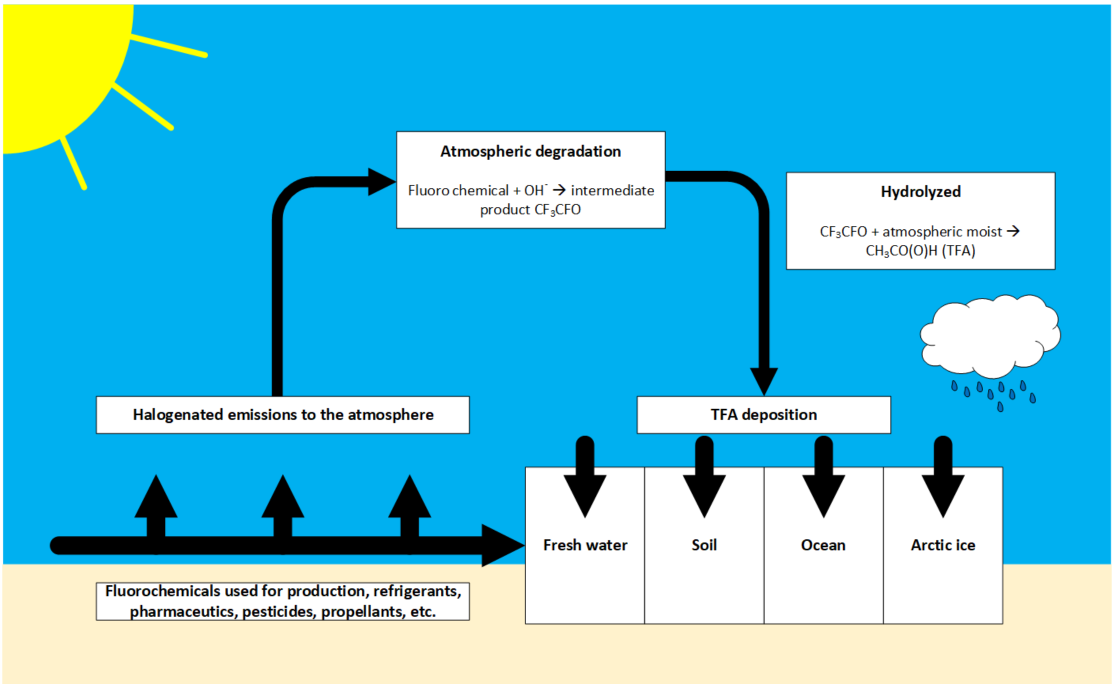
Report and statement of the downsides of HFO refrigerant usage

-Impact of fluorochemical refrigerants and their degradation products on the environment and health-



Published on: 22.02.2021

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Abstract

Refrigerants with a high Global Warming Potential (GWP) are phased out step by step by regulations such as the international Kigali amendment of the Montreal Protocol or the EU F-Gas-regulation. Besides a transition of the refrigeration market towards natural refrigerants, such as propane (R290; GWP_{100} = 3) for chillers, ammonia (R717; GWP_{100} = 0) for industrial applications, CO_2 (R744; GWP_{100} = 1) for commercial refrigeration and new promising technologies such as water (R718; GWP_{100} = 0) for server cooling or air (R729; GWP_{100} = 0) for temperatures down to −160 °C, new low GWP refrigerants made up of chemicals are introduced. The most considered low GWP refrigerant to be used in the future is HFO-1234yf and might replace R134a in mobile air conditioning technologies (MAC). It is known that some of the synthetic refrigerants result in TFA in the atmosphere. This substance is a scPFCA which is characterized by persistency in the environment, high mobility and it cannot be removed by current water treatment technology. TFA is of high concern, since it accumulates in local lakes, freshwater and soils and potentially harms the aquatic environment. Refrigerant producers often advertise HFOs as climate friendly and safe for the environment. This work demonstrates the current and future developments of persistent chemicals in the environment caused by past and future emissions of refrigerants into the atmosphere. The agglomeration of the degradation products in drinking water and natural waters is of major concern, therefore we demand to immediately stop the selling of all synthetic refrigerants and switch to natural refrigerants only.

Das Voranschreiten des Klimawandels setzt den Kälte-Klima-Umweltsektor unter Druck. Häufig werden in Kälteanlagen Kältemittel mit einem hohen Treibhauspotential (engl. Global Warming Potential GWP) verwendet, welche durch Regularien, wie z.B. dem Kigali Amendment des Montreal-Protokolls oder der EU F-Gase-Verordnung stufenweise reduziert werden. Neben einer Tendenz in Richtung der sogenannten „natürlichen“ Kältemittel, wie z.B. der bereits etablierten Kältemittel

- *Propan (R290; GWP100 = 3) für Kaltwassersätze,*
- *Ammoniak (R717; GWP100 = 0) für industrielle Kälte,*
- *CO_2 (R744; GWP100 = 1) für Supermarktkälte und kombinierte Warmwasser-/Wärmepumpen,*

und neuer vielversprechender Technologien, wie z.B.

- *Wasser (R718; GWP = 0) für Serverkühlung oder die Kunststoffindustrie,*
- *Luft (R729; GWP = 0) für Temperaturanwendungen bis -160 °C,*

wurden neue synthetische niedrig-GWP Kältemittel eingeführt.

Das in der Zukunft als meist verwendetes niedrig-GWP Kältemittel ist 2,3,3,3-Tetrafluorpropen (R1234yf; GWP_{100} *<3), welches das klimaschädliche Kältemittel 1,1,1,2-Tetrafluorethan (R134a;* GWP_{100} *= 1550) in Automobilklimaanalagen ersetzen soll. Es ist bereits bekannt, dass einige Kältemittel in der Atmosphäre zu Trifluoressigsäure (TFA) abgebaut werden. TFA gehört zu der Gruppe der kurzkettigen Perfluorcarbonsäuren (scPFCAs), welche persistent in der Umwelt und hoch mobil sind. Durch aktuelle Wasseraufbereitungsanlagen kann es nicht aus dem Trinkwasser nicht entfernt werden. TFA ist umweltbedenklich, da es sich in lokalen Seen, im Frischwasser und in Böden anreichern kann und wassergefährdende und gesundheitsschädliche Eigenschaften besitzt und in erhöhten Konzentrationen eine Gefahr für die Gesundheit darstellt. Die Hersteller der Kältemittel bewerben diese jedoch als klimafreundlich und sicher für die Umwelt.*

Dieser Report veranschaulicht die aktuelle und zukünftige Entwicklung von persistenten Chemikalien in der Umwelt, verursacht von derzeitigen und zukünftigen Kältemittelemissionen. Die Agglomeration der Abbauprodukte in Trinkwasser und Oberflächengewässern ist bedenklich, daher sollte umgehend ein Stopp der Inverkehrbringung von derartigen chemischen Kältemitteln erfolgen, um weitere Umweltauswirkungen zu verhindern

Keywords: refrigeration, natural refrigerants, HFO, TFA, environment and health.

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1. Introduction

Already two previous generations of chemical refrigerants have heavily influenced the environment with ozone depletion potential (ODP of CFCs and HCFCs) and global warming potential (GWP of HFCs), therefore one could assume that mankind has learned the lesson, that bringing a huge amount of persistent chemicals into nature can negatively impact our environment. Choosing and handling refrigerants correctly is important and a key factor in fighting climate change and maintaining environmental safety. The refrigeration industry causes approximately 7.8 % of the global greenhouse gas emissions, of which 37 % are caused by direct emissions of refrigerants and 63 % caused by indirect emissions due to production, transport and electricity production. The sector is expected to grow within the next decades, hence the emissions must be reduced to achieve a sustainable growth (IIF-IIR et al., 2017). In order to reduce direct emissions of refrigerants new chemical low-GWP refrigerants were introduced to the market and advertised as a promising solution. Already the previous HFC refrigerants (e.g. R134a) were found to yield trifluoroacetic acid (TFA) as a degradation product when released to the atmosphere (Wallington et al., 1996) causing concerns for environmental safety. Some of the newly introduced low-GWP refrigerants have higher yields of TFA (WMO, 2011) and therefore have a higher potential of polluting the environment. Since all refrigeration requirements can be perfectly solved with natural refrigerants like air, water, carbon dioxide, propane, and ammonia there is no need for any chemical refrigerants in the market. Many companies already prefer natural refrigerants over chemical ones, for example in commercial and industrial applications, industrial heat pumps, displacement chillers and mobile air conditioning (MAC forbus and train) applications (Shecco, 2020). However, the study shows that there is still a certain percentage that prefer chemical refrigerants over natural refrigerants. The impact of these refrigerants and their degradation products on the environment and the human body is presented in this report as well as the transition of the refrigeration market from the beginning of mechanical refrigeration towards the current situation.

2. History of refrigerants (It started natural and it will end natural)

The fundamentals of today's refrigeration systems were proposed in the early 1800s when Oliver Evans described the use of a closed cycle to freeze water (Evans Oliver, 1805). In 1834, Jacob Perkins patented his invention of the vapour compression system which was designed to use ethyl ether as a refrigerant (Perkins, 1834).

The first generation of refrigerants in the early years of refrigeration with vapour compression systems mainly consisted of solvents and natural refrigerants such as propane (R290) and ammonia (R717) that are still used today. Most of the refrigerants used back then were flammable, toxic and/or highly reactive causing many accidents. The first documentation of a systematic search for a refrigerant was performed by Carrier and R.W. Waterfill (1924). The refrigerants used until the 1930s are listed in Table 2 in the Appendix. Mainly researchers and engineers used whatever was available.

The Second generation of refrigerants: In the 1930s, refrigerants mainly shifted from natural refrigerants to chlorinated (and fluorinated) chemical refrigerants for safety and durability reasons. The first publication of Midgley and Henne (1930) shows how the variation of the chlorination and fluorination with hydrocarbons influences the boiling point, flammability and toxicity. They chose dichlorodifluoromethane (R12) due to its chemical properties. Commercial production of R12 began in 1931 followed by R11 in 1932. Chlorofluorocarbons (CFCs) and later hydrochlorofluorocarbons (HCFCs) dominated the second generation of refrigerants (James M. Calm, 2008). The environmental impact of these substances in the atmosphere, namely the depletion of the ozone layer, gained public interest in the early 1970s when Paul Crutzen warned that increasing the atmospheric concentration of nitrous oxide (N_2O) might deplete stratospheric ozone (Crutzen, 1970). Followed by Molina and Rowland's (1974) warning that chlorofluoromethanes (CFCs) would migrate to the stratosphere and deplete ozone, a harsh debate between scientists and the aerosol products industry about ozone depleting substances (ODS) started (Stephen O. Andersen et al., 2018) resulting in 24 nations signing the Montreal Protocol in 1987 beginning with controls on CFCs and halons.

The consequence of the 40-year use of CFCs before the first environmental concerns became public is still noticeable today. CFCs and long-lived chlorinated solvents were globally phased-out in 1996 and in 2010 for industrialised (A2 countries according to the Montreal Protocol) and developing (A5) countries, respectively. These substances had the most widespread usage amongst the second generation of refrigerants and hence reached the highest mole fractions in the atmosphere (Engel & Rigby, 2018). Due to the long atmospheric life-time these substances are still present in the atmosphere as the measurements at the Jungfrauenjoch in Switzerland show (Reimann et al., 2020).

The end of the CFC era, initiated by the Montreal Protocol, was at the same time the start of the **third generation of refrigerants,** the hydroflurocarbons (HFCs) yet another chemical substance which environmental impacts were undiscovered when introduced. Natural refrigerants such as, carbon dioxide (R744) ammonia (R717) and hydrocarbons (HCs) gained some interest, too, but fluorochemicals retained the primary focus. The Kyoto Protocol sets binding targets for greenhouse gases (GHG) and is implemented in national laws or regulations (e.g. EU-F-gas regulation). The restrictions of the Kyoto Protocol are forcing to shift towards refrigerants which have a low global warming potential (GWP). HFOs are commonly referred as the **fourth generation of refrigerants** or as low GWP-refrigerants.

The current main producers of the HFO refrigerant are Honeywell Fluorine Products (NL) and Chemours (CH) both members of the European Fluoro Carbons Technical Committee (EFCTC). The use of HFOs is highly controversial since producers and scientists argue about the consequences of the degradation product of the HFO refrigerants dominating the market, such as R1234yf, R1234ze(E), R1233zd(E), R1336mzz(Z) and their blends.

3. HFCs and HFOs and their by-products

Hydrofluorocarbons (HFC) replaced the ozone depleting CFC's and were used to an extend in the late 2000s. When these compounds are released to the troposphere, they can react with hydroxyl and chlorine radicals and hence, can be transformed to trifluoroacetylchloride (CF_3COCl) or trifluoroacetyl fluoride (CF_3COF), which are rapidly hydrolysed in the presence of atmospheric moisture to form TFA (Burkholder et al., 2015) (Tromp et al., 1995; Wallington et al., 1994). Trifluoroacetic acid (TFA; $CF_3CO(O)H$) is a short-chain per-fluorinated carbolic acid (scPFCA, $C_nF_{2n+1}CO_2H$ with $n \leq 3$), that has a high solubility in water, is very persistent in the environment and considered to be very mobile (Solomon et al., 2016). Even though, the potential for bioaccumulation in animals is low due to the low log K_{ow}, accumulation of scPFCAs in plants has been demonstrated. Findings of Zhaoyang Liu et al. (2019) indicate a preferential uptake of shorter-chain PFCAs for crops, as previously observed in controlled experiments of Johanna Krippner et al. (2014). The scPFCAs were taken up at a higher rate by the roots and were transported to the shoots. In an experiment of Likens et al. (1997) they demonstrated, that inputs of TFA to a northern hardwood forest and a small forest wetland ecosystem were not conservatively transported through these ecosystems, instead, they were retained within the vegetation and soils components. More TFA was retained by the wetland ecosystem. This will lead to a potential accumulation of TFA in wetlands, especially for wetlands lacking outflow, as suggested by Cahill et al. (2001) and Tromp et al. (1995).

Results from ocean water samples indicate that TFA is naturally occurring in ocean waters (Frank et al., 2002; Scott et al., 2005) but the TFA concentration in the atmosphere (Boya Zhang et al., 2018; Reimann et al., 2020; Wu et al., 2014) occurrence in freshwater (Marco Scheurer et al., 2017; Ole John Nielsen et al., 2001; Zihan Zhai et al., 2015) and even in the artic ice (Pickard et al., 2020) is more likely to originate from anthropogenic source.

The usage of HFC's have seen a significant increase over the last two decades. For instance, the concentration of R134a, which is mainly used for mobile air conditioning, at Mace Head, Ireland increased from 0.01 ppt in 1990 (Oram et al., 1996) to 100 ppt in

2018 (Reimann et al., 2018), making it the most abundant HFC in the earth's atmosphere (Freeling et al., 2020).

The HFO-1234yf was introduced to substitute R134a in mobile air conditioning units. In contrast to R134a, R1234yf rapidly degrades in the atmosphere with a molar and weight yield of 100 % (M.D. Hurley et al., 2008; Papadimitriou et al., 2011) and has a 12 day lifetime. That's much it is higher than the yield of 7-20 % for R134a (Wallington et al., 1996) with an atmospheric life time of 13.4 years (WMO, 2011), suggesting that TFA deposition from R1234yf will be enhanced and more localized (Henne et al., 2012; Wang et al., 2018). The time for degradation is also dependent on the amount of OH radicals in the atmosphere (Wang et al., 2018).

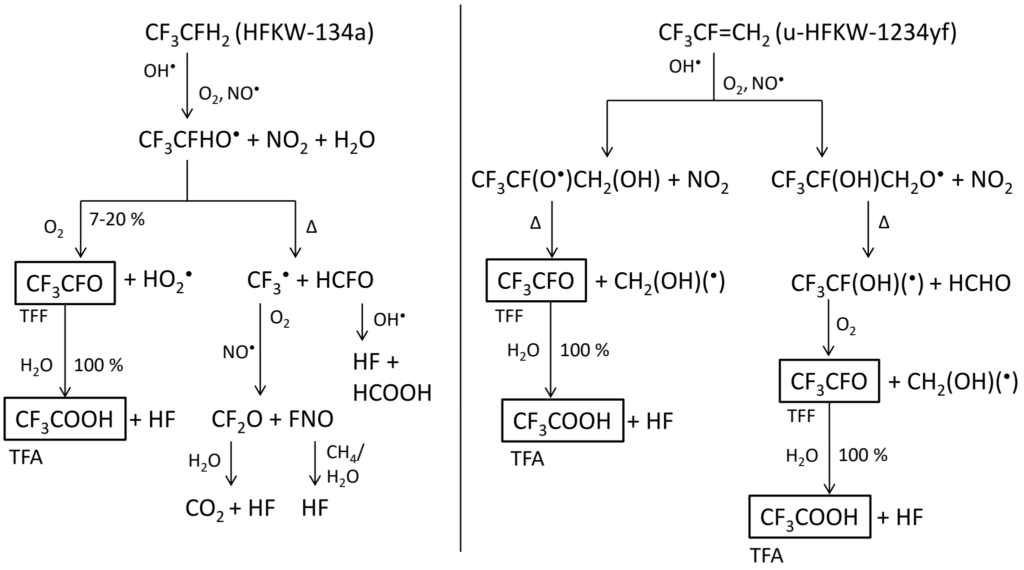

Figure 1: Atmospheric degradation of R134a and R1234yf (Behringer & Heydel, 2020)

Further refrigerants known to yield TFA are HFC-227a, HFC-236fa, HFC-245fa, HFC-365mfc, HFO-1234ze(E), HFO-1336mzz(E) and the mixtures R449A, R452C, R454C. The TFA yield of the most important refrigerants and propellants are summarized in Table 1.

Table 1: Most important refrigerants known to yield TFA

Refrigerant	Application	GWP	TFA yield	Source
R134a	Mobile air conditioning	3900	10-20 %	(Wallington et al., 1996)
R227ea	Replacement propellant for CFC-12 and firefighting for halon-1301	3580	100 %	(WMO, 2011)
R236fa	Firefighting replacement for halon-1211/1301, refrigerant	9820	<10 %	(WMO, 2011)
R245fa	Foams	1050	<10 %	(WMO, 2011)
R365mfc	Foams (replacing HCFCs)	842	<10 %	(WMO, 2011)
R1234yf	Replacing HFC-134a	4	100 %	(M.D. Hurley et al., 2008; Papadimitriou et al., 2011)
R1234ze(E)	Foams (for CFC-12)	7	<10 %	(WMO, 2011)

A recent review estimated the future deposition and accumulation of TFA in the ocean to be 3.7 – 7.4 ng/L increase in concentrations over the next 100 years with a constant global deposition of 50- 100 Gg/a (Tang et al., 2011) others estimated an increase of the TFA concentration of 15.3 ng/l in the ocean as terminal sink for the yield of HFO in the atmosphere from 1990 to 2050 (Solomon et al., 2016). Considering the conflicts in the literature about the consistency of a stable natural background, it is simplistic to assume a complete ocean mixing (Henne et al., 2012). On land, TFA is believed to have been transported by the mechanical action on the sea, just like sea salt aerosol (EFCTC, 2016).

However, this is not plausible since all substances solved in sea water with similar biological, chemical and relevant physiochemical properties for transport are transported similarly. With the assumptions that the sea contains 20 g/L chloride and 20 µg/L TFA as well as 10- 20 mg/l chloride in precipitation, only a TFA concentration of <0.001 µg/l in precipitation can be explained (Nödler et al., 2019). TFA is mainly scavenged from the atmosphere by wet deposition (Berg et al., 2000; D.J Bowden et al., 1996), therefore precipitation is considered to be the most important source of TFA to the nonmarine environment. The results of Berg et al. (2000) show that 96 % of TFA is deposited by wet deposition. Its high persistence also leads to the accumulation of TFA in the aquatic environment, especially in terminal water bodies with high evaporation rates (Cahill et al., 2001; Russell et al., 2012; Tromp et al., 1995).

TFA observed in precipitation is largely a result of urban activities (Scott et al., 2000). Different sources of TFA exposure to the environment is from direct discharge of wastewater from the industry (Marco Scheurer et al., 2017; Remmel, 2017; Xie et al., 2020), by thermolysis of fluoropolymers from household materials (Ellis et al., 2001; Jia'nan Cui et al., 2019). Pharmaceuticals and pesticides might also yield TFA as a terminal degradation product in the environment (Marco Scheurer et al., 2017). TFA was widely detected in human serum samples with median concentrations of 8.46 µg/l. Older persons showed a higher concentration of TFA than younger persons, suggesting a widespread human exposure among general population in China (Yishuang Duan et al., 2020).

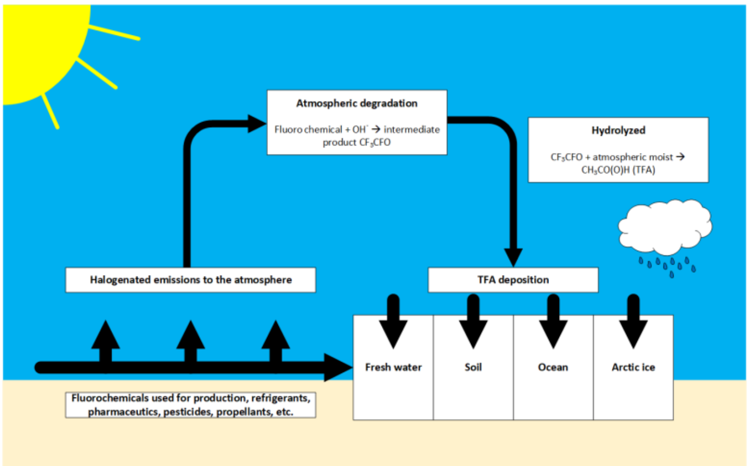

Figure 2: Deposition of TFA via. degradation of fluorochemical products

4. How are fluorinated refrigerants influencing the environment and humans?

Fluorides are agglomerating in the environment due to human emissions. The full potential outcome of fluoride emissions caused by refrigerants is hard to fully predict. That fluorides have an influence on functions in the human body, e.g. thyroid function is well known since the 1950s. The acute toxicity of TFA to mammals is well established (Solomon et al., 2016) and the predicted TFA concentrations are well below the NOEC (acute oral NOEC for rats is 250 mg/kg body wight (Boutonnet et al., 1999)), but the information of long-term effects of TFA is limited.

Human exposure to TFA

After concerning reports of high TFA concentrations in waters in NRW, Germany (Remmel, 2017) a long time toxicity assessment of TFA was performed (Umwelt Bundesamt, 2020). Rats were exposed for one year to TFA concentrations in of 0 ppm, 30 ppm, 120 ppm and 600 ppm in freshwater. The study showed an increase of the ALT-concentration (alanine aminotransferase) depending on the dosage of TFA (Umwelt Bundesamt, 2020). ALT is an indication of damage of the liver such as a liver-hypertrophy as it was observed in a 14 day study (*ECHA Dossier Für Trifluoressigsäure)*. In a study to developmental toxicity where TFA was given to pregnant rats (10-20th day of pregnancy) a temporary disfunction (~50 days) of the liver and kidney was observed (GESTIS-Stoffdatenbank).

The authors Safari et al. (2014) conclude that all halogenated inhalational anaesthetics, such as Halothane, enflurane, isofluorane and desfluorane are metabolized involving protein CYP2E1 and produce trifluoroacetylate components and are associated with liver injury. Halothane oxidation leads to production of trifluoroacetic acid (TFA), which acts on hepatocyte proteins to produce trifluoroacetylated components. A severe type of liver injury is associated with an acute increase of liver enzymes, alanine aminotransferase (ALT) and aspartate aminotransferase (AST), which remain elevated for one to two weeks following exposure and resolve without treatment (Wright et al., 1975), similar to the ALT concentrations measured in the study used by Umwelt Bundesamt (2020).

Based on the NOEC of 30 ppm (~1.8 mg/kg body wight), the maximum TFA concentration in freshwater in Germany is set to 60 µg/l, but at the same time the german environment agency (UBA) recommends not to exceed 10 µg/l.

TFA in aquatic environments

The toxicity of TFA on aquatic environments is well established. In aquatic environments the *selenastrum capricornutum* (freshwater green alga) is highly sensitive to TFA exposure with an NOEC of 0.12 mg/l (Boutonnet et al., 1999). A TFA concentration of 100 µg/l is considered to be safe for the aquatic ecosystem (Berends et al., 1999).

Fluoride in general

The effects of fluoride on the thyroid have long been observed. In the 1950s, fluoride was used pharmacologically to reduce the activity of the thyroid in people with hyperthyroidism. Even a low fluoride intake per day can influence the thyroid hormones TSH and T3 (Kheradpisheh et al., 2018). A daily intake of fluoride combined with low iodine diet increases the risk of a hypothyroidism (Malin et al., 2018; Peckham et al., 2015) for regions with low iodine intake such as e.g. Germany where almost 30 % of the populations shows a lower iodine intake than recommended (Johner et al., 2016). There are many ways to be exposed to fluoride, but the main path is water and nutrition (Guth et al., 2020; WHO, 2004). By releasing fluorinated gases to the atmosphere new ways of exposure are added, possibly effecting peoples that are already at a higher risk of exposure, such as e.g., refrigerant workers. Fleet et al. (2017) pointed out that there is a lack of literature on human health hazards of direct exposure to HFOs.

5. Concerning increase of HFO and TFA

The consideration of persistency of chemicals released to the environment is of great importance. A persistent substance that is constantly or increasingly emitted will result in continuously increasing concentration in the environment up to an point where it may exceed a no-effect thresholds (Cousins et al., 2019).

Cousins et al. (2019) summarise that the main concerns with highly persistent chemicals are:

“(1) The continuous release of highly persistent chemicals will lead to widespread, long-lasting, and increasing contamination.

(2) Increasing concentrations will result in increasing probabilities that known and unknown effects occur, be it by a single chemical and/or in a mixture with other substances.

(3) Once adverse effects are identified, it will be technically challenging, energy intensive, and thus costly, to reverse the chemical contamination and therefore the effects. These measures are limited to contamination hotspots, whereas, for most of the environment, no remediation or clean-up will be possible.”

The literature presented in the following section demonstrates the TFA agglomeration in the environment caused by the emission of fluorinated greenhouse gases over the last two decades and illustrates the importance of an immediate action on restricting the new generation of fluorinated greenhouse gases.

Continuous measurements at the Jungfrauenjoch in Switzerland show an increase in concentration and detection of R1234yf over the last decade. The measurements started in 2010 where R1234yf was not detected in the samples. In 2018, R1234yf was measured in 71 % of all the samples. The concentrations increased from 0.002 ppt to 0.050 ppt, respectively. In the urban area of Dubendorf, the mean mole fractions of R1234yf in 2018 were 3.0 ppt. R1234ze(E) was detected in 30 % of all measurements at the Jungfrauenjoch in 2011 and reached 85 % detection in all samples by 2018. At Dubendorf, it was detectable in all measurements from the beginning. The annual mean mole fraction of R1234ze(E) was 3.1 ppt in 2018. R1233zd(E) can be detected in all samples since 2015 at both stations but the mole fraction is still lower compared to R1234yf and R1234ze(E). (Vollmer et al., 2019).

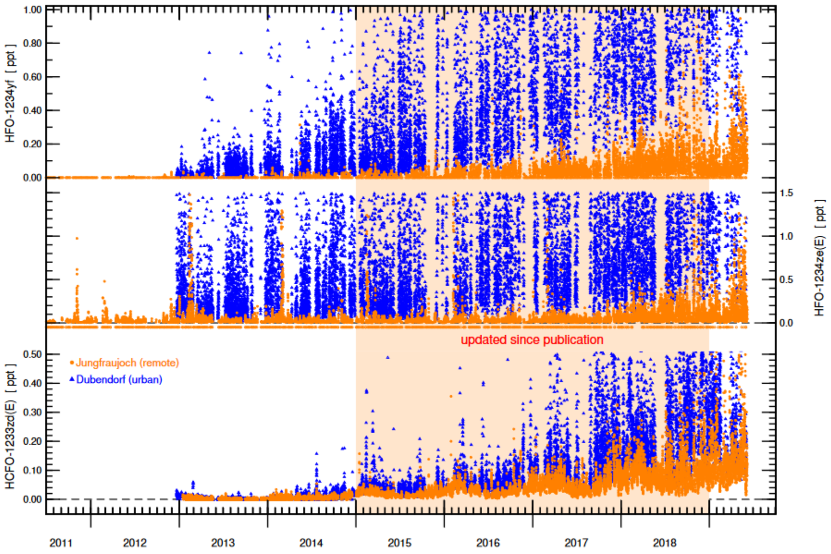

Figure 3: Measurements of HFO-1234yf and HCFO-1233zd(E) from 2011 to 2019 in Dubendorf and at the Jungfrauenjoch in ppt (Vollmer et al., 2019)

Measurements of landscape waters, tap waters and snows in Beijing, China in 2012 show a 17-fold increase in TFA concentrations compared with measurements in 2002 (Zihan Zhai et al., 2015). Findings of Xie et al. (2020) indicate that fluoride production plants are a serious problem to the surrounding aquatic life. The ratio of pollutant concentrations in the environment to the predicted no-effect concentration (PNC/PNEC) for TFA was greater than 1, indicating that TFA concentrations are potentially damageing the aquatic ecosystem of Jinan.

Multiple studies used modelling approaches to estimate future concentrations of TFA in precipitation due to the increasing use of R1234yf (Henne et al., 2012; Kazil et al., 2014; Russell et al., 2012; Wang et al., 2018). Simulation of Henne et al. (2012) show that, when all mobile air conditioning units of the vehicles in the EU are conversed to R1234yf, about 30-40 % of the European R1234yf emissions would be deposited as TFA within Europe, while the remaining fraction will be transported toward the Atlantic Ocean, Central Asia, Northern, and Tropical Africa. The highest annual mean TFA concentrations in rainwater were simulated over the Mediterranean and North Africa, reaching up to 2.5 µg/l. The total European annual R1234yf emissions were predicted to be between 11 to 19.2 Gg/a. The model does not consider any other use or introduction of refrigerants with a TFA yield, therefore even higher concentrations are expected in the future. Freeling et al. (2020) reported a three to four times higher TFA concentration in precipitation in Germany over the last two decades. The latest data of the measurement of TFA in precipitation in Germany shows a 3- fold increase compared to measurements of Berg et al. (2000). The measured average TFA precipitation concentration of 0.7 µg/l match the estimated concentration for the year 2020 in Europe of Henne et al. (2012), even though only 18 % of German cars are equipped with R1234yf in 2018 and the full substitution of R134a will not be completed before 2030. An annual wet deposition flux of 190 µg/m² or approximately 68 t was calculated for the sampling period from February 2018 to January 2019. Only 39 % of the annual TFA emission in precipitation in 2018 can be explained by the model of Henne et al. (2012). Based on estimations the mean annual TFA flux in Germany will increase by 10-folds by 2030 only considering the degradation of R1234yf (Behringer & Heydel, 2020).

Other similar studies predict the TFA concentration (caused by R1234yf emissions of mobile air conditioners) in terminal water bodies in North America to reach up to 1 to 15 µg/L with extreme concentrations up to 60-200 µg/L over the next 50 years (Russell et al., 2012).

While the environmental effects of TFA are considered to be negligible over the next few decades, potential longer-term impacts require further evaluations due to the environmental persistence of TFA and uncertainty in growth due to future uses of HFOs (Huret & Legras, 2014). In a study of environmental and health effects of HFO refrigerants by the Norwegian Environment Agency (Fleet et al., 2017) three possible scenarios of future TFA emissions were considered. Three different sets of models were performed for the scenarios 2025, 2100 phase-out (HFO use until 2050 then phased-out) and 2100 plateau (constant TFA emissions from 2050 to 2100). The RCR (Risk characterization ratio PNC/PNEC) were significantly higher than median and average algae risk assessments. The 2100 plateau scenario also suggests the highest RCR for TFA entering various environmental compartments. In comparison, the 2100 phase-out scenario has the lowest RCR, however some risk will remain in the environment due to the long-term persistence of TFA.

6. Natural alternatives

When it comes to justify if it is socially acceptable to use substances that yield persistent chemicals in the environment, one should always consider the availability of alternatives. Releasing chemicals that can last for generations in the environment, especially when there is an uncertainty about the environmental and health impacts, must be avoided when alternatives are available.

Natural refrigerants gained interest over the past decades and made technological progress to be competitive or even more efficient than refrigerant systems based on chemical refrigerants. Suitable natural refrigerants are available for mobile air conditioning. Carbon dioxide (R744; $GWP_{100} = 1$) is a promising solution for mobile air conditioning, especially since these systems are more efficient than existing ones (Lemks et al., 2011). In an official press release, the UBA (2010) recommends the use of R744 in mobile air conditioning instead of R1234yf and pointed out that R744 is neither toxic nor flammable, cost effective and has a good cooling capacity. The main concern when using R744 in MAC is the leakage of refrigerant into the passenger's room. Elevated CO_2 concentrations of > 4% can cause dizziness, unconsciousness, hearing and visual disturbance (EPA, 2015) and therefore increasing the risk of a car accident. At concentrations > 8 % CO_2 is deadly within a few minutes. Mixtures of hydrocarbons such as R436B (52 % R290 and 48 % R600a) were proposed at the ATMOsphere 2011 by Obrist (Graz & Busse, 2011). The system efficiency was significantly improved compared to R134a and hence more efficient than R1234yf, since the system performance of R1234yf is lower compared to R134a (Chi-Chuan Wang, 2014; J. Navarro-Esbrí et al., 2013). Additionally, the risk of using R1234yf in mobile air conditioning is higher due to the flammability and chemical reaction of R1234yf in case of a fire or hot surface temperatures. HFO-1234yf is classified by ASHRAE as A2L refrigerant meaning that it is not toxic with a lower flammability than the A2 refrigerants. During an fire or at surface temperatures above 350 °C, R1234yf will form hydrofluoric acid (HF) (BAM, 2009), which is acute toxic (PubChem.). In case of a burning car in a tunnel, the HF concentrations are expected to exceed the level considered to be safe (DMT GmbH & Co. KG, 2014).The Kraftfahrtbundesamt KBA (2013) summarized the investigations of crash tests and shoed that the use of R1234yf is in contradiction to the European aim of reducing the danger of traffic. In an experimental study on hydrocarbon mixtures to replace R134a the experiments showed that every mixing ratio of HCs outperformed R134a (Somchai Wongwises et al., 2006). HCs in general have proven to be energy efficient and have been found to be mostly suitable for small and medium sized domestic and commercial purposes, fluid chillers, heat pumps and low capacity automobile air conditioners. (K. Harby, 2017; Zunipa Roy & Gopinath Halder, 2020)

Overlooked applications in the present atmospheric models are large scale refrigeration applications using R1234ze(E). Such so-called ‘large tonnage chillers’ range from 20 kW up to 14 MW of cooling capacity and are primarily used in industrial refrigeration, server cooling, district cooling with systems ranging up to over 200 MW capacity if no free cooling is possible. Even though, R1234ze(E) has a lower yield of TFA compared to R1234yf, the atmospheric lifetime is 16 days (EFCTC) and hence favour more local TFA emissions, too. Natural refrigerants can cope with the challenge of these applications. For example, systems with water as refrigerant are very promising for temperatures above 0 °C. These systems are already used for server cooling and other industrial applications. The use of propane for chillers is well established. The state-of-the-art propane chillers use multi-cycle hydraulic system to minimize the refrigerant charge and are a perfect solution for cold water production in any size with high efficiency.

Every refrigeration application can be realised with natural refrigerants and hence reduce the risk of negative, long-term environmental effects such as climate warming, or pollution caused by chemicals.

7. Conclusion

History has already proven several times that emitting chemicals or substances in large quantities into the environment without knowing their exact impacts can result in global threats that prevail over generations and require regulations to avoid further damage. The impacts on the environment of the new HFO-refrigerants, more specifically the degradation product TFA, are well established with *selenastrum capricornutum* (freshwater green alga) being the most sensitive algae to TFA in the aquatic environment. There is no threat of acute TFA toxicity for humans at any of the current or expected concentrations, but long-term exposure with low concentrations showed elevated ALT-concentrations and indicate that TFA in drinking water can potentially damage the liver and have other impacts, for example on the hormone system. The current and expected future concentrations of TFA are lower than the concentrations known to have a negative effect on the environment. Nevertheless, exact concentrations are difficult to predict and concentrations might be higher than estimated by global atmosphere models in the future. The TFA concentrations in precipitation in Germany in 2018 only attributes to 39% (on average) of the predicted TFA concentrations of Henne et al. (2012). The more concerning TFA concentrations are those that we do not know yet, since they can lead to unexpected concentrations and exceed levels considered safe. Unexpected emissions with global effects occur as it was reported by Vollmer et al. (2021). They found unexpected emissions of three ozone depleting HCFCs that are believed to origin from chemical production processes as a by-product and have no known end use. Two of them are known compounds produced during refrigerant production such as HCFC-133a to produce HFC-134a. The second one, HCFC-31 is believed to form during the production of the refrigerant HFC-32 that is currently used in stationary air conditioning as a replacement for R410A. HCFC-132b was first spotted in 2015, but by analysing archived air, Vollmer concluded that its first appearance in the atmosphere was in the late 1990s. The measured emissions appear to come from sources in Asia and smaller emissions, originating from south-eastern France, stopped abruptly in early 2017 at the same time that a fluorocarbon factory near Lyon closed down. HFC-134a and HFC-32 are used in HFC/HFO blends and therefore will not only yield TFA but also cause ozone depletion due to the emissions of their by-products during production. The problem with risk assessments of TFA is the considerations of known thresholds only and neglecting the persistence of the chemicals since some negative effects might not be discovered yet.

“Concerns about a chemical are always related to effects, but for highly persistent chemicals, it should not be required that these effects are represented explicitly in the hazard assessment scheme. The hazard assessment of these chemicals should be based solely on their high persistence as a placeholder or proxy for effects.” (Cousins et al., 2019)

Due to the shorter lifetime of HFOs in the atmosphere their degradation product TFA lead to more local emissions causing higher concentrations in local precipitation, water reservoirs or wetlands, especially in those with lacking outflow. Not only refrigerant emissions from applications lead to more localized emissions, also fluorochemical production plants pollute the local environment with persistent chemicals (Xie et al., 2020). TFA is a very small molecule and therefore it cannot be removed by current water treatment technology.

There is a lack of information in the literature regarding the general effect of fluorochemical refrigerants on the thyroid. But it is known that halogen molecules influence the thyroid function. Therefore, HFO and TFA might also have the possibility to cause hypothyroidism and other consequences such as the brain development of children due to iodine deficiency during pregnancy (Bashash et al., 2017).

It is no question that sooner or later negative effects or an environmental disaster will happen; it is only a question of when it will happen. Before bringing tonnes of chemicals into the environment, it needs to be proven that they are harmless to human and the environment, especially regarding chemicals with high persistence such as TFA. “When high persistence is identified for a chemical, the uses of this chemical should be grouped into essential and nonessential uses as a basis for determining management actions. Non-essential uses, on the other hand, are uses for which there are alternatives or where a substance has no essential technical function in a product and the use is driven only by convenience or market opportunity. These nonessential uses of a substance with high persistence could then be phased out with highest priority, whereas for essential uses measures should be taken that help avoid emissions” (Cousins et al., 2019)

With the words of Maria Krautzberger, German Environment Agency's president 2018, “TFA cannot be removed [from drinking water] with the usual treatment methods, so further [use] must be avoided at all costs."

“Therefore, phasing out HFOs (and consequently TFA), or emission reduction strategies along with best practise measures that help ensure efficient capturing of HFO/TFA during recycling operations, will help reduce the risk to human and environmental health.” (Fleet et al., 2017). There is no technical need for these substances, since “HFOs are totally unnecessary in new refrigerant systems” (Statement of Hafner in (Stausholm, 2019)).

8. Literature

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Appendix

Table 2: Historical introduction of refrigerants (James M Calm & David A Didion, 1998)

Year	Refrigerant	Chemical formula of makeup
1830s	Choutchocine Sulfuric (ethyl) ether	Distillate of india rubber CH_3-CH_2-O-CH_2-CH_3
1840s	Methyl ether (R-E170)	CH_3-O-CH_3
1850	Water/sulfuric acid	H_2O/H_2SO_4
1856	Ethyl alcohol	CH_3-CH_2-OH
1859	Ammonia/water	NH_3/H_2O
1866	Chymogene Carbon dioxide	Petrol ether and naphta (hydrocarbons) CO_2
1860s	Ammonia (R717) Methyl amine (R630) Ethyl amine (R631)	NH_3 $CH_3(NH_2)$ CH_3-$CH_2(NH_2)$
1870	Methyl formate (R611)	$HCOOCH_3$
1875	Sulfur dioxide (R764)	SO_2
1878	Methyl chloride (R40)	CH_3Cl
1870s	Ethyl chloride (R160)	CH_3-CH_2Cl
1891	Blends of sulfuric acid with hydrocarbons	H_2SO_4, $C4H_{10}$, $C5H_{12}$, $(CH_3)_2CH$-CH_3
1900s	Ethyl bromide (R160B1)	CH_3-Ch_2Br
1912	Carbon tetrachloride	CCl_4

	Water vapour (R718)	H_2O
1920s	Isobutane (R600a) Propane (R290)	$(CH_3)_2CH-CH_3$ $CH_3-CH_2-CH_3$
1922	Dielene (R1130)	$CHCl=CHCl$
1923	Gasoline	Hydrocarbons
1925	Trielene (R1120)	$CHCl=CCl_2$
1926	Methylene chloride (R30)	CH_2Cl_2