to its widespread presence in the environment and high solubility in water, trifluoroacetic acid is most likely to affect terrestrial and aquatic organisms.

In a study with 2-year-old pine (Pinus ponderosa) seedlings exposed to TFA in fog chambers at concentrations of 150 and 10000 ng/L, no adverse physiological, morphological, or photosynthetic effects were observed. Higher concentrations were not tested, so the no-observed-effect concentration (NOEC) was not determined [43].

1.5.3 Risk assessment of TFA

The risks of TFA in various environments were assessed by comparing exposure values with toxicity values, specifically the most sensitive NOEC (no-observed-effect concentration). Exposure values were derived from the highest measured concentrations in surface waters discussed earlier. These comparisons, representing a worst-case scenario, were made by calculating the margin of exposure (MoE), which is the ratio of the exposure concentration to the toxicity value.

MoE is a widely used metric for assessing chemical toxicity risk. For non-carcinogenic compounds in humans, an MoE of 100 between the dose and the NOEC is deemed acceptable. For other organisms in the environment, acceptable MoEs range from 1 to 100, depending on the organism's response, its role in the ecosystem, and its ability to recover from any adverse effects.

Human exposure to TFA (salts) through drinking water was estimated based on the WHO standard of 2 liters per day for a 60 kg person. The highest concentration found in drinking and surface water was used as the exposure level, and the NOEC from rat studies served as the toxicity reference. The margin of exposure (MoE) was adjusted to reflect the daily intake for a 60 kg individual. This approach is considered conservative enough to ensure protection for other vertebrates in the environment.

For terrestrial plants directly exposed to TFA via fog or rain, the maximum TFA acid concentration reported in fog was used as the exposure value. The toxicity reference came from pine trees exposed to TFA acid in fog chambers. For plants exposed via soil, the highest measured TFA-salt concentration in soil was used as the exposure value, compared to the toxicity value for plants exposed via roots from an aqueous solution. In this analysis, soil density was assumed to be 1.5 kg/L, and the toxicity value was adjusted accordingly.

The margins of exposure (MoEs) for the described exposure scenarios are presented in Table 1-5. The risks from TFA for humans and terrestrial vertebrates are clearly minimal. The MoEs are extremely large, suggesting that even if exposures were to increase soon, the risks would likely remain negligible.

The risks to plants exposed via soil are negligible, with a Margin of Exposure (MoE) exceeding 100. In contrast, for plants exposed to TFA through fog or precipitation, the calculated MoE is low. However, this is based on a NOEC of 10000 ng/L, which represents the highest concentration tested in the study examining plant responses to TFA deposition. It is plausible that higher concentrations could yield a larger NOEC. Moreover, concentrations of 10000 ng/L are likely transient, occurring mainly at the onset of precipitation events. Subsequent precipitation typically contains lower TFA concentrations and washes off initial deposits from plants, thereby reducing TFA-acid exposures for terrestrial plants.

Exposure Scenario	Value	Toxicity value	MoE
Drinkingwater	183 ng salt/L	114000000 ng salt/kg/day	18698000
Surface freshwater	968 ng salt/L	114000000 ng salt/kg/day	3535000
Max concentration in soil	11092 ng salt/kg	3750000 ng salt/kg	338
Max concentration in fog and rain	3779 ng acid/L	10000 ng acid/L	3

Table 1-5 Margins of Exposure

1.5.4 Conclusions

This assessment report demonstrates a comprehensive understanding of TFA formation from HCFCs, HFCs, and HFOs, bolstered by reliable estimates of their usage and potential release thanks to the Montreal Protocol. The assessment aimed to determine whether the concentrations of TFA in the environment are greater than the no-observed-effect-concentration (NOEC) for various species. Using data from worst-case measured concentrations and extrapolations to 2050 of inputs from sources of TFA regulated and monitored under the Montreal Protocol, it was concluded that TFA is not expected to exceed these toxicity values. It was found that the current and estimated concentrations of TFA and its salts in the environment resulting from the degradation of HCFCs, HFCs, and HFOs do not present a risk to humans and the environment.

However, several critical uncertainties and issues undermine this conclusion:

- Lack of Comprehensive Data: There is insufficient information on the toxicity of TFA and its salts to terrestrial plants and no data on organisms found in salt lakes and playas, which are key accumulation sites due to their endorheic nature. This significant data gap calls for immediate attention to better understand the full impact of TFA on diverse ecosystems.
- 2. Underestimation of Risks: The report suggests that the risks to humans and the environment are minimal. Yet, it acknowledges that TFA is very persistent in the environment, and concentrations will continue to increase in terminal sinks. The long-term effects and potential bioaccumulation in vulnerable ecosystems have not been thoroughly assessed. The high persistence of TFA indicates that concentrations will likely continue to rise over time, necessitating more comprehensive risk evaluations.
- 3. Exponential Increase in Ambient Concentrations: The formation of TFA from the degradation of HCFCs, HFCs, and HFOs, as well as from other anthropogenic sources, is expected to lead to an exponential rise in ambient concentrations. This is particularly concerning given the widespread use of chemicals that can degrade into TFA, coupled with the lack of a global

inventory on the use and environmental release of these substances. The projected increase in TFA levels highlights the urgent need for continuous monitoring and more comprehensive studies.

Additionally, temporal and spatial sampling or measurements of TFA in oceans and flowing waters are limited, making it challenging to identify trends in TFA concentrations in these environments. It is crucial to initiate temporal monitoring of TFA in surface waters, particularly in vulnerable settings such as endorheic basins, to provide early assessments of potential accumulation trends.

While the assessment concludes that current and near-future levels of TFA in the environment pose minimal risks to humans and the environment, TFA exhibits high persistence, indicating that concentrations will likely continue to rise in terminal sinks over time. This persistence, coupled with the exponential rise of these substances in the environment, highlights the urgent need for more comprehensive data and a more cautious approach to assessing the risks of TFA.

Given these points, it is imperative that continuous monitoring and more comprehensive studies be undertaken to better understand the environmental fate and risks associated with TFA. Sustained attention is required due to TFA's exceptionally long environmental persistence and its potential longterm impact on ecosystems and human health.

2. Life Cycle Assessment

2.1 General Aspects of LCA

2.1.1 Set of Rules

In recent decades, the awareness of environmental importance has increased, and techniques have been developed to assess the environmental impacts associated with services and goods.

One of the techniques developed for this purpose is life cycle assessment. LCA can assist in:

- Identifying opportunities to enhance the environmental performance of products throughout their life cycle.
- Informing decision-makers in industry, government, or non-government organizations for strategic planning, priority setting, and product or process design or redesign.
- Selecting relevant indicators of environmental performance, including measurement techniques.
- Supporting marketing efforts, such as implementing an ecolabeling scheme, making environmental claims, or producing environmental product declarations [44].

The UNI EN ISO 14040 and 14044 standards provide a framework and guidelines for conducting Life Cycle Assessment (LCA). Here are the main topics covered in each standard:

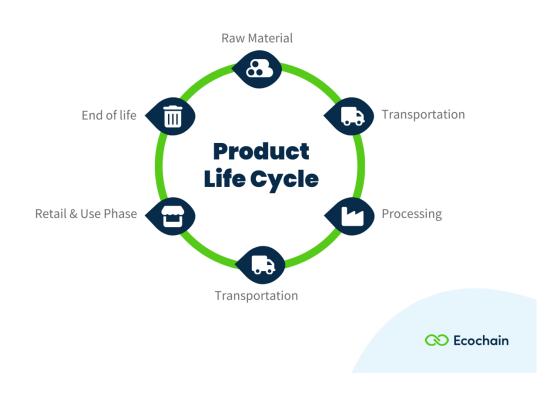
- UNI EN ISO 14040: Environmental Management, Life Cycle Assessment, Principles and Framework.
- UNI EN ISO 14044: Life Cycle Assessment, Requirements and Guidelines [45].

2.1.2 Product Life in LCA

To assess the life cycle of a product, we must first define its stages. Generally, the product life cycle consists of five main phases: Raw Material Extraction, Manufacturing & Processing, Transportation, Usage, and Disposal. Depending on the stages of interest or available data, certain phases can be included or excluded. Typically, four product life cycle models are available for LCA:

• Cradle-to-Grave: Analyzes a product's impact across all five life cycle stages—from raw material sourcing (cradle) to disposal (grave). Transportation, though listed as the third step, can occur between all stages.

- Cradle-to-Gate: Assesses a product until it leaves the factory, excluding the use and disposal phases. This simplifies the LCA and accelerates insights, especially for internal processes. This approach was common in environmental product declarations.
- Cradle-to-Cradle: A concept from the Circular Economy, this model replaces the waste stage with recycling, making the product reusable and effectively closing the loop. This is also known as closed-loop recycling.
- Gate-to-Gate: Focuses on a single value-added process within the production chain to reduce complexity. These assessments can later be combined for a comprehensive Life Cycle Assessment [46].



• Product Life Cycle

Figure 2-1 Product Life Cycle of LCA

2.1.3 Key steps of LCA

Let's delve deeper into the actual phases of an LCA, as defined in ISO standards 14040 and 14044.

Phases of a Life Cycle Assessment:

- Definition of Goal and Scope: Establishes the purpose, objectives, and boundaries of the LCA study.
- Inventory Analysis: Involves collecting and analyzing data on the inputs and outputs of the product system.
- Impact Assessment: Evaluates the potential environmental impacts associated with the inventory data.
- Interpretation: Analyzes results to draw conclusions, identify significant issues, and recommend improvements.

These phases are interdependent, as illustrated in Figure 2-2. The interpretation phase can occur alongside the other phases, even before the assessment is complete.

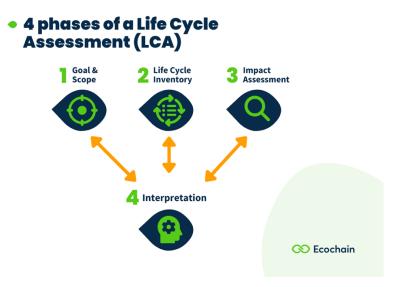


Figure 2-2 Key Steps of LCA

In more complex Life Cycle Assessments, continuously interpreting the results helps optimize the analysis as it progresses. Sometimes, it is necessary to revisit previous phases to incorporate new findings, which then influence subsequent phases. This iterative nature is a key characteristic of LCA [47].

2.2 SimaPro Software

SimaPro is a leading software tool designed for life cycle assessment (LCA) and sustainability analysis, offering a robust platform for evaluating the environmental impacts associated with products, services, and processes throughout their entire life cycle. Developed by PRé Sustainability, SimaPro is widely recognized and utilized by researchers, consultants, policymakers, and organizations across various industries to assess the ecological footprint of their operations and make informed decisions aimed at reducing environmental impact [48].

The software provides users with access to an extensive and regularly updated database of processes, materials, and energy sources. This rich dataset allows for precise modeling of complex systems, enabling users to analyze the environmental implications of every stage of a product's life, from raw material extraction and production to distribution, use, and end-of-life disposal or recycling. SimaPro's flexibility and comprehensive features make it suitable for a wide range of applications, from product design and innovation to corporate sustainability reporting and regulatory compliance.

One of SimaPro's key strengths is its ability to perform detailed life cycle impact assessments (LCIA), which include calculations of carbon footprints, resource depletion, human health impacts, and ecosystem damage. The software supports various impact assessment methods, such as ReCiPe, IPCC 2021 GTP100 and USEtox, allowing users to select the most appropriate approach for their specific needs. Moreover, SimaPro enables scenario analysis, sensitivity testing, and data comparison, providing valuable insights into how different design choices or operational changes can influence environmental outcomes.

Overall, SimaPro serves as an essential tool for those committed to advancing sustainability, offering the analytical depth and reliability needed to support environmental decision-making and drive meaningful progress toward more sustainable practices. Whether used for academic research, corporate strategy, or policy development, SimaPro empowers users to better understand and mitigate the environmental impacts of their products and processes, ultimately contributing to a more sustainable future [49].

2.3 Case of study

The scope of the study is to evaluate the environmental impact assessment based on the operation of a medium-sized supermarket with a total refrigeration capacity of 140 kW, divided into 120 kW for medium-temperature (MT) and 20 kW for low-temperature (LT) refrigeration systems. The analysis covers the impact of different refrigerant cascade configurations, specifically R455A MT + R744 LT, R1234ze MT + R744 LT, and a R744 transcritical configuration, across three distinct locations: Palermo, Ravenna, and Stockholm. The functional unit represents is the operation of the supermarket's refrigeration systems over a ten-year period under typical usage conditions.

2.3.1 Cascade Refrigeration Systems

A cascade refrigeration system is a sophisticated technology designed to achieve extremely low temperatures by utilizing multiple refrigeration cycles, each operating within its optimal temperature range. This approach is necessary in various industrial and scientific applications where conventional refrigeration systems, which typically operate using a single refrigeration cycle, would struggle to achieve the desired temperatures.

In a cascade refrigeration system, the cooling process is divided into multiple stages, each stage representing a complete refrigeration cycle. These cycles are connected in a series, where the evaporator of one cycle is used to cool the condenser of the subsequent, lower-temperature cycle. This cascading effect allows each stage to progressively lower the temperature, with the final stage achieving the ultra-low temperatures required for specific applications [50].

The operation of a cascade system begins with the high-temperature cycle, which functions similarly to a conventional refrigeration system. The primary purpose of this stage is to remove the initial heat from the system and cool down the condenser of the next cycle in the series. As the refrigerant in this stage absorbs heat, it evaporates and is then compressed, releasing heat in the condenser. This cooled condenser, in turn, serves as the evaporator for the next refrigeration stage.

The subsequent stage, or stages, operate at increasingly lower temperatures. These stages use refrigerants specifically chosen for their ability to function effectively at lower temperatures. The refrigerant in the second stage absorbs heat from the condenser of the first stage and evaporates at a lower temperature, further cooling the system. This process is repeated across as many stages as necessary to achieve the desired low temperature.

A critical component in the cascade refrigeration system is the heat exchanger, which is placed between the stages. The heat exchanger serves as the interface where heat is transferred from one refrigerant to the next. In a two-stage cascade system, the heat exchanger allows the high-temperature refrigerant to transfer its absorbed heat to the lower-temperature refrigerant. This heat transfer process is essential for the system's efficiency, as it allows the refrigerants to function within their optimal temperature ranges, reducing the energy required to achieve ultra-low temperatures [51].

Cascade refrigeration systems are highly efficient because they distribute the cooling load across multiple stages. Each stage operates under conditions where it is most effective, thereby reducing the overall energy consumption and mechanical wear on the compressors. By minimizing the temperature drop that each stage needs to achieve, the system reduces the pressure differential in each compressor, leading to lower energy usage and potentially longer system life.

In this case study, there are two configurations for the refrigeration system:

- First Configuration: This is a cascade cycle where R455A is used for the medium-temperature (MT) stage, and R744 is used for the low-temperature (LT) stage of the cascade system. Additionally, it includes an auxiliary glycol water circuit, which is used to transfer heat within the system and enhance overall efficiency.
- Second Configuration: This setup uses R1234ze as the refrigerant for the medium-temperature (MT) stage and R744 for the low-temperature (LT) stage. Also in this case is used the glycol water circuit.

2.3.2 Subcritical and Transcritical Behaviour of R744

In the case of transcritical configuration of R744 the role of the critical point of CO₂ is crucial. This chemical compound has a critical temperature of 31.1°C, a critical pressure of 7.38 MPa (73.8 bar) and presents several challenges when used as a refrigerant. Due to its relatively low critical temperature, CO₂ often operates at or above this critical point in many practical scenarios, particularly in warmer climates or high ambient temperatures. This behavior differs significantly from traditional refrigerants, leading to technical and operational difficulties [52].

One major issue is the lack of a phase change from vapor to liquid on the high-pressure side of the refrigeration cycle when operating above the critical temperature. In standard refrigeration systems using HFCs or HCFCs, the refrigerant condenses from vapor to liquid in the condenser, allowing efficient heat rejection at a nearly constant temperature. In contrast, in CO₂ systems that operate in the supercritical region, there is no distinct phase change. Instead, CO₂ behaves as a supercritical

fluid, and heat rejection occurs in a component called a gas cooler rather than a condenser. This process involves lowering the temperature of the supercritical fluid without the benefit of latent heat removal, making heat rejection less efficient and reducing overall cycle efficiency.

This inefficiency is especially noticeable in warm climates. In transcritical cycles, where CO_2 operates above its critical temperature, the system struggles with heat rejection because the temperature difference between the refrigerant and the environment is smaller. Consequently, the coefficient of performance (COP) of the system declines significantly in higher ambient temperatures. This limits the effectiveness of CO_2 refrigeration systems in hot climates and during summer, necessitating additional engineering solutions to maintain acceptable performance.

Another challenge is the high operating pressures required for CO₂ systems. Even in subcritical operation, CO₂ systems operate at much higher pressures compared to those using traditional refrigerants. In transcritical operation, pressures can exceed 100 bar, which imposes significant demands on system components. Compressors, heat exchangers, piping, and valves must be specially designed to handle these high pressures, increasing complexity, costs, and safety considerations. The need for high-pressure equipment is a major barrier to the widespread adoption of CO₂ systems in some markets.

Additionally, the increased pressures lead to higher compressor work. In transcritical operation, the compressor must work harder to achieve the necessary cooling effect, further reducing system efficiency. This additional energy consumption lowers the overall system performance, particularly compared to systems with refrigerants that can efficiently operate subcritically under similar conditions.

2.3.2.1 The Cycle

In a CO₂ transcritical refrigeration cycle, the evaporator operates in the subcritical region, while the gas cooler functions in the supercritical region. The pressure-enthalpy diagram illustrates the differences between conventional and transcritical refrigeration cycles. In transcritical cycles, heat absorption occurs below the critical temperature, keeping the evaporator pressure subcritical, similar to traditional vapor compression systems. However, during heat rejection, unlike subcritical cycles where the refrigerant changes phase at a constant temperature, the refrigerant's temperature decreases continuously in transcritical cycles without a phase change.

Although latent heat exchange during phase changes is highly efficient, the unique supercritical properties of CO₂ make it suitable for transcritical refrigeration systems. The large pressure difference

between heat absorption and heat rejection processes in transcritical cycles leads to significant thermodynamic losses during expansion. However, this pressure difference allows the use of expansion work recovery devices to partially recover energy lost during throttling in transcritical CO_2 cycles.

In terms of compression, conventional subcritical cycles usually operate with a pressure ratio up to eight, while transcritical cycles have a lower pressure ratio, typically between three and four. These lower compression ratios are beneficial for achieving high isentropic efficiency in transcritical heat pump systems [53].

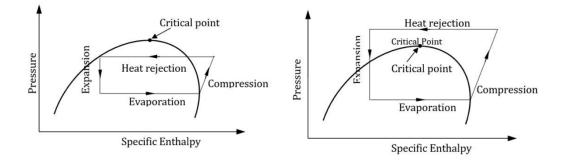


Figure 2-3 p-h Graphs for Subcritical and Transcritical Cycles [54]

2.4 Goal and Scope definition

To gain a more precise understanding of the environmental impact of supermarkets, it is essential to analyze each component of the system. This includes not only manufacturing processes, such as the use of raw materials, but also the operational phase, where both direct and indirect impacts come into play. Direct impacts involve factors like refrigerant and lubricant oil leaks, as well as maintenance activities. Indirect impacts are largely shaped by the supermarket's location, influencing aspects such as energy consumption. Furthermore, the disposal of materials at the end of the system's life cycle must also be carefully considered.

This study adopts a cradle-to-grave perspective, providing a comprehensive view of the environmental impacts from the production of materials through to their disposal.

However, it's important to note that this study has some limitations, primarily due to the reliance on data sourced from existing literature. While this provides a solid foundation, the study could be further enhanced and made more accurate by incorporating real-world data. This would help in refining the analysis and offering a more detailed understanding of the environmental impact of supermarkets.

2.5 Inventory analysis

2.5.1 Data Classification and Source

The data for this analysis were gathered from a variety of sources to ensure a comprehensive understanding:

- Literature: This includes research studies and academic papers that specifically examine the environmental impact of refrigeration systems. These studies provide valuable insights into the effects of refrigeration technologies on the environment and are crucial for contextualizing the data.
- Real-World Data: Data were obtained from an actual refrigeration facility located in Italy. This real-world data provides practical, on-the-ground information and helps to ground theoretical insights in actual operational conditions.
- Ecoinvent: Data were sourced from Ecoinvent, with a focus on version 3.10. It is a wellestablished database that offers detailed life cycle inventory data, which is essential for assessing the environmental impacts of various technologies and processes.

These diverse sources contribute to a robust and well-rounded analysis, integrating theoretical research with practical and standardized data.

2.5.2 Cabinets

In the context of a supermarket design study, the first components analyzed are the cabinets, which are placed in the supermarket according to the layout of a real system. The types of cabinets and their dimensions are based on actual specifications found on the manufacturer's website.

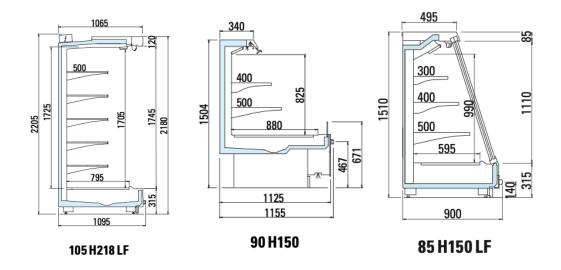


Figure 2-4 Section of LISBONA 2500/3750 105/218 2CLF [55], LONDON 3 90 H150 SE 2500 [56], SANTIAGO 3750 LF 85/150 [57]

The actual amount of raw materials used is taken from literature sources and is proportioned according to the size of the cabinets. This means that if the cabinets in the supermarket are larger or smaller than standard models, the quantity of raw materials considered will be adjusted accordingly. This approach ensures that the supermarket design accurately reflects the real specifications of the components used and the resources required for their construction and operation [58].

	LISBONA 2500 105/218 2CLF
Overall Dimensions	2,2 x 1,1 x 2,5
Dimensions of Cooling Area	1,72 x 0,80 x 2,2
Туре	Semi - Vertical
Product Life	10 years
Ambient Temperature	22°C
Relative Humidity	75%
ChillingTime	24 h/day
Material	Quantity [kg]
Alluminium, cast alloy	10,98
Flat glass, coated	7,28
Steel, low-alloyed	101,95
Synthetic rubber	8,40
Polyphenylene sulfide	10,31
Glass fibre reinforced plastic	9,52
	LISBONA 3750 105/218 2CLF
Overall Dimensions	2,2 x 1,1 x 3,75
Dimensions of Cooling Area	1,72 x 0,8 x 3,45
Туре	Semi - vertical
Product Life	10 years
Ambient Temperature	22°C
Relative Humidity	75%
ChillingTime	24 h/day
Material	Quantity [kg]
Alluminium, cast alloy	16,47
Flat glass, coated	10,92
Steel, low-alloyed	152,93
Synthetic rubber	12,60
Polyphenylene sulfide	15,46
Glass fibre reinforced plastic	14,28
	LONDON 2500 3 90 H150 SE
Overall Dimensions	1,5 x 1,08 x 2,5
Dimensions of Cooling Area	1,2 x 0,80 x 2,2
Туре	Display - case
Product Life	10 years
Ambient Temperature	22°C
Relative Humidity	75%
ChillingTime	24 h/day
Material	Quantity [kg]
Alluminium, cast alloy	7,35
Flat glass, coated	4,88
Steel, low-alloyed	68,25
Synthetic rubber	5,63
Polyphenylene sulfide	6,90
Glass fibre reinforced plastic	6,38

The general characteristics and main materials are resumed in the following table:

	SANTIAGO 3750 LF 85/150
Overall Dimensions	1,5 x 0,90 x 3,75
Dimensions of Cooling Area	1,2 x 0,75 x 3,45
Туре	Vertical
Product Life	10 years
Ambient Temperature	22°C
Relative Humidity	75%
ChillingTime	24 h/day
Material	Quantity [kg]
Alluminium, cast alloy	9,19
Flat glass, coated	6,09
Steel, low-alloyed	85,31
Synthetic rubber	7,03
Polyphenylene sulfide	8,63
Glass fibre reinforced plastic	7,97
	POZZETTO 250 [59]
Overall Dimensions	1,04 x 0,86 x 2,5
Dimensions of Cooling Area	0,90 x 0,70 x 2,2
Туре	Display - case
Product Life	10 years
Ambient Temperature	22°C
Relative Humidity	75%
ChillingTime	24 h/day
Material	Quantity [kg]
Alluminium, cast alloy	4,06
Flat glass, coated	2,69
Steel, low-alloyed	37,68
Synthetic rubber	3,11
Polyphenylene sulfide	3,81
Glass fibre reinforced plastic	3,52

Table 2-1 Materials of Cabinets

In the simulation, the following components were used to ensure the closest possible alignment with the reference real system in fact are used:

- 6 LISBONA 2500 105/218 2CLF
- 6 LISBONA 3750 105/218 2CLF
- 4 LONDON 3 90 H150 SE 2500
- 10 SANTIAGO 3750 LF 85/150
- 12 POZZETTO 250

This configuration was selected to maintain the highest fidelity to the actual reference system.

2.5.3 Condensing units

In the next table, all the other components of a refrigeration system will be included. As previously mentioned, there are different configurations, and not all components are always present. Their quantities may vary depending on the specific configuration used.

Abbreviations are used in the table: "MH" indicates components related to traditional refrigerants such as R455A or R1234ze, while "CN" to natural refrigerants like R744.

Component	Material	Quantity [kg]
Anti-condensation	Synthetic rubber	2,28
	Aluminium, cast alloy	6,4
	Aluminium, wrought alloy	13,6
	Cast iron	30
	Copper	20
	Polystyrene	10
Compressor 10 kW	Sheet rolling, aluminuim	20
Compressor 10 kw	Sheet rolling, chromium steel	16
	Sheet rolling, steel	40
	Steel, chromium steel	16
	Steel, low alloyed	40
	Synthetic rubber	3
	Wire drawing, copper	20
	Aluminium, cast alloy	15
	Aluminium, wrought alloy	31,8
	Cast iron	70,2
	Copper	46,8
	Polystyrene	23,4
0.0000000000000000000000000000000000000	Sheet rolling, aluminuim	46,8
Compressor 30 kW	Sheet rolling, chromium steel	37,4
	Sheet rolling, steel	93,6
	Steel, chromium steel	37,4
	Steel, low alloyed	93,6
	Synthetic rubber	7
	Wire drawing, copper	46,8
	Aluminium, cast alloy	23,4
	Aluminium, wrought alloy	49,8
	Cast iron	109,8
	Copper	73,2
	Polystyrene	36,6
	Sheet rolling, aluminuim	73,2
Compressor 60 kW	Sheet rolling, chromium steel	58,6
	Sheet rolling, steel	146,4
	Steel, chromium steel	58,6
	Steel, low alloyed	146,4
	Synthetic rubber	11
	Wire drawing, copper	73,2
	Copper cake	213,50
Condenser	Steel, low-alloyed	106,75
	Steel, chromium steel	36,75
Control Unit	Electronics, for control unit	8,35
Crankaass haster	Cable	1,23
Crankcase heater	Polyvinyldechloride	1,23
Drier filter CN	Steel, chromium steel	17,11
Drier filter MH	Steel, chromium steel	23,33
	Steel, chromium steel	178,50
Gascooler	Copper cake	106,75
	Steel, low-alloyed	141,75

Component	Material	Quantity [kg]
	Brass	6,30
Hardware, Collars, Fittings CN	Copper cake	15,75
Hardware, Collars, Hittings Civ	Steel, low-alloyed	4,73
	Polypropylene	3,15
	Brass	3,50
Hardware, Collars, Fittings MH	Copper cake	8,75
Hardware, Oottars, Hittings Hit	Steel, low-alloyed	2,63
	Polypropylene	1,75
Heat Exchanger	Steel, chromium steel	66,15
Liquid indicator	Brass	3,50
Liquid Receiver CN	Steel, chromium steel	140,00
Liquid Receiver MH	Steel, chromium steel	79,36
	Steel, chromium steel	84,00
Motor Fans	Aluminium, cast alloy	56,00
	Copper cake	66,50
Muffler	Steel, chromium steel	22,05
Pipes CN	Brass	28,18
Pipes MH	Brass	41,48
Pressure switches, Pressure proves and Gomax	Steel, low-alloyed	5,60
	Cast iron	60,00
	Aluminium, wrought alloy	1,00
Pump	Steel, chromium steel	46,00
rump	Copper	12,50
	Polyvinylchloride	1,5
	Synthetic rubber	0,35
Shut off valves and Solenoid valves CN	Brass	24,50
Shut off valves and Solenoid valves MH	Brass	28,00
Vibration Dampers	Brass	7,00
vibration Dampers	Steel, low-alloyed	7,00

Table 2-2 Materials	of Condensing Units
1 4010 2 2 1114101 1415	of condensing enns

The data were gathered from a combination of existing literature and, where available, from manufacturers' data sheets [60]. This approach ensures a comprehensive understanding by incorporating both published research and specific technical details provided by the manufacturers.

2.5.4 Refrigerants, Lubricating oil and Water Glycol

Another aspect to consider in the manufacturing phase is the initial quantity of refrigerant and lubricating oil. In this case, there are baseline data available from the literature that can be scaled according to the specific configuration being analyzed. For systems using traditional refrigerants, the data vary depending on the specific refrigerant used, particularly in relation to the liquid density [61].

The data are summarized in the following table:

Configuration	Refrigerant	CASNumber	Initial Quantity [kg]
R455A + R744	R455A	754-12-1	305,13
N433A + N744	R744	124-38-9	68,76
R1234ze + R744	R1234ze	29118-24-9	343,53
N123428 T N744	R744	124-38-9	68,76
R744 + R744	R744	124-38-9	481,32

Table 2-3 Initial Quantities of Refrigerants

Lubricating oil is vital in a refrigeration system because it reduces friction between moving parts, which helps prevent mechanical failure and wear. It also aids in heat transfer by absorbing and dissipating heat, seals gaps to improve efficiency, protects against corrosion by forming a protective layer on metal surfaces, and helps remove contaminants. The quantity is taken by literature.

Configuration	Initial Quantity [kg]
R455A + R744	14,28
R1234ze + R744	14,28
R744 + R744	4,2

Table 2-4 Initial Q	uantities o	of Lubricating	Oil
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In addition to traditional refrigerants, some refrigeration systems use a glycol-water (30%-70% by mass respectively) mixture to facilitate heat exchange between the medium temperature (MT) and low temperature (LT) sides of the system. In this case also the quantity is taken by literature [62].

Configuration	Initial Quantity [kg]
R455A + R744	1554,92
R1234ze + R744	1554,92

Table 2-5 Initial	Quantities	of	Glycol	Water
Tuble 2-5 Iniliai	Quantities	ΟJ	Giyeoi	muler

Refrigerants are not always available in the SimaPro database, so they were created manually by combining other chemical reagents. This process was guided by methodologies outlined in scientific articles, ensuring that the properties and environmental impacts of the refrigerants were accurately represented in the simulation. By following these established methods, it's possible to construct a reliable model of the refrigerants for use in the analysis.

2.5.4.1 R32

R-32, also known as difluoromethane, is a refrigerant commonly used in air conditioning and refrigeration systems. It belongs to the hydrofluorocarbon (HFC) family and has the chemical formula CH_2F_2 . It is valued for its lower global warming potential GWP of 675, which is significantly lower than that of many other refrigerants. R-32 is not available in the SimaPro database.

Fluorination of dichloromethane (DCM) with hydrogen fluoride (HF) involves a reaction where HF adds fluorine atoms to the molecule. DCM is a dichlorinated methane where both hydrogens are replaced by chlorine atoms [63]. The reaction is the following:

$$CH_2Cl_2 + 2HF \rightarrow CH_2F_2 + 2HCl$$

2.5.4.2 R1234yf

R-1234yf, chemically known as 2,3,3,3-tetrafluoropropene, is a next-generation refrigerant designed to be a more environmentally friendly alternative to traditional refrigerants with high Global Warming Potential (GWP), such as R-134a. R-1234yf has a GWP of 4, making it significantly less impactful on global warming compared to older refrigerants like R-134a, which has a GWP of about 1,430.

The formation of R-1234yf involves a series of chemical reactions, including fluorination and methylation steps. While the complete process includes several intermediate reactions, it can be simplified into a single overall reaction for clarity [64].

$$C_2ClF_3 + CH_3Cl + 2HF \rightarrow C_3H_2F_4 + HCl + HClF$$

In this simplified representation, HClF appears as a product but it is important to note that does not have a specific chemical role in this context. Its presence is a result of the simplifications made for the overall reaction and the focus on summarizing the process into a single, straightforward equation.

Chlorotrifluoroethylene (C₂HClF₃) is a starting reagent for this reaction. However, it is not included in SimaPro database, so it is necessary to synthesize or obtain chlorotrifluoroethylene separately to conduct this reaction.

To synthesize chlorotrifluoroethylene (C₂HClF₃) from trichloroethylene, zinc, and hydrogen fluoride (HF), the process involves a combination of reduction and fluorination steps.

Initially, trichloroethylene (C₂HCl₃) is reacted with zinc. Zinc acts as a reducing agent, helping to replace some of the chlorine atoms with hydrogen, which leads to the formation of an intermediate

compound. This intermediate is not always explicitly detailed, but it typically has fewer chlorine atoms.

This intermediate is treated with hydrogen fluoride (HF). HF provides the fluorine atoms needed to replace the remaining chlorine atoms. In this fluorination step, HF reacts with the intermediate to introduce fluorine atoms, resulting in chlorotrifluoroethylene (C₂HClF₃).

The overall reaction is:

$$C_2HCl_3 + 3HF + Zn \rightarrow C_2ClF_3 + 2HCl + H_2 + ZnCl_2$$

2.5.4.3 R1234ze

R-1234ze, chemically known as 1,3,3,3-tetrafluoropropene, is a refrigerant belonging to a group of hydrofluoroolefins (HFOs) designed to be more environmentally friendly alternatives to older refrigerants with higher Global Warming Potential (GWP). It has a very low GWP of 7.

To synthesize R-1234ze (1,3,3,3-tetrafluoropropene) starting from ethylene (C_2H_4) and carbon tetrachloride (CCl_4), the process involves a series of chemical reactions, primarily fluorination steps.

Initially, ethylene reacts with carbon tetrachloride in the presence of a fluorinating agent like hydrogen fluoride (HF). This reaction produces 1,1,2,2-tetrafluoroethane (C₂H₂F₄) as an intermediate, along with hydrochloric acid (HCl).

In the next step, 1,1,2,2-tetrafluoroethane undergoes further fluorination or rearrangement to produce 1,3,3,3-tetrafluoropropene (R-1234ze). This reaction also uses HF and produces additional HCl as a byproduct [65].

The overall reaction is:

$$5C_2H_4 + 8CCl_4 + 24HF \rightarrow 6C_3H_2F_4 + 32HCl$$

2.5.4.4 R455A

R-455A is a refrigerant designed as an environmentally friendly alternative to traditional refrigerants with higher Global Warming Potential (GWP). It has a low GWP of approximately 148, significantly lower than many conventional refrigerants.

The composition is the following [66]:

Material	Portion (%)	CASNumber
R1234yf	75,5	754-12-1
R32	21,5	75-10-5
R744	3	124-38-9

Table 2-6 Composition of R455A

In the results of chemical reactions, there are byproducts such as HCl (hydrochloric acid) that, although generated, are considered in Life Cycle Assessment (LCA) studies because they can be reused in industrial processes. The allocation of environmental impacts in such cases is based on mass, meaning the impacts are distributed according to the mass of each component, including reusable byproducts like HCl. This ensures that the benefits of recycling or reusing these substances are factored into the overall environmental assessment.

2.5.5 Assembly, Transport and Metal Working

The final part of the manufacturing phase is the assembly process. This step varies depending on the type of circuit and the specific refrigerant being used. The variations in the assembly process are determined by factors such as the physical properties of the refrigerant, the pressure and temperature requirements of the system, and the compatibility of materials used in the circuit. For instance, certain refrigerants may require specialized seals or insulation materials to prevent leaks or to ensure efficient operation, while others might necessitate different methods for connecting components within the circuit.

The transportation of components has not been manually included in the simulation to ensure the fairest possible comparison between different locations. The aim is to compare markets without the impact of transportation data affecting the results.

For instance, it wouldn't be realistic to assume that a single producer could serve both the Swedish and Italian markets, given the distance and logistical differences. Instead, the simulation uses "market" processes, which already account for transportation costs based on average values. This approach maintains consistency and fairness in the analyzed data, avoiding distortions from nonuniform transportation variables.

The metal working processes have been incorporated into SimaPro to achieve a more accurate and realistic simulation. Metal working refers to the various processes and techniques used to shape, treat, and finish metals, including activities such as casting, forging, welding, and machining. It is important to note that the values can vary depending on the specific systems and technologies used in these processes. By including these processes in the model, the simulation provides a more detailed and realistic analysis of the environmental impacts and energy consumption associated with metal products, thereby enhancing the quality and reliability of the assessments.

The chosen method involves directly integrating the metalworking processes of aluminum, chromium steel, copper, and steel into the "process" of the specific component under consideration. This means

that instead of treating the metalworking steps separately, they are included within the overall lifecycle of the component, reflecting the actual production workflow more accurately. This approach ensures that the environmental impacts and resource usage associated with the metalworking of these materials are directly accounted for in the analysis of the component itself.

2.6 Use Phase

2.6.1 Direct Emissions

Direct emissions refer to the release of greenhouse gases (GHGs) or other pollutants directly from a source into the atmosphere. These emissions occur because of activities where the emissions are physically produced on site.

They are primarily due to:

- Refrigerant Leakage: This is the most significant source of direct emissions. Two different annual leakage rates are considered: 5% and 10%. This involves adding new refrigerant to replace what has been lost, contributing to direct emissions. In the configurations with glycol water circuit, it's considered also a loss of it equal to the 10% annually.
- Lubricating Oil Loss: Lubricating oil used in the system is replaced annually. The process of replacing the oil results in emissions due to the handling and disposal of the used oil.
- Spare Parts Replacement: When spare parts are replaced, emissions can occur due to the production, transportation, and disposal of these components.

Together, these factors contribute to the overall direct emissions from the system.

	R455A (a) + R744 (b)	R1234ze (a) + R744 (b)	R744 + R744
Refrigerant leakage (5%) [kg]	152,57 (a) + 34,38 (b)	171,77 (a) + 34.38 (b)	240,66
Refrigerant leakage (10%) [kg]	305,13 (a) + 68,76 (b)	343,53 (a) + 68,76 (b)	481,32
Lubrificating oil [kg]	142,8	142,8	42
Polypopylene Granulate (condenser fan) [kg]	172,2	172,2	172,2
Glass (evaporator fan) [kg]	182	182	182
Synthetic Rubber [kg]	148,82	148,82	148,82
Glycol Water [kg]	1554,92	1554,92	0

Table 2-7 Use Phase Parameters

The condenser fan, constructed from fiber-reinforced polypropylene granulate, is designed to have a lifespan of 5 years. Over a 10-year period, this component is replaced twice. Similarly, the glass used in evaporator fans, which also has an estimated 5-year lifespan, is replaced twice within the same 10-year timeframe. Synthetic materials, often used in parts susceptible to condensation, follow the same replacement schedule, twice in 10 years.

2.6.2 Indirect emissions

Indirect emissions in a refrigeration system refer to the CO_2 and other greenhouse gas emissions associated with the energy consumption of the system. These emissions do not come directly from the refrigeration system itself but are instead linked to the electricity consumption required to operate various components of the system. Therefore, indirect emissions are related to the environmental footprint of the electricity generation used by the system.

Influence of Energy Mix and Ambient Temperature:

- Energy Mix: The footprint of the electricity used by the refrigeration system varies depending on the energy mix of the country. For example, in a country with a high proportion of renewable energy the indirect emissions associated with the system's energy consumption will be lower. Conversely, in a country where coal is the dominant energy source, indirect emissions will be higher due to the greater carbon intensity of coal-fired power plants.
- Ambient Temperature: The local climate also plays a crucial role in determining the energy consumption of a refrigeration system. In warmer climates, the system needs to work harder to maintain the desired temperatures, leading to increased energy consumption and, consequently, higher indirect emissions. Cooler climates, on the other hand, can reduce the system's workload and energy consumption.

To illustrate these factors, three different locations were chosen: Ravenna, Palermo, and Stockholm. These locations represent a range of climatic conditions and energy mixes:

- Ravenna (Italy): Located in northern Italy, Ravenna has a moderate climate. Italy's energy mix includes a significant share of natural gas, along with renewables like hydroelectric power.
- Palermo (Italy): Situated in southern Italy, Palermo experiences a warmer Mediterranean climate, requiring more energy for cooling. The energy mix is equal to that of Ravenna but with a higher demand for cooling energy.
- Stockholm (Sweden): Stockholm has a cold climate, which generally reduces the energy required for refrigeration. Sweden's energy mix is notably clean, with a large proportion of electricity coming from hydroelectric and nuclear power, resulting in lower indirect emissions.

By analyzing these three locations, it becomes clear how both the energy mix and ambient temperature can significantly influence the indirect emissions of refrigeration systems. This comparison highlights the importance of considering both factors when assessing the environmental impact of refrigeration systems across different regions.

Energy Mix	Energy Source	Electricity [GWh]	Share
	Natural Gas	138615	48,4%
	Hydro	30086	10,5%
	Solar PV	28121	9,8%
	Coal	27543	9,6%
Italy	Wind	20558	7,2%
	Oil	15554	5,4%
	Biofuels	15175	5,3%
	Geothermal	5816	2,1%
	Waste	4628	1,7%
	Hydro	70300	40,6%
	Nuclear	51944	30,0%
	Wind	33088	19,1%
Sweden	Biofuels	9435	5,4%
	Waste	5169	3,0%
	Solar PV	1963	1,1%
	Fossil Fuels	1296	0,8%

Table 2-8 Energy Mix of Italy and Sweden [67][68]

The first step in the analysis is to obtain hourly temperature data for the entire year for each of the three locations: Ravenna, Palermo, and Stockholm. This data can be sourced from reputable meteorological databases, which provide detailed historical weather information [69][70].

Once the hourly temperature data is collected for each location, the next step is to categorize the temperatures into six different ranges. The goal is to ensure that each temperature range covers approximately the same number of hours over the year. However, the specific temperature thresholds for these ranges will vary depending on the local climate, as each location has a unique temperature distribution.

After dividing the temperature data into the six ranges, the next step is to calculate the weighted average temperature for each location.

City	Min Temperature [°C]	Max Temperature [°C]	N. Hours [h]	Weighted Temperature [°C]
	-4	7	1551	3,92
	7	11	1462	8,46
Ravenna	11	16	1496	13,02
Navenna	16	20	1353	17,49
	20	25	1424	22,05
	25	36	1474	27,77
	4	12	1293	9,10
	12	15	1281	13,02
Palermo	15	19	1755	16,52
raterino	19	23	1614	20,56
	23	27	1548	24,45
	27	45	1269	29,68
	-14	-1	1321	-4,22
	-1	3	1629	0,45
Stockholm	3	7	1497	4,26
Stockhoth	7	13	1270	9,48
	13	17	1535	14,66
	17	29	1501	19,62

Table 2-9	Temperature	Ranges	for	each	City
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The cooling capacity is 120 kW for medium-temperature conditions and 20 kW for low-temperature conditions. Specifically:

- In the case of the R455A + R744 refrigerant system, there are two compressors of 30 kW and one compressor of 60 kW for medium-temperature, while there are two compressors of 10 kW for low-temperature.
- For the R1234ze refrigerant system, there are four compressors of 30 kW for medium-temperature conditions, and two compressors of 10 kW for low-temperature.
- In the case of the CO₂ transcritical system, there are three compressors for mediumtemperature with a total capacity of 120kW and two compressors for low-temperature with a total capacity of 20kW.

The evaporation temperature is consistently maintained at -10°C for medium-temperature conditions and -30°C for low-temperature conditions.

The condensation temperature is held at:

- 12.5°C above ambient temperature for cascade cycle systems.
- 10°C above ambient temperature for subcritical CO₂ systems.
- 2°C above ambient temperature for transcritical CO₂ systems (gas cooler output).

For indirect emissions related to the energy consumption of machines, calculations were based on the Seasonal Energy Performance Ratio (SEPR) from the European standard EN 14825:2006.

- Initially, the simulation is conducted using Bitzer or Dorin software to identify the most suitable compressor based on the analyzed configuration. Additionally, important data such as the Coefficient of Performance COP and the declared cooling capacity DCC, the specified amount of cooling that the refrigeration unit can provide under certain standard conditions, are obtained.
- Subsequently, the degradation coefficient C_d is introduced, which is useful to quantify the rate at which a material, system, or product loses its effectiveness or performance over time and it is set at 0.25 according to EN 14825. This coefficient accounts for the decrease in system performance over time or under certain conditions.
- The partial load is considered for each of the six temperature ranges, specifically 100% for the warmest, followed by 95%, 90%, 80%, 70%, and 60% for the coldest in cascade systems. Instead for CO₂ transcritical cycles they're assumed as 90%, 80%, 65%, 50%, 35%, 20%.
- 4. The Partial Load PL is calculated by multiplying these percentages by the initially required cooling capacity.
- 5. Then the Capacity Ratio CR is calculated dividing the Partial Load by the declared cooling capacity.
- 6. The COP at partial load COP_{PL} is:

$$COP_{PL} = COP * \left(1 - \left(C_d * (1 - CR)\right)\right)$$
[58]

7. Then is calculated the annual thermal energy output

$$PhTj = PL * h$$

8. To calculate the annual electrical energy consumption:

$$Electrical \ energy \ consumption \ [kWh] = \frac{PL * h}{COP_{PL}}$$

9. And the Seasonal Energy Performance Ratio, where the denominator is the sum of the electrical inputs.

$$SEPR = \frac{\sum_{j} PhT_{j}}{\sum_{j} PHT_{j}/COP_{DC}}$$

City	System	R455A + R744	R1234ze + R744	System	R744 + R744
		4JE-15Y-40P	6GE-34Y-40P		
	MT 30 kW	472-131-401	6GE-34Y-40P		4GTE30K
		4JE-15Y-40P	6GE-34Y-40P	MT	4DTE25K
Ravenna		472-131-401	6GE-34Y-40P		4DTE25K
	MT 60 KW	6GE-34Y-40P	/		
	LT	CDS301B	CDS301B	LT	2HSL3K
	LI	CDS301B	CDS301B	LI	2GSL3K
		4JE-15Y-40P	6GE-34Y-40P		
	MT 30 KW	4JE-131-40F	6GE-34Y-40P		4GTE30K
		4JE-15Y-40P	6GE-34Y-40P	MT	4DTE30K
Palermo		475-131-406	6GE-34Y-40P		4DTE30K
	MT 60 KW	6GE-34Y-40P	/		
	LT	CDS301B	CDS301B	LT	2HSL3K
	LI	CDS301B	CDS301B	LI	2GSL3K
		4NES-14Y-40P	6HE-28Y-40P		
	MT 30 KW	41120-141-401	6HE-28Y-40P		4HTE20K
	MI SO KW	4NES-14Y-40P	6HE-28Y-40P	MT	4FTE30K
Stockholm		4NE3-141-40F	6HE-28Y-40P		4FTE30K
	MT 60 kW	6HE-28Y-40P	/		
[LT	CDS301B	CDS301B	LT	2HSL3K
	LI	CDS301B	CDS301B	LI	2GSL3K

The choice of compressors is as follows:

Table 2-10 Compressor's Choice in Different Configurations

Subsequently, for each configuration, all parameters were calculated, and the values of SEPR and electrical energy consumption are reported below.

City	Configuration	System	SEPR	Energy Consumption [kWh]	Total Consumption [kWh]
		MT 30 KW	3,50	123222	
	R455A + R744	MT 60 kW	3,31	130478	279433
Ravenna		LT	5,59	25733	
Navenna	R1234ze + R744	MT 30 KW	3,43	251724	277457
	N123426 + N744	LT	5,59	25733	2/7437
	R744 + R744	/	2,38	288963	288963
		MT 30 KW	3,24	134453	
	R455A + R1234ze	MT 60 KW	3,07	141982	302434
Palermo		LT	5,59	25999	
Faterino	R1234ze + R744	MT 30 KW	3,18	274259	300258
	N123428 + N744	LT	5,59	25999	300238
	R744 + R744	/	2,18	321715	321715
		MT 30 KW	4,32	100553	
	R455A + R1234ze	MT 60 KW	4,21	102986	229379
Stockholm		LT	5,60	25840	
Stockhoth	R1234ze + R744	MT 30 KW	4,18	207740	233580
	K123428 + K744	LT	5,60	25840	20000
	R744 + R744	/	3,11	224700	224700

Table 2-11 Compressor's Energy Consumption in Different Configurations

In cascade systems, there is also a pump for the secondary water-glycol circuit, whose consumption is estimated to 7% of that of the compressors [71]. The energy consumption values reported below also take this into account.

City	Configuration	Energy Consumption [kWh]		
	R455A + R7AA	2989933		
Ravenna	R1234ze + R744	2968790		
	R744 + R744	2889630		
	R455A + R7AA	3236044		
Palermo	R1234ze + R744	3212761		
	R744 + R744	3217150		
	R455A + R7AA	2454355		
Stockholm	R1234ze + R744	2499306		
	R744 + R744	2247000		

Furthermore, the study is conducted over a period of 10 years, so the data is projected for that time frame.

Table 2-12 Energy Consumption of the entire System in 10 years

2.7 End of Life

Inventory data collection for the end-of-life phase was conducted in accordance with the guidelines provided by the WEEE directive (EU Regulation 2012/19, 2012), which applies to the product family in question. The environmental burdens associated with the remaining material fractions were estimated using typical recycling rates for material classes as specified in IEC/TR 62635 (2012).

All components were modeled using the 'Allocation, cut-off by classification' system model. This model does not credit producers for recycling their products at end-of-life (EoL) but instead allocates these benefits to secondary materials containing recycled content that are used in manufacturing. The full environmental impact of the virgin material is assigned to the first product produced, with the recycling impact allocated to the recycled material used in subsequent products, and the disposal impact allocated to the last product. As highlighted by Allacker et al. [72], this model does not require detailed knowledge of the recycling process at EoL. Therefore, this model was chosen to minimize uncertainty in EoL modeling, given the product's long lifespan and the challenges of accurately predicting specific EoL treatments for individual components. The environmental impact of landfill treatments for unrecycled material fractions was also included in the analysis.

Refrigerants are assumed to be released into the environment at the end of their lifecycle with a recycle rate of 70%.

The following table lists the materials and the quantities emitted into the environment, considering the unrecycled fraction:

Configuration	Material	Unrecycled Fraction [%]	Quantity [kg]
	Scrap Steel	5	335,7
	Scrap Copper	15	119,6
	Waste Rubber	50	219,32
	Scrap Aluminium	5	40,27
	Used Cable	100	1,23
R455A + R744	Waste Glass	15	60,59
	Waste Plastic	50	145,13
	Electronics Scrap	100	8,35
	Inert Waste	15	89,18
	Hazardous Waste (Refrigerant)	30	91,54
	Carbon Dioxide	30	20,62
	Scrap Steel	5	346,21
	Scrap Copper	15	125,72
	Waste Rubber	50	220,84
	Scrap Aluminium	5	42,31
	Used Cable	100	1,23
R1234ze + R744	Waste Glass	15	60,59
	Waste Plastic	50	145,13
	Electronics Scrap	100	8,35
	Inert Waste	15	90,71
	Hazardous Waste (Refrigerant)	30	103,06
	Carbon Dioxide	30	20,62
	Scrap Steel	5	336,08
	Scrap Copper	15	100,81
	Waste Rubber	50	219,14
	Scrap Aluminium	5	40,22
R744 + R744	Used Cable	100	1,23
	Waste Glass	15	60,59
	Waste Plastic	50	145,13
	Electronics Scrap	100	8,35
	Inert Waste	15	89,13
	Carbon Dioxide	30	144,4

Table 2-13 End of Life Materials and Quantities

3. Impact Assessment

3.1 Methods

In the simulation, the IPCC 2021 GWP 100 method, along with the ReCiPe 2016 Midpoint (H) and Endpoint (H) methods, were used to assess environmental impacts, with the analysis divided into smaller sections to focus on the most relevant data.

- The IPCC 2021 GWP 100 method measures the Global Warming Potential (GWP) over a 100-year time horizon, as defined by the Intergovernmental Panel on Climate Change (IPCC). It quantifies the impact of different greenhouse gases based on their capacity to trap heat in the atmosphere over 100 years, expressed in CO₂ equivalents. This method is widely used to compare the contributions of gases like methane, nitrous oxide, and carbon dioxide to long-term global warming [73].
- The ReCiPe 2016 Midpoint (H) method is a comprehensive life cycle impact assessment (LCIA) approach that evaluates environmental impacts across several categories, such as climate change, eutrophication, acidification, and ozone depletion. The "Midpoint" focuses on measuring impacts at an intermediate level of environmental damage, rather than the final stage. The "H" refers to the hierarchical perspective, which takes a balanced, long-term view of environmental effects [74].
- The ReCiPe 2016 Endpoint (H) method also assesses environmental impacts but focuses on the "endpoint" level of damage, meaning it measures the effects closer to the final damage in areas of protection, such as human health, ecosystems, and resource availability. This method provides a more comprehensive overview of long-term consequences, complementing the Midpoint approach [75].

In this simulation, these methods will vary based on the specific section being analyzed, ensuring that the most interesting and significant data are thoroughly examined. By breaking the analysis into smaller components, such as different stages of the refrigeration system's life cycle, each method can be applied in the most appropriate way, allowing for a detailed and insightful evaluation of environmental impacts.

3.2 Refrigeration System Assembly

The first aspect considered is the assembly of the refrigeration system. Three configurations were evaluated, and for each system analyzed, the results were very similar, as the components do not differ significantly from one another.

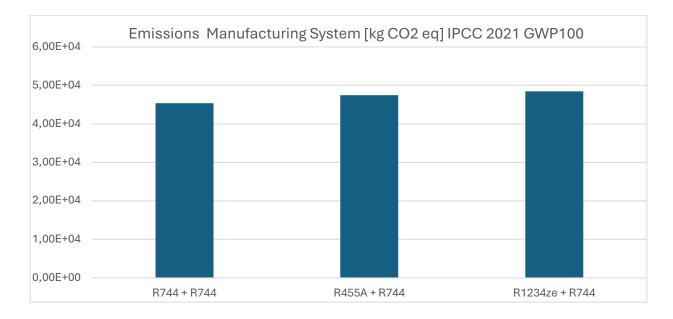


Figure 3-1 Emissions of Manufacturing system [kg CO2 eq] IPCC 2021 GWP100

As previously mentioned, the emissions are quite similar across the systems. They are slightly higher for systems using traditional refrigerants, not only due to the refrigerant itself but also because of the additional components required for this configuration (such as pumps, heat exchangers, and glycol water systems).

Component	R74	4 + R744	R455	6A + R744	R1234	ze + R744
	Emissions [kg CO2eq]	Percentage Emissions [%]	Emissions [kg CO2eq]	Percentage Emissions [%]	Emissions [kg CO2eq]	Percentage Emissions [%]
Total	45400	100,00%	47500	100,00%	48500	100,00%
Control Unit	477	1,05%	477	1,00%	477	0,98%
Anti Condensation	6	0,01%	6	0,01%	5	0,01%
Crankcase Heater	13	0,03%	13	0,03%	13	0,03%
Drier Filter	128	0,28%	168	0,35%	168	0,35%
Hardware,Collars, Fittings	165	0,36%	102	0,22%	102	0,21%
Liquid Receiver	1050	2,31%	658	1,39%	658	1,36%
Motor Fans	2360	5,20%	2360	4,97%	2360	4,87%
Pressure Switches and Probes	21	0,05%	21	0,04%	21	0,04%
Shut Off Valves and Solenoid Valves	127	0,28%	143	0,30%	143	0,29%
Muffler	165	0,36%	165	0,35%	165	0,34%
Vibration Damper	63	0,14%	63	0,13%	63	0,13%
Compressors	12330	27,16%	12330	25,96%	13590	28,02%
Cabinets	25390	55,93%	25390	53,45%	25390	52,35%
GasCooler	2610	5,75%	0	0,00%	0	0,00%
Pipes	146	0,32%	206	0,43%	206	0,42%
Liquid Indicator	18	0,04%	18	0,04%	18	0,04%
Condenser	0	0,00%	2140	4,51%	2140	4,41%
LubricatingOil	6	0,01%	20	0,04%	20	0,04%
Refrigerants	322	0,71%	770	1,62%	566	1,17%
Heat Exchanger	0	0,00%	992	2,09%	992	2,05%
Water Glycol	0	0,00%	888	1,87%	888	1,83%
Pump	0	0,00%	569	1,20%	569	1,17%

Table 3-1 Emissions and Percentage for each Component [kg CO₂ eq] IPCC 2021 GWP100

From this table, it is interesting to note that the most impactful components are the core elements of the system: the cabinets and compressors. Additionally, there is a significant impact from the motor fans and the gas cooler (in the case of transcritical CO_2 systems) and the condenser (in traditional refrigerant systems).

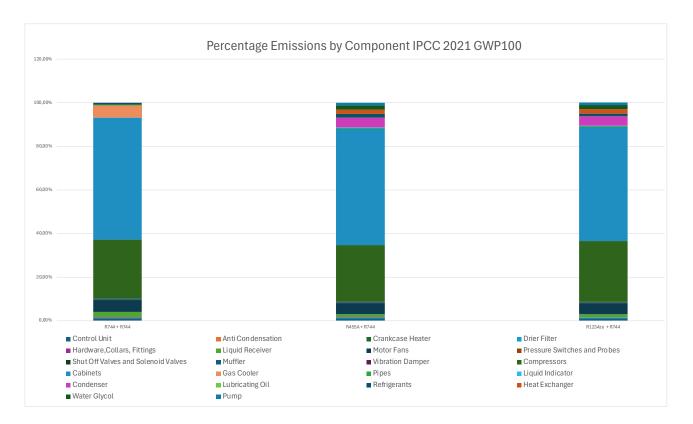


Figure 3-2 Percentage Emissions by Component IPCC 2021 GWP100

Regarding this topic, the flow diagram using the IPCC 2021 GWP100 method is also interesting. In this case, the compressor or cabinet package is not analyzed in a general way but is differentiated based on power or model. Consequently, it is interesting to see what percentage they influence the overall process. Moreover, with this type of chart, it is also possible to observe which processes have the greatest impact on emissions and how they branch out in the diagram (even just in the final part).

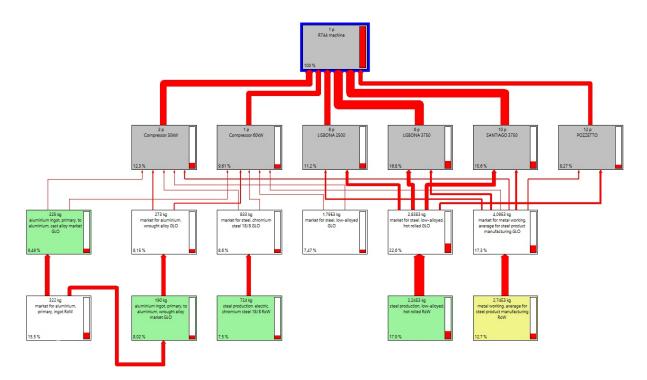


Figure 3-3 Flux Diagram of R744 + R744 Machine IPCC 2021 GWP100

In the case of the R744 + R744 and R455A + R744 configurations, as previously observed, the most impactful processes are the cabinets (except for London 2500, due to their lower quantity) and the compressor packages of 30 and 60 kW.

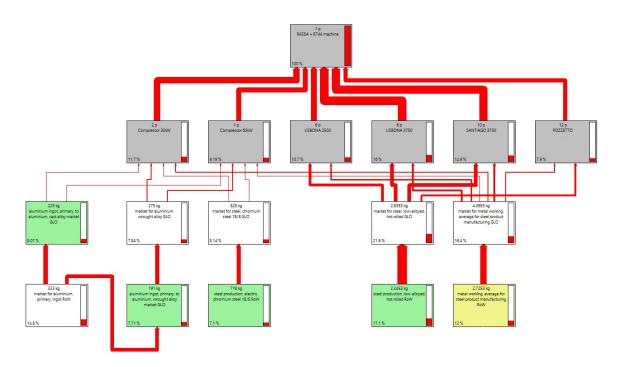


Figure 3-4 Flux Diagram of R455A + R744 Machine IPCC 2021 GWP100

Additionally, from these charts, the influence of raw materials is also interesting. In particular, the impact of aluminum wrought alloy, steel chromium steel, and steel low-alloyed, as well as the metalworking of the latter, is notable.

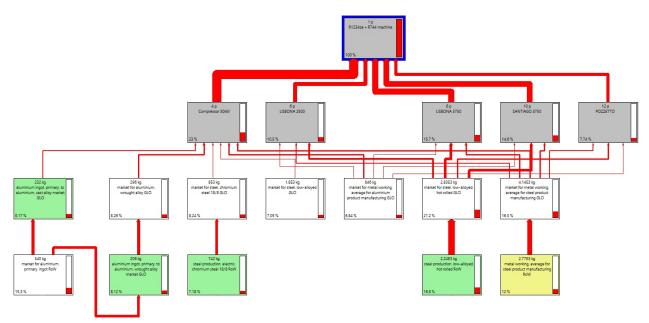


Figure 3-5 Flux Diagram of R1234ze + R744 Machine IPCC 2021 GWP100

The case of R1234ze + R744 is slightly different because the 60-kW compressor is not present, but there are four 30 kW compressors. However, it can be observed that the sum of the two percentages of the two compressor types from the previous cases is roughly similar to that of this case.

3.3 Use Phase

3.3.1 Direct Emissions

During the Use Phase, aside from the materials replaced in the various components, the difference in emissions is primarily driven by the leakage rate and the type of refrigerant used. Additionally, in systems using traditional refrigerants, the presence of the glycol-water circuit has a notable impact.

Component	nponent R744 + R744 10%		R455A	+ R744 10%	R1234ze + R744 10%		
	Emissions [kg CO2eq]	Percentage Emissions [%]	Emissions [kg CO2eq]	Percentage Emissions [%]	Emissions [kg CO2eq]	Percentage Emissions [%]	
Total	1360	100,00%	2830	100,00%	2630	100,00%	
R744	322	23,68%	46,1	1,63%	46,1	1,75%	
Lubricating Oil	58,2	4,28%	198	7,00%	198	7,53%	
Synthetic Rubber	407	29,93%	407	14,38%	407	15,48%	
Flat Glass	191	14,04%	191	6,75%	191	7,26%	
Polypropilene Granulate	379	27,87%	379	13,39%	379	14,41%	
R455A	0	0,00%	724	25,58%	0	0,00%	
R1234ze	0	0,00%	0	0,00%	520	19,77%	
Water Glycol	0	0,00%	888	31,38%	888	33,76%	

Component	Component R744 + R744 5%		R455A	+ R744 5%	R1234ze + R744 5%		
	Emissions [kg CO2eq]	Percentage Emissions [%]	Emissions [kg CO2eq]	Percentage Emissions [%]	Emissions [kg CO2eq]	Percentage Emissions [%]	
Total	1200	100,00%	2450	100,00%	2350	100,00%	
R744	161	13,42%	23	0,94%	23	0,98%	
LubricatingOil	58,2	4,85%	198	8,08%	198	8,43%	
Synthetic Rubber	407	33,92%	407	16,61%	407	17,32%	
Flat Glass	191	15,92%	191	7,80%	191	8,13%	
Polypropilene Granulate	379	31,58%	379	15,47%	379	16,13%	
R455A	0	0,00%	362	14,78%	0	0,00%	
R1234ze	0	0,00%	0	0,00%	260	11,06%	
Water Glycol	0	0,00%	888	36,24%	888	37,79%	

Table 3-2, Table 3-3 Emissions and Percentage emissions by Component of Use Phase (direct emissions) IPCC 2021 GWP100

This table shows the difference in emissions between the various configurations. As previously mentioned, the greatest impact is due to the traditional refrigerants R455A and R1234ze, with the former being more polluting.

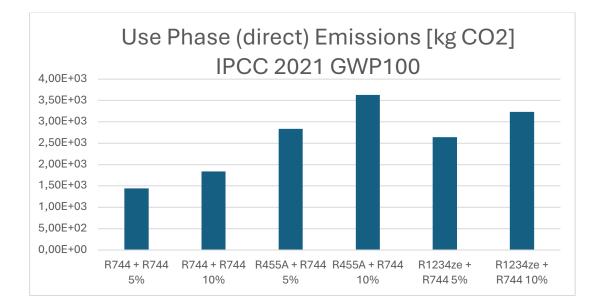


Figure 3-6 Emissions of Use Phase (direct emissions) [kg CO₂ eq] IPCC 2021 GWP100

Another interesting aspect of this part of the study is evaluating the impact of CFC-11, which are substances responsible for stratospheric ozone depletion. CFC-11 releases chlorine atoms when broken down by UV radiation in the stratosphere, and these chlorine atoms destroy ozone molecules, thinning the ozone layer that protects Earth from harmful UV rays. This impact is mainly due to the composition of the refrigerants: the impact is higher for R455A, lower for R1234ze, and nearly zero for R744.

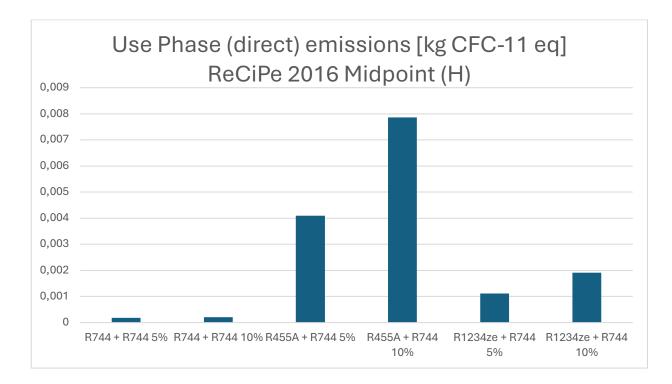


Figure 3-7 Emissions of Use Phase (direct emissions) [kg CFC-11 eq] ReCiPe 2016 Midpoint (H)

3.3.2 Indirect Phase

In the analysis of indirect emissions, nine different configurations were assessed, varying based on three locations and three systems. The locations influence emissions due to differences in energy mix and climate. For instance, Italy has a balanced energy mix that includes both fossil fuels and renewables, while Sweden relies more on clean, renewable energy. In terms of climate, Ravenna and Palermo have warmer temperatures, while Stockholm is much colder.

As for the systems, the CO₂-based system uses slightly less energy, partly because it doesn't require auxiliary circuits like the glycol-water system.

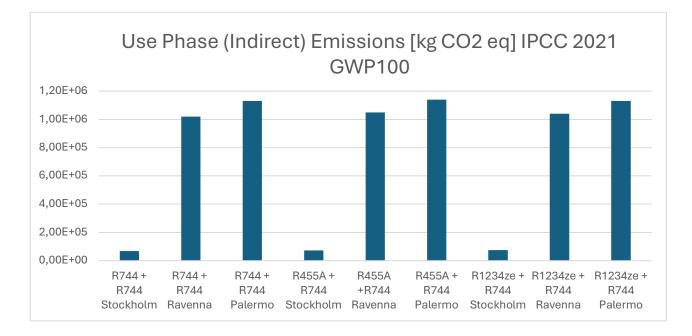


Figure 3-8 Emissions of Use Phase (indirect emissions) [kg CO2 eq] IPCC 2021 GWP100

The total amount of emissions in this phase is due to the electricity, calculated as mentioned earlier, consumed by the entire systems over the course of 10 years.

System	Emissions [kg CO2eq]
R744 + R744 Stockholm	67200
R744 + R744 Ravenna	1020000
R744 + R744 Palermo	1130000
R455A + R744 Stockholm	73400
R455A +R744 Ravenna	1050000
R455A + R744 Palermo	1140000
R1234ze + R744 Stockholm	74700
R1234ze + R744 Ravenna	1040000
R1234ze + R744 Palermo	1130000

Table 3-4 Emissions of Use Phase (indirect) [kg CO₂ eq] IPCC 2021 GWP100

3.4 End of Life

The data on emissions from the end-of-life phase has limited value on its own; it needs to be considered in relation to the rest of the study as a percentage. It is worth noting that, in the case of Stockholm, this figure stands at just under 1%, while for Italian cities it falls to around 0.1%. This is due to the much higher impact of the use phase in the latter.

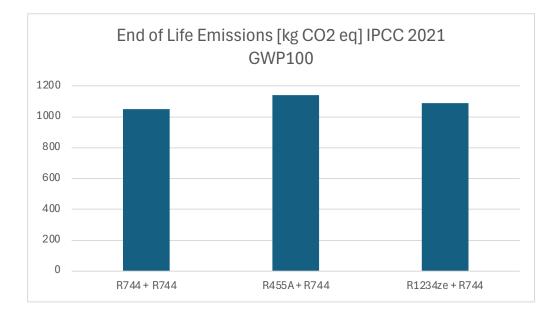


Figure 3-9 End of Life Emissions [kg CO₂ eq] IPCC 2021 GWP100

3.5 Entire Refrigeration System

3.5.1 IPCC 2021 GWP100

Now, the entire refrigeration system is analyzed, considering all the variables introduced in the study. The manufacturing phase changes depending on the configuration used. The use phase, on the other hand, can vary based on the city analyzed and the assumed leakage rate percentage. The end-of-life phase also differs according to the configuration.

Configuration	Emissions [kg CO2eq]
R744 + R744 Stockholm 5%	115090
R744 + R744 Stockholm 10%	115490
R744 + R744 Ravenna 5%	1067890
R744 + R744 Ravenna 10%	1068290
R744 + R744 Palermo 5%	1177890
R744 + R744 Palermo 10%	1178290
R455A + R744 Stockholm 5%	124880
R455A + R744 Stockholm 10%	125670
R455A + R744 Ravenna 5%	1101480
R455A + R744 Ravenna 10%	1101280
R455A + R744 Palermo 5%	1191480
R455A + R744 Palermo 10%	1192270
R1234ze + R744 Stockholm 5%	126930
R1234ze + R744 Stockholm 10%	127520
R1234ze + R744 Ravenna 5%	1092230
R1234ze + R744 Ravenna 10%	1092820
R1234ze + R744 Palermo 5%	1182230
R1234ze + R744 Palermo 10%	1182820

Table 3-5 Total Emissions for each Configuration [kg CO₂ eq] IPCC 2021 GWP100

It is evident that the aspect that causes the greatest variation in emissions is the city being analyzed. This is due both to the external temperature, which can make the system work harder or more efficiently, and to the country's energy mix. The method by which electricity is generated directly influences the overall emissions.

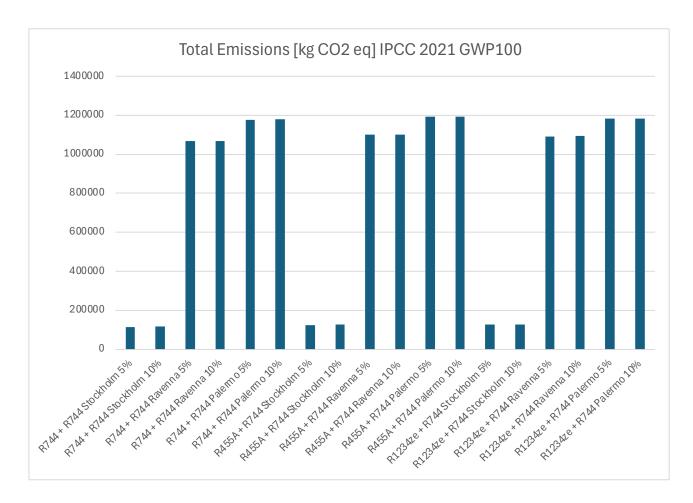


Figure 3-10 Total Emissions for each Configuration [kg CO2 eq] IPCC 2021 GWP100

Another interesting aspect is how, in the context of a study covering such a large and long-term system, the refrigerant leakage rate changes very little. As shown in the graph and table, this factor results in only a very slight variation in emissions.

Additionally, it can be observed how each phase proportionally influences the overall emissions. The contribution of each phase, manufacturing, use, and end-of-life can be seen in terms of percentage, highlighting their individual impact on the total emissions.

	R744 + R744 Stockholm 5%		R744 + R744 Stockholm 10%	[%]	R455A + R744 Stockholm 5%	[%]
Manifacturing Phase	45400	39,45%	45400	39,31%	47500	38,04%
Use Phase	68640	59,64%	69040	59,78%	76240	61,05%
End of Life	1050	0,91%	1050	0,91%	1140	0,91%

	R455A + R744 Stockholm 10%	[%]	R1234ze + R744 Stockholm 5%	[%]	R1234ze + R744 Stockholm 10%	[%]
Manifacturing Phase	47500	37,80%	48500	38,27%	48500	38,19%
Use Phase	77030	61,30%	77340	61,03%	77930	61,36%
End of Life	1140	0,91%	1090	0,86%	1090	0,86%

Table 3-6, Table 3-7 Total Emission for Stockholm IPCC 2021 GWP100

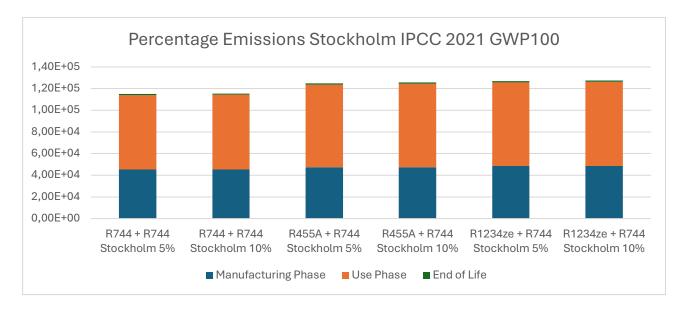


Figure 3-11 Percentage Emissions for Stockholm IPCC 2021 GWP100

In Stockholm, given that Sweden is more environmentally responsible in terms of electricity production, the manufacturing phase has a significant impact, accounting for approximately 40% of the total emissions. Additionally, the end-of-life phase contributes around 1% to the total emissions.

	R744 + R744 Ravenna 5%	[%]	R744 + R744 Ravenna 10%	[%]	R455A + R744 Ravenna 5%	[%]
Manifacturing Phase	45400	4,25%	45400	4,25%	47500	4,31%
Use Phase	1021440	95,65%	1021840	95,65%	1052840	95,58%
End of Life	1050	0,10%	1050	0,10%	1140	0,10%

	R455A + R744 Ravenna 10%		R1234ze + R744 Ravenna 5%	[%]	R1234ze + R744 Ravenna 10%	[%]
Manifacturing Phase	47500	4,31%	48500	4,44%	48500	4,44%
Use Phase	1052640	95,57%	1042640	95,48%	1043230	95,51%
End of Life	1140	0,10%	1090	0,10%	1090	0,10%

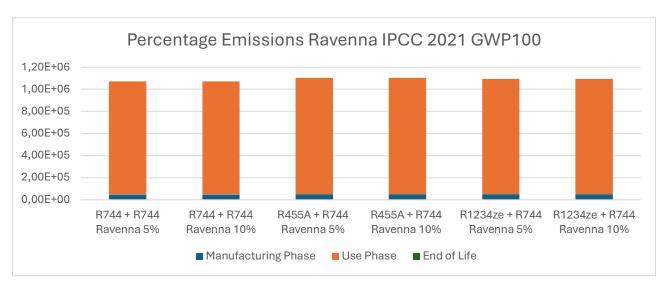


Table 3-8, Table 3-9 Total Emissions for Ravenna IPCC 2021 GWP100

Figure 3-12 Percentage Emissions for Ravenna IPCC 2021 GWP100

	R744 + R744 Palermo 5%	[%]	R744 + R744 Palermo 10%	[%]	R455A + R744 Palermo 5%	[%]
Manifacturing Phase	45400	3,85%	45400	3,85%	47500	3,99%
Use Phase	1131440	96,06%	1131840	96,06%	1142840	95,92%
End of Life	1050	0,09%	1050	0,09%	1140	0,10%

	R455A + R744 Palermo 10%	[%]	R1234ze + R744 Palermo 5%	[%]	R1234ze + R744 Palermo 10%	[%]
Manifacturing Phase	47500	3,99%	48500	4,10%	48500	4,10%
Use Phase	1143630	95,98%	1132640	95,82%	1133230	95,85%
End of Life	1140	0,10%	1090	0,09%	1090	0,09%

Table 3-10, Table 3-11 Total Emissions for Palermo IPCC 2021 GWP100

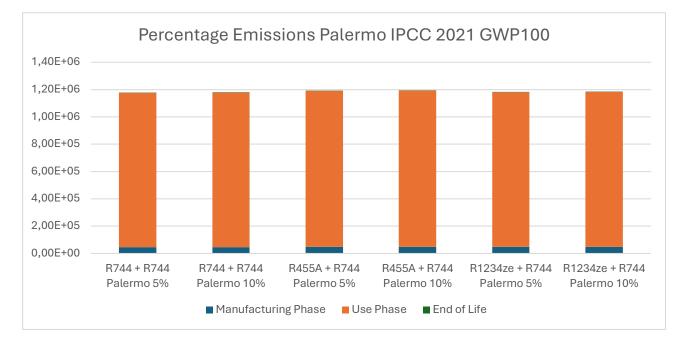


Figure 3-13 Percentage Emissions for Palermo IPCC 2021 GWP100

In contrast, for the two Italian cities, the manufacturing phase impacts emissions by less than 5%. The use phase has an even higher impact, particularly in Palermo, where the warmer climate leads to increased energy consumption. Due to the high emissions from the use phase, the end-of-life phase has a minimal impact, contributing only about 0.1% to the total emissions.

In the upcoming simulations, only the case of a 10% leakage rate will be analyzed. As observed, the differences in the overall system for different leakage rates are minimal, so reporting results for both 5% and 10% leakage rates would be redundant.

3.5.2 ReCiPe 2016 Midpoint (H)

3.5.2.1 Ozone Depletion

The characterization factor for ozone layer depletion accounts for the destruction of the stratospheric ozone layer by anthropogenic emissions of ozone depleting substances (ODS). The unit is kg CFC-11 equivalents.

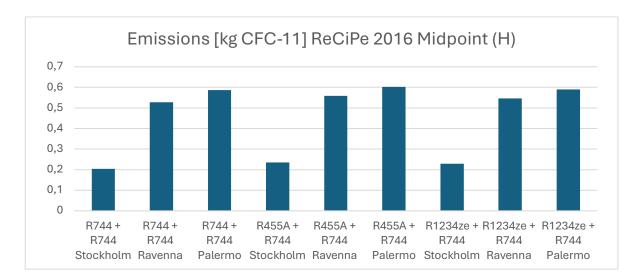


Figure 3-14 Total Emissions [kg CFC-11 eq] ReCiPe 2016 Midpoint (H)

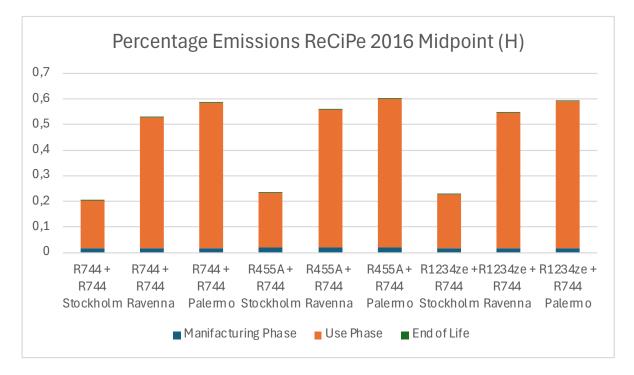


Figure 3-15 Percentage Emissions [kg CFC-11 eq] ReCiPe 2016 Midpoint (H)

The highest percentage corresponds to the indirect phase, while, in absolute terms, the difference between the Italian and Swedish scenarios is not as significant as for other parameters.

3.5.2.2 Terrestrial acidification

3500

1500 1000 500

0

R744 +

R744

Stockholm Ravenna

R744 +

R744

R744+

R744

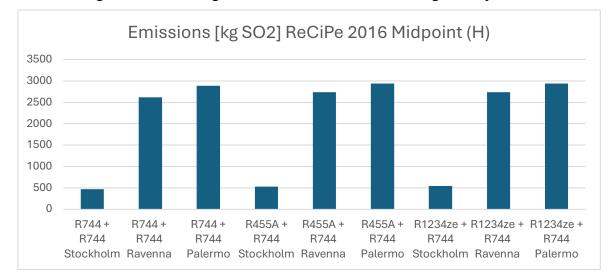
Manufacturing Phase

R455A +

R744

Palermo Stockholm Ravenna

The characterization factor for terrestrial acidification is Acidification Potential (AP) derived using the emission weighted world average fate factor of SO₂. The unit is kg SO₂ equivalents.



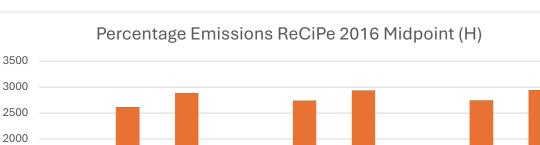


Figure 3-16 Total Emissions [kg SO2 eq] ReCiPe 2016 Midpoint (H)

Figure 3-17 Percentage Emissions [kg SO₂ eq] ReCiPe 2016 Midpoint (H)

R455A +

R744

Use Phase

R455A +

R744

R744

Palermo Stockholm Ravenna

End of Life

R1234ze + R1234ze + R1234ze +

R744

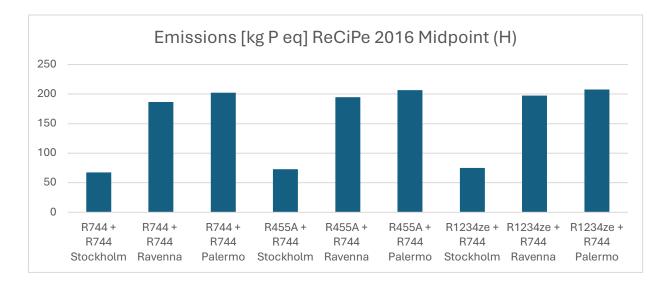
R744

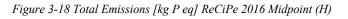
Palermo

In the Swedish scenario, the percentage of the manufacturing phase is almost 60% compared to that of the use phase.

3.5.2.3 Freshwater eutrophication

The characterization factor of freshwater eutrophication accounts for the environmental persistence (fate) of the emission of P containing nutrients. The unit is kg P to freshwater equivalents.





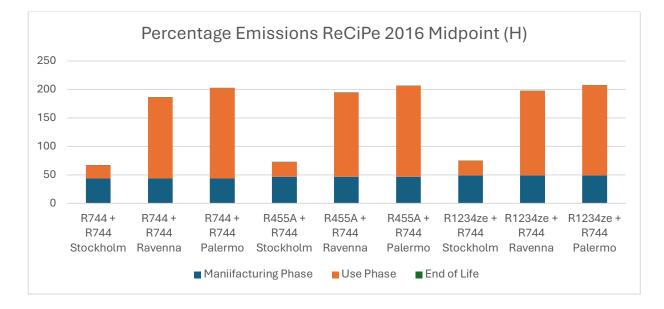


Figure 3-19 Percentage Emissions [kg P eq] ReCiPe 2016 Midpoint (H)

In this case, in the Swedish scenario, the manufacturing phase has twice the impact compared to the use phase. In the Italian scenario, although the impact is lower, it is still significant compared to other parameters, with the former accounting for one-third of the latter.

3.5.2.4 Fossil Resource Scarcity

The characterization factor of fossil resource scarcity is the fossil fuel potential, based on the higher heating value. The unit is kg oil equivalents.

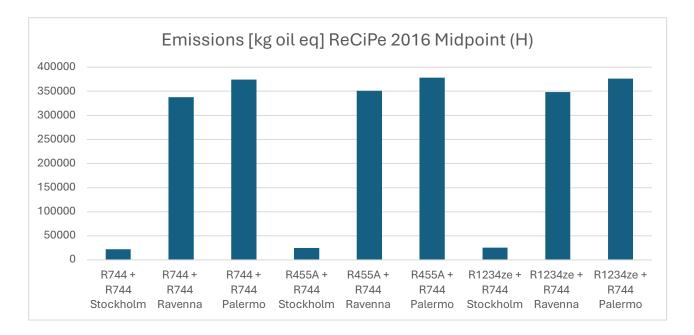


Figure 3-20 Total Emissions [kg oil eq] ReCiPe 2016 Midpoint (H)

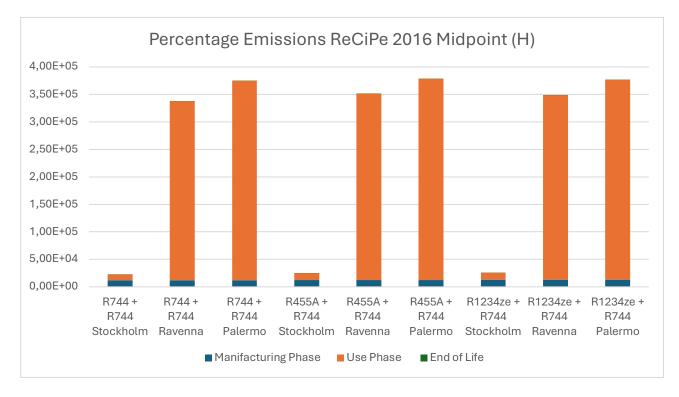


Figure 3-21 Percentage Emissions [kg oil eq] ReCiPe 2016 Midpoint (H)

In this simulation, for the Swedish scenario, the manufacturing and use phases are approximately equal. In absolute terms, the difference with the Italian scenario is quite significant.

3.5.3 ReCiPe 2016 Endpoint (H)

3.5.3.1 Human Health

Human Health, expressed as the number of year life lost and the number of years lived disabled. These are combined as Disability Adjusted Life Years (DALYs), an index that is also used by the World Bank and WHO.

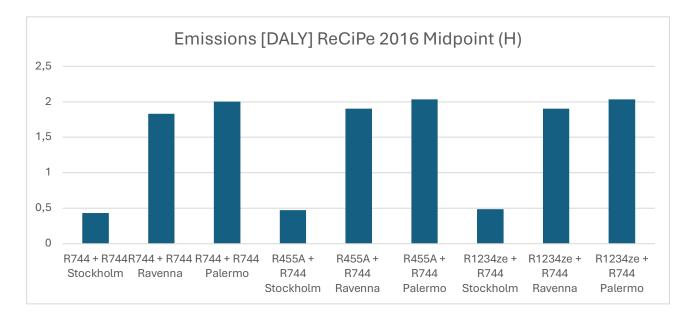


Figure 3-22 Total Emissions [DALYs] ReCiPe 2016 Endpoint (H)

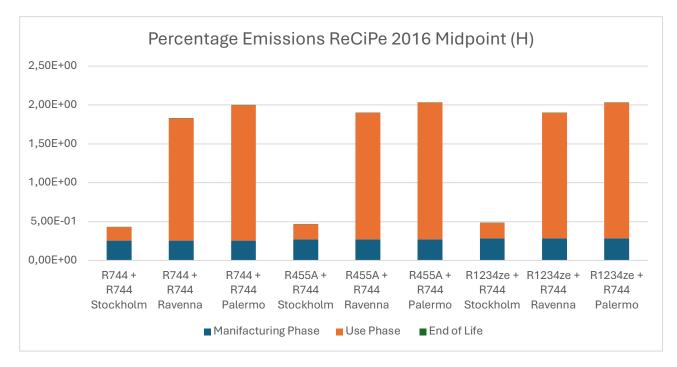
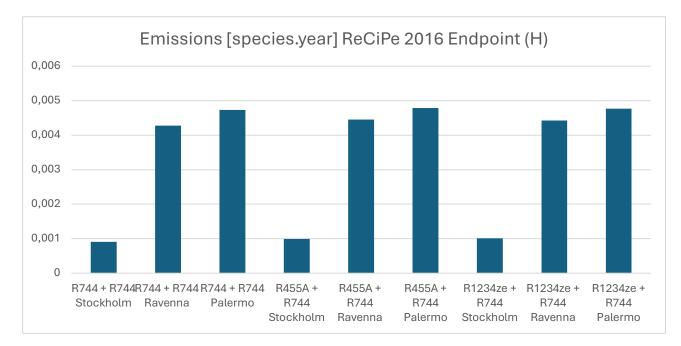


Figure 3-23 Percentage Emissions [DALYs] ReCiPe 2016 Endpoint (H)

The manufacturing phase accounts for around 60% of the impact, rather than the use phase.

3.5.3.2 Ecosystems



Ecosystems, expressed as the loss of species over a certain area, during a certain time. The unit is species.years.

Figure 3-24 Total Emissions [species.years] ReCiPe 2016 Endpoint (H)

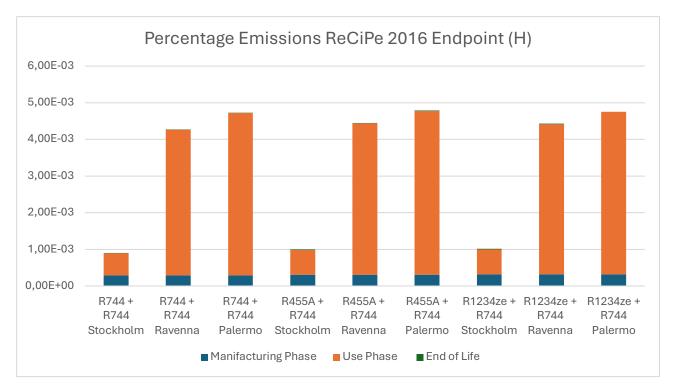


Figure 3-25 Percentage Emissions [species.years] ReCiPe 2016 Endpoint (H)

3.5.3.3 Resource Scarcity (USD 2013)

Resource scarcity, expressed as the surplus costs of future resource production over an infinitive timeframe (assuming constant annual production), considering a 3% discount rate. The unit is USD 2013. Mind that fossil resource scarcity does not have constant mid-to-endpoint factor but individual factors for each substance.

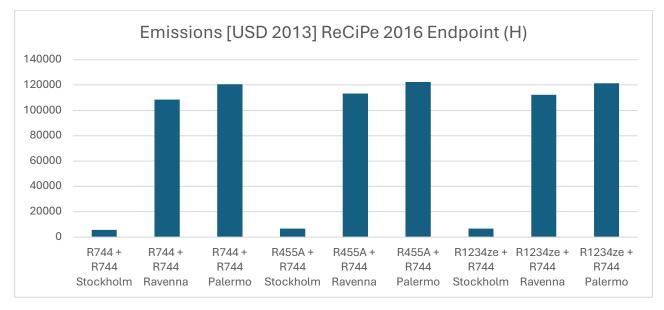


Figure 3-26 Total Emissions [USD 2013] ReCiPe 2016 Endpoint (H)

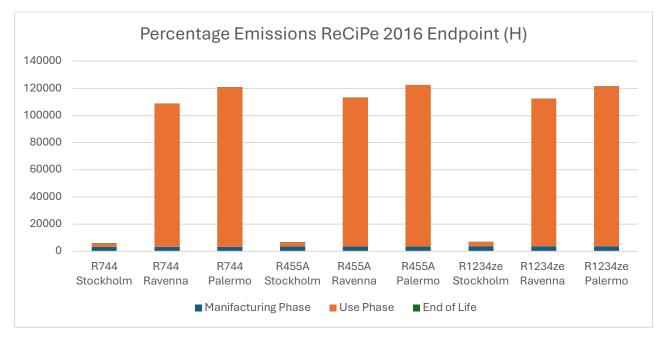


Figure 3-27 Percentage Emissions [USD 2013] ReCiPe 2016 Endpoint (H)

The difference between Italy and Sweden is very high; in fact, the Italian value is approximately 15 times higher.

3.5.4 Normalization of Results

With the previous simulations using the ReCiPe 2016 Midpoint (H) and ReCiPe 2016 Endpoint (H) methods, values for several key parameters were obtained. Additionally, it was observed that the overall trend of total emissions was similar in every scenario, while the variation occurred in the percentage of impact attributed to the different phases. For this reason, it is interesting to observe how each parameter varies in relation to the others through the normalization function.

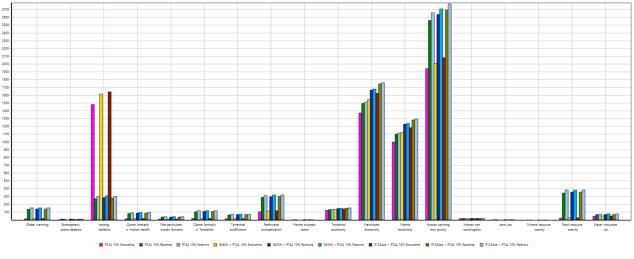


Figure 3-28 Normalization ReCiPe 2016 Midpoint (H)

It is observed that the parameters "Freshwater Ecotoxicity," "Marine Ecotoxicity," and "Human Carcinogenic Toxicity" show the highest values after normalization.

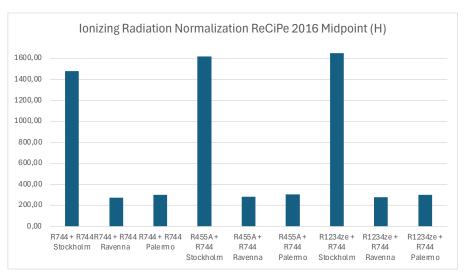


Figure 3-29 Ionizing Radiation Normalization ReCiPe 2016 Midpoint (H)

It is also interesting to note that the "Ionizing Radiation" parameter is the only one with higher values in the Swedish scenario. This is due to a series of processes that contribute to the generation of ionizing radiation throughout the life cycle of a product or service, such as nuclear energy production, which is part of the Swedish energy mix.and radioactive waste management.

3.6 Uncertainty Analysis

Uncertainty analysis is essential in a Life Cycle Assessment case study because it addresses the inherent variability and uncertainty in the input data. In an LCA, numerous parameters are often based on estimates or assumptions that can vary significantly. By conducting an uncertainty analysis, we can better understand how much these variations influence the results and, consequently, the reliability of the study's conclusions. This process helps ensure that decision-makers don't base their choices solely on single-point estimates, which may not fully capture the range of possible outcomes. Instead, uncertainty analysis provides a clearer picture of how sensitive the system is to changes in key inputs, highlighting which factors are most crucial and where further data collection might be needed to improve accuracy.

In the specific case of Ravenna, the 10% leakage rate is analyzed because it most closely resembles the real-world situation of the actual plant. Not only is this leakage rate a realistic assumption, but the climate in Ravenna is also similar to that of the real facility, making it the most suitable scenario for analysis. By incorporating both leakage and climate conditions that align with the actual plant, the study ensures that the results are more reliable and applicable to the real-world context. This provides a better basis for comparison and decision-making, as the outcomes are reflective of both the operational and environmental conditions likely to be encountered in practice. The method used is IPCC 2021 GWP.

3.6.1 R744 + R744 Configuration

The first configuration analyzed is the transcritical CO₂ system.

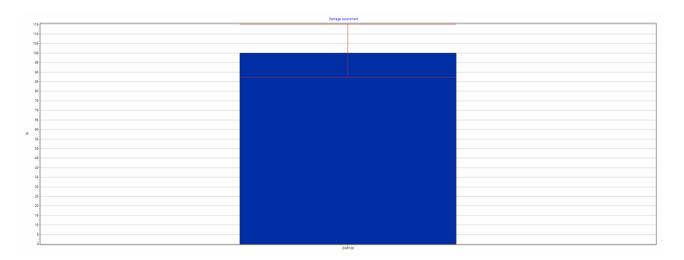


Figure 3-28 Uncertainty Analysis of R744 + R744 Configuration IPCC 2021 GWP

The error is approximately 15%. Additionally, the trend of the bell curve is as follows:

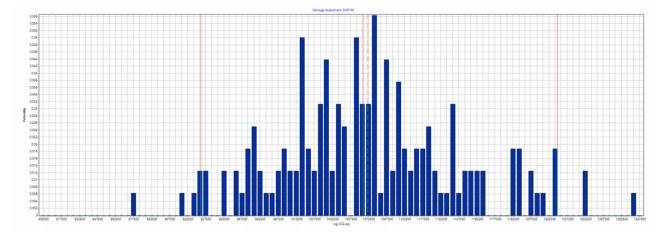


Figure 3-29 Bell-shaped Curve of R744 + R744 Configuration IPCC 2021 GWP

Mean	Median	Standard Deviation	Coefficient of Variation	2,50%	97,50%
1,06E+06	1,06E+06	7,56E+04	7,06%	9,33E+05	1,23E+06

Table 3-12 Parameters of R744 + R744 Configuration IPCC 2021 GWP

3.6.2 R455A + R744 Configuration

Then is analyzed the R455A + R744 Configuration. The error in this case is once again around 15%.

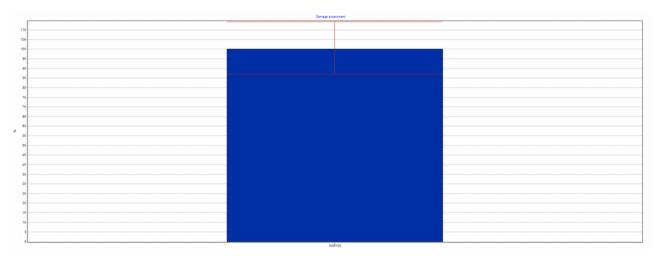


Figure 3-30 Uncertainty Analysis of R455A + R744 Configuration IPCC 2021 GWP

And the bell-shaped curve is:

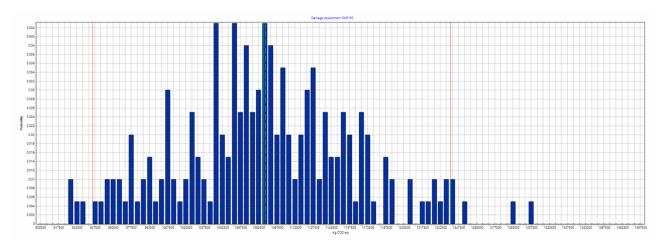


Figure 3-31 Bell-shaped Curve of R455A + R744 Configuration IPCC 2021 GWP

Mean	Median	Standard Deviation	Coefficient of Variation	2,50%	97,50%
1,10E+06	1,10E+06	7,32E+04	6,72%	9,46E+05	1,24E+06

Table 3-13 Parameters of R455A + R744 Configuration IPCC 2021 GWP

3.6.3 R1234ze + R744 Configuration

The R1234ze + R744 Configuration has an error around at 15%.

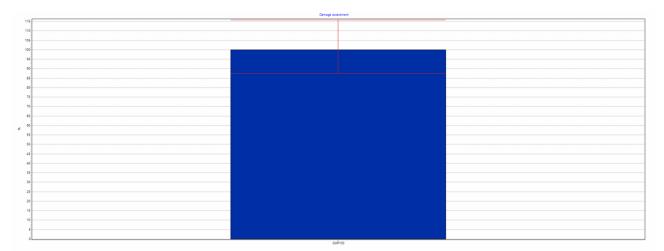


Figure 3-32 Uncertainty Analysis of R1234ze + R744 Configuration IPCC 2021 GWP

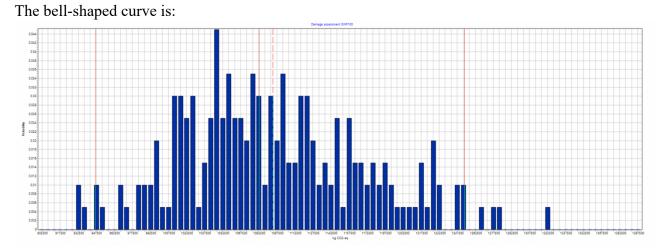


Figure 3-33 Bell-shaped Curve of R1234ze + R744 Configuration IPCC 2021 GWP

Mean	Median	Standard Deviation	Coefficient of Variation	2,50%	97,50 %
1,09E+06	1,09E+06	7,69E+04	7,03%	9,47E+05	1,25E+06

Table 3-14 Parameters of R1234ze + R744 Configuration IPCC 2021 GWP

3.6.4 Results

Following the uncertainty analysis, it is not possible to definitively conclude that one configuration is superior to the other, as there is a significant overlap in the values of both systems. This overlap prevents a clear distinction between their performances. However, a closer examination reveals that the trend of the transcritical CO₂ configuration tends to be slightly lower in comparison to the cascade systems. The cascade systems, in turn, exhibit very similar performance characteristics to each other, making it difficult to distinguish one from the other in terms of overall emissions.

Configuration	Mean	Minimum Value	Maximum Value
R744 + R744	1060000	901000	1219000
R455A + R744	1100000	935000	1265000
R1234ze + R744	1090000	926500	1253500

Table 3-15 Minimum and Maximum Values of emissions after Uncertainty Analysis [kg CO₂ eq] IPCC 2021 GWP100

3.7 Climate Data Variations

The uncertainty analysis previously conducted only considers the variations in data already integrated into the program, such as emissions related to raw materials or those associated with electricity production in each country. However, the climate factor is still not accounted for, even though it also influences emissions, as discussed earlier.

In this additional simulation, two different scenarios are considered: the first assumes that the external temperature is 1.5° Celsius higher than in the standard case study, while the second assumes it is 1.5° Celsius lower. These simulations are based on the compressor models previously used, and, following the same approach as outlined in paragraph 2.6.2, the electricity consumption of the systems is estimated under the two additional conditions.

The results are then analyzed and compared across the three meteorological simulations, dividing them by system and by city. This approach provides greater clarity in the presentation of the data and facilitates a more detailed commentary on the results. Only cases with a leakage rate of 10% are considered in this analysis.

3.7.1 Stockholm

The first case analyzed is for the city of Stockholm. In addition to the energy mix factor (which has already been observed to result in significantly lower emissions compared to Ravenna and Palermo), it is interesting to examine how the simulations with higher or lower temperatures impact emissions.

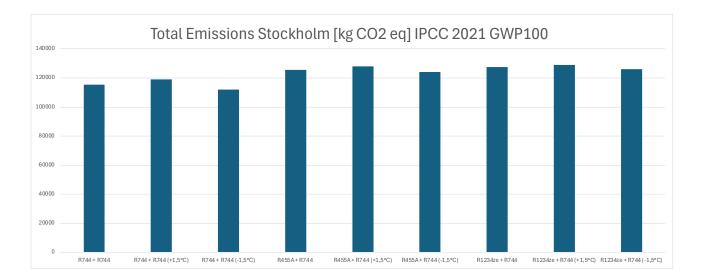


Figure 3-34 Total Emissions for Stockholm [kg CO₂ eq] IPCC 2021 GWP100

The variations due to temperature are minor compared to the standard conditions, but it is noteworthy how the performance of the transcritical CO_2 cycle, already very efficient in colder climates, allows for a greater improvement compared to the two Italian cities.

	R744 + R744 Stockholm 10%	[%]	R744 + R744 Stockholm 10% (+1,5°C)	[%]	R744 + R744 Stockholm 10% (-1,5°C)	[%]
Manifacturing Phase	45400	39,31%	45400	38,32%	45400	40,47%
Use Phase	69040	59,78%	72040	60,80%	65740	58,60%
End of Life	1050	0,91%	1050	0,89%	1050	0,94%

Table 3-16 Total Emissions for Stockholm R744 + R744 Configuration IPCC 2021 GWP100

	R455A + R744 Stockholm 10%	[%]	R455A + R744 Stockholm 10% (+1,5°C)	[%]	R455A + R744 Stockholm 10% (-1,5°C)	[%]
Manifacturing Phase	47500	37,80%	47500	37,15%	47500	38,38%
Use Phase	77030	61,30%	79230	61,96%	75130	60,70%
End of Life	1140	0,91%	1140	0,89%	1140,00	0,92%

Table 3-17 Total Emissions for Stockholm R455A + R744 Configuration IPCC 2021 GWP100

	R1234ze + R744 Stockholm 10%	[%]	R1234ze + R744 Stockholm 10% (+1,5°C)	[%]	R1234ze + R744 Stockholm 10% (-1,5°C)	[%]
Manifacturing Phase	48500	38,03%	48500	37,45%	48500	38,61%
Use Phase	77930	61,11%	79930	61,71%	76030	60,52%
End of Life	1090	0,85%	1090	0,84%	1090	0,87%

Table 3-18 Total Emissions for Stockholm R1234ze + R744 Configuration IPCC 2021 GWP100

In the case of Stockholm, the manufacturing phase shows an impact that varies by approximately 1.5% between the warmer and colder temperature scenarios.

3.7.2 Ravenna

For Ravenna, the analysis begins by examining the total emissions:

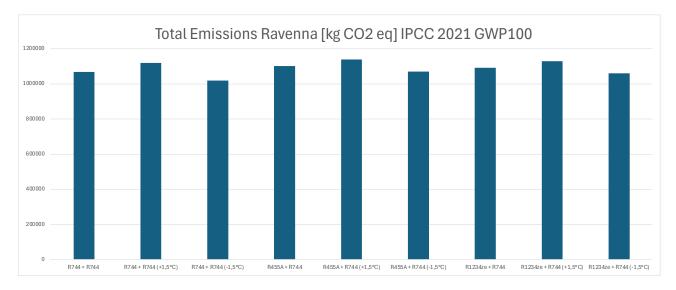


Figure 3-35 Total Emissions for Ravenna [kg CO2 eq] IPCC 2021 GWP100

Ravenna has the mildest temperature among all the cities, so there are no significant aspects to highlight in these simulations. The impact of the use phase compared to the rest varies by

approximately 0.5% across all simulations, between the most conservative configuration and the worst-case scenario.

	R744 + R744 Ravenna 10%	[%]	R744 + R744 Ravenna 10% (+1,5°C)	[%]	R744 + R744 Ravenna 10% (-1,5°C)	[%]
Manifacturing Phase	45400	4,25%	45400	4,06%	45400	4,47%
Use Phase	1021840	95,65%	1071840	95,85%	969840	95,43%
End of Life	1050	0,10%	1050	0,09%	1050	0,10%

Table 3-19 Total Emissions for Ravenna R744 + R744 Configuration IPCC 2021 GWP100

	R455A + R744 Ravenna 10%	[%]	R455A + R744 Ravenna 10% (+1,5°C)	[%]	R455A + R744 Ravenna 10% (-1,5°C)	[%]
Manifacturing Phase	47500	4,31%	47500	4,16%	47500	4,43%
Use Phase	1052640	95,58%	1093630	95,74%	1023630	95,46%
End of Life	1140	0,10%	1140	0,10%	1140,00	0,11%

Table 3-20 Total Emissions for Ravenna R455A + R744 Configuration IPCC 2021 GWP100

	R1234ze + R744 Ravenna 10%	[%]	R1234ze + R744 Ravenna 10% (+1,5°C)	[%]	R1234ze + R744 Ravenna 10% (-1,5°C)	[%]
Manifacturing Phase	48500	4,44%	48500	4,28%	48500	4,56%
Use Phase	1043230	95,46%	1083230	95,62%	1013230	95,33%
End of Life	1090	0,10%	1090	0,10%	1090	0,10%

Table 3-21 Total Emissions for Ravenna R1234ze + R744 Configuration IPCC 2021 GWP100

3.7.3 Palermo

The simulations for Palermo are made:

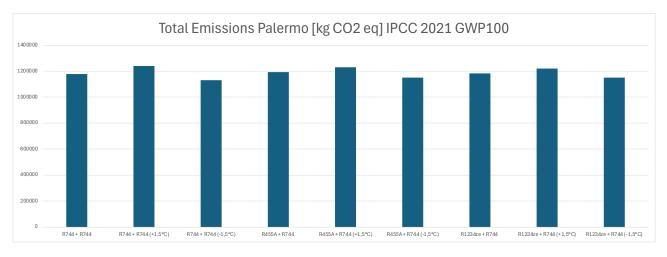


Figure 3-36 Total Emissions for Palermo [kg CO₂ eq] IPCC 2021 GWP100

In the case of Palermo, the very high summer temperatures lead to higher emissions during transcritical CO_2 operation. This is because the system operates in transcritical mode much more frequently compared to Stockholm, and significantly more than in Ravenna.

	R744 + R744 Palermo 10%	[%]	R744 + R744 Palermo 10% (+1,5°C)	[%]	R744 + R744 Palermo 10% (-1,5°C)	[%]
Manifacturing Phase	45400	3,85%	45400	3,67%	45400	4,02%
Use Phase	1131840	96,06%	1191840	96,25%	1081840	95,88%
End of Life	1050	0,09%	1050	0,08%	1050	0,09%

Table 3-22 Total Emissions for Palermo R744 + R744 Configuration IPCC 2021 GWP100

	R455A + R744 Palermo 10%	[%]	R455A + R744 Palermo 10% (+1,5°C)	[%]	R455A + R744 Palermo 10% (-1,5°C)	[%]
Manifacturing Phase	47500	3,98%	47500	3,89%	47500	4,12%
Use Phase	1143630	95,92%	1173630	96,02%	1103630	95,78%
End of Life	1140	0,10%	1140	0,09%	1140	0,10%

Table 3-23 Total Emissions for Palermo R455A + R744 Configuration IPCC 2021 GWP100

	R1234ze + R744 Palermo 10%	[%]	R1234ze + R744 Palermo 10% (+1,5°C)	[%]	R1234ze + R744 Palermo 10% (-1,5°C)	[%]
Manifacturing Phase	48500	4,10%	48500	3,97%	48500	4,21%
Use Phase	1133230	95,81%	1173230	95,94%	1103230	95,70%
End of Life	1090	0,09%	1090	0,09%	1090	0,09%

Table 3-24 Total Emissions for Palermo R1234ze + R744 Configuration IPCC 2021 GWP100

It can be observed that this increase in emissions leads to significant differences in the use phase for this configuration in Palermo, even though, in percentage terms, the variation remains within the range of approximately 0.4%.

4. Conclusions

In this thesis, the environmental impact of a 140 kW commercial refrigeration system (120 kW Medium Temperature, 20 kW Low Temperature) was studied by analyzing three different refrigerants across three distinct cities, with two varying leakage rates. The focus was on assessing both the overall results and the individual phases of the system's lifecycle: manufacturing, use, and end-of-life. Each case study provided insights into how refrigerant choice, geographic location, and leakage rates contribute to the system's total environmental footprint, allowing for a comprehensive understanding of the sustainability challenges posed by refrigeration systems in commercial settings.

The impact of the manufacturing phase is similar across all configurations, with the notable difference that the transcritical R744 system has a simpler configuration, resulting in a slightly lower environmental impact. Specifically, the R744 transcritical system contributes 45,400 kg CO₂ eq, compared to 47,500 kg CO₂ eq for the R455A + R744 configuration and 48,500 kg CO₂ eq for the R1234ze + R744 system. This difference highlights the relative advantage of using R744 in terms of reducing emissions during the manufacturing phase.

The use phase is heavily influenced by indirect emissions, which are affected both by the climate and, more importantly, by the energy mix of each country. This is evident in the stark difference in emissions between Sweden and Italy. In Sweden, the emissions are on the order of 10E+5 kg CO₂ eq, while in Italy, they reach 10E+6 kg CO₂ eq. This highlights how the carbon intensity of the energy grid plays a crucial role in determining the environmental impact during the operational phase of the refrigeration system.

Direct emissions are influenced by the leakage rate of the refrigeration system. Specifically, the depletion of the ozone layer is higher with the use of R455A. However, when considering the total study results, the difference in environmental impact between the refrigerants remains minimal. This indicates that while certain refrigerants may have a more pronounced effect on ozone layer depletion, the overall differences in emissions are relatively small within the context of the comprehensive analysis conducted.

The end-of-life phase has a minimal impact on the overall environmental footprint of the refrigeration system. In the Swedish scenario, it accounts for approximately 1% of the total impact, while in the Italian scenario, it contributes to even less than 0.1%. This suggests that the end-of-life phase,

although not negligible, has a relatively minor effect compared to other phases of the system's lifecycle.

In the study using ReCiPe midpoint and endpoint methods, the trend of greater environmental impact in Palermo, and to a slightly lesser extent in Ravenna, is confirmed. However, the extent of the impact varies in comparison to Stockholm depending on the specific environmental impact category analyzed. This indicates that while Palermo consistently shows higher environmental impacts, the relative difference from Stockholm can be pronounced depending on the category under consideration.

4.1 Limitations and Future developments

This thesis has some limitations, such as the lack of real data for the manufacturing phase. The data for the use phase were calculated through simulations, but they are plausible and comparable to data from real systems. Consequently, this research provides a solid foundation that can be further refined and validated with additional real-world data to achieve even more reliable results.

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