Chlorofluorocarbons

Chem 300a

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1.1: A Brief History of Chlorofluorocarbons

Chlorofluorocarbons (CFCs), also known as Freons, were first synthesized in 1928 by Thomas Midgley Jr, who was working for General Motors trying to find a safe refrigerant to use in commercial applications. (Rosenbaum, n.d.). They are an anthropogenic compound containing fluorine, carbon, and chlorine atoms, and are classified as halocarbons. CFCs are a family of chemicals based upon hydrocarbon skeletons, where most hydrogens have been replaced with chlorine and/or fluorine atoms. They are chemically stable freons that are non-flammable, tasteless and odourless. CFCs are very volatile, which makes for ideal refrigerant gases, having a boiling point close to zero degrees (Rosenbaum, n.d) They were originally created to replace the toxic gases used in the late 1800’s and early 1900’s. Examples of the toxic gases replaced by CFCs as refrigerants are ammonia (NH3), methyl chloride (CH3Cl), and sulfur dioxide (SO2) (Wilkins, 1999).

When first created dichlorodifloromethane was found to be less toxic than carbon dioxide, and as non-flammable as carbon tetrachloride (Midgley & Henne, 1930). The non-toxic, non-flammable, and non-reactive properties of CFCs made them ideal for use as refrigerants.

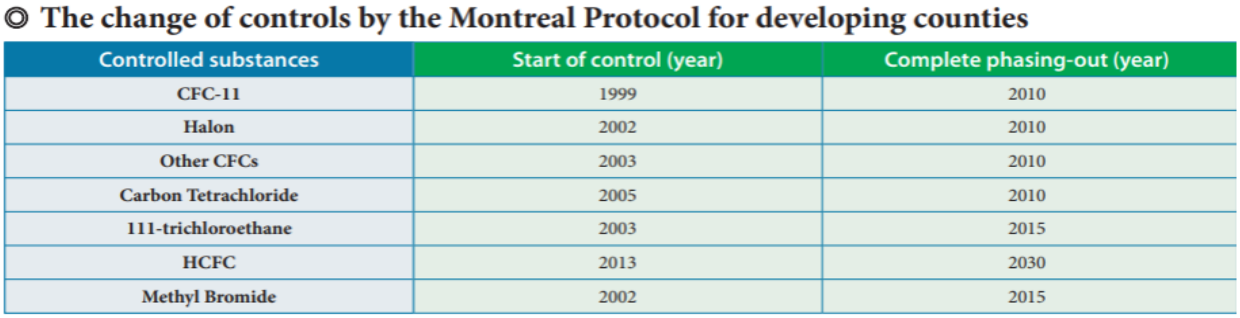
CFCs were used in many developed countries for consumption and production as they were inflammable and non-toxic towards humanity. Chlorofluorocarbons can be used as refrigerants, cleaning agents, foaming agents, and propellants for aerosol sprays (Welch, n.d.).

In 1974, Two University of California chemists, Professor F. Sherwood Rowland and Dr. Mario Molina, showed that CFCs contribute to the depletion of the ozone layer, as they are a major source of inorganic chlorine in the stratosphere (“CFCs,” n.d.).

In 1987, the Montreal Protocol on Substances was signed by 27 nations and put in place to protect the ozone layer (US Department of Commerce, n.d.). The Montreal Protocol is a global agreement to protect the stratosphere by eliminating the production and consumption of “ozone-depleting substances,” or ODS (“The Montreal Protocol on Substances That Deplete the Ozone Layer,” n.d.). The protocol has been led by the United States, taking domestic actions to phase out these CFCs from production and consumption. Since then, the Montreal Protocol has proven success, achieving universal ratification by all countries worldwide. By the end of the century, the protocol is hoping to have assisted in avoiding over 280 million cases of skin cancer, 1.6 million skin cancer deaths, and 45 million cases of cataracts (“The Montreal Protocol on

Substances That Deplete the Ozone Layer," n.d.). The implementation of the Montreal Protocol brings hopes towards full ozone recovery half-way through the 21st century.

Products banned due to the Montreal Protocol include halons (eliminated in 1994), other chemicals such as CFCs, HBFC's, carbon tetrachloride, and methyl chloroform (phased out in 1996), and methyl bromide (banned 2005). Hydrofluorocarbons are expected to be phased out by 2030 ("The Montreal Protocol on Substances That Deplete the Ozone Layer," n.d.).



◎ The change of controls by the Montreal Protocol for developing counties

Controlled substances	Start of control (year)	Complete phasing-out (year)
CFC-11	1999	2010
Halon	2002	2010
Other CFCs	2003	2010
Carbon Tetrachloride	2005	2010
111-trichloroethane	2003	2015
HCFC	2013	2030
Methyl Bromide	2002	2015

Table 2: ("History of Chlorofluorocarbons," n.d.)

A decade after the Montreal Protocol on Substances, the Kyoto Protocol was adopted by the United Nations after the Framework Convention on Climate Change in 1994 to control and diminish greenhouse gas emissions. It was signed and ratified by 192 countries making it the first agreement between nations placed to mandate reductions in greenhouse-gas emissions between countries (History of Chlorofluorocarbons, n.d.). The Kyoto Protocol was extended in 2012 up to 2020, but was replaced in 2015 by the Paris Agreement ("History of Chlorofluorocarbons," n.d.). In October 15 of 2016, multiple parties of the Montreal Protocol adopted the, "Kigali Amendment," which was put in place to deplete the production and consumption of HFCs around the world ("The Montreal Protocol on Substances That Deplete the Ozone Layer," n.d.).

1.2: Past and present applications of CFCs.

Since the invention of CFCs, this chemical family has been used for a variety of applications including as refrigerants, propellants, physical foaming agents for plastics, solvents, degreasing agents, and flame retardants (Gareau, 2011; Clark, 2015). The applications of CFCs are based around their high volatility (Rzepa et al., 2006) and stability (Clark, 2015). These compounds exist as gases at room temperature and pressure, and have low boiling points (Rzepa, et al., 2006). The slight variations in boiling points of the various CFC compounds is key for their versatility of applications.

Additionally, CFCs are inert, non-explosive, non-flammable, and non-toxic for humans (Clark, 2015) which contribute to their functions in a variety of applications, including for everyday use by humans. When CFCs were discovered to deplete the stratospheric ozone layer (Powell, 2002). This discovery led to protocols banning CFCs in certain circumstances, primarily as aerosol propellants and other uses where CFCs were purposely vented from their packages (Powell, 2002). Furthermore, banning protocols for CFCs vary with political borders, for example, in addition to banning the synthesis of CFCs the European Union banned the use of recycled CFCs as of January 2000 (Powell, 2002); whereas the US still allowed the recycling of CFCs as of 2002 (Powell, 2002). Regardless, it is interesting to understand the various past (and present) applications of CFCs.

The low boiling points of CFCs make these compounds ideal refrigerants, which are chemicals used in the vapour compression cycle of refrigerators, freezers, and air-conditioners (Bengston, n.d.). This cycle takes advantage of the low boiling points of CFCs, primarily CFC-13 (boiling point = -30^{o}C at standard temperature and pressure) (Rzepa et al., 2016), CFC-115, and CFC-14 (Vollmer et al., 2018). The basis of refrigeration is to transfer heat from one area to another (Bengston, n.d.), such as from inside a refrigerator to the external environment. The vapour compression cycle accomplishes this by compressing the refrigerant to a liquid, evaporating volatile the liquid with the heat from the target cold environment, recompressing the refrigerant and releasing the extra energy to the external environment (Figure 1), all within a continuous cycle (Bengston, n.d.). A low boiling point is crucial for this cycle because the refrigerant needs to be able to absorb heat and expand to a gas from environments cooled to below 0^{o}C (Bengston, n.d.). Since the refrigerant chemical remains in a closed-circuit environment (until the refrigeration appliance goes out of service), working appliances manufactured prior to CFC bans are still allowed to operate with CFCs in the US (National Institutes of Health, 2020). However, CFCs refrigerants still escape from these closed-circuit systems through leaking equipment (Powell, 2002): the US corporate-wide refrigerant leak rate is ~25% (Whitman, 2018). In the US, appliances manufactured prior to 2010 likely still contain CFC refrigerants (USDA Forest Service); this primarily consists of installed commercial and industrial refrigeration units (Powell, 2002). Due to the ban on the synthesis of CFCs, the have largely been replaced as refrigerants in new equipment by hydrofluorocarbons (Khemani, n.d.; Powell, 2002); ammonia gas is also used as a refrigerant in an alternative refrigeration cycle (Khemani, n.d.).

Manufacturers took advantage of the volatility of CFCs for products that require gas expansion, such as aerosol spray cans and asthma inhalers. These dispensing systems require an unreactive gas propellant to provide pressure to expel the main product and fill the empty space as the product is released (Kodrek Appliances Technology Co., 2013); this prevents the creation of negative pressure within the canister, allowing it to maintain its shape (Kodrek Appliances Technology Co., 2013). For asthma inhalers (also called pressurized metered dose inhalers), the propellant and the medication are suspended together in the canister; when the medication is ejected, the propellant expands to fill the empty space, a similar concept to aerosol cans (Asthma Canada, 2020). CFCs are ideal propellants because they are gases that readily expand at room temperature and are chemically inert to the other contents of the can (Kodrek Appliances Technology Co., 2013). In these disposable dispensing systems, the propellant is ultimately released into surrounding air. Since the recognition of CFCs' damaging effect on the ozone layer, they are no longer used as propellants: CFCs in most aerosols have been banned since 1980 (Powell, 2002); CFC asthma inhalers were completely phased out by 2013 (National Institutes of Health). For an example of a CFC replacement in inhalers see section 1.3.

The chemical properties which make CFCs ideal propellants also make them good physical blowing agents in the manufacture of plastic foam (Niyogi et al., 2014). This process involves the insertion of the blowing agent into the molten polymer mixture where the blowing agent evaporates using the heat from the exothermic plastic polymerization reaction (Niyogi et al., 2014). This gas expansion creates a cellular structure within the polymer, blowing it into a foam (Niyogi et al., 2014; Pantani et al., 2014). CFC gases expand at room temperature, and insoluble in- and do not react with- the molten plastic polymer (Niyogi et al., 2014). CFCs have been phased out as foam blowing agents in the US, European Union (EU), and other regions (Powell, 2002). Non-CFC physical blowing agents have been proposed, such as hydrochlorofluorocarbons in the US, and *c*-pentane in the EU (Powell, 2002). Furthermore, other foam extrusion methods exist, such as a chemical blowing process, which utilize non-CFC chemicals (Pantani et al., 2014).

CFCs have been used as gas solvents for dry-cleaning (NHDES, 2010). Dry-cleaning involves the use of a chlorinated solvent, such as CFC-113, to remove soils and stains in the place of detergents and water (MWDSC & EDF, 1991). The garment is washed with the solvent, after which the solvent is extracted, purified and stored for reuse (MWDSC & EDF, 1991). Although perchloroethylene (PERC) was the major solvent used in this industry, CFC-113 was used primarily for delicate items, because it is less chemically aggressive than PERC (MWDSC & EDF, 1991). It is also less hazardous to human health than PERC (MWDSC & EDF, 1991). In 1987, the US dry-cleaning industry used ~ 2000 metric tons of CFC-113, with ~ 460 metric tons expelled as waste (MWDSC & EDF, 1991). CFCs have been phased out in the dry-cleaning industry (Powell, 2002).

Throughout the 1990s, CFCs were used as the gaseous fire extinguishing agent in total-flooding extinguishing systems (Johnson et al, 1997), as well as in hand-held fire-extinguishers (Amarex, 2020). CFCs non-flammable and gaseous properties are ideal in this application; as a fire extinguishing agent. As CFCs leave no chemical residue they were promoted as extinguishers for delicate, sensitive, and expensive equipment such as computers, electrical equipment, automotive and aircraft engines, and laboratory chemicals and equipment (Amerex, 2020). Halon 1211 is the primary CFC used as a fire extinguishing agent (Powell, 2002). Since the banning of CFCs, Halon 1211 has been largely replaced as a fire-fighting agent by HFC227ea (Powell, 2002), however the manufacture of Halon 1211 extinguishers is still permitted given they use only recycled CFCs (Amarex, 2020)

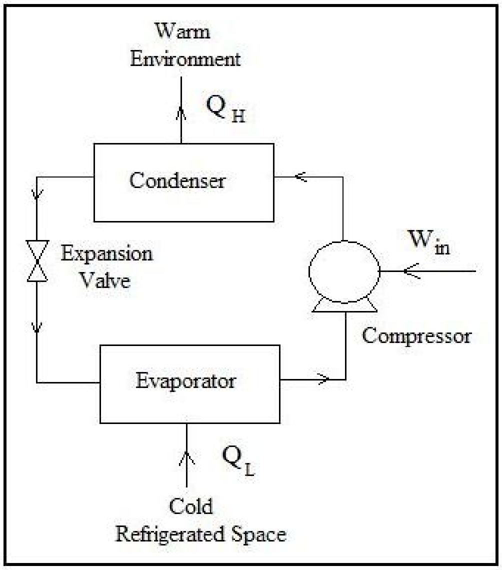


Figure 1: Vapour Compression Refrigeration Cycle.Q_L: heat absorbed by refrigerant from the refrigeration space; Q_H: heat released by the refrigerant to the external environment. (Bengston, n.d.).

1.3: A Future Replacement for Inhalers

Since the mid 1950s metered dose inhalers have been in use for personal respiratory aid through measured bronchodilators (pMDI) (Bronsky 1999). For most of that time inhalers were being used with a CFC called Beclomethasone dipropionate (BDP). It serves as a propellant to disperse medicated particles into air ways (Fireman 2001). With the discovery of CFCs reaction with the ozone layer and the ratification of the Montreal Protocol a new propellant was sought to create a safer and more efficient metered dose inhaler by the year 2005 (Fireman 2001).

Hydrofluoroalkane (HFA) was created as a replacement. HFA is a smaller particle that achieves greater dispersion by means of a warmer pressurized temperature. This allows for an increase of medication to reach more targeted areas of the lungs and less to the oropharynx, middle region of the pharynx, which the CFC-BDP reached (Fireman 2001).

With this finding, studies went underway to determine the likelihood of transferring patients to the HFA-BDP pMDI. Listed below are the designs and sample formats from a study conducted in the late 1990s early 2000s (Fireman et al. 2001).

1. Randomized, open, parallel study. Patients had at least 6 months of asmatic history with controlled symptoms using the CFC-BDP pMD above the age of 12.
2. Study was conducted in the USA, Belgium, The Netherlands, and the United Kingdom.
3. 473 patients were randomized. 354 to HFA-BDP, 119 to CFC-BDP.
4. Study conducted over 12 months to determine the efficacy and safety of switching patients from CFC-BDP pMDI to HFA-BDP pMDI.

After the year long trial ceased, results showed that asthma symptoms were maintained by the new HFA-BDP and maintained over the course of the year long study. It also expressed similarities between subgroups in breathing capabilities from baseline measurements to forced peak rates as shown in the chart below (Fireman et al. 2001).

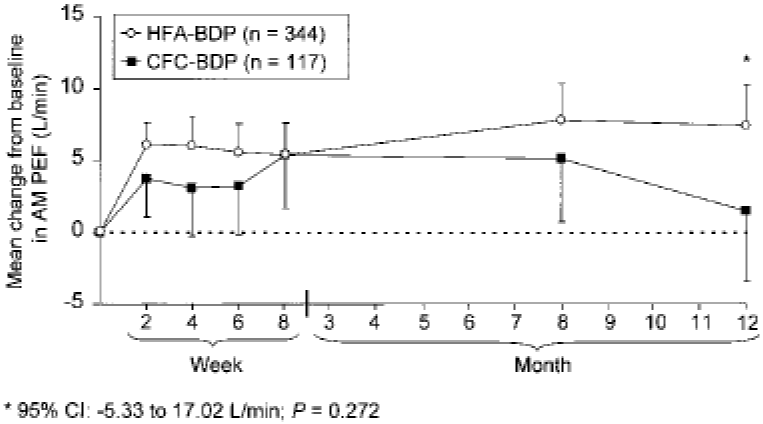


Figure 2: Pulmonary function parameters: mean (SE) change from baseline in AM PEFR (L/minute) (Fireman et al. 2001).

The only slight difference detected by some of the patients was a change in taste between the two favoring the CFC- BDP pMDI.

A study completed a few years prior to Fireman's with similar subject and control variables showed the same results with no significant differences in breathing quality, pulse rate, and blood pressure tracked (Bronsky 1999). With these and other successful trials it is possible to switch to HFA-BDP and move away from the harmful effects of the CFCs.

1.3: The Benefits and Costs of CFCs to society:

In 1932 the Carrier Engineering Corporation created the first home air conditioning unit using CFC-11. Due to CFCs record of non-toxicity CFCs became the preferred coolant in large air-conditioning systems. This preference was to such an extent that public health codes in American cities were rewritten to designate CFCs as the only allowed coolant in public buildings (Wilkins, 1999).

After World War 2 CFCs saw use as propellants for various products such as aerosol sprays, blowing agents for foams and packing materials, and solvents. (Wilkins, 1999). During the 1950's and 1960's CFCs provided the additional benefit of being a cheap method of providing air conditioning to automobiles, homes, and office buildings.

This caught on and CFCs, at their peak, had annual sales of one billion U.S. dollars with over one million metric tons annually produced (Wilkins, 1999). This provided an economic boon to the United States, along with the chemical benefits.

It was not until 1974 when two University of California chemists Professor F. Sherwood Rowland and Dr. Mario Molina demonstrated that there was a previously unforeseen problem with CFCs. While mostly inert in the troposphere due to the type of ultraviolet radiation that reaches the troposphere, they are a major source of inorganic chlorine in the stratosphere (Molina & Rowland, 1979).

As demonstrated above CFCs proved useful to society. However, the costs would come to outweigh the benefits. CFCs have a negative impact on both humans and ecosystems.

The lifetime of CFCs can be from 20 to 100 years ("The Ozone Hole", 2020). This provides time for them to ascend from the troposphere to the stratosphere. Once in the stratosphere, CFCs begin to break down the ozone. The process begins when ultraviolet radiation breaks down CFCs in the stratosphere.

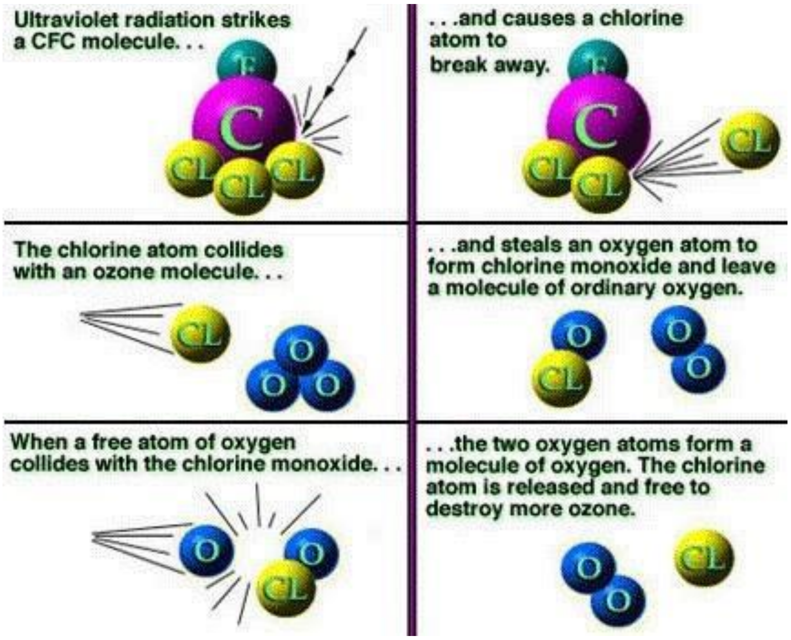


Figure 3: Interaction of CFCs with Ozone (http://www.theozonehole.com/ozonedestruction.htm)

Natural changes in the ozone throughout time have been observed. These natural regulations to the ozone are done by "the changing seasons, winds and long time scale sun variation”, and volcanic eruptions (“NASA - Ozone: What is it, and why do we care about it?” (2020)). Introduction of CFCs compromises the homeostasis of the ozone layer, causing an unnatural depletion of the ozone layer. The consequence of unnatural ozone depletion is UV-B and UV-C rays can reach the earth’s surface. Normally, the ozone layer is enough to block, and protect the earth’s surface from the sun’s high energy, ultraviolet rays. Consequences of these rays breaking through are a higher risk of people developing skin cancer, an increased chance of developing “cataracts, macular degeneration, and other eye damage (“Environmental Fact Sheet”, 2020).

CFCs not only have an impact on us through their effect on the atmosphere. They also damage us before leaving the troposphere. If inhaled, they can cause harm to the central nervous system (“Environmental Fact Sheet”, 2020). Inhalation produces similar behaviours to alcohol intoxication (“Environmental Fact Sheet”, 2020). Heart rhythm can also be affected, in some cases leading to death (“Environmental Fact Sheet”, 2020).

One atom of chlorine can destroy more than 100,000 ozone molecules (The facts about ozone depletion, 2020). The rate of ozone destruction caused by CFCs is greater than the rate at which it can repair itself. If our ozone layer continues to deplete, it can have a global impact on human life. UV-C rays do not simply pose a direct health risk to humans. These rays, if let through, have the ability to cause damage to all living materials and organisms due to their high energy levels (Canada, 2020).

The ocean is also susceptible to harm from exposure to UV-C radiation. Phytoplankton can be killed from high UV levels (Magazine & Ocean, 2020). Phytoplankton are the foundation of the aquatic food web (What are Phytoplankton, 2020). Without them, the entire food web will collapse. Phytoplankton are a primary food source for many organisms ranging from microscopic zooplankton to multi-ton whales. (What are Phytoplankton, 2020). If CFCs continue their damage multiple ecosystems will be affected. It is important that efforts are made to reduce ozone destruction to preserve not only human survival, but ecosystems worldwide.

1.4: Future Impact of CFC Removal

CFCs have been found to accumulate first in the troposphere where they then infiltrate to the stratosphere (Andino, 2011). Ozone (O_3) is usually thought to be dangerous to living things but within the stratosphere it acts as a protection mechanism from harsh ultraviolet rays (“The

Ozone Layer", 2018). Jean Andino (2011) suggests there are two main methods for removing compounds from the troposphere: disposition and reaction. Disposition occurs through rain moving these compounds out of the atmosphere and reaction is when the compounds react with radicals or ozone. CFCs are moved out from the troposphere mainly by using reaction because most of the CFCs are not water-soluble so they are unable to be disposed of by water (Andino,2011). The reactions that take CFCs out of the troposphere take long periods of time so the accumulation eventually starts making its way into the stratosphere (Andino, 2011). After entering the stratosphere CFCs are broken down by UV rays letting out Chlorine atoms which can further attach to ozone and thin out the ozone layer ("The Ozone Layer", 2018).

Because Ozone in the stratosphere is important to keeping living things protected and reducing global climate change, removing CFCs from the atmosphere would seem to be essential to getting the ozone levels back up ("The Ozone Layer", 2018). This removal isn't as easy as it sounds. Some studies in the late 1980s and early 1990s looked at using lasers to take out CFCs from the troposphere before it got to the stratosphere (Stix, 1989). The aim of these studies was to look at how cost effective and beneficial this would be to the environment. Experimental scientists proposed lasers would shoot UV rays from mountain ranges into a series of special mirrors then into space where the use of multi photon dissociation would break down CFCs (Stix, 1989). There were many difficulties with this proposal, Stix (1989) issued some including, ramen stability; where the length of wave needed to reach the CFCs may increase the instability of the wave in the atmosphere. Other things to consider were the lasers were not always targeting the CFC's and rather other molecules in the atmosphere (Stix, 1989) Although there was lots of work needed in the studies to ensure the efficacy, scientists still indicated that if done properly this method would be extremely expensive but would be just as great in its benefits (Stix 1989). In conclusion it seems that removing the CFCs from the atmosphere isn't easy, or cheap, and ultimately the laser proposal didn't go through. The best thing we can do to get rid of CFCs from the atmosphere safely is removing them from industrial and civilian use ("The Ozone Hole", 2020). CFCs will eventually break down and ozone levels will rise up naturally ("The Ozone Layer", 2018).

Scientists know from decades of data that long term CFC use decreases the amount of ozone in our stratosphere ("The Ozone Layer", 2018). If we were to see continuous use of CFCs in refrigerants, aerosols, etc. the problems occurring now in our atmosphere would become far more dangerous (Newman et al., 2009). Newman and his colleagues (2009) showed projections of what the ozone concentrations would be if CFCs use was not stopped and results were shocking showing near zero ozone concentrations in the stratosphere within 50 years (see figure 4)

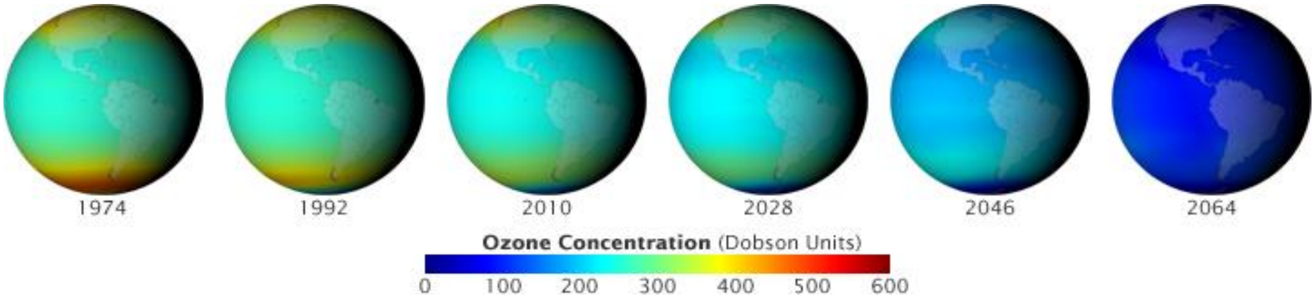


Figure 4: World projection of Ozone Concentrations in the stratosphere from 1974-2064 if CFCs are continuously used (Newman et al, 2009).

This is not likely to be a continuous problem as in 1985 the discovery of the ozone hole was made and by 1987 a ban was put into place to stop the global production of CFCs ("The Ozone Hole", 2020). The ban is known as the Montreal Protocol which was the first treaty to be followed universally to phase out CFCs in hopes of replenishing ozone levels in the stratosphere and protecting mankind (Govt. of Canada, 2019). Many scientists thought the Montreal protocol would be ineffective as CFCs were so popular in industrial use but in 2010 CFCs production stopped worldwide ("The Ozone Hole", 2020). The halt has increased ozone layers in just the last decade and Newman and colleagues (2009) interpolated that this will continue to get better in the next century but will unlikely go back to normal levels due to greenhouse gases still present (Figure 3).

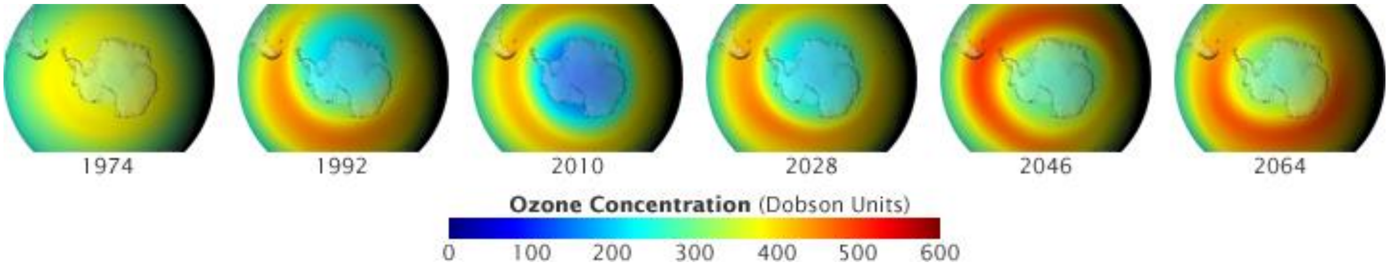
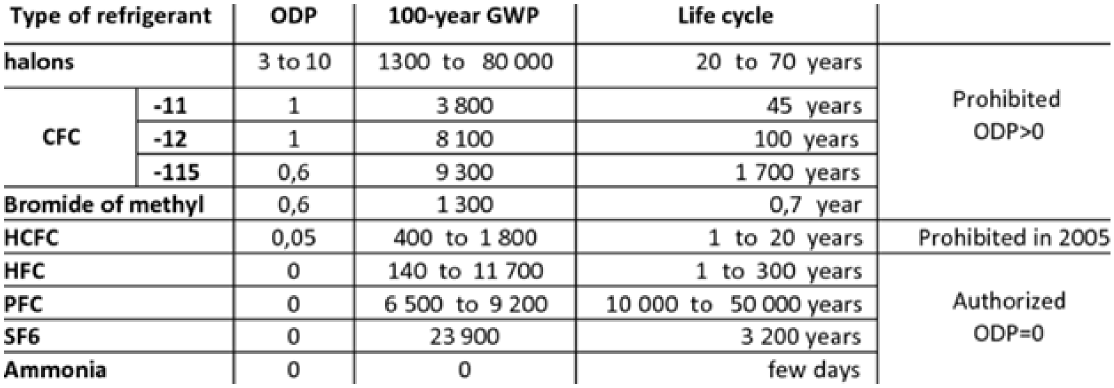


Figure 5: Scientist projection of Ozone concentrations from 2010-2064 since the Montreal Protocols ban on CFCs (Newman et al, 2009).

1.5: CFC Replacements

Once the Montreal Protocol was put in place, finding appropriate replacements for CFCs was crucial due to their diverse and widespread usage. The 1980's saw a sudden rise in the use of hydrochlorofluorocarbons (HCFCs) as an interim CFC replacement (Xiang et al., 2014). These molecules have one center carbon, with one chlorine, one hydrogen, and two fluorine atoms bonded to it. The environmental properties of HCFCs differ from those of CFCs in that they have a lower ozone depletion potential (ODP) and a lower global warming potential (GWP). IN terms of physical properties, HCFCs are similar to CFCs, which allowed seamless integration into existing industrial use. Some differences exist in the physical properties though, as HCFCs are less stable than CFCs, and more likely to break down in the troposphere rather than in the stratosphere. However, there is some percentage of HCFCs that do still stay intact until they reach the stratosphere. Once in the stratosphere these HCFCs, like CFCs, will react with sunlight to release chlorine radicals which interrupt the ozone production cycle. In response to this, a 1997 amendment to the Montreal Protocol was made, which added HCFCs to the list of restricted greenhouse gases. A HCFC phase out and management plan was put in place ("Montreal Protocol", 2020). Global consumption and production of HCFCs is set to be at zero by the year 2030.

The next option for CFC replacement is hydrofluorocarbons (HFCs). This molecule has a central carbon, with one hydrogen and three fluorine atoms bonded to it. Again, like the HCFCs, the physical properties of HFCs are similar to CFCs. The environmental properties are drastically different though, as removing the chlorine from this molecule sets the ODP to zero. However, the GWP of this molecule is much higher than that of HCFCs (Benhadid-Dib & Benzaoui, 2012). A 2016 amendment to the Montreal Protocol was made with the goal of reducing global HFC usage by 80% in the next 30 years (Montreal Protocol, 2020). There is currently no formal phase-out plan for HFCs.



Type of refrigerant		ODP	100-year GWP	Life cycle	
halons		3 to 10	1300 to 80 000	20 to 70 years	Prohibited ODP>0
CFC	-11	1	3 800	45 years	
	-12	1	8 100	100 years	
	-115	0,6	9 300	1 700 years	
Bromide of methyl		0,6	1 300	0,7 year	
HCFC		0,05	400 to 1 800	1 to 20 years	Prohibited in 2005
HFC		0	140 to 11 700	1 to 300 years	Authorized ODP=0
PFC		0	6 500 to 9 200	10 000 to 50 000 years	
SF6		0	23 900	3 200 years	
Ammonia		0	0	few days	

Table 2: ODP, GWP and lifetime of CFCs depending on the fluid type (Benhadid-Dib & Benzaoui, 2012)

Hydrofluoroethers (HFEs) have shown some potential as CFC replacements. Early studies into this molecule show that HFEs would be a suitable replacement for CFCs, as they have similar physical properties and usage possibilities (Sekiya & Misaki, 2000). Additionally, HFEs have lowered effects on the environment (0 ODP, low GWP), and have low toxicity levels. However, more recent studies have shown that the actual creation of HFEs for industrial use is a complicated and inefficient process (Kim et al, 2016). Most reactions for creating HFEs have low product selectivity, meaning that the products are impure and require further processing. This result has led to a downswing in HFE research.

All of the above CFC replacements have been used because of their similar physical properties to CFCs, meaning that they have been able to fill in for almost all of the varied uses and applications. However, some research has been done on molecules that are specific to only certain applications of CFCs. For example, one study found that a plant-based bio-surfactant material made from soybean oil is an efficient and biodegradable alternative for industrial cleaning purposes (Kim, Lee, Lee, Huh, Lee, 2016). Researching alternatives for each specific application of CFCs may be a more environmentally friendly approach, rather than continuing to use molecules that can take over all applications of CFCs, but still have high GWP ratings.

There are still some highly specialized uses of CFCs that are allowed, such as in fire suppression systems on submarines and airplanes, or in specific medical contexts (Simmonds et al., 2017)

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