September 2022 Report

The Rising Threat of HFOs and TFA to Health and the Environment

ATMO sphere

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Follow the Science on HFOs and TFA

This report is meant to shine a light on the threat to environmental and human health stemming from the rapidly increasing use of HFO-1234yf as a refrigerant in motor vehicle air-conditioning and, as part of blends with HFCs, in commercial and industrial refrigeration and other applications.

HFO-1234yf is considered a PFAS (forever chemical) by the Organisation for Economic Co-operation and Development (OECD). But more importantly, fugitive emissions of HFO-1234yf readily produce an atmospheric degradation product, trifluoroacetic acid (TFA), that is also a PFAS, according to the OECD. TFA descends to the Earth in rainfall across a wide geographic area, accumulating (because it doesn't break down) in waterways that supply drinking water.

Long-chain PFAS have already been determined to be extremely harmful chemicals. F-gases and TFA are shorter-chain PFAS but share the same chemical structure, persistence and potential for harm.

The proliferation of HFO-1234yf and TFA thus raises serious questions for the HVAC&R industry, end users of refrigerants and policymakers. The writing on the wall – in the form of numerous studies that are cited in this report – strongly points to the steady development of a new environmental and health problem stemming from the use of a fluorinated refrigerant, this time an HFO.

Even the chemical industry acknowledges the potential for harm by TFA after 2040, 17 years from now. Seventeen years ago, in 2005, HFCs were seen as a problematic refrigerant because of their high GWPs and contribution to climate change, which ultimately resulted in the Kigali Amendment and the phase down of HFCs around the world. Does the HVAC&R industry want yet another environmental calamity on its hands in 2040 – and possibly much sooner – because of the accumulation of TFA in the environment?

Seventeen years ago, natural refrigerants were still not widely used in retail grocery stores, so HFCs were dominant. But today, natural refrigerants like CO_2 and hydrocarbons are commonly employed by stores around the world, and there is simply no reason to use an HFO blend that incorporates HFO-1234yf, not to mention HFCs like R134a and R32 with their high GWPs. Even for mobile air-conditioning, CO_2 is a proven option, though car manufacturers have mostly opted for HFO-1234yf.

Natural refrigerants are considered future-proof because they exist in the environment and pose no threat to it. The same cannot be said about HFO-1234yf and its blends. Given the sizable investment that end users must make in refrigeration and air-conditioning, why would they spend that money on a solution that is not future-proof when a future-proof solution is available, tested and reliable?

Policymakers should also not turn a blind eye to the mounting evidence of TFA as an environmental threat. In Europe, beginning in January 2023, the European Chemicals Agency (ECHA) is planning to consider a proposal from five European nations to regulate TFA, HFO-1234yf and some other f-gases as PFAS under the EU's Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation. If the ECHA decides to regulate these chemicals as PFAS, it will send a resounding message throughout the world about their significant potential for harm.

As with climate change, the HVAC&R industry should follow the science when it comes to HFO-1234yf and TFA and work to avoid yet another environmental and health emergency in the years to come.

Marc Chasserot
Founder and Publisher, ATMOsphere

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Executive Summary

The chemical industry's replacement for HFCs – HFOs (hydrofluoroolefins) – have very low GWP values and thus don't present a problem for the climate or the ozone layer. But other environmental and health concerns have arisen for HFOs, particularly for HFO-1234yf (2,3,3,3-tetrafluoropropene), a mildly flammable (A2L) refrigerant that is the most widely used HFO.

The largest use of HFO-1234yf, beginning in Europe in 2012, has been as a replacement for R134a (100-year GWP of 1,430) in mobile air conditioning. Moreover, HFO blends such as R513A and R449A, which include HFO-1234yf as a key ingredient, are used in thousands of stores globally as well as in industrial facilities, ice rinks and other applications.

HFO-1234yf is marketed as an environmentally friendly refrigerant because of its low 100-year GWP (under 1). But when it leaks into the atmosphere, 100% of HFO-1234yf photo-oxidizes, in only 10-14 days, into trifluoroacetic acid (TFA), a short-chain per-fluoroalkylcarboxylic acid (scPFCA). TFA then descends in rainfall to Earth, where, as an extremely durable chemical, it accumulates mostly in water bodies, including rivers, streams, lakes and wetlands. While not currently regulated, the TFA is collecting in the environment, according to a number of recent studies, which largely attribute this to expanding emissions of HFO-1234yf.

Even at extremely small concentrations in drinking water, TFA is potentially harmful to human health. Moreover, it is difficult to remove from drinking water using conventional methods.

In Germany, where a host of TFA studies have been conducted, the German Environment Agency (UBA) has set a human health "orientation value" limit of 60 µg/L for TFA in drinking water and a "precautionary measure" of 10 µg/L. The concentration levels of TFA in the environment have begun to approach – or exceed – those levels in some studies.

Long-term exposure to TFA can potentially damage the liver and the thyroid function in humans, according to a report released in 2021 by Refolution Industriekälte, a German consulting and engineering firm focused on sustainable refrigeration.

Both TFA and HFO-1234yf fall under the definition of PFAS (per- and polyfluoroalkyl substances) established by the OECD (Organisation for Economic Co-operation and Development) and used by scientists around the world. PFAS encompass a well-known group of chemicals such as PFOA, PFOS and GenX, that have been linked to adverse health outcomes.

A myriad of studies have been conducted, mostly in Europe, on the accumulation of HFO-1234yf and TFA in the environment.

As it has with previous f-gas refrigerants, the chemical industry has rallied to the defense of HFO-1234yf, particularly in regard to the impact of TFA.

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Acronyms and Abbreviations

A2L (non-toxic, mildly flammable)
ALT (alanine transaminase)
CCl_4 (carbon tetrachloride)
CFC (chlorofluorocarbon)
CO_2 (carbon dioxide)
dw (dry weight)
ECHA (European Chemicals Agency)
ECOS (Environmental Coalition on Standards)
EEAP (Environmental Effects Assessment Panel
EFCTC (European Fluorocarbons Technical Committee)
EIA (Environmental Investigation Agency)
EPA (Environmental Protection Agency)
ESB (German Environmental Specimen Bank)
F-gas (fluorinated gas)
GSPI (Green Science Policy Institute)
GWP (global warming potential)
HCFC (hydrochlorofluorocarbon)
HCFO (hydrochlorofluoroolefin)
HFC (hydrofluorocarbon)
HFC-134a (1,1,1,2-tetrafluoroethane)
HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane)
HFO (hydrofluoroolefin)
HFO-1234yf (2,3,3,3-tetrafluoropropene)
HFO-1234ze (1,3,3,3-tetrafluoropropene)
MAC (mobile air-conditioning)
NOEC (no observed effect concentration)
ODP (ozone-depleting potential)
OECD (Organisation for Economic Co-operation and Development)
PEC (predicted environmental concentration)
PFAS (per-and polyfluoroalkyl substances)
PFOA (perfluorooctanoic acid)
PFOS (perfluorooctanesulfonic acid)
PNEC (Predicted No Effect Concentration)
R12 (Dichlorodifluoromethane)
R125 (pentafluoroethane)
R134a (1,1,1,2-tetrafluoroethane)
R227ea ((1,1,1,2,3,3,3-heptafluoropropane)
R32 (Difluoromethane)
REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals)
SCIs (stabilized Criegee intermediates)
scPFCA (short-chain perfluoroalkylcarboxylic acid)
TFA (trifluoroacetic acid or trifluoroacetate)
UBA (German Environment Agency)
UNEP (United Nations Environment Programme)

INTRODUCTION

The Rising Threat of HFOs and TFA to Health and the Environment

Numerous studies have pointed to increasing evidence of trifluoroacetic acid – HFO-1234yf's atmospheric degradation product and a potentially dangerous PFAS chemical – in the environment.

It has been well known since the 1970s that fluorinated gases used as refrigerants and in other applications pose a danger to the environment and human health

Developed in the 1920s, the original f-gases – chlorofluorocarbons (CFCs) such as R12 – were marketed as safe alternatives to refrigerants like sulfur dioxide and methyl chloride. However, by the 1970s, scientists, notably Mario Molina and F. Sherwood Rowland, discovered that CFCs significantly depleted the atmospheric ozone that protects people from cancer-causing ultraviolet radiation. Worldwide alarm led to the creation, in 1987, of the Montreal Protocol treaty, which began the process of phasing out CFCs and hydrochlorofluorocarbons (HCFCs) like R22 around the world. The health of the ozone layer has since improved.

CFCs and HCFCs also have high GWP values, making them a contributor to global warming as well as harmful to the ozone layer. Their replacements – hydrofluorocarbons (HFCs) – lack the chlorine atom that depletes the ozone layer, but HFCs still possess very high GWPs, hundreds or thousands of times higher than that of CO_2.

To address the global-warming impact of HFCs, the Kigali Amendment to the Montreal Protocol was created in 2016, setting up a phase-down program for these f-gases for developed and developing countries that will reduce their consumption by 80–85% over the next 25 years.

It's worth noting that chemical industry statements defending the safety of CFC and HFC refrigerants have proved to be false over time and were followed by regulatory action. (See page 9.)

The chemical industry's replacement for HFCs – HFOs (hydrofluoroolefins) – have very low GWP values and thus don't present a problem for the climate or the ozone layer. But other environmental and health concerns have arisen for HFOs, particularly for HFO-1234yf (2,3,3,3-tetrafluoropropene), a mildly flammable (A2L) refrigerant that is the most widely used HFO. U.S. manufacturers Chemours and Honeywell are the primary producers of HFO-1234yf, under the Opteon YF and Solstice YF brands, respectively.

The largest use of HFO-1234yf, beginning in Europe in 2012, has been as a replacement for R134a (100-year GWP of 1,430) in mobile air conditioning.

SHOULD THE CHEMICAL COMPANIES BE BELIEVED?

A Timeline of Chemical Industry F-Gas Comments

STATEMENT

1975:

The evidence that CFC refrigerants depleted the ozone layer was "a science fiction tale ... a load of rubbish ... utter nonsense."[1]

1986:

(on CFCs): "We believe that there is no immediate crisis that demands unilateral regulation.[1]

1990s:

"...environmentally acceptable alternatives, such as hydrofluorocarbon (HFC)134a" are being introduced.[2]

2019:

HFO refrigerants, including R513A "meet the long-term needs of the refrigeration... markets."[3]

2020:

"R513A is a transitional refrigerant."[4]

REGULATORY ACTION

1987:

Montreal Protocol is established to phase out CFCs.

2016:

The Kigali Amendment to the Montreal Protocol is established to phase down HFCs.

2030: ???

[1] (n.a.). (n.d.). "DuPont: A Case Study in the 3D Corporate Strategy." Greenpeace. Available online at: https://bit.ly/3pNziOD

[2] (n.a.). (n.d.) "DuPont HFC-134a Properties, Uses, Storage, and Handling." DuPont Suva. Available online at: https://bit.ly/3pFLvFb

[3] (n.a.). (2019). "Opteon™ XL41 (R-454B) and Opteon™ XP10 (R-513A) Refrigerants selected by Mitsubishi Electric Hydronics and IT Cooling Systems SpA (MEHITS) Applications." Chemours, May 27. Available online at: https://bit.ly/3jJtT7j

[4] Allgood, C., (2020). Video: "E16: Getting to Know Opteon™ XP10 (R-513A)." 5-minute mark, Chemours, September 22. Available online at: https://bit.ly/3xgRRfR

Refrigerant	Type	Composition	GWP (100 year)	GWP (20 year)
R448A	HFO/ HFC	26% R32 / 26% R125 / 21% R134a / 7% R1234ze / **20% R1234yf**	1,400	**3,100**
R449A	HFO/ HFC	24,3% R32 / 24,7% R125 / 25,7% R134a / **25,3% R1234yf**	1,400	**3,100**
R449C	HFO/ HFC	20% R32 / 20% R125 / 29% R134a / **31% R1234yf**	1,200	**2,900**
R452B	HFO/ HFC	67% R32 / 7% R125 / **26% R1234yf**	710	**2,100**
R513A	HFO/ HFC	44% R134a / **56% R1234yf**	600	**1,700**
R454B	HFO/ HFC	68.9% R32 / **31.1% R1234yf**	490	**1,700**

[1] Source: "Real GWP: 20 years vs 100 years: Impact of Refrigerants Fact Sheet #1 (V.1.1.)." ATMOsphere. Available online at: https://bit.ly/3HJOYJe

Chemours, a major producer of the gas, recently reported the number of vehicles on U.S. roads using HFO-1234yf as a refrigerant to be at least 80 million – about one in three vehicles registered in the U.S. in 2020.

Moreover, HFO blends such as R513A and R449A, which include HFO-1234yf as a key ingredient, are used in thousands of retail stores around the world as well as in industrial facilities, ice rinks and other applications. Because these blends contain HFCs, their GWPs, especially over 20 years, remain very high. (See chart, this page.)

HFO-1234yf is marketed as an environmentally friendly refrigerant because of its low 100-year GWP (under 1). But how environmentally friendly is it?
When it leaks into the atmosphere, 100% of HFO-1234yf photo oxidizes, in only 10-14 days, into trifluoroacetic acid (TFA), a short-chain per-fluoroalkylcarboxylic acid (scPFCA). TFA then descends in rainfall to Earth, where, as an extremely durable chemical, it accumulates mostly in water bodies, including rivers, streams, lakes and wetlands. In water bodies TFA can form trifluoroacetate (also abbreviated TFA) salts by reacting with minerals such as calcium and sodium; these salts are grouped with trifluoroacetic acid in terms of environmental effect.

Due to the shorter lifetime of HFOs in the atmosphere, their degradation product TFA leads "to more local emissions causing higher concentrations in local precipitation, water reservoirs or wetlands, especially in those with lacking outflow," noted a report released in 2021 by Refolution Industriekälte, a German consulting and engineering firm focused on sustainable refrigeration.

Another HFO, HFO-1234ze(E), also converts to TFA in the atmosphere, but to a smaller extent (less than 10%). Some HFCs also change into TFA: R134a (10-20%) and R227ea, a fire suppressant used in HFO/HFC blends (100%)

While not currently regulated, TFA is collecting in the environment, according to a number of recent studies, which largely attribute this to expanding emissions of HFO-1234yf. The environmental group Greenpeace has called on governments to list HFOs in the Annex of Controlled Substances of the Kigali Amendment in order to track HFO production, consumption and the amount released to the atmosphere.

In sufficient quantities, TFA can be a destructive substance. In pure form, it is harmful when inhaled, and causes severe skin burns. But even at extremely small concentrations in drinking water, TFA is potentially harmful to human health. Moreover, it is difficult to remove TFA from drinking water using conventionmal methods, though a new approach has recently been proposed.

In Germany, where a host of TFA studies have been conducted, the German Environment Agency (UBA) has set a human health "orientation value" limit of 60µg/L for TFA in drinking water and a "precautionary measure" of 10 µg/L. The concentration levels of TFA in the environment have begun to approach – or exceed – those levels in some studies.

Long-term exposure to TFA can potentially damage the liver and the thyroid function in humans, according to the Refolution report. The threat posed by TFA is particularly concerning, the report notes, because of its persistence in the environment, observing, "A persistent substance that is constantly or increasingly emitted will result in continuously increasing concentration in the environment up to a point where it may exceed a no-effect threshold."

Some aquatic life may already be feeling the effect of TFA, according to a wide-ranging 2017 HFOs/TFA study by the Norwegian Environment Agency. Exposure of freshwater green alga to existing levels of TFA in Malawi, Chile and Germany was found to "equate to there being an environmental risk," the report said.

Both TFA and HFO-1234yf fall under the definition of PFAS (per- and polyfluoroalkyl substances) established by the OECD (Organisation for Economic Co-operation and Development) and used by scientists around the world. PFAS encompass a well-known group of chemicals such as PFOA, PFOS and GenX, that have been linked to effects on the immune system and human development, cancer and other adverse health outcomes.

Reflecting the harm PFAS chemicals represent, the U.S. Environmental Protection Agency (EPA)'s health advisory on acceptable levels of PFAS, formerly 70ppt (parts per trillion) was revised on June 15, 2022, to 0.004ppt for PFOA, 0.02 parts per trillion for PFOS, and 10ppt for GenX.

Adopting the OECD definition of PFAS, five European countries announced last year their intention to submit a joint proposal to restrict some HFC and HFO refrigerants and TFA as PFAS under the EU's REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulation. The European Chemicals Agency (ECHA) is expected to take up the proposal next January and come to a decision by 2025, creating uncertainty about the use of HFOs in Europe.

Researchers at Northwestern University recently published a paper in the journal *Science* describing a method for destroying PFAS chemicals once they have been removed from contaminated soil or water. However, it remains to be seen how well these methods will work outside the lab, whether they can address the massive scale of worldwide PFAS contamination, or whether they apply to TFA, which is known to be extremely hard to remove from water.

Moreover, the Natural Resources Defense Fund (NRDC) recently reported that TFA is a byproduct of the process that breaks down longer-chains PFAS.

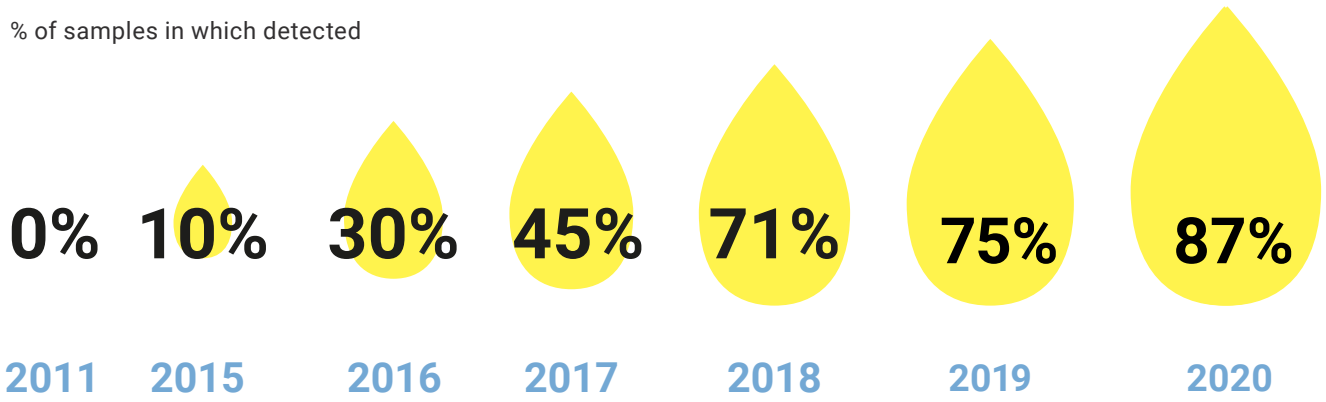
In the U.S., the EPA uses a different definition of PFAS that does not include f-gases or TFA; however, the agency's narrower definition has come under considerable criticism from U.S. scientists, and a bill has been put forward to change the EPA's definition to the OECD's.

Notwithstanding its PFAS definition, TFA is on the following EPA lists:

-- PFAS/EPA Toxcast Chemical Inventory
-- PFAS/EPA: Cross Agency Research List
-- PFAS/EPA: List of 75 Test Samples (Set 2)
And HFO-1234yf is in PFAS/EPA: PFAS structures in DSSTox (update August 2021).

Detection of R1234yf in the Atmosphere Over Europe

% of samples in which detected



Source: Empa, Update of "First observations of the fourth generation synthetic halocarbons HFO-1234yf, HFO-1234ze(E) and HCFO-1233zd(E)."Measurements taken at Jungfraujoch, Switzerland

RISING THREAT: TFA WARNINGS AROUND THE WORLD

TFA levels in the Arctic ice are 10 times higher than before 1987.[1]

The concentration of TFA in urban landscape waters in Beijing, China, increased 17-fold between 2002 and 2012.[3]

Monthly measurements of TFA in rainwater in Germany increased by three-to-five times in the last 25 years.[2]

High levels of TFA were found in the blood plasma of Chinese adults, with a median concentration of 8.46µg/L.[4]

TFA deposition is projected to be 10,000 metric tons per year by 2040 over European land, rising from about 2,000 metric tons in 2020.[2]

TFA has been found in beer samples from 23 countries.[5]

[1] Garry, M. (2020). "Canadian Researchers Find Elevated Levels of HFO-1234yf Byproduct in Arctic Ice." Hydrocarbons21. com, May 15. Available online at: https://bit.ly/3CtsB86

[2] Behringer, D. (2021). "Persistent degradation products of halogenated refrigerants and blowing agents in the Environment" [PowerPoint Presentation]. ATMO Europe Summit 2021. Available online at: https://bit.ly/3jJNV1L

[3] Zhai, Z et al. (2015). "A 17-fold increase of trifluoroacetic acid in landscape waters of Beijing, China during the last decade," Chemosphere, vol. 129, pp. 110-117. Available online at: https://bit.ly/3pRrICu

[4] Duan, Y et al. (2020). "Distribution of novel and legacy per-/polyfluoroalkyl substances in serum and its associations with two glycemic biomarkers among Chinese adult men and women with normal blood glucose levels," Environment International, vol. 134, no. 105295. Available online at: https://bit.ly/3BFRhbY

[5] Scheurer, M & Nödler, K. (2021). "Ultrashort-chain perfluoroalkyl substance trifluoroacetate (TFA) in beer and tea – An unintended aqueous extraction," Food Chemistry, vol. 351, no 129304. Available online at: https://bit.ly/3CDuqza bit.ly/3CDuqza

TFA in German Water	
Health orientation value:	60 µg/L[1]
Precautionary measure:	10 µg/L[1]
TFA concentrations in German water samples:	0.3 to 12.4µg/L[2]
Mean monthly TFA concentrations in German precipitation:	up to 4.874µg/L[3]

[1]German Environment Agency
[2] Ultra-Short-Chain PFASs in the Sources of German Drinking Water: Prevalent, Overlooked, Difficult to Remove, and Unregulated https://bit.ly/3TC45dK
[3] Persistent degradation products of halogenated refrigerants and blowing agents in the environment: type, environmental concentrations, and fate with particular regard to new halogenated substitutes with low global warming potential https://bit.ly/3TCYF2d

HFO/TFA on the rise

A myriad of studies have been conducted, mostly in Europe, on the accumulation of HFO-1234yf and TFA in the environment.

Empa, the Swiss Federal Laboratories for Materials Science and Technology, has studied the atmospheric presence of two HFOs and an HCFO in the atmosphere since 2011. In January 2021, it published an update of its 2015 study

Empa's measurements were made at two locations, Jungfraujoch in the Bernese Alps in Western Switzerland, and Dubendorf, the Zurich suburb where Empa is based. In its update, one of the researchers, Martin Vollmer reported that, since the initial Jungfraujoch and Dubendorf measurements were published in 2015, the three HFOs/HCFOs "have continued to grow in the atmosphere, both in frequency of detectable mole fraction as well as on their intensities/magnitudes."

For example, while HFO-1234yf at Jungfraujoch was detected in none of the 4,150 samples in 2011,, it was detected in 10% of all samples in 2015, in 30% in 2016, in 45% in 2017, in 71% in 2018, in 75% in 2019, and in 87% in 2020. Also, while the mean and median mole fractions in the first years remained at 0.002ppt, they increased to 0.15ppt and 0.10ppt by 2020, respectively.

The 2017 Norwegian Environment Agency study projected levels of HFO emissions (particularly HFO-1234yf) through 2100, and assessed how these emissions could affect the environment, pointing to many areas of concern as well as noting which areas need to still be investigated. For example, the study projected annual emissions of HFOs to be 228,641 metric tons from non-article 5 countries in 2050, and 860,582 metric tons from article 5 countries.

Given the persistence of TFA, the risk it presents increases if emissions of HFO-1234yf to the environment grow, the Norwegian report said. With that in mind, it stated that "phasing out HFOs (and consequently TFA), or emission reduction strategies along with best practice measures that help ensure efficient capturing of HFO/TFA during recycling operations, will help reduce the risk to human and environmental health."

Other studies suggest the impact the dissemination of HFO-1234yf and its conversion into TFA is starting to have. In January 2020, a study published in *Environment International* found TFA "in high concentrations" in more than 90% of blood serum samples in China, indicating "widespread human exposure" among the general population. "Our results provided support for future studies which need to further explore human exposure pathways and toxic effects on human health for these compounds," the study says.

TFA Concentrations Across Time from Precipitation in Germany	
1995/96:	54-69g/km²
2019/19:	190g/km²
2019/20:	276g/km²
2050 (projected):	4,000g/km²)

Source: Persistent degradation products of halogenated refrigerants and blowing agents in the environment: type, environmental concentrations, and fate with particular regard to new halogenated substitutes with low global warming potential https://bit.ly/3TCYF2d

Meanwhile, TFA has been found in in beer and tea at concentrations of 6ppb and 2ppb, respectively.

In a 2022 study funded by the German Environment Agency (UBA), growing concentrations of trifluoroacetate (TFA) were found in archived leaf samples of various tree species, with a two-to-five-fold increase between 1995 and 2018 – a sign that TFA bioaccumulates.

There have been several studies in Germany focused on TFA in bodies of water. For example, a 2017 study published in Water Research found levels of TFA in five locations along the Rhine River in Germany ranging from 0.4 to 1.4µg/L.

More recently, a 2022 study funded by the German government has found TFA "widespread and dominant" in 46 water samples collected from 13 different sources of German drinking water. The TFA concentrations found range from 0.3 to 12.4µg/L (exceeding Germany's precautionary measure of 10µg/L).

UBA also commissioned a two-year measurement of TFA in rainwater, carried out in Germany for the first time, from February 2018 to March 2020, with samples from eight German Meteorological Service measuring stations. The mean monthly TFA precipitation concentrations range from 0.330 to 0.398µgL, – three to five times the averages in 1996-1997 – reaching up to 4.874µg/L. One-year TFA inputs amounted to 190 g/km² in 2018/19 and 276 g/km² in 2019/20, an increase of at least three to four times compared to the period 1995/96 (54 to 69 g/km²). Based on that data, UBA modeled the "maximal future use and emissions" of HFOs up to 2050. "The projections show that in the future, especially the emissions of the refrigerant [HFO]-1234yf from mobile and stationary air conditioning will add a large additional share to the amounts of TFA or trifluoroacetate in the atmosphere."

The model calculation indicates that in 2050 the refrigerant R1234yf alone is expected to cause TFA inputs from precipitation of 2.5 kg/km^2 per year for Europe and up to 4 kg/km^2 per year for Germany; this would correspond to a ten-fold increase in today's TFA inputs, generating up to 50,000 metric tons of TFA load from refrigerant emissions for Europe in 2050.

From this study the UBA concluded that HFOs used as refrigerants, foam blowing agents and aerosol propellants "should be replaced by more sustainable solutions with halogen-free substances" such as natural refrigerants.

Denmark has also been studying the presence of TFA in water supplies. In 2021, the Danish Environmental

Protection Agency reported finding TFA in 219 out of 247 groundwater wells, as well as in some drinking water supplies. In the vast majority of groundwater wells, the concentration of TFA is lower than 1 µg/L.

In the U.K., a University of Bristol-led study simulated the effects of switching from R134a to R1234yf and found a 33-fold increase in the "global atmospheric burden of TFA." The amount of TFA would rise from 65 metric tons formed from the 2015 emissions of R134a to about 2,150 metric tons that would be formed in the future from an equivalent emission of HFO-1234yf.

In North America, a 2020 Canadian study looking at the composition of two Arctic ice cores found TFA levels 10 times higher than before 1987. The growth in the Arctic is particularly notable since "there is no direct use of HFOs or TFA in the Arctic," said Cora Young, , an atmospheric chemist at Toronto, Canada-based York University, and the corresponding author of the study

Chemical industry response

As it has with previous f-gas refrigerants, the chemical industry has rallied to the defense of HFO-1234yf, particularly in regard to the impact of TFA.

For example, the European Fluorocarbons Technical Committee (EFCTC) argues that the evidence is "clear and irrefutable" that TFA occurs naturally in "large quantities in the environment."

However, Canadian researchers have determined that there are "no compelling scientific arguments" to support the existence of naturally formed TFA. The study, "Insufficient evidence for the existence of natural trifluoroacetic acid," published on November 1, 2021, in *Environmental Science: Processes & Impacts,* concluded that in the absence of new evidence, "natural TFA should not be invoked in any discussions about the production and/or regulation of TFA."

EFCTC also contends that f-gases don't have the characteristics of longer-chain PFAS and should not be regulated as PFAS. But that is refuted by Lydia Jahl, a scientist with the Green Science Policy Institute (GSPI), who said "HFOs and TFA should be considered PFAS for their shared chemical structure, persistence and potential for harm."

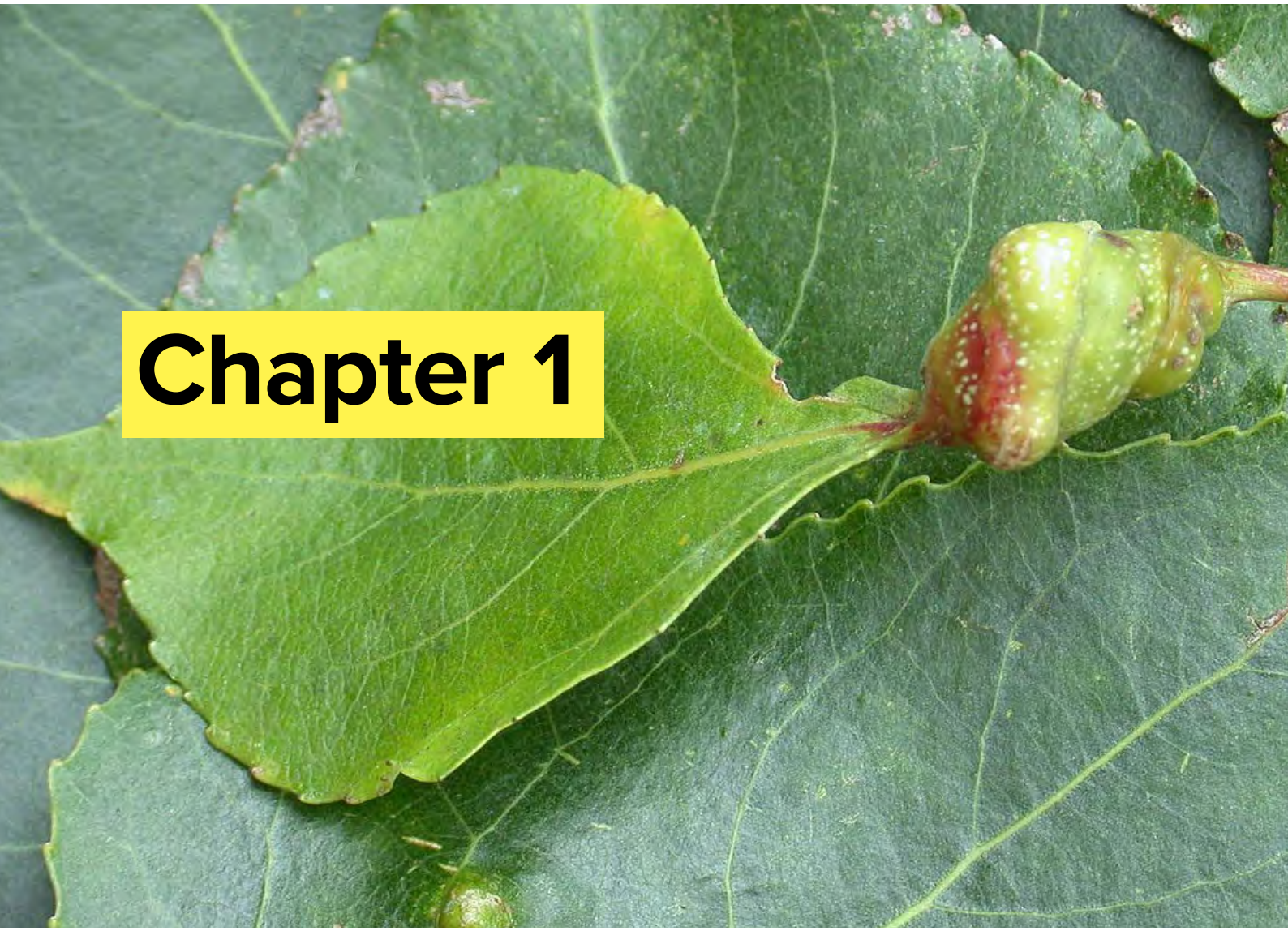
The EFCTC argues that TFA is not – and will not be – harmful to humans. However, the group often hedges on its assertions. In the following statement, quoting from the UNEP Environmental Effects Assessment Panel's Summary Update 2020 for Policymakers, EFCTC twice uses the word "current" to describe TFA risks. "The current low concentration of trifluoroacetic acid (TFA) produced by the degradation of several hydrofluorocarbons (HFCs) and hydrofluoroolefins (HFOs) is currently judged not to pose a risk to human health or to the environment" (emphasis added).

Quoting from the 2021 scientific assessment by the Environmental Effects Assessment Panel (EEAP) of the United Nations Environment Programme (UNEP): "Humans could be exposed to TFA via drinking water and food but there is no evidence to date of adverse effects on health" (emphasis added).

The EFCTC also does not commit to any assurances about TFA beyond 20 years, and acknowledges that TFA has the potential for harm even before then. For example, quoting from the 2018 Scientific Assessment of Ozone Depletion: "There is increased confidence that trifluoroacetic acid (TFA) produced from degradation of HFCs, HCFCs, and HFOs will not harm the environment over the next few decades. Periodic re-evaluation is prudent, given the uncertainties in the sources and sinks of TFA and because of its persistence in the environment" (emphasis added).

More recently, the chemical industry addressed the environmental deposition of TFA in an October 2021 study funded by the Global Forum for Advanced Climate Technologies (globalFACT), which represents f-gas producers Chemours, Honeywell, Arkema and Koura (and equipment manufacturer Daikin). The study concluded that "with the current knowledge of the effects of TFA on humans and ecosystems, the projected emissions through 2040 would not be detrimental" (emphasis added). But the study also acknowledged that "the major uncertainty in the knowledge of the TFA concentrations and their spatial distributions is due to uncertainties in the future projected emissions" (emphasis added).

The following is a review of recent studies and developments involving the accumulation of TFA in the environment and its potential impact on human health.



Chapter 1

Lombardy Poplar leaf samples

Leaf Samples Found to Have Increasing Amounts of TFA Over Time

In a 2022 study funded by the German Environment Agency (UBA), growing concentrations of trifluoroacetate (TFA) were found in archived leaf samples of various tree species, with a two-to-five-fold increase between 1995 and 2018.

The study attributed the TFA growth to "increasing emissions of gaseous TFA precursors" such as certain HFC and HFO refrigerants.

The study – "Levels and Temporal Trends of Trifluoroacetate (TFA) in Archived Plants: Evidence for Increasing Emissions of Gaseous TFA Precursors over the Last Decades" – was published April 18, 2022, in *Environmental Science & Technology*. Its authors are Finnian Freeling, Marco Scheurer, Jan Koschorreck, Gabriele Hoffmann, Thomas A. Ternes, and Karsten Nödler.

Scheurer and Nödler also participated in another recent German TFA study that found TFA, among other similar chemicals, "widespread and dominant" in 46 water samples collected from 13 different sources of German drinking water.

In its acid form (trifluoroacetic acid), TFA is produced in the atmosphere by the 100% breakdown of HFO-1234yf, and is carried in rainfall to Earth, where it is found in acetate form. Between 7% and 20% of HFC-134a breaks down into TFA in the atmosphere.

According to the leaf-study authors, this is the first study to describe the "concentrations and temporal trends of TFA in biota by analyzing archived leaf samples of various tree species from the German Environmental Specimen Bank [ESB]." They regard plants as "an efficient biomonitoring tool" to evaluate the presence of TFA in the environment over time.

In total, 55 tree leaf samples from the German ESB were analyzed for TFA. Samples of the same leaf species from different locations each had a similar concentration range of TFA. The highest concentrations (up to about 1,000µg/kg dry weight) were found in Lombardy poplar leaves.

A "statistically significant positive trend" in the TFA concentration within the study period was found for most species and sites. This trend, the study says, is "likely the result of both bioaccumulation as well as increasing emissions of gaseous TFA precursors over the last three decades."

Widespread contamination

Since TFA was detected in all analyzed plant samples, these results show that "the ubiquitous presence of TFA in dry and wet deposition leads to a widespread contamination of terrestrial ecosystems, even at near-natural and remote locations," says the study.

While the study authors do not know of any "ecotoxicological effect data" for the tree species at higher TFA levels, they see the study results contributing to the "current discussion on the regulation of per- and polyfluoroalkyl substances (PFAS) to protect human and environmental health." TFA is considered an ultra-short-chain PFAS, according to the Organisation for Economic Co-operation and Development (OECD).

The study noted that TFA manifests a very high persistence and mobility in the environment, which means it has "a much higher likelihood for long-lasting and widespread adverse effects." Consequently, the study says, TFA and its precursors "should be considered for regulation to reduce the risk of potentially irreversible harm in the future."

TFA sources include industrial discharges and the degradation of many pesticides and pharmaceuticals. However, the study assumed that the predominant source of TFA in the studied plant matrices was atmospheric deposition from f-gas degradation.

The leaf study encompassed the species European beech, Lombardy poplar, Norway spruce, and Scots pine. The TFA concentrations of investigated tree leaf samples generally ranged from tens to hundreds of µg/kg of dry weight (dw).

TFA concentrations ranged between 24.6µg/kg dw in 1989 and 312µg/kg dw in 2019 in the European beech leaf samples; between 42.8µg/kg dw (1992) and 538 µg/kg dw (2020) in the Norway spruce leaves; between 98.5µg/kg dw (1992) to 453µg/kg dw (2018) in the Scots pine samples; and between 156µg/kg dw (1991) and 1,060µg/kg dw (2020) in leaves of the Lombardy poplar.

The high levels of TFA in recent tree leaf samples in Germany are comparable to the observations made by two studies in China, which reported TFA concentrations between approximately 280 and 3,000µg/kg dw for similar plant matrices, the study says.

TFA Concentrations in German Leaves Over Time (µg/kg dw)	
European beech leaf	
1989	24.6
2019	312
Norway spruce leaves	
1992:	42.8
2020	538
Scots pine	
1992:	98.5
2018:	453
Lombardy poplar	
1991:	156
2020:	1,060

Source: Levels and Temporal Trends of Trifluoroacetate (TFA) in Archived Plants: Evidence for Increasing Emissions of Gaseous TFA Precursors over the Last Decades, Environmental Science & Technology.

ATMO Conferences

UPCOMING EVENTS

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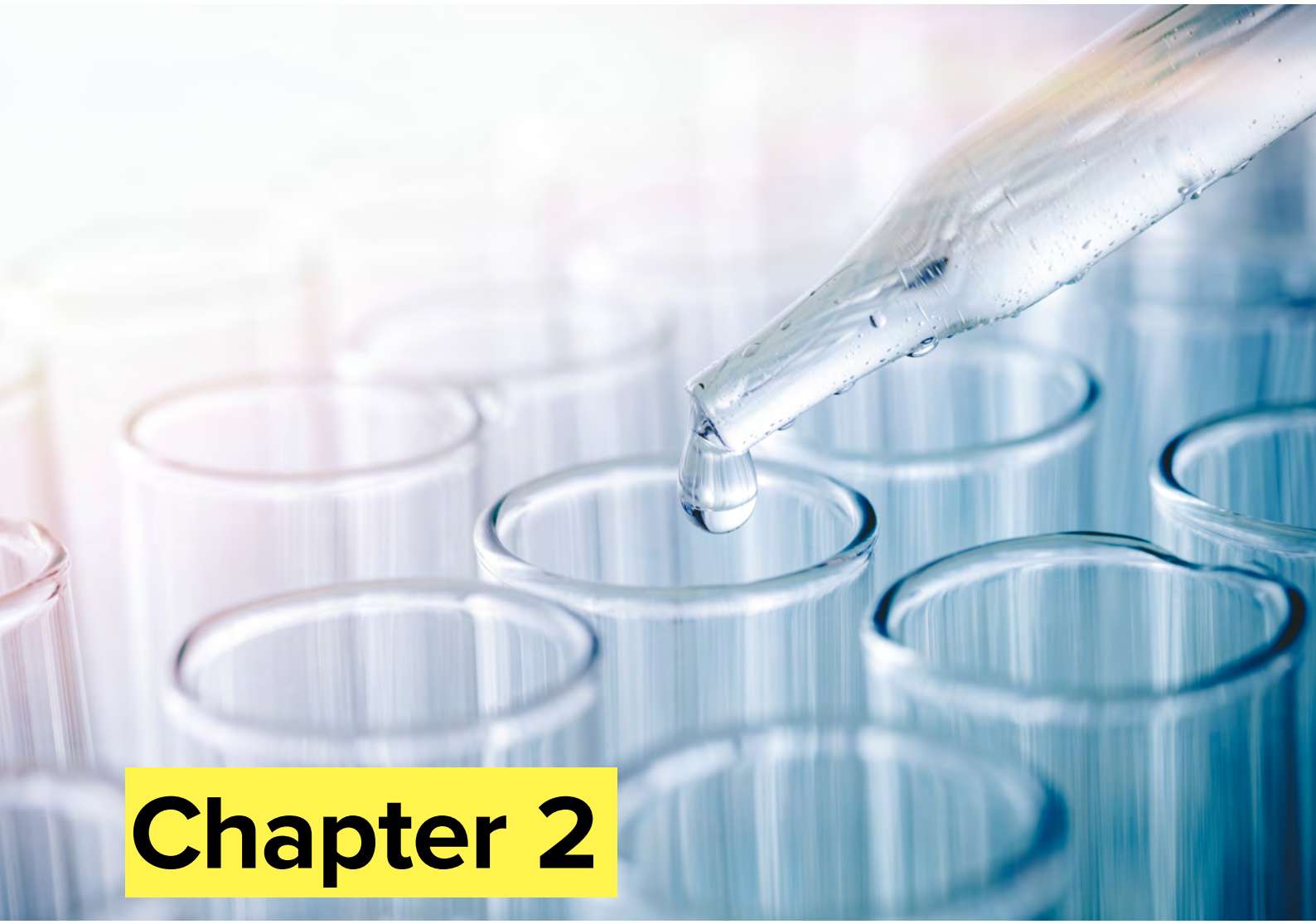


Chapter 2

German Study Finds Significant Amount of TFA in Drinking Water

A 2022 study funded by the German government has found trifluoroacetate (TFA), a degradation product of certain HFCs and HFOs, "widespread and dominant" in 46 water samples collected from 13 different sources of German drinking water.

The study – "Ultra-Short-Chain PFASs in the Sources of German Drinking Water: Prevalent, Overlooked, Difficult to Remove, and Unregulated" – was published May 4 in *Environmental Science & Technology*. Its authors are Isabelle J. Neuwald, Daniel Hübner, Hanna L. Wiegand, Vassil Valkov, Ulrich Borchers, Karsten Nödler, Marco Scheurer, Sarah E. Hale, Hans Peter H. Arp, and Daniel Zahn.

Scheurer and Nödler also participated in another 2022 German TFA study that found TFA in archived leaf samples of various tree species, with a two-to-five-fold increase between 1995 and 2018.

Funded by Germany's Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, the study looked for the presence of short chain and ultra-short-chain PFAS (known as "forever chemicals" for the durability in nature). TFA is considered an ultra-short-chain PFAS, according to the Organisation for Economic Co-operation and Development (OECD). The samples were taken between October 27 and November 4, 2020.

In its acid form (trifluoroacetic acid), TFA is produced in the atmosphere by the 100% breakdown of HFO-1234yf, and is carried in rainfall to the Earth, where it is found in acetate form. Between 7% and 20% of HFC-134a breaks down into TFA in the atmosphere.

Short-chain and ultra-short-chain PFASs "generally fulfill" the proposed criteria for persistent, mobile, and toxic (PMT) or very persistent and very mobile (vPvM) substances, established by the German Environment Agency (UBA), the study says. Consequently, ultra-short-chain PFASs "represent a major challenge for drinking water production and show that regulation in the form of preventive measures is required to manage them."

TFA was the most dominant PFAS found in the study, accounting for more than 90% of the total concentration of PFAS analyzed in all samples, with a maximum and median concentration of 12.4 and 0.9 µg/L, respectively. "From the data presented herein, it is evident that short-chain PFASs and especially the ultra-short-chain PFASs TFA, TFMS [trifluoromethanesulfonate], and PFPrA [perfluoropropanoate] are widespread and dominant in these samples from drinking water sources," the study says.

The TFA results are "in line with previous monitoring programs in German surface waters," the study says. A 2020 study done on behalf of the German Environment Agency (UBA) across eight locations in Germany measured the concentration of TFA in rainwater. From February 2018 to January 2019, an average of 0.330µg/L of TFA was found in 566mm (22.3in) of precipitation; from February 2019 to January 2020, an average of 0.398µg/L was found in 694mm (27.3in), with a maximum value of 4.87µgL. Compared to earlier studies done in 1995–1996 and 1996–1997, the average amount of TFA has increased by three-to-five times.

In Germany, TFA has a "drinking water health guidance value of 60 µg/L" based on consumption of 2L of water daily, and "a target value as a plant protection agent metabolite" (precautionary value) of 10 µg/L, the study says.

Denmark has also been studying the presence of TFA in water supplies. In 2021, the Danish Environmental Protection Agency reported finding TFA in 219 out of 247 groundwater wells, as well as in some drinking water supplies. In the vast majority of groundwater wells, the concentration of TFA is lower than 1 µg/L.

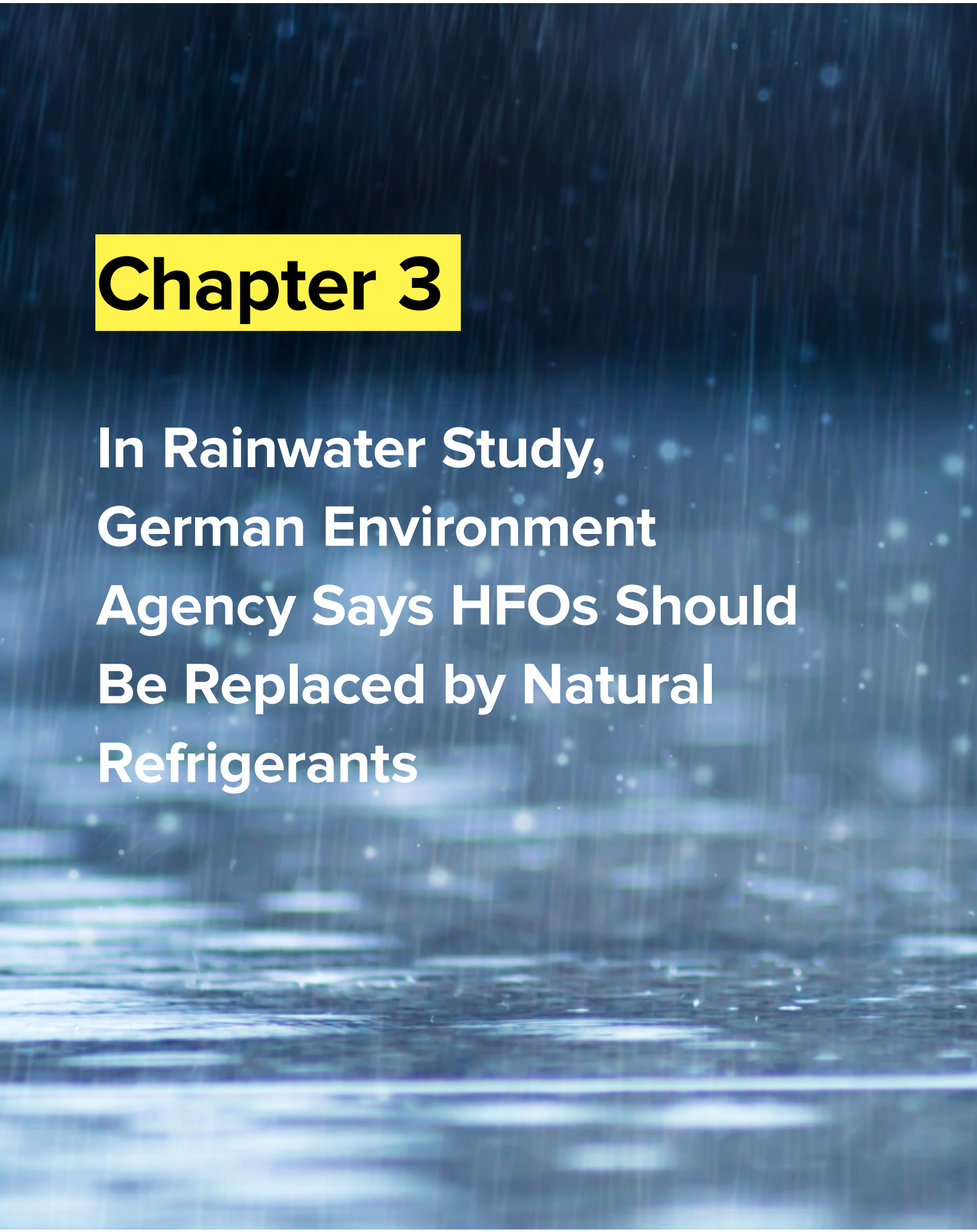
Potential health effects

The ultra-short-chain PFAS, which were the most prevalent PFASs found in the drinking water sources, are also the ones that are the most difficult to remove during drinking water production, the study says. "This raises questions both about the costs of removing these substances and the potential health effects these chemicals might cause."

The study acknowledges that there is currently little to no data about long-term exposure of ultra-short chain PFAS like TFA. However, "PFASs will remain in the environment for decades once released due to their persistent nature," and "remediation is either unfeasible or exceedingly expensive if adverse effects from these PFASs occur."

The study suggests that the results can be used to "better account for ultra-short-chain PFASs in fresh water and drinking water sources and to support monitoring campaigns, policy development, and risk assessment of these problematic substances."

The study does not attempt to identify the source of the TFA found in water samples. It notes that TFA can be introduced into the water cycle through industrial processes and as a transformation product of pharmaceutical and agricultural products, among others. But it also observes that TFA is a "transformation product of hydrofluorocarbon refrigerants in the atmosphere and may reach the aqueous environment via atmospheric deposition."



Chapter 3

In Rainwater Study, German Environment Agency Says HFOs Should Be Replaced by Natural Refrigerants

In a new 259-page study of the environmental impact of HFOs , the German Environment Agency (UBA) concludes that HFOs used as refrigerants, foam blowing agents and aerosol propellants "should be replaced by more sustainable solutions with halogen-free substances" such as natural refrigerants.

The report – "Persistent degradation products of halogenated refrigerants and blowing agents in the environment: type, environmental concentrations, and fate with particular regard to new halogenated substitutes with low global warming potential" – focuses on the degradation products of HFOs, notably the conversion of HFO-1234yf into trifluoroacetic acid (TFA) in the atmosphere. Atmospheric TFA descends to Earth in rainfall, and the report noted that higher levels of TFA have been found in rainwater.

TFA, according to UBA, is "classified as hazardous to water." Moreover, because of the persistence of TFA in the environment and the difficulty of removing it from groundwater and drinking water, the UBA says in the report that the use of HFOs as substitutes for HFCs "must be regarded as problematic."

Consequently, the report says, HFO refrigerants, foam blowing agents and aerosol propellants "should be replaced by more sustainable solutions with halogen-free substances."

"Alternatives with natural refrigerants should be preferred and promoted," the report adds.

In support of these conclusions, UBA commissioned a two-year TFA measurement program, carried out in Germany for the first time, from February 2018 to March 2020, with samples from eight German Meteorological Service measuring stations.

From February 2018 to January 2019, an average of 0.330µg/L of TFA was found in 566mm (22.3in) of precipitation; from February 2019 to January 2020, an average of 0.398µg/L was found in 694mm (27.3in). The mean monthly TFA precipitation concentrations reached up to 4.87µg/L. Compared to earlier studies done in 1995-1996 and 1996-1997, the avferage amount of TFA increased by three-to-five times.

One-year TFA inputs amounted to 190 g/km² in 2018–19 and 276 g/km² in 2019–20, an increase of at least three to four times compared to the period 1995–96 (54 to 69 g/km²).

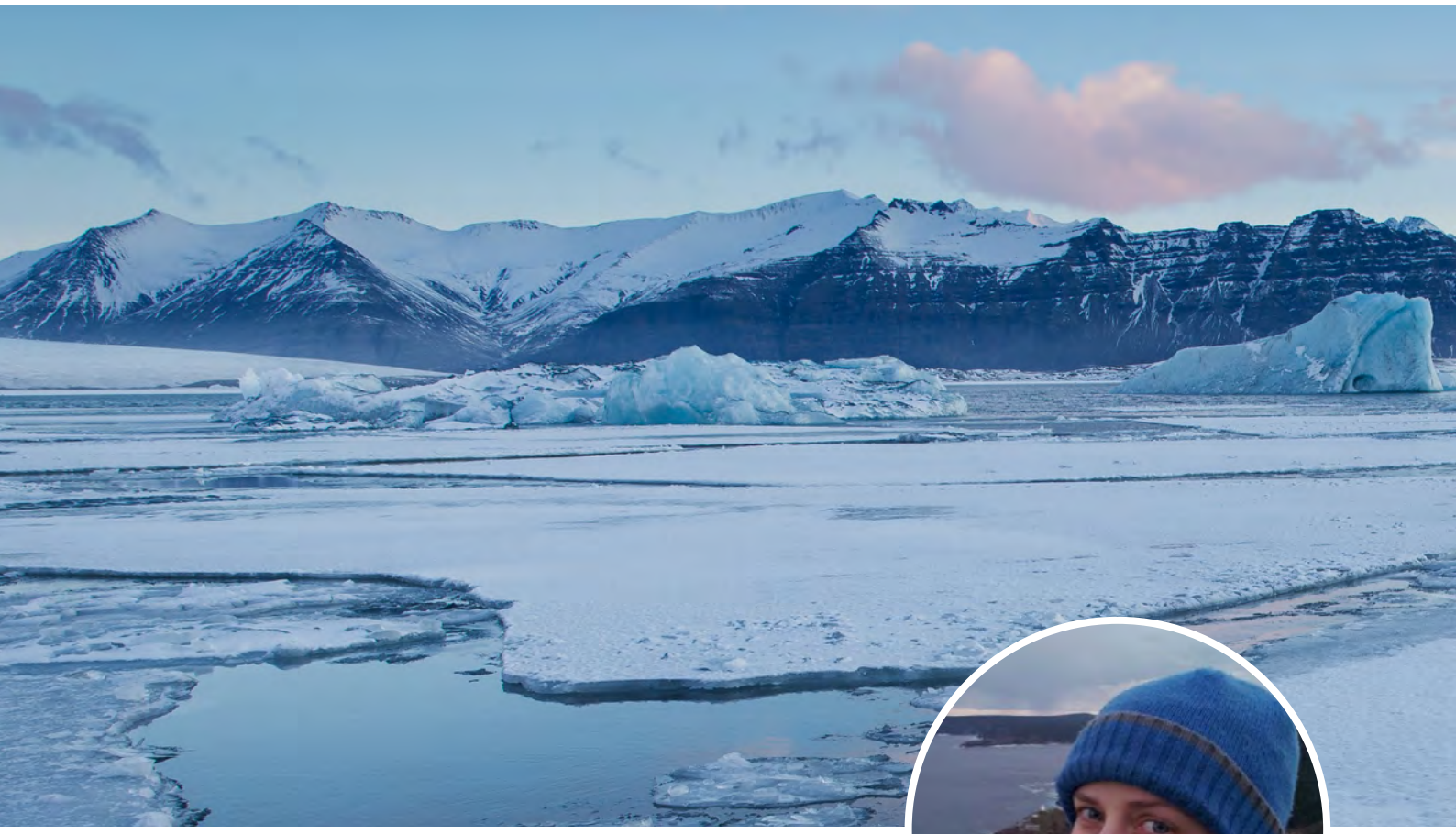
Based on that data, UBA modeled the "maximal future use and emissions" of HFOs up to 2050. "The projections show that in the future, especially the emissions of the refrigerant [HFO]-1234yf from mobile and stationary air conditioning, will add a large additional share to the amounts of TFA or trifluoroacetate in the atmosphere."

The model calculation indicates that in 2050 the refrigerant HFO-1234yf alone is expected to cause TFA inputs from precipitation of 2.5 kg/km^2 per year for Europe and up to 4 kg/km^2 per year for Germany; this would correspond to a ten-fold increase in today's TFA inputs, generating up to 50,000 metric tons of TFA load from refrigerant emissions for Europe in 2050.

"If manufacturers and operators now change over to systems using natural substances with a low global warming potential, such as hydrocarbons, carbon dioxide or ammonia, both the emissions of TFA can be significantly reduced and the climate can be protected," said UBA President Dirk Messner.

Among the authors of the report are:

- Dr. David Behringer, Dr. Felix Hedel, Barbara Gschrey, Steffi Osterheld, Winfried Schwarz and Kristina Warncke, all with Öko-Recherche, Frankfurt, Germany
- Finnian Freeling and Dr. Karsten Nödler, both with Technologiezentrum Wasser (TZW), Karlsruhe, Germany



Cora Young, York University

Chapter 4

Canadian Researchers Find Elevated Levels of TFA in Arctic Ice

A 2020 Canadian study looking at the composition of two Arctic ice cores since 1990 points to the accumulation of trifluoroacetic acid (TFA), an atmospheric byproduct of HFO-1234yf that is raising concerns about the refrigerant's long-term effect on the environment and human health.

TFA is one of three short-chain perfluoroalkylcarboxylic acids (scPFCAs) identified in the study – titled "Ice Core Record of Persistent Short-Chain Fluorinated Alkyl Acids: Evidence of the Impact From Global Environmental Regulations" – which was published on April 23, 2020, in *Geophysical Research Letters*. The other two are perfluoropropionic acid (PFPrA), and perfluorobutanoic acid (PFBA).

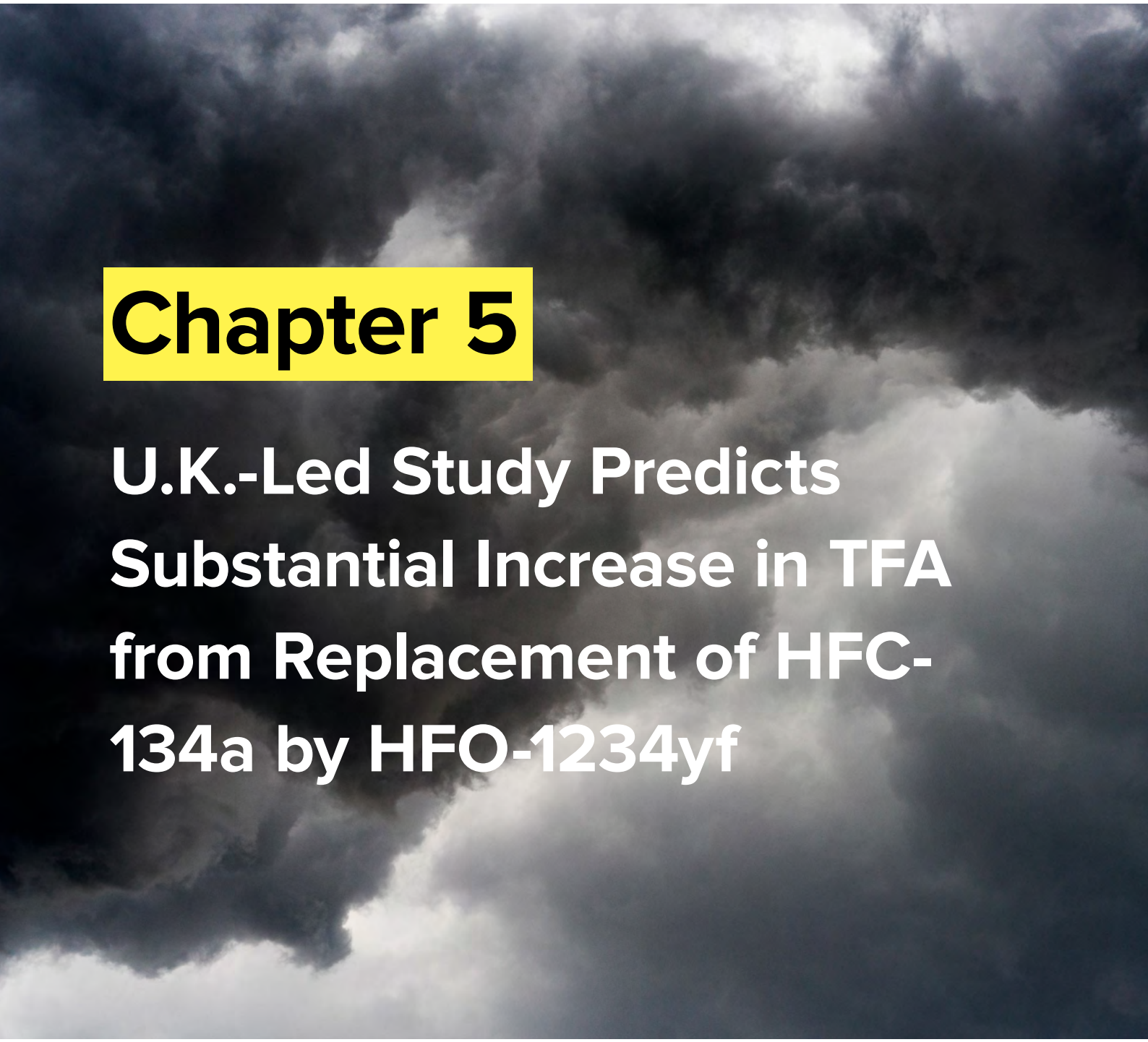
The study, which determined the content of the ice cores from the Devon Ice Cap in Nunavut, Canada, on a yearly basis, verified that levels of these "persistent compounds" have increased since 1990, following the adoption in 1987 of the Montreal Protocol; that global treaty resulted in ozone-depleting CFC and HCFC gases being replaced by HFCs, and more recently by HFOs.

"We observe the importance of CFC replacements in the increased deposition of TFA," says the study. "Deposition of TFA is expected to increase as new CFC replacement compounds are phased in. This work demonstrates the increased environmental burden of persistent and potentially toxic scPFCAs as a result of global regulation."

Cora Young, an atmospheric chemist at Toronto, Canada-based York University, and the corresponding author of the study, is quoted by the BBC in a May 14, 2020, article as saying that the levels of scPFCAs found in the Arctic ice is "on the order of 10 times higher now than we saw before the Montreal Protocol." While the potential toxicity of the compounds is still to be determined, "we do know that we are committing the environment to a great deal of contamination," she added.

In addition to identifying these compounds, the study's researchers, including Young and Amila De Silva, a chemist at Environment and Climate Change Canada, used atmospheric modeling to try to deduce the sources of the compounds, according to an article published May 2 in *Chemical & Engineering News*. The researchers determined that the TFA was a byproduct of HFC-134a and its replacement gas, HFO-1234yf, both used as refrigerants in car air conditioners. HFO-1234yf produces far more TFA than HFC-134a in the atmosphere (a 100% conversion vs. up to 20%), with the TFA descending to Earth in rainfall. Young was quoted in the article as saying TFA is "likely circulating throughout the Northern Hemisphere."

The analysis suggests that PFBA is also a byproduct of CFC replacements, but the researchers were unable to pinpoint the source of PFPrA.



Chapter 5

U.K.-Led Study Predicts Substantial Increase in TFA from Replacement of HFC-134a by HFO-1234yf

A 2021 study comparing the environmental effects of HFC-134a (R134a) and HFO-1234yf predicts that the replacement of the former by the latter, such as in mobile air-conditioning (MAC), would lead to substantially more production of trifluoroacetic acid (TFA) in the atmosphere, and ultimately on the surface of the Earth.

The study – "Investigation of the Production of Trifluoroacetic Acid from Two Halocarbons, HFC-134a and HFO-1234yf and Its Fates Using a Global Three-Dimensional Chemical Transport Model" – was conducted largely by researchers at the University of Bristol, U.K., and published in March, 2021, in *ACS Earth and Space Chemistry*.

Because of its high 100-year GWP (1,430), R134a production is being phased down globally under the Kigali Amendment to the Montreal Protocol. It has been widely replaced in MAC applications by HFO-1234yf, which has a 100-year GWP of less than one.

In the atmosphere, the two gases vary in their degradation into TFA. While emissions of HFO-1234yf completely convert into TFA, only 7–20% of R134a does so. Moreover, R134a has a lifetime of 14 years while HFO-1234yf breaks down in 10–14 days.

The University of Bristol-led study simulated the effects of switching from R134a to HFO-1234yf and found a 33-fold increase in the "global atmospheric burden of TFA." The amount of TFA would rise from 65 metric tons formed from the 2015 emissions of R134a to about 2,150 metric tons that would be formed in the future from an equivalent emission of HFO-1234yf.

Moreover, in specific geographic areas, the amount of TFA was seen as greater, including an increase of up to 250-fold across Europe and significant increases (up to 50-fold) in regions of the southern hemisphere, under the R134a-replacement-by-HFO-1234yf scenario.

Two outside experts weighed in on these findings in a 2021 article. "This is – to our knowledge – the first study predicting such high increases in regional TFA depositions. If the findings can be verified, it would most likely mean the end of widespread use of HFOs," wrote Michael Kauffeld, Professor at the Karlsruhe University of Applied Sciences – Institute of Refrigeration, Air-Conditioning, and Environmental Engineering, and Mihaela Dudita, Project Manager at SPF Institute for Solar Technology, Eastern Switzerland University of Applied Sciences (OST).

The University of Bristol-led researchers also noted that, while their investigation assumed that future HFO-1234yf consumption would match the peak consumption of R134a seen in 2015, "it is likely that [HFO-1234yf] consumption will increase beyond this point and emissions will grow accordingly." In fact, HFO-1234yf use, they said, is expected to exceed current R134a usage by around 290,000 metric tons per year by 2100.

"This investigation shows that a transition from HFC-134a to HFO-1234yf use will result in a significant overall increase in tropospheric TFA as loss processes cannot compensate sufficiently," the study says. "As such, natural cycles of TFA and the proportions that reside in air, land, and sea reservoirs will be altered as environmental contamination increases."

The researchers also studied the ways by which TFA is lost in the atmosphere through a reaction with what are called stabilized Criegee intermediates (SCIs). The effect of SCIs on TFA was found to be greatest over forested regions, such as the Amazon and Congo, where TFA atmospheric lifetime may be reduced to two days. But SCI-induced loss of TFA is "mostly negligible" over water and ice-covered regions.

Globally, they found that these reactions accounted for only about 0.4% of the total loss. "Even with consideration of the effects of SCIs, the percentage increase in tropospheric TFA resulting from the switch to HFO use remains substantial," their report said.

Another study looking at the accumulation of TFA in rainwater, released in 2021 by the German Environment Agency (UBA), predicted a ten-fold increase in today's TFA production from HFO-1234yf atmospheric degradation by 2050; this would generate up to 50,000 metric tons of TFA in Europe.

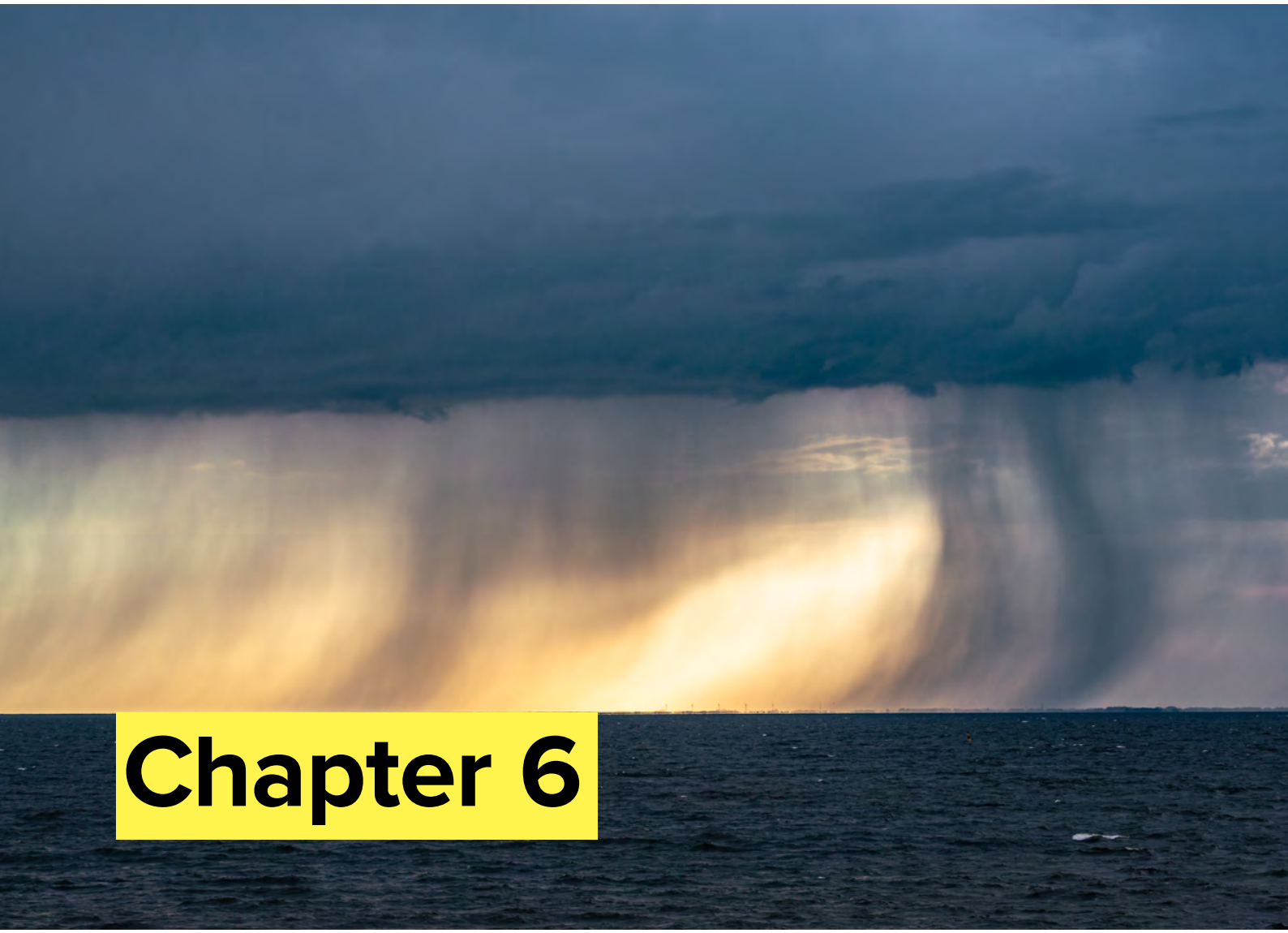
Effects of TFA

In terms of what the additional TFA would do to the environment, the University of Bristol-led study cites a 2020 study suggesting that atmospheric TFA may contribute to the formation of aerosols, "which would have a significant impact on climate change."

Other recent studies have addressed the potential impact of TFA, a highly durable substance, on the health of humans and other living species.

.While current levels of TFA in the environment are not considered a threat, the UBA says in its report that TFA is "classified as hazardous to water." Moreover, because of the persistence of TFA in the environment and the difficulty of removing it from groundwater and drinking water, the UBA report says that the use of HFOs as substitutes for HFCs "must be regarded as problematic" and encourages the use of natural refrigerants.

Commenting on TFA's stability in water, Kauffeld and Dudita cited concerns that "any HFO regulation will come into force too late once the negative consequences of an increased amount of TFA in rainwater becomes evident." Already, they said, TFA is "not particularly healthy for some aquatic organisms."



Chapter 6

Norwegian Study Assesses Impact of HFOs on Environment

A major 2017 study conducted for the Norwegian Environment Agency projects levels of HFO emissions (particularly HFO-1234yf) through 2100, and assesses how these emissions could affect the environment, pointing to many areas of concern as well as noting which areas need to still be investigated.

Conducted for Norway by U.K.-based Risk & Policy Analysts, the wide-ranging study, called "Study on environmental and health effects of HFO refrigerants," tracked the state of knowledge on HFOs and HFO-1234yf atmospheric degradation product TFA.

Information for the Norwegian study was gathered from academic and grey literature as well as consultations with various stakeholders, including a manufacturer of HFO refrigerants, a company involved in the reclamation of HFO refrigerants, academic experts, a nongovernment organization and a refrigeration industry association.

Among the Norwegian study's contributions is its projection of HFO refrigerant emissions up to the year 2100 for Non-Article 5 (developed) countries and Article 5 (developing) countries. It tracks emissions from the commercial, industrial, transport, stationary AC and mobile AC sectors.

The study uses different projection models, including business-as-usual (BAU) and two MIT (mitigation)-5 scenarios (worst and best case), which assume the conversion of key Non-Article 5 refrigeration and air conditioning equipment to HFOs by 2025 and the commencement of similar conversions in Article 5 countries by the same date. One MIT-5 scenario looks at HFO emissions frozen from 2050 to 2100 and another looks at a phase out after 2050.

For projections up to 2050, the study uses the UN's September 2016 TEAP (Technology and Economic Assessment Panel) Task Force Report (XXVII/4), which encompasses all low-GWP refrigerants, including natural refrigerants.

The study projects annual emissions of HFOs (focusing on HFO-1234yf) to be 228,641 metric tons from Non-Article 5 countries in 2050, and 860,582 metric tons from Article 5 countries.
The study acknowledged the "aggressive" nature of its emissions analysis but said that this made its environmental risk assessment "appropriately conservative."

While the study does not link emissions projections to specific environmental impacts, it does note that the "margin of safety (MOS) for human health is reduced in 2100 for the plateau of HFO emissions from 2025." (The lowest MOS for human health was for maternal and developmental toxicity.)

The 2100 plateau, adds the report, "might be particularly concerning as the precipitation is likely to cause a significant increase in levels of TFA not only in the expected final compartment (the aquatic environment) but also those compartments which TFA enters (soils) on its way to entering the final compartment."

Toxicity study

The Norwegian study's assessment of TFA finds that its projected toxicity risk to organisms and human health "appears to be low." But the study does locate one exception – the effect on the most sensitive algae species, Raphidocelis subcapitata (freshwater green alga).

In its analysis of the impact of TFA on aquatic biotic communities, the Norwegian study used EUSES (European Union System for the Evaluation of Substances) to do a basic analysis of PEC (predicted environmental concentration) and PNEC (Predicted No Effect Concentration) – the limit of what can be tolerated with no adverse effects – in different regions of the world. The calculations are based on ecotoxicity and environmental concentrations identified in the scientific literature.

The study finds the predicted upper environmental TFA concentrations in the soils of Malawi and Chile and the surface waters of Germany to be equivalent to 0.0075, 0.0094 and 0.14 mg/L a.e. (acid equivalents), respectively.

For the freshwater green alga, these levels would be greater than its most toxic freshwater PNEC of 0.0062 mg/L, using an assessment factor (reflecting data uncertainty) of 100; this, the report says, "would equate to there being an environmental risk." The report also says TFA's NOEC (no observed effect concentration) for freshwater green alga is 0.12mg/L.

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Many of the knowledge gaps cited by the Norwegian report involved TFA toxicity data deemed "inadequate or missing, not allowing a thorough assessment of the effects this may have on the wider environment."

As examples, the report points to the absence of data on toxicity to organisms found in salt lakes and playas, which are terminal sinks for TFA and where TFA is expected to become concentrated. In addition, no measurements have been reported on the concentrations of TFA in crops for human consumption.

About one third of TFA is moved by rivers, which results in "a considerable amount introduced in terrestrial environments where TFA is susceptible to leaching into the groundwater," the report says.

But there have been few studies on TFA concentrations in groundwater. "This needs to be addressed due to potential implications for drinking water," it said.

The study recommends periodic monitoring of TFA concentrations in well-known U.S. terminal water bodies such as Mono Lake, California, and Pyramid Lake, Nevada, and appropriate endorheic (terminal) basins in Europe. These would provide "an early indication of the rate of TFA accumulation following the large-scale use of HFO-1234yf in MAC [mobile air-conditioning]."

Generally, more research is needed to fully understand the cycle of TFA in the atmosphere and hydrosphere, as well as other sources of the acid, the report says.

Given the persistence of TFA, the risk it presents increases if emissions of HFO-1234yf to the environment increase, the Norwegian report says. With that in mind, it concludes that "phasing out HFOs (and consequently TFA), or emission reduction strategies along with best practice measures that help ensure efficient capturing of HFO/TFA during recycling operations, will help reduce the risk to human and environmental health."

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atmosphere.cool/natural-refrigerants-label/

Lydia Jahl, Green Science Policy Institute

Chapter 7

Scientist Urges U.S. EPA to Broaden Definition of PFAS to Include F-Gases, TFA

The definition of PFAS (per- and polyfluoroalkyl substances) used by the U.S. Environmental Protection Agency (EPA) should be broadened to include chemicals such as certain HFC and HFO refrigerants, as well as refrigerant byproduct trifluoroacetic acid (TFA), according to a scientist from the Green Science Policy Institute (GSPI).

The scientist, Lydia Jahl, Science and Policy Associate for GSPI, presented this view via Zoom at a session on the impact of refrigerants on health, safety and climate at the ATMOsphere (ATMO) America Summit 2022. ATMO America, held June 7-8, 2022, in Alexandria, Virginia, was organized by ATMOsphere, publisher of this report.

The PFAS category comprises thousands of "forever chemicals" that are toxic, bioaccumulate in humans, animals and plants, and are extremely durable in the environment due to the tremendously strong carbon-fluorine chemical bond. They have been employed in hundreds of consumer products, including non-stick cookware, stain repellent, food packaging, cosmetics and clothing. The ubiquity of PFAS has led to their being found in drinking water, among other places in the environment.

Two PFAS chemicals – PFOA, used in Teflon non-stick pans, and PFOS, an ingredient in 3M's Scotchgard stain repellent – were phased out in the U.S. by the EPA after the discovery of their health hazards, which include cancer, reproductive problems and endocrine disruption.

Because of the difficulty of regulating thousands of individual PFAS chemicals, scientists have urged that PFAS be addressed as a class. However, two differing definitions of this class have emerged.

A definition published last year by the OECD (Organization for Economic Co-operation and Development) describes PFAS as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom. This definition is accepted by "leading PFAS scientists around the world," said Jahl. It is also used by the National Defense Authorization Act (NDAA) and several U.S. states.

The OECD's definition of PFAS includes certain f-gases like R134a (an HFC) and R1234yf (an HFO), as well as TFA, which is formed in the atmosphere by the breakdown of 100% of R1234yf and up to 20% of R134a.

But the EPA, through its Office of Chemical Safety and Pollution Prevention (OCSPP), defines PFAS more narrowly than the OECD, saying it contains at least two adjacent carbon atoms, where one carbon is fully fluorinated and the other is at least partially fluorinated. The EPA's definition excludes f-gases and TFA, and many other harmful chemicals.

In Europe, five countries are expected to ask the European Chemicals Agency (ECHA) in January to regulate PFAS under the OECD definition, including some f-gases and TFA. A decision is expected by 2-025. The f-gas industry in Europe has pushed back against the classification of HFCs and HFOs as PFAS. "HFCs, HFOs and HCFOs are a distinct subset and due to their properties are not commonly regarded as PFAS," says the European Fluorocarbons Technical Committee (EFCTC) on its website.

Because TFA and f-gases may have only one fluorinated carbon atom, they are called ultra-short-chain PFAS under the OECD definition. The best-known PFAS, which have been subjected to the most regulation, are long-chain PFAS such as PFOA and PFOS, which have eight carbon atoms. However, short-chain and ultra-short-chain PFAS share many of the characteristics of long-chain PFAS, and are even harder to remove from drinking water than long-chain PFAS.

"HFOs and TFA should be considered PFAS for their shared chemical structure, persistence and potential for harm," said Jahl. "There's no indication that ultra-short-chain [PFAS] molecules are safe. EPA's incomplete PFAS definition leaves room for harm."

Jahl cited Linda Birnbaum, formerly the head of the National Institute for Environmental Health Sciences, who told *The Guardian* that the definition the EPA's toxics office uses is "a lot more like industry's" rather than like the definition used by the international scientific community. "This highlights the importance of listening to the scientists who are actually studying these chemicals in depth," Jahl added.

Jahl acknowledged that more toxicology data is needed "to be 100% certain" of TFA's potential effect on human health in water supplies and other places where it is collecting. "But we need that toxicity data before it would be wise to continue using TFA and products that results in TFA formation."

This is especially true, Jahl added, given the availability of natural refrigerants as "safer alternatives."

The EPA's more restrictive definition of PFAS has prompted criticism from a number of quarters in the past year. Last September, scientists from GSPI and several other groups (including the Environmental Working Group and the Natural Resources Defense Council) sent a letter to EPA Administrator Michael Regan urging the agency to use the OECD's definition of PFAS, which they called "scientifically sound and consistent with definitions that have been included in federal and state laws regulating PFAS."

The letter also noted that the EPA's definition excluded many HFC and HFO refrigerants as well as TFA, which "poses risk to human and ecological receptors." The scientists pointed out that TFA has been recognized as a PFAS by the California Department of Toxic Substance Control, among others.

U.S. legislators have also weighed in. In November, 2021, Representatives Deborah Ross (Democrat from North Carolina) and Nancy Mace (Republican from South Carolina) introduced the PFAS Definition Improvement Act (HR 5987), which would define PFAS as the OECD does.

In a suit against the EPA in April, 2022, Public Employees for Environmental Responsibility (PEER), a Washington, D.C.-based NGO, alleged that the agency was "withholding documents explaining why it has adopted an exceedingly limited definition of [PFAS]."

EPA subsequently released more than 2,500 pages of documents, but on June 10 PEER said in a statement that it found "no scientific basis" for the EPA's working definition of PFAS, and "no reasons given for excluding thousands of chemicals included in State definitions." PEER added that it will challenge in court redactions in the EPA's documents that "may mask the scientific basis" for its PFAS definition.

The EPA did not respond to a request for comment on the reasons for its PFAS definition.

TFA accumulation

In her presentation, Jahl cited a number of studies finding growing amounts of TFA in the environment, which she attributed to "the broad use of HFCs and HFOs that react in the atmosphere to cause TFA formation."

While a significant generator of TFA, f-gases are not its only source, noted David Behringer, Project Manager for Öko-Recherche, a German environmental consultancy, who participated in the impact of refrigerants session with Jahl. TFA, used in labs, is emitted directly from its manufacturing process and is the degradation product of many herbicides and pesticides. "No one knows exactly how those sources contribute to the TFA in the environment," he said.

However, added Behringer, the continued use of HFO-1234yf in mobile air-conditioning "could well result in a situation where in the future the RAC [refrigeration and air-conditioning] sector is the main contributor [of TFA]."

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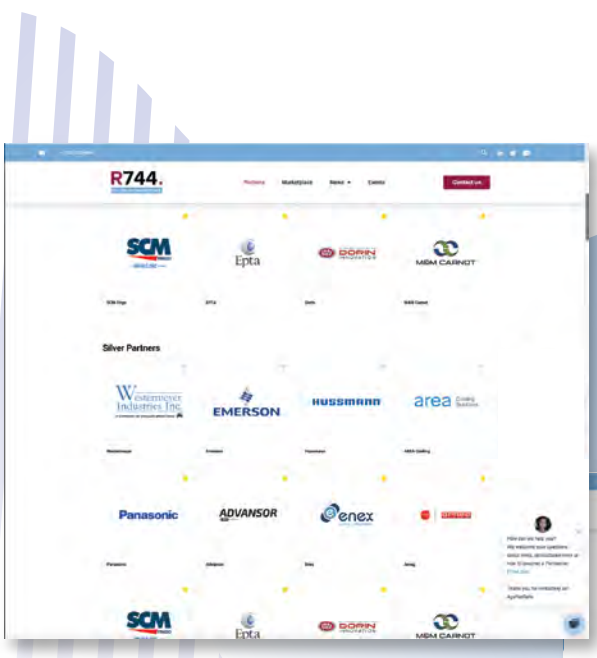

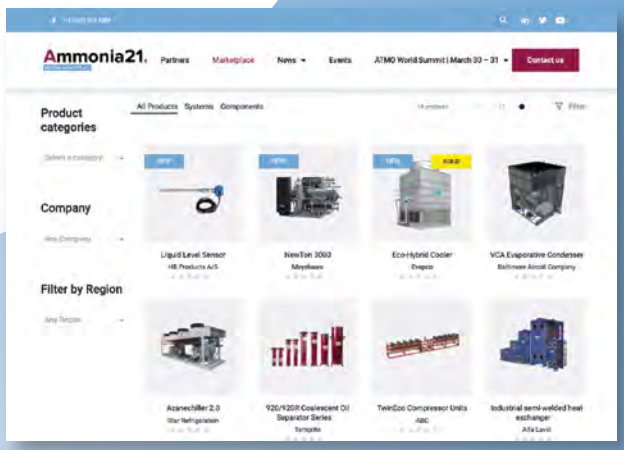

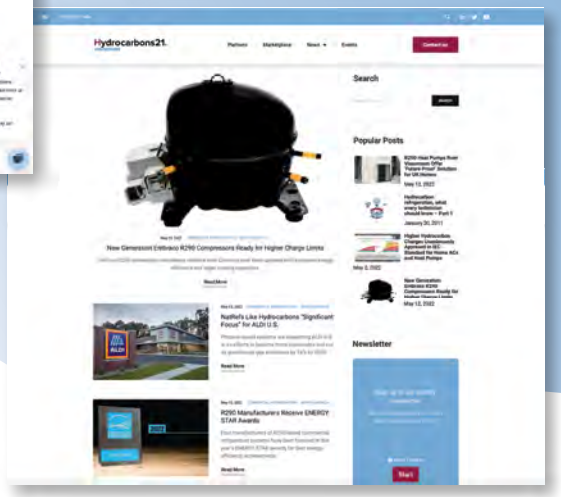

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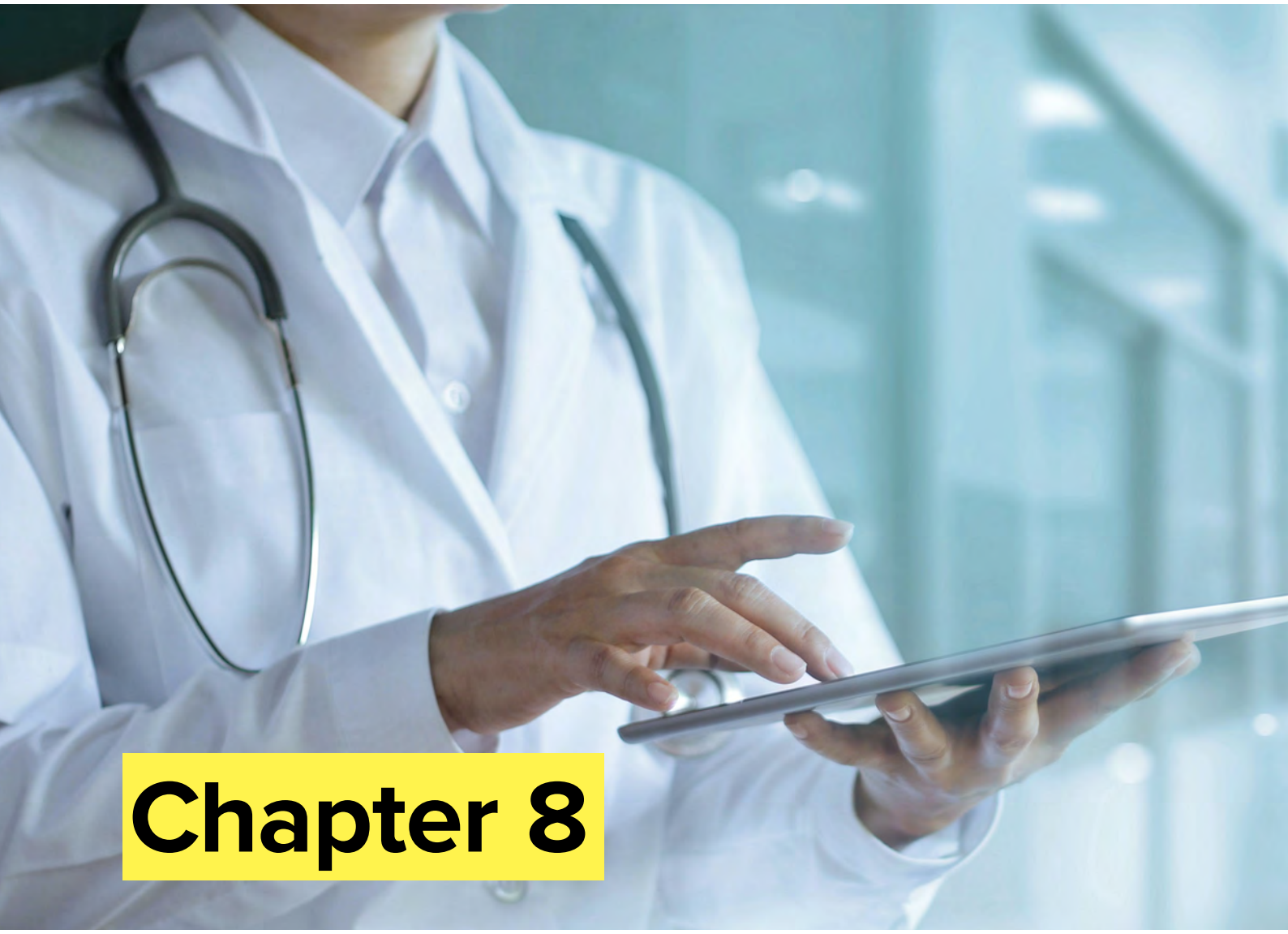

Chapter 8

Report on HFO/TFA Effects Points to Potential Harm to Liver and Thyroid Function

Long-term exposure to HFO byproduct trifluoroacetic acid (TFA) can potentially damage the liver and the thyroid function in humans, according to a report released in 2021 by Refolution Industriekälte, a Karlsruhe, Germany-based consulting and engineering firm focused on sustainable refrigeration.

The report – "Report and statement of the downsides of HFO refrigerant usage – Impact of fluorochemical refrigerants and their degradation products on the environment and health" – is available here.

While the report acknowledges that there is no threat of acute TFA toxicity for humans at any of the "current or expected concentrations," it says that "long-term exposure with low concentrations [of TFA] showed elevated ALT [alanine transaminase]-concentrations and indicate that TFA in drinking water can potentially damage the liver and have other impacts, for example on the hormone system," in particular thyroid function.

An elevated blood level of ALT, an enzyme, is an indication of liver damage. In regard to the thyroid, the report nots that, while there is a lack of information in the literature regarding the general effect of fluorochemical refrigerants on the thyroid, "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."

TFA is readily formed in the atmosphere from the degradation of HFO-1234yf and, to a lesser degree, other fluorinated refrigerants. It comes down to the Earth's surface as a form of "acid rain" and accumulates in the aquatic environment, especially in terminal water bodies with high evaporation rates. HFO-1234yf is widely used as a replacement for HFC-134a in mobile air-conditioning, and as part of HFO blends (such as R449A and R513A) used in commercial refrigeration and ice rink systems.

TFA's impact on the environment is "well established" with regard to freshwater green alga (selenastrum capricornutum, also called or raphidocelis subcapitata), which is the most sensitive algae to TFA in the aquatic environment, the report noted. The report acknowledged that in other environmental impacts, the current and expected concentrations of TFA are lower than the concentrations known to have a negative effect.

However, it notes, "exact concentrations are difficult to predict and concentrations might be higher than estimated by global atmosphere models in the future."

The report's overarching message is a warning to the HVAC&R industry: "Before bringing tonnes of chemicals into the environment, it needs to be proven that they are harmless to humans and the environment, especially regarding chemicals with high persistence such as TFA."

If this warning goes unheeded, the report says, "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."

Indeed, history has already demonstrated that emitting refrigerants and other 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 report says.

Taking this risk is unnecessary, the report noted, given that natural refrigerant alternatives are widely available for a myriad of applications. "We demand to immediately stop the selling of synthetic refrigerants and switch to naturals only," says the report.

TFA toxicity in rats

The report described "a long-time toxicity assessment of TFA," which was performed after "concerning reports of high TFA concentrations in waters in [North Rhine-Westphalia], Germany."

In this study, rats were exposed for one year to TFA concentrations in of 0 ppm, 30ppm, 120ppm and 600ppm in freshwater. "The study showed an increase of the ALT-concentration (alanine aminotransferase) depending on the dosage of TFA," the report says.

In another study where TFA was given to pregnant rats (on the 10th–20th day of pregnancy) a temporary dysfunction (at about 50 days) of the liver and kidney was observed, the report says.

The report also notes the connection between the use of halogenated inhalational anesthetics, notably halothane, and the production of TFA and subsequently trifluoroacetylate components that are associated with liver injury. Here, too, there is an "acute increase" of ALT, as well as aspartate aminotransferase (AST), which "remain elevated for one to two weeks following exposure and resolve without treatment," says the report.

Concerns about TFA have influenced Germany policy on allowable TFA concentrations in freshwater. Based on the NOEC (no observed effect concentration) threshold of 30 ppm for humans (about 1.8mg/kg body weight), the maximum TFA concentration in freshwater in Germany has been set to 60 µg/l; however, the German Environment Agency recommends not exceeding 10µg/l.

The mean annual TFA concentration in Germany is estimated to increase by 10-fold by 2030, "only considering the degradation of R1234yf," the report says.

Refolution has initiated a petition on change.org that urges European Union authorities to effectively allow only natural refrigerants to be used in new installations starting in 2022.

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Chapter 9

Other HFO-1234yf Concerns

In addition to its production of TFA in the atmosphere, there are other concerns related to HFO-1234yf. Carbon tetrachloride (CCl_4) – a probable carcinogenic liquid that can damage the liver, kidneys and central nervous system – is reportedly used as a feedstock in the production of HFO-1234yf. CCl_4, which evaporates easily, is also a potent ozone-depleting substance, almost as harmful as CFCs, as well as a high-GWP (1,730) gas.

CCl_4 production in the U.S. has been increasing due to its use as a feedstock in the manufacture of HFO-1234yf and HFO-1234ze, according to a 2017 report by Safer Chemicals, Healthy Families' Environmental Health Strategy Center Healthy Building Network. The U.S. Environmental Protection Agency has reported CCl_4 leaks from facilities operated by Honeywell and Chemours that produce HFO-1234yf.

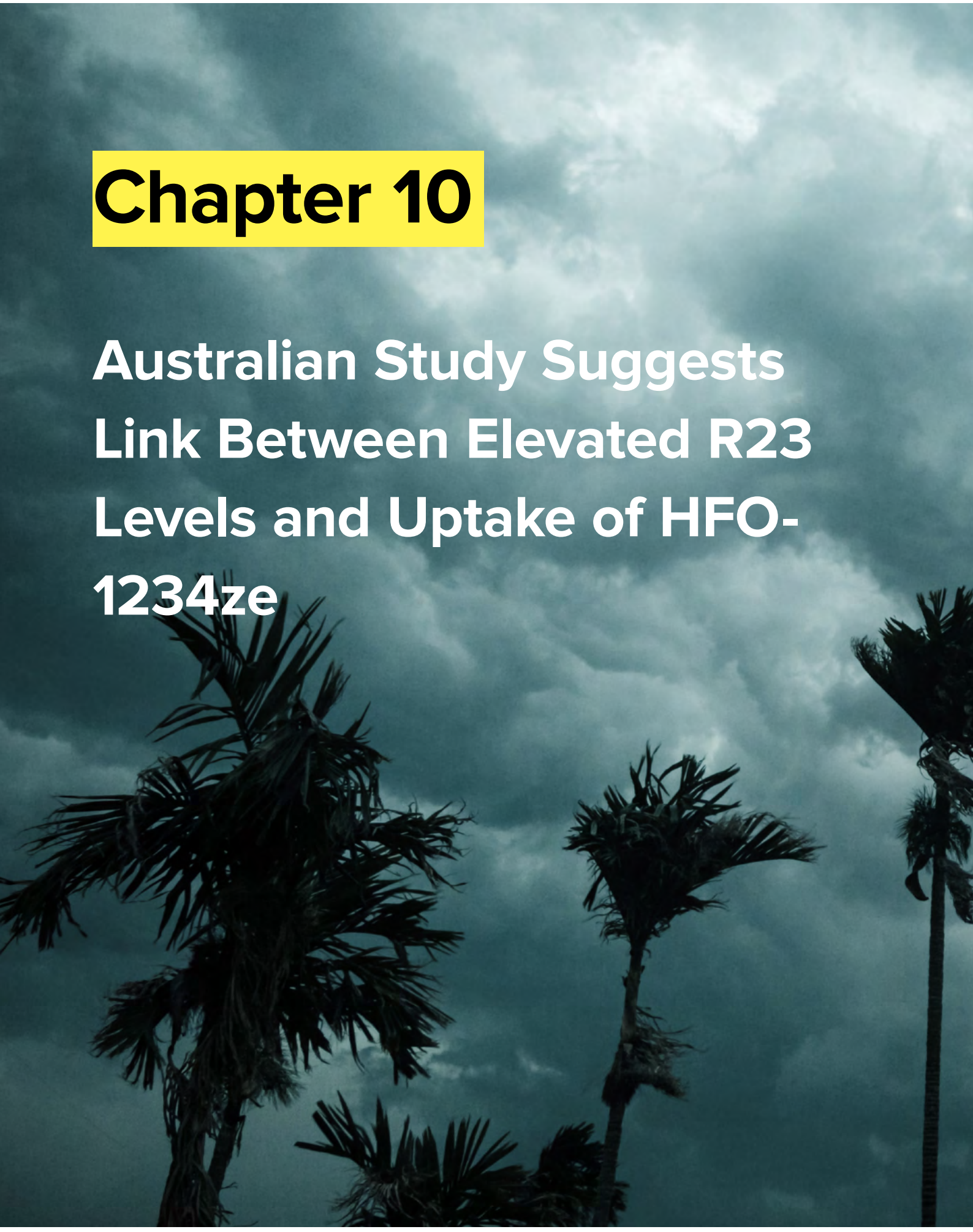
In August, Chemours announced that it will be increasing production of HFO-1234yf at its facility near Corpus Christi, Texas, by about 40%.

In a study of the emissions related to the production of refrigerants, HFO-1234yf was found to generate 10.9lbs (4.9kg) of CO_2e for every pound produced, while CO_2 generates 0.8lbs (0.36kg) and ammonia 2.1lbs (0.95kg).

The climate impact of refrigerants' manufacturing processes and their atmospheric degradation products – in addition to their direct global warming effect – should be considered in what ECOS (Environmental Coalition on Standards), a Brussels, Belgium-based NGO, calls the "lifecycle GWP".

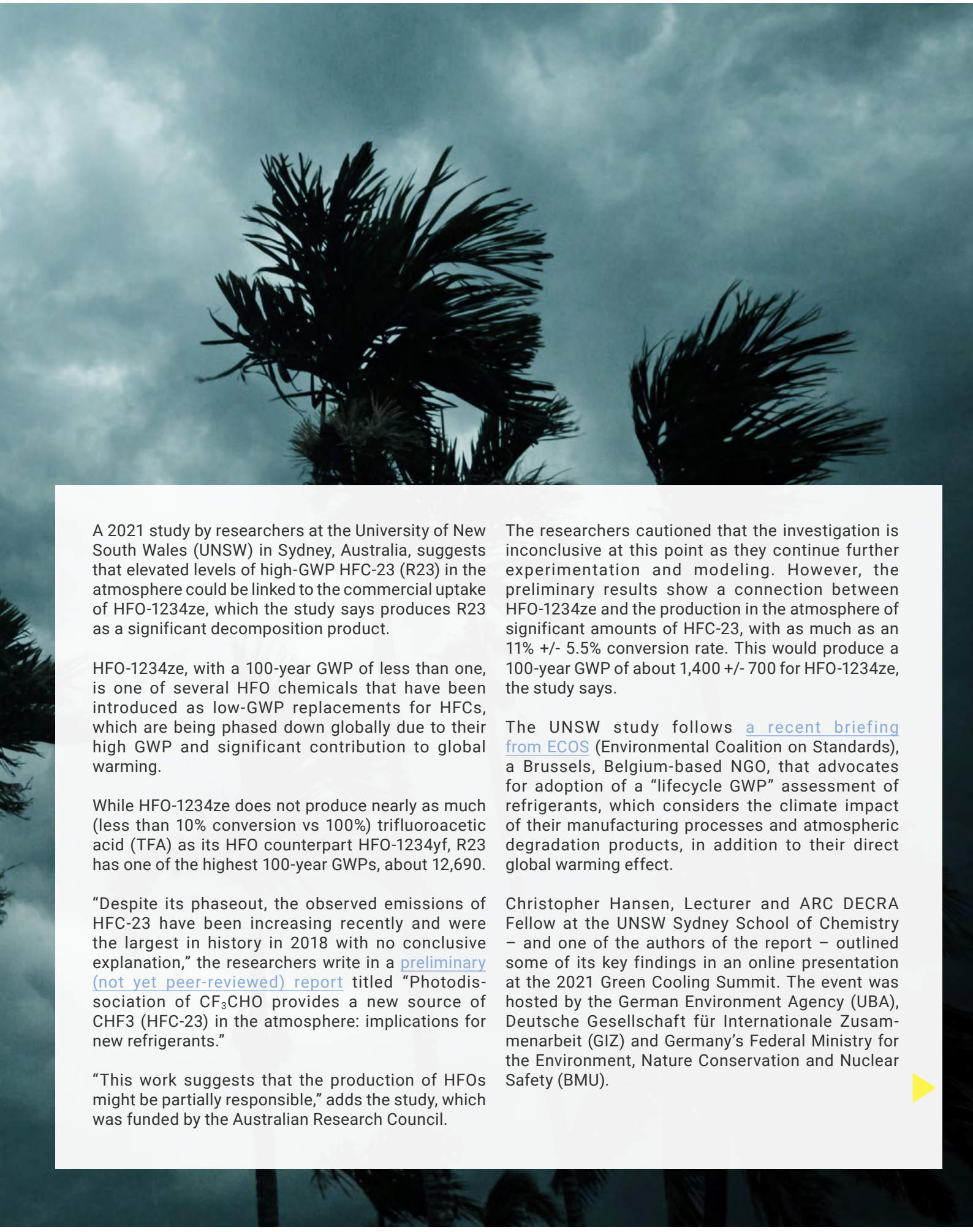
Yet another issue related to HFO-1234yf has been identified in the automobile industry. In a few instances, HFO-1234yf poured into air-conditioning service units is thought to have previously undergone polymerization, resulting in a silicone-like solid mass that irreparably damages the service unit, according to a report in *Krafthand*, a German technical magazine. Polymerization of the refrigerant would have occurred in its original container as a result of high temperatures (70–90°C/158–194°F) due to exposure to the sun, for example, and the ingress of air.

In stationary refrigerant cycles, "some of the mixtures with R1234yf will polymerize and I think in some plants it has already happened, but nobody had in mind that the 'white residue' may also be related to the refrigerant, said Alexander Türke, a researcher at the Institute for Ventilation and Refrigeration Technology (ILK), Dresden, Germany, He added that polymerization should only happen in oil-free systems.



Chapter 10

Australian Study Suggests Link Between Elevated R23 Levels and Uptake of HFO-1234ze



A 2021 study by researchers at the University of New South Wales (UNSW) in Sydney, Australia, suggests that elevated levels of high-GWP HFC-23 (R23) in the atmosphere could be linked to the commercial uptake of HFO-1234ze, which the study says produces R23 as a significant decomposition product.

HFO-1234ze, with a 100-year GWP of less than one, is one of several HFO chemicals that have been introduced as low-GWP replacements for HFCs, which are being phased down globally due to their high GWP and significant contribution to global warming.

While HFO-1234ze does not produce nearly as much (less than 10% conversion vs 100%) trifluoroacetic acid (TFA) as its HFO counterpart HFO-1234yf, R23 has one of the highest 100-year GWPs, about 12,690.

"Despite its phaseout, the observed emissions of HFC-23 have been increasing recently and were the largest in history in 2018 with no conclusive explanation," the researchers write in a preliminary (not yet peer-reviewed) report titled "Photodissociation of CF_3CHO provides a new source of CHF3 (HFC-23) in the atmosphere: implications for new refrigerants."

"This work suggests that the production of HFOs might be partially responsible," adds the study, which was funded by the Australian Research Council.

The researchers cautioned that the investigation is inconclusive at this point as they continue further experimentation and modeling. However, the preliminary results show a connection between HFO-1234ze and the production in the atmosphere of significant amounts of HFC-23, with as much as an 11% +/- 5.5% conversion rate. This would produce a 100-year GWP of about 1,400 +/- 700 for HFO-1234ze, the study says.

The UNSW study follows a recent briefing from ECOS (Environmental Coalition on Standards), a Brussels, Belgium-based NGO, that advocates for adoption of a "lifecycle GWP" assessment of refrigerants, which considers the climate impact of their manufacturing processes and atmospheric degradation products, in addition to their direct global warming effect.

Christopher Hansen, Lecturer and ARC DECRA Fellow at the UNSW Sydney School of Chemistry – and one of the authors of the report – outlined some of its key findings in an online presentation at the 2021 Green Cooling Summit. The event was hosted by the German Environment Agency (UBA), Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) and Germany's Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU).

Hansen explained that HFO-1234ze, used as a refrigerant, foam-blowing agent and propellant, decomposes in the atmosphere into trifluoroacetaldehyde (CF_3CHO) "with 100% molar yield."

What happens to the CF_3CHO is the focus of Hansen's research. The photolysis (action of light) on this substance in the atmosphere is largely thought to produce molecular "radicals" (CF_3 and CHO) that lead to benign compounds in the atmosphere (CO_2 and HF). However, Hansen noted, "most studies" observe evidence for a "molecular channel" with a 2% yield of R23 from the breakdown of CF_3CHO.

"This is concerning to me," he said. "Even a small amount of R23, multiplied by a large number, would be a quite significant, or even disastrous, outcome."

Comparison to a well-studied chemical

To gain further insight into this process, Hansen and his team looked at the atmospheric breakdown of an analogous compound, acetaldehyde (CH_3CHO), which has been "well-studied," he said.

"There is nothing here that should preclude the fluorinated species [CF_3CHO] from accessing the same rich chemistry that the well-studied acetaldehyde [CH_3CHO] does," he said.

In particular, CH_3CHO can decompose into CH_4 (methane) and CO, which is analogous to CF_3CHO forming CHF_3 (R23) and CO, he said.

In lab experiments at zero pressure, the researchers concluded that there is "unequivocally a unimolecular pathway to HFC-23 from CF_3CHO." This, Hansen said, "raises a red flag," though it's not necessarily the same in the atmosphere.

However, in comparing the reaction rate in the atmosphere of CF_3CHO to CH_3CHO, he said the reaction rate of CF_3CHO is 30 times slower, and has 11 chances to access this photochemistry, compared to two for CH_3CHO.

From this he concluded that "by analogy with CH_3CHO, under a simple atmospheric chemistry model, 11% +/- 5.5% of emitted CF_3CHO molecules become HFC-23." This, he added, "would lead to an effective 100-year GWP of about 1,400 +/- 700 for HFO-1234ze."

To verify these findings, the researchers are engaged in an experimental and modeling program "to determine the fate of CF_3CHO in the atmosphere explicitly," Hansen said.

Early results from flow-tube reactor experiments are yielding findings "in agreement with our current results," he noted.

U.S.-based Honeywell, a producer of HFO-1234ze, describes it as a "sustainable alternative to traditional refrigerants" that "meets your business criteria in performance, cost effectiveness, environmental impact and safety." Honeywell did not respond to a request for comment on the UNSW study.

The European Fluorocarbons Technical Committee (EFCTC) has disputed the UNSW study.

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• Leaf Samples Found to Have Increasing Amounts of TFA: https://bit.ly/3dVVB1h

Chapter 2

• German Study Finds Significant Amount of TFA in Drinking Water: https://bit.ly/3vCl2dx

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