TEXTE
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Final 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

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Abstract

This report describes the current status and the development of the use and emissions of halogenated refrigerants, foam blowing agents and aerosol propellants in Germany and in the EU. The focus is on hydrofluorocarbons (HFCs) and unsaturated hydrofluorocarbons with low global warming potential (u-HFCs and u-HCFCs) and their atmospheric degradation products. In addition to hydrogen fluoride, trifluoroacetic acid (TFA) or trifluoroacetate have been identified as persistent degradation products of some halogenated refrigerants foam blowing agents and aerosol propellants. The demand, the emissions, and the amount of degradation products of halogenated refrigerants, foam blowing agents and aerosol propellants were modelled in a scenario with maximal future use and emissions of unsaturated halogenated substances up to the year 2050. The projections show that in the future, especially the emissions of the refrigerant u-HFC-1234yf from mobile and stationary air conditioning will add a large additional share to the amounts of TFA or trifluoroacetate in the atmosphere. In order to quantify the atmospheric input of trifluoroacetate via precipitation, a two-year nationwide measurement programme was carried out in Germany for the first time, from February 2018 to March 2020. Compared with earlier measurements in the context of other projects, significantly higher concentrations of trifluoroacetate were found in rainwater. Based on the projections and the results of the measurement programme, the expected maximal input of TFA or trifluoroacetate from the atmospheric degradation of halogenated refrigerants, foam blowing agents and aerosol propellants in Germany and the EU were calculated.

The use of halogenated substitutes with a low global warming potential must be regarded as problematic in view of the persistence of TFA or trifluoroacetate in the environment. TFA or trifluoroacetate inputs into groundwater and drinking water can only be removed with considerable effort. Therefore, fluorinated refrigerants, foam blowing agents and aerosol propellants should be replaced by more sustainable solutions with halogen-free substances.

Kurzbeschreibung

Dieser Bericht beschreibt den Ist-Zustand und die Entwicklung der Verwendung und der Emissionen halogenierter Kälte- und Treibmittel in Deutschland und in der EU. Der Fokus liegt auf teilfluorierten Fluorkohlenwasserstoffen (HFKW) und ungesättigten halogenierten Kohlenwasserstoffen mit kleinem Treibhauspotential (u-HFKW und u-HFCKW) sowie deren atmosphärischen Abbauprodukten. Neben Fluorwasserstoff wurde insbesondere Trifluoressigsäure (TFA) bzw. Trifluoracetat als persistentes Abbauprodukt einiger halogenierter Kälte- und Treibmittel identifiziert. Der Bedarf, die Emissionen und die Menge der Abbauprodukte von halogenierten Kälte- und Treibmitteln wurden bis zum Jahr 2050 in einem Szenario mit maximaler zukünftiger Verwendung und Emission ungesättigter halogenierter Stoffe modelliert. Die Projektionen zeigen, dass zukünftig insbesondere die Emissionen des Kältemittels u-HFKW-1234yf aus der mobilen und stationären Klimatisierung einen hohen zusätzlichen Anteil zu den TFA- bzw. Trifluoracetat-Mengen in der Atmosphäre beitragen werden. Um den atmosphärischen Eintrag von Trifluoracetat über den Niederschlag zu quantifizieren, wurde erstmalig ein zweijähriges deutschlandweites Messprogramm von Februar 2018 bis März 2020 durchgeführt. Im Vergleich zu früheren Messungen im Rahmen anderer Projekte ergaben sich deutlich erhöhte Konzentrationen von Trifluoracetat im Regenwasser. Basierend auf den Projektionen und den Ergebnissen des Messprogramms konnte der zu erwartende maximale Eintrag von TFA bzw. Trifluoracetat aus dem atmosphärischen Abbau halogenierter Kälte- und Treibmittel in Deutschland und der EU abgeschätzt werden.

Die Verwendung von halogenierten Ersatzstoffen mit kleinem Treibhauspotential ist angesichts der Persistenz von TFA bzw. Trifluoracetat in der Umwelt als problematisch anzusehen. TFA bzw. Trifluoracetat-Einträge in Grund- und Trinkwasser können nur mit erheblichem Aufwand wieder entfernt werden. Daher sollten fluorierte Kälte- und Treibmittel durch nachhaltigere Lösungen mit halogenfreien Stoffen ersetzt werden.

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List of abbreviations

AGAGE	Advanced Global Atmospheric Gases Experiment
AHRI	Air Conditioning, Heating and Refrigeration Institute
AnaFgas	Analysis of Fluorinated Greenhouse Gases (emissions model for the EU)
ASHRAE	American Society of Heating, Refrigerating and Air-Conditioning Engineers
BR	Abbreviation for the rainwater measuring station Brocken (Germany)
CAS	Chemical Abstracts Service
CFC	chlorofluorocarbon (fully halogenated)
CoRAP	Community Rolling Action Plan
CRI-STOCHEM	name of the chemical transport model
DFG	German Research Foundation
DKV	German Society for Refrigeration and Air Conditioning e.V.
DL	detection limit
DNEL	derived no-effect level
DUE	abbreviation for the atmospheric measuring station Dübendorf (Switzerland)
DW	dry weight
ECHA	European Chemicals Agency
EC_x	concentration that leads to a change in the reaction of x % in a given time (e.g. EC_{10} or EC_{50})
EC_{50}	average effective concentration (effect in 50 % of the studied population)
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
EEA	European Environment Agency
Empa	Swiss Federal Laboratories of Materials Science and Technology
EPA	United States Environmental Protection Agency
ES	abbreviation for the rainwater measuring station Essen (Germany)
EU	European Union
EU-28	European Union with 28 Member States (including United Kingdom)
EU-28+	European Union with 28 Member States (including United Kingdom) plus Norway, Switzerland and Turkey
FELS-test	Fish, Early-Life Stage Toxicity Test
FLEXPART	FLEXible PARTicle dispersion model
FW	fresh weight
PFC	perfluorocarbon (fully halogenated)
F-gas	fluorinated (greenhouse) gas
HCFC	hydrochlorofluorocarbon (partially halogenated)

GC-MS	gas chromatography-mass spectrometry
GHG	greenhouse gas
GOW	health orientation value (German: Gesundheitlicher Orientierungswert)
GW	abbreviation for the rainwater measuring station Greifswald
GWP	global warming potential
HCFE	hydrochlorofluoroether
HCC	partially chlorinated hydrocarbon
HF	hydrogen fluoride
HFE	hydrofluoroether
HFC	hydrofluorocarbon (partially fluorinated)
HFO	hydrofluoroolefin (older Anglo-Saxon name for unsaturated HFCs; see u-HFC)
IPCC	Intergovernmental Panel on Climate Change
ISO	International Organisation for Standardization
JFJ	abbreviation for the atmospheric measuring station Jungfraujoch (Switzerland)
LC_{50}	average lethal concentration
LOEC	lowest observed effect concentration
LOESS	locally estimated scatterplot smoothing
MAC	mobile air conditioning
MAK	maximum work place concentration (German: Maximale Arbeitsplatzkonzentration)
MHD	abbreviation for the atmospheric measuring station Mace Head (Ireland)
MDI	metered-dose inhaler
MIN-scenario	scenario of minimal HFC-use, i.e. of minimal HFC-emissions
MO	abbreviation for the rainwater measuring station Munich-Oberschleißheim (Germany)
MP	Montreal Protocol on Substances that Deplete the Ozone Layer
NHN	standard elevation zero (German:Normalhöhennull)
NIR	National Inventory Report: detailed description and numerical information for reporting to UNFCCC
NLKWN	Lower Saxony State Agency for Water Management, Coastal Protection and Nature Conservation (Germany)
NOEC	no observed effect concentration
OECD	Organisation for Economic Co-operation and Development
ODP	ozone depletion potential
ODS	ozone depleting substance
OH-radical	hydroxyl radical
OICA	Organisation Internationale des Constructeurs d'Automobiles (international organization of automobile producers)

PD	abbreviation for the rainwater measuring station Potsdam (Germany)
PFA	partially fluorinated alcohol
PFMP	perfluoro(2-methyl-3-pentanone)
PFOA	perfluorooctanoic acid
PFOS	perfluorooctanesulfonic acid
PNEC	predicted no effect concentration
PU	polyurethane
QSAR	quantitative structure-activity relationship model
REACH	Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals
ROS	regression on order statistics
SCAS-Test	semi-continuous activated sludge test
SD	standard deviation
SU	abbreviation for the rainwater measuring station Stuttgart (Germany)
SW	abbreviation for the rainwater measuring station Schleswig (Germany)
TCA	trichloroacetic acid
TEAP	Technology and Economic Assessment Panel
TFA	trifluoroacetic acid
TFAC	trifluoroacetyl chloride
TFF	trifluoroacetyl fluorid
TNS	abbreviation for the atmospheric measuring station Taunus (Germany)
TOC	total organic carbon
TZW	DVGW-Technologiezentrum Wasser (German Water Centre) (Karlsruhe, Germany)
u-HCFC	unsaturated HCFC
u-HFC	unsaturated HFC
UBA	German Environment Agency
UNEP	United Nations Environment Programme
UNFCCC	United Nations Framework Convention on Climate Change
UStatG	German Environmental Statistics Act
VRF	variable refrigerant flow
WAM-scenario	with-additional-measures-scenario
WD	wet deposition
WK	abbreviation for the rainwater measuring station Wasserkuppe (Germany)
WMO	World Meteorological Organization
XPS	extruded polystyrene

Summary

Halogenated hydrocarbons are often used as refrigerants and blowing agents in foams. Further areas of application include the use as propellant for aerosols and metered dose inhalers as well as solvents and fire extinguishing agents. This report provides an overview of the status of the use of halogenated refrigerants and blowing agents and possible future developments. The study particularly includes substance aspects of the life cycle and focuses on the introduction of persistent degradation products of halogenated refrigerants and blowing agents into the environment in Germany and Europe (EU-28)[1]. Particular consideration is given to new halogenated substances with low global warming potential (GWP).

Motivation

Fully halogenated chlorofluorocarbons (CFCs), which are largely responsible for the depletion of the ozone layer and have a high global warming potential, were as a result of the Montreal Protocol replaced by hydrochlorofluorocarbons (HCFCs) with a smaller ozone-depleting potential. Due to a further tightening of the Montreal Protocol, HCFCs had to be replaced by hydrofluorocarbons (HFCs) since the 1990s as well.

On the grounds of their high global warming potential, HFCs are gradually being withdrawn from the market now. Since 2006, HFCs have been subject to restrictive regulations in the European Union (EU)[2]. The revised F-Gas Regulation[3] stipulates a progressive shortage of HFC-quantities since 2015, based on the global warming potential of the regulated substances. In 2016, HFCs were included in the Montreal Protocol with the Kigali Agreement. In the future, therefore, only small quantities of HFCs will be available in Europe and worldwide and will tend to be reserved for use in essential niche applications.

As of today, halogen-free refrigerants such as hydrocarbons, carbon dioxide (CO_2) and ammonia (NH_3) are established alternatives to halogenated substances in many applications. These substances were used as refrigerants prior to halocarbons and are now often referred to as “natural refrigerants”. The best example is the almost exclusive use of isobutane (R600a) as a refrigerant in household refrigerators (fridges) in Europe, which has been used since the mid-1990s and is now accepted worldwide. Large industrial refrigeration systems often use natural refrigerants such as ammonia. In commercial refrigeration, the proportion of systems with CO_2 and hydrocarbons is steadily increasing.

Halogenated substances from the group of unsaturated HFCs (u-HFCs, often referred to as HFOs[4]) with short atmospheric lifetimes and low global warming potentials are increasingly offered on the market. In addition, chlorinated substances are being developed in the form of unsaturated HCFCs (u-HCFCs, often referred to as HCFOs[5]) that (again) have an ozone-depleting potential. Unsaturated HFCs and HCFCs have low global warming potentials, albeit the impact of the large-scale use of these substances and in particular their persistent degradation products on the environment has not been extensively investigated. This report is intended to contribute to this question.

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[1] Unless otherwise stated, “Europe” is used synonymously with “EU-28” in this report. The EU-28 includes all 28 Member States of the European Union as it existed until February 1, 2020 (including the United Kingdom of Great Britain and Northern Ireland).

[2] F-gas Regulation (EC) No 842/2006 and Directive 2006/40/EC (MAC-Directive)

[3] F-gas Regulation (EU) No 517/2014

[4] Short for hydrofluoroolefin, a term used by industry in the Anglo-Saxon region

[5] Short for hydrochlorofluoroolefin, a term used by industry in the Anglo-Saxon region

Assessment of the current status

In a first step, the current status was analysed (Chapter 2). The entire life cycle of of the investigated halogenated refrigerants, foam-blowing agents and aerosol propellants including the atmospheric degradation was mapped. Applications, quantities, and compositions of halogenated greenhouse gases in Germany and Europe as well as their emissions during production, use and disposal are presented. Furthermore, information on by-products from the manufacture and secondary components of the investigated substances was compiled. The degradation routes and degradation products of halogenated greenhouse gases were identified in detail and their pathways into the environment quantified. Finally, the impact of these degradation products on the environment was evaluated.

Relevant substitutes with low GWP, which are already currently used in large quantities as refrigerants, foam blowing agents and aerosol propellants are listed in Table S 1. These are u-HFC-1234yf, as a replacement for HFC-134a in mobile air conditioning systems for cars since 2011, u-HFC-1234ze(E), as a replacement for HFCs with high GWP as a foam blowing agent and propellant for aerosols, as well as u-HFC-1336mzz(Z) and u-HCFC-1233zd(E) as replacements for HFCs as foam blowing agents. The u-HFC-1234yf and the u-HFC-1234ze(E) are also components of many new refrigerant mixtures (so called blends) that are used in refrigeration and air conditioning.

Table S 1: List of unsaturated halogenated refrigerants, foam blowing agents and aerosol propellants with low global warming potential currently commercially available in Europe (EU-28).

Substance name	Chemical name	Molecular formula	Main use
u-HFC-1234yf	2,3,3,3-tetrafluoropropene	$CF_3CF=CH_2$	refrigerant
u-HFC-1234ze(E)	(1E)-1,3,3,3-tetrafluoropropene	trans-$CF_3CH=CHF$	refrigerant, foam blowing agent, aerosol propellant
u-HCFC-1233zd(E)	(E)-1-chloro-3,3,3-trifluoropropene	trans-$CF_3CH=CHCl$	refrigerant, foam blowing agent
u-HFC-1336mzz(Z)	(2Z)-1,1,1,4,4,4-hexafluorobutene	cis-$CF_3CH=CHCF_3$	foam blowing agent
u-HFC-1336mzz(E)	(2E)-1,1,1,4,4,4-hexafluorobutene	trans-$CF_3CH=CHCF_3$	refrigerant
u-HCFC-1224yd(Z)	cis-1-chloro-2,3,3,3-tetrafluoropropene	cis-$CF_3CF=CHCl$	refrigerant, foam blowing agent

Emissions from the manufacture, use and disposal of HFCs, u-HFCs and u-HCFCs

The production of halogenated greenhouse gases in Europe is limited to a few HCFCs and HFCs. HFC-134a, HFC-365mfc, HFC-227ea, HFC-143a, and HCFC-22 are produced in relevant quantities. Halogenated substitutes with low GWP are mainly produced in the US and in China as well as in Japan and in India. Quantitatively, the most relevant by-product in Europe is HFC-23, which is formed especially during the production of HCFC-22. The emissions from production have rarely been investigated and are usually neither identified nor quantified. The tables in Chapters 2.4.1 and 2.4.2 (Table 4 and Table 5) list some of the by-products and intermediates, as well as chemical precursors and potential secondary components, based predominantly on analysis of literature and patents.

A solid data basis on the use of halogenated greenhouse gases in Europe and Germany are freely available annual reports from the European Environment Agency (EEA) based on the reporting obligations set out by the EU F-Gas Regulation[6] as well as annual surveys of the German Federal Statistical Office[7]. The data show that HFC-134a contributes by far the largest share of the halogenated greenhouse gases used in the EU and especially in Germany. In 2018, this share was 38 % for the EU and 46 % for Germany. The share of u-HFC-1234yf was 13 % in the EU and 24 % in Germany (Table 6 in Chapter 2.5.1). From 2016 to 2018, the share of u-HFC-1234yf in the EU increased almost three times, in Germany even four times, mainly due to the substitution of HFC-134a with u-HFC-1234yf in mobile air conditioning (for passenger cars). The largest area of application for fluorinated greenhouse gases in 2018 was the refrigeration sector with 74 % in the EU and 77 % in Germany. Foam blowing agents were used with a share of 12 % in the EU and 15 % in Germany, propellants for aerosols had a share of 10 % and 7 %, respectively (Table 7 in Chapter 2.5.1). In all sectors, the use phase is responsible for the largest contribution to total emissions (Table 10 in Chapter 2.5.2).

The disposal or intended destruction of halogenated greenhouse gases was also quantified based on the EU F-gas reporting. HFCs account for 85 % of the destroyed amount of halogenated greenhouse gases, about half of which is HFC-23. As a result of operational and vehicle accidents, halogenated greenhouse gases can be inadvertently destroyed. The products of an uncontrolled combustion depend on many factors, in particular the temperature and the available reaction partners. Complete thermal decomposition primarily produces hydrogen fluoride (HF), which forms in contact with moisture highly toxic hydrofluoric acid. The new halogenated substitutes with low GWP generally have a higher flammability than their predecessors with high GWP, which also increases the probability of the formation of toxic hydrofluoric acid in the event of accidental release.

Atmospheric Degradation

Once these gases have been released into the atmosphere, atmospheric degradation starts with an initial reaction, primarily with OH radicals. Halogenated carbonyl compounds are formed as intermediate products. The type of intermediate product determines the further degradation pathway in the atmosphere. For HFCs, u-HFCs and u-HCFCs, most of the halogenated carbonyl compounds formed are further broken down to hydrogen fluoride (HF) and carbon dioxide (CO_2), except for the two compounds trifluoroacetyl fluoride (TFF, CF_3CFO) and trifluoroacetaldehyde (CF_3CHO). With water, TFF reacts completely to the highly persistent and highly mobile trifluoroacetic acid (TFA, CF_3COOH). For trifluoroacetaldehyde, a TFA formation rate of up to 10 % can be assumed. Now and in the future, large quantities of two substances that strongly form TFA will be used, namely HFC-134a, of which 7-20 % is degraded to TFA on a molar basis and u-HFC-1234yf, which completely degrades to TFA (Figure S 1). Additionally, there are further halogenated gases that form TFA during atmospheric degradation (see Table 14 in Chapter 2.7.4 and Table 15 in Chapter 2.8).

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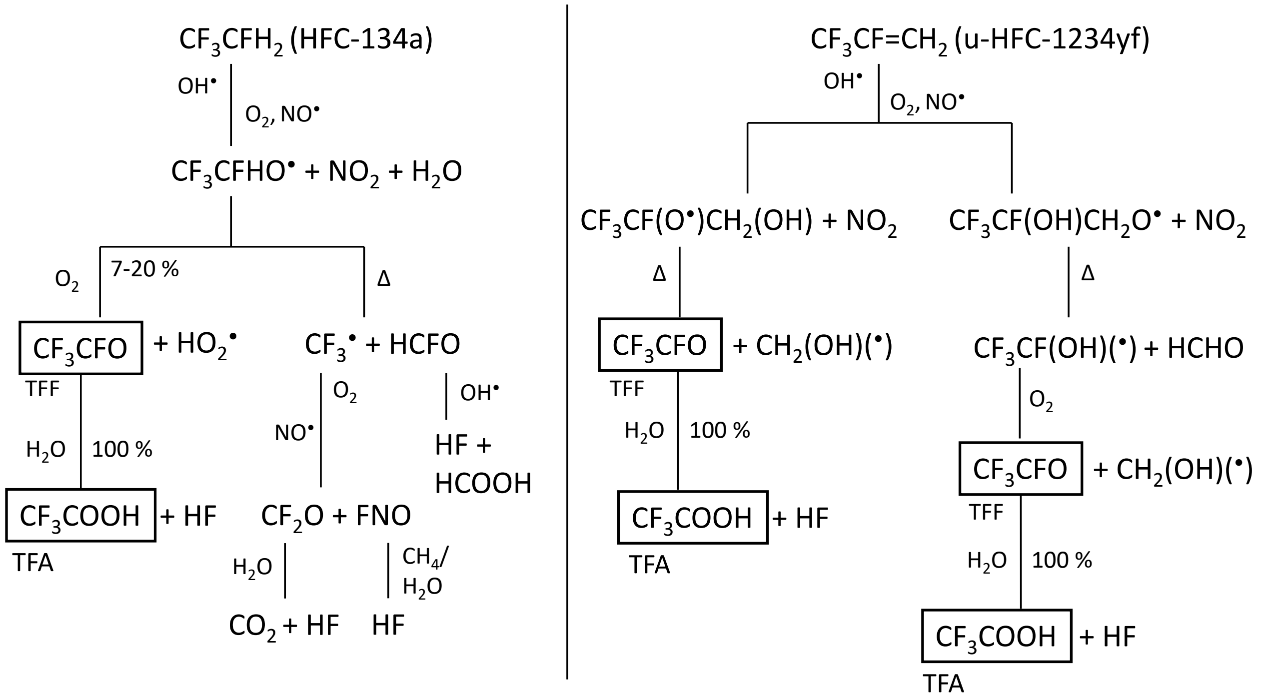
[6] Article 19 of Regulation (EU) Nr. 517/2014

[7] Report on the collection of certain climate-relevant substances by the German Federal Statistical Office.

Figure S 1: Atmospheric degradation of HFC-134a (left) and u-HFC-1234yf (right) via the fluorinated intermediates trifluoroacetyl fluoride (TFF, CF_3CFO), CF_3 radicals and HCFO to the terminal fluorinated degradation products trifluoroacetic acid (TFA) and hydrogen fluoride (HF).



Source: own research, Öko-Recherche

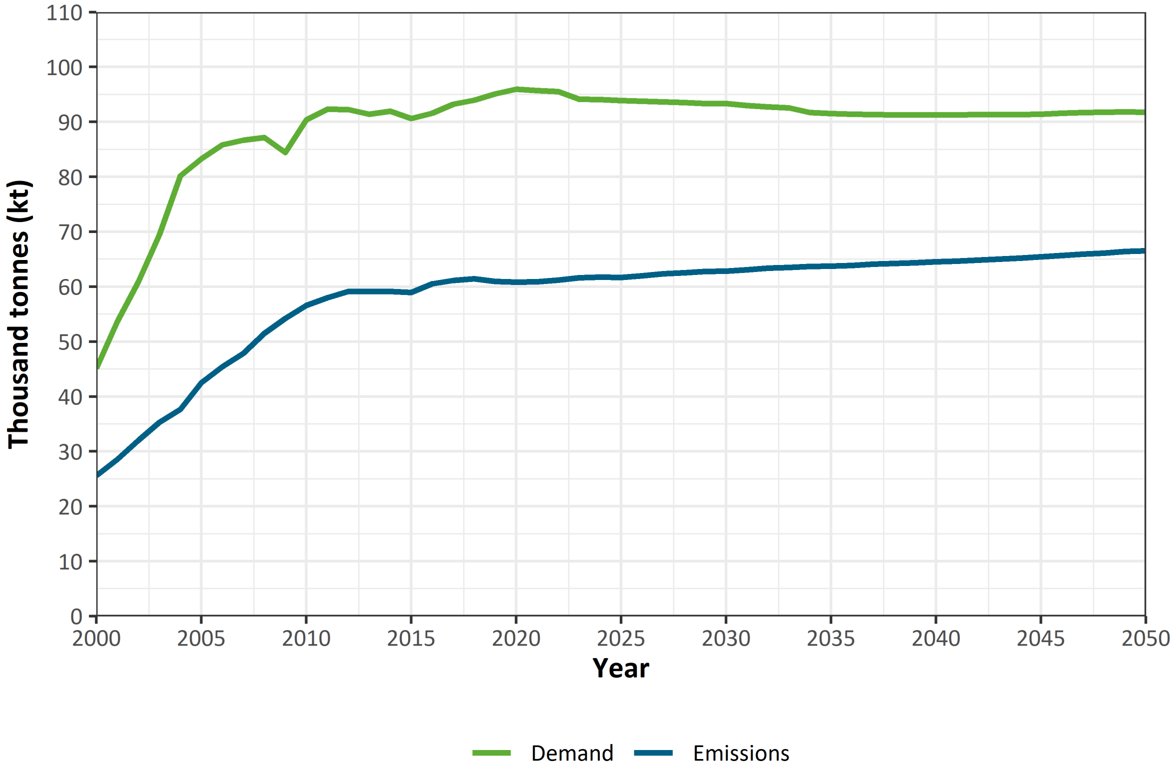
Demand for and emissions of halogenated refrigerants and blowing agents up to the year 2050

For a comprehensive assessment of the use and emissions of halogenated refrigerants and blowing agents up to the year 2050 and the resulting TFA amount in the 28 EU Member States (EU-28), a model for the projection of halogenated greenhouse gases was used (Chapter 3). This model comprises all relevant sectors in which fluorinated greenhouse gases are used in Europe and projects the demand and emissions for each substance in each sector up to the year 2050. The model includes new halogenated substitutes with low GWP and all available data from the reporting to the UN Climate Secretariat, as well as other models, market information and expert surveys.

The aim of the projections was to develop a scenario in which a maximum market penetration of halogenated substitutes in relation to natural substances is assumed in every application in the refrigeration, air conditioning, foam blowing and aerosol propellant sector, unless an alternative with halogen-free substitutes is already established or very likely to be established from the current perspective. The annual emissions calculated by the model were then offset against the substance-specific TFA formation rates in order to determine the maximum annual TFA quantities to be expected from the atmospheric degradation of halogenated substances in Europe (EU-28).

The projections show only a very small decrease in the total demand for HFCs, u-HFCs and u-HCFCs from about 96,000 tonnes in 2020 to approximately 92,000 tonnes in 2050. The total emissions continue to rise from about 61,000 tonnes in the year 2020 to around 67,000 tonnes in 2050 (Figure S 2, Table 23). In the air-conditioning and refrigeration sector, the demand consists of the initial refrigerant charge if units are manufactured in the EU-28, part of which emits in the course of the equipment's lifetime, and the refilling quantities added during servicing. Emissions typically occur with a time lag to the initial charging and include the release of gases during the use phase and the disposal of end-of life equipment.

Figure S 2: Demand and emissions of HCFCs (up to 2015)[8], HFCs, u-HFCs and u-HCFCs in Europe (EU-28) in kilotonnes for the period from 2000 until 2050.



Source: own research, Öko-Recherche

In 2020, the mobile air conditioning sector accounted for both the highest refrigerant demand of around 31,600 tonnes and the highest emissions of about 29,500 tonnes. At present, existing vehicles using HFC-134a are the main emission source, while from 2030, u-HFC-1234yf will be the refrigerant with the highest demand and emissions. Mobile air conditioning systems in passenger cars have the largest share in every case.

Stationary air conditioning, which includes room air conditioners, heat pumps and chillers, does not show an increase in demand of around 25,000 tonnes in the projections from 2020 onwards, while emissions will rise from around 9,000 tonnes in 2020 to around 16,000 tonnes in 2050. For the refrigeration sector, a demand of around 17,000 tonnes in 2020 is calculated, followed by a demand of around 13,000 tonnes for foam blowing. While the demand in the refrigeration sector will drop to around 13,000 tonnes by 2050, it will remain constant at around 13,000 tonnes for foam blowing agents.

In terms of emissions, the sectors differ largely: While emissions from the refrigeration sector will decrease by almost half from around 9,000 tonnes to around 5,000 tonnes in the period from 2020 to

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[8] Since 1 January 2010 the refill of refrigeration and air conditioning units with virgin HCFCs is banned in the EU according to EU Regulation No 1005/2009. Since 1 January 2015 also the use of recycled HCFCs for the servicing of refrigeration and air conditioning units is prohibited.

2050, projected emissions from the foam sector will increase from approximately 5,000 tonnes to around 6,000 tonnes. In the remaining sectors, demand and emissions will grow just slightly in the years from 2020 to 2050: Demand will rise from about 9,000 tonnes to around 10,000 tonnes and emissions are projected to increase from ca. 5,000 tonnes to around 6,000 tonnes.

When looking at demand and emissions by substance, it becomes apparent that especially HFC-125, HFC-134a, HFC-32, u-HFC-1234yf and u-HFC-1234ze will play a greater role in the period from 2000 to 2050. The quantities of substances with a higher GWP such as HFC-125 and HFC-134a will decrease sharply by 2050.

TFA quantities arising from halogenated substances

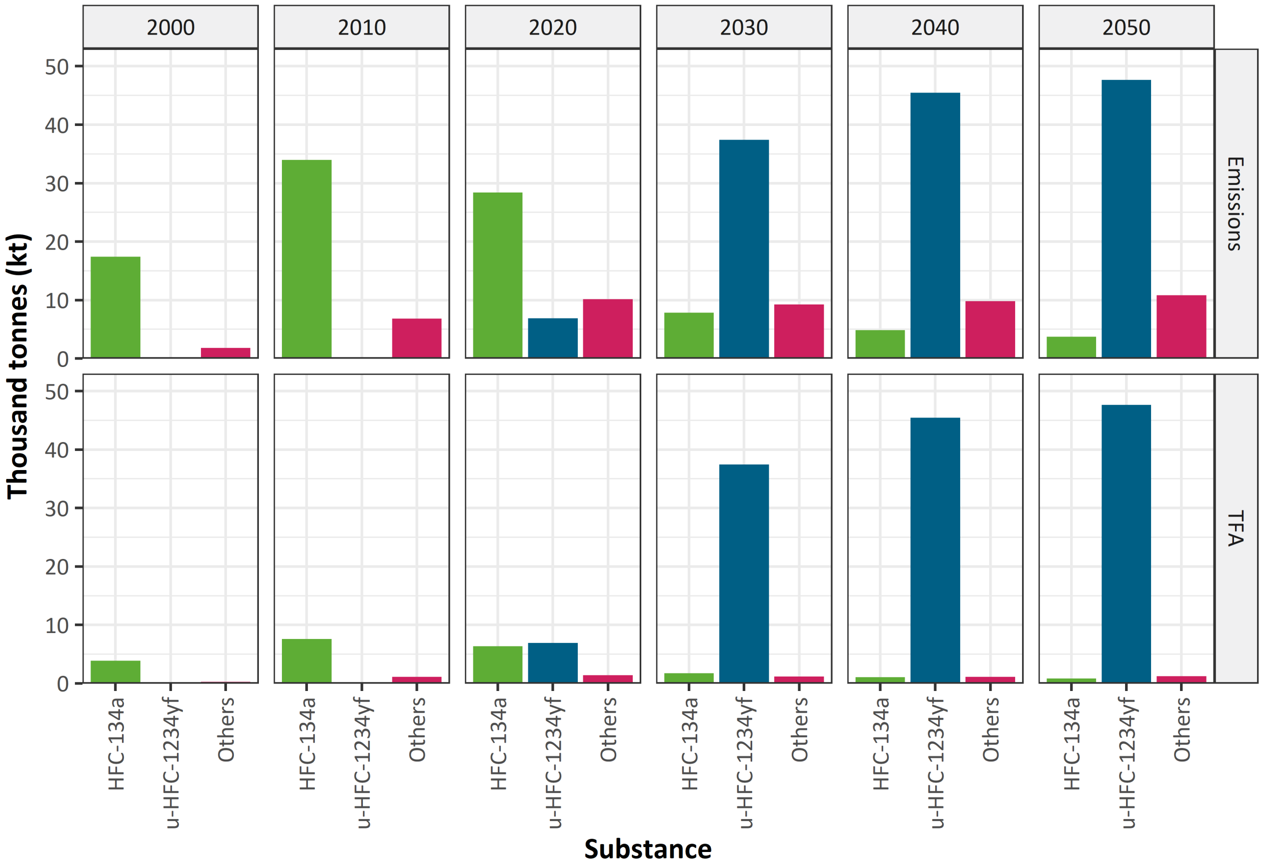
On the basis of the projected emissions, the amount of TFA arising from each substance in the various application areas was calculated. For 2020, this resulted in a total TFA quantity of slightly less than 15,000 tonnes in the EU-28, which will rise continuously until 2050 and then amount to around 50,000 tonnes per year (Table 26 in Chapter 3.4.3.1). For Germany, the respective TFA quantity ranges just over 2,000 tonnes in 2020 and around 6,500 tonnes in 2050.

With regard to the formation of TFA during atmospheric degradation, HFC-134a and u-HFC-1234yf are particularly relevant (Figure S 3, Table 27 in Chapter 3.4.3.2). While HFC-134a accounts for almost half of the emissions of all projected substances in Europe up to 2020, this proportion will decrease to around 10 % by 2030 and to around 5 % by 2050. The emissions of u-HFC-1234yf only amount to around 10 % of the total emissions in 2020. This share will increase to around 60 % by 2030 and to approximately 70 % by 2050.

In 2020 around 7,000 tonnes of TFA result from the degradation of u-HFC-1234yf emissions in Europe alone. This corresponds to 47 % of the total TFA formed in that year from all substances projected in the model. The emissions of HFC-134a account for around 6,000 tonnes, 43 % of the total amount of TFA.

By 2030, the amount of TFA from the degradation of u-HFC-1234yf will increase significantly to approximately 37,000 tonnes, while TFA resulting from the degradation of HFC-134a will decrease to about 2,000 tonnes.

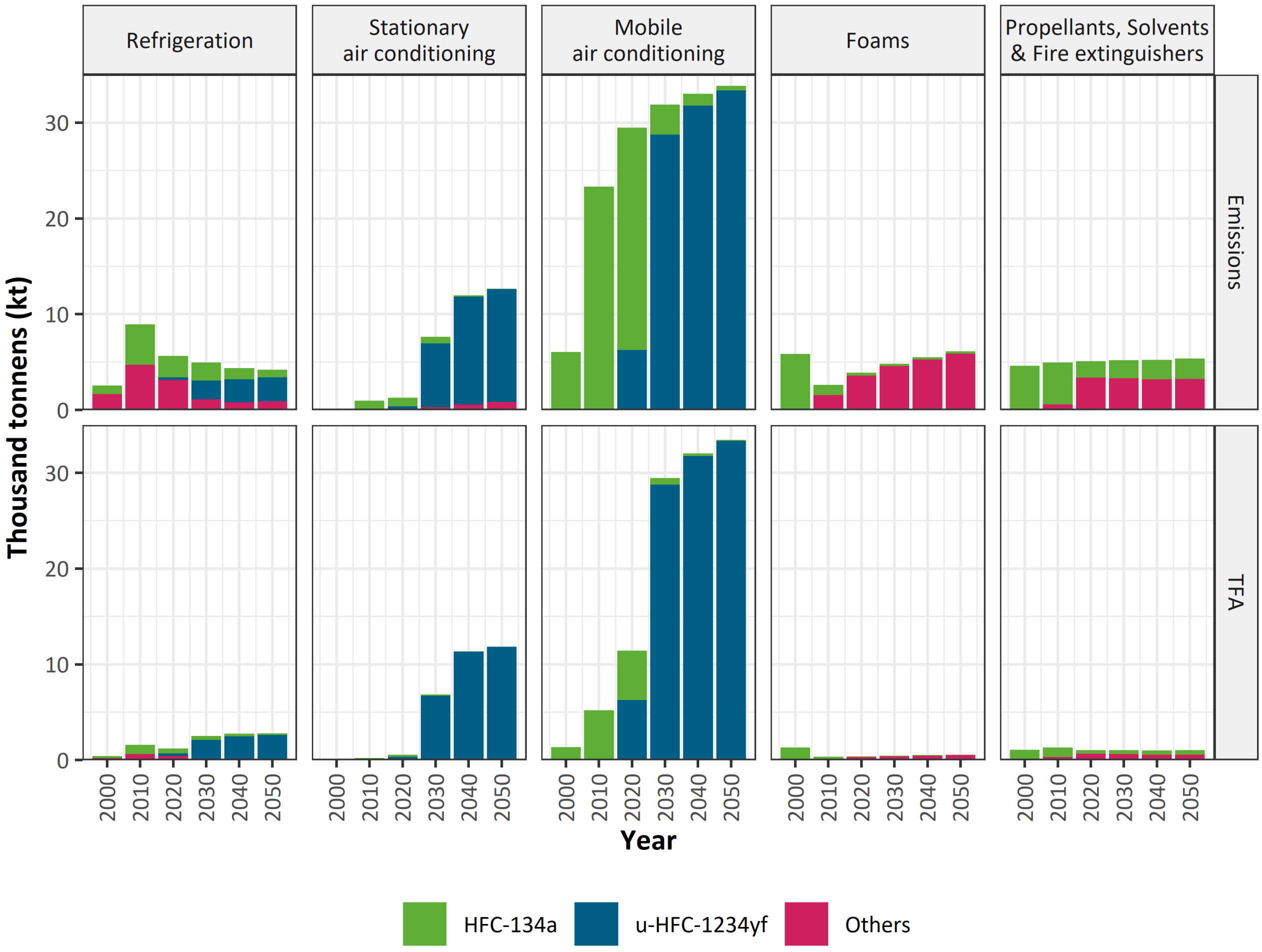
Figure S 3: Trends of European emissions (EU-28) and resulting TFA quantities formed by relevant HFCs, u-HFCs and u-HCFCs used as refrigerants and blowing agents in various applications in kilotonnes in the period from 2000 to 2050. All other projected substances that form TFA are summarized as “Others”.



Source: own research, Öko-Recherche

In 2050, the contribution of HFC-134a accounts for only 2 %, while u-HFC-1234yf is responsible for almost 96 % of the total amount of TFA from the projected substances. Therefore, sectors in which HFC-134a and u-HFC-1234yf are used in large quantities contribute greatly to TFA formation. The highest amount of TFA relates to mobile air conditioning. In stationary air conditioning, the greatest growth in emissions and resulting TFA formation is expected from 2020 onwards (Figure S 4). For Germany, the picture for substances and sectors is similar to that of Europe.

Figure S 4: European (EU-28) emissions of important HFCs, u-HFCs and u-HCFCs in refrigerants and blowing agents, and resulting trifluoroacetic acid (TFA) quantities in kilotonnes by sector for the years 2000 to 2050 in 10-year steps. All other projected TFA-forming substances are summarized as "Others". The sector "Others" is not shown, as the TFA quantities here are at a maximum of about 0.03 kilotonnes (30 tonnes).

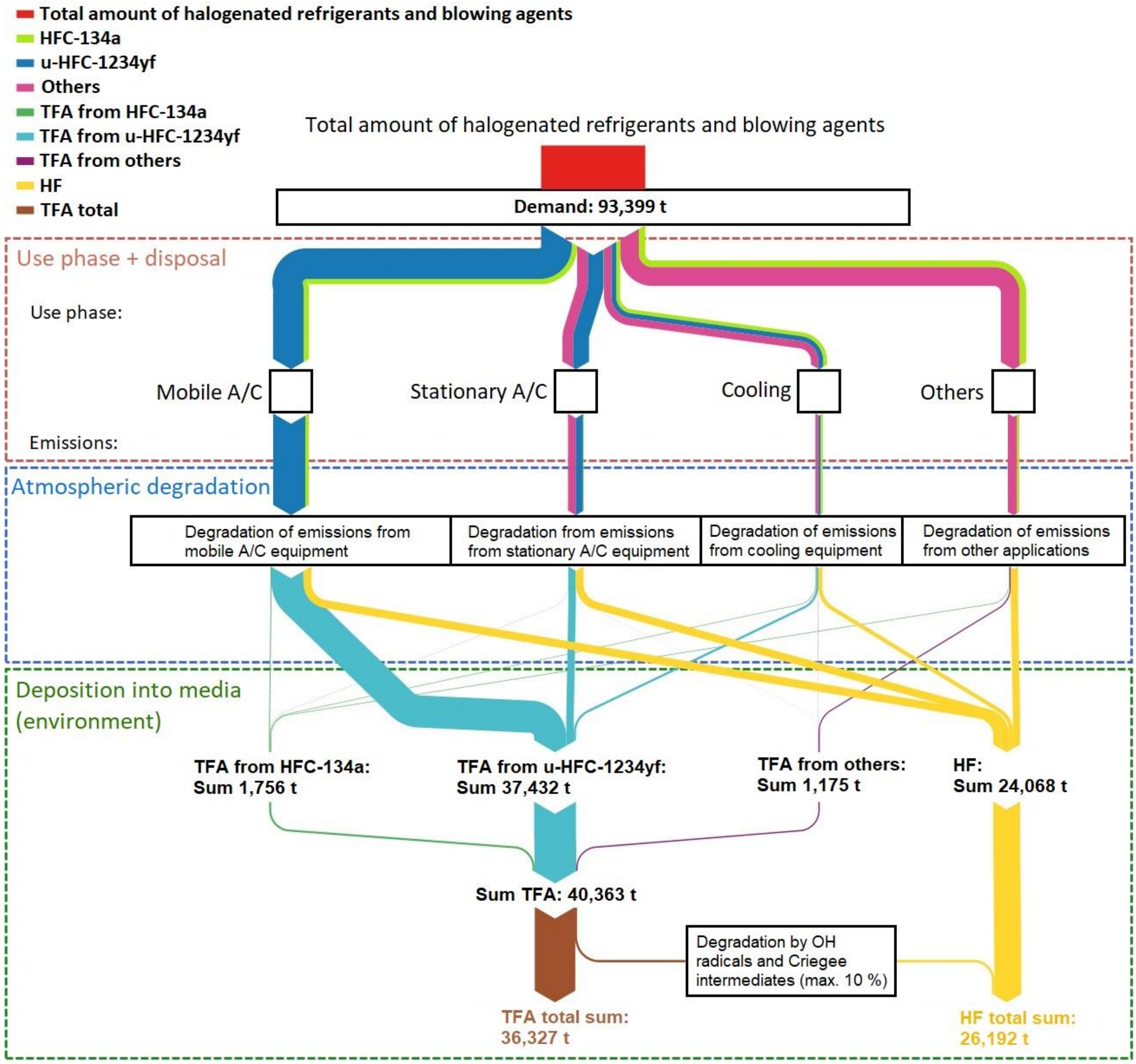


Source: own research, Öko-Recherche

Visualization of the mass flows for the year 2030

In order to estimate the contribution of halogenated refrigerants and blowing agents in the different application sectors, Figure S 5 shows a visualization of the mass flow of total European emissions from the various sectors for the year 2030 for different substances and the resulting TFA quantities that are deposited regionally and globally. The increasing trend in TFA emissions from substances with high TFA formation rates that are used and emitted in large quantities - such as HFC-134a now and u-HFC-1234yf in the future - is clearly evident. With the increasing use of halogenated substitutes with low global warming potentials, the deposition of TFA into the environment will grow sharply.

Figure S 5: Sankey mass flow diagram of the total European (EU-28) emissions of the modelled halogenated substances from use and disposal in the various sectors and the atmospheric degradation products trifluoroacetic acid (TFA) and hydrogen fluoride (HF) for the year 2030. The sectors foam blowing agents, aerosol propellants, solvents, and fire extinguishing agents as well as the semiconductor industry and emissions from HFC production are summarized as "Others".



Source: own research, Öko-Institut and Öko-Recherche

Occurrence of TFA or trifluoroacetate and input into the environment

It has so far been assumed that TFA, in the form of its salt trifluoroacetate (CF_3COO^-), occurs naturally only in the oceans, although the exact sources are unknown. The concentration in the oceans was 10 ng/L to 250 ng/L in the 1990s and early 2000s. However, with a high degree of certainty TFA or trifluoroacetate found on the mainland and in surface waters, originates mainly from anthropogenic sources. Trifluoroacetate gets into the soil and groundwater by means of wet deposition (via precipitation, snow, or fog) or by means of dry deposition with salt formation (e.g. sodium trifluoroacetate). Due to its high mobility, trifluoroacetate finally enters drinking water and subsequently accumulates there due to its high persistence.

Singular measurements in Germany in the 1990s showed a ubiquitous distribution of trifluoroacetate in rainwater, fog water, surface waters and anthropogenically influenced spring waters. The concentrations ranged from 10 ng/L to 410 ng/L in rainwater. Only in fog water, higher concentrations of 20 ng/L to 930 ng/L were measured, whereby it should be noted that fog water generally contains higher concentrations of haloacetic acids such as TFA and of inorganic ions as compared to rainwater measured at the same location. More recent measurements in Germany from 2017 usually showed higher concentrations of trifluoroacetate of up to 2,400 ng/L in rainwater.

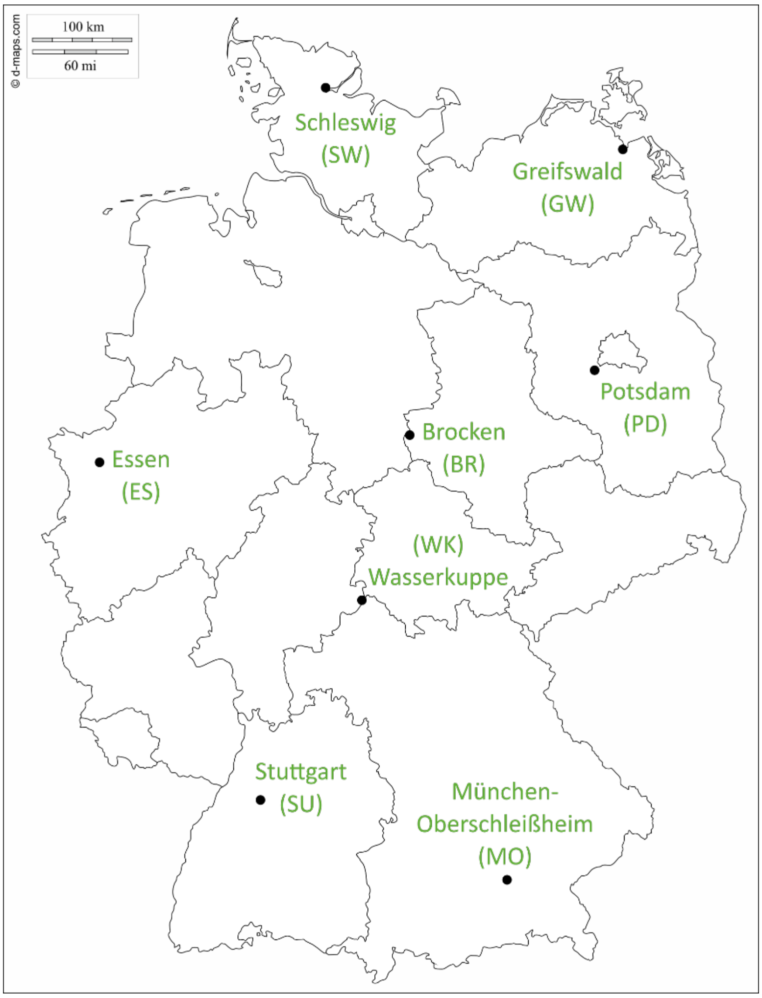
Since refrigerants, foam blowing agents and aerosol propellants are mainly emitted into the atmosphere, their degradation products such as trifluoroacetate are predominantly introduced via the precipitation path. Due to the complete conversion of u-HFC-1234yf to TFA and its widespread use as a replacement for HFC-134a in mobile air conditioning systems in cars and in new refrigerant mixtures, a high input of TFA through precipitation into the groundwater and drinking water is to be expected. This conclusion was also made in a simulation study from 2012 by Henne et al. (2012). The study assumed a complete refrigerant conversion from HFC-134a to u-HFC-1234yf in mobile air conditioning systems in cars in Europe by 2020 and calculated concentrations of TFA in precipitation averaging 600 ng/L to 800 ng/L with peaks of 2,000 ng/L in Southern Germany. In this study, however, only u-HFC-1234yf from emissions from mobile air conditioning systems in cars was considered as the source for TFA.

Trifluoroacetate measurements in rainwater

The entry of trifluoroacetate as a degradation product of emitted halogenated refrigerants, foam blowing agents and aerosol propellants occurs mainly via precipitation. An extensive literature analysis showed that to date no studies on the overall input of trifluoroacetate via the precipitation path for Germany or Europe have been published. In order to quantify this input, a Germany-wide measurement program was carried out for the first time (Chapter 4). Rainwater samples were taken at eight active measurement sites of the German Weather Service (DWD, Figure S 6) over a period of two years and analysed for their trifluoroacetate content by the Technology Centre for Water (TZW) in Karlsruhe.

In the period from February 2018 to January 2020 (March 2018 to February 2020 at the Stuttgart station), at each of the eight measuring stations samples of the precipitation collected on site were taken for every precipitation event. Based on the respective amount of precipitation collected, volume-equivalent monthly composite samples could be created for each site. The trifluoroacetate concentrations of the monthly composite samples were analysed in the laboratory. To validate the results, the trifluoroacetate concentration of each of the 1,187 individual precipitation samples was determined for the period February 2018 to January 2019 (March 2018 to February 2019 at the Stuttgart station). The respective area-related trifluoroacetate input was calculated from the trifluoroacetate concentration and the associated amount of precipitation.

Figure S 6: Locations of the rainwater sampling in Germany; the abbreviations used for each of the stations is indicated in brackets.

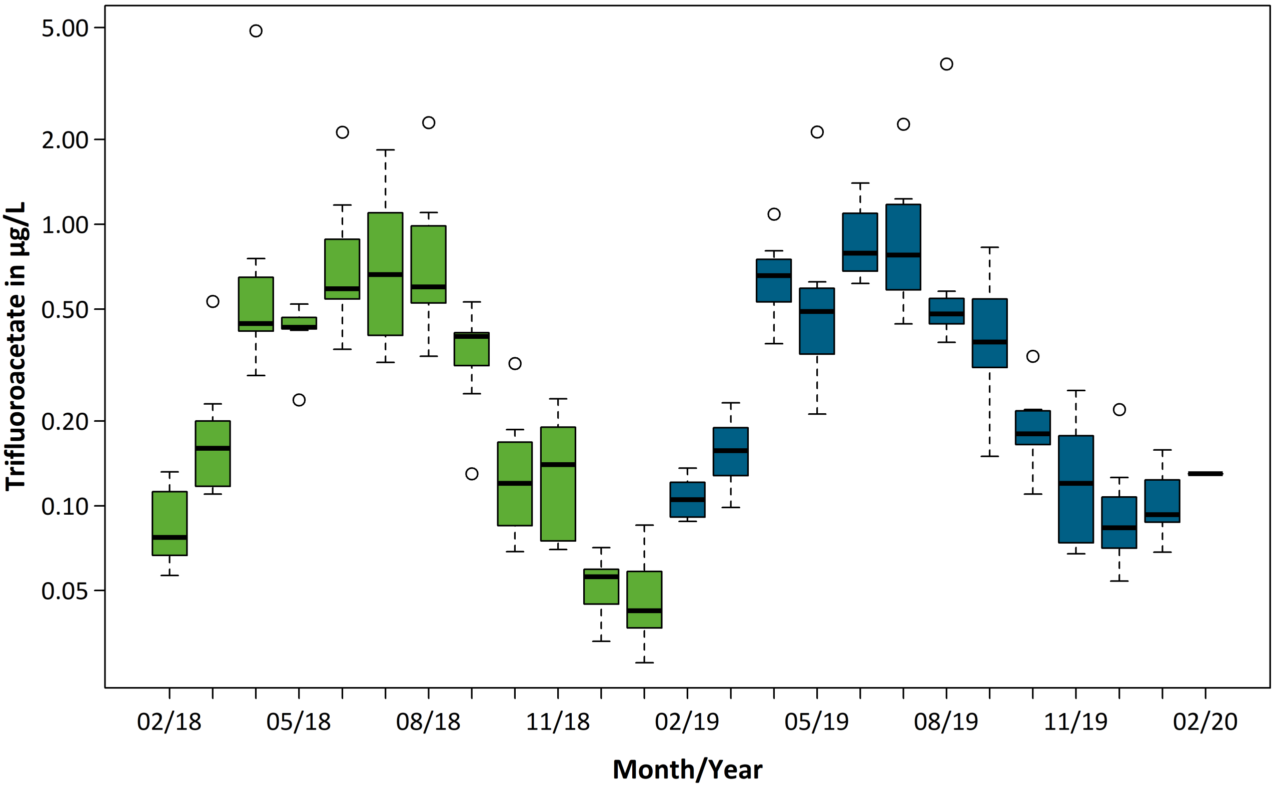


Source: copyright d-maps.com, edited by TZW Karlsruhe

Assessment of the trifluoroacetate concentrations of the monthly composite samples

The monthly composite samples of the precipitation show a pronounced annual variation with regard to the trifluoroacetate concentration, with the samples from the summer months containing significantly higher concentrations than those from the winter months (Figure S 7). The mean trifluoroacetate concentration in the period 2018/2019 was 0.429 µg/L (range from 0.028 µg/L to 4.780 µg/L), in the period 2019/2020 it was 0.453 µg/L (range 0.054 µg/L to 3.710 µg/L). The median concentrations were almost identical (0.245 µg/L and 0.244 µg/L).

Figure S 7: Box plots of the precipitation-weighted trifluoroacetate concentrations of the volume-equivalent monthly composite samples of precipitation from February 2018 (02/18) to February 2020 (02/2020) from seven measuring stations that only collected wet deposition samples. Grouping of data is based on time (month and year). The periods from February to January are separated by colour. The y-axis is shown on a binary logarithmic scale. Station Stuttgart is not included in 02/18. For February 2020 there is only one monthly composite value for the Stuttgart station.



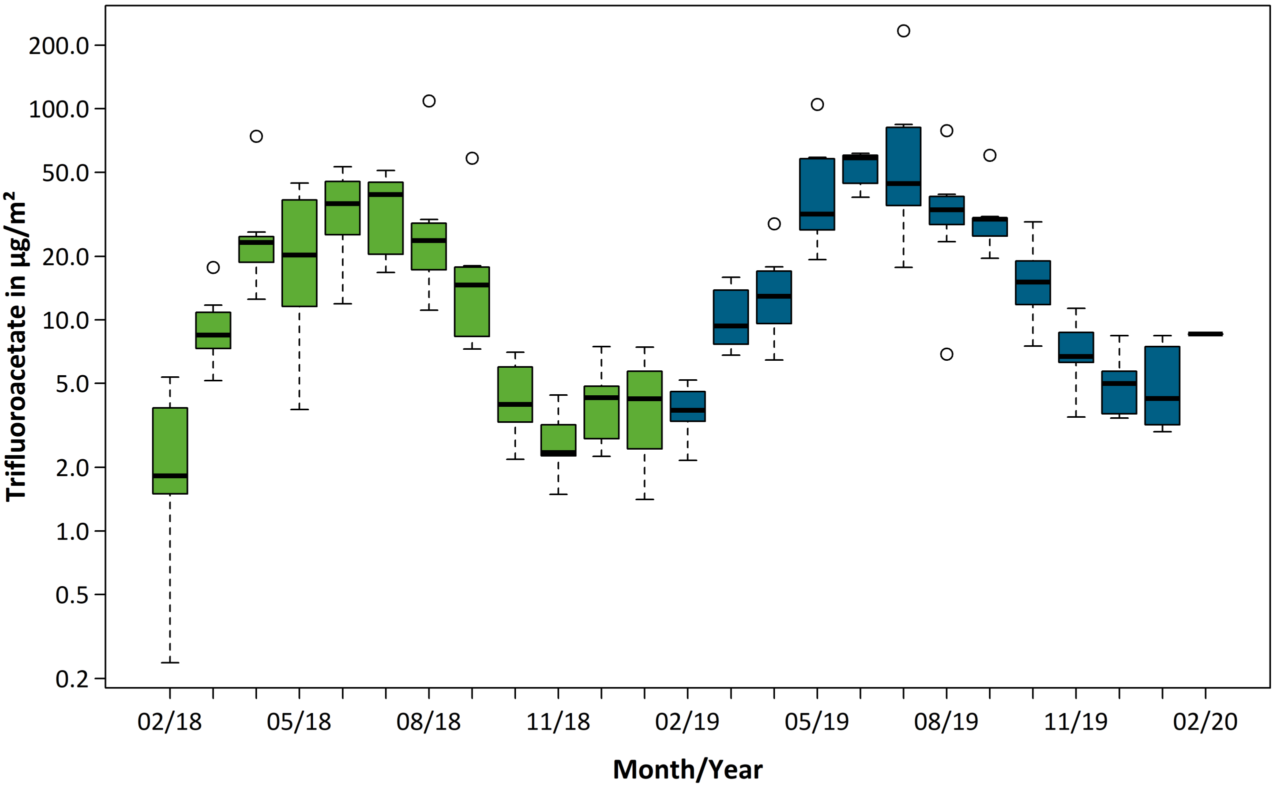
Source: own research, Öko-Recherche and TZW Karlsruhe

The data for the Brocken station is not shown in Figure S 7 and Figure S 8. In contrast to the results of the other stations, they contain not only the wet, but the sum of wet and dry deposition.

Area-related trifluoroacetate deposition

The trifluoroacetate deposition also showed maxima in the summer months and significantly lower values in the winter months (Figure S 8). On average, the trifluoroacetate deposition was 16.719 µg/m^2 (0.238 µg/m^2 to 108.790 µg/m^2) in the period 2018/2019 and 25.463 µg/m^2 (2.158 µg/m^2 to 234.037 µg/m^2) in the period 2019/2020. Even if the medians are used (8.292 µg/m^2 and 14.863 µg/m^2), the deposition in the period 2018/2019 was lower than in 2019/2020. Since the median trifluoroacetate concentrations in the precipitation were the same in both periods, the increase in the trifluoroacetate deposition in 2019 relates to higher amounts of precipitation compared to the very dry year 2018. These findings underline that it is necessary for comparisons to not only determine the concentrations in the precipitation, but to also refer to the amount of precipitation at different sites and over longer periods of time, as was done in this project.

Figure S 8: Box plots of the trifluoroacetate deposition over the precipitation from February 2018 (02/18) to February 2020 (analysis of the volume-equivalent monthly composite samples) of all seven measuring stations that only recorded the wet deposition. Grouping of data based on time (month and year). The periods from February to January are separated by colour. The y-axis is shown on a binary logarithmic scale. Station Stuttgart is not included in 02/18. For February 2020 there is only one monthly composite value for the Stuttgart station.



Source: own research, Öko-Recherche and TZW Karlsruhe

Significantly smaller variations in trifluoroacetate concentration and deposition were observed between the individual measuring stations than between months. Urban centres (Munich, Essen, and Stuttgart) showed the highest values. No increased TFA concentrations or depositions were found at the coastal monitoring stations in Greifswald and Schleswig.

Analysis of individual precipitation samples

The analysis of the individual precipitation samples for the period 2018/2019, without considering the related amount of precipitation, resulted in a mean concentration of 0.703 µg/L. The mean precipitation-weighted trifluoroacetate concentration over all measuring stations for the period 2018/2019 was 0.335 µg/L. This confirmed the results of the monthly composite samples. The high maximum concentrations of up to 38 µg/L were particularly striking at the Munich-Oberschleißheim site. On average, for all stations, a daily trifluoroacetate deposition of 1.28 µg/m^2 was derived for the period 2018/2019.

Annual trifluoroacetate deposition in Germany

The precipitation-weighted average concentration of all analysed individual samples (0.335 µg/L, Table 36 in Chapter 4.5.1.2) multiplied by the average total precipitation in Germany of 566 mm during the same period (DWD 2020) results in an average wet trifluoroacetate deposition of 190 µg/m^2 or approximately 68 tonnes in Germany in the period February 2018 to January 2019. In 2018, however, there was unusually low rainfall in Germany. If one refers to the multi-year average of 819 mm precipitation in Germany (reference period 1981-2010; DWD 2020), the annual wet deposition of trifluoroacetate amounts to 274 µg/m^2 or for the whole area of the Federal Republic of Germany a total of about 98 tonnes.

Trifluoroacetate concentrations in soil samples and plants

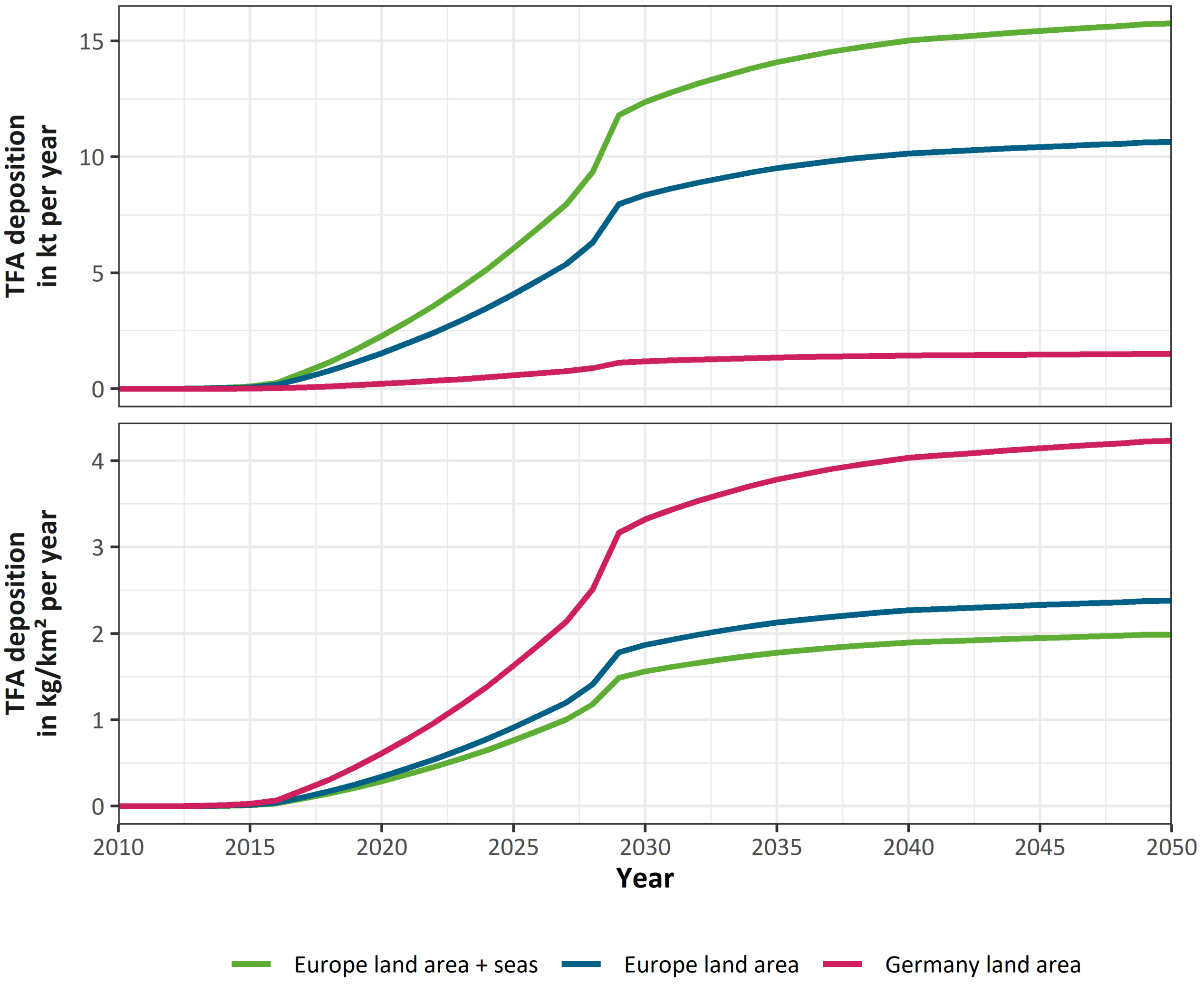
In addition to sampling the rainwater, soil samples were taken near the eight measuring stations in July and October 2019 and their trifluoroacetate concentration was determined. The soil samples showed trifluoroacetate concentrations of <0.2 µg/kg to 0.97 µg/kg dry weight (<0.2 µg/kg to 0.77 µg/kg fresh weight) and the maximum concentrations were found at the Brocken station. Furthermore, six typical herbaceous plant species were sampled at the Munich-Oberschleißheim station in July 2019. In the plant samples, the trifluoroacetate concentration was 35 µg/kg to 120 µg/kg dry weight (7.3 µg/kg to 39 µg/kg fresh weight). This corresponds to an enrichment factor in relation to the trifluoroacetate concentration of the rainwater of 16-87. Overall, the measured values for the soil and plant samples were within the range of the concentrations measured in other studies.

Model for the quantification of the TFA rainfall-concentration and TFA deposition

For further evaluation, the results of the projections and the measurement program were used by the Swiss Federal Laboratories for Materials Science and Technology (Eidgenössische Materialprüfungs- und Forschungsanstalt, Empa) to update an existing model for the quantification of TFA concentration in precipitation and TFA deposition. For this purpose, new data on the atmospheric concentration of u-HFCs and u-HCFCs from the vicinity of Frankfurt am Main were considered. The model included u-HFC-1234yf and important HCFCs and HFCs (HCFC-123, HCFC-124, HFC-134a, HFC-245fa, HFC-143a, HFC-365mfc and HFC-227ea). The modelled trifluoroacetate concentrations arising from these halogenated substances comprised less than 50 % of the precipitation measurements concentration. The remaining share could not be explained by degradation of the halogenated refrigerants and blowing agents involved. Since the model shows large uncertainty ranges due to simplified assumptions, it could still be improved, however this was beyond the scope of this project.

For u-HFC-1234yf, the future deposition of TFA from atmospheric degradation was also calculated using this model (Figure S 9). According to this, the absolute annual TFA deposition in tonnes in Germany and Europe (EU-27, Great Britain, Switzerland, and Turkey) will increase very sharply until 2030 and thereafter increase more slowly but continuously until 2050. In Germany, the average TFA deposition per area (kg/km^2) is well above the European average. Up to 2050, an increase in TFA deposition of approximately 4 kg/km^2 is to be expected. Compared to the mean deposition rates measured in this study, this would be an increase by a factor of 10. For Europe, an average annual TFA deposition rate of 2.5 kg/km^2 can be expected by 2050.

Figure S 9: Estimated future TFA deposition (input in kilotonnes per year) (top) and TFA deposition rates (input in kg/km² per year) (bottom) from the atmospheric degradation of u-HFC-1234yf for Europe (EU-27, Great Britain, Switzerland and Turkey) with surrounding seas (Europe land area + seas), the land area of Europe (Europe land area) and Germany (Germany land area).



Source: own research, Empa and Öko-Recherche

Comparison of fluoroacetate deposition with other studies

For comparison of the measurement results of this study with the existing scientific publications, the trifluoroacetate deposition for the two 12-month periods from February 2018 to January 2019 (2018/2019) and February 2019 to January 2020 (2019/2020) were calculated for the entire area of Germany. Based on the concentrations of the monthly composite samples, these amounted to a deposition of 187 g/km² or 67 tonnes of trifluoroacetate in the period 2018/2019 and 276 g/km² or 99 tonnes in the period 2019/2020. Based on the individual samples' depositions of 190 g/km² or 68 tonnes (precipitation-weighted) and 398 g/km² or 142 tonnes (not precipitation-weighted) were determined.

Only a few studies measured TFA or trifluoroacetate in precipitation over long periods of time. However, due to the strong seasonality and variation within a site, this is essential to make valid statements. The few studies that carried out continuous measurements showed gaps in the data collection or the calculated average values were only based on a small number of samples. Compared to two studies by Klein (1997) and Jordan and Frank (1999) on trifluoroacetate measurements in precipitation in Bayreuth in the period of 1995 to 1996, the concentration and deposition of trifluoroacetate in Germany in the period from 2018 to 2020 found in this study was three to four times higher.

Outlook

Within this study, some knowledge gaps were identified. Little is known about the formation and emission of halogenated substances in the production of HFCs, u-HFCs and u-HCFCs. Since a large number of different environmentally and health relevant substances can occur in the production process, their identification and the quantification of emissions are relevant. The same applies to the secondary components in HFCs, u-HFCs and u-HCFCs.

The formation potential of TFA from the atmospheric degradation of trifluoroacetaldehyde, which is an intermediate product of some relevant halogenated refrigerants and blowing agents, must also be clarified. So far unknown sources of emissions of saturated and unsaturated HFCs and HCFCs should be identified, for example the source of the increased emissions of u-HFC-1234ze in winter in Europe. It is of great interest to clarify the origin of the proportion of the measured amount of trifluoroacetate in the precipitation, which cannot be directly explained by the common emissions of refrigerants and blowing agents. In addition to the revision of the model used for TFA deposition, further possible atmospheric sources that have already been discussed in the literature, such as the combustion of fluoropolymers at low temperatures or the emission of fluorinated inhalation anaesthetics and solvents, should be analysed in more detail.

Due to the extremely high persistence and mobility of TFA and trifluoroacetate, the increasing use of halogenated substitutes with low global warming potentials leads to growing pollution of the groundwater and drinking water resources. Since persistent substances remain in the environment for a long time and neither effective natural mechanisms nor acceptable technical processes for removing TFA from drinking water resources are known, potential harm to the environment and humans can only be prevented by minimizing the input of TFA and its precursors. Even if the deposition of TFA and its precursors were to cease immediately, an extremely long-lived substance such as TFA or trifluoroacetate would remain in the environment for at least several decades.

The results of the analyses and projections underline the need for action to avoid further deposition of TFA and TFA-forming substances into the environment. The use of halogenated refrigerants, foam blowing agents, aerosol propellants and further TFA precursors should therefore be avoided. Alternatives with natural refrigerants should be preferred and promoted.

This report presents and describes the substance aspects and environmental effects of recently introduced halogenated refrigerants and blowing agents in greater detail. Therefore, the results of this report are also relevant for the implementation and further development of the EU F-Gas Regulation. The results of this report can also be used to analyse the effects of regulations or funding measures that refer to the use of HFCs, u-HFCs and u-HCFCs and which, in addition to economic and social impacts, also require assessment of environmental effects.

The TFA formation and accumulation from the use of halogenated refrigerants and blowing agents should also be examined and discussed for Europe and worldwide in order to be considered internationally in the implementation of the Kigali Amendment to the Montreal Protocol. This is needed urgently in view of the ongoing phase-out of ozone-depleting substances in developing countries and related introduction of alternatives to ozone-depleting substances because alternatives with non-halogenated substances already exist for most applications.

Zusammenfassung

Halogenierte Kohlenwasserstoffe werden bevorzugt als Kältemittel und als Treibmittel in Schäumen eingesetzt. Weitere Anwendungsgebiete umfassen die Nutzung als Treibmittel für Aerosole sowie als Löse- und Feuerlöschmittel. Der vorliegende Bericht gibt einen Überblick über den Stand der Verwendung halogenierter Kälte- und Treibmittel und die zukünftige Entwicklung. Die Studie beinhaltet insbesondere stoffliche Aspekte im Lebenszyklus und legt den Schwerpunkt auf den Eintrag persistenter Abbauprodukte halogenierter Kälte- und Treibmittel in die Umwelt in Deutschland und Europa (EU-28)[9]. Besonders werden dabei neue halogenierte Stoffe mit kleinem Treibhauspotenzial (GWP) betrachtet.

Motivation

Vollhalogenierte Fluorchlorkohlenwasserstoffe (FCKW), die maßgeblich für den Abbau der Ozonschicht verantwortlich sind und ein hohes Treibhauspotential haben, wurden in Folge des Montrealer Protokolls durch teilhalogenierte Fluorchlorkohlenwasserstoffe (HFCKW) mit kleinerem ozonschichtschädigendem Potential ersetzt. Durch eine Verschärfung des Montrealer Protokolls mussten auch HFCKW seit den 1990er Jahren durch teilfluorierte Kohlenwasserstoffe (HFKW) ersetzt werden.

Aufgrund ihres hohen Treibhauspotentials werden nun auch die HFKW schrittweise vom Markt genommen. In der Europäischen Union (EU) wurden HFKW bereits seit dem Jahr 2006 einschränkenden Regelungen[10] unterworfen. Zusätzlich wird mit der überarbeiteten F-Gas-Verordnung seit dem Jahr 2015[11] die HFKW-Menge progressiv verknappt, wobei die Berechnung der Mengen auf dem Treibhauspotential der geregelten Stoffe basiert. Im Jahr 2016 wurden die HFKW mit dem Kigali-Abkommen in das Montrealer Protokoll aufgenommen. Zukünftig werden daher in Europa und auch weltweit nur noch kleine HKFW-Mengen zur Verfügung stehen und tendenziell dem Einsatz in essentiellen Nischenanwendungen vorbehalten sein.

Als Ersatz für halogenierte Stoffe haben sich für viele Anwendungen bereits halogenfreie Kältemittel wie Kohlenwasserstoffe, Kohlendioxid (CO_2) und Ammoniak (NH_3) durchgesetzt. Diese schon vor den halogenierten Stoffen als Kältemittel bekannten Stoffe werden heute oft als natürliche Kältemittel bezeichnet. Bestes Beispiel ist die nahezu ausschließliche Verwendung von Isobutan (R600a) als Kältemittel in Haushaltskühlschränken in Europa, das seit Mitte der 1990er Jahre eingesetzt wird und mittlerweile weltweit akzeptiert ist. Auch große Industriekälteanlagen verwenden oftmals natürliche Kältemittel wie Ammoniak. In der Gewerbekälte nimmt der Anteil an Anlagen mit CO_2 und Kohlenwasserstoffen stetig zu.

Als Ersatzstoffe für HFKW mit hohem Treibhauspotential werden aber auch zunehmend halogenierte Stoffe aus der Gruppe der ungesättigten HFKW (u-HFKW, oft als HFO[12] bezeichnet) mit kurzen atmosphärischen Lebensdauern und niedrigen Treibhauspotentialen angeboten. Zusätzlich werden chlorierte Stoffe in Form von ungesättigten HFCKW (u-HFCKW, auch als HCFO[13] bezeichnet) entwickelt, die (wieder) ein ozonschichtschädigendes Potential aufweisen. Ungesättigte HFKW und HFCKW haben zwar ein niedriges Treibhauspotential aber der Einfluss der großskaligen Verwendung dieser Stoffe

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[9] Wenn nicht anders erwähnt, wird in diesem Bericht „Europa“ synonym mit „EU-28“ verwendet. Die EU-28 umfasst alle 28 Mitgliedsstaaten der Europäischen Union, wie diese bis zum 1. Februar 2020 bestand (inklusive Vereinigtes Königreich von Großbritannien und Nordirland).

[10] EU F-Gas-Verordnung Nr. 842/2006 und MAC-Richtlinie Nr. 2006/40/EG

[11] EU F-Gas Verordnung Nr. 517/2014

[12] Kurz für Hydrofluorolefin, eine Bezeichnung, die im angelsächsischen Raum von der Industrie verwendet wird

[13] Kurz für Hydrochlorfluorolefin, eine Bezeichnung, die im angelsächsischen Raum von der Industrie verwendet wird

und insbesondere ihrer persistenten Abbauprodukte auf die Umwelt ist bisher nicht weitreichend untersucht worden. Hierzu soll dieser Bericht einen Beitrag liefern.

Ermittlung des Ist-Zustandes

In einem ersten Schritt wurde der Ist-Zustand analysiert (Kapitel 2). Dazu wurde der gesamte Lebenszyklus der untersuchten halogenierten Kälte- und Treibmittel einschließlich des atmosphärischen Abbaus abgebildet. Dargestellt sind sowohl Anwendungen, Mengen und Zusammensetzungen halogenierter Treibhausgase in Deutschland und Europa sowie deren Emissionen bei der Produktion, Verwendung und Entsorgung. Weiterhin wurden Informationen zu Nebenprodukten aus der Herstellung und Nebenbestandteilen der untersuchten Stoffe zusammengestellt. Ausführlich wurden die Abbauwege und -produkte halogenierter Treibhausgase identifiziert und deren Eintragspfade in die Umwelt quantifiziert. Abschließend wurde die Wirkung dieser Abbauprodukte auf die Umwelt evaluiert.

Relevante halogenierte Stoffe mit niedrigem GWP, die derzeit bereits in großer Menge als Kälte- und Treibmittel Verwendung finden, sind in Tabelle S 1 aufgelistet. Dabei handelt es sich um u-HFKW-1234yf, als Ersatz für HFKW-134a in Pkw-Klimaanlagen seit 2011, u-HFKW-1234ze(E), als Ersatz für HFKW mit hohem GWP als Treibmittel für Aerosole und Schäume sowie u-HFKW-1336mzz(Z) und u-HFCKW-1233zd(E) als Ersatz von HFKW als Schaumtreibmittel. Der u-HFKW-1234yf und der u-HFKW-1234ze(E) sind zudem Bestandteile vieler neuer Kältemittelgemische, die in der Kälteerzeugung und Klimatisierung zum Einsatz kommen.

Tabelle S 1: Auflistung von derzeit in Europa (EU-28) kommerziell verfügbaren ungesättigten halogenierten Kälte- und Treibmitteln mit kleinem Treibhauspotential.

Stoffbezeichnung	Chemische Bezeichnung	Summenformel	Hauptverwendung
u-HFKW-1234yf	2,3,3,3-Tetrafluorpropen	$CF_3CF=CH_2$	Kältemittel
u-HFKW-1234ze(E)	(1E)-1,3,3,3-Tetrafluorpropen	trans-$CF_3CH=CHF$	Kältemittel, Schaumtreibmittel, Aerosoltreibmittel
u-HFCKW-1233zd(E)	(E)-1-Chlor-3,3,3-trifluorpropen	trans-$CF_3CH=CHCl$	Kältemittel, Schaumtreibmittel
u-HFKW-1336mzz(Z)	(2Z)-1,1,1,4,4,4-Hexafluorbuten	cis-$CF_3CH=CHCF_3$	Schaumtreibmittel
u-HFKW-1336mzz(E)	(2E)-1,1,1,4,4,4-Hexafluorbuten	trans-$CF_3CH=CHCF_3$	Kältemittel
u-HFCKW-1224yd(Z)	Cis-1-Chlor-2,3,3,3-tetrafluorpropen	cis-$CF_3CF=CHCl$	Kältemittel, Schaumtreibmittel

Emissionen bei Herstellung, Verwendung und Entsorgung von HFKW, u-HFKW und u-HFCKW

Die Herstellung halogenierter Treibhausgase in Europa beschränkt sich auf wenige HFCKW und HFKW. In relevanten Mengen produziert werden insbesondere HFKW-134a, HFKW-365mfc, HFKW-227ea, HFKW-143a und HFCKW-22. Halogenierte Ersatzstoffe mit kleinem GWP werden hauptsächlich in den USA und China produziert sowie in Japan und Indien. Das quantitativ relevanteste Nebenprodukt in Europa ist das fluorierte F-Gas HFKW-23, das insbesondere bei der Produktion von HFCKW-22 anfällt. Die Emissionen aus der Produktion sind wenig untersucht und werden in der Regel weder identifiziert noch quantifiziert. In Table 4 in Kapitel 2.4.1 und Table 5 in Kapitel 2.4.2 sind einige vorwiegend aus der Literatur und Patenten ermittelte Neben- und Zwischenprodukte sowie Ausgangsstoffe und potentielle Nebenbestandteile aufgelistet.

Zur Verwendung halogenierter Treibhausgase in Europa und Deutschland sind aufgrund der Berichtspflicht gemäß EU F-Gas-Verordnung[14] jährlich erscheinende und frei verfügbare Berichte der europäischen Umweltagentur („European Environment Agency“, EEA) und die jährlichen Erhebungen des Statistischen Bundesamtes[15] eine solide Datengrundlage. Hieraus geht hervor, dass HFKW-134a in Europa und insbesondere in Deutschland den mit Abstand größten Anteil der verwendeten halogenierten Treibhausgase ausmacht. Im Jahr 2018 belief sich dieser Anteil auf 38 % für Europa und 46 % für Deutschland. Der Anteil von u-HFKW-1234yf war 13 % in Europa bzw. 24 % in Deutschland (Table 6 in Kapitel 2.5.1). In den Jahren von 2016 bis 2018 nahm der Anteil von u-HFKW-1234yf in Europa um fast das Dreifache zu, in Deutschland sogar um das Vierfache, was hauptsächlich auf die Umstellung von HFKW-134a auf u-HFKW-1234yf in der mobilen Klimatisierung (Pkw) zurückzuführen ist. Der größte Einsatzbereich fluorierter Treibhausgase war im Jahr 2018 sowohl in Europa mit 74 % als auch in Deutschland mit 77 % der Kältemittelsektor. Schaumtreibmittel fanden mit Anteilen von 12 % in Europa und bzw. 15 % in Deutschland Verwendung, Treibmittel für Aerosole hatten einen Anteil von 10 % bzw. 7 % (Table 7 in Kapitel 2.5.1). In allen Sektoren liefert die Nutzungsphase den größten Beitrag zu den Gesamtemissionen (Table 10 in Kapitel 2.5.2).

Die Entsorgung bzw. gezielte Zerstörung halogenierter Treibhausgase wurde ebenfalls anhand der EU F-Gase-Berichterstattung quantifiziert. 85 % der zerstörten Menge an halogenierten Treibhausgasen sind HFKW, davon ist etwa die Hälfte HFKW-23. In Folge von Betriebs- und Fahrzeugunfällen kann es zur unbeabsichtigten Zerstörung halogenierter Treibhausgase kommen. Die Produkte einer unkontrollierten Verbrennung sind dabei von vielen Faktoren abhängig, insbesondere der Temperatur und den verfügbaren Reaktionspartnern. Bei vollständiger thermischer Zersetzung entsteht vor allem Fluorwasserstoff (HF), der in Kontakt mit Feuchtigkeit zur hochgiftigen Flusssäure reagiert. Die neuen halogenierten Ersatzstoffe mit kleinem GWP weisen in der Regel eine höhere Brennbarkeit als ihre Vorgänger mit hohem GWP auf, womit auch die Wahrscheinlichkeit der Bildung toxischer Flusssäure bei unbeabsichtigter Freisetzung gestiegen ist.

Atmosphärischer Abbau

Sind diese Gase in die Atmosphäre gelangt, beginnt der atmosphärische Abbau über eine initiale Reaktion vorrangig mit OH-Radikalen. Als Zwischenprodukte entstehen halogenierte Carbonylverbindungen. Die Art des Zwischenproduktes entscheidet über den weiteren Abbau in der Atmosphäre. Bei HFKW, u-HFKW und u-HFCKW werden die meisten der entstandenen halogenierten Carbonylverbindungen weiter zu Fluorwasserstoff (HF) und Kohlendioxid (CO_2) abgebaut, ausgenommen sind die beiden Verbindungen Trifluoracetylfluorid (TFF, CF_3CFO) und Trifluoracetaldehyd (CF_3CHO). Trifluoracetylfluorid (TFF) reagiert mit Wasser vollständig zur hochgradig persistenten und hochmobilen Trifluoressigsäure (TFA, CF_3COOH), für Trifluoracetaldehyd kann von einer TFA-Bildungsrate von bis zu 10 % ausgegangen werden. In großen Mengen werden heute und in Zukunft insbesondere zwei stark TFA-bildende Stoffe eingesetzt, das sind der HFKW-134a, der zu 7-20 % und der u-HFKW-1234yf, der zu 100 % zu TFA abgebaut wird (Abbildung S 1). Daneben gibt es noch weitere halogenierte Gase, die beim atmosphärischen Abbau TFA bilden (Table 14 in Kapitel 2.7.4 und Table 15 in Kapitel 2.8).

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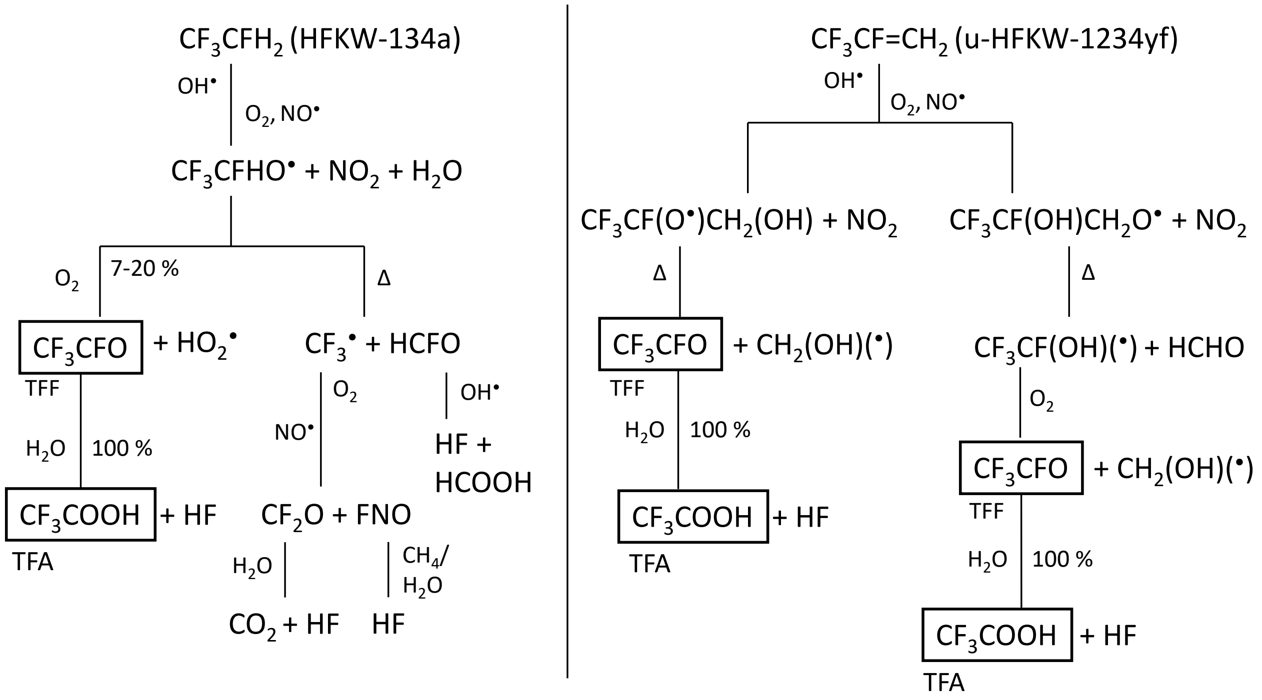
[14] Artikel 19 der Verordnung (EU) Nr. 517/2014

[15] Bericht zur Erhebung bestimmter klimawirksamer Stoffe des Statistischen Bundesamtes.

Abbildung S 1: Atmosphärischer Abbau von HFKW-134a (links) und u-HFKW-1234yf (rechts) über die fluorierten Zwischenprodukte Trifluoracetylfluorid (TFF, CF_3CFO), CF_3-Radikale und HCFO zu den terminalen fluorierten Abbauprodukten Trifluoressigsäure (TFA) und Fluorwasserstoff (HF).



Quelle: Eigene Darstellung, Öko-Recherche

Bedarf und Emissionen halogenierter Kälte- und Treibmittel bis zum Jahr 2050

Für eine umfassende Einschätzung der Verwendung und Emission halogenierter Kälte- und Treibmittel bis zum Jahr 2050 und der daraus gebildeten TFA-Menge in Europa (EU-28)[16], wurde ein Modell zur Projektion halogenierter Treibhausgase verwendet (Kapitel 0). Dieses Modell umfasst alle relevanten Sektoren, in denen fluorierte Treibhausgase in Europa Verwendung finden und projiziert den Bedarf und die Emission für jeden einzelnen Stoff in jedem Sektor bis ins Jahr 2050. Im Modell wurden neue Ersatzstoffe mit kleinem GWP und alle verfügbaren Daten aus der Berichterstattung an das Klimasekretariat, anderen Modellierungen, Marktinformationen und Expertenbefragungen berücksichtigt.

Das Ziel der Projektionen war die Entwicklung eines Szenarios, bei dem in jeder Anwendung im Kälte-, Klima- und Treibmittelbereich eine maximale Marktdurchdringung halogenierter Ersatzstoffe im Verhältnis zu natürlichen Stoffen angenommen wird, außer wenn eine Alternative mit halogenfreien Kältemitteln bereits etabliert oder aus heutiger Sicht sehr wahrscheinlich ist. Die vom Modell berechneten jährlichen Emissionsmengen wurden schließlich mit den stoffspezifischen TFA-Bildungsraten verrechnet, um die jährlich maximal zu erwartenden TFA-Mengen aus dem atmosphärischen Abbau halogenierter Stoffe in Europa zu ermitteln.

Die Projektionen ergeben nur einen sehr geringen Rückgang des Gesamtbedarfs an HFKW, u-HFKW und u-HFCKW von ca. 96.000 metrischen Tonnen im Jahr 2020 auf ca. 92.000 Tonnen im Jahr 2050.

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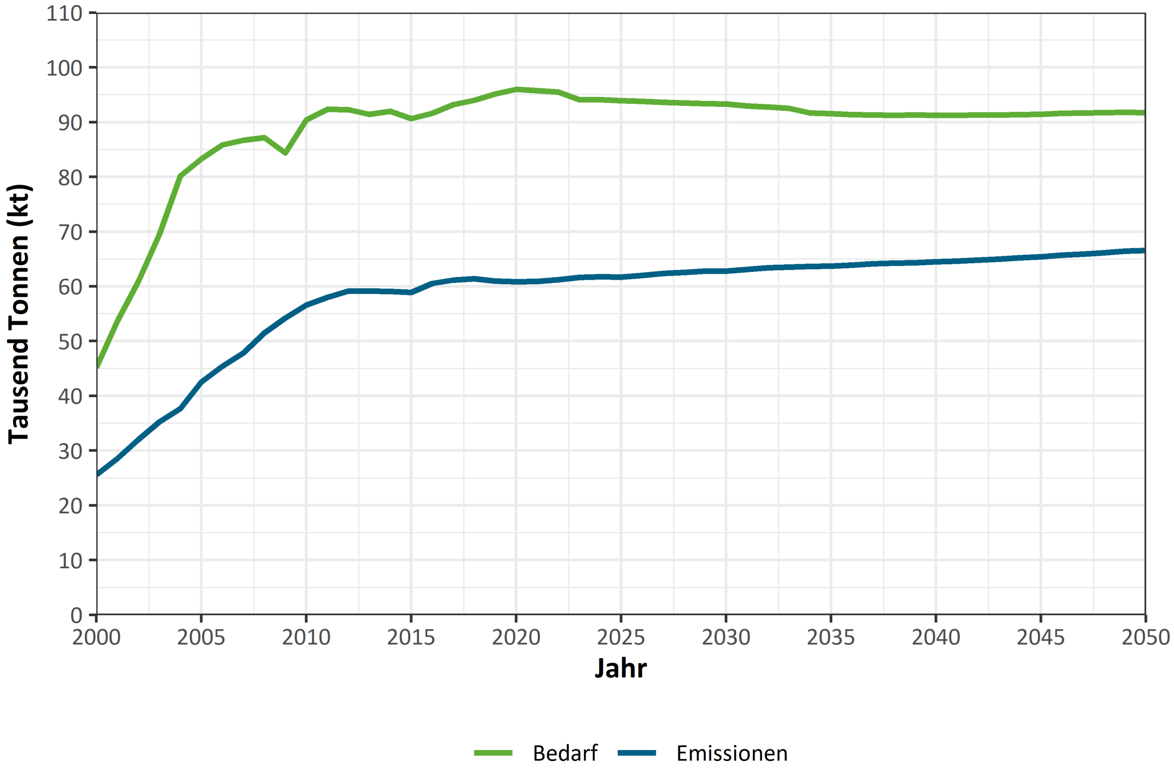
[16] Die Modellierung umfasst für den gesamten Zeitraum von 2000 bis 2050 alle 28 Staaten, die im Januar 2020 Mitglied der EU waren.

Während der Bedarf an HFKW stark zurückgeht, der Kältemittelbedarf insgesamt aber hoch bleibt, werden die HFKW-Mengen durch einen vermehrten Einsatz von u-HFKW und u-HFCKW ersetzt. Die Gesamtemissionen steigen noch weiter an von ca. 61.000 Tonnen im Jahr 2020 auf ca. 67.000 Tonnen im Jahr 2050 (Abbildung S 2, Table 23 in Kapitel 3.4.1). In der Kältetechnik setzt sich der Bedarf aus der Menge für die Erstbefüllung von Geräten innerhalb Europas die im Laufe der Lebenszeit der Geräte entweicht und den Nachfüllmengen im Rahmen der Gerätewartung zusammen. Die Emissionen erfolgen in aller Regel zeitversetzt zum Bedarf und umfassen die Freisetzung der Gase während der Nutzungsphase und der Entsorgung von Altgeräten.

Abbildung S 2: Bedarf und Emissionen von HFCKW (bis 2015)[17], HFKW, u-HFKW und u-HFCKW in Europa (EU-28) in Kilotonnen für den Zeitraum der Jahre 2000 bis 2050.



Quelle: Eigene Darstellung, Öko-Recherche

Die mobile Klimatisierung hat im Jahr 2020 mit etwa 31.600 Tonnen sowohl den höchsten Kältemittelbedarf als auch mit etwa 29.500 Tonnen die höchsten Emissionen. Heute tragen dazu noch hauptsächlich Bestandsfahrzeuge mit HFKW-134a bei, während ab dem Jahr 2030 der höchste Bedarf beim u-HFKW-1234yf bestehen wird, wobei Pkw-Klimaanlagen jeweils den größten Anteil haben.

Die stationäre Klimatisierung, dazu gehören Raumklimageräte, Wärmepumpen und Flüssigkeitskühlsätze, zeigt in den Projektionen ab dem Jahr 2020 keine Zunahme des Bedarfs von ca. 25.000 Tonnen, die Emissionen steigen von ca. 9.000 Tonnen im Jahr 2020 auf ca. 16.000 Tonnen im Jahr 2050 an. Der Kältesektor hat einen errechneten Bedarf von ca. 17.000 Tonnen im Jahr 2020, gefolgt von den

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[17] Seit dem 1. Januar 2010 ist die Befüllung und Nachfüllung von Kälte- und Klimaanlagen mit HFCKW-Frischware nach Verordnung (EG) Nr. 1005/2009 in der EU verboten. Seit 1. Januar 2015 ist die Verwendung aller HFCKW in Kälte- und Klimaanlagen in der EU verboten.

Schaumtreibmitteln mit ca. 13.000 Tonnen. Während der Bedarf im Kältesektor bis zum Jahr 2050 auf ca. 13.000 Tonnen sinkt, bleibt er bei Schaumtreibmitteln konstant bei ca. 13.000 Tonnen.

Hinsichtlich der Emissionen unterscheiden sich die Sektoren: Während im Bereich der Kälte die Emissionen in den Jahren 2020 bis 2050 um fast die Hälfte von ca. 9.000 Tonnen auf ca. 5.000 Tonnen abfallen, steigen die projizierten Emissionen im Schaumsektor in der gleichen Zeit von ca. 5.000 Tonnen auf ca. 6.000 Tonnen. In den restlichen Sektoren zeigen Bedarf und Emissionen in den Jahren 2020 bis 2050 nur geringes Wachstum, von ca. 9.000 Tonnen auf ca. 10.000 Tonnen im Bedarf und von ca. 5.000 Tonnen auf ca. 6.000 Tonnen bei den Emissionen.

Betrachtet man die Bedarfs- und Emissionsmengen nach Substanz, wird ersichtlich, dass insbesondere HFKW-125, HFKW-134a, HFKW-32, u-HFKW-1234yf und u-HFKW-1234ze im Zeitraum von 2000 bis 2050 eine größere Rolle spielen. Die Einsatzmengen der Stoffe mit höherem GWP wie HFKW-125 und HFKW-134a nehmen bis 2050 stark ab.

TFA-Mengen aus halogenierten Stoffen

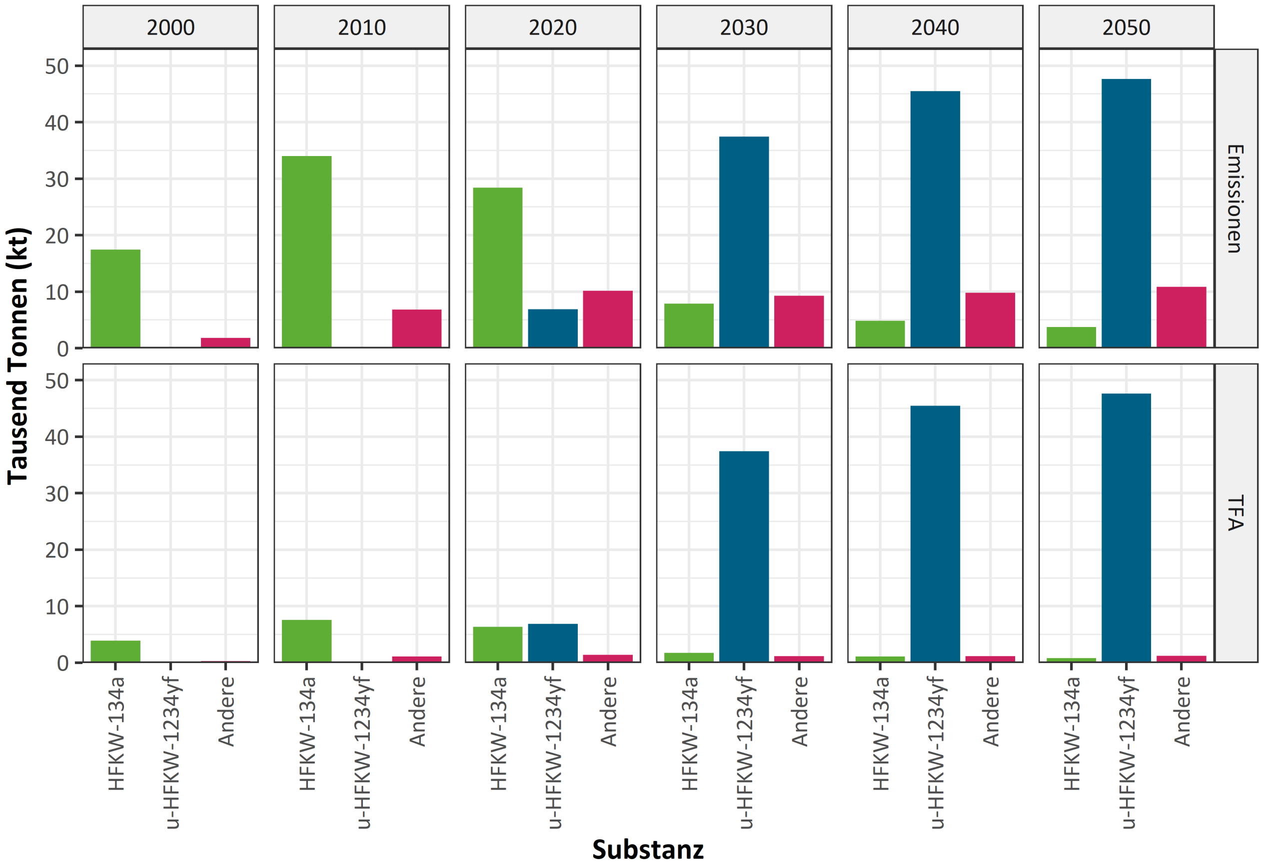
Auf der Basis der projizierten Emissionen wurde die aus den einzelnen Stoffen in den unterschiedlichen Einsatzbereichen entstehende TFA-Menge berechnet. Für das Jahr 2020 ergab dies in Europa eine TFA-Gesamtmenge von etwas unter 15.000 Tonnen, die bis zum Jahr 2050 kontinuierlich steigt und dann bei ca. 50.000 Tonnen pro Jahr liegt (Table 26 in Kapitel 3.4.3.1). Für Deutschland ergeben sich etwas über 2.000 Tonnen im Jahr 2020 und ca. 6.500 Tonnen im Jahr 2050.

Hinsichtlich der Bildung von TFA beim atmosphärischen Abbau sind insbesondere HFKW-134a und u-HFKW-1234yf relevant (Abbildung S 3, Table 27 in Kapitel 3.4.3.2). Während HFKW-134a bis ins Jahr 2020 knapp die Hälfte der Emissionen aller projizierter Stoffe in Europa ausmacht, geht dieser Anteil bis zum Jahr 2030 auf ca. 10 % und bis zum Jahr 2050 auf ca. 5 % zurück. Die Emissionen von u-HFKW-1234yf betragen im Jahr 2020 erst ca. 10 % der Gesamtemissionen. Dieser Anteil steigt bis 2030 auf ca. 60 % und bis 2050 auf ca. 70 %.

Bereits ab dem Jahr 2020 ergeben sich in Europa ca. 7.000 Tonnen TFA aus dem Abbau von u-HFKW-1234yf-Emissionen. Dies entspricht 47 % der in diesem Jahr gebildeten TFA-Gesamtmenge aus allen im Modell projizierten Stoffen. Die Emissionen von HFKW-134a tragen mit ca. 6.000 Tonnen 43 % zur TFA-Gesamtmenge bei.

Bis ins Jahr 2030 steigt die TFA-Menge aus dem Abbau von u-HFKW-1234yf auf ca. 37.000 Tonnen deutlich an, während die des HFKW-134a auf ca. 2.000 Tonnen zurückgeht.

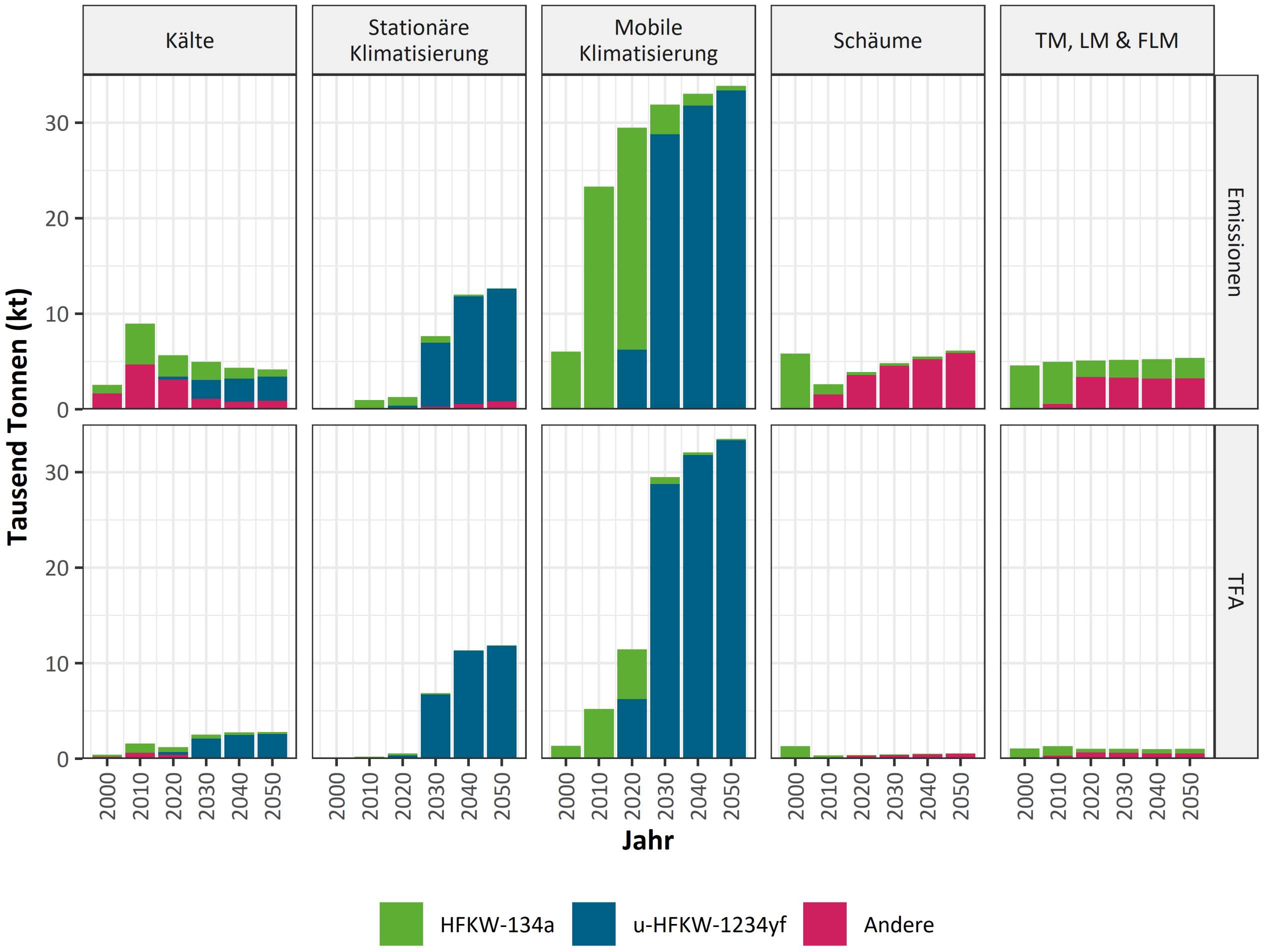
Abbildung S 3: Entwicklung der europäischen (EU-28) Emissionen und daraus resultierenden Mengen an Trifluoressigsäure (TFA) von wichtigen TFA-bildenden HFKW-, u-HFKW- und u-HFCKW-haltigen Kälte- und Treibmitteln über alle Sektoren in Kilotonnen für die Jahre 2000 bis 2050 in 10-Jahres-Schritten. Alle weiteren projizierten TFA-bildenden Substanzen sind unter der Bezeichnung „Andere" subsummiert.



Quelle: Eigene Darstellung, Öko-Recherche

Im Jahr 2050 liegt der Beitrag von HFKW-134a an der gesamten TFA-Menge aus den projizierten Stoffen nur noch bei 2 %, während u-HFKW-1234yf für fast 96 % verantwortlich ist. Daher tragen Sektoren, in denen HFKW-134a und u-HFKW-1234yf in großen Mengen verwendet werden, stark zur TFA-Bildung bei. Die höchste Menge an TFA entsteht aus Kältemitteln, die aus mobilen Anlagen in die Atmosphäre emittiert wurden. In der stationären Klimatisierung wurde ab dem Jahr 2020 das größte Wachstum der Emissionen und der daraus gebildeten TFA-Menge ermittelt (Abbildung S 4). Für Deutschland ergibt sich für die Stoffe und Sektoren ein analoges Bild zu Europa.

Abbildung S 4: Europäische (EU-28) Emissionen von wichtigen HFKW-, u-HFKW- und u-HFCKW-in Kälte- und Treibmitteln und daraus gebildete Menge an Trifluoressigsäure (TFA) in Kilotonnen nach Sektor für die Jahre 2000 bis 2050 in 10-Jahres-Schritten. Alle weiteren projizierten TFA-bildenden Substanzen sind unter der Bezeichnung „Andere“ subsummiert. Der Sektor „Weitere“ wird nicht gezeigt, da die TFA-Mengen hier im Maximum bei ca. 0,03 Kilotonnen (30 Tonnen) liegen. TM = Treibmittel, LM = Lösemittel, FLM = Feuerlöschmittel.

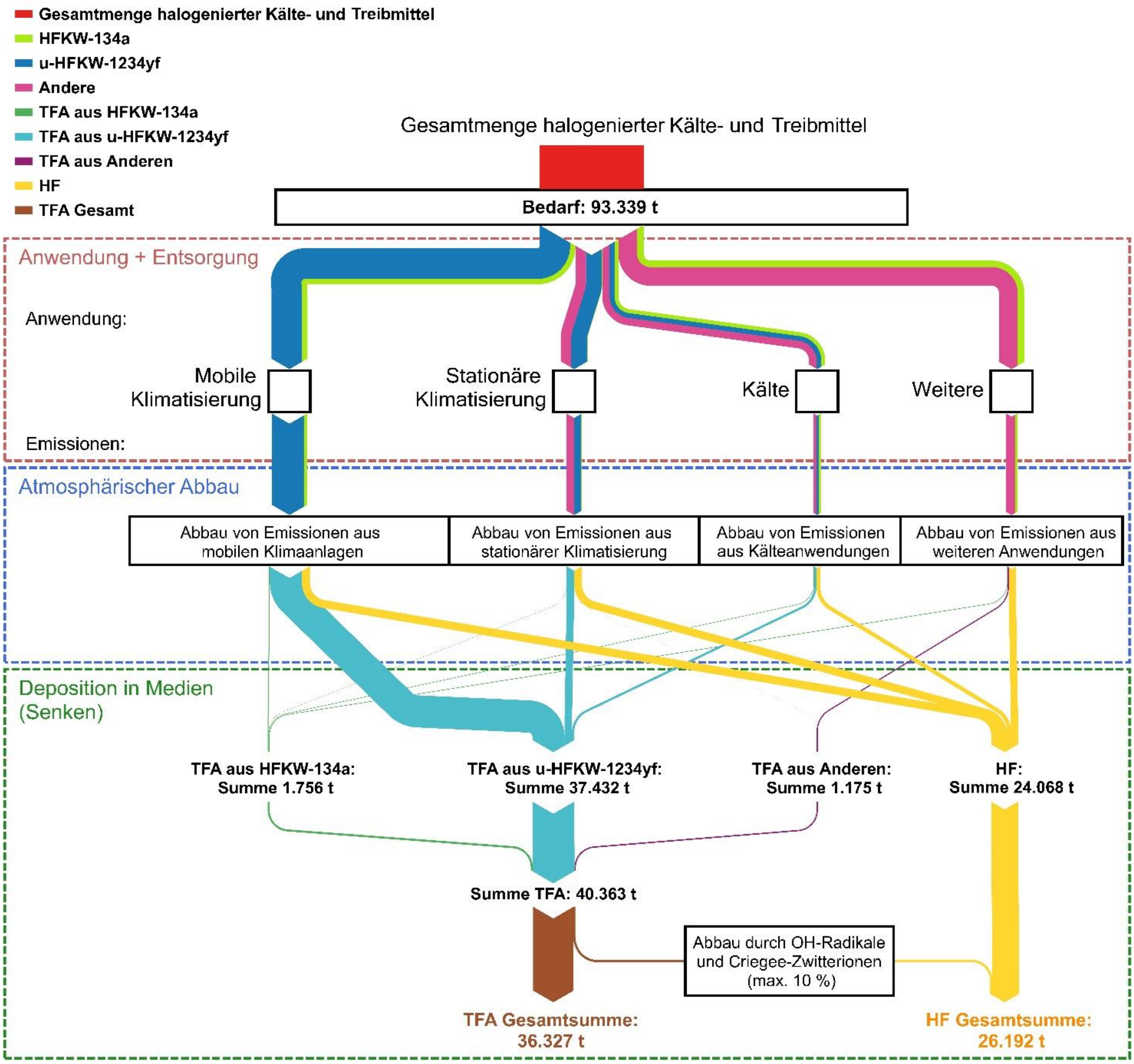


Quelle: Eigene Darstellung, Öko-Recherche

Visualisierung der Stoffströme für das Jahr 2030

Um den Beitrag der halogenierten Kälte- und Treibmittel in den unterschiedlichen Anwendungssektoren mengenproportional einschätzen zu können, zeigt Abbildung S 5 bespielhaft für das Jahr 2030 eine Visualisierung des Mengenflusses der europäischen Gesamtemissionen aus den unterschiedlichen Sektoren für die verschiedenen Stoffe und die sich daraus ergebenden TFA-Mengen, die regional und global deponiert werden. Der weiter ansteigende Trend der TFA-Einträge aus Stoffen, die in großen Mengen verwendet und emittiert werden und hohe TFA-Bildungsraten haben - wie heute HFKW-134a und zukünftig u-HFKW-1234yf - ist klar ersichtlich. Mit zunehmender Verwendung von halogenierten Ersatzstoffen mit kleinem Treibhauspotential wird der Eintrag von TFA in die Umwelt stark zunehmen.

Abbildung S 5: Sankey-Mengenflussdiagramm der europäischen (EU-28) Gesamtemissionen der modellierten halogenierten Stoffe aus der Verwendung und Entsorgung in den verschiedenen Sektoren und die atmosphärischen Abbauprodukte Trifluoressigsäure (TFA) und Fluorwasserstoff (HF) für das Jahr 2030. Die Sektoren Schäume, Treib-, Lösungs- und Feuerlöschmittel sowie Halbleiterindustrie und Emissionen aus der HFKW Produktion sind unter „Weitere“ subsumiert.



Quelle: Eigene Darstellung, Öko-Institut und Öko-Recherche

Vorkommen und Eintrag von TFA bzw. Trifluoracetat in die Umwelt

Man geht bisher davon aus, dass TFA, in Form des Salzes Trifluoracetat (CF_3COO^-), nur in den Ozeanen natürlich vorkommt, wobei die genauen Quellen unbekannt sind. Die Konzentration in den Ozeanen lag in den 1990er und frühen 2000er Jahren bei 10 ng/L bis 250 ng/L. Auf dem Festland und in Oberflächengewässern stammt TFA bzw. Trifluoracetat dagegen mit hoher Sicherheit maßgeblich aus anthropogenen Quellen. Trifluoracetat wird mittels nasser Deposition (über den Niederschlag, Schnee oder Nebel) oder mittels trockener Deposition unter Salzbildung (z.B. Natriumtrifluoracetat) in die Böden und das Grundwasser eingetragen. Von dort gelangt es durch seine hohe Mobilität schließlich bis ins Trinkwasser und reichert sich dort aufgrund seiner hohen Persistenz an.

Vereinzelte Messungen in Deutschland aus den 1990er Jahren zeigen eine ubiquitäre Verteilung von Trifluoracetat in Regenwasser, Nebelwasser, Oberflächengewässern und anthropogen beeinflussten Quellwassern. Die Konzentrationen beliefen sich auf 10 ng/L bis 410 ng/L in Regenwasser. Nur in Nebelwasser wurden höhere Konzentrationen von 20 ng/L bis 930 ng/L gemessen, wobei zu beachten ist, dass Nebelwasser im Verhältnis zu am gleichen Standort zeitnah gemessenem Regenwasser generell eine höhere Konzentration an Halogenessigsäuren wie TFA und anorganischen Ionen aufweist. Neuere Messungen in Deutschland aus dem Jahr 2017 ergaben in der Regel höhere Konzentrationen von Trifluoracetat mit bis zu 2.400 ng/L in Regenwasser.

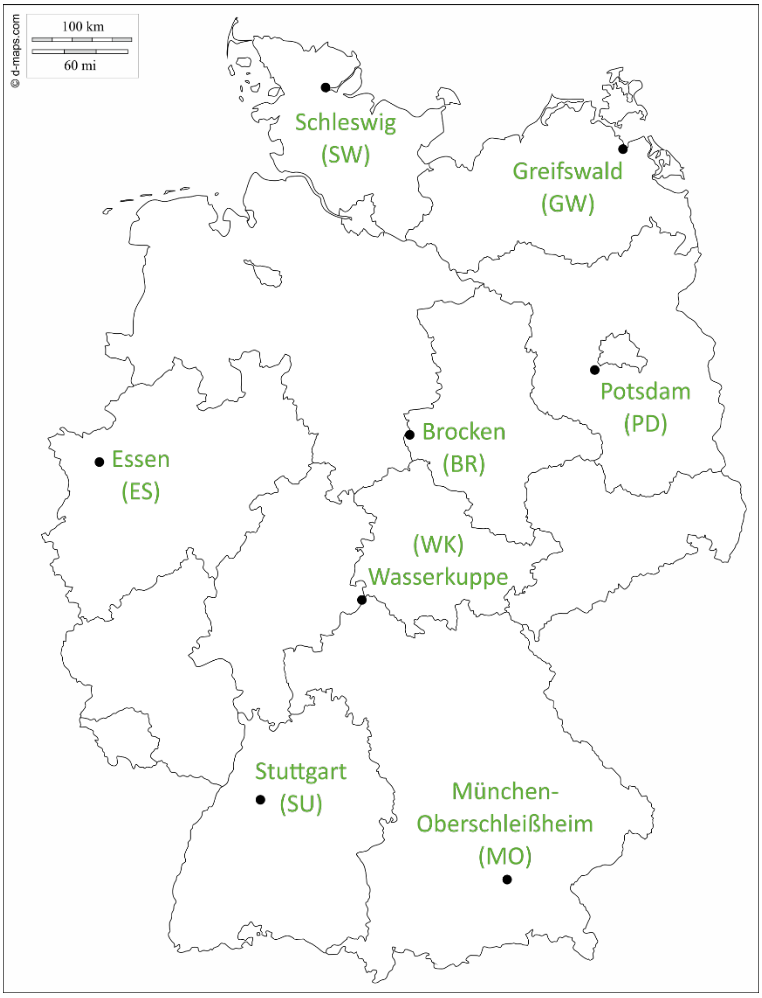
Da Kälte- und Treibmittel vorwiegend in die Atmosphäre emittieren, werden deren Abbauprodukte wie Trifluoracetat hauptsächlich über den Niederschlagspfad eingetragen. Aufgrund der vollständigen Umwandlung von u-HFKW-1234yf zu TFA und dessen großflächiger Verwendung als Ersatz für HFKW-134a in Pkw-Klimaanlagen und in neueren Kältemittel-Gemischen ist mit einem starken Eintrag von TFA durch den Niederschlag bis ins Grund- und Trinkwasser zu rechnen. Zu diesem Ergebnis kam auch eine Simulationsstudie aus dem Jahr 2012 von Henne et al. (2012). Bei einer angenommenen vollständigen Kältemittelumstellung von HFKW-134a auf u-HFKW-1234yf in Pkw-Klimaanlagen in Europa im Jahre 2020 wurden in der Studie Konzentrationen von TFA im Niederschlag von durchschnittlich 600 ng/L bis 800 ng/L mit Maxima in Süddeutschland von 2.000 ng/L berechnet. Als Quelle für TFA wurde in dieser Studie jedoch ausschließlich u-HFKW-1234yf aus der Emission von Pkw-Klimaanlagen berücksichtigt.

Trifluoracetat-Messungen im Niederschlag

Der Eintrag von Trifluoracetat als Abbauprodukt freigesetzter halogenierter Kälte- und Treibmittel erfolgt hauptsächlich über den Niederschlagspfad. Eine intensive Literaturrecherche zeigte, dass es bisher keine Studien zum Eintrag von Trifluoracetat über den Niederschlagspfad für Deutschland oder Europa gibt. Um diesen Eintrag zu quantifizieren, wurde erstmals eine deutschlandweites Messprogramm durchgeführt (Kapitel 4). An acht bestehenden Stationen des Deutschen Wetterdienstes (DWD, Abbildung S 6) wurden über den Zeitraum von zwei Jahren Regenwasserproben entnommen und vom Technologiezentrum Wasser (TZW) in Karlsruhe auf ihren Trifluoracetat-Gehalt analysiert.

An allen acht Messstationen wurden in der Zeit von Februar 2018 bis Januar 2020 (März 2018 bis Februar 2020 an der Station Stuttgart) bei jedem Niederschlagsereignis Proben des vor Ort aufgefangenen Niederschlags genommen. Anhand der jeweiligen Niederschlagsmenge wurden volumenäquivalente Monatsmischproben für jeden Standort erstellt. Die Trifluoracetat-Konzentrationen der Monatsmischproben wurden im Labor analysiert. Zur Validierung der Ergebnisse wurden für den Zeitraum Februar 2018 bis Januar 2019 (März 2018 bis Februar 2019 an der Station Stuttgart) die Trifluoracetat-Konzentration von jeder der 1.187 Einzelniederschlagsproben bestimmt. Aus der Trifluoracetat-Konzentration und der zugehörigen Niederschlagsmenge wurde der Trifluoracetat-Eintrag pro Fläche berechnet.

Abbildung S 6: Standorte der Niederschlagsprobenahme; im weiteren Verlauf verwendete Kürzel der Stationen in Klammern.



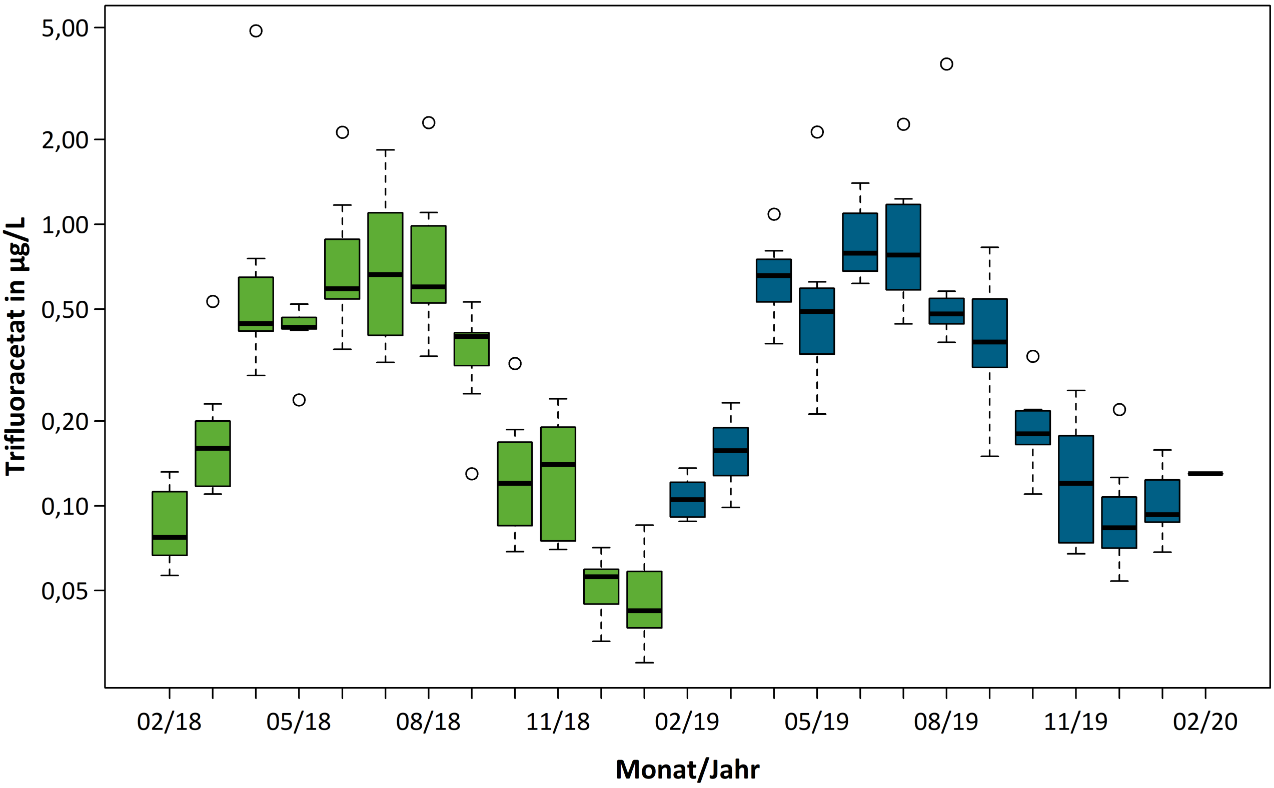
Quelle: copyright d-maps.com, verändert von TZW Karlsruhe

Auswertung der Trifluoracetat-Gehalte der Monatsmischproben

Die Monatsmischproben der Niederschläge weisen hinsichtlich der Trifluoracetat-Konzentration einen ausgeprägten Jahresgang auf, wobei die Proben der Sommermonate deutlich höhere Konzentrationen im Niederschlag enthielten als die der Wintermonate (Abbildung S 7). Im Mittel lag die Trifluoracetat-Konzentration im Zeitraum 2018/2019 bei 0,429 µg/L (Spanne von 0,028 µg/L bis 4,780 µg/L), im Zeitraum 2019/2020 im Mittel bei 0,453 µg/L (Spanne 0,054 µg/L bis 3,710 µg/L). Im Median konnten für beide Zeiträume praktisch die gleichen Konzentrationen (0,245 µg/L und 0,244 µg/L) bestimmt werden.

Die Daten für die Station Brocken sind in Abbildung S 7 und Abbildung S 8 nicht dargestellt, da diese im Gegensatz zu den Ergebnissen der anderen Stationen nicht nur die nasse, sondern die Summe aus nasser und trockener Deposition beinhalten.

Abbildung S 7: Boxplots der niederschlagsgewichteten Trifluoracetat-Konzentrationen der volumenäquivalenten Monatsmischproben des Niederschlags von Februar 2018 (02/18) bis Februar 2020 (02/2020) von sieben Messstationen, die ausschließlich die nasse Deposition erfassen haben. Gruppierung der Daten anhand der Zeit (Monat und Jahr). Die Zeiträume Februar bis Januar sind farblich getrennt. Die y-Achse ist binär logarithmisch skaliert. Station Stuttgart ist nicht in 02/18 enthalten. Für Februar 2020 gibt es nur einen Monatsmischwert für die Station Stuttgart.



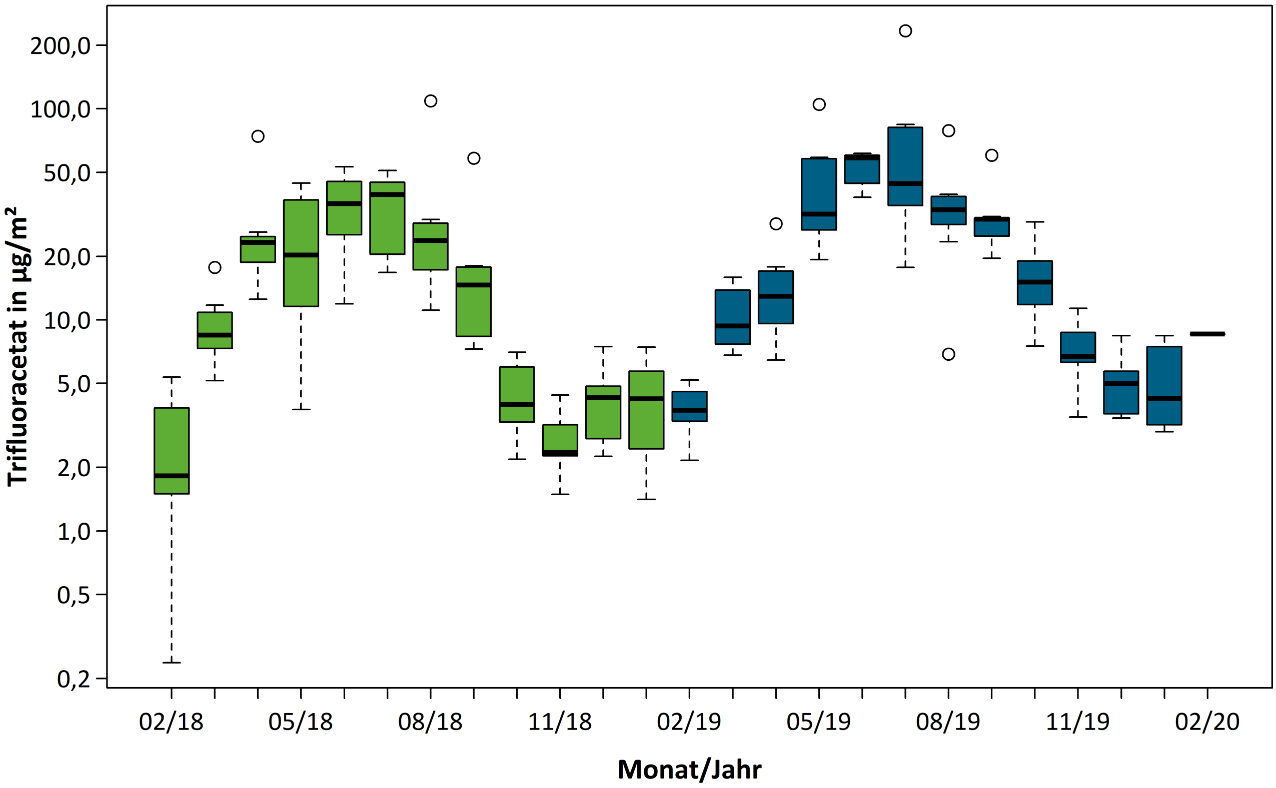
Quelle: Eigene Darstellung, Öko-Recherche und TZW Karlsruhe

Flächenbezogener Trifluoracetat-Eintrag

Der Trifluoracetat-Eintrag zeigte ebenfalls Maxima in den Sommermonaten und deutlich geringere Werte in den Wintermonaten (Abbildung S 8). Im Mittel lag der Trifluoracetat-Eintrag im Zeitraum 2018/2019 bei 16,719 µg/m^2 (0,238 µg/m^2 bis 108,790 µg/m^2) und im Zeitraum 2019/2020 bei 25,463 µg/m^2 (2,158 µg/m^2 bis 234,037 µg/m^2). Auch wenn man die Mediane heranzieht (8,292 µg/m^2 und 14,863 µg/m^2), ist der Eintrag im Zeitraum 2018/2019 kleiner als 2019/2020. Da die Trifluoracetat-Konzentrationen in den Niederschlägen im Median in beiden Zeiträumen gleich waren, ist die Erhöhung des Trifluoracetat-Eintrags im Jahr 2019 auf höhere Niederschlagsmengen als im sehr trockenen Jahr 2018 zurückzuführen. Dies verdeutlicht, dass es für Vergleiche notwendig ist, nicht allein nur die Konzentrationen im Niederschlag zu erheben, sondern wie in diesem Projekt durchgeführt, auch den Eintrag über die Niederschlagsmenge verschiedener Orte und über längere Zeiträume heranzuziehen.

Zwischen den einzelnen Messstationen wurden deutlich geringere Unterschiede in Trifluoracetat-Konzentration und -Eintrag beobachtet als zwischen den einzelnen Monaten. Urbane Zentren (München, Essen und Stuttgart) wiesen die höchsten Werte auf. An den küstennahen Messtationen Greifswald und Schleswig wurden keine erhöhten TFA-Konzentrationen bzw. Einträge beobachtet.

Abbildung S 8: Boxplots der Trifluoracetat-Einträge über den Niederschlag von Februar 2018 (02/18) bis Februar 2020 (Analyse der volumenäquivalenten Monatsmischproben) aller sieben Messstationen, die ausschließlich die nasse Deposition erfasst haben. Gruppierung der Daten anhand der Zeit (Monat und Jahr). Die Zeiträume Februar bis Januar sind farblich getrennt. Die y-Achse ist binär logarithmisch skaliert. Station Stuttgart ist nicht in 02/18 enthalten. Für Februar 2020 gibt es nur einen Monatsmischwert für die Station Stuttgart.



Quelle: Eigene Darstellung, Öko-Recherche und TZW Karlsruhe

Analyse der Niederschlags-Einzelproben

Die Analyse der Niederschlags-Einzelproben für den Zeitraum 2018/2019 ergab - ohne Berücksichtigung der zugehörigen Niederschlagsmenge - eine mittlere Konzentration von 0,703 µg/L. Die mittlere niederschlagsgewichtete Trifluoracetat-Konzentration über alle Messstationen für den Zeitraum 2018/2019 betrug 0,335 µg/L. Dies bestätigten die Ergebnisse der Monatsmischproben. Auffallend waren hohe maximale Konzentrationen, insbesondere am Standort München-Oberschleißheim, von bis zu 38 µg/L. Im Mittel aller Stationen konnte für den Zeitraum 2018/2019 ein täglicher Trifluoracetat-Eintrag von 1,28 µg/m^2 abgeleitet werden.

Jährlicher Trifluoracetat-Eintrag in Deutschland

Aus dem niederschlagsgewichteten Mittelwert aller untersuchten Einzelproben (0,335 µg/L, Table 36 in Kapitel 4.5.1.2) multipliziert mit der durchschnittlichen Niederschlagssumme für Deutschland desselben Zeitraums von 566 mm (DWD 2020) ergibt sich eine durchschnittliche nasse Trifluoracetat-Deposition von 190 µg/m^2 bzw. ca. 68 Tonnen für Deutschland für den Zeitraum Februar 2018 bis Januar 2019. Im Jahr 2018 gab es allerdings ungewöhnlich geringe Niederschläge in Deutschland. Bezieht man sich auf den mehrjährigen Mittelwert von 819 mm Niederschlag in Deutschland (Referenzperiode 1981-2010) (DWD 2020), beträgt die jährliche nasse Deposition von Trifluoracetat 274 µg/m^2 bzw. für die Gesamtfläche der Bundesrepublik Deutschland insgesamt ca. 98 Tonnen.

Trifluoracetat-Konzentrationen in Bodenproben und Pflanzen

Neben der Beprobung des Regenwassers wurden im Juli und Oktober 2019 Bodenproben in der Nähe der acht Messstationen genommen und deren Trifluoracetat-Konzentration bestimmt. Die Bodenproben wiesen Trifluoracetat-Konzentrationen von <0,2 µg/kg bis 0,97 µg/kg Trockengewicht (<0,2 µg/kg bis 0,77 µg/kg Frischgewicht) auf, wobei die Maximalkonzentrationen an der Station Brocken gemessen wurden. Zusätzlich wurden im Juli 2019 an der Station München-Oberschleißheim sechs typische krautige Pflanzenarten beprobt. Bei den Pflanzenproben lag die Trifluoracetat-Konzentration bei 35 µg/kg bis 120 µg/kg Trockengewicht (7,3 µg/kg bis 39 µg/kg Frischgewicht). Dies entspricht einem Anreicherungsfaktor in Bezug auf die Trifluoracetat-Konzentration im Niederschlag von 16-87. Insgesamt lagen die gemessenen Werte der Boden- und Pflanzenproben innerhalb der Spannbreite der in anderen Studien gemessenen Konzentrationen.

Modell zur Quantifizierung von TFA-Konzentrationen im Niederschlag und TFA-Eintrag

Die vorliegende Studie quantifiziert erstmals die Konzentration von Trifluoracetat im Regenwasser in Deutschland in räumlicher und zeitlicher Auflösung. Die hier durchgeführten Messungen zeigen einen deutlich erhöhten Eintrag von TFA bzw. Trifluoracetat über den Niederschlagspfad in die Umwelt im Vergleich zu früheren Messungen.

Zur weiteren Auswertung wurden die Ergebnisse der Projektionen und des Messprogramms von der Eidgenössischen Materialprüfungs- und Forschungsanstalt (Empa) verwendet, um ein bestehendes Modell zur Quantifizierung von TFA-Konzentration im Niederschlag und TFA-Eintrag für Europa[18] zu aktualisieren. Hierzu wurden auch neue Daten zur atmosphärischen Konzentration von u-HFKW und u-HFCKW aus der Nähe von Frankfurt am Main mit einbezogen. Anhand dieser Modellierung konnte der Beitrag von u-HFKW-1234yf sowie wichtiger HFCKW und HFKW (HFCKW-123, HFCKW-124, HFKW-134a, HFKW-245fa, HFKW-143a, HFKW-365mfc und HFKW-227ea) an den gemessenen Trifluoracetat-Konzentrationen im Niederschlag ermittelt werden. Dieser betrug unter 50 %. Die übrigen Anteile konnten nicht durch den Abbau der einbezogenen halogenierten Kälte- und Treibmittel erklärt werden. Da das Modell aufgrund vereinfachter Annahmen große Unsicherheiten aufweist, könnte es noch verbessert werden, was den Rahmen dieses Projektes überstieg.

Für u-HFKW-1234yf wurde anhand dieses Modells auch der zukünftige Eintrag von TFA aus dem atmosphärischen Abbau berechnet (Abbildung S 9). Demnach wird in Deutschland und Europa bis ins Jahr 2030 der absolute jährliche TFA-Eintrag in Tonnen sehr stark ansteigen und danach bis zum Jahr 2050 langsamer aber weiter kontinuierlich zunehmen. In Deutschland liegt der TFA-Eintrag pro Fläche (kg/km^2) deutlich über dem europäischen Durchschnitt, es muss hier mit mittleren TFA-Depositionsraten von ca. 4 kg/km^2 pro Jahr bis 2050 gerechnet werden. Im Vergleich zu den in dieser Studie gemessenen mittleren Depositionsraten wäre dies ein Zuwachs um einen Faktor 10. Im europäischen Durchschnitt kann eine mittlere TFA-Depositionsrate von 2,5 kg/km^2 pro Jahr bis 2050 erwartet werden.

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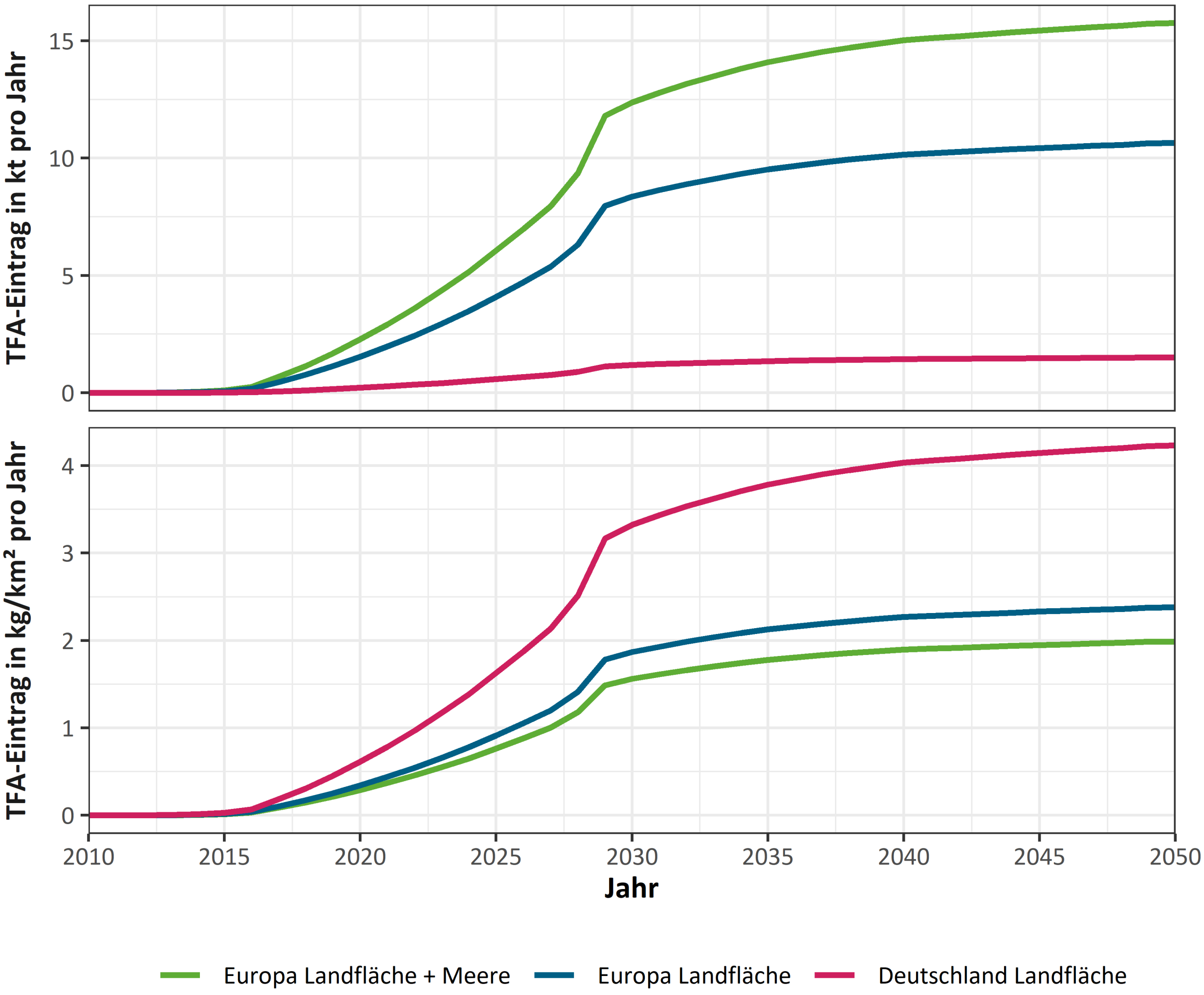
[18] Die Modellierungen der Empa schließen neben der EU-28 auch die Schweiz und die Türkei mit ein.

Abbildung S 9: Abgeschätzte zukünftige TFA-Deposition (Eintrag in Kilotonnen pro Jahr) (oben) bzw. TFA-Depositionsraten (Eintrag in kg/km² pro Jahr) (unten) aus dem atmosphärischen Abbau von u-HFKW-1234yf für Europa (EU-28, Norwegen, Schweiz und Türkei) mit umliegenden Meeren (Europa Landfläche + Meere), die Landfläche Europas (Europa Landfläche) und von Deutschland (Deutschland Landfläche).



Quelle: Eigene Darstellung, Empa Zürich und Öko-Recherche

Vergleich der Trifluoracetat-Einträge mit denen in anderen Studien

Zum Vergleich der Messergebnisse dieser Studie mit der Fachliteratur wurden die Trifluoracetat-Einträge der gesamten beiden 12 Monats-Zeiträume in Zeitraum von Februar 2018 bis Januar 2019 (2018/2019) und Februar 2019 bis Januar 2020 (2019/2020) für ganz Deutschland berechnet. Diese beliefen sich, basierend auf den Konzentrationen der Monatsmischproben, auf 187 g/km^2 bzw. 67 Tonnen Trifluoracetat im Zeitraum 2018/2019 und 276 g/km^2 bzw. 99 Tonnen im Zeitraum 2019/2020. Anhand der Einzelproben konnten Einträge von 190 g/km^2 bzw. 68 Tonnen (niederschlagsgewichtet) und 398 g/km^2 bzw. 142 Tonnen (nicht niederschlagsgewichtet) ermittelt werden.

In der Literatur finden sich nur wenige Studien, die TFA bzw. Trifluoracetat im Niederschlag über längere Zeiträume gemessen haben. Aufgrund der starken Saisonalität und Streuung innerhalb eines Standortes wäre dies aber zwingend für eine valide Aussage erforderlich. Die wenigen Studien, die kontinuierliche Messungen durchgeführt haben, wiesen stets Lücken in der Datenerfassung auf oder die berechneten Mittelwerte beruhen nur auf einer sehr kleinen Anzahl von Stichproben. Im Vergleich zu zwei Studien von Klein (1997) und Jordan und Frank (1999), die Trifluoracetat im Niederschlag in Bayreuth im Zeitraum 1995 bis 1996 gemessen haben, lag in der Zeit von 2018 bis 2020 die Konzentration und der Eintrag von Trifluoracetat in Deutschland, die in dieser Studie ermittelt wurden, drei- bis viermal höher.

Ausblick

Im Rahmen dieser Studie wurden einige Wissenslücken identifiziert. Nur wenig ist bekannt zur Bildung und Emission halogenierter Stoffe bei der Herstellung von Kälte- und Treibmitteln. Da beim Herstellungsprozess verschiedene umwelt- und gesundheitsrelevante Substanzen entstehen können, ist deren Identifikation und die Quantifikation dieser Emissionen von Relevanz. Ebenso verhält es sich mit den Nebenbestandteilen in halogenierten Kälte- und Treibmitteln.

Es bedarf auch der Abklärung des Bildungspotentials von TFA aus dem atmosphärischen Abbau von Trifluoracetaldehyd, das als Zwischenprodukt einiger relevanter halogenierter Kälte- und Treibmitteln entsteht. Bisher nicht bekannte Emissionsquellen von gesättigten und ungesättigten HFKW und HFCKW sollten identifiziert werden, so beispielsweise die Quelle der erhöhten Emissionen von u-HFKW-1234ze im Winter in Europa. Von großem Interesse ist es zu klären, woher der Anteil der gemessenen Trifluoracetat-Menge im Niederschlag stammt, der durch die bekannten Kälte- und Treibmittelemissionen nicht unmittelbar erklärt werden kann. Neben der Überarbeitung des verwendeten Modells zum TFA-Eintrag wären mögliche weitere atmosphärische Quellen, die bereits in der Literatur diskutiert wurden, wie die Verbrennung von Fluorpolymeren bei niedrigen Temperaturen oder die Emission von fluorierten Inhalationsanästhetika und Lösemitteln, näher zu analysieren.

Aufgrund der extrem hohen Persistenz und Mobilität von TFA bzw. Trifluoracetat führt die steigende Verwendung von halogenierten Ersatzstoffen mit kleinem Treibhauspotential zu einer zunehmenden Belastung des Grund- und Trinkwassers. Da persistente Stoffe lange in der Umwelt verbleiben und weder wirksame natürliche Mechanismen noch vertretbare technische Verfahren zur Entfernung von TFA aus Trinkwasserressourcen existieren, kann ein potentieller Schaden für Umwelt und Mensch nur durch die Minimierung des Eintrags von TFA und seiner Vorläuferverbindungen verhindert werden. Selbst bei sofortiger Beendigung des Eintrags von TFA und dessen Vorläufern würde ein extrem langlebiger Stoff wie TFA bzw. Trifluoracetat noch mindestens mehrere Jahrzehnte in der Umwelt verbleiben.

Die Ergebnisse der Untersuchungen und Projektionen unterstreichen den Handlungsbedarf zur Vermeidung des weiteren Eintrages von TFA und TFA-bildenden Stoffen in die Umwelt. Auf den Einsatz von halogenierten Kälte- und Treibmitteln sollte daher verzichtet werden und Alternativen mit natürlichen Kältemitteln präferiert und gefördert werden.

Im Bericht werden die stofflichen Aspekte und Umweltauswirkungen kürzlich eingeführter halogenierter Kältemittel vertieft dargestellt und erweitert. Daher sind die Ergebnisse der vorliegenden Untersuchungen auch von Belang für die Umsetzung und Weiterentwicklung der EU F-Gas-Verordnung. Herangezogen werden können die Ergebnisse dieses Berichtes auch für die Analyse der Auswirkungen von Regelungen oder Fördermaßnahmen, die den Einsatz von HFKW, u-HFKW und u-HFCKW beinhalten und die neben wirtschaftlichen und sozialen Effekten auch die Betrachtung der Umweltwirkungen erfordern.

Die TFA-Bildung und Anreicherung aus der Verwendung von halogenierten Kälte- und Treibmitteln sollte auch für Europa und weltweit untersucht und thematisiert werden, um in der Umsetzung des Kigali-Abkommens auf internationaler Ebene Berücksichtigung zu finden. Dies ist vor allem vor dem

Hintergrund des derzeit stattfindenden Ausstiegs aus Ozonschicht zerstörenden Substanzen in Entwicklungsländern und der damit verbundenen Einführung von Ersatzstoffen dringend erforderlich, da es für die meisten Anwendungen schon Lösungen mit halogenfreien Stoffen gibt.

1 Introduction

1.1 Halogenated greenhouse gases with potential to form persistent degradation products in the atmosphere

For over six decades, halogenated hydrocarbons have been produced and used in products and processes worldwide. Halogenated hydrocarbons are those in which at least one hydrogen atom has been replaced by one of the halogens fluorine, chlorine, bromine, or iodine.

Formerly used halogenated hydrocarbons are now banned because of their potential to deplete the ozone layer. In the meantime, halogenated substitutes have also been severely restricted in many applications due to their high global warming potential (GWP)[19]. The European F-gas Regulation (EU) No. 517/2014 (in the following EU F-gas Regulation) limits the use of hydrofluorocarbons (HFCs) with high GWP directly by bans for use in certain applications, and indirectly by a gradually limiting the permitted quantities, which are weighted according to their GWP (the so-called HFC phase-down). On an international level, the Montreal Protocol was extended to cover HFCs in 2016. This decision, taken in Kigali, is the basis for the worldwide HFC reduction, with the first reduction stage for industrialized countries came into force at the beginning of 2019.

Due to the restrictions on substances that deplete the ozone layer and have a greenhouse potential, there is an increasing need for substitutes now. Natural refrigerants such as carbon dioxide, hydrocarbons and ammonia are available as halogen-free solutions. However, the use of previously unused unsaturated halogenated hydrocarbons is also increasing.

This study provides an overview of the short-lived halogenated gases and their use, as well as current and future quantities, especially in the refrigeration and air conditioning sector. More specifically, the potential of these gases to form persistent and mobile degradation products through atmospheric degradation and their fate in the environment is discussed.

1.2 The progression from fully halogenated CFCs to u-HFCs and u-HCFCs

In Germany and other industrialized countries, for decades, the quantitatively most important halogenated hydrocarbons belonged to the group of fully halogenated chlorofluorocarbons (CFCs). Their main areas of application were foam blowing agents, aerosol propellants, solvents, and refrigerants. In addition, there were brominated halogenated hydrocarbons, the so-called halons, which were widely used as fire extinguishing agents and are to a lesser extent still used now (UNEP 2015). These substance groups are regulated worldwide by the Montreal Protocol for the protection of the ozone layer.

Partially halogenated CFCs (abbreviation HCFCs) were considered a temporary substitute for CFCs because of their lower ozone depleting potential and were mainly used in refrigeration technology and the production of foams. On the other hand, in the case of aerosols, solvents, fire extinguishing agents, household refrigerators and many foams, CFCs and halons could mostly be directly replaced by halogen-free substances. This has significantly reduced the use of ozone-depleting substances since the early 1990s.

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[19] In this study the GWP is always given over a time horizon of 100 years. Unless otherwise stated, the source used is the 4th Assessment Report of the IPCC (IPCC 2007), which is also the basis for the GWPs listed in Annex I and II of the European F-Gas Regulation (EU) No. 517/2014.

HCFCs were also included in the Montreal Protocol soon after the CFCs and were also heavily regulated in Europa[20] and Germany[21]. Regulation (EC) No. 1005/2009 bans HCFCs in the EU since 2015. HCFCs are still widely used in developing countries; their use will end there by 2040 at the latest. The use of HCFCs as a starting material for other production processes and for certain niche applications has not yet been restricted worldwide.

Use of the terms Europe and EU in this report

Unless otherwise stated, "Europe" in this report always refers to the 28 Member States of the European Union as it existed until February 1, 2020 (including the United Kingdom of Great Britain and Northern Ireland). In some cases, "EU-28" is also used synonymously for emphasis.

Whenever national borders cannot be included, such as in the case of geographical modelling using atmospheric models, "Europe" or "European", unless otherwise stated, refers to the geographical area of these 28 EU Member States plus Norway, Switzerland, and Turkey. Sometimes "EU-28+" is also used synonymously.

Due to the bans on CFCs, halons and HCFCs, the chemical industry developed halogenated hydrocarbons without chlorine or bromine as substitutes in the early 1990s. The hydrofluorocarbons (HFCs) contain only fluorine as halogens. For niche applications, such as cryogenic cooling (less than minus 40 °C), fully halogenated fluorocarbons (PFCs) were also introduced in some cases. HFCs and PFCs no longer harm the ozone layer, but continue to contribute to the greenhouse effect. They are still used in large quantities in industrialized countries, especially as refrigerants and, to a lesser extent, as blowing agents for foams and propellants for aerosols.

The high global warming potential (GWP) of HFCs and PFCs is the reason why they are also subject to legal restrictions.[22] At the international level, under the Montreal Protocol, the Kigali Amendment was adopted in October 2016 and came into force in 2019. The resolution provides for a significant reduction in HFC consumption, in terms of CO_2 equivalents, worldwide within a few decades. The aim is to replace HFCs with high GWP by climate and environmentally friendly alternatives, whereby the total amount (mass) of HFCs used will not necessarily decrease.

1.3 Unsaturated HFCs as substitutes for saturated HFCs

At the European level, the regulation of HFCs began much earlier than at the international level. The first European F-gas legislation from 2006 not only imposed restrictions on HFCs in stationary applications (Regulation (EC) No. 842/2006), but also included a ban on fluorinated greenhouse gases with a GWP above 150 in car air conditioning systems in the 2006/40/EC (MAC Directive) directive - starting in 2011.

Since 2006, it was already clear that the market for the quantitatively most important HFC-134a, which was used in large quantities in passenger car air conditioning systems, would collapse in the medium term, as the GWP of HFC-134a is 1,430. While the European automotive industry has been developing and testing passenger car air conditioning systems for the refrigerant CO_2 since the late 1990s, since the end of 2006, in response to the MAC directive, two US refrigerant manufacturers in

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[20] Regulation (EC) No 1005/2009 on substances that deplete the ozone layer.

[21] For Germany, the "FCKW-Halon-Verbots-Verordnung" (CFC-halon-ban regulation) of 1991 and the following „Chemikalien-Ozonschicht-Verordnung" (chemical ozone layer regulation), in force since 2006, should be mentioned.

[22] Regulation (EU) No. 517/2014 on fluorinated greenhouse gases and annual emission reporting requirements under the Framework Convention on Climate Change (UNFCCC).

particular have brought several unsaturated HFCs (u-HFCs) with a GWP of less than 150 into the discussion within a short time.

Following an international agreement reached by the automotive industry at the beginning of 2010 on a general replacement refrigerant, u-HFC-1234yf became available on the market in sufficient quantities following supply bottlenecks in 2013. However, the use of CO_2 or hydrocarbons as refrigerants is still under investigation, for example in cars with new drive types.

The u-HFCs are also HFCs, i.e. fluorinated greenhouse gases, which are chemically more unstable and therefore have a low global warming potential.[23] The most important single u-HFC, u-HFC-1234yf, has a GWP of four (WMO 2010), the GWP of the second important u-HFC-1234ze(E) is seven (WMO 2010).[24] Due to the development of unsaturated HFCs, new chlorinated hydrocarbons are now being developed and marketed, which are abbreviated as u-HCFCs in this report. Like u-HFCs, these have a low global warming potential, but due to their chlorine content they have an ozone depleting potential. Due to their relatively short atmospheric lifetimes, this potential is lower than that of HCFCs.

Table 1 gives an overview of the environmentally relevant properties of halogenated greenhouse gases by substance group according to their historical development up to the u-HFCs and u-HCFCs: the ozone depleting potential (ODP), the global warming potential (GWP) and the atmospheric lifetime. In addition, the most important individual substances are listed as refrigerants (R for "refrigerant", designation according to the ISO 817 (ISO 2017) standard).

Table 1 shows that by replacing CFCs and HCFCs with PFCs and HFCs, substances with high ODP are avoided.[25] In terms of global warming potential (GWP), the differences between CFCs, HCFCs, PFCs and HFCs are only small. Similar to the halogen-free refrigerants, the u-HFCs and u-HCFCs have a small GWP because their chemical stability and thus their atmospheric lifetime are low.

The chemical instability of u-HFCs leads to higher flammability. The chemical industry has always emphasized that the main advantage of the so-called "safety refrigerants" CFCs, HCFCs and HFCs over non-halogenated substances is that they are not flammable. Therefore, if non-flammable refrigerants are required for stationary refrigerant applications, u-HFCs can only be used in combination with saturated HFCs, which increases the GWP of the mixture.[26]

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[23] In industrial linguistic use, unsaturated HFCs are often called HFOs, which stands for Hydro-Fluoro-Olefins, in order to distinguish the group of substances more clearly from conventional HFCs.

[24] The GWP of u-HFC1234yf and u-HFC-1234ze(E) has now been reduced to <1 each (WMO 2018), but in the present study the GWPs from the older WMO report (WMO 2010) are used, as they are also mentioned in Annex II of the EU F-Gas Regulation.

[25] In theory, ODP values can also be calculated for certain HFCs. However, they are minimal and have not yet been taken into account in environmental policy.

[26] Refrigerant mixtures ("blends") are currently used in large quantities, they are developed for different temperature ranges and refrigeration and air-conditioning applications.

Table 1: Overview of groups of halogenated greenhouse gases used in the past and present and key figures on their effect in the atmosphere. ODP, ozone depleting potential. GWP, global warming potential.

Substance group	ODP[a]	GWP[b]	Atmospheric lifetime[c]	Examples for single substances
CFCs and Halons	0.6 - 10	4,750 - 14,400	45 - 1,020 Jahre	R11, R12, R13B1
HCFCs	0.02 - 0.11	77 - 2,310	1 - 17.2 Jahre	R22, R141b
PFCs	no ODP	7,390 - 12,200	2,600 - 50,000	R14, R116
HFCs	no ODP	124 – 14,800	<1 - 242 years	R32, R134a, R125
u-HFCs	no ODP	4[d] - 16[e]	few days	R1234yf, R1234ze
u-HCFCs	<0.0004[e]	0.4 - 3.7[e]	few days	R1233zd, R1233xf

[a] unless otherwise stated, ODP based on Annex I of Regulation (EC) No 1005/2009

[b] unless otherwise stated, GWP based on the 4th IPCC Assessment Report (IPCC 2007)

[c] Lifetimes of the individual substances from Myhre et al. (2013), Table 8.A.1[27]

[d] Table 1-11 in WMO (2010)

[e] Table A-1 in WMO (2018)

The replacement of HFCs by u-HFCs, u-HCFCs or by mixtures of HFCs, u-HFCs and u-HCFCs leads - like the use of halogen-free substances - to a reduction of the contribution to the greenhouse effect in the respective applications. Due to the EU F-gas Regulation and the Kigali Amendment[28] agreed under the Montreal Protocol, strong growth of unsaturated HFCs is expected in applications where saturated HFCs have been used so far (see Chapter 3). The Kigali Amendment demands the reduction of HFC consumption converted into CO_2-equivalents. However, the mass of the substances used may also increase, which is likely to be due to the expected further increase in refrigeration and air conditioning systems, especially in emerging and developing countries.

Therefore, the question of the environmental relevance of new halogenated refrigerants is even more pressing than before. In addition to the environmentally harmful consumption of critical raw materials such as fluorite[29] and costly manufacturing processes for the u-HFCs and u-HCFCs, their low chemical stability inevitably leads to degradation in the atmosphere and to the release of degradation products into the environment more quickly than with halogenated substances used in the past. As a result, knowledge about which new substances are used in what quantities, which decomposition and degradation products are produced, where they remain and what environmental effects they have, is becoming increasingly important.

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[27] Viewable under URL https://www.ipcc.ch/site/assets/uploads/2018/02/WG1AR5_Chapter08_FINAL.pdf (last access: 19.08.2020)

[28] https://ozone.unep.org/sites/default/files/Handbooks/MP_Handbook_2019.pdf (last access: 06.04.2020)

[29] Fluorite (CaF_2), also called fluorspar or calcium fluoride, is the most common raw material for hydrogen fluoride, which in turn serves as a source of fluorine in the production of fluorinated hydrocarbons.

1.4 Atmospheric degradation products of halogenated refrigerants and blowing agents

If halogenated refrigerants and blowing agents enter the atmosphere, they are gradually being degraded. Via precipitation, the degradation products reach the earth's surface and water bodies and can be harmful to the environment.

As quantitatively relevant, halogenated, and thus potentially persistent or toxic substances, the atmospheric degradation of HCFCs, HFCs, u-HCFCs and u-HCFCs produces, among others, trifluoroacetic acid (abbreviation: TFA) and hydrogen fluoride (HF). Hydrogen fluoride is not persistent in the environment. TFA, however, is extremely persistent and highly mobile. Recent analyses indicate increasing TFA concentrations in drinking water close to the precautionary health value. Since TFA cannot be removed from the water in a practical and economical way with common water treatment methods, such as ozonation or activated carbon treatment, it must be monitored in the water with special attention.

Little is known at present about the expected quantities of the new halogenated refrigerants and blowing agents with small GWP in existing and future applications, as well as the concentrations and accumulation of the degradation products and their fate in water, soil, and organisms.

1.5 Objective of this project

The aim of the project was to describe and evaluate the environmental impact of halogenated refrigerants, foam blowing agents and aerosol propellants[30] in Germany and Europe. The entire life cycle of these halogenated substances from production to use and disposal was considered. Against the background of current climate policy regulations, it is to be expected that the quantities of unsaturated HFCs used, and therefore their emissions into the atmosphere, will increase significantly in the coming years. Therefore, the current use levels of halogenated substances were quantified and projections of future use were developed. In addition, the knowledge about these substances, their atmospheric degradation pathways and degradation products, input, occurrence, point of deposition and environmental impact was systematized. An indicative measurement program for the determination of environmental concentrations was also carried out.

The present report consists of five chapters. Chapter 1 introduces the topic and explains the problems that are covered by this report. Starting with the current state (Chapter 2) and the preparation of projections of demand and emissions of certain partially halogenated substances and their degradation products up to the year 2050 (Chapter 3), the indicative measurements performed on the concentration of TFA in rainwater and the input of TFA into soil and plants within the scope of a Germany-wide measuring program are described and their results are presented in Chapter 4. Finally, an overall evaluation and processing of the results of the projections and the performed measurements is carried out in Chapter 5.

This project focuses on persistent degradation products of halogenated refrigerants and blowing agents with a special focus on halogenated substitutes with low global warming potential. It should be noted that some pesticides, flame retardants, solvents, pharmaceuticals, etc. may also be halogenated substances that can form persistent degradation products.

This study focuses on halogenated refrigerants and blowing agents that can emit into the atmosphere through their use and whose degradation products are released into the environment along this path. Other halogenated substances that are not used as blowing agents or refrigerants, but which form per-

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[30] In the following, foam blowing agents and aerosol propellants are commonly referred to as "blowing agents".

sistent degradation products when emitted into the atmosphere, are discussed in passing. Unless otherwise stated, the term "halogenated substances" in the following refers exclusively to the group of halogenated refrigerants and blowing agents.

The present report is intended to contribute to a better understanding of the contribution of relevant substances that are mainly responsible for the atmospheric input of degradation products of halogenated substances. The focus lies on the halogenated greenhouse gases currently used as refrigerants and blowing agents, i.e. HFCs, u-HFCs and u-HCFCs. All other substance groups of halogenated greenhouse gases are dealt with in summary.

2 Analysis of the current situation

2.1 Objective

This chapter provides a comprehensive assessment of the current situation for HFC, u-HFC and u-HCFC use and emissions in Germany and the EU (where data is available[31]). This is necessary also because the current state of HFCs, u-HFCs and u-HCFCs use and emissions forms the basis for the projections, in order to estimate which substances with low GWP will replace HFCs in the future.

In addition to non-halogenated, so-called natural refrigerants such as CO_2, ammonia, or simple hydrocarbons such as propane or butane, fluorinated gases with a small GWP, mainly u-HFCs and u-HCFCs, are also offered as substitutes for HFCs.

Furthermore, the results of this analysis also served to identify environmentally relevant atmospheric degradation products of the halogenated refrigerants and blowing agents investigated, which determined the direction of the measurement program during the course of the project.

The aim is to present and evaluate the current state of research with a focus on the use of halogenated refrigerants and blowing agents and the associated emissions, degradation products, by-products as well as their occurrence and effects in the environment. The thematic focus is on unsaturated halogenated substances with low global warming potentials.

For the unsaturated halogenated substances with a low global warming potential, the current state with regard to the life cycle phases

- production (Chapter 2.4),
- use (Chapter 2.5),
- destruction (Chapter 2.6),
- atmospheric degradation (Chapter 2.7, 2.8) and
- persistence in the environment (Chapter 2.9, 2.10)

is reviewed on the basis of a comprehensive literature review. The following questions are answered by a systematic evaluation of the relevant technical literature and interviews with experts from industry and science:

1. Which halogenated refrigerants and blowing agents are currently used alone or in mixtures to replace substances that are relevant regarding the greenhouse effect, in which applications, in which quantities and in which compositions in Germany and in the EU?
2. What emissions (type and quantity) are produced during production, use and disposal?
3. Which degradation products in what quantities are produced from the individual halogenated substances?
4. Which by-products are formed during the production of the substances?
5. Which by-products are contained in the halogenated substances?
6. Where are the new halogenated substances and their degradation products found in the environment and in what chemical form and bioavailability?
7. What is known about the effects of these substances?

Open questions are then identified and presented.

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[31] At the time of writing, reported data for Germany and the EU on halogenated substances were available up to the year 2018 (status: March 2020).

2.2 Methods

In order to work on the research questions, the technical literature was analysed and systematized. Relevant halogenated substances with low global warming potential were identified and described. A complete list of literature can be found in the bibliography.

2.2.1 Use and emissions of fluorinated gases

First, the substances were identified on which the focus should be placed in the evaluation of environmental effects (Chapter 2.1). Relevant for the assessment are saturated or unsaturated halogenated hydrocarbons, which have a potential to form persistent and toxic degradation products.

The data for all existing applications of halogenated refrigerants and blowing agents up to the year 2018 were determined for Germany and Europe (EU-28) as a whole. The assessment of the relevance of the substances was based on the reporting according to the EU F-gas Regulation (EU) No. 517/2014 and the UNFCCC emissions reporting for Germany and the European Union (EU-28; CRF, NIR)[32,33,34]. For the substances reported under the EU F-gas Regulation, those halogenated gases were considered relevant whose annual use quantities (sum of packaged goods and prefilled equipment) exceeded 50 tonnes[35]. The emissions resulting from production, use and disposal were also taken from the sources mentioned in the emissions reporting.

2.2.2 Scientific Literature

2.2.2.1 Scientific studies on the degradation of halogenated refrigerants and blowing agents

Studies on the degradation of halogenated refrigerants and blowing agents have only been carried out by a relatively small number of scientific groups. By far the most publications on this subject come from the working groups of Timothy J. Wallington and Ole J. Nielsen. Timothy J. Wallington is associated with the US-American Ford Motor Company. Ole J. Nielsen holds a professorship at the Department of Chemistry at the University of Copenhagen in Denmark. The focus of their scientific cooperation is on the degradation processes of HCFCs, HFCs, u-HFCs and u-HCFCs. This often includes an assessment of the environmental impact, e.g. in terms of determining an ODP, GWP or possible harmful atmospheric degradation products. Usually, the investigations are laboratory experiments under artificially generated conditions.

James B. Burkholder has published a series of papers on the atmospheric degradation of halogenated substances. Most of his work is summarized in a review from 2015 in collaboration with Richard A. Cox and Akkihebbal R. Ravishankara.

In addition, further studies of a large number of other scientists were evaluated. A complete overview can be found in the bibliography.

2.2.2.2 Technical books on the degradation of halogenated refrigerants and blowing agents

To a lesser extent, scientists have prepared information from the scientific literature on the atmospheric degradation of halogenated refrigerants and blowing agents in reference books. For the present report, the reference book "The Primary Photochemical Processes in the Alkenes" by Jack G. Calvert

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[32] Regulation (EU) No 525/2013: Mechanism for monitoring and reporting greenhouse gas emissions. URL: http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32013R0525

[33] Commission Implementing Regulation (EU) No 749/2014: Reporting requirements for the Member States pursuant to Regulation 525/2013. URL: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32014R0749

[34] Commission Delegated Regulation (EU) No 666/2014 – Regquirements for a Union Inventory system pursuatn to Regulation 525/2013. URL: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:32014R0666

[35] Unless otherwise mentioned in the text, tons always refer to the unit metric tons.

and colleagues from 2008 was used in particular. This is also used as a source for other publications, including those of organizations such as the "World Meteorological Organization" (WMO).

2.2.2.3 Reports from governmental and non-governmental organizations

In addition to the publications, most of which are the result of experimental studies, there is a series of reports of a non-experimental nature that have been summarized by experts for various organizations. These are information that have been compiled and prepared from the scientific literature. Extensive reports, which also include the atmospheric degradation of halogenated refrigerants and blowing agents, are in particular the reports of the WMO with the title "Scientific Assessment of Ozone Depletion", which are published every four years (the last one at the end of 2018). Apart from that, the "Technology and Economic Assessment Panel" (TEAP) of the United Nations Environment Programme (UNEP) provides technical information on alternative technologies to ozone depleting substances upon request from Parties to the Montreal Protocol. These reports contain, among other things, estimates of potential new halogenated substances and their future use quantities and have been published regularly every year in recent years.

2.2.2.4 Biodegradability and environmental toxicity

A systematic literature and database search was carried out for the halogenated refrigerants and blowing agents with low global warming potential, the u-HFCs and u-HCFCs, which were classified as relevant. The same was done for the persistent degradation product trifluoroacetic acid (TFA). The sources used are listed in the annex to this report (Annex A.1).

The results were compared with information from standard works on substance data (Verschueren 1996, Gangolli 2007). The entries for trifluoroacetic acid, tetrafluoroethene and hexafluoropropene in the DOSE database (Gangolli 2007) did not yield any further information. Searches in databases require a unique assignment of the CAS number[36].

For the keywords "trifluoroacetic acid" or "halogenated hydrogen carbon" or "HCFC" and "ecotoxicity" or "degradability", an internet and literature search was conducted in Pubmed[37], Scopus or Science Direct (publisher Elsevier) and the SETAC website (journal Environmental Toxicology and Chemistry).

2.2.2.5 Patents

Information on the production of halogenated refrigerants and blowing agents was mainly obtained from patents. In many cases, these represent the only publicly available source of possible production routes, as they are not published by the producers, especially for newer substances. With the help of the patents, an attempt was made to identify possible starting materials and by-products and, if evident, secondary components.

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[36] CAS - Chemical Abstracts Service, CAS Number - international standard for the identification of chemical substances by unique registration number, findable e.g. in Wikipedia, the toxnet database ChemIDplus or the substance database Gestis.

[37] http://www.ncbi.nlm.nih.gov/pubmed/

2.2.3 Other sources

2.2.3.1 REACH database

All substances that are manufactured or imported in the EU in quantities of more than one ton per year per company must be registered with the European Chemicals Agency (ECHA). This also applies to substances in mixtures. The legal basis for this is Article 10 of the REACH[38] regulation[39]. A registration dossier is prepared for all substances subject to registration. This consists of a technical dossier with information on safe use and, in the case of annual production of more than ten tons, a chemical safety report, which must provide information on the environmental impact and environmental behaviour.[40] For all substances and degradation products, the dossiers were evaluated, if available, in particular with regard to ecotoxicity and environmental fate.

2.2.3.2 Reportable emission and use data of halogenated refrigerants and blowing agents

Data on emissions and use of halogenated greenhouse gases for Germany and the EU were mostly taken from publicly available reports. For F-gases, the data reported under Article 19 (1) to (5) of the EU F-gas Regulation were taken from the publications of the European Environmental Protection Agency (EEA) (EEA 2017 & 2019). National data reported under the German Environmental Statistics Act (UStatG) on the production, imports, exports and use of fluorinated refrigerants and blowing agents were taken from the corresponding publication of the German Federal Statistical Office (Statistisches Bundesamt 2018 & 2019). As the publications of the Federal Statistical Office are not published annually and detailed data are only available for 2016 and 2018, but not for 2017, the same years were considered for the EU, which are included in the EEA reports of 2017 and 2019, in order to ensure comparability.

2.2.3.3 Research on niche applications of halogenated refrigerants and blowing agents

The starting point for the analysis was a study already carried out by the Federal Environment Agency (UBA 2010). In addition, a literature and internet search was carried out to determine the data and information on u-HFCs and u-HCFCs in niche applications and, if necessary, to identify and, where possible, quantify data from other sources. Literature from scientific journals and product descriptions of u-HFCs and u-HCFCs available on the internet and other publications were evaluated. Table A 1 in Annex A.1 contains a list of the search terms used.

2.2.4 Expert surveys

A series of expert discussions have been conducted as semi-structured interviews in person or by telephone since April 2018. Some of the questionnaires were sent out in advance. The content of the questionnaires was adapted according to the professional background of the interviewees in order to conduct the interviews in the most targeted manner possible. The main questions that were asked in all interviews are summarized in Annex A.3.

In order to assess possible synthesis routes of new halogenated substances, production processes and the by-products and intermediates, by-products, products resulting from the destruction or unintentional combustion and atmospheric degradation of halogenated greenhouse gases, employees at universities with a focus on fluorine chemistry and who have already worked on the topic of refrigerants and blowing agents were surveyed.

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[38] Registration, Evaluation, Authorisation of Chemicals

[39] Regulation (EC) No 1907/2006

[40] https://www.reach-clp-biozid-helpdesk.de/de/REACH/Registrierung/Registrierung.html (last access: 08.04.2020)

Experts from industry were asked primarily about the current and future market penetration of halogenated substances, based on their mostly long-standing experience with halogenated refrigerants and blowing agents. Experts from industry and science were asked for their assessment of the production processes.

In order to obtain a picture of developments in the refrigerant, foam blowing agent and aerosol propellant market as up-to-date and comprehensive as possible, various congresses and events by associations and organizations were attended, and presentations by experts in the field of halogenated refrigerants and blowing agents were followed and evaluated. Whenever possible, these experts were asked about the market development of the various new substances. This served to identify future developments, and thus also potentially relevant new substances and mixtures. A list of the events attended is given in Table A 2 in Annex A.4.

The names and institutions of the interviewed experts are documented in this report exclusively for the Federal Environment Agency in the form of a confidential annex. All experts were given the opportunity to comment on the documentation of their statements before they were made available to the Federal Environment Agency.

2.3 Identification of relevant substances

In the following, the most important halogenated refrigerants and blowing agents currently sold on the European market are presented.

The research on unsaturated halogenated refrigerants and blowing agents with small GWP showed that the estimation of their future relevance is much more difficult to make than was the case for saturated HFCs. On the one hand this is due to the large number of potentially available substances. On the other hand, the experts from industry and science were hardly able to make reliable statements about the expected future market penetration of new substances. However, some substitutes that will probably also be relevant in the future were identified in the expert discussions.

Table 2 shows an overview of the unsaturated halogenated refrigerants and blowing agents with small GWP that can be considered relevant.

In addition to the individual substance u-HFC-1234yf, which is used as a substitute refrigerant for HFC-134a in car air conditioning systems and in mixtures, u-HFC-1234ze(E) was named primarily for use as a blowing agent in foam production and in chillers. For chillers of high-performance classes, relevant appliance manufacturers have named u-HCFC-1233zd(E) and the mixture R513A (mixture of u-HCFC-1234yf and HFC-134a)[41].

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[41] The mixture R513A is composed of u-HFC-1234yf (56%) and HFC-134a (44%), has a GWP of 631 and is non-flammable. In addition, R513A shows hardly any noticeable loss of performance compared to pure HFC-134a, as it has similar thermodynamic properties. The conversion of the system is possible without modifications and without renewing oil and seals.

Table 2: Listing of (potentially) relevant and currently in the EU commercially available unsaturated halogenated refrigerants and blowing agents with small GWP.

Substance name (CAS number)	Trade name	Chemical name	Molecular formula	Main use	Annual use quantity[a] in tonnes according to REACH[b] (expert estimation)
u-HFC-1234yf (754-12-1)	Honeywell Solstice® yf, Chemours Opteon™ XL10	2,3,3,3-tetrafluoropropene	$CF_3CF=CH_2$	refrigerant	1,000 - 10,000 (>10,000)
u-HFC-1234ze(E) (29118-24-9)	Honeywell Solstice® ze	(1E)-1,3,3,3-tetrafluoropropene	trans-$CF_3CH=CHF$	refrigerant, foam blowing agent, aerosol propellant	100 - 1,000 (1,000 - 5,000)
u-HCFC-1233zd(E)[c] (102687-65-0)	Honeywell Solstice® zd, Arkema Forane® HTS and FBA	(E)-1-chloro-3,3,3-trifluoropropene	trans-$CF_3CH=CHCl$	refrigerant, foam blowing agent	100 - 1,000 (1,000 - 5,000)
u-HFC-1336mzz(Z) (692-49-9)	Chemours Opteon™ 1100	(2Z)-1,1,1,4,4,4-hexafluorobutene	cis-$CF_3CH=CHCF_3$	foam blowing agent	>100[d] (>100)
u-HFC-1336mzz(E) (66711-86-2)	no data available	(2E)-1,1,1,4,4,4-hexafluorobutene	trans-$CF_3CH=CHCF_3$	refrigerant[e]	10 - 100 (<100)
u-HCFC-1224yd(Z) (111512-60-8)	AGC Chemicals AMOLEA™-yd	Cis-1-chloro-2,3,3,3-tetrafluoropropene	cis-$CF_3CF=CHCl$	refrigerant, foam blowing agent	No data available (<100)

[a] Production (does not play a role in the EU) + Import into the EU

[b] https://echa.europa.eu/de/information-on-chemicals (status: March 2020)

[c] Isomer u-HCFC-1233zd(Z) is very rarely offered as a solvent.

[d] Here it is unclear what quantity is involved. REACH specifies 100+ tons on the one hand (https://echa.europa.eu/de/substance-information/-/substanceinfo/100.217.885, https://echa.europa.eu/de/brief-profile/-/briefprofile/100.217.885, letzter Zugriff: 06.03.2020) and 1000+ tons on the other (https://echa.europa.eu/de/registration-dossier/-/registered-dossier/10030/1, last access: 06.03.2020). According to expert estimation, production does not take place in the EU and imports are between 100 and 1,000 t, but rather in the range of >100 t.

[e] Possible use in high temperature heat pumps and Organic Rankine Cycles (ORC).

In view of the bans on blowing agents with a GWP above 150 - for example u-HCFC-1233zd(E) and u-HFC-1336mzz(Z) - which came into force on January 1, 2020 under the EU F-gas Regulation, u-HCFC-1233zd(E) and u-HFC-1336mzz(Z) will be used as substitutes in foam production. Further possible substitutes were identified in the literature, including u-HCFC-1224yd(Z), which could be used as a substitute for HFC-245fa (used in PU foam production, solvents, and ORC systems) and u-HCFC-1233zd (used in high-capacity water chillers)[42].

For use in high temperature heat pumps, u-HFC-1336mzz(Z), u-HFC-1336mzz(E), u-HFC-1234yf, u-HFC-1234ze(E), u-HCFC-1233zd(E) and u-HCFC-1224yd(Z) are suitable (Arpagaus 2019).

In addition to their use as refrigerants and blowing agents, unsaturated perfluorinated hydrocarbons are partly used as substitutes in the production of fluoropolymers and as process gases. Worth mentioning here are tetrafluoroethene (tetrafluoroethylene, R1114) and hexafluoropropene (R1216, Fleet et al. 2017, see Chapter 2.8).

In the following, u-HFC-1234ze, u-HCFC-1233zd, u-HCFC-1224yd and u-HFC-1336mzz, in no more detailed specification, stand for u-HFC-1234ze(E), u-HCFC-1233zd(E), u-HCFC-1224y(Z) and u-HFC-1336mzz(Z), respectively.

2.4 Production of halogenates refrigerants and foaming agents

In 2018, 19,270 tons of HFCs were produced in the EU (EEA 2019). According to experts, only a small number of HFCs were produced in the EU, namely HFC-23, HFC-134a, HFC 143a, HFC-227ea and HFC-365mfc (EEA 2016). All other HFCs and all u-HFCs and u-HCFCs were produced and imported outside the EU. Table 3 gives an overview of the HFCs produced in the EU and the order of magnitude of production volumes for 2018, based on expert estimates.

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[42] https://www.agcce.com/amolea-yd-a-non-flammable-low-gwp-hcfo-refrigerant/ (letzter Zugriff: 21.08.18)

Table 3: Overview of the HFCs produced in the EU in 2018 with the respective main use and the annual production capacity in metric tons, as well as the production sites in the EU according to expert information.

ASHRAE designation	IUPAC designation	Molecular formula	Main use	Production in tons	Production site in the EU
HFC-23	trifluoromethane (fluoroform)	CHF_3	By-product of HCFC-22 production	<1,000	Germany, Netherlands, France, Italy (4 HCFC-22-plants)
HFC-134a	1,1,1,2-tetrafluoroethane	CF_3CH_2F	Refrigerant, aerosol propellant, blowing agent	<10,000	Germany (1 plant), France (1 plant)
HFC-143a	1,1,1-trifluoroethane	CF_3CH_3	Refrigerant	<1,000	France (1 plant)
HFC-227ea	1,1,1,2,3,3,3-heptafluoropropane	CF_3CHFCF_3	Fire extinguishing agent, metered dose aerosol (MDI), refrigerant, blowing agent	>1,000	Germany (1 plant)
HFC-365mfc	1,1,1,3,3-pentafluorobutane	$CF_3CF_2CH_2CH_2F$	Refrigerant, blowing agent, ORC systems, solvent	<10,000	France (1 plant)

2.4.1 Production routes and emissions of HFCs produced in the EU

The quantitatively most important by-product from the production of HCFC-22 ($CHClF_2$) is **HFC-23** (CHF_3, GWP 14,800). Almost 90,000 tons of HCFC-22 are produced annually in the EU, which is about 50 % of the total production volume of ozone depleting substances in the EU (EEA 2019). HCFC-23 is produced as a by-product to about 2-3 % (Gschrey & Zeiger 2015). HCFC-22 is produced in the Netherlands, Italy, France, and Germany, mainly as a starting material for further manufacturing processes in the chemical industry.

In this context, the production of HFC-32 (CH_2F_2) is relevant, which is used as a refrigerant in air conditioning units, both as a single substance and as a component of various mixtures[43]. The production of HFC-32 is - in simplified terms - mostly done by fluorination of HCFC-22 (Cuzzato 2001). It should be noted that HCFC-22 is also an intermediate product in the production of other partially halogenated refrigerants and blowing agents (e.g. **HFC-227ea**), so that the emissions of HFC-23 must be regarded in part as by-products of these substances.

The production route of the halogenated ether HCFE-235da2 (isoflurane, chemical name (1-chloro-2,2,2-trifluoroethyl)(difluoromethyl)ether, molecular formula $C_3H_2ClF_5O$) also has HCFC-22 as an intermediate product.

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[43] For example, the R407 series with 10-30 % HFC-32 and the mixture R410A with an HFC-32 share of 50 %.

For **HFC-134a**, the only production route in the EU is via HCFC-133a. This is a two-stage process in two separate reactors (Belter 2010):

Reactor 1:

1. $CCl_2=CHCl$ (HCC-1120, trichloroethene) + HF → $CFCl_2CH_2Cl$ (HCFC-131a) + HCl
2. $CFCl_2CH_2Cl$ (HCFC-131a) + HF → CF_2ClCH_2Cl (HCFC-132b) + HCl
3. CF_2ClCH_2Cl (HCFC-132b) + HF → CF_3CH_2Cl (HCFC-133a)

Reactor 2:

1. CF_3CH_2Cl (HCFC-133a) + HF → CF_3CH_2F (HFC-134a) + HCl

This process produces the toxic **u-HCFC-1122** (1-chloro-2,2-difluoroethene, $CF_2=CHCl$) as a by-product, which is fed back into the cycle at 280-300 °C and reacts further to form HCFC-133a[44]. However, an emission of this by-product is not excluded in principle.

HFC-365mfc is produced in the EU in relevant quantities as a foam blowing agent substituting HCFC-141b. HFC-365mfc can be produced from a pentachlorobutane compound, hydrogen fluoride and a fluorination catalyst (Brosch et al. 2000). The 1,1,1,3,3-pentafluorobutane produced in this way can contain hydrogen chloride, hydrogen fluoride or unsaturated (chlorine)-fluorocarbon compounds (including 2-chloropropene) as minor components, which originate from the fluorination reaction or the feedstock (Bertocchio et al. 1998).

The following Table 4 shows the identified by-products and intermediates, as well as potential minor components that can occur and emit during the production processes of HFCs.

Table 4: By-products and intermediates potentially formed during the production of HFCs, as well as starting materials and minor components.

Target substance	Starting materials, intermediates, by-products, and potential minor components	Literature
HFC-32	HCC-30 (dichloromethane) HCC-20 (trichloromethane, chloroform) HCFC-22 HFC-23	Cuzzato (2001)
HFC-227ea	HCC-20 (trichloromethane, chloroform) hexafluoropropene (HFP, R1216) tetrafluoroethene (R1114) HCFC-124 HCFC-22 HFC-23	Gschrey & Zeiger (2015)
HFC-134a	HCC-1120 (trichloroethene) HCFC-131a HCFC-132b HCFC-133a u-HCFC-1122	Belter (2010)
HFC-365mfc	pentachlorobutane 2-chloropropene	Brosch et al. (2000) Bertocchio et al. (1998)

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[44] Personal communication with an HFC-134a plant operator

2.4.2 Production routes and emissions of u-HFCs and u-HCFCs

For the production of u-HFCs and u-HCFCs, publicly available sources were only available to a limited extent. Therefore, the potentially applied production processes were derived from the large number of published patents. The in-depth investigation of patented production processes for u-HFCs and u-HCFCs showed that a large number of potential by-products, intermediates and minor components can occur. Table 5 shows the identified by-products and intermediates as well as potential minor components that can occur and emit during the production processes of u-HFCs and u-HCFCs. The substances listed in the column "Starting materials, intermediates, by-products and potential minor components" can be contained in the product in addition to the target substance, mostly in the form of the isomers existing for the substance. The detailed textual presentation of the mentioned patents can be found in Annex A.5.

Already in 1960, Maley (1960) described the synthesis of u-HFC-1234yf via the reaction of chloromethane (CH_3Cl, HCC-40) with HCFC-22 or tetrafluoroethene ($CF_2=CF_2$, TFE) at 700 to 950 °C. However, it is not known whether u-HFC-1234yf is currently commercially produced in this way. A Honeywell patent from 2009 describes a synthesis route that also starts with chloromethane (Van der Puy 2009). This is reacted with u-HCFC-1113 ($CF_2=CFCl$, CTFE) to form u-HFC-1233 isomers, which in turn form u-HFC-1234yf via reaction with HF. Depending on the reaction conditions, a yield of up to 87 % u-HFC-1234yf can be achieved. The major by-products are HFC-245fa (optimally not more than 6 %) and other undefined HFCs, HCFCs, u-HCFCs and u-HCFCs with more than two carbon atoms (optimally not more than 7 %).

According to industry experts, hexafluoropropene ($CF_3CF=CF_2$, HFP, R1216) is used in China as the starting substance for u-HFC-1234yf (for example, described in Smith et al. 2009). The reaction chain here proceeds via the formation of HFC-236ea (1,1,2,3,3,3-hexafluoropropane), which forms u-HFC-1225ye (1,2,3,3,3-pentafluoropropene) by dehydrofluorination, which in turn reacts with HF to form HFC-245eb (1,2,3,3,3-pentafluoropropane). A final dehydrofluorination step then yields u-HFC-1234yf. The starting substance hexafluoropropene is usually obtained by the pyrolysis of HCFC-22, which is used for the production of tetrafluoroethene (TFE), producing hexafluoropropene and HFC-23 as by-products and intermediates, respectively (Halliwell 1967, Siegemund et al. 2000).

For u-HFC-1234yf, the production path often runs via isomers of HCFC-244 and HFC-245 as well as u-HCFC-1233. The u-HCFC-1233 synthesis route, starting from CTFE, is most likely the preferred method in modern plants, for example in the U.S., based on expert information. However, new production routes for the manufacture of u-HFC-1234yf are continuously being researched and published. In 2018, for example, a patent was published for the production of the cyclic butane derivative TFMCB (1,1,2-trifluoro-2-(trifluoromethyl)cyclobutane), which contains a C-CF_3 group and can react further to vinylidene fluoride (1,1-difluoroethene, u-HFC-1132a) and/or u-HFC-1234yf (Nair et al. 2018).

Table 5: By-products and intermediates potentially formed during the production of u-HFCs and u-HCFCs as well as potential minor components. Toxic substances are marked with †. If not specified, all isomers are potentially included. This list is not exhaustive.

Target substance	Starting materials, intermediate products, by-products, and potential minor components	Literature
u-HFC-1234yf	chloromethane (CH_2Cl, HCC-40) HCFC-22 ($CHClF_2$) tetrafluoroethene (C_2F_4, TFE)	Du Pont (Maley 1960)
u-HFC-1234yf	HFC-245 ($C_3H_4F_4$) HFC-254 ($C_3H_4F_4$) u-HFC-1225 (C_3HF_5)†	Du Pont (Rao et al. 2007)
u-HFC-1234yf	HCFC-235 ($C_3H_2ClF_5$) HFC-245 ($C_3H_4F_4$) u-HCFC-1224 (C_3HClF_4)	Du Pont (Nappa et al. 2011)
u-HFC-1234yf	HCFC-244 ($C_3H_3ClF_4$) HFC-245 ($C_3H_4F_4$) u-HCFC-1233 ($C_3H_2ClF_3$)	Honeywell (Mukhopadhyay et al. 2009)
u-HFC-1234yf	u-FCC-1113 (C_2ClF_3, CTFE)† u-HCFC-1233 ($C_3H_2ClF_3$) u-HCC-1232 ($C_3H_2Cl_2F_2$) HCFC-243 ($C_3H_3Cl_2F_3$) HCFC-244 ($C_3H_3ClF_4$) HFC-41 (CH_3F) HFC-245fa ($C_3H_4F_4$) chlorotrifluorocyclopropane ($C_3H_2ClF_3$)	Honeywell (Van Der Puy 2009)
u-HFC-1234yf	hexafluoropropene (C_3F_6, HFP, R1216) HFC-236ea ($C_3H_2F_6$) u-HFC-1225ye (C_3HF_5)† HFC-245eb ($C_3H_3F_5$) HFC-254eb ($C_3H_4F_4$)	Ineos Fluor Holdings Limited (Smith et al. 2009)
u-HFC-1234yf	u-HCC-1230xa ($C_3H_2Cl_4$) u-HCC-1233xf ($C_3H_2ClF_3$) HCFC-244bb ($C_3H_3ClF_4$) HFC-245cb ($C_3H_3F_5$) HFC-245eb ($C_3H_3F_5$)	Arkema (Elsheikh & Bonnet 2009, Pigamo et al. 2011)
u-HFC-1234yf	HCC-240db ($C_3H_3Cl_5$) u-HCFC-1233xf ($C_3H_2ClF_3$) HFC-245cb ($C_3H_3F_5$) u-HCFC-1233zd ($C_3H_2ClF_3$) u-HFC-1234ze ($C_3H_2F_4$) HFC-245fa ($C_3H_3F_5$) u-HFC-1243zf ($C_3H_3F_3$) u-HCC-1230xa ($C_3H_2Cl_4$) u-HCC-1232xf ($C_3H_2Cl_2F_2$) u-HCC-1231xf ($C_3H_2Cl_3F$) HCFC-242dc ($C_3H_3Cl_3F_2$) HCFC-241db ($C_3H_3Cl_4F$)	Daikin (Nose & Komatsu 2014)

Target substance	Starting materials, intermediate products, by-products, and potential minor components	Literature
u-HFC-1234yf	HFC-134a ($C_2H_2F_4$) u-HFC-1225ye (C_3HF_5)† u-HCC-1140 (C_2H_3Cl)† u-HCFC-1131 (C_2H_2ClF)	Fleet et al. (2017)
u-HFC-1234ze(E)	HFC-245 ($C_3H_4F_4$) u-HFCW-1234 ($C_3H_2F_4$)	Honeywell (Cottrell et al. 2010)
u-HFC-1336mzz(E) and u-HFC-1336mzz(Z)	HCFC-123 ($C_2HCl_2F_3$) HCFC-133 ($C_2H_2ClF_3$) HFC-143a ($C_2H_3F_3$) HFC-236fa ($C_3H_2F_6$) u-HFC-1132a ($C_2H_2F_2$)	Du Pont (Sun et al. 2013)
u-HCFC-1233zd(E) and u-HCFC-1233zd(Z)	HCFC-240fa ($C_3H_3Cl_5$) HCFC-241fa ($C_3H_3Cl_4F$) HCFC-242fa ($C_3H_3Cl_3F_2$) HCFC-243fa ($C_3H_3Cl_2F_3$) HCFC-244fa ($C_3H_3ClF_4$) HFC-245fa ($C_3H_3F_5$) u-HCFC-1233 ($C_3H_2ClF_3$)	Honeywell (Tung et al. 2005, Cottrell et al. 2013)
u-HCFC-1233zd(E)	HCFC-240fa ($C_3H_3Cl_5$) HCFC-244fa ($C_3H_3ClF_4$) HFC-245fa ($C_3H_3F_5$) u-HFC-1234ze ($C_3H_2F_4$) u-HCFC-1233zd(Z) (C_3HClF_3)	Honeywell (Tung et al. 2015)
u-HFC-1123	u-HFC-1132 ($C_2H_2F_2$)	Asahi Glass Company (Tasaka et al. 2016)

2.4.3 Fugitive emissions from the production of halogenated refrigerants and blowing agents

The production of halogenated refrigerants and blowing agents inevitably leads to fugitive emissions[45] which, depending on the exhaust gas treatment, may become environmentally relevant and potentially contribute to the formation of persistent degradation products.

In Germany, emissions of HFC-23, HFC-134a and HFC-227ea result from the production of halogenated refrigerants and blowing agents. The production quantities and emissions of these HFCs, including fugitive emissions, are reported annually to the German Federal Environment Agency. This data is not publicly available and may only be used for national emissions reporting to the Climate Secretariat in accordance with the reporting obligations of the United Nations Framework Convention on Climate Change (UNFCCC). This applies to the majority of fluorinated greenhouse gases in the EU reported under the Framework Convention on Climate Change. Therefore, these data cannot be explicitly mentioned in this report, but are included in the data basis for the projections in Chapter 3.

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[45] Fugitive emissions are emissions if the intended product emits into the atmosphere, by-product emissions are emissions of substances that are produced in the manufacture of other substances but do not correspond to the final product (IPCC 2006).

2.4.4 Minor components in halogenated refrigerants and blowing agents

During the production of a substance, further substances are produced as a result of chemical reactions, which are not necessarily completely removed from the end product and are circulated with the end product and finally emitted into the atmosphere. These further substances in the final product are referred to in this report as minor components and are, if disclosed or published, also listed in Table 5. Although the majority of u HCFCs and u HFCs used in the EU are imported, the additional minor components in the main products are of particular interest due to their use within the EU and will be discussed below.

According to AHRI ("Air Conditioning, Heating and Refrigeration Institute") Standard 700-2012[46] , refrigerants should not contain more than 0.5 % by weight of minor components. For HFC-134a, for example, up to 5,000 ppm contamination with u-HFC-1234yf is acceptable. An investigation of the contamination of HFC-134a with HCC-40 (chloromethane or methyl chloride, CH_3Cl) by the AHRI resulted in an HCC-40 content of less than 100 ppm[47] when HFC-134a is purchased from trusted manufacturers or distributors. Usually, individual substances are not specified separately, but the contamination is generally quantified. Therefore, manufacturers and distributors often quantify minor components as <1 %. Which substances exactly are present as minor components in a sold product (e.g. a refrigerant) and in what quantity is not further investigated. Therefore, there is very little information on possible minor constituents. The only clue is provided by patents, some of which list possible substances that may occur during production.

A U.S. patent for the production of u-HCFC-1234yf lists substances that are used or generated during production (including HCC-240db, HFC-245cb and u-HCFC-1233xf, see Annex A.5) and as such may remain in the final product (Nose & Komatsu 2014). However, this is a patent of the company Daikin, which is not allowed to produce u-HCFC-1234yf for patent reasons. This is reserved for Honeywell and Chemours only. In the patents of the two companies (Mukhopadhyay et al. 2009, Van Der Puy 2011) no measurement of the minor components is made. There are only data on other substances with more than two carbon atoms (6-10 % depending on the mixing ratio of the starting substances), but not for certain individual substances.

Recently, a risk analysis of current and potentially future important u-HFCs and u-HCFCs in refrigerant use was conducted as part of a study for the Norwegian Environmental Agency (Fleet et al. 2017). Discussions with scientists and gas producers revealed that refrigerants are generally of high purity, but that contamination with other HFCs, u-HFCs and u-HCFCs is a regular occurrence. Honeywell states that u-HFC-1234yf is contaminated with small amounts of HFC-134a and u-HFC-1225ye(Z) as well as other unidentified unsaturated fluorinated alkenes. According to the product specifications of a leading manufacturer of u-HFCs, the cumulative impurities should not exceed 40 ppm for unsaturated fluorinated alkenes and 150 ppm for u-HFC-1225ye(Z) (Fleet et al. 2017). However, some of the industry experts interviewed by Fleet et al. state that impurities only need to be identified and labelled if the concentration exceeds 1,000 ppm. The majority of impurities are non-reacted starting materials and are usually not further identified. Fleet et al. (2017) state further possible minor components in u-HCFC-1234yf, namely u-HCC-1140 (CH_2=CHCl) and u-HCFC-1131 (CH_2CFCl and/or trans-/cis-CHF=CHCl). Impurities with these substances can be up to 0.1 % by weight.

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[46] http://ahrinet.org/App_Content/ahri/files/STANDARDS/AHRI/AHRI_Standard_700-2016_with_Addendum_1.pdf (last access: 08.04.2020)

[47] http://www.ahrinet.org/App_Content/ahri/files/Product%20Section/AHRI_R_40_Contamination_white_paper.pdf (last acces: 08.04.2020)

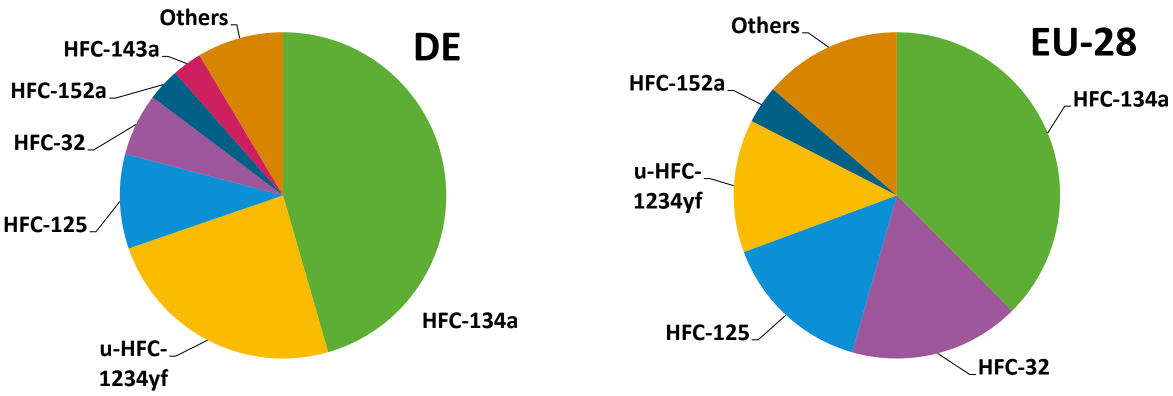
Long-chain perfluorinated substances such as perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), which are particularly hazardous due to their bioaccumulation and toxicity, have not been found as impurities in u-HFCs and u-HCFCs and, according to consultations with major producers, do not occur in the production of u-HFCs and u-HCFCs (Fleet et al. 2017).

2.5 Use of halogenated refrigerants and blowing agents

2.5.1 Application quantities of halogenated refrigerants and blowing agents

Since 2006, the use of HFCs has been restricted by law in the EU, currently by the EU F-gas Regulation. In 2018, HFC-134a was by far the most widely used substance in Germany with 46 % (Statistisches Bundesamt 2019) and in the EU with 38 % by mass of all reportable saturated and unsaturated HCFCs and HFCs (EEA 2019) (Figure 1). The input quantities of HFC-32 and HFC-125 and, to a much smaller extent, HFC-152a and HFC-143a are also relevant. The u-HFC-1234yf is the only unsaturated HFC that was used in larger quantities and reported individually. The u-HFC-1234ze is also statistically surveyed, but the quantities used are not publicly available. In the EU, the usage quantities of u-HFC-1336mzz, u-HCFC-1233xf and u-HCFC-1233zd are collected. This data is also confidential.

Figure 1: Distribution of use volumes of reportable saturated and unsaturated HCFCs and HFCs in Germany (DE)[48] and the EU-28 for 2018.[49]



Source: Statistisches Bundesamt (2019) and EEA (2019), own illustration, Öko-Recherche

The u-HFC-1234yf is primarily used in new vehicle air conditioning systems. The "Directive 2006/40/EC relating to emissions from air conditioning systems in motor vehicles" had already prohibited the use of refrigerants with a global warming potential above 150 in air conditioning systems of new types in passenger cars (class M1) and smaller car-like commercial vehicles (class N1, group 1) since January 1, 2011. Since January 1, 2017, the ban applies to all new vehicles in categories M1 and N1, Group 1. The previous refrigerant HFC-134a is still contained in existing vehicles. HFC-134a is also still used in cars intended for export outside the EU and in larger vehicles.

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[48] The mixtures reported for Germany were broken down into their individual components according to their mass proportions and added to the respective individual substances. However, not all data on individual substances and mixtures are publicly available. For Germany, the category "Other" includes substances with very low use volume, confidential substance quantities and confidential mixture quantities. The substances in "Others" for Germany are only partially identical to those in the group "Others" for the EU-28.

[49] The substances shown are partly used as single substances, but also in refrigerant mixtures (blends). In the figure, the proportions of the substances in the various mixtures have already been taken into account and included in the total quantity used.

The u-HFC-1234yf is also a component of some new refrigerant mixtures (e.g. R448A, R449A and R513A), which are used in increasing quantities.

Table 6 shows the shares of the individual HFCs and u-HFCs and u-HCFCs in the collected total use volume of all reportable HFCs, u-HFCs and u-HCFCs in Germany and the EU for 2016 and 2018.

Table 6: Usage quantities of reportable HFCs, u-HFCs and u-HCFCs in Germany[a] in 2016 (Statistisches Bundesamt 2018) and 2018 (Statistisches Bundesamt 2019) and the EU for 2016 (EEA 2017) and 2018 (EEA 2019). Under the heading "Other" all substances are subsumed which had a share of less than 1 % of the total amount used (only HFC, u-HFC and u-HCFC) or which were not used in public.

Substance name	Germany in tons 2016 (share of the total quantity)	Germany in tons 2018 (share of the total quantity)	EU in tons 2016 (share of the total quantity)	EU in tons 2018 (share of the total quantity)
HFC-32	344 (4 %)	490 (6 %)	11.022 (11 %)	14.647 (17 %)
HFC-125	841 (9 %)	744 (9 %)	18.701 (19 %)	12.938 (15 %)
HFC-134a	6.126 (69 %)	3.615 (46 %)	44.166 (45 %)	32.543 (38 %)
HFC-143a	464 (5 %)	232 (3 %)	7.205 (7 %)	confidential
HFC-152a	244 (3 %)	258 (3 %)	3.431 (4 %)	3.245 (4 %)
HFC-227ea	91 (1 %)	<1 %	1.754 (2 %)	1.387 (2 %)
Other HFCs[a]	274 (3 %)	680 (9 %)	5.296 (5 %)	4.124 (5 %)
u-HFC-1234yf	495 (6 %)	1.920 (24 %)	5.214 (5 %)	11.437 (13 %)
Other u-HFCs and u-HCFCs	see Table 9[b]	see Table 9[b]	1.091 (1 %)	6.314 (7 %)
Total	**8.879 (100 %)**	**7.936 (100 %)**	**97.880 (100 %)**	**86.708 (100 %)**

[a] For Germany, this quantity includes all u-HFCs and u-HCFCs except u-HFC-1234yf.

[b] This quantity is confidential and therefore not mentioned. However, there are data on this, based on expert estimates, which are listed in Table 9.

With almost half of the HFC, u-HFC and u-HCFC consumption in the EU and almost 70 % in Germany, HFC-134a had the highest share in 2016. As a single material, HFC-134a is still mainly used as a refrigerant in vehicle air conditioning systems and stationary refrigeration systems, as well as a foam blowing agent and aerosol propellant. This was followed by HFC-125 with a mass share of 19 % in the EU and 9 % in Germany (as a component of refrigerant mixtures). The third most used substance in the EU in 2016 was HFC-32, followed by HFC-143a, for Germany it is inversely. HFC-152a is also used relatively frequently, for example as a blowing agent for XPS foam and propellant for technical aerosols. HFC-227ea has only a very small share of the total amount used in Germany and the EU.

For 2016, a use quantity of 495 tons for Germany and 5,214 tons for the EU of u-HFC-1234yf was reported. These quantities are mainly used in pre-filled products, especially in vehicle air conditioning systems. The u-HFC-1234ze is also statistically surveyed, but its usage quantities are not publicly available as separate data. For the EU in 2016, total use quantities of 1,091 tonnes of u-HFC-1234ze, u-HFC-1336mzz, u-HCFC-1233zd and u-HCFC-1233xf have been reported. This amount is also primarily contained in prefilled products. The data of the individual substances are confidential.

By 2018, the share of HFC-134a had declined noticeably, by 7 % in the EU and by as much as 23 % in Germany. In contrast, the amount of u-HFC-1234yf used rose sharply, especially in Germany. While an increase of 8 % was recorded in the EU, the reported amount in Germany increased fourfold.

For Germany and the EU in 2016 and 2018, Table 7 shows the used quantities of fluorinated greenhouse gases subject to reporting requirements by application areas as published by the Federal Statistical Office on the basis of the German Environmental Statistics Act (UStatG) (Statistisches Bundesamt 2018 & 2019) and the EEA reports on fluorinated greenhouse gases (EEA 2017 & 2019).

Table 7: Quantities of use of reportable fluorinated greenhouse gases (including mixtures) in the various applications and their share of the total quantity used in Germany 2016 (Statistisches Bundesamt 2018) and 2018 (Statistisches Bundesamt 2019) and the EU-28 2016 (EEA 2017) and 2018 (EEA 2019).[a]

Application	Use in Germany 2016 (tonnes)	Use in Germany 2018 (tonnes)	Use in the EU 2016 (tonnes)	Use in the EU 2018 (tonnes)
Refrigerant	6,730 (75 %)	6,214 (77 %)	77,998 (78 %)	65,190 (74 %)
Blowing agent for Foams	1,434 (16 %)	1,193 (15 %)	10,157 (10 %)	10,530 (12 %)
Propellant for aerosols	624 (7 %)	520 (7 %)	8,728 (9 %)	8,744 (10 %)
Others	186 (2 %)	109 (1 %)	3,150 (3 %)	3,177 (4 %)
Total	**8,974[b] (100 %)**	**8,036[c] (100 %)**	**100,032[d] (100 %)**	**87,640[e] (100 %)**

[a] For the EU, the total amount used includes HFCs, u-HFCs, u-HCFCs, PFCs, HFEs, alcohols, SF6 and NF3 and other perfluorinated substances. For Germany, however, only HFCs, u-HFCs and PFCs.

[b] In 2016, the use of 95.3 tonnes of PFC was reported for Germany. HFC and u-HFC quantities together amount to 8,879 tonnes.

[c] In 2018, the use of 97.9 tonnes of PFCs was reported for Germany. HFC and u-HFC quantities together amount to 5,651 tonnes.

[d] In 2016, the use of 97,880 tonnes of HFCs, u-HFCs and u-HCFCs was reported for the EU.

[e] In 2018, the use of 86,708 tonnes of HFCs, u-HFCs and u-HCFCs was reported for the EU.

With regard to the different application sectors, it can be seen that the use of HFCs as refrigerants was the most relevant in 2016 and 2018 both in Germany and in the EU. In both years, HFCs accounted for approximately three quarters of the total amount of fluorinated greenhouse gases used in Germany and the EU. The HFC quantity for Germany in 2016 also includes 495 tonnes of u-HFC-1234yf for passenger car air conditioning systems, with 99 % of the quantity being used for the first filling of new air conditioning systems. Based on our own research, we assume that the total use of HFCs, u-HFCs and PFCs was greater.[50] In 2018, the quantity of u-HFC-1234yf used for the first filling of passenger car air conditioning systems rose to 1,786 tonnes (Statistisches Bundesamt 2019).

In quantitative terms, the use of halogenated substances as foam blowing agents is much less important, with extruded polystyrene (XPS) accounting for the largest proportion in Germany in 2018 with 77 % (Statistisches Bundesamt 2019). This is followed by its use as a propellant for medical and

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[50] The statistics for use in Germany only take "packaged goods" into account. This means that the quantities imported by HFC-filled products are not included. The 390 tonnes of u-HFC-1234yf contained in air conditioning systems of imported cars in 2016 were therefore not included in the statistics, although they were "used" in Germany: Warncke et al (2017).

technical aerosols and finally all other applications, including fire extinguishing agents, working materials for ORC systems and solvents.

In addition, approximately 180 tonnes of hydrofluoroethers (HFE) were used for anaesthesia in Germany in 2018 (Warncke et al. 2020). Since they are not yet covered by the German Environmental Statistic Law, they are not included in Table 7. In the EU F-gas reporting, however, they are included but are not listed individually for reasons of confidentiality.

2.5.1.1 Use of unsaturated halogenated refrigerants and blowing agents in mixtures

The HFCs, u-HFCs and u-HCFCs listed in Table 6 are not only used as individual substances but also as part of refrigerant mixtures. Thus, the EU figures in Table 6 refer to applications of HFCs, u-HFCs and u-HCFCs in single substances and mixtures. In EU reporting, mixtures are not listed separately, but calculated separately according to the substances they contain. For example, 10 tonnes of the mixture R404A is separated according to its HFC content (44 % HFC-125, 4 % HFC-134a, 52 % HFC-143a) and the individual HFC quantities (4.4 tonnes of HFC-125, 0.4 tonnes of HFC-134a, 5.2 tonnes of HFC-143a) are added to the quantities reported as individual substances.

In Germany, HFCs, u-HFCs and u-HCFCs are only treated as single substances, mixtures are listed separately. For Germany it is therefore possible to quantify the proportion of the mixtures in the total quantity. In 2016 the share of mixtures was 23 % of the total quantity of 8,879 tonnes of HFCs and u-HCFCs (Statistisches Bundesamt 2018). HFC-32, HFC-125 and HFC-143a were used almost exclusively in mixtures and only to a small extent as single substances. For HFC-143a, for example, the use as a single substance was only 0.9 %. In contrast, more than 90 % of the total amount of HFC-134a is used as a single substance.

Due to the reduced quantities of halogenated greenhouse gases available on the EU market, as a consequence to the EU F-gas Regulation and the upcoming bans on refrigerants with high GWP and against the background of the Kigali Decision, substances and mixtures with lower global warming potentials are increasingly being developed and marketed. In particular, the refrigerants R404A (GWP 3,922), R407C (GWP 1,744) and R410A (GWP 2,088), which together account for 81 % of all mixtures used in Germany[51] (Statistisches Bundesamt 2018), are to be replaced. This share decreased to 59 % in 2018 (Statistisches Bundesamt 2019), mainly due to a decrease in the use of R404A from 794 tonnes in 2016 to 412 tonnes in 2018. However, the total amount of mixtures used in Germany increased by 208 tonnes during this period. This is mainly due to the increasing use of newer mixtures with lower GWP, especially R449A, which in 2018 with 441 tonnes already accounted for 19 % of all mixtures used in Germany.

Table 8 shows the HFCs and u-HFCs currently used in relevant quantities in older and newer mixtures. The selection of these substances is mainly based on the mixtures that are already commercially available or are currently in the test phase or certification phase by ASHRAE (TEAP 2016) and have become known by March 2020.

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[51] R404A: 38 %, R407C: 21 %, R410A: 21 % (the total results in only 80 % due to rounding errors)

Table 8: List of HFCs and u-HFCs currently used in relevant quantities as single substances and in older and newer mixtures (status: March 2020).

	GWP	Substance fractions
Older mixtures		
R404A	3,922	HFC-125 (44 %), HFC-134a (4 %), HFC-143a (42 %)
R407C	1,744	HFC-32 (23 %), HFC-125 (25 %), HFC-134a (52 %)
R410A	2,088	HFC-32 (50 %), HFC-125 (50 %)
Newer mixtures		
R448A	1,387	HFC-32 (26 %), HFC-125 (26 %), HFC-134a (21 %), u-HFC-1234yf (20 %), u-HFC-1234ze(E) (7 %)
R449A	1,397	HFC-32 (24,3 %), HFC-125 (24,7 %), HFC-134a (25,7 %), u-HFC-1234yf (25,3 %)
R450A	605	HFC-134a (42 %), u-HFC-1234ze(E) (58 %)
R452A	2,140	HFC-32 (11 %), HFC-125 (59 %), u-HFC-1234yf (30 %)
R452B	698	HFC-32 (67 %), HFC-125 (7 %), u-HFC-1234yf (26 %)
R455A	148	HFC-32 (21,5 %), u-HFC-1234yf (75,5 %)
R466A	733	HFC-32 (49 %), HFC-125 (11,5 %), CF_3I (39,5 %)
R513A	631	HFC-134a (44 %), u-HFC-1234yf (56 %)
R514A	13	u-HFC-1336mzz(Z) (74,7 %), HCC-1130(E)[a] (25,3 %)

[a] Trans-1,2-dichlorethene (CHCl=CHCl)

Newer mixtures often achieve a lower GWP by combining classical refrigerants with high GWP[52] (e.g. HFC-125 or HFC-134a) with unsaturated compounds from the group of u-HFCs and u-HCFCs. For example, the mixture R449, which is marketed by Chemours as a substitute for R404A, has a GWP of 1,397, due to the low GWP of the u-HFC-1234yf contained in the mixture. Honeywell offers the R448 compound as a replacement for R404A with a similar GWP of 1,387. In addition to u-HFC-1234yf, a smaller amount of u-HFC-1234ze(E) is also contained here.

Although R448 and R449 have a significantly lower GWP than R404A, which they are intended to replace, both mixtures can only be regarded as a medium-term solution due to their still comparatively high GWP. The reason for this is the relatively large proportion (about half of the mixture) of HFC-125 and HFC-134a, which have a high GWP of 3,500 and 1,430, respectively. In order to reduce the GWP of the mixture significantly, more unsaturated HFC would have to be added[53].

However, the addition of u-HFC causes problems. Although the GWP decreases with increasing amounts of unsaturated substances, since unsaturated substances are degraded much faster in the atmosphere than saturated substances due to their double bond (Hurley et al. 2008). At the same time, however, the flammability of the mixture increases. Older mixtures are generally classified as non-flammable and therefore in safety class 1 according to ISO 817 (ISO 2014, 2017) and ASHRAE Standard 34 (ASHRAE 2016, 2018). In contrast, newer mixtures containing u-HFCs with a low GWP of less

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[52] This report follows the classification of GWP levels by the RTOC (UNEP 2015): ultra-low or negligible <30, very low <100, low <300, medium 300-1000, high >1000, very high >3000, ultra-high >10.000.

[53] A low GWP of a mixture can also be achieved by adding hydrocarbons (e.g. isobutane, R600a). However, these substances are not halogenated and thus lie outside the scope of this report.

than 300 are usually classified in class 2L (lower flammability with low flame speed)[54]. Due to their flammability, new challenges arise when dealing with refrigerant mixtures, especially for ensuring plant safety by technical personnel.

To address the problem of flammability, Honeywell is seeking to launch a new mixture (R466A) containing trifluoroiodomethane (CF_3I, sometimes referred to as trifluoro-iodomethane, CF_3J) in addition to HFC-125 and HFC-32[55]. R466A has been certified by ASHRAE and classified in safety class 1 (non-flammable)[56]. The reason that R466A is not flammable is the addition of a not inconsiderable amount of CF_3I, which is also used as a flame retardant (McCain & Macko 1999). Due to its ODP of 0.01 to 0.02, CF_3I is listed in Annex II of the European Regulation on Substances that Deplete the Ozone Layer (EC No. 1005/2009), so its production, import and export are subject to reporting. It remains to be seen to what extent this mixture will prevail. In addition to the ODP of CF_3I, the mixture still has a rather high GWP of 733[57]. Furthermore, there are probably health risks such as mutagenicity [58,59], and possibly other problems. Honeywell already tried to develop CF_3I in a mixture with u-HFC-1234yf under the name "Fluid H", ready for the market in the time around 2007[60], which, however, failed due to material compatibility and stability problems[61].

Non-flammable mixtures with small GWP could also be produced by using chlorinated unsaturated compounds such as u-HCFCs, but would have the disadvantage of a (small) ODP. So far, no mixtures with u-HCFCs are known on the market (as of March 2020).

2.5.1.2 Inventory of unsaturated halogenated refrigerants and blowing agents in Germany

In Germany, u-HFCs have been in use since 2012: Initially mainly as a propellant in foam production, in technical aerosols and in the mobile air conditioning of cars. Since 2014/2015 they have also been used in refrigerant mixtures for stationary applications (Table 9).

Table 9 shows that the stock of u-HFC-1234yf in 2018 was more than 25 times as high as in 2014. Most of these quantities were used for the initial filling of air conditioning systems in passenger cars produced in Germany. The use in passenger car air conditioning systems also has the highest growth potential for the future, especially since the quantities needed to replenish the inventory losses of the entire fleet of passenger cars equipped with u-HFC-1234yf are being added and are slowly increasing. It should be noted that the figures in Table 9 refer to the stock in a specific year, while those in Table 6 refer to consumption during one year. The stock is the existing quantity of gas that is influenced by previous years, for example in the form of stored quantities. Consumption is only the quantity used in one year and is usually less than the stock for that year. For u HFC-1234yf, 495 and 1,920 tonnes were used in 2016 and 2018, respectively (Table 6), but the inventory was significantly higher in these years at 1,332 and 5,042 tonnes, respectively (Table 9).

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[54] http://www.unep.fr/ozonaction/information/mmcfiles/7679-e-International_Standards_in_RAC.pdf (last access: 10.08.18)

[55] https://www.coolingpost.com/world-news/secret-of-honeywells-new-refrigerant/ (last access: 10.08.18)

[56] https://www.coolingpost.com/world-news/ashrae-confirms-r466a-as-non-flammable-a1/ (last access: 10.01.20)

[57] https://www.coolingpost.com/world-news/secret-of-honeywells-new-refrigerant/ (last access: 10.08.18)

[58] https://echa.europa.eu/de/registration-dossier/-/registered-dossier/24892 (last access: 10.08.18)

[59] Classification trifluoroiodomethane: H341: May probably cause genetic defects. (http://gestis.itrust.de/nxt/gateway.dll/gestis_de/000000.xml?f=templates$fn=default.htm$vid=gestisdeu:sdbdeu$3.0, last access: 10.09. 2018)

[60] http://docplayer.net/15419428-Update-on-a-low-gwp-refrigerant-fluid-h.html (last access: 10.09. 2018)

[61] https://www.honeywell-refrigerants.com/europe/wp-content/uploads/2013/03/honeywell-solstice-yf-technical-bulletin.pdf (last access: 10.09. 2018).

Table 9: Stock of u-HFC-1234yf and u-HFC-1234ze(E) as single substance and in mixtures in various applications since 2012 in Germany in tonnes (only u-HFC, without HFC in mixtures). Survey by Öko-Recherche for the German Federal Environment Agency. Deviations from reported data possible. Sources: unpublished data from inventory survey & Warncke et al. (2017, 2020).

Application	2012	2013	2014	2015	2016	2017	2018
u-HFC-1234yf							
Car air conditioning	9.3	58.2	15.6	33.9	1,284.6	2,986.9	4,715.3
Supermarkets (R448A, R449A)	-	-	2.1	10.2	37.7	136.3	271.7
Refrigerated vehicles (R452A)	-	-	-	1.7	9.6	25.2	54.9
Total	**9.3**	**58.2**	**17.7**	**45.8**	**1,331.9**	**3,148.4**	**5,041.9**
u-HFC-1234ze(E)							
Supermarkets (R448A)	-	-	<0.1	0.2	2.1	9.1	18.9
Turbo compressor, XPS and technical aerosols[62,63]	-	23.7	45.7	73.6	101.9	193.9	298.6
Total	**-**	**23.7**	**45.7**	**73.8**	**104.0**	**203.0**	**317.5**
Total quantity used	**9.3**	**81.9**	**63.4**	**119.6**	**1,435.9**	**3,351.4**	**5,359.4**

Compared to u-HFC-1234yf, u-HFC-1234ze(E) had a smaller usage quantity (317.5 tonnes), which was mainly used for the production of XPS insulation materials, which a German producer uses as a substitute for HFC-152a. Here, too, there is a steady increase in the amount used over the years, with deviations.

The use of u-HFCs in newer refrigerant mixtures (R448A, R449A and R452A) has also shown a moderate increase in recent years. Refrigerant mixtures with u-HFCs or u-HCFCs did not yet play a major role in Germany with <4 % of all mixtures used in 2016 (Statistisches Bundesamt 2018), whereas this proportion has already risen to at least 19 %[64] in 2018 (Statistisches Bundesamt 2019). The two mixtures R448A and R449A with a relatively high GWP of about 1,390 were used exclusively for the conversion of existing R404A plants (GWP 3,922).

2.5.2 Emissions of halogenated refrigerants and blowing agents

The application quantities considered in the previous Chapter 2.5.1 provide information about the applications and the type of halogenated refrigerants and blowing agents. These serve as a basis for the calculation of the emissions into the atmosphere from which degradation products are later formed.

During the entire "life cycle" of products filled with halogenated refrigerants and blowing agents – namely production, use and disposal - emissions occur that contribute to the destruction of the ozone

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[62] In the case of technical aerosols, it is not the inventory but the consumption for the first filling that is assumed here, since the substances regularly emit during consumption.

[63] For reasons of confidentiality, these sectors are grouped together.

[64] Only R449A is mentioned by the German Federal Statistical Office in its public report for 2018 (Statistisches Bundesamt 2018). There are, however, other mixtures containing u-HFCs (especially R448A, R513A, R450A and R452A), without quantities that are available publicly, but which experts estimate will certainly be used in Germany in 2018. The proportion of mixtures containing u-HFCs in Germany is more likely to be around 25 %.

layer and/or global warming, and, entering the atmosphere, are exposed to rapid or slow degradation processes.

The emission shares of production (filling), use (inventory) and disposal in the total emissions differ considerably depending on the application and especially on whether the systems are open or closed. The highest emissions of refrigerants occur during use (Table 10). For aerosols, inventory emissions account for 99 % of total emissions. Emissions from the initial filling of refrigeration and air conditioning systems account for approximately 1 % of emissions. In the production of XPS insulation materials, approx. 30 % of the blowing agent emissions are released during the entire life cycle and 35 % in the use phase; for PU foams, 10 % are released during production and 50 % from the use phase (1 % in each year of the life cycle). Assuming a life cycle of 50 years for foam/insulation materials, 35 % to 40 % of blowing agents remain at the end of their life cycle for which there is no recovery to date.

Table 10: Shares of emissions from the three phases of the "life cycle" of total emissions by application from the reporting for the German Federal Environment Agency in percent for the year 2015. Source: Warncke et al. (2016).

Application	Production/Filling	Inventory/use phase	Disposal
Refrigeration and air conditioning	1 %	90 %	9 %
PU foams	10 %	50 %	40 %
XPS insulation materials	30 %	35 %	35 %
Aerosols	1 %	99 %	0 %

The estimated annual emissions of HFCs from all applications in Germany in 2018 were approximately 6,100 metric tonnes (Warncke et al. 2020). The major part, approx. 4,700 tonnes (77 %), are refrigerant emissions. Regarding the emissions of u-HFCs from refrigeration and air conditioning applications in Germany, data are available for Germany (not for the EU) until 2018 (Table 11). (Status: March 2020)

Disposal emissions for the vehicles filled with u-HFC-1234yf are not yet generated, as these vehicles have only been in use since 2012 and have therefore not yet reached the end of their service life.

Total emissions of u-HFC-1234yf and u-HFC-1234ze(E) were already more than 10 times higher in 2018 than in 2014, at 597 tonnes (Table 11). With 514 tonnes in 2018, u-HFC-1234yf was emitted significantly more than u-HFC 1234ze(E) with 83 tonnes. The majority of u-HFC-1234yf emissions came from car air conditioning systems (482 tonnes, 94 %).

Table 11: Total emissions of HFC-1234yf and u-HFC-1234ze(E) in stationary and mobile applications in Germany in tonnes for the years 2012 to 2018 -, no data available. Source: Warncke et al. (2017, 2020).

	2012	2013	2014	2015	2016	2017	2018
u-HFC-1234yf							
Car air conditioning	0.9	5.8	15.7	33.9	131.4	311.0	482.3
Supermarkets (R448A + 449A)	-	<0.1	0.2	1.1	4.5	15.9	30.1
Refrigerated vehicles (R452A)	-	-	-	<0.1	0.4	0.9	1.9
Total emissions	**0.9**	**5.9**	**15.9**	**35.1**	**136.3**	**327.8**	**514.3**
u-HFC-1234ze(E)							
Supermarkets (R448A)	-	-	-	<0.1	0.2	0.9	1.7
Turbo compressor, XPS and technical aerosols[a]	-	34.4	38.8	36.9	44.4	74.2	81.0
Total emissions	**-**	**34.4**	**38.8**	**37.0**	**44.6**	**75.1**	**82.7**
Total emissions of u-HFC-1234yf and u-HFC-1234ze(E)	**0.9**	**40.3**	**54.7**	**71.9**	**180.5**	**402.9**	**597.0**

[a] For reasons of confidentiality, these sectors are grouped together.

2.5.3 Emissions from the production of u-HFC-containing products in Germany

As already explained in Chapter 2.5.1, emissions are not only generated during the use of a product, but also during its production. During production, substances are either filled in, introduced as part of the final product (e.g. technical aerosols) or removed from the product in a test procedure (e.g. after leakage tests in the production of air conditioners). Even if all measures to prevent leakage are included, a small amount of chemicals can still be released. These emissions are referred to as manufacturing emissions.

In general, the emission factors for the manufacture of mass products such as household and commercial refrigerators and freezers, split air conditioners, etc. are below 5 % (Schwarz et al. 2013). General estimates of emission factors for manufacturing are in the range of 1-2 % per unit.

As Table 12 shows, emissions from production have almost doubled since 2013. Due to the sharp increase in the use of u-HFC-1234yf in passenger car air conditioning systems and the associated filling, emissions from this area will increase significantly. The emissions from passenger car production are assumed to be very low at 0.003 kg per vehicle, so despite the high amount of u-HFC-1234yf used, total production emissions are relatively low. The opposite is true for foam production, where manufacturing emissions of 30 % are generated, which is why very high emissions are released in comparison to the amount of u-HFC-1234yf used.

Table 12: Emissions of u-HFCs from the production of u-HFC-filled appliances in Germany in tonnes from 2013 to 2018. For the year 2012, there were no manufacturing emissions for u-HFC-1234yf, since passenger cars with u-HFC-1234yf were imported into Germany before 2013 but no domestic production took place yet. -, No data available. Source: Warncke et al. (2017, 2020).

Year	2013	2014	2015	2016	2017	2018
u-HFC-1234yf						
Car air conditioning	<0.1	<0.1	<0.1	2.97	12.31	10.76
Supermarkets (R448A, 449A)	<0.1	<0.1	<0.1	0.3	1.2	1.6
Refrigerated vehicles (R452A)	-	-	<0.1	<0.1	<0.1	<0.1
Total emissions	**<0.1**	**<0.1**	**<0.1**	**3.3**	**13.6**	**12.5**
u-HFC-1234ze(E)						
Supermarkets (R448A)	-	-	<0.1	<0.1	<0.1	0.1
Turbo compressors, XPS and technical aerosols[a]	34.2	38.1	34.4	41.6	56.6	56.7
Total emissions	**34.2**	**38.1**	**34.5**	**41.7**	**56.7**	**56.8**
Total emissions of u-HFC-1234yf and u-HFC-1234ze(E)	**34.3**	**38.2**	**34.6**	**45.0**	**70.3**	**69.3**

[a] For reasons of confidentiality, these sectors are grouped together.

2.5.4 Niche applications of u-HFCs and u-HCFCs

In addition to the main applications (refrigeration and air conditioning systems, blowing agents for PU and XPS insulation materials etc.), u-HFCs and u-HCFCs can be used in many other niche applications. In some cases, special technical requirements must be met. The distinction between main applications and niche applications is not clear and therefore cannot be clearly defined.

Identified niche applications are the use of u-HFCs and u-HCFCs as propellants in technical and other aerosols in various sprays for the refrigeration and compressed air industry, in cosmetic products, in household products or for the maintenance of pressure expansion vessels (for heating and solar collector systems) (Table 13). Currently, applications use u-HFC-1234ze(E) and mixtures containing this substance.

However, no data on usage quantities are currently available. Examples of use - without claiming to be complete - are given in Table 13. Whether further applications with u-HFCs or u-HCFCs will be used in the near future cannot be assessed at this time. A list of the identified product names can be found in Table A 3 in Annex A.6.

Table 13: Application examples for niche applications of u-HFCs and u-HCFCs as propellants or technical gases.

Market segment	Category	Substance	Examples of use in niche applications
Fine Chemicals	Aerosol formulation (propellant gas) for technical sprays for industrial purposes (2 hits)	u-HFC-1234ze as well in blend: u-HFC-1234ze/HFC-134a	Troubleshooting of electronic components as well as assembly and disassembly of fitting parts (printed circuit boards and semiconductors)
Technical sprays for industrial purposes	Cold spray (4 hits)	u-HFC-1234ze, concentrations up to 100 %	Troubleshooting of electronic components as well as assembly and disassembly of fitting parts (printed circuit boards and semiconductors)
Technical sprays for industrial purposes	Cooling spray (3 hits)	u-HFC-1234ze	Test circuits, heat dissipation during soldering or desoldering
Technical sprays for industrial purposes	Compressed air spray (9 hits)	u-HFC-1234ze	Precision cleaner
Technical sprays for industrial purposes	Compressed air spray (9 hits)	u-HFC-1234ze	Dust removal from electronic components
Technical sprays for industrial purposes	Compressed air spray (9 hits)	u-HFC-1234ze/ dimethyl ether	Dust removal from electronic components
Technical sprays for industrial purposes	Compressed air spray (9 hits)	u-HFC-1234ze as replacement for HFC-134a, u-HFC-1234ze alone or u-HFKW-1234ze blended with up to 10 % HFC-134a is used.	For checking and supplementing the pressure cushion of expansion vessels in heating and tank technology.
Sprays with biological active ingredients	Propellant gas	u-HFC-1234ze as replacement for HFC-134a in Europe	Aircraft insecticide
Cosmetic sprays	Propellant for barrier spray (1 hit)	u-HFC-1234ze	Skin protection products
Cosmetic sprays	Propellant gas for hair mousse spray (1 hit)	u-HFC-1234ze	Hair mousse

It has been shown that the use of u-HFCs and u-HCFCs as a propellant for sprays represents a wide range of applications, especially in products that previously contained HFC-134a.

Technical sprays are used especially in trade, industry and handicraft and are used for maintenance, care, repair in the construction industry, the automotive industry, in household products as well as other industries and handicraft. The largest proportion in terms of volume is accounted for by cold sprays and compressed air sprays.

Cold sprays with various propellants and gas mixtures are used for cooling on the most diverse material surfaces, for troubleshooting (temperature-dependent) electronic components and for the assembly and disassembly of fitting parts. Problems can arise from the fact that electrostatic charging can occur during spraying due to the ingredients and the aerosol can ignite. For this reason, cold sprays that are used on electronics in operation must be tested for safety in accordance with the aerosol directive 75/324/EEC[65,66].

Compressed air sprays are used to de-dust precision mechanics and electronic components (precision cleaners). Another field of application is the refilling of membrane pressure expansion vessels in heating systems.

Furthermore, particles that are hollow inside are used as vectors for active pharmaceutical ingredients. Active pharmaceutical ingredients are introduced into the hollow spaces and slowly diffuse out of them in the body. Products for household, body, car care as well as food and medication are also offered as sprays.

HBFC-1233xfB (2-BTP, $CF_3CBr=CH_2$, 2-bromo-3,3,3-trifluoropropene)[67], which is being discussed as a substitute for halon-1211, which is still used as a fire extinguishing agent in the aircraft industry, has not been used in the EU to date.

In order to obtain specific data for Germany and the EU on the use in processes or the inventory of products, publicly available statistics were used. There is no information available on production figures, the content of u-HFCs and u-HCFCs in products, the resulting waste streams and recycling processes, and information on emissions during the waste phase. Based on the search hits according to Table A 1 in Annex A.2, it can be concluded that u-HFC-1234ze(E) is currently being increasingly used in aerosols.

According to the expert interviews conducted so far, there is no information available on the potential of u-HFCs and u-HCFCs as propellants in spray cans. A quantification of emissions caused by the use of these substances in sprays could not be made due to the lack of production figures, application quantities and concentrations.

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[65] http://www.bmas.de/DE/Themen/Arbeitsschutz/Produktsicherheit/aerosolpackungen.html (last access: 28.03.2020)

[66] http://www.bmas.de/SharedDocs/Downloads/DE/Thema-Arbeitsschutz/richtlinie-75-324-ewg.pdf;jsessionid=531C73A36911940883F45DAE684BF60C?__blob=publicationFile&v=1 (last access: 28.03.2020)

[67] https://www.epa.gov/sites/production/files/2016-03/documents/snap_action_factsheet.pdf (last access: 28.03.2020)

2.6 Destruction of halogenated refrigerants and blowing agents

The destruction of halogenated greenhouse gases must be reported in the EU according to the EU F-gas Regulation. Since 2007, this includes all PFCs and HFCs listed in Annex I to the Regulation and since 2014 also the u-HFCs and u-HCFCs listed in Annex II. The destruction of F-gases has increased steadily in almost all years since 2008, but decreased sharply in 2016 by slightly more than half of the previous year, to about 620 tonnes, and then rose again to about 670 tonnes by 2018 (EEA 2019). With 97 %, HFCs had by far the largest share of the destroyed quantity of fluorinated gases in the EU in 2018.

Since the service companies or end users did not deliver the refrigerants for disposal by type but as mixtures, in the past it was rarely possible to distinguish between individual HCFCs and HFCs from the return of used refrigerants. It is to be assumed, however, that due to the ban on the use of virgin HCFCs as refrigerants since 2010 and of recycled HCFCs since 2015, higher quantities of these substances have also been disposed of for destruction during this period.

The rising prices for virgin HFCs in recent years have also led to an increase in the importance of recycling and reclamation of HFCs, especially of mixtures with high greenhouse potential such as R404A, but also of HFC-134a. The recovery of refrigerants by type is a prerequisite for efficient recycling and reclamation. As a result, more precise information on the quantities of refrigerants recovered for reclamation and destruction has recently become available.

The most important substance in terms of quantities destroyed in Europe is, according to our current state of knowledge, HFC-23 (see Chapter 2.4.1). In the EU in 2018, it accounted for approx. 50% of the destroyed quantities, based on all HFCs (EEA 2019). The destruction of HFC-23 has been practiced in the EU for years and has led to greatly reduced emissions of this HFC since the 1990s (Schwarz et al. 2011). Some applications of HFC-23 have been important for a long time[68], while HFC-23 is still produced in Europe primarily as a by-product of HCFC-22 production[69]. The EU F-gas Regulation (Article 7) now requires that the destruction of HFC-23 from production processes must be reported using best available techniques.

2.6.1 Unintentional destruction

In addition to the intentional destruction of halogenated refrigerants and propellants, there is also the possibility of unintentional destruction, e.g. in industrial or car accidents, on hot surfaces or in fires.

Only hexa- and pentafluoropropenes are clearly non-flammable. The tetrafluoropropenes are typically on the borderline between flammability and non-flammability (Lindley & Noakes 2010), except, e.g. u-HFC-1234yf, which is flammable. According to the data sheet, u-HFC-1234yf has a self-ignition temperature of 405 °C and an explosion range of 6.2 to 12.3 volume % (Honeywell safety data sheet[70]). For

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[68] For example, as a fire extinguishing agent (mainly as a replacement for halon-1301) and etching gas in the semiconductor industry. HFC-23 is still used in small quantities as a low temperature refrigerant.

[69] According to expert information, HFC-23 is a by-product of the production of HCFC-22, accounting for approximately 2 %. The larger part of the HFC-23 is collected and destroyed in the plant. A smaller part of the collected quantity is sold as raw material. HFC-23 is used as an intermediate product in the production of bromine trifluoromethane ($CBrF_3$, halon 1301), which in turn is used as a feedstock in the production of the biocide Fipronil.

[70] http://www51.honeywell.com/sm/lgwp-it/common/documents/msds-documents/FP_LGWP_IT_HFO-1234yf_it_MSDS.pdf (last access: 21.09.2018)

transport and storage based on the harmonized classification procedure, u-HFC-1234yf is classified as an extremely flammable gas (category 1)[71] (Regulation (EC) No 1272/2008 (CLP)[72]).[73]

The issue of flammability and the resulting reaction products have been the subject of intense discussion, especially for **u-HFC-1234yf**, since it was proposed as a refrigerant for passenger car air conditioning systems in 2007. Meanwhile, u-HFC-1234yf is used worldwide in passenger car air conditioning systems and in mixtures as a replacement for the non-flammable HFC-134a. Due to its flammability, the refrigerant u-HFC-1234yf is not only an additional ignition source in the crash area of passenger cars, but also in stationary systems, during re-filling of systems, in the workshop and during disposal. There exist no special statistics on the cause of fires for this in Germany.

Among others, the German Federal Institute for Materials Research and Testing (BAM) tested the fire behaviour of u-HFC-1234yf in application-oriented tests. These tests showed that u-HFC-1234yf is flammable in several scenarios and at temperatures such as those encountered in cars, and that dangerous quantities of hydrogen fluoride (HF) are formed during combustion and in contact with hot surfaces (BAM 2010, UBA 2010a).

The vehicle manufacturer Daimler AG carried out special tests with passenger cars on the fire behaviour of u-HFC-1234yf in 2012 in order to safeguard the use as a refrigerant. These tests simulated the leakage of refrigerant in the engine compartment during real driving. It was shown that even after small amounts of u-HFC-1234yf have leaked when the engine is hot, an ignition with HF formation can occur and lead to vehicle fire. In more than two thirds of the tests, ignition occurred. Comparable tests with HFC-134a showed no ignition (VDA 2012). As a result, certain models with newly developed air conditioning systems were equipped with the non-flammable refrigerant carbon dioxide (CO_2, R744) or with extinguishing devices. Daimler cited the higher ignition potential of u-HFC-1234yf compared to HFC-134a as the reason for this (Daimler 2015).

In 2013, the German Federal Motor Transport Authority (KBA), in its function as a market surveillance authority, carried out orienting tests on four passenger cars on the flammability of u-HFC-1234yf and the associated HF exposure in car air conditioning systems (KBA 2013). In the frequent cases used to evaluate product safety and derived from accident situations, the KBA did not identify any serious danger with regard to ignition and critical HF formation. In scenarios to validate the results, the KBA measured dangerous amounts of hydrofluoric acid (HF) in the event of fire and the emission of u-HFC-1234yf when the engine was hot without any discernible flame formation. Further tests were strongly recommended by the KBA. The EU Commission did not follow this recommendation (European Commission Joint Research Centre 2014)[74].

Hydrofluoric acid (also called fluoric acid), the aqueous solution of hydrogen fluoride, is a highly corrosive acid. Skin or mucous membrane burns with hydrofluoric acid often proceed apparently harmlessly without warning pain; pain only occurs after hours or days. Very poorly healing, painful ulcers then form on the skin and mucous membranes. Burns, the size of the palm of the hand, can cause death if medical assistance is not immediately provided. Even exceeding the inhalation of 95 ppm hydrogen

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[71] https://echa.europa.eu/de/information-on-chemicals/cl-inventory-database/-/discli/details/15639 (last access: 21.09.2018)

[72] https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:353:0001:1355:EN:PDF (last access: 21.09.2018)

[73] Due to a formal amendment to the CLP Regulation, the classification of u-HFC-1234yf will be "flammable gas (category 1B)" from 17 October 2020 (Regulation (EU) 2019/521) https://eur-lex.europa.eu/legal-content/DE/TXT/PDF/?uri=CELEX:32019R0521 (last access: 21.09.2018)

[74] A critical evaluation of the EU-process was performed by the German Federal Environment Agency (UBA 2014).

fluoride (HF) for an exposure time of 10 minutes (severity level AEGL-2[75]) leads to irreversible damage to human health. Inhalation of approx. 100 ppm HF over a period of 30 to 60 minutes can be fatal (LMU 2018).

According to studies by Feller et al (2014), the combustion of u-HFC-1234yf produces not only hydrogen fluoride but also the toxic **carbonyl fluoride (COF_2)**. Carbonyl fluoride reacts very quickly with water to form hydrofluoric acid and CO_2. This reaction can also occur when COF_2 is inhaled through the humid mucosa of the respiratory tract, whereby the resulting hydrofluoric acid is absorbed by the body. Contact with skin, eyes or mucous membranes causes severe irritation.[76] The greatest risk potential is the inhalation of carbonyl fluoride. A recent publication by Januszkiewicz et al. (2018) reports on short-term inhalation tests on rats and concludes that COF_2 is even more toxic than hydrogen fluoride and almost 45 times more lethal. Carbonyl fluoride should therefore be considered in the risk analyses for u-HFC-1234yf in car air conditioning systems.

The **u-HFC-1234ze(E)** is also flammable. Although u-HFC-1234ze(E) is declared non-flammable in safety data sheets, this only applies to transport and storage based on the globally harmonized classification procedure (CLP 2008), for which the flammability is tested at 20 °C. But already at about 30 °C, u-HFC-1234ze(E) has an explosion limit. In addition, an explosion range starts to develop at about 10 % humidity already at 23 °C (Kondo et al. 2012). For classification as a refrigerant according to the ISO 817 standard, the higher reference temperature of 60 °C (ISO 2014, 2017) applies. At this temperature u-HFC-1234ze(E) is flammable and the refrigerant is therefore classified in the same safety group A2L as u-HFC-1234yf.

2.6.2 Disposal of equipment and devices

If a system is taken out of service without prior recovery of the substance, the substance is emitted. Emissions can also occur during proper disposal. When the system is evacuated and the refrigerant is recovered, small amounts of refrigerant remain in the oil and piping and are then released.

Up to now, there are no disposal emissions from u-HFCs or u-HCFCs in Germany, as the end of the service life of the systems and devices filled with them has not yet been reached.

2.7 Atmospheric degradation products of halogenated refrigerants and blowing agents

2.7.1 Initiation of degradation

The halogenated refrigerants and blowing agents are either saturated (group of CFCs, HCFCs and HFCs), i.e., the substances contain only single carbon bonds, or they are unsaturated (group of u-HCFCs and u-HCFCs), i.e., the substances contain - usually one - carbon double bond. If the gases are emitted into the atmosphere, saturated and unsaturated gases have different degradation paths and degradation times.[77]

The atmospheric degradation of saturated partially halogenated organic substances (HCFCs and HFCs) is usually initiated by an abstraction reaction[78] with OH radicals (Figure 2). In this process, a hydrogen

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[75] AEGL: „Acute exposure guideline levels" (Störfallbeurteilungswert according to the Störfallverordnung, 12. BImschV).

[76] Entry for carbonyl fluoride in the GESTIS-database: http://gestis.itrust.de/nxt/gateway.dll/gestis_de/490953.xml?f=templates$fn=default.htm$3.0 (last access: 24.08.2018)

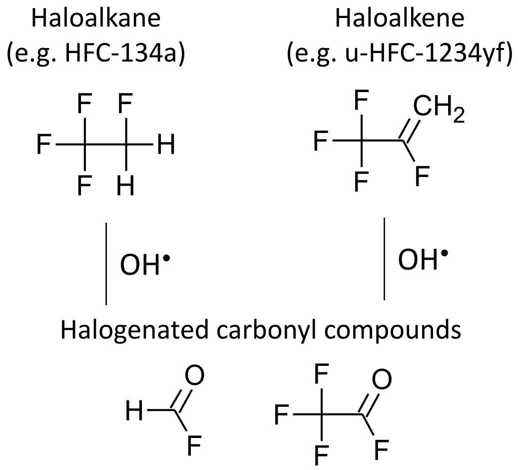
[77] The atmospheric degradation of PFCs is not discussed because it has been very little studied (Burkholder et al. 2015) and PFCs have an extremely long lifetime of more than 2,500 years (see Table 1 in Chapter 1.2).

[78] A reaction that removes an atom from a chemical compound.

atom is removed from the substance. The resulting radical reacts with oxygen from the air and is converted to a relatively stable halogenated carbonyl compound[79] by further reactive intermediate steps (Calvert et al. 2008). This abstraction reaction can also take place with chlorine radicals. However, these are about 100 times rarer in the atmosphere than the OH radicals.

For the unsaturated partially halogenated substances (u-HFCs and u-HCFCs), degradation is largely initiated by the addition of the OH radical. In a first step, carbonyl compounds are also formed. The addition of a chlorine radical is also possible with the unsaturated substances. This reaction can lead to chlorinated end products that have a longer lifetime than the original chlorine-free substances (Burkholder et al. 2015). Due to the much lower concentration of the Cl radical compared to the OH radical in the atmosphere, this reaction is likely to be relatively insignificant.

Figure 2: The initial degradation of saturated HCFCs and HFCs (haloalkanes, e.g. HFC-134a) and unsaturated HFCs and HCFCs (haloalkenes, e.g. u-HFC-1234yf) via reaction with OH radicals in the atmosphere leads to halogenated carbonyl compounds, e.g. formyl fluoride (HCFO) or trifluoroacetyl fluoride (TFF, CF_3CFO)



Source: Own representation, Öko-Recherche

In addition to the reaction with the OH radical, which dominates degradation, halogenated refrigerants and blowing agents can also be degraded by other, proportionally less significant routes, which are briefly described here.

In the stratosphere, atmospheric degradation of HCFCs and HFCs can be initiated by UV-photolytic means (Burkholder et al. 2015). Similarly, degradation is possible by an initial addition of singlet oxygen ($O(^1D)$), but this reaction is relatively insignificant for HFCs. For u-HFCs and u-HCFCs, degradation can also be initiated to a small extent by the addition of ozone (O_3) or a nitrate radical (NO_3), whereby other intermediates and end products can result.

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[79] Carbonyl groups are compounds in which a carbon atom is connected to an oxygen atom by a double bond.

2.7.2 Formation of intermediates

Since the atmospheric degradation of halogenated refrigerants and blowing agents generally occurs, as described above, via OH radical-initiated oxidation, only this degradation path will be discussed in more detail in the following. For the halogenated substances investigated in this report, the following halogenated carbonyl compounds in particular are formed as intermediates (Wallington et al. 1994, Burkholder et al. 2015):

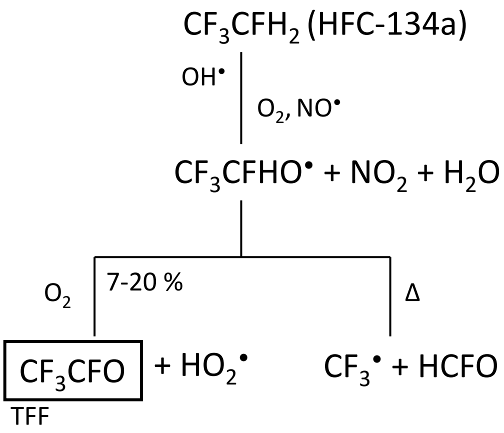
- carbonyl fluoride (CF_2O),
- formyl fluoride (HCFO),
- carbonyl chloride fluoride (CClFO),
- trifluoroacetaldehyde (CF_3CHO) and
- trifluoroacetyl fluoride (**TFF**, CF_3CFO).

The type of intermediate products determines which end products are produced during atmospheric degradation.

In the following, the atmospheric degradation path of four important substances - HFC-134a, u-HFC-1234yf, u-HFC-1234ze(E) and u-HCFC1233zd(E) - via OH radical-initiated oxidation is shown schematically.

In the case of HFC-134a (Figure 3), the OH-initiated abstraction reaction produces the alkoxy radical (CF_3CFHO) via the reaction with oxygen and in the presence of NO. Most of this is decomposed thermally and a smaller part (7-20%, Wallington et al. 1996) forms the halogenated intermediate TFF.[80]

Figure 3: Simplified degradation scheme for the OH-initiated addition of HFC-134a. The result is 7-20 % trifluoroacetyl fluoride (TFF, CF_3CFO).



Source: Modified after Wallington et al. (1992) and WMO (2010), own illustration, Öko-Recherche

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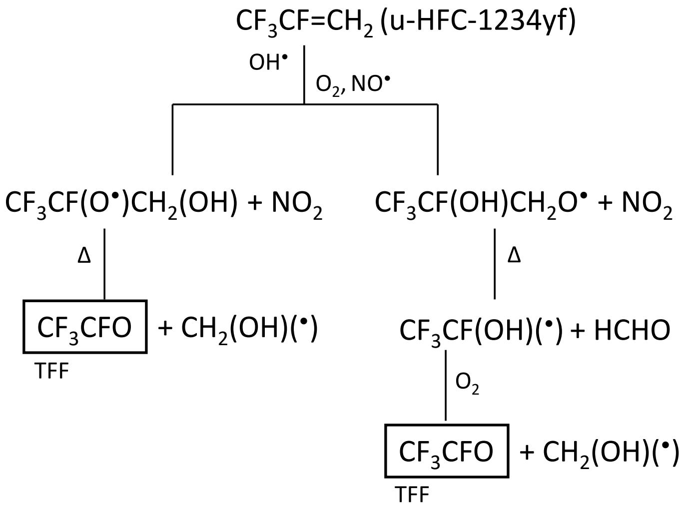
[80] Luecken et al. (2010) give a TFA yield of "~21 %" for HFC-134a, but without giving a citation and without carrying out own measurements. Therefore, this value is not listed here, even if it was cited by other authors (Solomon et al. 2016).

In contrast to HFC-134a, OH addition can be performed as an initial step of atmospheric degradation in halogenated propenes (u-HFC-1234yf, u-HFC-1234ze(E), u-HFC-1233zd(E)) at either the first or the second carbon atom. Depending on the attacked carbon atom, this leads to the formation of two different radical compounds, which react further in the atmosphere.

For u-HFC-1234yf (Figure 4), further degradation of the radical compounds, as a result of OH addition, occurs via reaction with oxygen and nitrogen monoxide radicals with subsequent complete thermal decomposition to form TFF as a halogenated intermediate (Hurley et al. 2008).

Figure 4: Degradation scheme for the OH-initiated addition of u-HFC-1234yf. The result is exclusively trifluoroacetyl fluoride (TFF, CF_3CFO).



Source: Modified after Hurley et al. (2008), own illustration, Öko-Recherche

The degradation of u-HFC-1234ze(E) (Figure 5) initially behaves very similar to that of u-HFC-1234yf (Figure 4). Different radical compounds are formed, which, however, do not form TFF but decompose thermally, or decompose thermally and react with oxygen to finally form trifluoroacetaldehyde (CF_3CHO) as a halogenated intermediate (Javadi et al. 2008).[81]

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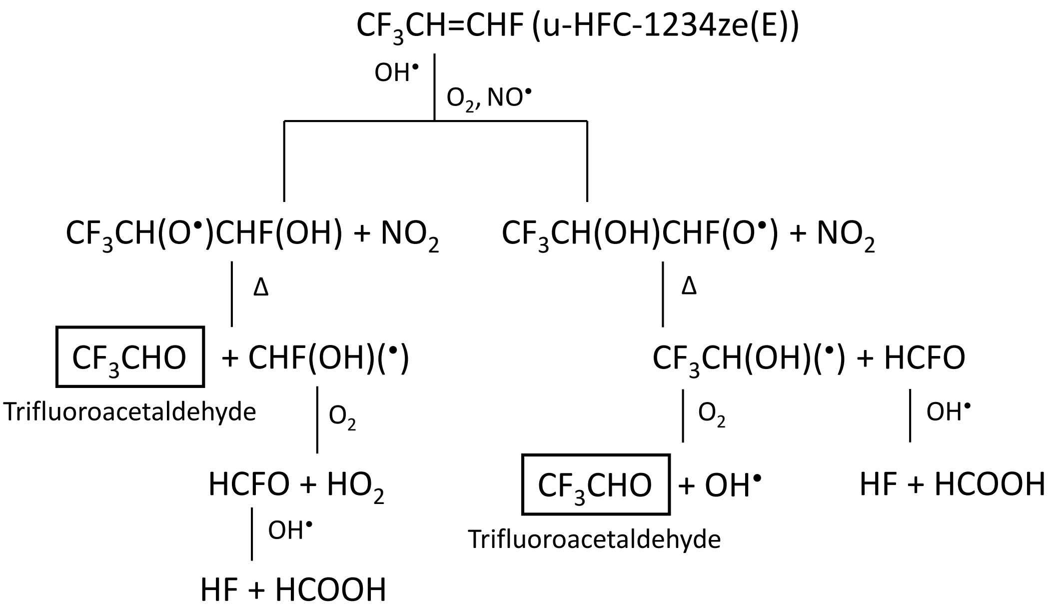
[81] Nilsson et al (2009) determined the same degradation products for u-HFC-1234ze(Z) (cis-$CF_3CH=CHF$) as for u-HFC1234ze(E) (namely CF_3CHO and HCFO).

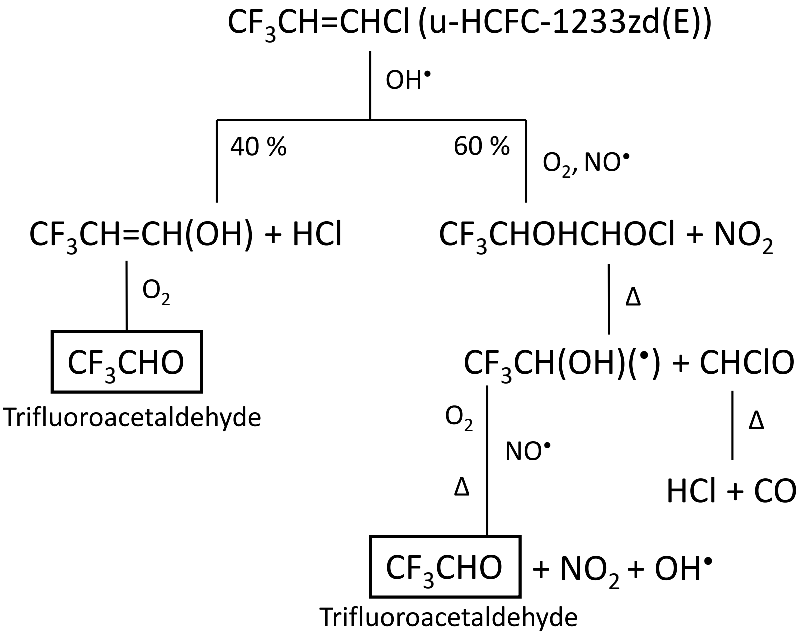
Figure 5: Degradation scheme for the OH-initiated addition of u-HFC-1234ze(E). Trifluoroacetaldehyde (CF_3CHO) is formed, but not trifluoroacetyl fluoride (TFF, CF_3CFO).



Source: Modified after Javadi et al. (2008), own illustration, Öko-Recherche

In a similar way to u-HFC-1234ze(E), the degradation of u-HCFC-1233zd(E), independent of the location of the initial OH addition, leads to the formation of trifluoroacetaldehyde as a halogenated intermediate (Figure 6). Due to the bonded chlorine atom, however, chlorinated compounds are formed in addition to trifluoroacetaldehyde, which are finally degraded to hydrogen chloride (HCl) by reaction with OH radicals (Burkholder et al. 2015).

Figure 6: Degradation scheme for the OH-initiated addition of u-HCFC-1233zd(E). Trifluoroacetaldehyde (CF_3CHO) is formed, but not trifluoroacetyl fluoride (TFF, CF_3CFO).



Source: Modified after Sulbaek Andersen et al. (2018), own illustration, Öko-Recherche

2.7.3 Atmospheric degradation of the halogenated intermediates

The various halogenated intermediates are finally further degraded via different pathways. Figure 7 shows an example of this with the decomposition of HFC-134a and u-HFC-1234yf.

Hydrogen fluoride (HF) is always one of the end products of atmospheric degradation for the halogenated refrigerants and blowing agents investigated. For some of the degradation pathways, trifluoroacetic acid (TFA) is formed.

Many fluorinated compounds are degraded via the formation of the toxic carbonyl fluoride (COF_2) or via formyl fluoride (HCFO) as an intermediate (Burkholder et al. 2015). Carbonyl fluoride hydrolyses to CO_2 and hydrofluoric acid (Javadi et al. 2008), while formyl fluoride reacts relatively slowly with OH radicals to form FCO radicals in the atmosphere or hydrolyses to HF and HCOOH due to the probably much faster reaction with water (Wallington & Hurley 1993).

In addition, hydrogen fluoride (HF) is produced during the hydrolysis of trifluoroacetyl fluoride (TFF). HF is also formed during the photolytic and thermal decomposition of trifluoroacetaldehyde. In aqueous solution, HF is present as hydrofluoric acid, which is acutely toxic and corrosive[82]. Wallington et al. (2015) estimated the additional fluoride input due to the atmospheric degradation of u-HFCs and u-HCFCs and the associated acidification of the precipitation as negligible. Wallington et al. (2015) assumed an annual emission of 100,000 tons of u-HFCs and u-HCFCs for the calculation of the fluoride input. Assuming an empirical formula for the unsaturated halocarbons of -CHX- (where X can be fluorine or chlorine), a homogeneous distribution in the atmosphere and a global precipitation of 4.9×10^{17} L per year, the authors conclude that the additional input of HF and HCl from the degradation of unsaturated halocarbons in the atmosphere is 10^{-9} to 10^{-8} mol/L. Taking into account the probably inhomogeneous distribution of unsaturated halocarbons due to their short atmospheric lifetime, Wallington et al. (2015) estimate regional concentration peaks of 10^{-8} to 10^{-7} mol/L[83].

The halogenated greenhouse gases examined in this report form one of the following end products via intermediates after complete degradation in the atmosphere (Wallington et al. 1994, 2015, 2017, Newsted et al. 2002, Harnisch et al. 2004):

- carbon dioxide (CO_2),
- formic acid (HCOOH),
- hydrogen chloride (HCl),
- hydrogen fluoride (HF) and
- **trifluoroacetic acid** (CF_3COOH, **TFA**).

With the exception of TFA and formic acid, the above-mentioned possible atmospheric degradation products are inorganic substances, which as such do not show any persistence.[84] Formic acid decomposes in water to CO_2 and H_2 and in air to CO and H_2O (Akiya & Savage 1998) and is therefore not persistent in the environment.[85]

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[82] http://gestis.itrust.de/nxt/gateway.dll/gestis_de/520038.xml?f=templates$fn=default.htm$3.0 (last access: 06.04.2020)

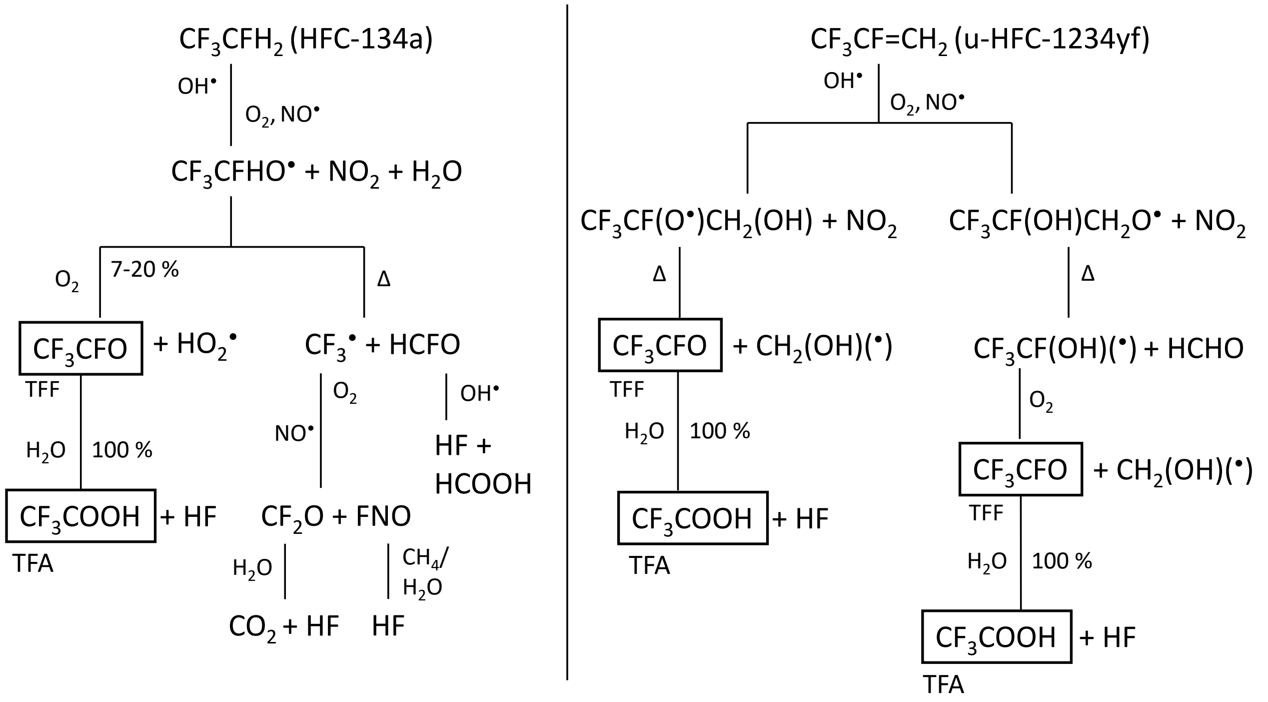
[83] 10^{-7} mol/L per year correspond to an additional amount of fluorine per year of 0.0018988 mg/L for fluorine with a molar mass of 18.988 g/mol. For comparison, the German Drinking Water Regulation (TrinkwV 2001) specifies a limit value for fluoride in drinking water of 1.5 mg/L in Annex 2 (to § 6 para. 2 TrinkwV 2001 + amendment Nov. 2011).

[84] The term "persistent" is only used for organic substances; see also entry on "persistence" in Römpp (1995).

[85] During atmospheric decomposition by reaction with NO radicals (nitrogen monoxide), NO_2 (nitrogen dioxide) is also produced. NO_2 decomposes photolytically to an NO radical and an oxygen radical (Altenstedt & Pleijel 1998). The oxygen radicals thus formed finally react with oxygen and form ground-level ozone. This reaction mechanism is a characteristic

An end product of the atmospheric decomposition of halogenated refrigerants and blowing agents is trifluoroacetic acid (TFA). In contrast to the above-mentioned degradation products, it is highly persistent in the environment and also highly mobile (Scheurer et al. 2017).[86]

Figure 7: Atmospheric degradation of HFC-134a (left) and u-HFC-1234yf (right) via the fluorinated intermediates trifluoroacetyl fluoride (TFF, CF_3CFO), CF_3 radicals and HCFO to the terminal fluorinated degradation products trifluoroacetic acid (TFA) and hydrogen fluoride (HF). The degradation pathways are only completely shown here for the halogenated substances.



Source: Data from Wallington & Hurley (1993), Wallington et al (1994), Javadi et al (2008) and Burkholder et al (2015), own illustration, Öko-Recherche

2.7.3.1 Formation of trifluoroacetic acid (TFA) from fluorinated intermediates

Trifluoroacetic acid (**TFA**, CF_3COOH) can generally be formed from different substance classes of organic molecules, whereby the presence of a C-CF_3 group is considered a prerequisite for the potential for TFA formation. Many unsaturated HFCs and HCFCs as well as hydrofluoro- and hydrochlorofluoroethers (HFEs and HCFEs) have one or, in the case of some HFEs and HCFEs, several C-CF_3 groups.

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of many short-lived organic substances (so-called "volatile organic compounds", or VOCs for short), since only these are broken down near the ground due to their short atmospheric lifetime. Contrary to its protective effect in the form of the ozone layer in the upper atmosphere (stratosphere), ground-level ozone in the lower atmosphere (troposphere), as an irritant gas, poses a health hazard to people. Therefore, some of the most important u-HFCs were tested for their photochemical ozone creation potential (POCP). Basically, it can be said that u-HFCs have a significantly higher POCP than corresponding analogous HFCs, but a significantly lower POCP than corresponding pure hydrocarbons (Wallington et al. 2015). A model study on the complete replacement of HFC-134a with u-HFC-1234yf in automotive air conditioning systems in the U.S. estimated the contribution of u-HFC-1234yf to the formed ground-level ozone to be less than 0.01 % (Luecken et al. 2010). In the following, the topic of ground-level ozone formation by halogenated greenhouse gases will not be discussed further, as this report focuses on persistent degradation products of halogenated refrigerants and blowing agents and ozone is not such a degradation product.

[86] TFA (CAS number 76-05-1) is a substance registered under the REACH regulation, which is classified as vPvM (very persistent in the environment and very mobile in the aquatic environment) (Arp & Hale 2019).

Therefore, all these substances can, at least potentially, form TFA during atmospheric degradation. For the halogenated substances treated in this study, TFA is formed mainly by hydrolysis of the intermediate trifluoroacetyl fluoride (**TFF**, CF_3CFO) (Burkholder et al. 2015). According to Wallington et al. (1994), TFF is practically only degraded hydrolytically, because the reaction with OH radicals and photolysis is too slow to be significant.

In the less likely case of an initial reaction of halogenated refrigerants and blowing agents with a Cl radical, trifluoroacetyl chloride (**TFAC**, CF_3CClO) is formed as an intermediate product. TFAC is also formed during the OH-initiated degradation of chlorinated substances, such as HCFC-123 (Kotamarthi et al. 1998), but not during the OH-initiated degradation of u-HCFC-1233zd (see Figure 6). The further degradation of TFAC can potentially contribute to TFA formation in the atmosphere, whereby TFAC does not react with OH radicals, but is only degraded photolytically or hydrolytically (Wallington et al. 1994). The hydrolytic degradation of TFAC ends exclusively in the formation of TFA and competes with the photolytic degradation, in which no TFA is formed. Kotamarthi et al. (1998) assume that 93.9 % of TFAC reacts hydrolytically to form TFA, while only 2.6 % is degraded photolytically (the remaining 3.5 % is attributed to dry deposition in oceans and on surfaces). The photolysis yields CF_3, CO and Cl, as well as traces of CF_3Cl (CFC-13). The latter molecule is long-lived and, as such, can reach the stratosphere, in which it also transports chlorine. Due to the small quantities involved, Wallington et al (1994) do not assume a significant damaging effect to the ozone layer.

2.7.3.2 Formation of TFA from the intermediate trifluoroacetaldehyde

Furthermore, TFA can be produced via the intermediate **trifluoroacetaldehyde (CF_3CHO)**. This degradation pathway is much more complicated than the two above mentioned, but could play an important role for the total TFA input, because many halogenated refrigerants and blowing agents form trifluoroacetaldehyde as an intermediate in atmospheric degradation. The literature still treats the formation of TFA from trifluoroacetaldehyde controversially, therefore the formation path via the intermediate product trifluoroacetaldehyde (CF_3CHO) is described in detail in the following.

The atmospheric degradation of trifluoroacetaldehyde can occur via three competing reactions (Calvert et al. (2008), Figure 8):

a) the OH-initiated abstraction reaction[87],
b) hydrolysis or
c) photolysis.

In the degradation pathway via an OH radical attack (a), CF_3CO is formed in a primary reaction step (Hurley et al. 2006). CF_3CO finally reacts almost completely to CF_3COO_2 (99 % at 1 standard atmosphere and 298 K). CF_3COO_2 can in turn react with NO, NO_2 and HO_2 radicals (Calvert et al. 2008). The reaction with NO produces CF_3COO radicals, which, through the formation of CF_3 radicals, ultimately produce CO_2 and HF. In contrast, the reaction with NO_2 only leads to the formation of CF_3COO_2 radicals and NO_2. The reaction with HO_2 radicals can take place in three ways (Hurley et al. 2006):

More than half of the CF_3COO_2 radicals (52 % at 298 K and 700 Torr air pressure) that react with HO_2 radicals are converted to CF_3COO radicals. A smaller part (39 %) is converted to TFA, while CF_3COOOH is formed only to a small percentage (9 %). CF_3COOOH probably reacts further via photolysis and reaction with OH radicals to form various CF_3COO_x radicals (Calvert et al. 2008).

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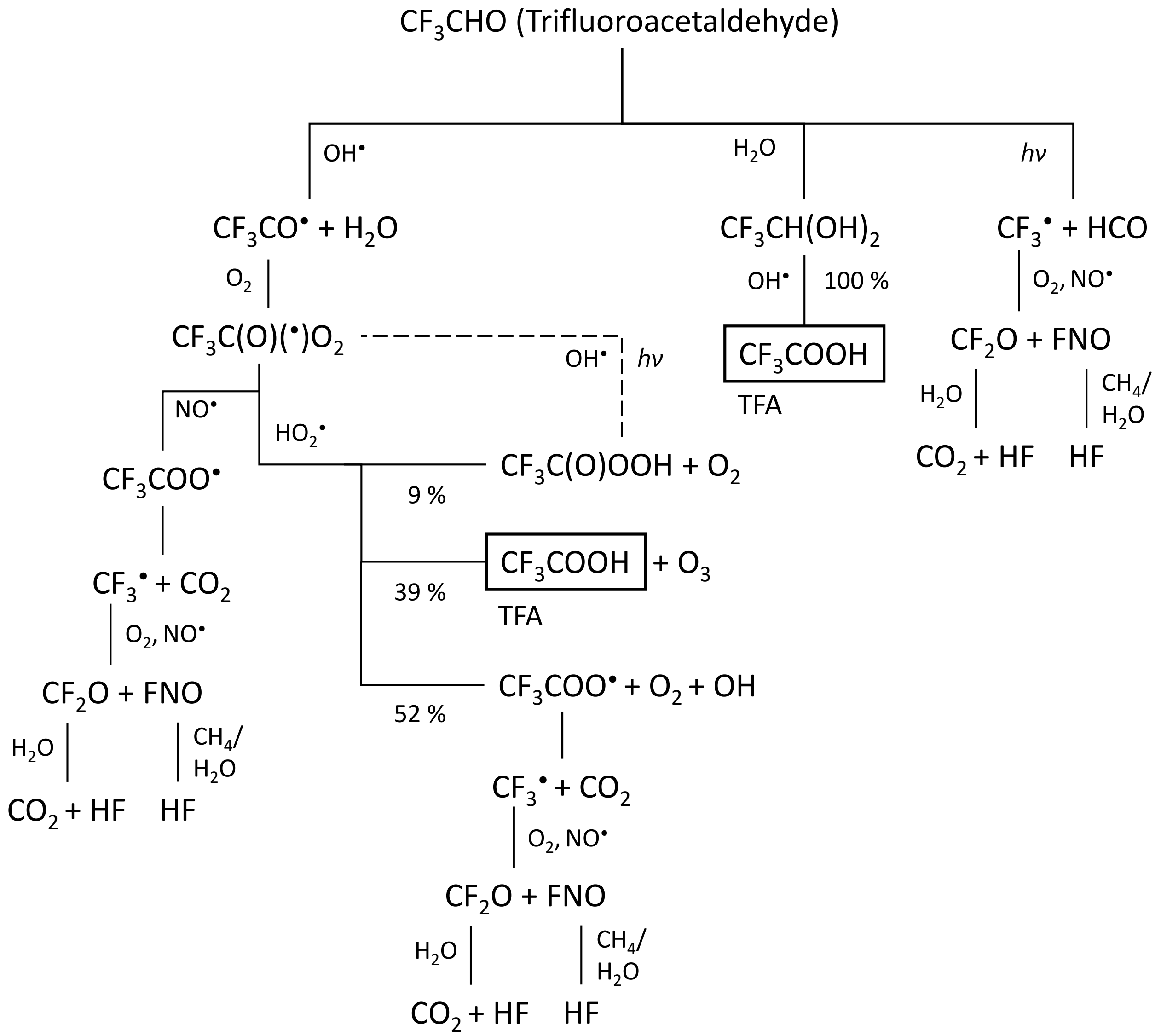
[87] In principle, degradation via reaction with chlorine radicals is also possible. However, this will not be further discussed in the context of this report.

The hydrolysis of trifluoroacetaldehyde (b) leads to complete formation of TFA. The reaction with water leads to the formation of the hydrate $CF_3CF(OH)_2$, which is converted to TFA by oxidation (Sulbaek Andersen et al. 2006).

The photolysis of trifluoroacetaldehyde (c) does not lead to the formation of TFA, but to CF_3 and HCO radicals (Chiappero et al. 2006).

Figure 8: Atmospheric degradation pathway of trifluoroacetaldehyde (CF_3CHO) via an OH-initiated abstraction reaction (OH-), hydrolysis (H_2O) and photolysis (hv).



Source: Data from Wallington et al (1994), Sellevåg et al (2004a, 2005), Sulbaek Andersen et al (2006), Chiappero et al (2006), Hurley et al (2006), Javadi et al (2008) and Calvert et al (2008), own illustration, Öko-Recherche

Decisive for the formation of TFA in substances that form trifluoroacetaldehyde as an intermediate is the competition of reactions (a-c) in the atmospheric degradation of trifluoroacetaldehyde. If the degradation is primarily by photolysis, no TFA formation occurs. However, if the degradation is carried out via another route, a certain percentage of TFA can be formed. The atmospheric lifetime of trifluoroacetaldehyde influences which degradation path is taken. Various results have been published in the scientific literature.

For the **OH-initiated degradation** (a) an atmospheric lifetime of approx. 26 days is assumed. This was determined by Sellevåg et al (2004a) and used by other relevant authors (Chiappero et al. 2006). Estimates of other authors do not deviate far from this with 24 days (Scollard et al. 1993).

Hydrolytic degradation (b) is likely to be significantly influenced by the time it takes for trifluoroacetaldehyde to come into contact with water surfaces (Chiappero et al. 2006). For trifluoroacetyl fluoride (TFF) and trifluoroacetyl chloride (TFAC), measurements and calculations on tropospheric lifetime under hydrolysis have been performed (DeBruyn et al. (1995) and citations contained therein). While DeBruyn et al. (1995) determined 2 to 10 days for TFAC and 0.5 to 3 days for TFF, other authors determined significantly shorter times of about 0.06 and about 0.05 days for tropospheric lifetimes for the hydrolysis of TFAC and TFF, respectively. However, DeBruyn et al. (1995) point out that tropospheric lifetimes of less than 5 days cannot be readily calculated, because cloud formation probabilities must be included in the calculation. DeBruyn et al (1995) therefore assume a lower limit of 5 to 10 days. Similarly, Wallington et al. (1994) give 5 days as the lower limit of the lifetime for hydrolysis. They justify this with transport limitations, i.e. the time needed for the transport of material into clouds.

Regarding **photolysis** (c), there are several studies, some of which have come to very different conclusions. These studies determine the quantum yield of the photon-induced degradation process of trifluoroacetaldehyde, which indicates how likely a trifluoroacetaldehyde molecule is split by an absorbed photon. Very briefly: The higher the quantum yield, the shorter the atmospheric lifetime of a molecule during photolytic degradation[88]. Dodd & Smith (1957) determined a quantum yield of 0.12 at a light wavelength of 313 nm. Chiappero et al. (2006) found a very similar quantum yield of 0.17 at 308 nm. A study by Sellevåg et al. (2004a), on the other hand, found a yield of less than 0.02.

Accordingly, the authors interpret the relevance of photolysis in the atmospheric degradation of trifluoroacetaldehyde differently. While Sellevåg et al. (2004a) consider OH-initiated degradation and photolysis to be approximately equally frequent due to the very similar atmospheric lifetime of about 26 days for OH and more than 27 days for photolysis, Chiappero et al. (2006) consider photolysis to be the dominant degradation pathway for trifluoroacetaldehyde.[89] Based on comparisons with other studies and a follow-up study by Sellevåg et al. (2005), in which the authors conclude, based on their own calculations, that trifluoroacetaldehyde should have a relatively low threshold for photolytic degradation, Chiappero et al. (2006) assume an error in the measurements by Sellevåg et al. (2004a).

Accordingly, some authors, some of whom were also involved in the study by Chiappero et al. (2006), assume in further investigations that trifluoroacetaldehyde does not contribute to the formation of TFA in the atmosphere. Sulbaek Andersen et al. (2012a), for example, assume an atmospheric lifetime for photolysis of less than 2 days, with reference to Chiappero et al. (2006). Interestingly, Chiappero et al. (2006) never explicitly mention a lifetime of less than 2 days for trifluoroacetaldehyde. Only in one figure (Figure 11 in Chiappero et al. (2006)) a minimum lifetime with respect to photolysis of slightly more than 2 days is presented for trifluoroacetaldehyde at an altitude of about 10.75 km.[90] However,

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[88] Trifluoroacetaldehyde can be split photolytically in two ways. On the one hand, photolysis can cleave CF_3CHO to (i) CF_3 radicals and HCO, but there is also the possibility that (ii) CF_3H and CO are formed by photolytic cleavage (Chiappero et al. 2006). The wavelength of the photons determines the type of cleavage. For example, at a wavelength of 313 nm, reaction (i) probably does not play a significant role (Dodd & Smith 1957, Pearce & Whytock 1971), but at 254 nm it does (Chiappero et al. 2006). Reaction (ii) is probably the dominant reaction at 308 nm and 313 nm (Dodd & Smith 1957, Chiappero et al. 2006). Since CF_3CHO has the highest probability of absorption (probability of a CF_3CHO molecule absorbing a photon of this wavelength) in the region around 300 nm (Sellevåg et al. 2004a, Chiappero et al. 2006, Calvert et al. 2008), only the results for reaction (i) are described in the following text,

[89] The study by Chiappero et al (2006) was financed exclusively by E.I. duPont de Nemours.

[90] Calvert et al. (2008) quote here very precisely a lifetime of 2.1 and 5.7 days at 0 and 11.7 km altitude, respectively.

since a lifetime of <2 days is actually stated for three other substances that were also investigated in the study by Chiappero et al. (2006), it can be assumed that other authors have erroneously assumed this for trifluoroacetaldehyde. Wallington et al. (2015) also state less than 2 days for the photolysis of trifluoroacetaldehyde, with reference to Sulbaek Andersen et al. (2004). However, since this information is not found in the given source[91], it can be assumed that a corresponding quotation is missing and that the information was also erroneously taken from Chiappero et al. (2006).

Chiappero et al. (2006) also acknowledge that their results are based on a calculation that uses a wavelength-independent quantum yield. However, according to the authors, this dependency should be considered in the calculation, as it corresponds to reality. However, since no data for trifluoroacetaldehyde were available for this purpose, the results of the calculation were subsequently corrected linearly based on the wavelength dependence of CH_3CHO as an approximate value. As a result of this correction, the authors arrived at a photolysis rate that was approximately 2.8 times lower. Therefore, the assumption that trifluoroacetaldehyde is photolytically degraded in less than two days cannot be supported by Chiappero et al. (2006).

Following the investigations of Chiappero et al. (2006), Calvert et al. (2008) have also looked at the photolysis of trifluoroacetaldehyde. Since no data on the wavelength dependency of trifluoroacetaldehyde were available, Calvert et al. (2008) estimate the photochemical lifetime of trifluoroacetaldehyde for an overhead Sun in the lower troposphere to be approximately 19 hours, based on calculations using the quantum yield of 0.17 from Chiappero et al. (2006).

This has far-reaching consequences for the estimation of the TFA formation rate of unsaturated HFCs as presented in the reports of the "World Meteorological Organization" (WMO) for the years 2010 and 2014. In their reports on the scientific assessment of ozone depletion, the authors assumed a TFA formation rate of less than 10 % for substances that form trifluoroacetaldehyde as an intermediate (WMO 2010), but it is not explained exactly how this estimated value was determined.[92] In the following WMO report, this estimate was revised and no TFA formation is assumed for substances that form trifluoroacetaldehyde as an intermediate (WMO 2014). In the WMO Report from the year 2018, the subject of the intermediate product is finally completely abandoned (WMO 2018). However, it is not explicitly mentioned that substances that form trifluoroacetaldehyde as an intermediate cannot be degraded to TFA.

If one assumed that photolysis was the main degradation pathway for trifluoroacetaldehyde in the atmosphere and that radical attack and hydrolysis would play no role at all, trifluoroacetaldehyde would not contribute to the formation of TFA in the atmosphere. This argumentation is apparently followed by the WMO report from the year 2014 (WMO 2014). However, it can be assumed that at least parts of the trifluoroacetaldehyde are degraded, if not by radical attacks, then by hydrolysis. Under natural conditions, trifluoroacetaldehyde will find a certain amount of humidity in the atmosphere and form the stable aldehyde hydrate $CF_3CH(OH)_2$ by absorbing a water molecule[93]. Sulbaek Andersen et al. (2006) also assume that hydration could be an important atmospheric degradation pathway for trifluoroacetaldehyde. The aldehyde hydrate is again almost completely oxidized to TFA (Sulbaek Andersen et al. 2006, Calvert et al. 2008).

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[91] In a later publication from the same year, Sulbaek Andersen et al. (2004b), with reference to Sellevåg et al. (2004a), also give a lifetime for the photolysis of trifluoroacetaldehyde of more than 27 days.

[92] Interestingly, Solomon et al. (Solomon et al. 2016) with reference to Javadi et al. (2008) give a TFA yield of <10 % for u-HFC-1234ze(E). However, this statement cannot be found in Javadi et al. (2008).

[93] Personal communication from Prof. Andreas Kornath, Faculty of Chemistry and Pharmacy, Ludwig-Maximilians-University Munich.

Based on the above data, the TFA formation potential of substances that form trifluoroacetaldehyde as an intermediate is not generally assumed to be zero in this study. Instead, the TFA yield is calculated within the range given in the WMO 2010 Ozone Report (WMO 2010), assuming a possible TFA formation rate of up to 10 %. However, this rate of formation could also be higher. The lack of clear indications in the literature prevents a more exact estimation of the TFA formation rate.

2.7.4 Substance-specific TFA formation rates

For the determination of TFA formation rates of the substances under consideration, the entire degradation pathway, from the halogenated starting material, via the fluorinated intermediates to the degradation end product, has to be considered and, if possible, quantified. Decisive for the TFA-yield of a substance are

- the rate of formation of fluorinated intermediates that can be further converted to TFA and
- the rate of conversion of these intermediates to TFA.

Point 2, the rate of conversion of the intermediate products to TFA, was presented in detail in Chapter 2.7.3. In case of formation of trifluoroacetyl fluoride (TFF) and trifluoroacetyl chloride (TFAC), a practically complete conversion to TFA can be assumed. For trifluoroacetaldehyde, however, we assume a conversion rate of up to 10 %.

The decisive factor is now point 1: the rate of formation of the intermediates. Data on the identity of the intermediates involved in the atmospheric degradation of many halogenated greenhouse gases are available from various scientific studies, which have been compiled in the comprehensive review article by Burkholder et al. (2015). However, the proportion of these intermediates is only known for a few substances, such as HFC-134a (see Chapter 2.7.2). Since 7-20 % of TFF is produced during the degradation of HFC-134a, the TFA yield can be quantified. In some cases, the same intermediate product is always produced, regardless of the possible degradation path. For example, u-HFC-1234yf can be quantified exactly because TFA is always produced during the degradation process. Sulbaek Andersen et al. (2018) concluded in an atmospheric modelling study that the molar TFA yield during atmospheric degradation of u-HCFC-1233zd(E) is approximately 2 %[94].

For the majority of the investigated substances, information on TFA yield is not available. If no data are available, we postulate, based on the fluorinated intermediates in Burkholder et al. (2015), a complete conversion to TFA in case of formation of trifluoroacetyl fluoride (TFF) or trifluoroacetyl chloride (TFAC) and a conversion of up to 10 % in case of formation of trifluoroacetaldehyde. In cases where TFF or TFAC can be formed in addition to trifluoroacetaldehyde, we conservatively assume a complete conversion to TFA as well.

For halogenated propenes (u-HFCs or u-HCFCs with a C_3-body) a more precise estimation of the TFA formation rate can be made, which is explained in the following.

2.7.4.1 Importance of the occupation of the central carbon atom in halogenated propenes with C_3-body

For u-HFCs and u-HCFCs with a C_3-body (fluorinated propenes), the composition of the carbon atom closest to the CF_3-group ("central carbon atom ") is of decisive importance in atmospheric degradation. If a fluorine atom is bonded here, degradation takes place primarily via trifluoroacetyl fluoride (TFF), which is completely hydrolysed to TFA (WMO 2014). The TFA yield in this case is therefore estimated

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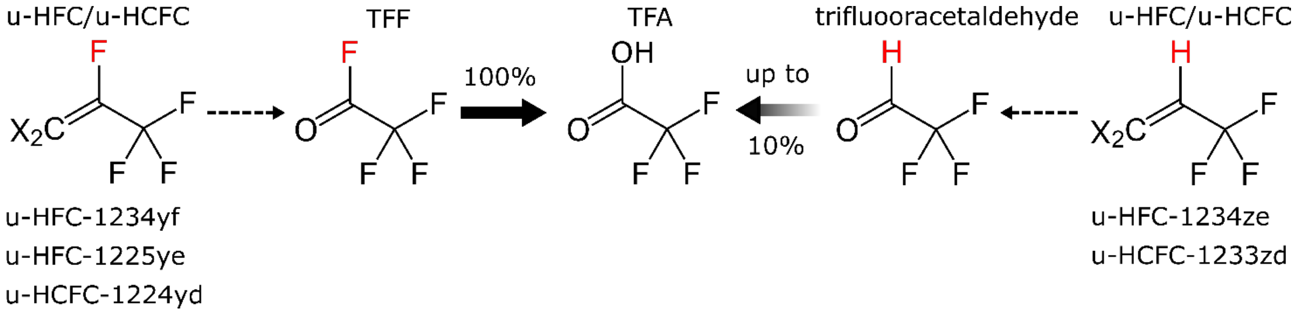
[94] Sulbaek-Andersen et al. (2018) use the quantum yield from Chiappero et al. (2006) for their modelling of the photolytic degradation of CF_3CHO. For the degradation via OH radicals, however, they use data from Calvert et al. (2011), which in turn refer to Sellevåg et al (2004a), among others. The modeling in Sulbaek-Andersen et al. (2018) thus assumes photolysis as the dominant degradation path of CF_3CHO and thus a minimal formation of TFA.

to be high. If the central carbon atom is occupied by a hydrogen atom, trifluoroacetaldehyde is usually formed and a low TFA formation rate can be expected.

The following Figure 9 summarizes the relationship for u-HFCs and u-HCFCs with a hydrogen or fluorine atom at the central carbon atom in schematic form. Basically, u-HFCs and u-HCFCs with C_3-body can be grouped approximately on the basis of these assumptions regarding their TFA formation rate, even if no explicit data on atmospheric degradation are available.

Figure 9: Interrelationships for various u-HFCs and u-HCFCs with a hydrogen or fluorine atom on the central carbon atom: Depending on the fluorine or hydrogen atom on the central carbon atom , atmospheric degradation of u-HFCs and u-HCFCs with C_3-bodies produces primarily trifluoroacetyl fluoride (TFF) or trifluoroacetaldehyde, which influences the further conversion rate to trifluoroacetic acid (TFA). X stands for F, Cl or H.



Source: WMO (2014), own representation, Öko-Recherche

However, this rule regarding the occupation of the CF_3-nearest carbon atom cannot be generalized easily beyond the group of u-HFCs and u-HCFCs with C_3-bodies. For example, while the atmospheric degradation of u-HCFC-1336mzz ($\mathbf{CF_3CH}=\mathbf{CHCF_3}$) may produce trifluoroacetaldehyde and not trifluoroacetyl fluoride (TFF), u-HCFC-1345fz ($\mathbf{CF_3CF_2}CH=CH_2$) does not form TFF during degradation (Burkholder et al. 2015). The reason for this could be the position of the double bond. Thus, trifluoroacetaldehyde is formed during the degradation of u-HFC-1438mzz(E) (trans-$\mathbf{CF_3CF_2}CH=\mathbf{CHCF_3}$), but no TFF is formed. The composition of the carbon atom closest to the CF_3-group seems to be decisive only in combination with a double bond following this carbon atom.

For the group of u-HFCs and u-HCFCs the rule is also not easy to apply. Many of the u-HFCs and u-HCFCs listed in Burkholder et al. (2015) form TFF as an intermediate product when the carbon atom next to the CF_3-group is fluorinated (e.g. HCFC-124, HFC-134a, HFC-227ea, HFC-245eb, HFC-236ea and HFC-43-10mee) and, accordingly, when this is not the case, only trifluoroacetaldehyde (e.g. HCFC-234fb and HFC-143a). However, this does not apply to all substances (e.g. HFC-227ca and HFC-236fa). In addition, many of these substances have a hydrogen atom in addition to fluorine, close to the CF_3-group. HFC-134a is such a case and, as already mentioned, TFF is formed to 7-20 %, but no trifluoroacetaldehyde is formed. In general, HCFCs and HFCs with a fluorinated CF_3-adjacent carbon atom, which also carries a hydrogen molecule, seem to form TFA, but no trifluoroacetaldehyde (e.g. HCFC-124, HFC-245eb, HFC-236ea and HFC-227ea).

If a chlorine atom is bonded to the carbon atom closest to the CF_3-group, as is the case with HCFC-123, HCFC-124 and HCFC-133a, for example, only limited information can be derived about the formation rate of the fluorinated intermediates for corresponding substances based on the current state of research. During the OH-initiated degradation of HCFC-123 and HCFC-133a, trifluoroacetyl chloride (TFAC) is formed as an intermediate, but not in the case of HCFC-124, possibly because the carbon atom next to the CF_3-group also contains a fluorine atom (Burkholder et al. 2015). A generalization cannot be made for chlorinated substances based on the available data.

For all u-HFCs and u-HCFCs with C_3-body considered in this study, it is therefore possible to roughly estimate the TFA formation rate based on the fluorination of the carbon atom closest to the CF_3-group, even if no scientific data are available. However, for all other substances there are not enough reliable data to make such an estimation.

2.7.4.2 Quantification of the TFA yield during atmospheric degradation

With the above-described procedure for estimation and with data from the scientific literature, the TFA yield of the substances investigated in this report can be derived (Table 14). A complete list of further substances and all intermediates can be found in Annex A.7 (Table A 4).

Table 14: Overview of selected halogenated substances that can form trifluoroacetic acid (TFA) during atmospheric degradation. The complete table is given in Annex A.7.

Substance	TFA molar yield	Source
HFC-245fa	<10 %	WMO (2010)
HFC-134a	7-20 %	Wallington et al. (1996)
HFC-143a	<10 %	own estimate
HFC-365mfc	<10 %	WMO (2010)
HFC-227ea	100 %	WMO (2010)
u-HFC-1234yf	100 %	Hurley et al. (2008)
u-HFC-1234ze(E)	<10 %	WMO (2010)
u-HFC-1336mzz(Z)	<20 %[95]	Qing et al. (2018)
u-HFC-1225ye(E and Z)	100 %	own estimate
u-HCFC-1233zd(E)	2 %	Sulbaek Andersen et al. (2018)
u-HCFC-1224yd(Z)	100 %	own estimate

2.7.4.3 TFA formation for mixtures

Many of the newer mixtures used in refrigeration and air conditioning contain u-HFCs, especially u-HFC-1234yf and u-HFC-1234ze(E). These, as well as the single substance (e.g. u-HFC-1234yf), are to be considered as a TFA source, which can be measured according to the proportion of substances contributing to TFA formation (e.g. u-HFC-1234yf). Thus, a mixture of 60 % u-HFC-1234yf and 40 % HFC-134a has a TFA formation potential of up to 68 %.[96]

2.7.4.4 Deviations from published data on TFA yield of certain substances

In the WMO report of 2014 (WMO 2014), with reference to Young & Mabury (2010), a number of substances that form TFA during atmospheric degradation are mentioned as examples. These include HFC-125 and HFC-143a, which only form carbonyl fluoride (CF_2O) and trifluoroacetaldehyde as intermediates, respectively (Burkholder et al. 2015). Following this assessment, both HFCs are also classified as TFA producers in a briefing note of the UNEP Ozone Secretariat (Seki 2015). The "European

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[95] u-HFC-1336mzz(Z) is probably >90 % degraded to one CF_3CHO molecule and one CF_3CHOH radical (Qing et al. 2018). The latter reacts with oxygen to form CF_3CHO.

[96] TFA yield of u-HFC-1234yf is 100 % and of HFC-134a is 20 % (conservative estimate): (60 % * 100 %) + (40 % * 20 %) = 68 %

Fluorocarbons Technical Committee" (EFCTC) has taken a position on this issue, pointing out that neither HFC-125 nor HFC-143a are significantly degraded to TFA in real life.[97] As mentioned above, carbonyl fluoride is hydrolytically decomposed to CO_2 and hydrofluoric acid, whereby no TFA is formed. However, trifluoroacetaldehyde can be degraded to TFA, the yield for HFC-143a has been conservatively estimated at 100 % by Solomon et al (2016). In the present report a TFA yield of up to 10 % is assumed for HFC-143a, while HFC-125 does not form TFA.

2.8 Other relevant halogenated substances forming TFA

In addition to the use of halogenated hydrocarbons as refrigerants and blowing agents, which are the focus of this report, other fluorinated substances are used in other applications whose emissions can lead to the formation of TFA in the atmosphere.

In general, also HCFC-123 and HCFC-124 can form TFA during atmospheric degradation. While HCFC-123 is mainly used as a starting material for the production of other halogenated substances, HCFC-124 is mainly a by-product in the production of other halogenated substances. While HCFC-123 is completely converted to trifluoroacetyl chloride (TFAC) and finally to 94 % to TFA during OH-initiated degradation in the atmosphere, HCFC-124 is completely converted to trifluoroacetyl fluoride (TFF) and thus 100 % to TFA (Kotamarthi et al. 1998, Burkholder et al. 2015).

With regard to an atmospheric degradation to TFA, the applications as solvents (e.g. in the precision cleaning of electronic components), heat carriers and inhalation anaesthetics (e.g. desflurane, sevoflurane and isoflurane), in which representatives of the substance groups of hydrofluoroethers (HFEs) and hydrochlorofluoroethers (HCFEs) are used, should also be mentioned. Besides carbon, hydrogen, and fluorine, HFEs have an oxygen atom in the molecule. HCFEs additionally have a chlorine atom.

Table 15 shows important groups of halogenated greenhouse gases that are not used as refrigerants or blowing agents.

Table 15: Environmentally relevant data of further groups of halogenated substances which are not used as refrigerants or blowing agents but may form TFA during atmospheric decomposition. PFAs, partially fluorinated alcohols. HFEs, hydrofluoroether. HCFEs, hydrochlorofluoroether.

Substance group	ODP	GWP	Atmospheric lifetime	Examples for single substances	TFA-yield of the sample substances
HCFCs	0.005 – 0.520[a]	77 – 2,310	1 – 19.5 years[b]	HCFC-123 HCFC-124	94 %[c] 100 %[c]
PFAs	-	1 - 18[d]	20 - 120 days[d]	2,2,2-trifluoroethanol	<10 %[e]
HFEs and HCFEs	0 – 0.08[f]	11 – 14,900	3 - 50 years[b]	HFE-7500 HFE-236ea2 (desflurane) HFE-347 (sevoflurane) HCFE-235da2 (isoflurane)	100 %[g] 3 %[h] 7 %[i] 95 %[j]
Unsaturated PFCs	-	<1[k]	1 - 5 days[k]	hexafluoropropene (R1216)	100 %[l]

[a] Annex I to Regulation (EC) No 1005/2009 (EU ODS Regulation)
[b] Burkholder et al. (2015)

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[97] https://www.fluorocarbons.org/wp-content/uploads/2016/09/EFCTC_Learn_about_TFA_from_HFCs_HFOs.pdf (last access: 23.08.2018)

[c] Kothamarti et al. (1998)

[d] Sellevåg et al. (2004b); the given values are only valid for TFE (CF3CH2OH), CHF2CH2OH and CH2FCH2OH

[e] Trifluoroacetaldehyde is formed as a degradation product (Sellevåg et al. 2004b, Vasil'ev et al. 2006), therefore a TFA formation rate of <10 % is assumed.

[f] Langbein et al. (1999)

[g] Newsted et al. (2002)

[h] Sulbaek Andersen et al. (2012b) give a probability of 17 % for the degradation of desflurane to form CF_3CFHO radicals via OH or Cl radical degradation. These radicals are also generated during HFC-134a degradation (see Figure 7 in Chapter 2.7.3.1) and according to Wallington et al. (1996) are degraded to TFA by 7-20 %. This corresponds to a TFA formation rate of 1.2-3 % during the degradation of desflurane. In fact, Sulbaek Andersen et al. (2012b) could prove the formation of 3 % trifluoroacetyl fluoride (TFF, CF_3CFO), which completely hydrolyses to TFA (see Chapter 2.7.3.1). The detection of 3 % TFF indicates that the degradation rate of CF_3CFO to TFF - and thus also the TFA formation rate of HFC-134a - is closer to 20 % than to 7 %. Sulbaek Andersen et al. (2012b) state this accordingly with 18 %.

[i] According to Sulbaek Andersen et al. (2012b), sevoflurane is degraded to $(CF_3)_2CHOC(O)F$ (93 %) and $CF_3C(O)CF_3$ (7 %) via an initial OH or Cl radical reaction. While $(CF_3)_2CHOC(O)F$ according to Sulbaek Andersen et al. (2012b) is presumably dissolved in sea water, whereby the degradation products are unknown, the hydrolysis leads to the formation of TFA. According to Jackson et al. (2011) also the photolysis of $CF_3C(O)CF_3$, via the formation of a CF_3O and a CF_3 radical, leads to TFA. CF_3O radicals are further degraded to TFA (Jackson et al. 2011), CF_3 radicals are further degraded to HF and CO_2 (see Figure 8 in Chapter 2.7.3.2). It can therefore be assumed that the atmospheric degradation of sevoflurane with respect to non-marine sinks has a TFA yield of 7 %.

[j] Wallington et al. (2002)

[k] Hodnebrog et al. (2013)

[l] Mashino et al. (2000)

Hydrofluoroethers (HFE) are also used to replace long-chain saturated HFCs, such as perfluorooctanoic acid (PFOA), which has been used in fluoropolymer production for a very long time. However, since PFOA is bioaccumulative and toxic, HFEs are used as substitutes, but those can be persistent and toxic as well (Gordon 2011, Beekman 2016). In some cases, long-chain polyfluorinated HFEs are emitted into the atmosphere during the production process (e.g. $CF_3(CF_2)_2OCHFCF_3$, heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether, Beekman 2016). All these substitutes carry several C-CF_3 groups and could therefore potentially form TFA during atmospheric degradation.

For HFEs and chlorinated HFEs (HCFEs), atmospheric degradation is only partially realistic, since gaseous emissions to the atmosphere are unlikely to occur in many heat transfer fluid (HTF) applications. According to scientific experts[98], at least long-chain HFEs are unlikely to enter the gas phase, and the alcohols that might be produced by degradation would not necessarily be gaseous. However, Newsted et al. (2002) assume that HFE-7500 ($C_7F_{15}OC_2H_5$, with three C-CF_3 groups) could possibly be completely degraded to TFA in the atmosphere. Other representatives of the HFE-7000 series, like HFE-7500, carry C-CF_3 groups and are shorter-chained. Thus, these could as well form TFA during atmospheric degradation. An example of a member of the HFE series in possible new applications is HFE-7200, which consists of two isomers ($(CF_3)_2CFCF_2OC_2$ and $CF_3CF_2CF_2CF_2OC_2H_5H$), is marketed as a high-tech liquid and could be used in the battery cooling of electric vehicles in the future[99]. Some manufacturers of electric cars, however, use air cooling (e.g. Nissan Leaf) or a water-glycol mixture (e.g. Tesla).[100] BMW uses the refrigerant of the car air conditioning system (currently u-HFC-1234yf) for battery cooling in its electric car model i3.

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[98] Personal discussion with Prof. Thomas Braun, Dr. Mike Ahrens and Dr. Gisa Meißner (Humboldt University Berlin, Institute of Chemistry, June 26, 2018).

[99] https://chargedevs.com/newswire/xing-mobilitys-electric-supercar-uses-novel-battery-cooling-system/ (last access: 18.01.2018)

[100] https://jingweizhu.weebly.com/blog/summary-of-electric-vehicle-battery-cooling-systems (last access: 18.01.2018)

Regarding a possible TFA formation via atmospheric degradation, **shorter-chain HFEs and HCFEs**, which carry C-CF_3 groups and are emitted in gaseous form, are probably of greater importance. Inhalation anaesthetics are worth mentioning here, since these are practically completely released into the atmosphere as gas when used. This concerns HCFE-235da2 (isoflurane), HFE-236ea2 (desflurane) and HFE-347 (sevoflurane), of which only the last two are used in significant quantities in Germany in the field of human medicine (Warncke et al. 2017). Isoflurane, however, is still the standard inhalation anaesthetic in veterinary medicine in Germany[101] and is also approved for the mandatory anaesthesia for piglet castration which has been mandatory since January 2017 (then postponed to January 2019 and now to January 2021)[102, 103].

Isoflurane is degraded in the atmosphere by OH radical attack to a relatively inert ester ($CF_3COOCHF_2$), which probably only hydrolyses to TFA through contact with a body of water (Wallington et al. 2002). The molar yield is about 95 %. TFA can also be formed during the atmospheric degradation of **desflurane**, whereby Sulbaek Andersen et al. (2012b) assume that only 17 % of the degradation takes place via the formation of the CF_3CHFO radical. This radical reacts with 18 % oxygen to form TFF and thus TFA. The TFA yield of desflurane is therefore about 3 % (see also Table 15). **Sevoflurane** is oxidized in the atmosphere to $(CF_3)_2CHOCOF$ by 93 % and decomposed to formyl fluoride (HCFO) and CF_3COCF_3 by 7 %, whereby the latter is completely hydrolysed to TFA (Sulbaek Andersen et al. 2012b, see also Table 15). According to Sulbaek Andersen et al. (2012b), $(CF_3)_2CHOCOF$ is probably dissolved in seawater within one to three years. The TFA yield of **sevoflurane**, related to non-marine sinks, is therefore about 7 %.

HFEs and HCFEs, together with PFCs, SF_6 and alcohols, accounted for about two to three percent of the total reported use of fluorinated gases in 2018 (expert statement, the exact figures are confidential). Therefore, HFEs and HCFEs do not represent a quantitatively relevant group of substances so far.

Furthermore, **partially fluorinated alcohols (PFAs)** have been considered as substitutes for CFCs and HCFCs for certain applications (Sellevåg et al. 2004b). These alcohols are also formed during the atmospheric degradation of, among others, CFCs and their substitutes and, if they carry a C-CF_3 group, can be atmospherically degraded to TFA (Hurley et al. 2004b, Burkholder et al. 2015). In part, the TFA yield has been studied. For example, the atmospheric degradation of 2,2,2-trifluoroethanol (TFE, CF_3CH_2OH) via reaction with OH radicals leads to trifluoroacetaldehyde (Sellevåg et al. 2004b, Vasil'ev et al. 2006). Furthermore, wet deposition accounts for about 30 % of the total deposition of 2,2,2-trifluoroethanol (Chen et al. 2003).

Some PFAs are produced on purpose, e.g. 2,2,2-trifluoroethanol, 2,2,3,3,3-pentafluoro-1-propanol ($CF_3CF_2CH_2OH$) or 2,2,3,3,4,4,4-heptafluoro-1-butanol ($CF_3CF_2CF_2CH_2OH$). 2,2,2-trifluoroethanol is used as a solvent (Bégué et al. 2004), while 2,2,3,3,3-pentafluoro-1-propanol is used as a derivatization reagent in laboratory diagnostics[104]. 2,2,3,3,4,4,4-heptafluoro-1-butanol is used as a derivatization reagent (Northen et al. 2008). It is an isomer of HFE-7000, but much more reactive (Díaz-de-Mera et al. 2008).

Another important group are unsaturated perfluorinated hydrocarbons (unsaturated PFCs). These consist exclusively of carbon and fluorine, but have a very short atmospheric lifetime (Acerboni et al. 2001). Interesting representatives of this group are in particular R1114 and R1216, whose tonnage in

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[101] Personal communication with staff of small and large animal clinics in Germany.

[102] https://www.bundestag.de/dokumente/textarchiv/2018/kw45-de-tierschutzgesetz-577236 (last access 06.03.2020)

[103] https://www.bvl.bund.de/SharedDocs/Fachmeldungen/05_tierarzneimittel/2018/2018_11_23_Fa_Isofluran.html (last access 06.03.2020)

[104] https://www.sigmaaldrich.com/catalog/product/aldrich/257478?lang=de&region=DE (last access: 20.08.2018)

the EU under REACH is estimated at 10,000 to 100,000 tonnes each[105,106]. R1114 is better known as tetrafluoroethene (tetrafluoroethylene[107], $CF_2=CF_2$) and is used as monomer in the production of polytetrafluoroethylene (PTFE). Tetrafluoroethene is produced using HCFC-22, which in turn is used as a starting material for the production of R1216 (hexafluoropropene, $CF_3CF=CF_2$) (Freudenreich et al. 1993). This serves as a co-monomer in fluoropolymer production. As an unwanted product, however, it can also be released into the atmosphere during the combustion of fluoropolymers (Ellis et al. 2001b). Once there, it is completely degraded to TFA (Mashino et al. 2000). Tetrafluoroethene cannot degrade to TFA. The combustion of fluoropolymers can also lead directly to the formation and emission of TFA into the atmosphere (Ellis et al. 2001b).

In principle, many other fluorinated substances with C-CF_3 bodies can be potential sources of TFA from the atmosphere. However, these are often little studied or do not play a relevant role in terms of quantity at present. For example, Jackson et al. (2011) report the theoretically possible formation of TFA through the photolytic degradation of the liquid extinguishing agent Novec 1230 (PFMP, perfluoro(2-methyl-3-pentanone), $CF_3CF_2C(O)CF(CF_3)_2$).

2.9 Trifluoroacetic acid (TFA) and trifluoroacetate in the environment

2.9.1 Input path of trifluoroacetic acid (TFA) into the environment

Trifluoroacetic acid (TFA) was identified as the quantitatively most important persistent degradation product from halogenated refrigerants and blowing agents in this project (Table 16). TFA is formed in aqueous solution by hydrolysis, especially of trifluoroacetyl fluoride (TFF)[108], e.g. in the form of humidity or precipitation, but also by the degradation of trifluoroacetaldehyde. Since TFA is highly soluble in water, wet deposition in surface water occurs during precipitation events. Furthermore, dry deposition, in the form of deposition of airborne solid and gaseous particles, can occur on soil and vegetation.

TFA released into the environment forms salts (trifluoroacetates) with ions such as sodium, potassium, magnesium, or calcium (Solomon et al. 2016, see also Table 16) and can eventually be released into waters such as the oceans. In surface waters, trifluoroacetate can also remain for longer periods of time, for example under conditions of lack of runoff and high transpiration rates.

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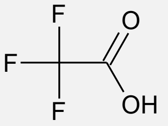
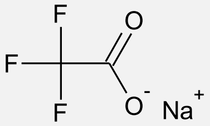
[105] https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15453 (last access: 06.04.2020)

[106] https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15192 (last access: 06.04.2020)

[107] The abbreviation TFE is identical to that of 2,2,2-trifluoroethanol. To avoid confusion, the abbreviation TFE is not used in this report.

[108] TFA can also be produced with a very high molar yield by hydrolysis of TFAC (trifluoroacetyl chloride). However, the substances discussed in this report are usually degraded atmospherically via TFF or trifluoroacetaldehyde, since they do not contain chlorine in the case of HFCs and the u-HCFCs investigated so far are not degraded via TFAC (see Chapter 0).

Table 16: Some characteristics of trifluoroacetic acid (TFA) and trifluoroacetate (here for example the sodium salt of trifluoroacetic acid, sodium trifluoroacetate).

Name	Trifluoroacetic acid	Sodium trifluoroacetate
Structural formula		
Synonyms	perfluoroacetic acid, trifluoroethanoic acid, 2,2,2-trifluoroethanoic acid, TFA	sodium perfluoroacetate, sodium salt of trifluoroacetic acid, sodium 2,2,2-trifluoroacetate, partly also "TFA" (in this report TFA always refers to trifluoroacetic acid)
Molecular formula	CF_3COOH, $C_2HF_3O_2$	$CF_3COO^- Na^+$, $C_2F_3NaO_2$
Family of chemicals	perfluorocarboxylic acid	salt of perfluorocarboxylic acid
CAS number	76-05-1	2923-18-4
Molar mass	114.023 g/mol	136.005 g/mol

Trifluoroacetate is only slightly retained in **soil** (Likens et al. 1997, Richey et al. 1997) and remains in the hydrosphere. Mass transport in soil is influenced by conservative transport processes (diffusion and dispersion) and non-conservative transport processes (adsorption and chemical and biological degradation reactions). Trifluoroacetate seems to show differences in the specific transport process depending on the degree of soil water saturation (Likens et al. 1997). Mineral aerobic soils can favour diffusion and transport with the soil water. In water-influenced ecosystems, trifluoroacetate is retained to a higher degree in soil and vegetation. Due to the increased bioaccumulation of trifluoroacetate in plant communities of water-saturated soils, there is an increased potential for damage.

Standley & Bott (1998) investigated the biomolecular uptake of trifluoroacetate in **aquatic organisms**. Because of the structural similarity of sodium trifluoroacetate (the sodium salt of trifluoroacetic acid, see Table 16) to the salt of acetic acid (CH_3COO^-), a biochemical intermediate and microbial nutrient, trifluoroacetate is potentially used by organisms in lipids or acetylated proteins. In fact, Standley & Bott (1998) demonstrated in mesocosm experiments with radioactively labelled sodium trifluoroacetate the uptake and metabolic transformation of trifluoroacetate in aquatic organisms such as annelids (ringed worms), beetle larvae, water stars (*Callitriche spec.*), duckweed (*Lemna sp.*), and the orange-red balsam (*Impatiens capensis*).

Trifluoroacetate is absorbed by higher plants via the sap flow (transpiration) (Rollins et al. 1989, Likens et al. 1997) and accumulates in leaves (Jordan & Frank 1999, Benesch et al. 2002). In experiments on the sunflower (*Helianthus annuus*), accumulations in leaves, stem and roots were measured in varying degrees (Boutonnet et al. 1999).

Due to its persistence and high mobility, TFA or trifluoroacetate is to be classified as problematic with regard to its environmental impact and especially with regard to accumulations in **ground and drinking water**. Trifluoroacetate measurements for Germany have only been carried out in a few studies in the relevant technical literature so far (Table 17). Maximum concentrations in rainwater and water bodies were determined that are both well below the toxicity threshold for aquatic organisms and below the precautionary limit[109] of 10 µg/L (UBA 2008). It should be noted that many of these measurements date back up to 20 years.

Current measurements of the German Water Centre (TZW-Technologiezentrum Wasser Karlsruhe) showed trifluoroacetate concentrations in rainwater, surface water and spring water, which are in part significantly higher than the older measurements (see also Chapter 4). If one considers the TFA concentration in rainwater, which was calculated for the complete replacement of HFC-134a by u-HFC-1234yf from cars by Henne et al. (2012), the extreme case values predicted for Europe[110] are significantly higher and lie with up to 12 µg/L (12,000 ng/L) above the health orientation value (3 µg/L) (UBA 2019) as well as the precautionary measures value (10 µg/L) (UBA 2008).

Table 17: Concentrations of trifluoroacetate based on measurements in the hydrosphere for various sites in Germany and modelled trifluoroacetic acid (TFA) concentrations worldwide.

Medium	Place	Period	Trifluoroacetate concentration	Source
Rainwater				
	Bayreuth	1995	25-280 ng/L (mean: 100 ng/L)	Frank et al. (1996)
	Bayreuth	1995-1996	10-410 ng/L (mean: 110 ng/L)	Jordan & Frank (1999)
	Waldstein (mountain range in north-east Bavaria)	1998-1999	marine air: 3-64 ng/L (median: 35 ng/L), nonmarine air: 3-141 ng/L (median: 15 ng/L),	Römpp et al. (2001)
	Karlsruhe	2017	<50-2,400 ng/L	TZW internal measurements (2017)
	Berlin	2018^{a}	1,556 ng/L (after a long dry period), 370 ng/L (after 12 h rain)	Dorgerloh et al. (2019)
Surface water				
	Fichtelsee (Bavaria)	1995	70 ng/L	Frank et al. (1996)
	Weißenstädter See (Bavaria)	1995	115 ng/L	Frank et al. (1996)
	Lake Constance (Baden-Württemberg)	1995	60 ng/L	Frank et al. (1996)

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[109] Exceeding this value is intended to trigger immediate measures that serve as a precautionary defense against avoidably high pollution (UBA 2011),

[110] EU-28 plus Norway, Switzerland and Turkey

Medium	Place	Period	Trifluoroacetate concentration	Source
	Bayreuth (Roter Main)	1995	60-280 ng/L (mean: 140 ng/L)	Frank et al. (1996)
	Bayreuth	1995-1996	60-280 ng/L (mean: 140 ng/L)	Jordan & Frank (1999)
	Karlsruhe (Rhein)	2017	350-490 ng/L	TZW internal measurements (2017)
	Basel (Rhein)	2017	350-510 ng/L	TZW internal measurements (2017)
Spring water				
	Fichtelgebirge	1995	70-320 ng/L	Frank et al. (1996)
	Antonien spring (<1 % younger spring water content[b])	1995-1996	<10 ng/l	Jordan & Frank (1999)
	Thüringer Wald spring (<1 % younger spring water content)	1995-1996	<10 ng/l	Jordan & Frank (1999)
	Bayern spring (10 % younger spring water content)	1995-1996	13 ng/L	Jordan & Frank (1999)
	Rennsteig spring (15 % younger spring water content)	1995-1996	25 ng/L	Jordan & Frank (1999)
	Gallus spring (Swabian Alb)	2017	440-500 ng/L	TZW internal measurements (2017)
Fog water				
	Waldstein (mountain range in northeast Bavaria)	1998-1999	marine air: 20-930 ng/L (median: 100 ng/L), nonmarine air: 20-420 ng/L (median: 230 ng/L)	Römpp et al. (2001)
Model calculations for the concentration of TFA in rainwater from different HCFCs, HFCs and u-HFCs				
	Worldwide[c]	2010	160 ng/L	Tromp et al. (1995)
	Worldwide[c]	2010	120 ng/L	Kotamarthi et al. (1998)
	Europe in July[c]	2010	300 ng/L	Kotamarthi et al. (1998)
	Europe (EU-28 + Norway, Switzerland & Turkey)[d]	2016[e]	annual mean: 620 ng/L[f], max.: 2,099 ng/L[f]	Wang et al. (2018)

Medium	Place	Period	Trifluoroacetate concentration	Source
	Europe (EU-28 + Norway, Switzerland & Turkey)[d]	2020[e]	annual mean: 600-800 ng/L[g], summer max.: 12,000 ng/L[h]	Henne et al. (2012)
	Southern Germany[d]	2020[d]	annual max.: 2,000 ng/L[g]	Henne et al. (2012)

[a] This is an assumption. In the article by Dorgerloh et al. (2019) it is not stated when the rainwater samples were taken.

[b] Younger spring water is anthropogenically influenced, e.g. because it is connected to water cycles that are contaminated with trifluoroacetate by human activity and thus also introduce trifluoroacetate into the spring water. The age of spring water is determined by radioisotope analysis (Jordan & Frank 1999).

[c] Only for TFA from the emission of HCFC-123, HCFC-124 and HFC-134a.

[d] Only for TFA from the emission of u-HFC-1234yf from car air conditioning systems.

[e] Assuming the complete replacement of HFC-134a with u-HFC-1234yf in car air conditioning systems.

[f] Based on the high emission scenario from Henne et al. (2012).

[g] High emission scenario, simulation over the whole year.

[h] High emission scenario, simulation for summer (mid-June to end of August), peak values only in Mediterranean areas with low precipitation.

Trifluoroacetate cannot be detected in older spring waters (Table 17), which indicates that the significant input of trifluoroacetate into the environment is of anthropogenic origin (Jordan & Frank 1999). This is supported by the fact that rivers in less industrialized areas have lower trifluoroacetate concentrations. Overall, a long-term accumulation of trifluoroacetate must be expected. In fact, trifluoroacetate can now be detected ubiquitously in anthropogenically influenced waters.

Due to considerable industrial discharges (e.g. in the Neckar river in 2016), TFA or trifluoroacetate has become the focus of attention of drinking water suppliers and analytical research institutes. The maximum trifluoroacetate concentrations of >100 µg/L found in the Neckar River in this context (Scheurer et al. 2017) have induced systematic investigations on the removal of trifluoroacetate during drinking water treatment. The TZW Karlsruhe therefore examined the suitability of common water treatment methods such as activated carbon treatment, ozonation and chlorination as well as special methods such as ion exchange and reverse osmosis. Of the tested processes, an effective removal of trifluoroacetate is only possible with the very cost-intensive reverse osmosis (Scheurer et al. 2017).

So far, applied simulation models for the future concentration of TFA in rainwater are based on the assumption that all car air conditioning systems are operated with the refrigerant u-HFC-1234yf. Based on this assumption, a 2.5-month regional 3D atmosphere model for North America was developed by Luecken et al. (2010). The model revealed a locally different deposition and concentration of TFA with less global transport compared to HFC-134a. This can be attributed to the faster atmospheric degradation of u-HFC-1234yf. Luecken et al. (2010) found an average deposition of 0.24 kg/m^2 TFA, which is significantly higher than the highest estimates for all HFC sources, with concentration peaks in rain of 1,264 ng/L, which would be below the lowest concentration by around a factor of 44 for which no damage to aquatic organisms is assumed (PNEC = 56,000 ng/L[111]).

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[111] Predicted No-Effect Concentration (PNEC) from the REACH registration dossier for TFA (https://echa.europa.eu/de/brief-profile/-/briefprofile/100.000.846, last access: 28.03.2020)

Another simulation was carried out for Europe[112] by Henne et al. (2012), who also assumed that all car air conditioning systems are operated with the refrigerant u-HFC-1234yf. Based on the FLEXPART and CRI-STOCHEM models used, the authors arrived at a total emission level of u-HFC-1234yf for Europe in 2020 (after complete replacement of HFC-134a in the model) of 11.0-19.2 kilotonnes per year. About 30-40 % of these emissions are deposited within Europe in the form of TFA, the rest is transported in the atmosphere towards the Atlantic, Central Asia and Africa. The maximum annual concentration in rainwater is estimated at 2,000 ng/L for southern Germany. This concentration would be 28 times lower than the PNEC for aquatic organisms. At the maximum, Henne et al. (2012) arrived at 12,000 ng/L TFA, which would be less than 5 times below the PNEC.

Similarly, Wang et al. (2018) came to a maximum annual concentration of TFA in rainwater of 2,099 ng/L for Europe in a simulation study. They assumed that in 2016 all air conditioning systems of the entire car fleet were operated exclusively with u-HFC-1234yf. The annual deposition rate of TFA according to this assumption was 5.87 kilotonnes per year. Wang et al. (2018) calculated the annual deposition rate of TFA also under the assumption that the number of passenger cars will increase until 2030 and the higher number of vehicles resulted in an annual deposition rate of 6.14 kilotonnes per year.

The atmospheric degradation of HCFCs, HFCs, u-HFCs and u-HCFCs represents a relevant TFA source, since the amount of continuously formed TFA from halogenated substances will increase strongly in the future, mainly due to the increased use of the refrigerant u-HFC-1234yf in mobile passenger car air conditioning systems and in refrigerant mixtures for mobile and especially stationary systems. The input of TFA and trifluoroacetate into water bodies (incl. drinking water) has been examined in the course of this project by a nationwide measuring program (Chapter 4).

On the basis of these current research results, an estimation of the future development of TFA and trifluoroacetate inputs into water bodies is indispensable also in terms of sustainable resource protection.

2.9.2 Natural TFA sources

TFA is on the one hand anthropogenically introduced into the environment by the degradation of fluorinated substances (see Chapter 2.7), on the other hand TFA is also formed naturally. Thus, a certain amount of TFA can be detected in the oceans, which was measured at individual places. In the North Atlantic the concentration of TFA was 70 ng/L (Ireland) and 250 ng/L (France), in the South Atlantic (South Africa) 160 ng/L and in the South Pacific (Australia) 200 ng/L (Frank et al. 1996, Jordan & Frank 1999).

Frank et al. (2002) made further measurements at different depths in the southern North Atlantic and Southern Ocean, measuring concentrations of 190 to 220 ng/L TFA. Frank et al. (2002) assume on the basis of all above mentioned measurements a homogeneous concentration of TFA in the oceans of about 200 ng/L worldwide. Assuming 1.34 x 10^{21} L of water in the oceans, the authors assume a total amount of 268 million tons of TFA in the oceans.

In contrast, Scott et al. (2005) have measured very heterogeneous TFA concentrations in the oceans, ranging from less than 10 ng/L in the Pacific to over 150 ng/L in the Atlantic. While 60 to 160 ng/L TFA were measured in the Arctic Ocean (Canada Basin) down to 700 m depth, the concentration in deeper waters (water older than 1,000 years) was constant at 150 ng/L. In the Northwest Pacific the TFA concentration was low up to 100 m depth and from there up to 60 ng/L. In the South Pacific the TFA concentration was generally low, only in some places with a depth of more than 800 m it was

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[112] EU-28 plus Norway, Switzerland and Turkey

50 ng/L or more. In general, high and homogeneous values were measured by Scott et al. (2005) in waters of the Atlantic and Arctic Oceans, but lower and less homogeneous values were measured in the Pacific. Based on their own measurements, Scott et al. (2005) assume a quantity of 61 to 205 million tons of TFA in the oceans. According to the authors, the origin of TFA in the oceans cannot be explained by natural input from deep-sea vents alone. In summary it can be stated that at present only a limited state of knowledge exists concerning the occurrence of TFA in the oceans, whereby, as explained above, the results and statements of different authors (Frank et al. 2002, Scott et al. 2005) contradict each other partially. Current measurements of TFA in seawater could help to clarify existing contradictions and questions and furthermore could provide knowledge about the existence and nature of natural TFA sources.

According to the present state of knowledge, the TFA in the ocean originates from natural sources as well as from the input of anthropogenically introduced TFA into the environment, which passes into the water phase and then into the oceans. TFA salts can also be transported from the oceans back to the land. This discharge is probably analogous to other salts, which can be transported away as aerosols by physical processes such as the bursting of air bubbles at the sea surface (Gong et al. 1997). In a "Special Review" the EFCTC estimates the amount of TFA transported globally from the oceans to the mainland to be about 4,000 tons per year (EFCTC 2016). The authors of the "Special Review" come to this conclusion based on the concentration ratio of chloride to TFA in seawater. Since a further description of the method was not provided by EFCTC, even upon request, the results cannot be reproduced and validated.

However, if one assumes - as the EFCTC does - that TFA behaves like chloride, a different scenario emerges: seawater has an average salinity of 35 g per litre, with chloride accounting for 55 %. This results in a concentration of about 19 g chloride per litre of seawater. The relevant studies on the concentration of TFA in seawater were quoted above, where 150 ng/L can be considered realistic and corresponds to the 200 million tons of TFA reported by the EFCTC in its "Special Review"[113]. The concentration of chloride in the precipitation above the mainland is about 10 to 20 mg/L. If one assumes that a maximum concentration of 20 mg/L is only fed by the seawater discharge, the discharge of TFA would be analogous to the global annual discharge of 0.16 ng/L, i.e. very small. If one follows the assumption of the EFCTC regarding the comparability of chloride and TFA, in relation to the discharge from the sea, the contribution of TFA from the sea can be estimated as negligible.

2.9.3 Further reactions of trifluoroacetic acid (TFA) in the atmosphere

Trifluoroacetic acid (TFA) is highly persistent in the atmosphere, but there are two chemical reaction paths that can partially lead to the degradation of TFA in the atmosphere. However, these are far less likely than the entry of TFA into the environment via the precipitation from the atmosphere.

2.9.3.1 Reaction with OH radicals

On the one hand, TFA can react with OH radicals, producing CF_3COO radicals and water (Møgelberg et al. 1994). As described in Chapter 2.7.3, these radicals are further decomposed in the atmosphere to HF and CO_2. However, TFA has an atmospheric lifetime of about 230 days with respect to the reaction with OH radicals (Hurley et al. 2004a), which is much longer than the lifetime with respect to wet and dry deposition of 9 days (Kotamarthi et al. 1998) and 10 to 30 days (Tromp et al. 1995), respectively.

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[113] Based on the assumption that the global volume of the oceans is approx. 1.3 x 10^9 km^3 and thus 1.3 x 10^{21} L, at 150 ng TFA per liter this results in a total amount of 200 million tons TFA.

Therefore, contrary to the estimate of Møgelberg et al. (1994) that the reaction with OH radicals accounts for 10-20 % of the TFA loss in the atmosphere[114], this degradation path can be neglected with high probability. Kanakidou et al. (1995) estimate that the loss of TFA by reaction with OH radicals reduces the amount of TFA in rainwater by a maximum of 5 %. Therefore, Kotamarthi et al. (1998), for example, do not include the loss of OH radicals in their model study on the formation of TFA by the degradation of HCFCs and HFCs. Henne et al. (2012) found in their models a degradation rate of TFA by OH radicals of about 1 % to 3 %.

2.9.3.2 Reaction with Criegee intermediates

There is the possibility that TFA molecules react with Criegee intermediates[115] in the atmosphere (Chhantyal-Pun et al. 2017). The reaction with Criegee intermediates could, according to Chhantyal-Pun et al. (2017), represent the dominant reaction path of TFA in forested regions with 4 days of atmospheric lifetime, in contrast to approximately 10 days for wet and dry deposition[116]. Model calculations showed that the reaction of TFA with Criegee intermediates in the atmosphere could account for about 13.5 % of all degradation processes (including degradation by OH radicals, as well as wet and dry deposition) for Central Europe and approximately 9.2 % to 17.1 % for Germany.[117]

This reaction takes place preferentially over wooded areas due to the more frequent occurrence of Criegee intermediates.[118] The products of the reaction are hydroperoxyester (HPE) adducts,[119] which in turn can be broken down by OH radicals. For example, if a TFA molecule reacts with the Criegee zwitterion e.g. CH_2OO, the HPE $CF_3C(O)OCH_2OOH$ is formed. This can further react with OH radicals in the atmosphere[120]:

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[114] The reason for this estimate is the assumption of Møgelberg et al. (1994) that the atmospheric lifetime of TFA with respect to OH radical degradation is 68 days. This was clearly corrected upwards by Hurley et al. (2004a). It should be mentioned that Timothy J. Wallington and Michael D. Hurley were involved in both publications.

[115] Criegee intermediates or zwitterions are short-lived carbonyl oxides with two individual radical centers (https://www.internetchemie.info/chemie-lexikon/stoffe/c/criegee-intermediat.php, last access 20.07.2020). They are formed during the reaction of alkenes with ozone in the air and in plant cells (source: Lexikon waldschädigende Luftverunreinigungen und Klimawandel, http://bfw.ac.at/rz/wlv.lexikon?keywin=375, last accessed 20.07.2020).

[116] Chhantyal-Pun et al. (2017) assume a rate of approx. 10 days for TFA with regard to wet and dry deposition, with reference to Hurley et al. (2004a), who only determined rates for the reaction of TFA with OH radicals. Hurley et al. (2004a) cite the deposition rates from Kotamarthi et al. (1998) and Tromp et al. (1995) and summarize both deposition rates for perfluorocarboxylic acids with approx. 10 days each.

[117] Personal communication with Dr. Anwar Khan (School of Chemistry, University of Bristol on April 30, 2020). The 13.5% relate to the approximate center of Central Europe in the north of the Czech Republic (coordinates: 50 ° 22'42.4992 "N 14 ° 58'14.1528" E), the 9.2% to 17.1% to the locations of measuring stations of precipitation from Chapter 4 (for coordinates, see Table 28 in Chapter 4.3). The numbers were provided by Dr. Anwar Khan based on model calculations with the updated Criegee field from Holland et al. (2020). This update lowers the modeled value of contribution of the reaction of TFA and other perfluorocarboxylic acids with Criegee intermediates in relation to the other loss processes from Chhantyal-Pun et al. (2017) and Chhantyal-Pun et al. (2018) significantly.

[118] Forested areas are the world's largest source of alkenes that react with ozone to produce Criegee intermediates (personal communication with Dr. Rabi Chhantyal-Pun, School of Chemistry, University of Bristol on September 20, 2018)

[119] Compound molecules from the two original molecules without the formation of by-products

[120] Personal communication with Dr. Rabi Chhantyal-Pun (School of Chemistry, University of Bristol) on September 24th, 2018

1. $CF_3C(O)OCH_2OOH$ (HPE) + OH → $CF_3C(O)OCH_2OO + H_2O$
2. $CF_3C(O)OCH_2OO + NO → CF_3C(O)OCH_2O + NO_2$
    a. $CF_3C(O)OCH_2O + N_2 → CF_3C(O)O + H_2CO$ (C-C bond breaking)
    b. $CF_3C(O)OCH_2O + O_2 → CF_3C(O)OC(O)H + HO_2$
        i. $CF_3C(O)OC(O)H + H_2O →$ **$CF_3C(O)OH$ (TFA)** + HC(O)OH (hydrolysis)

Here, C-C bond breaking and hydrolysis compete, with the former irreversibly destroying TFA (see degradation path of the CF_3COO radical in Figure 8 in Chapter 2.7.3.2, while TFA is re-formed by hydrolysis. The latest studies have shown that perfluorooctanoic acid (PFOA) reacts with Criegee intermediates to produce another HPE, that is most certainly deposited in aqueous media where PFOA is regenerated, thus accelerating the transfer of PFOA to aqueous phases in the process (Holland et al. 2020). This very probably applies in the same way to other perfluorocarboxylic acids such as TFA, so that their irreversible destruction should only be about 10 %.121 For Germany, about 0.9 % to 1.7 % of the TFA molecules in the atmosphere would be destroyed by Criegee intermediates. The reaction with Criegee intermediates therefore does not represent a significant degradation path for TFA in Germany, but merely accelerates the wet deposition.

This might also explain why Jordan & Frank (1999) measured a 2.6-fold higher TFA concentration in rain that had fallen through the canopy of a spruce forest than that collected in an adjacent open area. The authors explain this with an evaporative concentration of rain on the leaf surface, as well as with a dry deposition of TFA on the plant surface with subsequent rinsing by rain. However, it is also possible that the wet deposition of TFA over the forested area was accelerated by the higher concentration of Criegee intermediates.

2.10 Biodegradability and ecotoxicity of halogenated low-GWP refrigerants and blowing agents and their persistent atmospheric degradation products

2.10.1 Halogenated refrigerants and blowing agents with small GWP

2.10.1.1 Biodegradability

The data on the biodegradability of the halogenated refrigerants and blowing agents with small GWP considered in detail in this study is incomplete and based partly on estimates. However, the data unanimously show that the substances are not hydrolytically split and are not biodegradable. Im et al. (2014) conducted aerobic and anoxic microcosm experiments with u-HFC-1234yf in closed serum bottles inoculated with 5 g/100 mL sediment or soil (no standard tests). In these tests, u-HFC-1234yf was not susceptible to microbial, cometabolic[122] or abiotic degradation. However, the transferability of the results from closed systems to the real environment and thus the question whether u-HFC-1234yf can enter the groundwater is controversially discussed (Im et al. 2015). Recent work does not provide any more recent data either (Fleet et al. 2017). Review articles on the degradability and ecotoxicity of HFCs and HCFCs based on the corresponding ECETOC substance dossiers concern compounds other than those under consideration, but they demonstrate the poor degradability and moderate ecotoxicity of these substance groups (Berends et al. 1999b).

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[121] Personal communication with Dr. Rabi Chhantyal-Pun and Prof. Dr. Dudley E. Shallcross (School of Chemistry, University of Bristol) on April 22nd, 2020

[122] Cometabolism: Metabolism of a substance by a cell or a microorganism, in which the cell neither obtains energy from the metabolism nor can further utilize the products of this metabolism.

2.10.1.2 Ecotoxicity

With the exception of u-HFC-1234yf, u-HFC-1234ze, u-HCFC-1233zd and u-HFC-1336mzz, the ecotoxicity data is weak and based mainly on QSAR estimates. The available information is summarized in Table 18. Detailed information on the biodegradability and ecotoxicity of the above substances is provided in Annex A.8.

Table 18: Toxicity of various halogenated refrigerants and blowing agents with small GWP according to REACH registration dossiers. LC_{50}, medium lethal concentration (death of 50 % of the untested population). EC_{50}, medium effective concentration (effect in 50 % of the untested population). LOEC, "lowest observed effect concentration" (lowest concentration at which an effect on the organism occurs). NOEC, "no observed effect concentration" (highest dose at which no effect on the organism occurs). -, no data available. (Status: March 2020)

Group of organisms	u-HFC-1234yf	u-HFC-1234ze	u-HCFC-1233zd	u-HFC-1336mzz
Fish (acute)	33 mg/L (LC_{50})	>117 mg/L (LC_{50})	38 mg/L (LC_{50})	76.1 mg/L (LC_{50})
Fish (chronic)	2.7 mg/L (NOEC) 5.4 mg/L (LOEC) 22 mg/L (EC_{50})	-	-	9.58 mg/L (NOEC)
Daphnia (acute)	34 mg/L (NOEC) 65 mg/L (EC_{50})	160 mg/L (EC_{50})	82 mg/L (EC_{50})	22.5 mg/L (EC_{50})
Daphnia (chronic)	15.2 mg/L (NOEC)	-	-	10.2 mg/L (NOEC)
Aquatic algae and cyanobacteria	>75 mg/L (NOEC) >100 mg/L (EC_{50})	170 mg/L (NOEC)	115 mg/L (NOEC) 215 mg/L (EC_{50})	6.92 mg/L (NOEC) 23.7 mg/L (EC_{50})
Microorganisms	-	-	-	1,000 mg/L (EC_{50})

Based on the data from the various tests in Table 18, REACH lists concentrations for substances for which no negative environmental effects are to be expected ("Predicted No-Effect Concentration", PNEC). The PNEC is derived from the lowest available NOEC or EC10 values obtained in chronic tests. Depending on the number and type of available tests, the NOEC or EC10 value is divided by a safety factor of up to 100 (ECHA 2017). Available PNECs are listed in Table 19 for some partially halogenated greenhouse gases with small GWP.

Table 19: Ecotoxicological information for u-HFC-1234yf, u-HFC-1234ze(E) and u-HCFC-1233zd(E) from the REACH dossiers. Shown is the concentration at which no negative environmental effects are to be expected (PNEC - Predicted No-Effect Concentration). -, no data available. (Status: March 2020)

Danger for	u-HFC-1234yf	u-HFC-1234ze(E)	u-HCFC-1233zd(E)
Aquatic organisms			
Fresh water	100 - 250 µg/L	100 µg/L	38 µg/L
Fresh water (intermittent release)	330 - 1,000 µg/L	1 mg/L	380 µg/L
Seawater	25 µg/L	-	3.8 µg/L
Sea water (intermittent release)	no dangers detected	-	-
Sewage treatment plant	no emissions to be expected	-	no dangers detected

Danger for	u-HFC-1234yf	u-HFC-1234ze(E)	u-HCFC-1233zd(E)
Sediment (fresh water)	1.35 mg/kg dry weight	-	691 µg/kg dry weight
Sediment (sea water)	135 µg/kg dry weight	-	69.1 µg/kg dry weight
Air	no dangers detected	-	no dangers detected
Terrestrial organisms (soil)	720 µg/kg dry weight	-	126 µg/kg dry weight
Predators (secondary poisoning)	no bioaccumulation potential	-	no bioaccumulation potential

2.10.1.3 Toxicity

In general, HFCs have a rather low toxicity. Because of their low boiling points, they are highly volatile. HFC gases and vapours are heavier than air, can accumulate in enclosed spaces, especially on the ground or in lower areas, and can reach high concentrations. Very high concentrations of HFCs can lead to life-threatening cardiac arrhythmia and suffocation due to oxygen displacement.

There are several potential risks associated with u-HFCs and u-HCFCs, including flammability, especially with u-HFCs, and the potential for the formation of hydrofluoric acid and TFA.

Combustion products

Hydrofluoric acid is the name for the aqueous solution of the gas hydrogen fluoride (HF), which like the gas is highly corrosive and very toxic. In connection with the discussion about safety in passenger car air conditioning systems, it has been shown many times that hydrogen fluoride, among other things, can be produced during combustion of the refrigerant u-HFC-1234yf (see Chapter 2.6.1). While HFC-134a is classified as A1 according to the refrigerant standard ISO 817[123], i.e. as a non-flammable refrigerant with low toxicity, u-HFC-1234yf has the classification A2L and is therefore considered a refrigerant with low toxicity and low flammability. At high temperatures, on hot surfaces and in fires, u-HFC-1234yf forms hydrogen fluoride, which forms corrosive hydrofluoric acid on contact with air humidity or water (BAM 2010, KBA 2013). The u-HFC-1234ze(E) also forms toxic fluorinated gases such as hydrogen fluoride in the event of ignition or fire (see Chapter 2.6.1).

Workplace limit value

In 2014, the German Research Foundation (DFG) published an 8-hour workplace limit value (Maximum Workplace Concentration German: Maximale Arbeitsplatzkonzentration, MAK) for 2,3,3,3-tetrafluoropropene (u-HFC-1234yf) of 100 mL/m^3 (ppm) (DFG 2014), which was raised to 200 ml/m^3(ppm) in 2015 following objections (DFG 2015a, DFG 2015b) and continues to be stated as such (DFG 2018). Since its publication in the Joint Ministerial Gazette (GMBl 2016) in Germany in June 2016, the value of 200 ppm is a legally binding occupational exposure limit in Germany and is listed in the Technical Rules for Hazardous Substances (TRGS 900)[124].

According to the international standard ISO 817 No. 6.1.2, a refrigerant with an occupational exposure limit below 400 ppm is classified in Class B (higher chronic toxicity), based on occupational exposure

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[123] ISO 817 divides refrigerants into different classes of toxicity and flammability. A stands for "lower toxicity", B for "higher toxicity". The number 1 stands for "no flame propagation", 2L for lower flammability, 2 for flammable and 3 for higher flammability.

[124] TRGS 900: Technical Rules for Hazardous Substances: Occupational Exposure Limits. BArBl magazine 1/2006 p. 41-55, edition: January 2006, admissible modified and supplemented: GMBl 2018 p.542-545 [No.28] (version 07.06.2018) https://www.baua.de/DE/Angebote/Rechtstexte-und-Technische-Regeln/Regelwerk/TRGS/pdf/TRGS-900.pdf?__blob=publicationFile (last access: 23.10.2018)

limits such as the MAK value (ISO 2017). An occupational exposure limit value of 200 ppm would result in the refrigerant being classified as Class B (higher chronic toxicity). However, the u-HFC-1234yf is currently listed there as a Class A refrigerant (lower chronic toxicity). The classification of u-HFC-1234yf in ISO 817 and in the U.S. ASHRAE 34 (ASHRAE 2016) refrigerant standard as a Class A refrigerant is based on the 2008 Workplace Environmental Exposure Levels Committee (WEEL) value of 500 ppm. However, the U.S. EPA ("Environmental Protection Agency") had already specified a stricter workplace exposure limit of 250 ppm over 8 hours in 2011 in the approval of u-HFC-1234yf for passenger cars and repeatedly in 2016 for larger vehicles (EPA 2011, EPA 2016). So far, neither ASHRAE nor ISO have complied with the request of the German standardization institute DIN in 2017 to classify u-HFC-1234yf as a Class B refrigerant (higher chronic toxicity) based on the new DFG MAK value of 200 ppm for u-HFC-1234yf. Instead, refrigerant manufacturers are discussing new criteria for the classification of refrigerants in order to maintain the classification in Class A.

In some German safety data sheets for u-HFC-1234yf the value of 200 ppm was specified (Honeywell 2016, Friedrichs 2017), but in a current German safety data sheet the value of 500 ppm (Honeywell 2018) is found again or the specification is missing completely (Linde 2016).

Substance evaluation u-HFC-1234yf

Due to the hazardous degradation products, consumer exposure, the high expected volumes in the field of mobile air conditioning, the widespread use, and the high environmental impact, u-HFC-1234yf[125] was included in 2012 in the Community Rolling Action Plan (CoRAP[126]) for substance evaluation of chemicals under the European REACH regulation in Europe. The aim of the substance evaluation is to examine the above-mentioned risk-based concerns regarding the use of u-HFC-1234yf and, if necessary, to make follow-up demands or propose measures. The publication of the substance evaluation is still pending due to additional requests from the EU Commission to the registrants with regard to a possible mutagenicity. A publication of the substance evaluation by the European Chemicals Agency (ECHA) has not yet taken place (status: September 2020).

Toxicity data from the ECHA database

Registration dossiers for u-HFC-1234yf, u-HFC-1234ze(E) and u-HCFC-1233zd(E) are available in the ECHA database in accordance with the EU REACH Regulation[127]: **u-HFC-1234yf** has been described as low-risk by inhalation, skin, eye or oral exposure, with only a derived no-effect level (DNEL) for repeated intake defined at 950 mg/m^3 for workers.[128] For **u-HFC-1234ze**, no hazard has been identified so far for inhalation exposure, although the long-term limit for repeated intakes is 3,902 mg/m^3 for workers and 830 mg/m^3 for the general population. There are no data for skin, eye, and oral exposure. There is no known risk to the general population for local inhalation effects.[129] According to the REACH dossier, both u-HFCs are only slightly absorbed, minimally metabolized, and quickly excreted from the body. For **u-HCFC-1233zd**, no hazard has been demonstrated for inhalation, skin, eye, or oral exposure. However, there is a long-term inhalation limit of 1,779 mg/m^3 for workers and 379 mg/m^3 for the general population. There is also a long-term limit for oral exposure for the general population of 109 mg/kg body weight per day.[130]

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[125] The u-HFC-1234yf is called "polyhaloalkene" here.

[126] https://echa.europa.eu/de/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table/-/dislist/details/0b0236e1807e4409 (last access: 08.04.2020)

[127] For u-HFC-1336mzz(Z), a dossier is available but it does not contain any usable toxicological information.

[128] https://echa.europa.eu/de/brief-profile/-/briefprofile/100.104.879 (last access: 08.04.2020)

[129] https://echa.europa.eu/de/brief-profile/-/briefprofile/100.104.972 (last access: 08.04.2020)

[130] https://echa.europa.eu/de/brief-profile/-/briefprofile/100.149.148 (last access: 08.04.2020)

Further toxicity potentials

Halogenated compounds with a $=CF_2$ group are often associated with toxic effects because this group is highly reactive (McLinden et al. 2017), which is also called "$=CF_2$ structural alert" (Lindley & Noakes 2010). Relevant substances that carry a $=CF_2$ group include u-HFC-1345czf, u-CFC-1113, tetrafluoroethylene (R1114) and hexafluoropropene (R1216) (Lindley & Noakes 2010). The high correlation of reactivity and toxicity is also shown for u-HFC-1225zc, which also has a =CF2 group.

Only u-HFC-1123, which is marketed as a refrigerant, is an exception, as the substance carries a $=CF_2$ group, but is comparable in its acute toxicity to the currently used refrigerant u-HFC-1234ze(E) (Fukushima & Hashimoto 2015, McLinden et al. 2017). No data are available on the chronic toxicity of u-HFC-1123 (McLinden et al. 2017).

Some initially promising substitutes for HFCs are no longer considered or used due to their (potential) toxicity. These include both isomers (Z and E) of u-HFC-1225ye, which have potential sub-chronic and chronic toxicity (Lindley & Noakes 2010). The u-HFC-1225ye is a minor component of u-HFC-1234yf, and other possible minor components of u-HFCs and u-HCFCs have been shown to be harmful to health, e.g. the carcinogenic u-HCFC-1140, which can be formed during the production of u-HFC-1234yf (see Chapter 2.4.4).

2.10.2 Trifluoroacetic acid (TFA)

In 2000, the photolytic degradation of HCFC-123, HCFC-124 and HFC-134a was identified as the main source of TFA in the environment (Berg et al. 2000). Ellis and Mabury (2000) identified as a further source the substance 3-trifluoromethyl-4-nitrophenol (TFM), which is used in the large lakes against parasitic sea lampreys and is photolytically degraded to TFA at a wavelength of 365 nm. The surface-active perfluorooctanoic acid (PFOA), which is itself classified as persistent, is also converted to TFA by electrochemical treatment (Gong et al. 2014). During the ozonation of sewage treatment plant effluents, TFA can be formed from several precursors. In addition, TFA is also formed during the combustion of fluoropolymers such as polytetrafluoroethylene (trade name Teflon) (Scheurer et al. 2017). For TFA a detailed environmental risk analysis of Boutonnet et al. (1999) is available, so that the following research concentrates on the period starting in the year 2000.

2.10.2.1 Biodegradability

Different degradation results from standard tests with (extended) closed bottle tests (OECD 301 D) or the SCAS test (OECD 302 A) are available. The tests consistently report a negligible degradability of TFA. There is evidence that trifluoroacetic acid is degraded in both oxic (oxygen-containing) and anoxic (oxygen-free) marine sediments (Visscher et al. 1994, Oremland et al. 1995). The results could not be reproduced and are therefore questioned by Boutonnet et al. (1999). During bank filtration (26 meters in 8 days) TFA showed a conservative behaviour (Berg et al., 2000). Scheurer et al. (2017) confirm that TFA is neither degraded in sewage treatment plants nor in soil filters. Franco et al. (2014) describe that the mycorrhizal fungus *Pisolithus tinctorius* tolerates and is able to degrade TFA. Ellis et al. (2001a) observed in a field study no degradation of TFA even after one year. Kim et al (2000) report anaerobic TFA degradation via cometabolism[131] by reductive dehalogenation in a 90-week study.

2.10.2.2 Toxicity and ecotoxicity

Trifluoroacetic acid (TFA), as a concentrated acid, may pose a hazard to humans upon contact and ingestion. However, such exposure is highly unlikely due to the relatively low concentration in the atmosphere (Solomon et al. 2016). For workplaces where very high concentrations of TFA may be hand-

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[131] Cometabolic degradation has been demonstrated here in a mixed culture containing naturally occurring microorganisms commonly found in natural water systems.

led, inhalation and oral exposure limit values of 2,67 mg/m^3 and 16 mg/m^3 for long- and short-term inhalation and 42 µg/kg body weight per day for repeated oral intake apply[132]. TFA is not metabolised[133] in mammals according to Tang et al. (1998) and trifluoroacetate shows no genotoxicity according to Blake et al. (1981).

There are numerous ecotoxicity studies on trifluoroacetate, which indicate a low ecotoxic potential (see REACH registration dossier for TFA[132], Table 20). Trifluoroacetate is shown to have little ecotoxicological effect on the organisms studied, but most likely on the green freshwater algae *Raphidocelis subcapitata*.

Table 20: Ecotoxicological effects of trifluoroacetic acid (TFA) on various algae and land plants (REACH registration dossier for TFA[a]). EC_{10}, mean effective concentration (effect in 10 % of the investigated population). EC_{50}, mean effective concentration (effect in 50 % of the investigated population). LC_{50}, mean lethal concentration (death of 50 % of the investigated population). LOEC, "lowest observed effect concentration" (lowest concentration at which an effect on the organism occurs). NOEC, "no observed effect concentration" (highest dose at which no effect on the organism occurs). -, no data available. (Status: March 2020)

organism	EC_{10} (mg/L)	EC_{50} (mg/L)	LC_{50} (mg/L)	LOEC (mg/L)	NOEC (mg/L)
Raphidocelis subcapitata (freshwater green algae, former name Selenastrum capricornutum)	5.59	237	-	-	2.5
Lemna gibba (duckweed)	-	915[b], 999[c]	-	-	250[b,c]
Daphnia magna (water flea), short-term test	-	>999	-	-	999
Daphnia magna (water flea), long-term test	-	>25	-	>25	≥25
Danio rerio (zebrafish), short-term test	-	-	>999	-	≥999
microorganisms of a wastewater treatment plant near Darmstadt (Germany)	>832	>832	-	-	>832

[a] https://echa.europa.eu/de/registration-dossier/-/registered-dossier/5203 (last access: 28.03.2020)

[b] Effect on number of fronds.

[c] Effect on biomass.

The lowest TFA threshold (0.12 mg/L) was measured for the freshwater algae *Raphidocelis subcapitata* (formerly *Selenastrum capricornutum*) until 2017 (Boutonnet et al. 1999). Since the algae recovered when citric acid was added, the authors suspect a possible influence of trifluoroacetate on the citric acid cycle. Higher thresholds were found for other organisms such as duckweed and various higher land plants (Table 20). No interfering effects of TFA were observed in the anaerobic milieu (Emptage et al. 1997). In 2017, the results of previous studies on the effect of TFA on aquatic organisms and especially the freshwater algae *Raphidocelis subcapitata* were re-examined in a new study by INERIS (Chabot 2017). This study fulfilled the requirements of OECD TG 201 (OECD Testing Guideline 201,

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[132] https://echa.europa.eu/de/registration-dossier/-/registered-dossier/5203 (last access: 28.03.2020)

[133] Oral intake and inhalation studies in mice and rats.

version of 23.03.2006) and showed an EC_{50}[134] of 237 mg/L, an EC_{10}[135] of 5.59 mg/L and a NOEC[136] of 2.5 mg/L.

More recent work includes that of Smit et al. (2009), who investigated the effect of trifluoroacetate on garden beans (*Phaseolus vulgaris*) and maize (*Zea mays*). A significant inhibition of photosynthetic parameters was demonstrated at elevated trifluoroacetate concentrations. The growth of garden beans from day 7 to 14 showed a dose-dependent inhibition of 13 % at 0.625 mg/L Na-TFA and 76 % at 160 mg/L Na-TFA. The corresponding values for corn were 17 % to 70 %.

Hanson et al. (2002) investigated the mixed toxicity of trichloroacetic acid (TCA) and trifluoroacetic acid in aquatic microcosms for 49 days in the concentration range of 0.1 to 10 mg/L each and found no significant risk from TCA/TFA mixed toxicities in the environmentally relevant concentration range.

Ulhaq et al. (2013) investigated the effect of TFA in the fish embryo test with *Danio rerio* and determined an EC_{50} (6 days after fertilization) of 700 mg/L. Further ecotoxicity data are cited by Fleet et al. (2017) and complete the overall picture without providing significant new findings: Berends et al. (1999a) report the inhibitory effect of trifluoroacetate on various algae species (EC_{50} always >100 mg/L). Hanson et al. (2002) investigated the trifluoroacetate toxicity to the aquatic plants *Myriophyllum sibiricum* and *Myriophyllum spicatum* (EC_{50} = 357 mg/L and 313 mg/L).

A REACH registration dossier is available for TFA, in which further ecotoxicity data are documented.[137] In the acute daphnia test according to OECD Guideline 202, no toxicity of TFA to *Daphnia magna* (large water flea) was observed at concentrations up to 999 mg/L after 48 hours. In the chronic Daphnia test according to OECD Guideline 211, a NOEC ("No Observed Effect Concentration") ≥ 25 mg/L was observed after 21 days in relation to the survival rate of the parent animals and the reproduction rate. For acute toxicity in zebrafish over four days, a study according to OECD Guideline 203 showed a NOEC of 999 mg/L. However, there are no chronic data available for fish (e.g. "Fish early life stage test", FELS OECD Guideline 210). Furthermore, a study according to OECD Guideline 209 was performed on microorganisms, which showed a NOEC of more than 832 mg/L.

Based on the various toxicity tests, the PNEC ("Predicted No-Effect Concentration") for TFA, which is used to assess the environmental risk of a substance, was determined by ECHA for the different media (Table 21). According to the REACH dossier, it is 56 µg/L in fresh waters. The health orientation value (GOW) is 3 µg/L (UBA 2019). The precautionary value for TFA, which is only temporarily acceptable, is stated by the German Federal Environment Agency, following an EU recommendation, as 10 µg/L (SANCO 2003, UBA 2008)[138].

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[134] Average effective concentration (effect in 50 % of the investigated population).

[135] Average effective concentration (effect in 10 % of the investigated population).

[136] „No observed effect concentration" (highest dose at which no effect on the organism occurs).

[137] https://echa.europa.eu/de/registration-dossier/-/registered-dossier/5203 (last access: 28.03.2020)

[138] The derivation of a guide value for TFA in drinking water is under discussion (status May 2020).

Table 21: Ecotoxicological information for trifluoroacetic acid (TFA) from the REACH dossiers. If available, the Predicted No-Effect Concentration (PNEC) is given. (Status: March 2020)

Danger for	TFA
Aquatic organisms	
Fresh water	560 µg/L
Fresh water (intermittent release)	2.37 mg/L
Seawater	56 µg/L
Sea water (intermittent release)	no data available
Sewage treatment plant	83.2 mg/L
Sediment (fresh water)	2,36 mg/kg dry weight
Sediment (sea water)	236 µg/kg dry weight
Air	no dangers detected
Terrestrial organisms (soil)	4.7 µg/kg dry weight
Predators (secondary poisoning)	no bioaccumulation potential

In laboratory tests on various groups of organisms, TFA concentrations as found in the environment so far did not show any harmful effects. Due to the persistence of the substance TFA, however, a long-term increase in concentration in the environment is to be expected.

3 Projections of halogenated refrigerants and blowing agents until the year 2050

3.1 Objectives

This chapter quantifies the consumption and emission quantities of halogenated refrigerants and blowing agents in a scenario of maximum future use and emissions of halogenated substitutes with small GWP (u-HFCs and u-HCFCs) in order to estimate present and future maximum quantities of persistent degradation products formed in Germany and the EU-28 countries[139]. The following questions will be answered:

1. Which halogenated refrigerants and blowing agents will be used by 2050 as single substances or in mixtures to replace greenhouse-relevant substances in which applications, in which quantities and in which compositions in Germany and in Europe (EU-28), based on a u-HFC and u-HCFC maximum scenario from 2018?
2. What emissions (type and quantity) will occur during production, use and disposal by 2050?
3. Which degradation products are to be expected in what quantities by 2050?

To answer these questions, previous, current and future usage quantities (hereinafter referred to as "demand", i.e. quantities required for the initial filling of new devices and refill quantities for existing devices) and emissions of halogenated refrigerants and blowing agents are mapped in a suitable model.

u-HFC and u-HCFC maximum scenario for estimating the environmental impact

Since the present study focuses on the assessment of environmental impact of persistent degradation products of halogenated refrigerants and blowing agents, future demand and emission quantities of refrigerants and blowing agents in Germany and the EU-28, as well as the derived quantities of atmospheric degradation products, were projected within the framework of a scenario with maximum use and emissions of halogenated substitutes with small GWP. This means that priority was given to the conversion from HFCs to u-HFCs and u-HCFCs over the conversion to non-halogenated substances (e.g. propane and CO_2). The only exception are sectors where non-halogenated substances are already established on the market (e.g. ammonia in large industrial refrigeration plants). For all sectors it was assumed that the change to halogenated refrigerants and blowing agents with low GWP would not be accompanied by a reduction in leakage rates or an increase in the recovery of gas volumes. The projections presented here therefore do not necessarily reflect the real development on the refrigeration and blowing agent market or the development of emissions, but allow an estimate of the possible maximum amount of persistent degradation products.

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[139] The United Kingdom was not excluded from the analysis even after 2020, as the aim of the projections was to achieve the most comprehensive ecological assessment possible.

3.2 Method description

3.2.1 Description of the model and its further development

For the projections, a model already developed for the revision of the EU F-gas Regulation by Öko-Recherche and Öko-Institut on behalf of the EU Commission was used (Schwarz et al. 2011). The so-called AnaFgas model ("Analysis of fluorinated greenhouse gases in EU-27"), which projects the demand and emissions of fluorinated greenhouse gases in the EU in various scenarios, could be adapted to the specific questions of this project.

The AnaFgas model is a "bottom-up" inventory model that determines demand and emission scenarios for F-gases in relevant sectors and sub-sectors for the EU-27[140] Member States (Schwarz et al. 2011). It models the demand and emissions of HFCs and HCFC-22 for the period 1995 to 2050, based on market data and estimates of the annual sales of equipment[141] containing these substances and the amount of substances needed to manufacture and/or maintain appliances within the EU.

All demand and emission estimates are derived from bottom-up processes, with demand and emissions being calculated per sector based on underlying factors (Figure 10). These include annual changes in equipment inventory, composition, and filling of equipment, as well as leakage rates during the use phase (lifetime) and destruction of equipment at the end of its lifetime (disposal). Some of these components are influenced by other factors, such as population development, gross domestic product growth or technological changes. Based on these factors, annual stocks and emissions as well as demand can be calculated for each year by sub-sector and EU member state.

Basically, the demand is derived from the amount of initial filling of equipment in Europe (EU-28) and the amount of gas needed to replenish the amount emitted during the use phase from the inventory of equipment in the EU during equipment maintenance (Figure 10). This equipment can either have been produced and filled in Europe or imported prefilled from other European countries. The quantity of emissions is calculated from the emissions during the use phase and the emissions from the disposal of old equipment. Specific emission factors for use and disposal per gas and sector are assumed, which can change over time due to technological developments.

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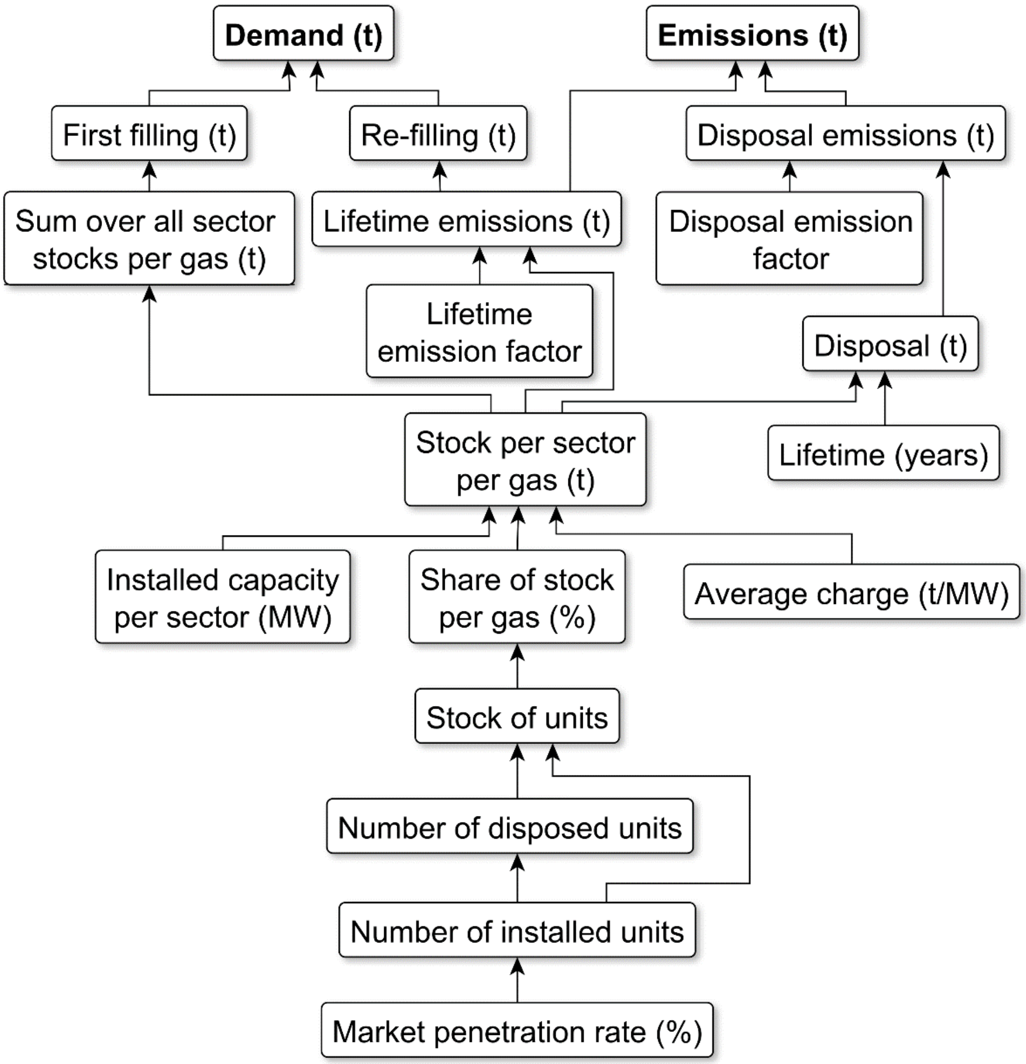
[140] EU-27 refers here to the 27 EU Member States in 2011. Croatia joined the EU in 2013 and, unlike the United Kingdom, is not part of the EU-27 mentioned here.

[141] Here, the term equipment includes systems (e.g. refrigeration or air conditioning units) and products (e.g. insulating foam or compressed gas containers).

Figure 10: Simplified illustration of the basic structure of the AnaFgas model for calculating demand and emissions of halogenated HCFCs, HFCs, u-HFCs and u-HCFCs in Europe (EU-28) per sector and gas in metric tons. The actual calculations are highly sector-specific and consider additional factors such as population development in the different EU Member States and technological developments. The first filling refers only to equipment filled in Europe (EU-28).



Source: Own illustration, Öko-Recherche

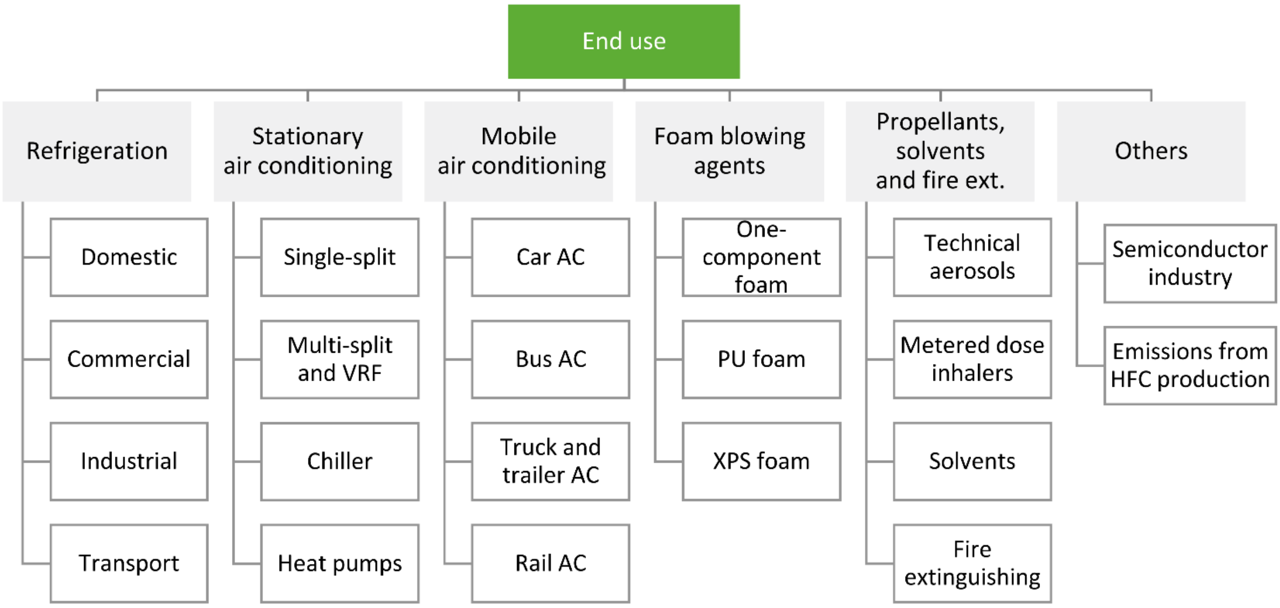
AnaFgas uses market information to collect inventories of the stock of equipment in each application sector in each EU country. This includes the percentage of the equipment inventory that contains the different F-gases. These modelled inventories are maintained by adding new equipment or new F-gases annually and decommissioning old equipment after an appropriate number of years. Annual leakage rates, maintenance emissions and disposal emissions are estimated separately for each end-use application.

For statements regarding the use and emissions of u-HFCs in 2050, the projections focus on Europe (EU-28). Thus, statements on the depositions of possible degradation products (especially TFA) can be derived from large-scale emission estimates using the atmospheric simulation studies mentioned in the analysis of the current situation (e.g. by Henne et al. 2012).

The following adaptations to the AnaFgas model were made within the scope of this project in the sectors of stationary refrigeration and air conditioning, mobile air conditioning, blowing agents, and propellants shown in Figure 11:

- Updating the database until 2016 for refrigerants, foam blowing agents and aerosol propellants
- Integration of the new refrigerants, foam blowing agents and aerosol propellants (see Table 22)
- Integration of country data for Croatia for the entire timeline[142,143]
- No adjustments were made for the solvent and fire-extinguishing agent sectors and the category "Others" in Figure 11, as they are not refrigerants or foam blowing agents or aerosol propellants. Nevertheless, the projections for these sectors from the original AnaFgas model were adopted unchanged for HCFCs and HFCs, as this allowed a more realistic projection. In addition, the sectors of this group contain some substances that can form TFA during atmospheric degradation.

Figure 11: Applications of HCFCs, HFCs, u-HFCs and u-HCFCs in the AnaFgas model adapted for this purpose; VRF stands for variable refrigerant flow, PU for polyurethane, XPS for extruded polystyrene.



Source: Schwarz et al (2011), own illustration, Öko-Recherche

The original AnaFgas model comprises 30 different single substances and four mixtures. For the current project, the selection of the single substances and mixtures was extended based on the results of the analysis of the current situation and then narrowed down again according to the project's focus on halogenated refrigerants and blowing agents (Table 22).

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[142] To this end, necessary adjustments to the AnaFgas model were developed and implemented in a workshop with the project partner Öko-Institut.

[143] In consultation with the German Federal Environment Agency, the United Kingdom will remain included in the adapted AnaFgas model beyond March 2019, as emissions are to be analyzed at the European level - and not only at the EU level.

Sometimes different gas producers offer almost identical mixtures for the same application area. Since some of these mixtures are not yet established on the market, no statement can be made as to which mixture will eventually prevail or in what proportion the market shares will be. In these cases, the respective mixtures were standardized for modelling purposes by averaging the individual mixture components[144]. The mixtures R454C and R455A as well as R448A and R449A were always standardized. R513A and R450A have been combined in the industrial refrigeration sector, in transport refrigeration for refrigerated trucks and trailers and in train air conditioning.

For the foam sector, it was not yet clear at the time of modelling how strongly the newer u-HFCs and u-HCFCs will be established in the market. For gaseous foam blowing agents, u-HFC-1234ze(E) in particular should be mentioned here. Furthermore, u-HCFC-1224yd(Z) is also sold as a foam blowing agent with the focus on its use as a refrigerant. For the projections u-HCFC-1224yd(Z) has not been considered as it is not yet clear whether it will be able to stand up to the strong competition on the EU market. Candidates for liquid foam blowing agents in the EU market are u-HFC-1336mzz(Z) and u-HCFC-1233zd(E).

Table 22: List of substances and mixtures in the AnaFgas model for the calculations in this project. The substances and mixtures newly added to the 2011 model are written in italics. The double marked mixtures R448A/R449A, R450A/R513A, R454C/R455A are not existing refrigerants but have been combined for the projections.

Group of substance	Substance name	Chemical formula or composition for mixtures
HCFCs		
	HCFC-22	$CHClF_2$
HFCs		
	HFC-23	CHF_3
	HFC-32	CH_2F_2
	HFC-125	CHF_2CF_3
	HFC-134a	CH_2FCF_3
	HFC-143a	CH_3CHF_2
	HFC-152a	CH_3CHF_2
	HFC-227ea	CF_3CHFCF_3
	HFC-236fa	$CF_3CH_2CF_3$
	HFC-245fa	$CHF_2CH_2CF_3$
	HFC-365mfc	$CH_3CF_2CH_2CF_3$
	HFC-43-10-mee	$CF_3CHFCHFCF_2CF_3$
u-HFCs und u-HCFCs		
	u-HFC-1234yf	$CF_3CF=CH_2$
	u-HFC-1234ze(E)	*trans-*$CF_3CH=CHF$
	u-HFC-1336mzz(Z)	*cis-*$CF_3CH=CHCF_3$

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[144] For example, the mixtures R454C and R455A both have a GWP of 148 and are offered primarily as a replacement for R404A. R454C consists of 21.5 % HFC-32 and 78.5 % u-HFC-1234yf. R455A on the other hand consists of 21.5 % HFC-32, 75.5 % u-HFC-1234yf and 3 % CO_2. Both mixtures were averaged according to their proportions for modelling in AnaFgas: R454C/R455A thus consists of 21.5 % HFC-32, 77 % u-HFC-1234yf and 1.5 % CO_2.

Group of substance	Substance name	Chemical formula or composition for mixtures
	u-HCFC-1233zd(E)	*trans-*$CF_3CH=CHCl$
Mixtures		
	R404A	HFC-125 (44 %), HFC-134a (4 %), HFC-143a (42 %)
	R407C	HFC-32 (23 %), HFC-125 (25 %), HFC-134a (52 %)
	R410A	HFC-32 (50 %), HFC-125 (50 %)
	R507A	HFC-125 (50 %), HFC-143a (50 %)
	R448A	*HFC-32 (26 %), HFC-125 (26 %), HFC-134a (21 %), u-HFC-1234yf (20 %), u-HFC-1234ze(E) (7 %)*
	R449A	*HFC-32 (24.3 %), HFC-125 (24.7 %), HFC-134a (25.7 %), u-HFC-1234yf (25.3 %)*
	R450A	*HFC-134a (42 %), u-HFC-1234ze(E) (58 %)*
	R452A	*HFC-32 (11 %), HFC-125 (59 %), u-HFC-1234yf (30 %)*
	R454C	*HFC-32 (21.5 %), u-HFC-1234yf (78.5 %)*
	R455A	*HFC-32 (21.5 %), u-HFC-1234yf (75.5 %),* CO_2 *(3 %)*
	R466A	*HFC-32 (49 %), HFC-125 (11.5 %),* CF_3I *(39.5 %)*
	R513A	*HFC-134a (44 %), u-HFC-1234yf (56 %)*
Mixtures merged for projections		
	R448A/R449A	*HFC-32 (25.15 %), HFC-125 (25.35 %), HFC-134a (23.35 %), u-HFC-1234yf (22.65 %), u-HFC-1234ze(E) (3.5 %)*
	R450A/R513A	*HFC-134a (43 %), u-HFC-1234yf (28 %), u-HFC-1234ze (29 %)*
	R454C/R455A	*HFC-32 (21.5 %), u-HFC-1234yf (77 %),* CO_2 *(1.5 %)*

The AnaFgas model already contains a WAM scenario (with-additional-measures-scenario), which corresponds to a scenario for the HFC phase-down in Europe (EU-28). The WAM scenario is based on assumptions about the introduction of alternatives to HFCs in all applications and thus the reduction of HFC demand and emissions. The identified technical replacement options with possible market penetration rates in 2015, 2020 and 2030 were considered. The market penetration rates for the various applications were estimated by experts. A cost threshold for emission avoidance of 50 Euros per ton of CO_2 equivalent was applied. The level of abatement costs also served as a criterion for selecting HFC-free alternatives if more than one alternative is technologically feasible and financially viable ("penetration mix"). This assumption was no longer taken into account when updating the model. All new substitutes with a small GWP were estimated independent of any cost threshold. Existing data on older high GWP refrigerants and blowing agents were not changed.

In the AnaFgas model, the use of u-HFCs as an alternative to HFCs in various sectors has already been established (especially with regard to the refrigerants u-HFC-1234yf and u-HFC-1234ze(E)) and was further detailed in the course of this project. For this purpose, background research and discussions were conducted with manufacturers, importers, and distributors of refrigerants in different EU countries as well as important market participants in all refrigerant application areas (see Chapter 2.2.4). Especially in the next decade, the use of refrigerant mixtures consisting of u-HFCs and HFCs is expected for retrofitting of existing systems (currently still using HFCs), which will reach the end of their service life only in a few years. In the course of this background research and discussions a manageable number of newer u-HFC single substances and mixtures could be identified which are relevant now and in the future (see Chapters 2.3 and 2.5.1). These were included in the adapted AnaFgas model and their demand and emissions were projected until 2050.

After the further development of the WAM scenario to a "u-HFC and u-HCFC maximum scenario" for the use of u-HFCs and u-HCFCs (see Chapter 3.3), an analysis of the modelling results enabled the identification of those sectors in which relevant use quantities of u-HFCs and u-HCFCs are expected in the future. In combination with the findings of Chapter 2, these assumptions were validated for relevant sectors and, if necessary, adjusted.

As a basis for the assumptions of the u-HFC maximum scenario (see Chapter 3.3), another model could be included: the German F-gas model, which is generally used for annual emission reporting. This model was further developed analogous to the calculation methodology for the EU (AnaFgas model) within the framework of a project for the German Federal Environment Agency.[145] The German F-gas model is supplemented annually with current data as part of the national F-gas reporting for the UBA. Methodological enhancements and adaptations of the model to changing reporting requirements for F-gas emissions have been developed and implemented in recent years in various UBA projects[146,147] by Öko-Recherche.

In this project the German F-gas model was used to update the data set for Germany in the adapted AnaFgas model and to validate the assumptions for the introduction of u-HFCs in the EU.

Relevant here is the so-called MIN scenario (scenario of minimum HFC consumption or minimum HFC emissions) of the German F-gas model, which projects the development of F-gas consumption and emissions for all 28 HFC sectors analysed up to 2030, assuming a change to alternatives to HFCs. As in the AnaFgas model, the reduction in demand for HFCs results from the increase in demand for technologies and processes without HFCs, which in turn follow the market penetration rates contained in the model.

As a result of the modelling, statements can be made on the use and emissions of u-HFCs in the EU up to the year 2050.

3.2.2 Conversion of emissions of relevant substances into TFA quantities

Based on the determined substance-specific TFA formation rates (see Chapter 2.7.4), a conversion of the annual emissions of relevant HCFCs, HFCs, u-HFCs and u-HCFCs in Europe (EU-28) estimated by the modelling into expected TFA amounts until the year 2050 was performed. For this purpose, the annual emission quantity of each substance (S) in metric tons was multiplied by its respective TFA formation rate and corrected by the ratio of the molar mass[148] (M) of TFA for the respective substance:

$$TFA\text{ quantity } (S)_{year} = emission\ quantity\ (S)_{year} * TFA\ formation\ rate\ (S) * \frac{M\ (TFA)}{M\ (S)}$$

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[145] In contrast to the AnaFgas model for the EU-27 (excluding Croatia), the initial data set in the German F-Gas model is more detailed and takes country-specific differences into account in numerous places. Beyond EU legislation, specific German requirements are also taken into account (Gschrey et al. 2015a).

[146] See Schwarz et al. (2012)

[147] See Gschrey et al. (2015b)

[148] The molar masses of all substances were taken from the publicly accessible PubChem database (https://pubchem.ncbi.nlm.nih.gov/, last access: 27.06.2019).

3.2.3 Conversion of emissions of relevant substances into quantities of hydrogen fluoride

Analogous to the calculation of the TFA amount, the amount of hydrogen fluoride (HF) produced was calculated from the emitted amounts of the relevant HCFCs, HFCs, u-HFCs and u-HCFCs in Europe (EU-28) until the year 2050. The number of HF molecules formed for each substance was determined depending on its TFA formation rate and number of fluorine atoms. The basic assumption was that each fluorine atom of a substance that is not bound in TFA will eventually produce an HF molecule when degraded in the environment. TFA contains three fluorine atoms and during degradation via trifluoroacetyl fluoride (TFF), an HF molecule is always formed in addition to TFA. For u-HFC-1234yf, which is completely degraded to TFF and finally TFA, three of the four fluorine atoms remain in the formed TFA molecule and one fluorine atom is released as a HF molecule.

For those substances which are not completely degraded to TFA during atmospheric degradation, the HF formation rate cannot be determined unambiguously. This is true for HFC-134a and especially for all substances that form trifluoroacetaldehyde during degradation, since 10 % of the trifluoroacetaldehyde molecules react to form TFA and 90 % react to form three HF molecules[149]. In order to consider all degradation pathways, a weighted arithmetic mean value of the HF formation rate was calculated for each substance. For HFC-134a, for example, this calculation results in 3.4 HF molecules, since HFC-134a is degraded to one TFA and one HF molecule with a probability of 20 % and to four HF molecules with 80 % probability:

$$average\ HF\text{-}formation\,rate\ (\text{HFC-134a}) = 0.2 \cdot 1 + 0.8 \cdot 4 = 3.4$$

In the same way, the average HF formation rate can be calculated for each substance (S) that forms trifluoroacetaldehyde during degradation[150]:

$$average\ HF\ \text{formation rate}\ (S)\ = \\ 0.1 \cdot (number\ of\ fluorine\ atoms\ (S) - 3) + 0.9 \cdot number\ of\ fluorine\ atoms\ (S)$$

Finally, the average HF formation rate can be used analogous to the TFA formation rate to calculate the HF quantity formed from the emission quantity for each substance in each year:

$$HF\ quantity\ (S)_{year} = emission\ quantity\ (S)_{year} \cdot average\ HF\ formation\,rate\ (S) \cdot \frac{M\ (HF)}{M\ (S)}$$

3.3 Assumptions for a u-HFC and u-HCFC maximum scenario until 2050

3.3.1 Legal and political guidelines

In the u-HFC and u-HCFC maximum scenario of emissions of fluorinated gases up to the year 2050 modelled here, the framework of the current legislation was represented as follows:

The implementation of the EU F-gas Regulation No. 517/2014 was ensured in the model by considering the prohibitions of the placing on the market of products and equipment listed in Annex III to the Regulation. In particular, the prohibitions in the sectors of refrigeration, air conditioning, foams, and aerosols were considered to determine the market penetration rates and mapped by corresponding assumptions. The assumptions made were developed in consultation with industry experts. In terms of an environmentally relevant estimation, the scenario primarily considers the use of u-HFCs and u-

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[149] Trifluoroacetaldehyde (CF_3CHO) contains three fluorine atoms and can thus form three HF molecules.

[150] Exceptions are HFC-236fa and u-HFC-1336mzz, as these can form two CF_3CO radicals and two trifluoroacetaldehyde molecules respectively. All six fluorine atoms can therefore be bound in two TFA molecules each, whereby no HF molecule is produced.

HCFCs and corresponding mixtures in various application sectors. The previous introduction of alternatives to fluorinated greenhouse gases with a small GWP that do not contain u-HFCs and u-HCFCs, i.e. with halogen-free, so-called natural refrigerants and blowing agents, was considered proportionately in the assumptions for the various sectors.

For automotive air conditioning systems, the model was based on the European Directive 2006/40/EC on vehicle air conditioning systems (MAC Directive), according to which the refrigerant HFC-134a, which had been used until then, was no longer permitted in new types of passenger cars and small commercial vehicles from 2011 onwards. Since 2017, only refrigerants with a GWP of less than 150 are permitted in the air conditioning systems of all new passenger cars and small commercial vehicles.

Beyond 2030, compliance with the Kigali amendment on the HFC phase-down is assumed, the objectives of which partly exceed the requirements and timeframe of current EU legislation.

3.3.2 Database for Germany

Within the framework of the German emissions reporting (German F-gas model), a detailed analysis has been carried out in the last two years, among other things, on the extent to which the distribution of halogen-free alternatives has changed in commercial refrigeration and car air conditioning (for the years 2010 to 2016, see Table A 5 in Annex A.9). Using the German F-gas model, realistic basic values for the market penetration of various halogenated greenhouse gases in the various sectors can be assumed for Germany and, based on these, future developments in other EU countries can be estimated.

3.3.3 Assumptions for Europe (EU-28)

Industry experts were consulted to estimate future market penetration rates of u-HFCs and u-HCFCs as single substances and in newer mixtures. The assumptions made were presented at the annual conference of the German Society of Refrigeration and Air Conditioning, DKV e.V. (German: Deutscher Kälte- und Klimatechnischer Verein, DKV e.V.) in Aachen from 21 to 23 November 2018 and discussed with the participants for the purpose of possible adjustments.[151] For the presentation all expert interviews were evaluated and the market penetration of unsaturated alternatives in the different application areas was estimated, against the background of the change from fluorinated substances with high (e.g. HFC-134a) and medium GWP (e.g. HFC-32) to fluorinated substances with low GWP (u-HFCs and u-HCFCs) and available natural substances with low GWP (e.g. propane or CO_2). After the presentation, intensive discussions were held with the experts present, which allowed an assessment of the assumptions regarding the market penetration of fluorinated greenhouse gases. The results of the expert assessments were incorporated into the assumptions made here for the various substances up to the year 2050, which are summarized in Table A 6 in Annex A.9. These evaluated assumptions were finally incorporated into the adapted AnaFgas model to project demand and emissions up to 2050.

In the EU, fluorinated refrigerants have already been almost completely replaced by natural refrigerants in the field of **household refrigerators** (refrigerators and freezers).[152] Since 1995, new appliances in Germany may no longer contain CFCs as refrigerants[153]. In contrast to the USA, for example, the use of natural refrigerants has become established in the EU in this area and it is not to be expected

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[151] The speech was entitled „Perspektiven von HFKW-Alternativen in Europa“ ("Perspectives of HFC alternatives in Europe") and was presented by Felix Heydel and David Behringer on November 23, 2018.

[152] Only refrigerants are considered under the term household refrigeration appliances. Foaming agents for insulating foams in refrigerators and freezers are included in the foam sector.

[153] CFC Halon Prohibition Ordinance (“FCKW-Halon-Verbots-Verordnung“) of May 6, 1991.

that halogenated substances will be found in this sector in the future. According to the EU F-gas Regulation, the marketing of household refrigerators with refrigerants with a GWP greater than 150 is no longer permitted since 2015.

In the **commercial refrigeration** sector, we generally expect a dynamic shift from high GWP refrigerants (HFC-134a and R404A), partly via mixtures with an average GWP of about 600 (e.g. R513A as a substitute for R404A, also in deep-freezing[154]), to low GWP mixtures. In order to remain competitive on the market alongside natural refrigerants, the latter would have to have a GWP of less than 150.

In the case of individual plug-in devices, natural refrigerants (propane and CO_2) already have a certain market share and will probably be able to maintain this in the future. With the reduction in the availability of HFC-134a, a u-HFC mixture with a GWP of less than 150 will increasingly establish itself (e.g. R454C or R455A).

For centralized commercial refrigeration systems, we also expect the dynamic transition to low GWP mixtures with a GWP below 150 described above. The main reason for this is the EU F-gas Regulation, which stipulates that from January 2022, multi-component centralized refrigeration systems with a nominal capacity of 40 kW and above can only use refrigerants with a GWP of less than 150. Only in the primary refrigerant circuit in cascading systems may fluorinated greenhouse gases with a GWP of up to 1,500 still be used. We therefore assume that mixtures with a medium GWP, such as R513A, will continue to be available on the refrigerant market in the future.

The refrigerant CO_2 is increasingly used in centralized refrigeration systems now and probably in the future, although it can be assumed that u-HFC and u-HCFC mixtures with low GWP will be established on the EU market as well, especially in Southern Europe[155]. In addition, we assume that some of the applications will undergo a change in technology instead of a change of refrigerant, e.g. to plug-in devices and chillers.

In liquefaction units, in addition to propane and CO_2, u-HFC mixtures with a small GWP and u-HFC-1234ze(E) as a single substance will probably play a major role in the future. The use of R448A and R449 will probably only be a temporary solution, especially for existing plants, as these mixtures still have a rather high GWP of just under 1,400. Thus, they would only offer an advantage in GWP compared to R404A. Mixtures with a medium GWP of about 600, such as R513A, will also be increasingly displaced from the market from 2020 onwards.

In the sector of large **industrial refrigeration** plants, ammonia has a very high market share, which will continue to increase. Up to now, HFC-134a and R404A have been used primarily, but these will soon be replaced by low-GWP solutions due to the F-gas regulation. We assume that there will be a transition from u-HFC mixtures with a medium GWP of about 600 to u-HFC-1234ze(E) and to a lesser extent to hydrocarbons, which will dominate the market together with ammonia.

In the **transport refrigeration** sector, HFC-134a or the mixtures R404A and R452A are currently mainly used. In the truck, trailer and refrigerated container sector, a change is being made to the substitute refrigerant mixture R452A in particular, which will probably have to be replaced again in the future as a result of the F-gas Regulation due to its high GWP. In the area of smaller refrigerated vehicles, HFC-134a is currently used primarily, as well as the mixtures R404A and R452A. In the field of

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[154] https://www.kka-online.info/artikel/kka_R-513A_geeignet_fuer_TK-Anwendungen_3241612.html (last access: 06.04.2020)

[155] This assumption is based on the fact, that CO_2 systems lose more efficiency than F-gas systems as the condensing temperature increases. Therefore, the use of CO_2 systems in regions with high ambient temperatures, such as Southern Europe, requires more complex technologies, which may be associated with a higher price.

transport refrigeration, a development from u-HFC mixtures with medium GWP to low GWP mixtures is likely for both areas mentioned. The mixture R513A is conceivable in smaller refrigerated vehicles, at least in the meantime, as a replacement for HFC-134a due to its comparable refrigerating capacity and efficiency[156] and will in all probability play a greater role in the future. Flammable natural refrigerants have not been introduced in direct cooling circuits in the EU due to safety concerns for transport refrigeration. The development of systems with the refrigerant CO_2 has not been further advanced.

In the field of **stationary air conditioning**, the refrigerant mixture R410A and HFC-32 are currently used. We assume that these will be replaced by u-HFC mixtures with low GWP and that natural refrigerants (especially propane) and single substance u-HFCs will become only niche applications. In general, a long-term transition to a mixture with GWP below 150 is assumed for this sector. However, it can be assumed that HFC-32 with a GWP of 675 will at least temporarily establish itself on the market and will displace the high GWP substances (R410A and R407C) that will still be mainly used in 2018. Due to the significantly larger filling quantity of VRF systems[157], compared to mobile room and split air conditioning units, the non-combustible mixture R466A could establish itself on the market. In case of safety concerns due to the filling quantity, R466A would be the only known alternative of the safety class A1, with the disadvantage of a GWP of 733. Whether and how R466A will assert itself in the market, cannot be classified at present, since at the time of the data collection the ASHRAE certification was not yet finalized and the mixture possesses an ozone-depleting potential due to the trifluoriodomethane (CF_3I) contained in it. In expert interviews R466A was assessed very ambivalently. Some experts did not give the mixture any chance on the market, others stated that the demand for an A1 refrigerant in this area was so great that R466A could dominate the market due to the lack of an alternative. In our assumptions we assume conservatively that R466A will only be able to assert itself on the market to a limited extent.

In the field of **mobile air conditioning**, it can be assumed that u-HFC-1234yf will prevail as a replacement for HFC-134a. Although a natural alternative would be available here with CO_2, car manufacturers have been very hesitant to implement this alternative so far. In the field of electromobility, a significant use of this technology[158] or, alternatively, of hydrocarbons, which is also being developed, can potentially be assumed[159]. Contrary to initial expectations at the time of the market research in 2018, new electric cars are mainly sold with u-HFC-1234yf as a refrigerant, such as the new ID.3 from VW. The installation of a heat pump with CO_2 as a refrigerant is only available as a chargeable addition.[160]

In the area of train air conditioning, a non-flammable u-HFC refrigerant mixture is expected to be used primarily as a substitute for HFC-134a. Halogen-free alternatives include systems with compressed air, which are currently only hesitantly used on the market, or hydrocarbons and CO_2 that are being developed.

For **chillers**, we assume that, as in air conditioning systems, a transition from the high GWP mixtures R407C and R404A to low GWP u-HFC mixtures will occur in systems with positive displacement compressors. In addition to the natural refrigerant ammonia, u-HFC-1234ze(E) will gain a certain market

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[156] https://www.opteon.de/products/refrigerants/xp10 (last access: 06.04.2020)

[157] Multi-split air conditioning systems with a ‘variable refrigerant flow’ (VRF).

[158] Since electric cars have no combustion engine, there is a need to heat the interior of the vehicle in cold ambient temperatures without engine waste heat. The use of the air conditioning system in the form of a heat pump is a suitable solution here. This solution is clearly preferable, as it means that no additional components have to be installed in the vehicle. The use of CO_2 has proven to be the most energy-efficient option here, especially for Europe (Westerloh et al. 2018).

[159] OPTEMUS tests R290 heat pump in electric vehicles (https://hydrocarbons21.com/articles/8919/optemus_tests_r290_heat_pump_in_electric_vehicles, last access 30.04.2019)

[160] Official information on the vehicle equipment of the ID.3 series model from Volkswagen AG upon request on August 6, 2020.

share. In the field of centrifugal compressors (turbo compressors), however, we expect u-HFC-1234ze(E) and u-HCFC-1233zd(E) to become clearly established. However, it is currently not yet possible to predict in what proportion these two u-HFC refrigerants will be established on the market. Therefore, we assume a share of 50 % for both refrigerants.

We also assume that single substance u-HFCs and u-HCFCs will become strongly established as **foam blowing agents** for PU and XPS foam. For XPS foams we see u-HFC-1234ze(E) as the most likely candidate. In the field of PU foams, however, it is not yet clear in which form the possible substances (u-HFC-1336mzz(Z) and u-HCFC-1233zd(E)) will ultimately be established on the market. Therefore, we project these substances as a group and calculate a medium GWP and a medium TFA formation potential. For one-component foams we see a clear dominance of hydrocarbons in the future.

As **propellant** in aerosols, we expect in the future mainly u-HFC-1234ze(E), which replaces or has already replaced HFC-134a. For the medical application of metered-dose inhalers (MDIs), no successor is yet apparent and HFC-134a remains the most important propellant. Replacement in this sector is much more difficult than in other sectors, as propellants in medical applications, such as asthma sprays, are subject to increased safety and toxicity requirements. Therefore, the use of HFCs in MDIs is exempted by the F-gas Regulation since January 2018[161].

The application area “**others**” contains various sectors in which halogenated greenhouse gases are used, but not as refrigerants or blowing agents. For solvents, only the demand and emissions of HFC-43-10mee are projected in the AnaFgas model. Other solvents are not included, so no market penetration rate can be given here. For fire extinguishing agents we assume that HFCs will be completely replaced by fluoroketones and already have a very small market share of 10 %. We assume that the use of HFCs in the semiconductor industry only accounts for a very small share of the market. Fugitive emissions and by-product emissions from the production of halogenated hydrocarbons are assumed to remain constant and include various HFCs. HFC-23, which is a by-product of the production of HCFC-22 and others, accounts for the largest share.

3.4 Results of projections on demand, emissions, and degradation products

3.4.1 Demand and emission quantities of HCFCs, HFCs, u-HFCs and u-HCFCs in the EU-28 until the year 2050

The projected demand, of the HCFCs, HFCs, u-HFCs and u-HCFCs investigated in this project (see Table 22 in Chapter 3.2.1), will double in the period from 2000 to 2010 from approx. 45,000 tonnes to approx. 90,000 tonnes (Figure 12 and Table 23). From 2010 onwards, the demand for halogenated refrigerants and blowing agents will increase only moderately. In 2050 there is a projected demand of approx. 92,000 tons of halogenated refrigerants and blowing agents.

The projected emission quantities of the investigated substances in the EU across all application sectors amount to approx. 26,000 tonnes in 2000 and will more than double to approx. 57,000 tonnes by 2010 (Figure 12 and Table 23). Emissions will rise sharply by 2010 and increase only slowly in the following years. The total amount of emissions in the EU in 2050 will be about 67,000 tons.

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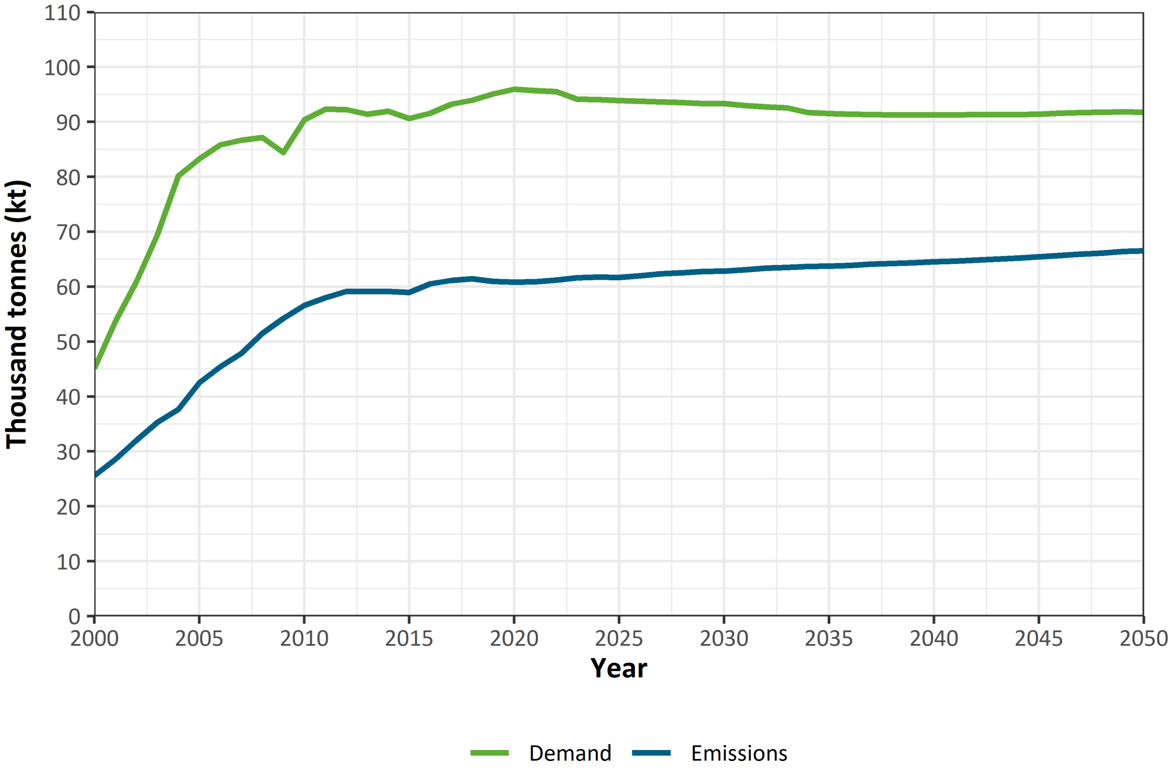
[161] Article 15 2 (f), Regulation (EU) No. 517/2014

Figure 12: Demand and emissions of HCFCs, HFCs, u-HFCs and u-HCFCs in the EU-28 in metric kilotonnes for the period 2000 to 2050 for the “u-HFC and u-HCFC maximum scenario”.



Source: Own illustration, Öko-Recherche

Looking at the demand and especially the emissions of the projected HCFCs, HFCs, u-HFCs and u-HCFCs by use sector, **mobile air conditioning** is the largest sector (Figure 13 and Table 23). In this sector, the increase in demand and emissions follows the respective trend that is also evident across all sectors, i.e. after an initial strong increase, the annual demand remains constant.

For the projections, the data on passenger car production in the EU for the years 1999 to 2017 are taken from the statistics of the International Automobile Manufacturers Association (Organisation Internationale des Constructeurs d'Automobiles, OICA). Based on this data, the production volume of passenger cars in the EU has not changed significantly between 1999 and 2017 (Figure A 1 in Annex A.9). A constant production rate is therefore assumed for the period 2018 to 2050, based on the OICA's 2017 figures.

In the case of mobile air conditioning, emissions will exceed the demand in the period between 2035 and 2050. The reason for this is the share of cars imported into the EU of the total number of all cars in the EU. Mobile air conditioning systems in imported passenger cars are filled for the first time in non-EU countries and this initial filling quantity is not added to the demand for these cars. In this case, the demand only results from the refilling of emitted quantities during the use phase. However, the first fill of refrigerant only emits within the EU[162]. In contrast, cars produced in the EU are first filled within the EU. If the passenger cars were produced for use in the EU, they also emit the refrigerant completely within the EU. The emission levels are identical for imported cars and cars produced in the EU

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[162] In the adapted AnaFgas model, we assume an emission rate of 10 % during the service life, just like the original AnaFgas model. The emission rate in case of destruction of the vehicle is 70 % for passenger cars.

(and for the EU), but the refrigerant requirement is lower for imported vehicles. However, as the total number of passenger cars in the EU is rising continuously in the model, the share of passenger cars produced in the EU will decrease continuously from 2018 onwards and the share of imported vehicles will increase. Since imported passenger cars contribute less to the demand but to the same extent to emissions, the emissions ultimately exceed the demand.

The second largest sector, **stationary air conditioning**, includes air conditioners, heat pumps and water chillers. Here, differences between the course of demand and emissions become apparent. While the emissions, similar to the mobile air conditioning sector, show a continuous, small increase after an initial growth, the demand does not increase from 2020 onwards and is slightly decreasing until the end of the time series. The reason for stagnating demand is mainly the assumed saturation of the market with regard to new installations of air conditioning units from 2030 on and to a small extent attributable to the expected increasing use of non-halogenated refrigerants, namely ammonia, propane, and water. The emissions follow the course of demand with a time lag, and here is no sign of a decrease of emissions by 2050.

The third largest sector is **refrigeration**. Here the demand and especially the emissions of HCFCs, HFCs, u-HFCs and u-HCFCs rise sharply in the period 2000 to 2010 and then fall to levels slightly above those of 2000. The decline in the demand for fluorinated greenhouse gases and thus also their emissions is due to the projected increasing market penetration of natural refrigerants and alternative technologies (see Chapter 3.3.3).

The **foam sector** shows a strong increase in demand in the years 2000 to 2010, which then decreases slightly until 2020 and remains stable at around 13,000 tonnes until 2050. At the same time, emissions decrease slightly until 2030 and then rise again until 2050 to similar levels as in 2010 with 6,125 tonnes. In principle, the foam sector is very much determined by the market penetration of the various foam blowing agents. For example, while HFC-134a was by far the most important blowing agent in the PU foam sector in 2000, HFC-365mfc and HFC-245fa increasingly entered the market in the early 2000s and led to an increase in demand for the entire sector. The share of HFC-134a decreased accordingly. In the further course of time, we expect the market to saturate and only shifts in the market penetration of individual foam blowing agents will follow. We assume that for XPS foams, u-HFC-1234ze(E) and for PU foams, u-HFC-1336mzz(Z) and u-HCFC-1233zd(E) will replace the halogenated high-GWP foam blowing agents on the market.

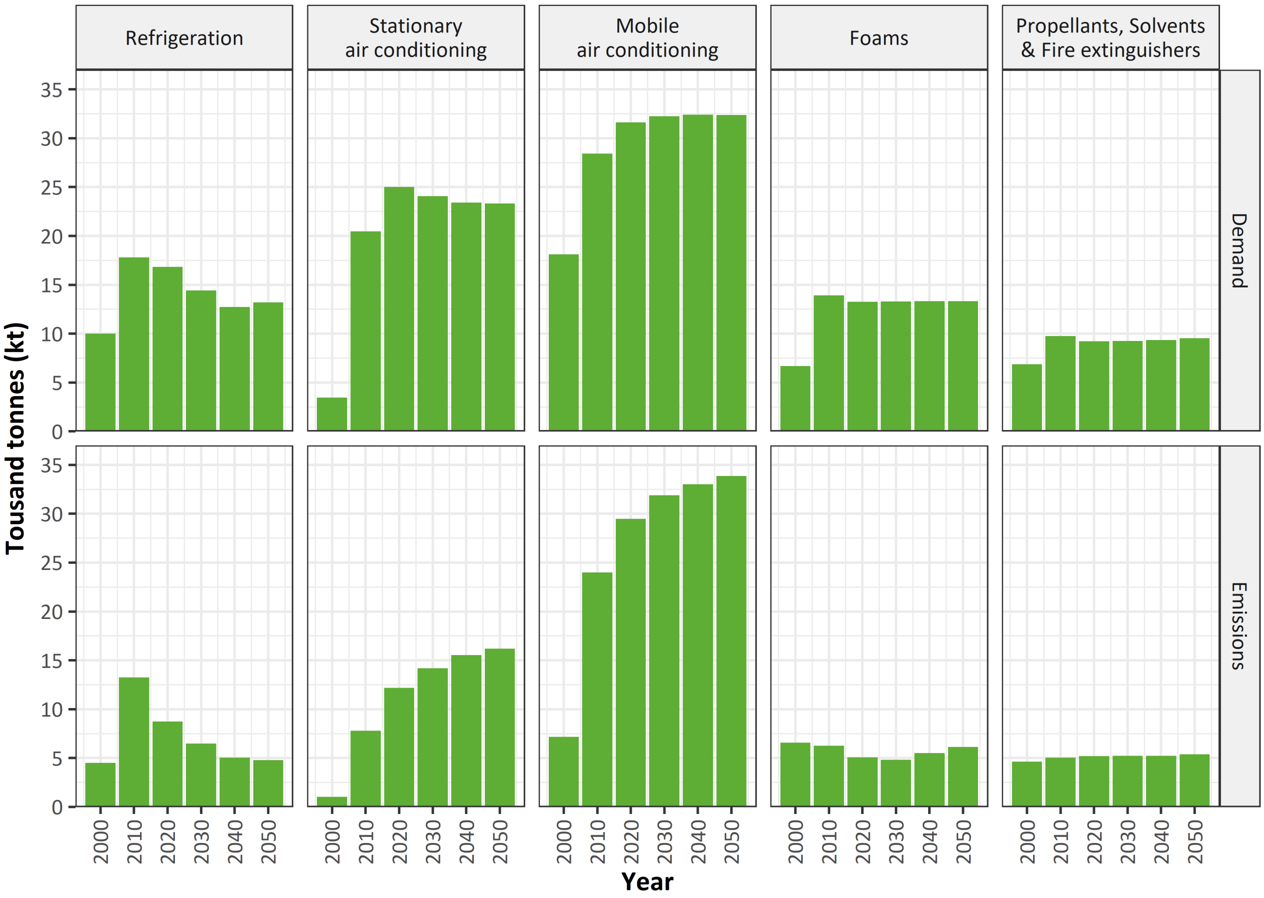
The demand for **propellants, solvents and fire extinguishing agents** also increased in the years 2000 to 2010, but less strongly than in the foam sector and will eventually reach approximately 9,500 tonnes in 2050. Emissions also increased by about 500 tonnes in the years 2000 to 2010 and will then remain at slightly more than 5,000 tonnes until 2050.

For the **others** sector, a constant HFC demand of the semiconductor industry of 27 tonnes until 2050 is assumed. The emissions from the semiconductor industry, together with the emissions from HFC production show a strong decrease in the years 2000 to 2010 and finally remain constant at just over 200 tonnes until 2050.

Table 23: Demand and emissions of HCFCs, HFCs, u-HFCs and u-HCFCs in Europe (EU-28) in metric tons from 2000 to 2050 in 10-year steps across all sectors for the "u-HFC and u-HCFC maximum scenario".

Year	2000	2010	2020	2030	2040	2050
Demand	**45,138**	**90,409**	**95,969**	**93,338**	**91,264**	**91,756**
Mobile air conditioning	18,116	28,427	31,616	32,264	32,413	32,361
Stationary air conditioning	3,447	20,459	25,028	24,059	23,412	23,314
Refrigeration	10,002	17,815	16,825	14,417	12,742	13,190
Foams	6,686	13,933	13,261	13,303	13,316	13,316
Propellants, solvents and fire extinguishing agents	6,860	9,748	9,212	9,268	9,354	9,548
Others (semiconductor industry only)	27	27	27	27	27	27
Emissions	**25,597**	**56,606**	**60,859**	**62,825**	**64,524**	**66,554**
Mobile air conditioning	7,187	23,983	29,466	31,889	33,017	33,856
Stationary air conditioning	1,030	7,799	12,193	14,189	15,533	16,208
Refrigeration	4,510	13,253	8,736	6,487	5,028	4,777
Foams	6,584	6,277	5,074	4,829	5,505	6,125
Propellants, solvents and fire extinguishing agents	4,633	5,051	5,187	5,228	5,238	5,385
Others (semiconductor industry and HFC production)	1,653	243	203	203	203	203

Figure 13: Quantity of projected demand and emissions of HCFCs, HFCs, u-HFCs and u-HCFCs in Europe (EU-28) in metric kilotonnes (kt) in the years 2000 to 2050 in 10-year increments by sector for the “u-HFC and u-HCFC maximum scenario”. The sector "Others" is not shown because the quantities of demand and emissions over the period 2000 to 2050 average 0.03 kt and 0.45 kt respectively.



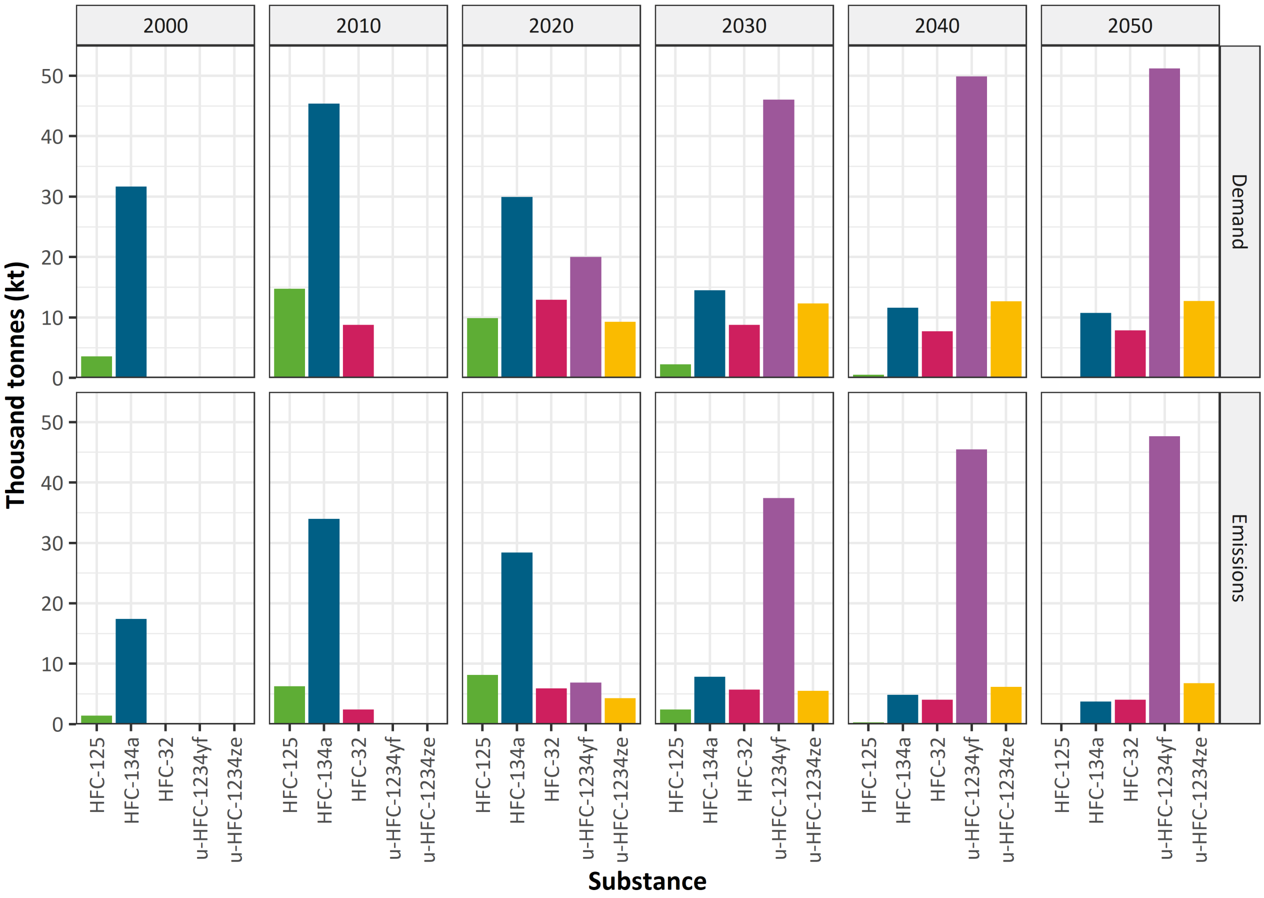
Source: Own illustration, Öko-Recherche

The breakdown of demand and emission quantities by individual substances for the period from 2000 to 2050 shows high levels of use, especially for HFC-125, HFC-134a, HFC-32, u-HFC-1234yf and u-HFC-1234ze, with HFCs with a high GWP being replaced by substances with a lower GWP (Table 24 and Figure 14).

Table 24: Overview of the demand and emission quantities of the individual HCFCs, HFCs, u-HFCs and u-HCFCs in Europe (EU-28) in metric tons in the years 2018, 2020, 2030 and 2050 for the “u-HFC and u-HCFC maximum scenario”. D, Demand. E, emissions.

Year	2018		2020		2030		2050	
Substance	**D**	**E**	**D**	**E**	**D**	**E**	**D**	**E**
HCFC-22	86	159	0	0	0	0	0	0
HFC-23	13,801	5,362	79	154	42	107	27	80
HFC-32	13,975	8,235	12,951	5,916	8,762	5,731	7,865	4,056
HFC-125	34,399	32,048	9,863	8,149	2,260	2,424	230	169
HFC-134a	5,245	3,497	29,950	28,416	14,484	7,858	10,743	3,742
HFC-143a	3,036	3,036	4,523	3,084	894	668	57	76
HFC-152a	482	437	1,191	1,191	0	0	0	0
HFC-227ea	10	8	468	435	376	374	342	292
HFC-236fa	1,611	498	16	8	37	11	37	11
HFC-245fa	5,343	1,518	1,220	469	0	281	0	214
HFC-365mfc	201	201	4,048	1,432	0	872	0	680
HFC-43-10mee	11,600	3,479	201	201	201	201	201	201
u-HFC-1234yf	4,016	2,926	20,003	6,903	46,030	37,439	51,223	47,658
u-HFC-1234ze	35	4	9,289	4,289	12,339	5,491	12,717	6,769
u-HFC-1336mzz	129	8	878	99	3,513	637	3,513	1,159
u-HCFC-1233zd	86	159	1,291	113	4,400	732	4,800	1,447
Total	**93,971**	**61,415**	**95,970**	**60,860**	**93,339**	**62,825**	**91,757**	**66,554**

Figure 14: Demand and emissions of HCFCs, HFCs, u-HFCs and u-HCFCs in Europe (EU-28) in metric kilotonnes in 10-year increments from 2000 to 2050 for the "u-HFC and u-HCFC maximum scenario". Only substances that have exceeded an annual demand of 10,000 tonnes or an annual emission of 5,000 tons between 2000 and 2050 are included.



Source: Own illustration, Öko-Recherche

3.4.2 Validation of the projections

To validate the plausibility of the modelled quantities of demand and emissions, the results for the past were compared with reported data. Data on demand in metric tonnes as well as in CO_2 equivalents (CO_2-eq) from the annual F-gas reporting are available for the period from 2007 to 2018 (EEA 2019). It should be noted that prefilled equipment did not have to be reported up to and including 2013. From 2014 onwards, however, they are included in the data. In the AnaFgas model, the quantities of refrigerants and blowing agents imported in prefilled equipment are also projected, so the data for the demand in metric tonnes and CO_2 equivalents from 2007 to 2013 from the F-gas reporting have been corrected by the approximate quantities in prefilled equipment to ensure comparability of the data. In addition, the reported quantities for the years 2007 and 2008 were corrected by the estimated quantity for Croatia[163]. For the approximate determination of the demand of HFCs in prefilled equipment, the average value of the reported HFC quantities in devices for the years 2014 to 2017 of 7,913 metric tonnes or 15.5 million tonnes CO_2-eq (EEA 2019) was added to the reported HFC quantities for

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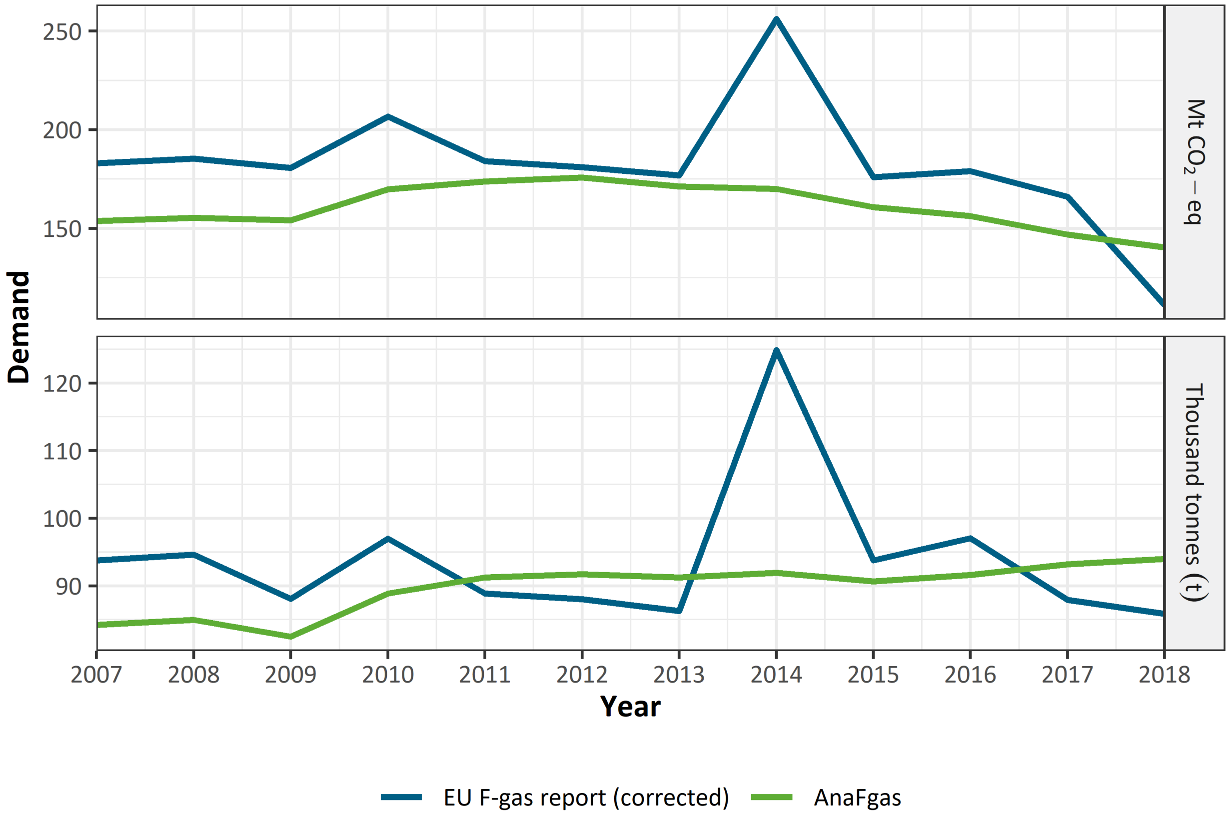
[163] This is an expert estimate of the Öko-Institut.

the years 2007 to 2013. Finally, the amount of HFCs imported for the sole purpose of export in pre-filled equipment was subtracted from the corrected demand in metric tonnes and CO_2 equivalents, as these quantities do not remain on the EU market[164].

A comparison of the demand for HFCs, u-HFCs and u-HCFCs in the EU from 2007 to 2018 shows that the projection by the AnaFgas model in CO_2 equivalents is rather conservative, as in most cases smaller demand quantities were determined than those actually reported according to the EU-F-gas Report (EEA 2019) (Figure 15). In general, the data series are in good agreement, especially for metric tons, although the data from the AnaFgas model are only slightly below the reported values and slightly above them at the end of the comparison period. Only the year 2014 is an exception. Here, the reported data show that demand in metric tons and especially CO_2 equivalents is above the respective projected values. The reason for this is that before the EU F-gas Regulation came into force in 2015, fluorinated gases were still traded on the EU market without restriction and were stockpiled due to the expected shortage.

Figure 15: Comparison of the demand in megatonnes CO_2-eq (top) and metric kilotonnes (bottom) of HFCs, u-HFCs and u-HCFCs in Europe (EU-28) from 2007 to 2018 according to the adapted AnaFgas model for the "u-HFC and u-HCFC maximum scenario" and the EU F-gas report (EEA 2019). The reported data have been corrected to ensure comparability with the projected data.



Source: Own illustration, Öko-Recherche and Öko-Institut

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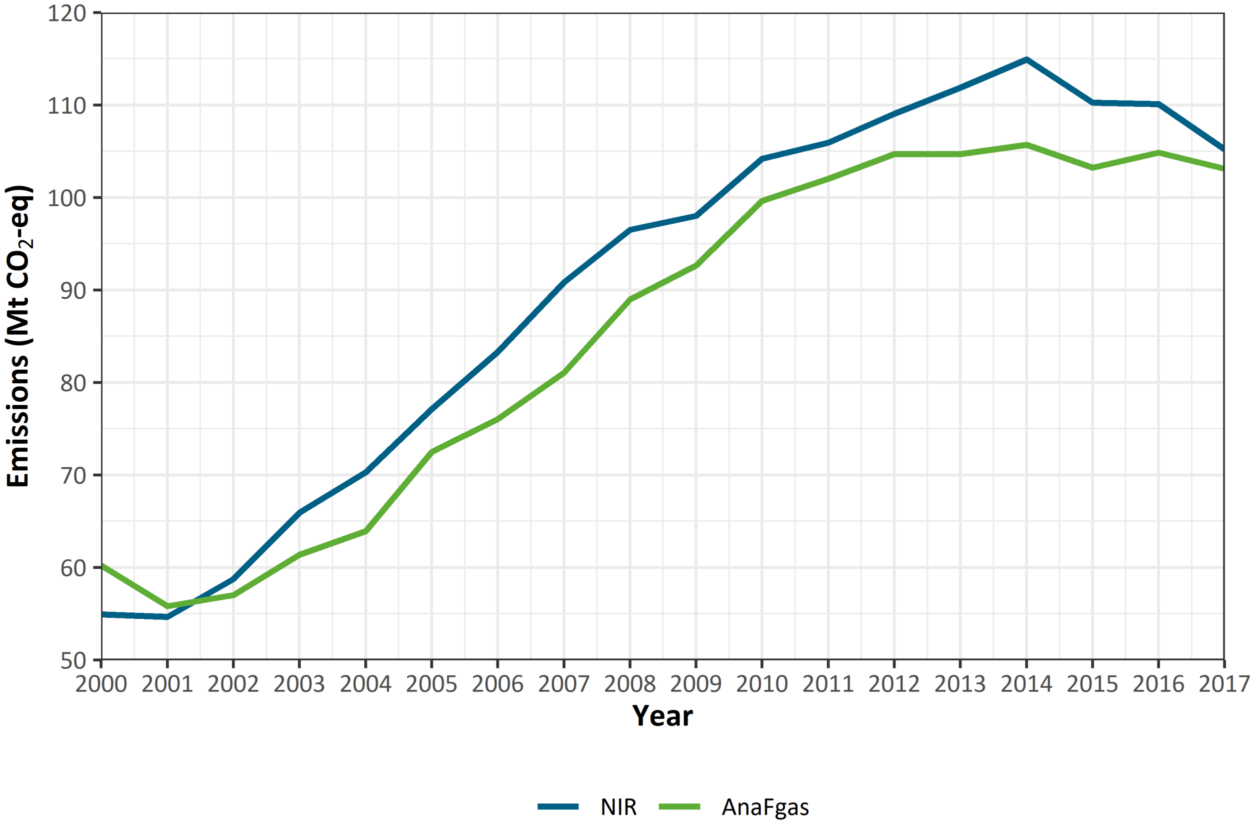
[164] This is an expert estimate of the Öko-Institut.

All EU Member States and the EU as a community of states committed to report annual emissions of greenhouse gases within the framework of the United Nations Framework Convention on Climate Change (UNFCCC). These National Inventory Reports (NIR) with their data tables in a Common Reporting Format (CRF) submitted annually by all countries are freely available online and were used to validate the projections of the adapted AnaFgas model. The EU also has its own NIR, which was used for comparison purposes. Since the greenhouse gas inventories are not collected according to metric tonnes but according to greenhouse gas potential, the results of the projected emission data for the different substances were converted accordingly. The comparison of the emission data from 2000 to 2017 shows a high degree of agreement between the reported and projected amounts of HFCs, u-HFCs and u-HCFCs (Figure 16). Only in the period from 2000 to 2001, the projections overestimate the reported NIR emissions for the EU. From 2004 to 2017, the projected emission quantities slightly underestimate the reported ones, but follow an analogous course and are very close again in 2017.

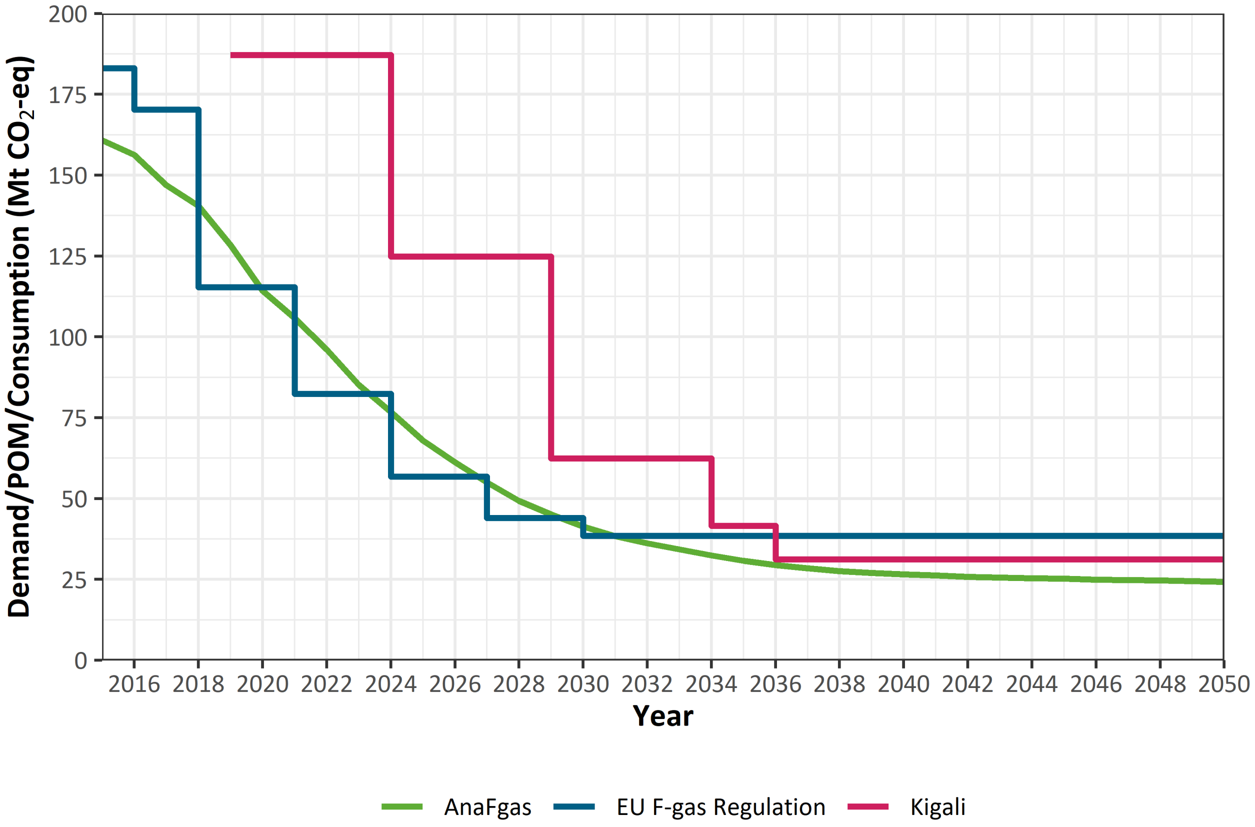
Figure 16: Comparison of emissions in megatons (Mt) CO_2-eq of HFC, u-HFC and u-HCFC in Europe (EU-28) from 2000 to 2017 according to the adapted AnaFgas model for the "u-HFC and u-HCFC maximum scenario" and the "National Inventory Report" (NIR) of the EU-28.



Source: Own illustration, Öko-Recherche

For further validation, the projected demand quantities from the AnaFgas model were compared with the maximum permitted amounts for placing on the market (POM) of HFCs in the EU under the F-gas Regulation and the maximum permitted consumption of HFCs under the Kigali Amendment. As can be seen in Figure 17, the quantities required under the AnaFgas model correspond well to the maximum permitted consumption of HFCs in the EU for the period 2015 to 2030, even if the reduction levels of the F-gas Regulation are not exactly reflected year by year. Moreover, the limits of the HFC reduction targets of the Kigali Amendment are not exceeded.

Figure 17: Comparison of the projected demand in megatons (Mt) CO_2-eq of HFCs, u-HFCs and u-HCFCs in Europe (EU-28) from 2015 to 2050 according to the adjusted AnaFgas model for the “u-HFC and u-HCFC maximum scenario” with the maximum permitted amount for placing on the market (POM) of HFCs in the EU-28 under the EU F-gas Regulation and the maximum permitted consumption of HFCs according to the Kigali Amendment.



Source: Own illustration, Öko-Recherche

3.4.3 Emissions of important TFA precursor substances and TFA quantities formed

3.4.3.1 Projections for Europe (EU-28)

Regarding the potential formation of TFA during atmospheric degradation, not all projected HCFCs, HFCs, u-HFCs and u-HCFCs are relevant. The emission quantities of the relevant substances for the period from 2000 to 2050 are summarized in Table 25. In particular for HFC-134a and u-HFC-1234yf, very high emissions occur. Other substances such as HFC-236fa play a minor role.

Table 25: Emission quantities of refrigerants and propellants from the groups of HFCs, u-HFCs and u-HCFCs, which form trifluoroacetic acid (TFA) during atmospheric decomposition, for Europe (EU-28) in metric tons in the years from 2000 to 2050 for the “u-HFC and u-HCFC maximum scenario”.

Substance	2000	2010	2020	2030	2040	2050
HFC-134a	17,427	33,982	28,416	7,858	4,851	3,742
HFC-143a	1,715	4,725	3,084	668	131	76
HFC-227ea	75	363	435	374	276	292
HFC-236fa	1	8	8	11	9	11
HFC-245fa	0	396	469	281	245	214
HFC-365mfc	0	1,160	1,432	872	770	680
HFC-43-10mee	40	201	201	201	201	201
u-HFC-1234yf	0	0	6,903	37,439	45,477	47,658
u-HFC-1234ze	0	0	4,289	5,491	6,172	6,769
u-HFC-1336mzz	0	0	99	637	911	1,159
u-HCFC-1233zd	0	0	113	732	1.093	1,447
Total	**19,258**	**40,835**	**45,449**	**54,564**	**60,136**	**62,249**

As described in Chapter 3.3.3 the expected total emissions of refrigerants and blowing agents were converted into the resulting TFA amounts according to their degradation rates (Chapter 2.7.4.2). Table 26 shows a summary of the TFA amounts in Europe (EU-28) for the period from 2000 to 2050, calculated from the emissions of the projected TFA-forming HFCs, u-HFCs and u-HCFCs (Table 25) and the substance-specific TFA formation rates (see Chapter 2.7.4). The atmospheric decomposition of HFC-134a and u-HFC-1234yf provides the highest TFA contributions at the total input of the refrigerants and blowing agents (see also Figure 18).

The sum of the TFA input of HFC-134a and u-HFC-1234yf of the total sum has a share of 96 % in the EU in the period from 2000 to 2050 (HFC-134a: 14.7 %; u-HFC-1234yf: 81.3 %) (Table 26). Over time, the opposite trend in the use of HFC-134a and u-HFC-1234yf is apparent. HFC-134a is responsible for 93 % and 87 % of the projected annual TFA amount in 2000 and 2010, respectively. From 2020 onwards, the TFA share of HFC-134a will decrease to 43 % and the share of u-HFC-1234yf will then dominate with 47 %. In the period from 2030 to 2050 the use of HFC-134a will continue to decrease. After 2020, u-HFC-1234yf will dominate the projected TFA amount from refrigerant and foam blowing applications and finally have a share of 96 % in 2050 (47,650 t of 49,717 t). All other projected TFA-forming substances contribute, on average, almost 6 % to the annual projected TFA amount in the EU in the period of 2000 to 2050.

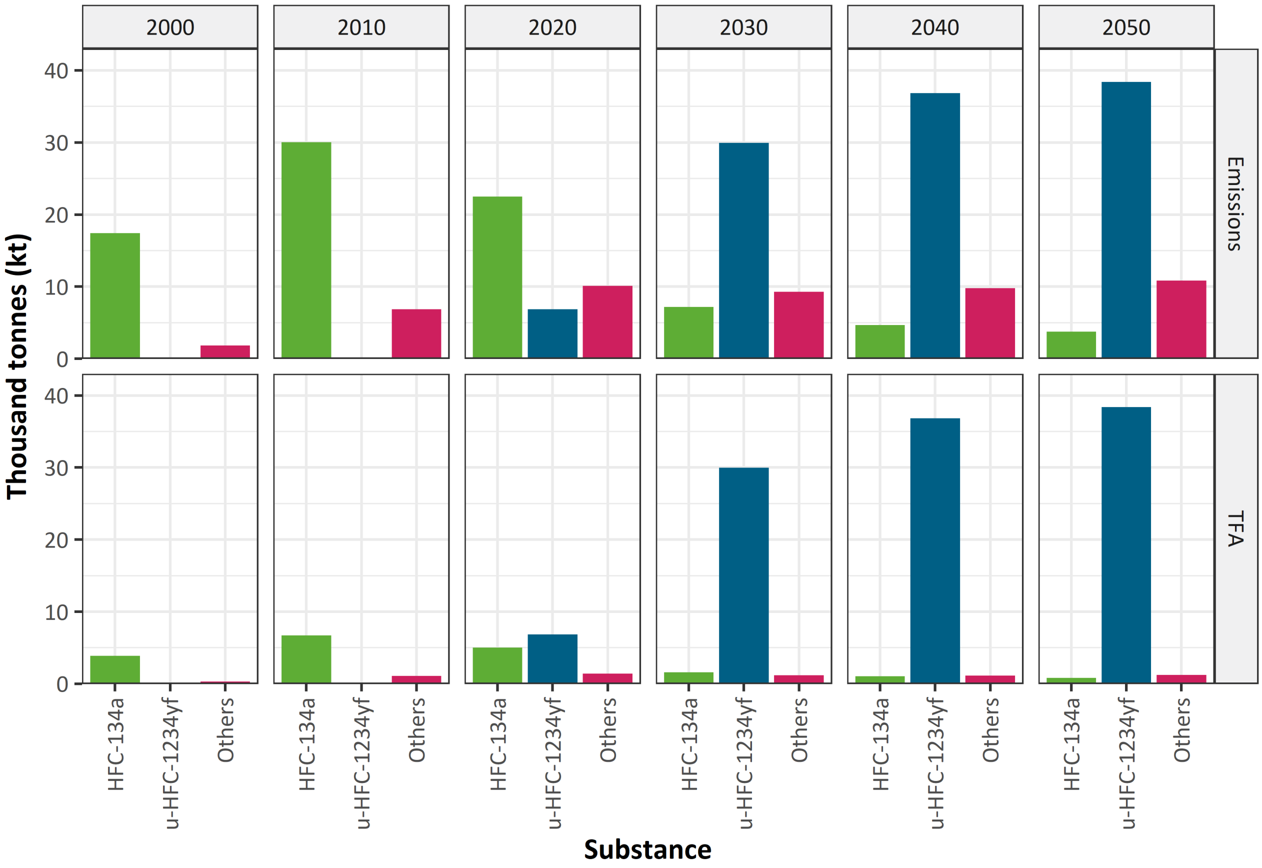
Clarifying remarks on the TFA deposition calculated from the emissions

The actual deposition of a TFA molecule from the degradation of any HFC, u-HFC or u-HCFC molecule depends on the location of wet or dry deposition. Although this is influenced by the location of the emission of the precursor substance, it is also influenced by its lifetime in the atmosphere and weather conditions. Therefore, the TFA quantities converted from the emissions here do not show the direct temporal and local deposition on the territory of the EU or Germany. A deposition rate can only be estimated by means of modelling (see Chapter 5.2.2.5). However, the following TFA-quantities will occur as a consequence of the emissions of halogenated refrigerants and blowing agents, if the substances are used in the quantities projected here. The TFA deposition, following the decomposition of refrigerants and foam blowing agents, will not take place completely in Germany or the EU, and, in case of longer-lived substances, especially not in the year when the emissions of the refrigerant or foam blowing agent occurred. In the foreseeable future, however, all TFA quantities and all other degradation products will be deposited into the environment.

Table 26: Summary of the quantities of trifluoroacetic acid (TFA) calculated from European (EU-28) emissions of all TFA-forming HFC, u-HFC and u-HCFC containing refrigerants and blowing agents in metric tons in the years from 2000 to 2050 for the “u-HFC and u-HCFC maximum scenario”.

Substance	2000	2010	2020	2030	2040	2050	Total TFA sum (2000-2050)	Share of total sum
HFC-134a	3,895	7,595	6,351	1,756	1,084	836	202,781	14.7 %
HFC-143a	233	641	418	91	18	10	12,736	0.9 %
HFC-227ea	50	243	292	251	185	196	11,121	0.8 %
HFC-236fa	0	1	1	1	1	1	31	0.0 %
HFC-245fa	0	34	40	24	21	18	1,297	0.1 %
HFC-365mfc	0	89	110	67	59	52	3,598	0.3 %
HFC-43-10mee	18	91	91	91	91	91	4,295	0.3 %
u-HFC-1234yf	0	0	6,902	37,432	45,469	47,650	1,125,699	81.3 %
u-HFC-1234ze	0	0	429	549	617	677	18,741	1.4 %
u-HFC-1336mzz	0	0	14	89	127	161	3,233	0.2 %
u-HCFC-1233zd	0	0	2	13	19	25	486	0.0 %
Total	**4,196**	**8,694**	**14,650**	**40,364**	**47,691**	**49,717**	**1,384,018**	**100 %**

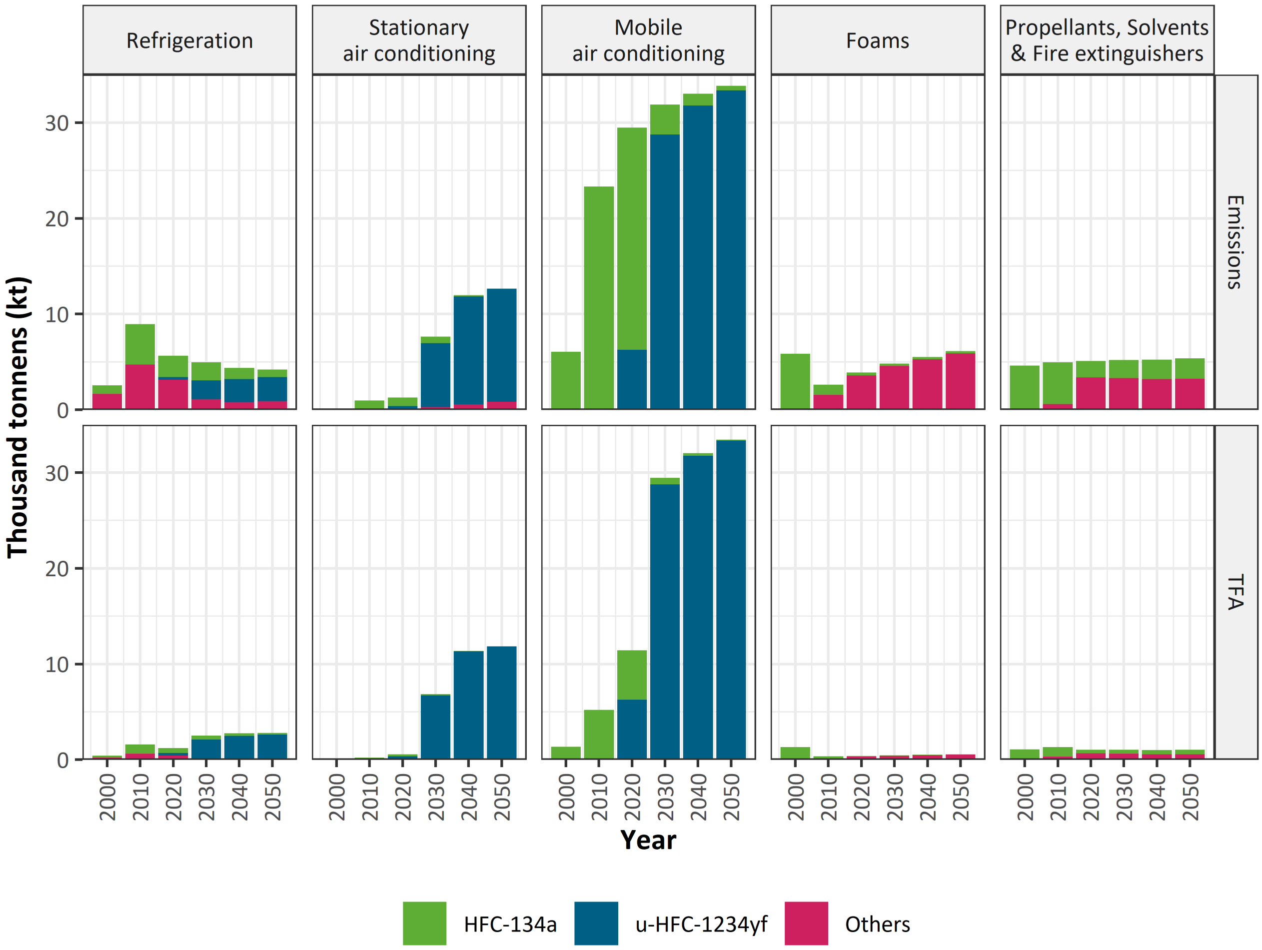
Figure 18: Development of European (EU-28) emissions and resulting quantities of trifluoroacetic acid (TFA) of major TFA-forming HFCs, u-HFCs and u-HCFC-containing refrigerants and blowing agents across all sectors in metric kilotonnes for the years 2000 to 2050 in 10-year steps for the "u-HFC and u-HCFC maximum scenario". All other projected TFA-forming substances are subsumed under the heading "Others".



Source: Own illustration, Öko-Recherche

Looking at the TFA amounts formed by sector, mobile air conditioning plays the largest role in 2020 (Figure 19). While the contribution from this sector more than doubles by 2030 and continues to increase moderately by 2050, the stationary air conditioning sector in particular shows a strong TFA increase by 2030 and further growth by 2050. The TFA contribution from the refrigeration sector also increases significantly between 2020 and 2030, and then remains roughly the same until 2050 and is below the values of air conditioning. Due to the use of fewer TFA-forming substances, the foam sector contributes to a lesser extent to the TFA burden on the environment, despite increasing emissions. The situation is similar with the other projected sectors.

Figure 19: Quantities of European (EU-28) emissions and formed trifluoroacetic acid (TFA) of major TFA-forming HFC-, u-HFC- and u-HCFC-containing refrigerants and blowing agents in metric kilotonnes by sector for the years 2000 to 2050 in 10-year steps for the "u-HFC and u-HCFC maximum scenario". All other projected TFA-forming substances are subsumed under the heading "Others". The sector "Others" is not shown, because the TFA amounts here are at a maximum of approx. 0.03 kt.



Source: Own illustration, Öko-Recherche

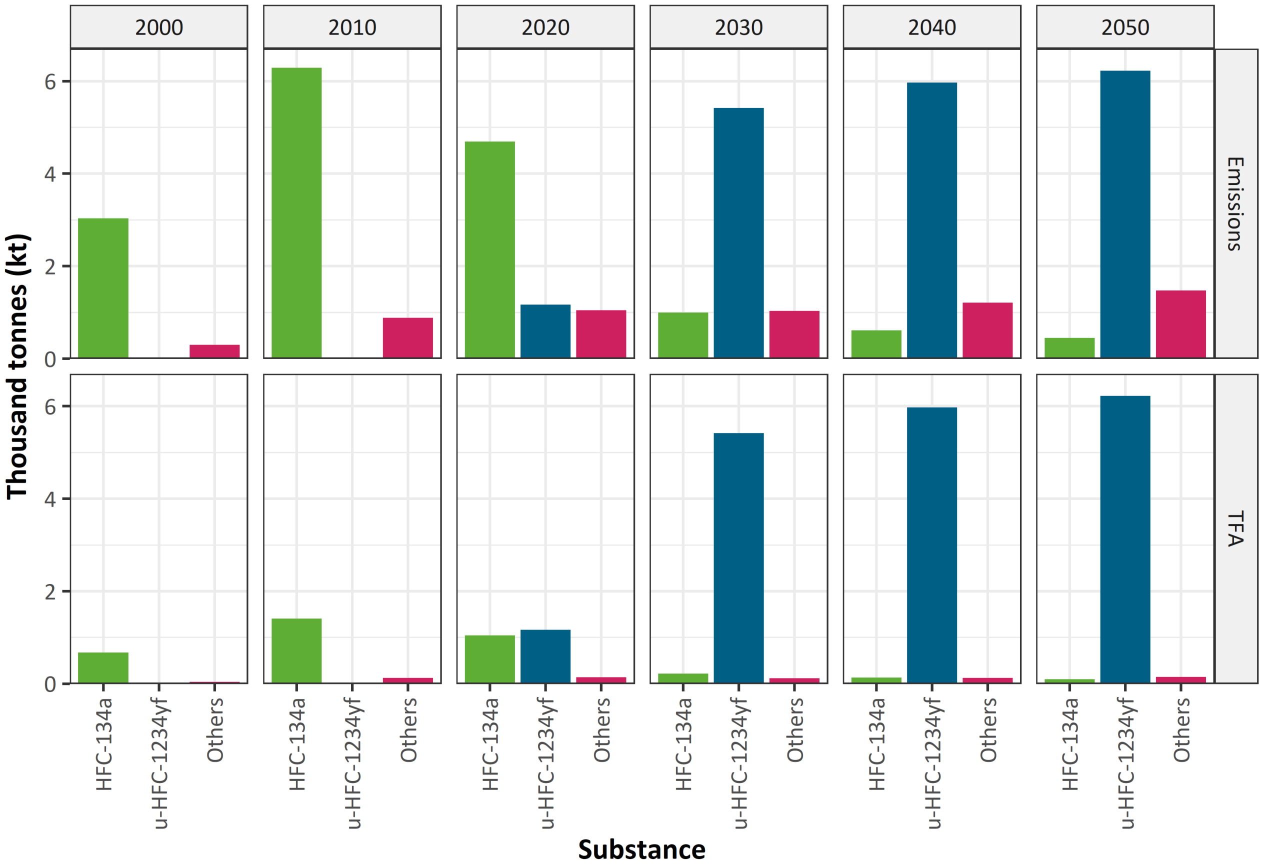
3.4.3.2 Projections for Germany

Germany shows a similar picture as the EU with regard to the amount of TFA formed from emissions of relevant substances and contributes in total with approx. 14 % to the amount of TFA formed from all EU emissions (Table 27). By far the most important substances are, as with the EU, HFC-134a and from the year 2020 increasingly u-HFC-1234yf (Figure 20).

Table 27: Summary of the amount of trifluoroacetic acid (TFA) of all TFA-forming refrigerants and blowing agents containing HFCs, u-HFCs and u-HCFCs in metric tons in the years 2000 to 2050, calculated from the German emissions for the "u-HFC and u-HCFC maximum scenario". The share of the German (DE) and European (EU-28) total refers to the respective substance.

Substance	2000	2010	2020	2030	2040	2050	Total TFA Germany (2000-2050)	Share of DE total	Share of EU-28 total
HFC-134a	679	1,406	1,050	223	137	101	37,941	19.12 %	2.74 %
HFC-143a	40	99	61	14	2	0	2,051	1.03 %	0.15 %
HFC-227ea	1	15	26	22	21	22	927	0.47 %	0.07 %
HFC-236fa	0	0	0	0	0	0	4	0.00 %	0.00 %
HFC-245fa	0	4	3	2	2	1	112	0.06 %	0.01 %
HFC-365mfc	0	6	4	3	3	2	167	0.08 %	0.01 %
HFC-43-10mee	1	1	1	1	1	1	35	0.02 %	0.00 %
u-HCFC-1233zd	0	0	0	2	3	4	74	0.04 %	0.01 %
u-HFC-1234yf	0	0	1,170	5,419	5,970	6,220	154,427	77.83 %	11.16 %
u-HFC-1234ze	0	0	45	72	90	108	2,540	1.28 %	0.18 %
u-HFC-1336mzz	0	0	1	4	5	7	138	0.07 %	0.01 %
Total	**721**	**1,531**	**2,361**	**5,760**	**6,233**	**6,467**	**198,416**	**100 %**	**14.3 %**

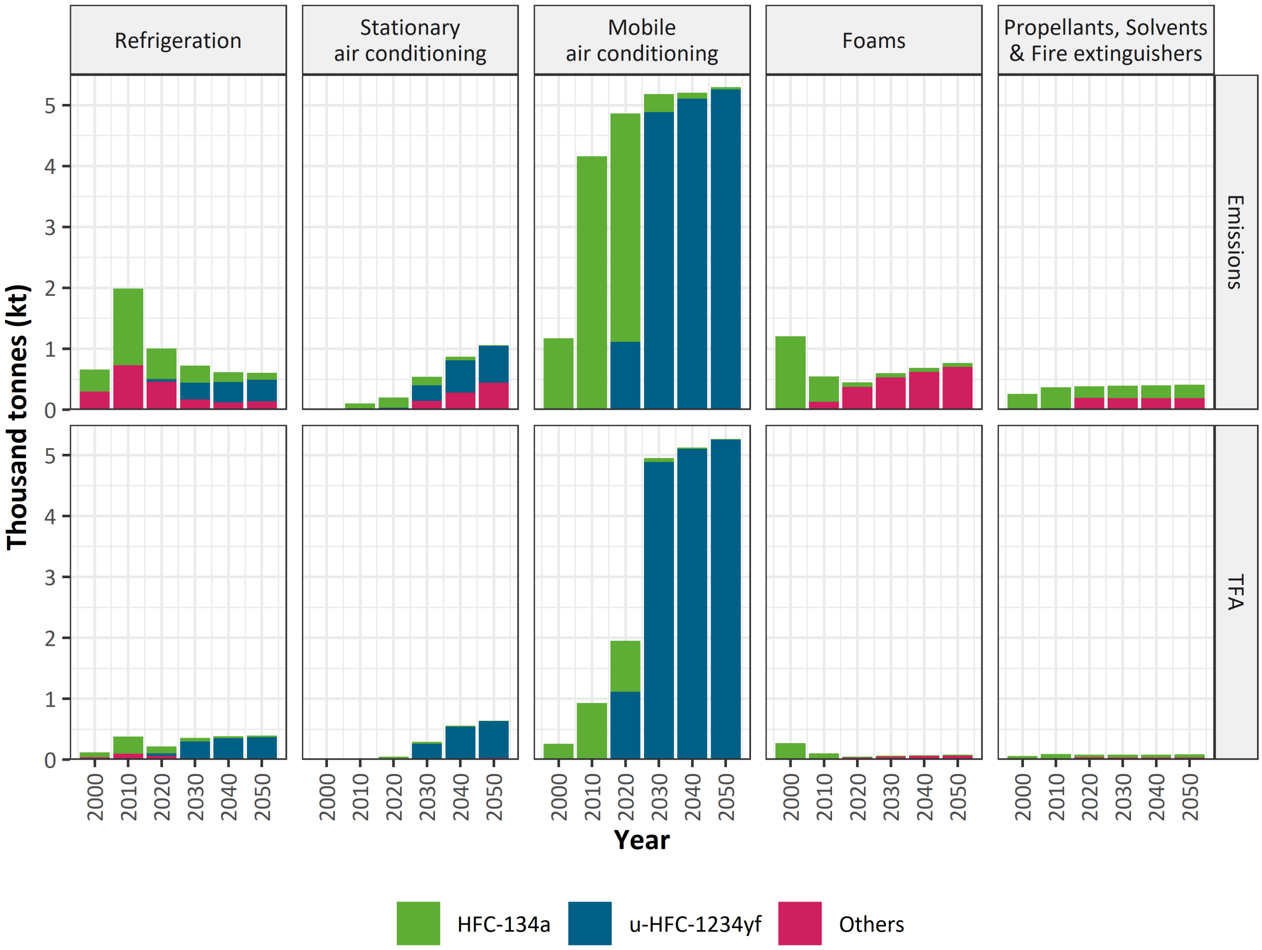
Figure 20: Development of German emissions and resulting amount of trifluoroacetic acid (TFA) of important TFA-forming HFC-, u-HFC- and u-HCFC-containing refrigerants and blowing agents across all sectors in metric kilotonnes for the years 2000 to 2050 in 10-year steps for the “u-HFC and u-HCFC maximum scenario”. All other projected TFA-forming substances are subsumed under the heading “Others”.



Source: Own illustration, Öko-Recherche

Looking at the sectors, the picture is similar to that of the EU as a whole, although emissions from the stationary air conditioning sector play a smaller role, especially with regard to the use of u-HFC-1234yf (Figure 21).

Figure 21: Development of German emissions and resulting amount of trifluoroacetic acid (TFA) of major TFA-forming HFC-, u-HFC- and u-HCFC-containing refrigerants and blowing agents in metric kilotonnes by sector for the years 2000 to 2050 in 10-year steps for the "u-HFC and u-HCFC maximum scenario". All other projected TFA-forming substances are subsumed under the heading "Others". The sector "Others" is not shown, because the TFA-amounts here are at a maximum of about 0.006 kt.

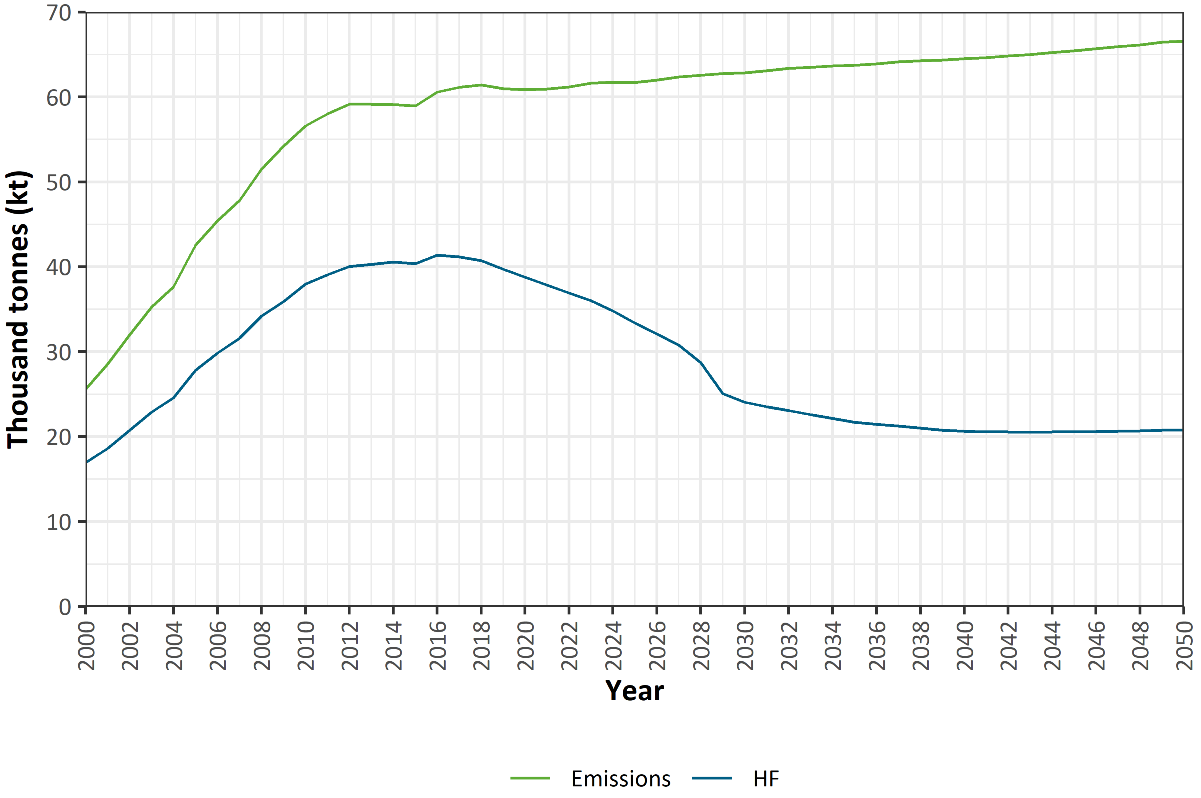


Source: Own illustration, Öko-Recherche

3.4.4 Emission of halogenated greenhouse gases and formed quantities of hydrogen fluoride for Europe (EU-28)

The quantities of hydrogen fluoride (HF) calculated from the projected emissions of HCFCs, HFCs, u-HCFCs and u-HCFCs follow the trend in emissions over the period from 2000 to about 2017 (Figure 22 and Table 28). While the total emission quantities continue to increase slightly, the HF quantities formed will decrease significantly from 2018 onwards. From around 2030, the HF quantities remain at slightly more than 20 kilotonnes per year. The main reason for this is the decrease in the emission of HFC-134a, which produces four HF molecules in 80 % of atmospheric degradation, and HFC-125, which forms five HF molecules. The u-HFC-1234yf, whose emissions increase significantly, forms only one HF molecule.

Figure 22: Emissions of all projected HCFC, HFC, u-HFC and u-HCFC containing refrigerants and propellants in Europe (EU-28) and the resulting quantities of hydrogen fluoride (HF) in metric kilotonnes for the years 2000 to 2050 for the “u-HFC and u-HCFC maximum scenario”.



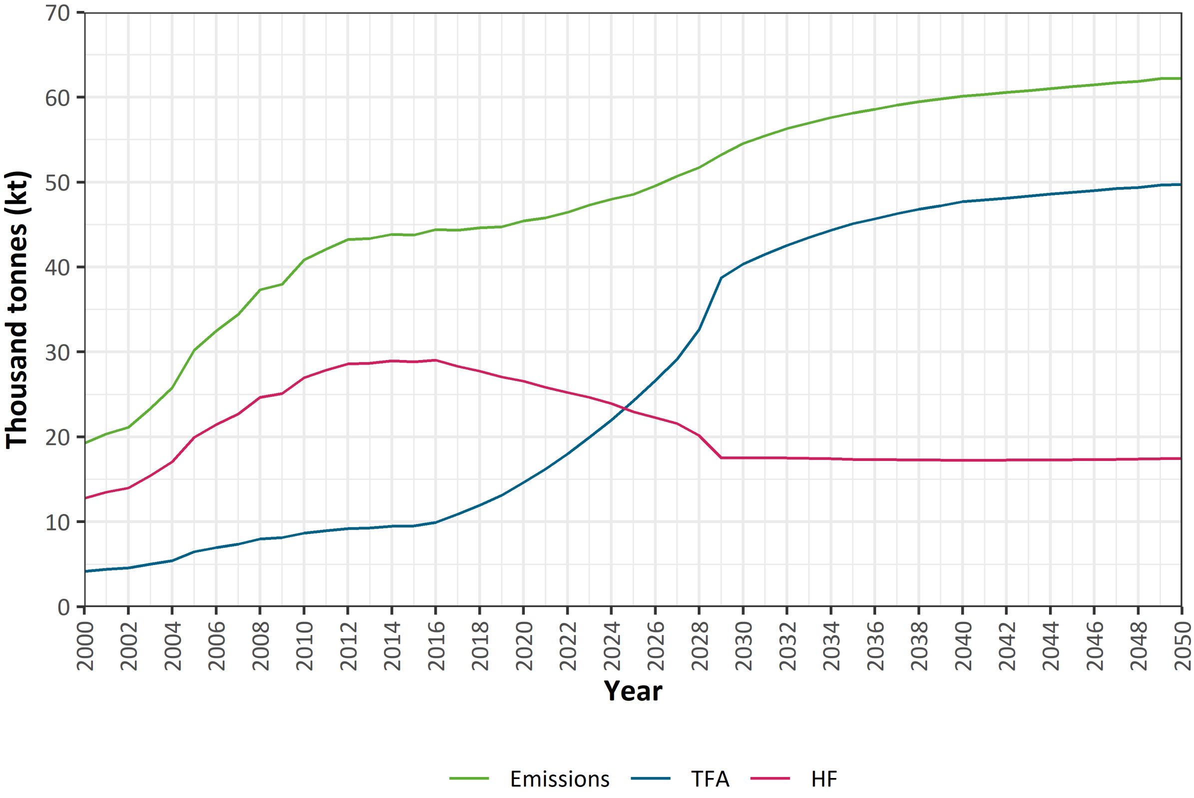
Source: Own illustration, Öko-Recherche

Table 28: Summary of the quantity of hydrogen fluoride (HF) calculated from European (EU-28) emissions of all projected HCFC, HFC, u-HFC and u-HCFC containing refrigerants and blowing agents in metric tonnes in the years 2000 to 2050 for the "u-HFC and u-HCFC maximum scenario".

Substance	2000	2010	2020	2030	2040	2050	Total HF sum 2000-2050
HCFC-22	1,226	1,469	0	0	0	0	21,525
HFC-125	1,199	5,240	6,791	2,020	238	141	151,739
HFC-134a	11,618	22,655	18,944	5,239	3,234	2,495	604,845
HFC-143a	1,102	3,037	1,982	429	84	49	60,335
HFC-152a	450	2,225	721	0	0	0	46,062
HFC-227ea	35	171	205	176	130	138	7,805
HFC-23	1,285	170	132	91	68	68	9,268
HFC-236fa	<1	5	6	7	6	7	290
HFC-245fa	0	278	329	197	172	150	10,695
HFC-32	7	1,876	4,550	4,407	3,093	3,120	154,632
HFC-365mfc	0	736	909	554	489	432	29,674
HFC-43-10mee	22	112	112	112	112	112	5,275
u-HCFC-1233zd	0	0	51	330	492	652	12,530
u-HFC-1234yf	0	0	1,211	6,568	7,978	8,360	197,510
u-HFC-1234ze	0	0	2,784	3,564	4,006	4,393	121,662
u-HFC-1336mzz	0	0	58	373	533	678	13,615
Total	**16,945**	**37,973**	**38,785**	**24,068**	**20,637**	**20,796**	**1,447,461**

If only the TFA-forming substances are considered (Figure 23), the same trend can be seen that for emissions from the EU-28, the amount of TFA formed increases from about 2025 onwards, while the amount of HF decreases, i.e. instead of HF, increased amounts of TFA are formed.

Figure 23: Emissions of TFA-forming HCFC-, HFC-, u-HFC- and u-HCFC-containing refrigerants and propellants in Europe (EU-28) and quantities of trifluoroacetic acid (TFA) and hydrogen fluoride (HF) formed therefrom in metric kilotonnes for the period from 2000 to 2050 for the “u-HFC and u-HCFC maximum scenario”.



Source: Own illustration, Öko-Recherche

3.5 Flow Analysis for Europe (EU-28) for the year 2030

If we consider the total degradation path of TFA-forming substances in Europe (EU-28) for the year 2030 from the AnaFgas model, a total demand of 93,339 metric tonnes of halogenated substances[165] can be assumed (Figure 24). The largest share of this (35 %) is accounted for by the passenger car air conditioning sector, with u-HFC-1234yf accounting for the largest share (85 %). This is followed by the stationary air conditioning sector with 26 %, and then all other sectors except refrigeration with 24 %. The refrigeration sector itself accounts for 15 % of the total demand. The u-HFC-1234yf represents almost 50 % of the demand with 46,030 tonnes, while HFC-134a only covers 16 %. Accordingly, 60 % of the 62,825 tonnes of total emissions are accounted for by u-HFC-1234yf. The main burden of emissions comes from the mobile and stationary air conditioning sectors, which account for almost three quarters of total emissions with 51 % and 23 % respectively. Depending on the substance in the atmosphere, the emitted quantities are decomposed to TFA or HF. The mobile air conditioning sector accounts for the largest share (73 %), followed by stationary air conditioning with 17 %. In both sectors the TFA-emissions with 98 % originate particularly from u-HFC-1234yf. In all sectors, u-HFC-1234yf accounts for 93 % of the total TFA quantity of 40,363 tonnes. The total amount of HF formed is approx. 24,000 tonnes.

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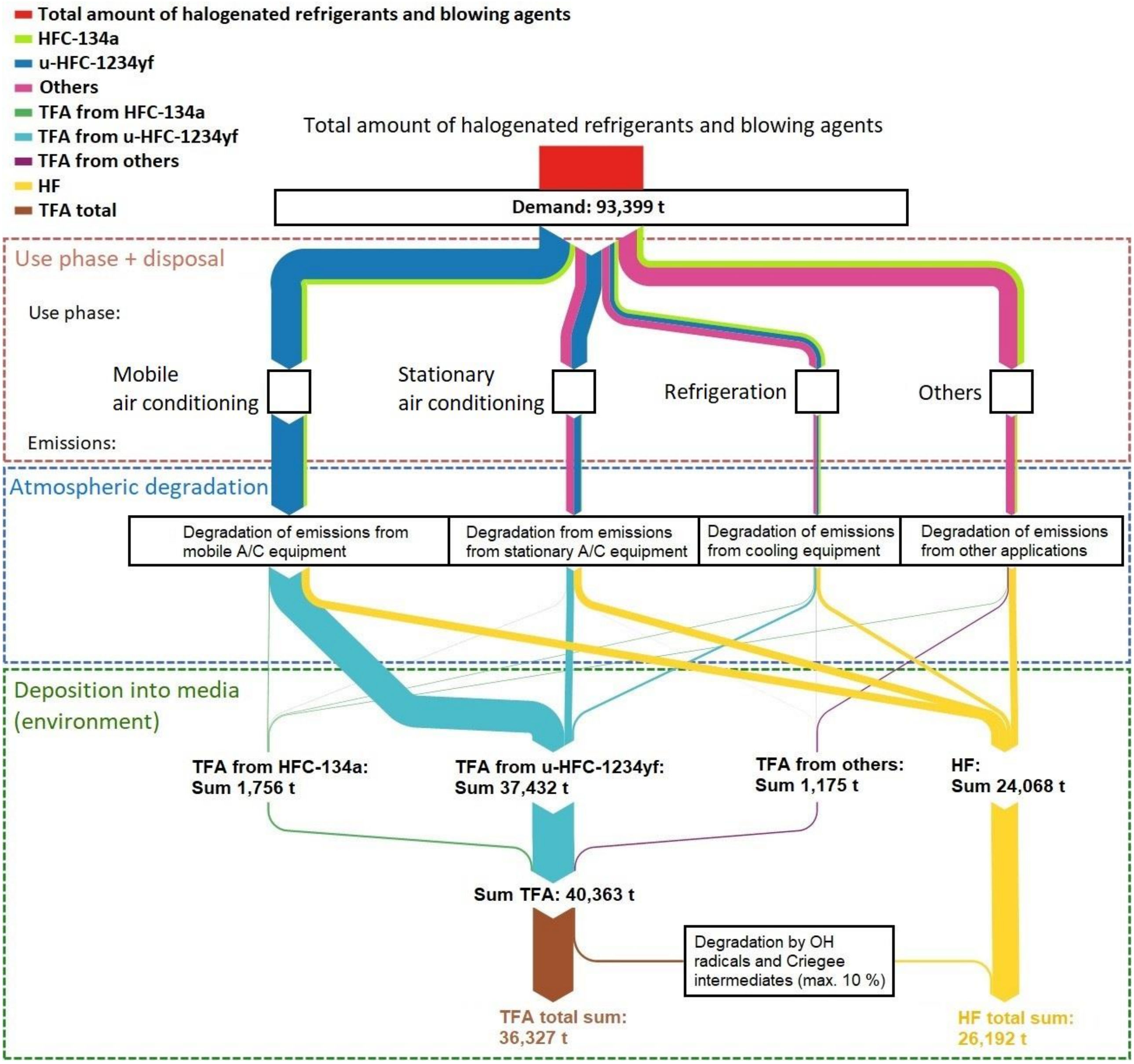
[165] This includes all substances and applications that were modeled in Chapter 3, i.e. besides refrigerants and blowing agents also other sectors and substances.

It can be assumed that only a very small portion of the formed TFA is degraded in the atmosphere. If one assumes a maximum loss of TFA by the reaction with OH radicals of 5 %, 38,345 tonnes of TFA remain in the atmosphere, which are introduced into the media soil and water via precipitation or dry deposition. The rate of the loss of TFA by the reaction with Criegee intermediates in the atmosphere is probably negligible, but should not exceed 2 % in Europe (see Chapter 2.9.3.2). Even under the assumption of a significantly higher degradation rate of 5 %, a total of 36,327 tonnes of TFA would remain.

Figure 24: Sankey flow diagram of the European (EU-28) total emissions of modelled halogenated substances from use and disposal in the various sectors and the atmospheric degradation products TFA and HF for the year 2030 for the “u-HFC and u-HCFC maximum scenario”. The sectors foams, propellants, solvents, and fire extinguishing agents, as well as semiconductor industry and emissions from HFC production, are subsumed under „Others”.



Source: Own illustration, Öko-Institut and Öko-Recherche

3.6 Limitations of the AnaFgas model

3.6.1 Selection of projected substances

The adapted AnaFgas model projects emissions only for halogenated refrigerants and blowing agents. This includes certain HCFCs, HFCs, u-HFCs and u-HCFCs and their mixtures (see Table 22). As described in Chapter 2.8, further halogenated substances may form the persistent degradation product TFA. However, since these are not refrigerants, foam blowing agents or aerosol propellants, their emissions are not modelled within the scope of this project. Exceptions are the fluorinated hydrocarbons already included in the original AnaFgas model in the sectors solvents and fire extinguishing agents as well as in the production of halogenated hydrocarbons and the semiconductor industry. These were adopted without adjustment and included in the TFA calculation.

3.6.2 Limits of the assumptions

The assumptions in this project are estimates based on projections of certain developments and various factors. These include technical developments and political conditions that may change over time. For the years from 2000 to 2018 robust and realistic estimates of the TFA amounts could be made considering the reported emission data. The projections, which continue the development, were calculated based on the year 2018 and take into account the existing F-gas regulations. The so-called u-HFC and u-HCFC maximum scenario generated here assumes that the transition to u-HFC and u-HCFCs has priority over the transition to non-halogenated substances (such as propane and CO_2), except in sectors where non-halogenated substances are already established on the market. Therefore, it cannot be ruled out that the actual development may deviate from the scenario on which this report is based. In general, the further the assumptions reach into the future, the greater the inaccuracy.

There may be deviations in the future from various estimates or assumptions on which the projections are based. These include the uncertainty of future political requirements. The model is based on the current legislation, which was detailed in Chapter 3.3.1. It considers certain measures, such as regular leakage checks, which should lead to a reduction in certain emission factors. However, the implementation of these measures differs widely across EU Member States and application sectors (Schwarz et al. 2011).

Increased tightness and targeted recovery of the refrigerant at the end of life can lead to a reduction in emissions. In particular in the case of mobile air conditioning systems that have higher emissions and use a very high proportion of TFA-forming u-HFC-1234yf, this would have a reduction effect. Technical developments or measures that could improve the tightness of the systems or measures to increase the recovery rates were not taken into account under the maximum scenario.

Newly registered vehicles with mobile air conditioning systems in the EU are not always disposed at the end of their lives. Research for Germany showed that around 76 % of the 2.75 million cars and small trucks (class N1) put out of service in 2013 were transported abroad (Sander et al. 2017). 55 % remained within the EU and 91 % were re-registered there, while 21 % were exported to other EU countries. Of the 24 % decommissioned vehicles that remained in Germany, 80 % were subjected to authorised and 20 % to non-authorised disposal. Since there are no precise data on residual quantities and recovery of refrigerants in air conditioning systems of end-of-life vehicles for the EU, it must be assumed, especially under a scenario of maximum environmental pollution, that complete emissions are possible.[166] In addition, the 6.15 million cars and small trucks (class N1) reported as end-of-life vehicles in the EU in 2014 are offset by 4.66 million vehicles whose whereabouts are unknown

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[166] For the projections in this study, the assumptions of Schwarz et al. (2011) were retained, who assumed that the remaining amount of 70 % of the filling capacity would be completely emitted when disposing of car air conditioning systems.

(Mehlhart et al. 2018). In order to quantify the overall environmental impact, all emissions from the EU inventory were thus included and converted into TFA quantities. Therefore, the emissions in the present projections exceed the emissions directly allocated to the EU alone and may therefore deviate from other calculations. However, these emissions must be considered in order to quantify the total environmental impact.

Furthermore, many assumptions are based on expert estimates and not on facility-related data. In general, expert assessments and industry forecasts form the basis of the assumptions regarding the development of the various application sectors up to the year 2050. In the course of this long period, deviations from current assessments and forecasts may occur. In principle, therefore, the model must allow for systematic uncertainty.

A major uncertainty factor is the reaction of market participants. The projections of future demand are based on decisions by users, plant manufacturers and equipment manufacturers in favour of u-HFCs and u-HCFCs. This means, for example, that a u-HFC or u-HCFC solution will be chosen when purchasing a new system at a comparable price. Conventional HFC technologies are no longer considered for new plants if an alternative technology is financially preferable due to the scarcity and consequently higher price of HFCs as a result of the F-gas Regulation. Since the aim of this project is to estimate the maximum possible environmental impact of the degradation products of halogenated refrigerants and blowing agents, natural refrigerants, which represent a realistic alternative to conventional HFC technologies in many application sectors, are less strongly considered and, if available, HFC or HCFC solutions are preferred.

The extent to which financial incentives lead to consistent changes in the choice of certain refrigerants and blowing agents is generally not precisely assessable. For example, unforeseeable events and developments can have a major impact on the price of various refrigerants and blowing agents and thus reduce their market share. For example, stockpiling and illegal trade of refrigerants in Europe in 2018 is likely to have had a significant impact on the availability of HFC-134a, for example for car repair shops, and the price development of the mixture R404A. Economic crises or technological leaps can also change the market significantly. However, such developments cannot be considered in the model.

4 Field monitoring campaign to determine the wet deposition of trifluoroacetic acid (TFA)/trifluoroacetate

4.1 Objectives

The analysis of the current situation showed that certain halogenated refrigerants and blowing agents can be transformed in the atmosphere to the persistent and highly mobile compound trifluoroacetic acid (TFA). TFA is primarily scavenged from the atmosphere as trifluoroacetate by wet deposition which results in the contamination of water resources. So far, only very few studies are available that have systematically determined the concentration of TFA/trifluoroacetate in precipitation. However, such monitoring efforts are necessary to adequately describe the atmospheric deposition of TFA/trifluoroacetate of a specific region. In this study, a nation-wide field monitoring network including eight sampling sites was established in Germany. At each site, precipitations samples were taken over the duration of two years and were analyzed for trifluoroacetate. The aim of this monitoring effort was to quantify the current annual wet deposition of trifluoroacetate in Germany. The characterization of the nonpoint source pollution of TFA that results from precipitation is a vital step in evaluating potential environmental and human-health risks related to the TFA contamination of water resources. Furthermore, the obtained data set can be used as a benchmark for future studies.

4.2 General Information

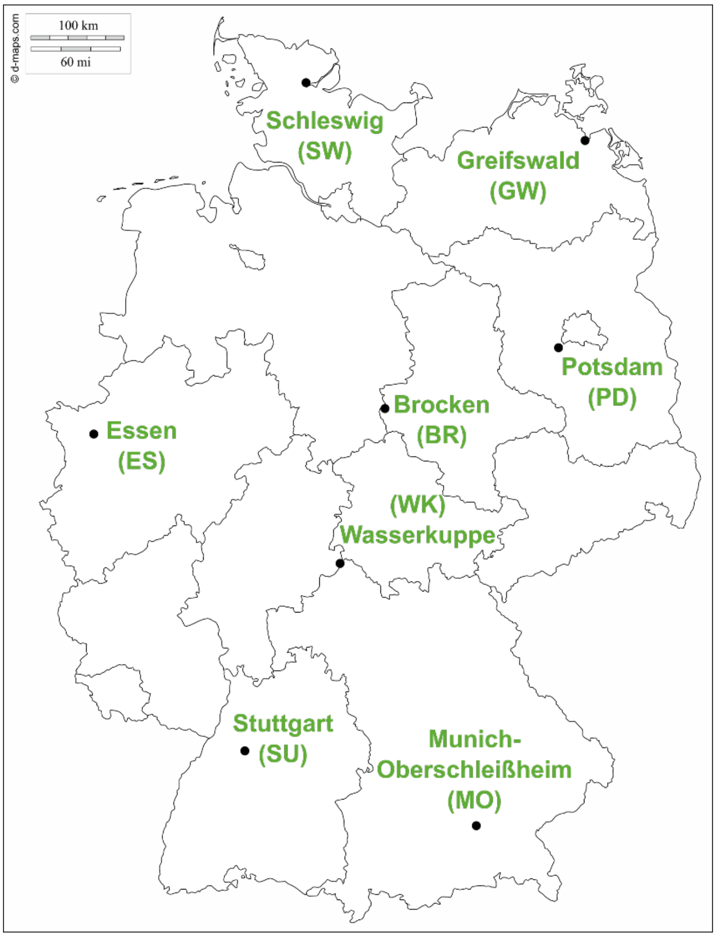
Due to its strong tendency to deprotonate, trifluoroacetic acid (TFA, CF_3COOH) is present in the aquatic environment almost exclusively in the form of its anion trifluoroacetate (CF_3COO^-). The abbreviation TFA is used in the literature for both the acid and the anion (see also Table 16 in Chapter 2.9.1). The analytical results presented in the following do always refer to trifluoroacetate.

Sampling of spring and groundwater in order to determine the wet deposition of trifluoroacetate was not considered in this study due the unknown contribution of additional sources of TFA in the respective areas (e.g. agricultural activities). A surface water monitoring campaign carried out by TZW and NLKWN (Lower Saxon State Department for Waterway, Coastal and Nature Conservation) also showed the difficulties to identify and quantify individual contributions of different TFA sources to the total amount of trifluoroacetate present in the collected water samples (Nödler et al. 2019). Consequently, the project presented here focused on the quantification of trifluoroacetate in precipitation samples. In addition, soil and plant samples were collected in the immediate vicinity of the precipitation sampling sites and were also analyzed for trifluoroacetate.

4.3 Sampling of precipitation, soil, and plant material

The monitoring campaign was supported by the German Meteorological Service (German: Deutscher Wetterdienst, DWD). Eight DWD sampling sites systematically distributed over Germany were selected for the trifluoroacetate monitoring campaign. Since these sites were part of the DWD network for radionuclide monitoring, existing infrastructure could be used and only a small additional expenditure for the local personnel was necessary. The selected sampling sites are shown in Figure 25. Additional geographical information can be found in Table 29.

Figure 25: Geographic location and of studied sampling site in Germany. Sampling site abbreviations in parentheses.



Source: d-maps.com, modified by TZW Karlsruhe

Table 29: Geographical coordinates and altitudes (in m above sea level) of the precipitation sampling sites in different federal states of Germany.

Sampling site	Abbrev.	Federal State	Latitude	Longitude	Altitude in m above sea level
Brocken	BR	Saxony-Anhalt	51°47'55.0" N	10°37'05.9" E	1.134
Essen	ES	North Rhine-Westphalia	51°24'14.8" N	6°58'03.7" E	150
Greifswald	GW	Mecklenburg-Vorpommern	54°05'48.1" N	13°24'20.2" E	2
Munich-Oberschleißheim	MO	Bavaria	48°14'38.4" N	11°33'10.8" E	484
Potsdam	PD	Brandenburg	52°22'52.7" N	13°03'43.9" E	81
Schleswig	SW	Schleswig-Holstein	54°31'39.0" N	9°32'55.3" E	43
Stuttgart	SU	Baden-Württemberg	48°49'41.2" N	9°12'00.0" E	314
Wasserkuppe	WK	Hesse	50°29'50.3" N	9°56'34.1" E	921

4.3.1 Precipitation sampling

Sampling at the sites Brocken, Essen, Greifswald, Munich-Oberschleißheim, Potsdam, Schleswig, and Wasserkuppe started in February 2018. At the Stuttgart site, sampling started in March 2018 due to reconstruction work. In order to cover an extended period of time and due to the high temporal variation in trifluoroacetate concentration in precipitation described in the literature, the duration of the monitoring campaign was set to two years. With the exception of the site Brocken, the collection pans and containers were rinsed with deionized water on a daily basis in periods without precipitation. The resulting samples of dissolved/suspended dry-deposited material were included for radionuclide monitoring by the German Meteorological Service but not used for trifluoroacetate analysis. The rinsing step ensured that the concentrations of precipitation samples were not altered by the amount of dry-deposited trifluoroacetate from periods without precipitation. Consequently, it can be assumed that the precipitation samples from the sites Essen, Greifswald, Munich-Oberschleißheim, Potsdam, Stuttgart, Schleswig, and Wasserkuppe were not substantially influenced by dry-deposited trifluoroacetate and were therefore representative for the amount of wet-deposited trifluoroacetate. In contrast to the other sampling locations, site Brocken is characterized by extreme weather conditions due to its altitude and exposed location. Consequently, the setup used for sample collection at the site Brocken consisted of a rain gauge specifically designed for precipitation sampling at high-altitude locations affected by strong winds and high annual snowfall. The collection pan and the containers were not rinsed with deionized water between precipitation collection periods. Consequently, samples from the site Brocken contained dry- and wet-deposited trifluoroacetate and therefore represent the total amount of atmospherically deposited trifluoroacetate. As such, the data from the site Brocken is displayed and discussed separately from the other sites.

All locations were equipped with all material necessary for sample collection and shipping. The provided sample tubes (centrifuge tubes) were identified as being suitable for sample storage (no losses of trifluoroacetate due to sorption; contamination-free). The provided material is shown in Table A 7 in Annex A.10.1. The sampling protocol is listed in Annex A.10.2.

During periods of very low precipitation, the collection pans were rinsed with a defined amount of deionized water. Analytical results for these specific samples were later dilution-corrected. Since the rinsing water was produced on site, each monitoring station was required to include a sample of the rinsing water (field blank) to the first batch of shipped precipitation samples. No contamination was detected in any of the blank samples, i.e. the trifluoroacetate concentrations were always below the detection limit (DL) of 0.025 µg/L. It has to be noted that rinsing of the collection pan was rarely done. In 2018, only about 10 % of all samples contained rinsing water.

In order to prevent concentration effects, water samples must be taken and stored in such manner that evaporation losses do not occur. Securely sealed sample containers, such as the centrifuge tubes used in this study, are unproblematic in that regard. Only two samples were leaking when they arrived at the laboratory.

Due to the high environmental persistence of trifluoroacetate, analyte losses during storage (in this study: weeks to months at 4 °C) are highly unlikely. This could already be shown by a storage test which was done as part of the validation of the analytical method. Evaporation from the DWD's precipitation collection containers can also be considered as insignificant, as the containers were emptied daily in most instances (90 % of all samples taken in 2018). Even with longer intervals, i.e. up to 1 week, evaporation losses are expected to be of little relevance (<10%). Not all stations were able to provide daily emptying of the collection containers over the entire two-year period. For example, the site Essen had to change from daily to weekly sampling after March 2019. This was due to personnel reasons and was communicated in advance by the DWD.

In the two-year observation period, a total of 2,410 precipitation samples were collected. On average, 96 precipitation samples (Minimum/Maximum: 56/163 samples) were taken per month and site on average. On average, most samples per month (18 samples) were provided by the station Brocken, the smallest number (9 samples) by the stations Munich-Oberschleißheim (in the following figures partly also briefly referred to as Munich) and Essen, although the smaller number of samples at the station Essen was mainly due to the change from daily to weekly sampling after March 2019. Note that the number of individual samples cannot be equated with the number of days with precipitation, since the collection periods of individual samples varied. The total precipitation amount during the studied periods at each site is shown in Table 30.

Table 30: Precipitation amounts at the studied sites during the periods 2018/19 (February 2018 to January 2019) and 2019/20 (February 2019 to January 2020); for the Stuttgart site: March 2018 to February 2019 (2018/19) and March 2018 to February 2020 (2019/20).

Measurement site	Precipitation amount in mm	
	February 2018 - January 2019	February 2019 - January 2020
Brocken	1,330	1,475
Essen	653	877
Greifswald	440	526
Munich-Oberschleißheim	772	749
Potsdam	337	521
Stuttgart	502	661
Schleswig	681	1,057
Wasserkuppe	890	1,009

4.3.2 Sampling of soil and plant material

In July and October 2019, soil samples were taken in the vicinity of all DWD stations involved in the project. Only vegetated areas were sampled. The highest trifluoroacetate concentrations in precipitation were detected at the Munich-Oberschleißheim site. As a result, soil samples were taken at this site at two different times- Additionally, samples of six plant species (above-ground material) were collected in July 2019 at this site. An influence of additional trifluoroacetate sources at the sites, such as from the degradation of pesticides containing carbon-bound trifluoromethyl moieties ($C\text{-}CF_3$), is unlikely.

A total of eight individual soil samples were taken with a soil sampler (Figure 26). The soil profile was divided into two depth ranges (0-30 cm and 30-60 cm). A composite sample was prepared from these individual samples for each depth range. Samples of six common plant species (above-ground material) were collected in plastic bags. In addition, herbariums of the collected species were prepared for plant identification purposes.

Figure 26: Soil profile within the soil sampler.

Source: TZW Karlsruhe/ Rolf Benesch

4.4 Methods for trifluoroacetate analysis

4.4.1 Analysis of precipitation samples

Monthly (volume-equivalent) composite samples were prepared for each site and month from individual precipitation samples. Volume-equivalent means that the volume ratio between the individual sample and the composite sample is identical to the volume ratio between the precipitation amount of the respective individual sample and the precipitation amount of all individual samples that make up the composite sample.

In addition, all individual samples from the period February 2018 to January 2019 (site Stuttgart: March 2018 to February 2019) were analyzed for trifluoroacetate individually. The rationale behind this was to get a better understanding of the temporal variations of trifluoroacetate concentration in precipitation. In addition, the individual measurements enabled the calculation of volume-equivalent (i.e. precipitation-weighted) average concentrations. Hence, analytical results of the monthly composite samples prepared in the laboratory could be compared to the calculated monthly averages (based on measurements of individual samples), which, in theory, should be identical to each other. Both efforts produced very similar results (average deviation: 11 %).

Detailed information regarding the analytical method for the determination of trifluoroacetate can be found in Scheurer et al. (2017) and only a brief description will be given here. A precipitation sample was centrifuged (15 min, 4,000 × g), 1 mL of the supernatant was transferred to a 2 mL HPLC vial, spiked with internal standard ($^{13}C_2$-trifluoroacetate) and mixed. Ion chromatography coupled to tandem mass spectrometry (IC-MS/MS) was used for used for analysis. The injection volume was set to 100 µL. An IonPac AS17-C (Dionex) with a corresponding pre-column was used for chromatographic separation. The mobile phase consisted of methanol (MeOH) and an aqueous ammonium bicarbonate solution. The detection limit for trifluoroacetate (DL; 0.025 µg/L) was determined according to DIN 32645.

4.4.2 Analysis of soil and plant samples

4.4.2.1 Sample preparation

Soil samples were freeze-dried, grinded and homogenized. For the analysis of the plant samples, the plant material was first cut into approx. half-cm pieces and dried at 40 °C for 48 h. For each sample, fresh and dry weights (FW and DW) were recorded to normalize the determined trifluoroacetate concentrations to the fresh weight.

4.4.2.2 Extraction

The described extraction methods were developed and validated in a previous TZW research project (Sacher et al. 2019). For the extraction of trifluoroacetate from soil matrix, 2 g of soil sample were mixed with 1.6 g of sodium sulfate in a polypropylene centrifugation tube. Subsequently, a defined amount of internal standard and 4 mL of MeOH were added to the tube. The obtained suspension was sonicated for 15 min and shaken for another 15 min using a reciprocating shaker. The suspension was centrifuged (15 min, 4.000 *x* g) and the supernatant was transferred to a 10 mL glass vessel. The extraction was repeated with fresh MeOH to optimize the extraction yield. Finally, the combined extracts were evaporated to dryness using a gentle stream of nitrogen and dissolved again in 1 mL of acetonitrile.

For the extraction of trifluoroacetate from plant matrix, 1 g of the dried and homogenized plant material was weighed into 15 mL polypropylene centrifugation tube, spiked with a defined amount of internal standard and mixed with 3 mL of MeOH (+1 % (v/v) formic acid) and 3 mL of ultrapure water. The obtained suspension was sonicated for 15 min and shaken for another 15 min using a reciprocating shaker. After centrifugation (15 min, 4,000 *x* g), the supernatant was transferred to another 15 mL polypropylene centrifugation tube. This procedure was repeated twice with fresh solvent to optimize the extraction yield. The trifluoroacetate contents usually found in plant material allow for a five-fold dilution of the combined extract with ultrapure water, leading to a reduction of matrix effects in subsequent IC-MS/MS-analysis.

Since grinded soil material can easily be homogenized, the analysis of replicates of a soil sample was considered unnecessary. Three of the six plant samples were analyzed in triplicates. The other plant samples could only be extracted and analyzed once (only little sample material was available after drying, almost the total sample quantity was used). The good precision of analytical method, expressed by the low variance of the concentrations of the triplicate plant samples however shows, that homogeneous sample material was produced by cutting the plant material in very small pieces as described above.

4.4.2.3 Analysis

The quantification of trifluoroacetate in soil and plant extracts was performed analogously to the analytical method used for the determination of trifluoroacetate in precipitation. Laboratory blanks were used to detect potential contamination during sample preparation and extraction by analyzing aliquots of ultrapure water (laboratory blanks) that were treated as the environmental samples. No contamination was detected in any of the blanks. The limit of quantitation of trifluoroacetate for plants was 32 µg/kg and for soils 0.2 µg/kg dry weight. In addition to the trifluoroacetate analysis, the total organic carbon (TOC) content was determined by a combustion method.

4.4.2.4 Methods for interpreting left-censored data

Left-censored observations, sometimes referred to as “non-detects” or “less than” values (e.g. < 0.025 µg/L), are concentrations that are known only to be somewhere between zero and the DL. Commonly used methods in environmental chemistry to deal with values below the DL, is to substitute a fraction of the DL for each censored value or to exclude them from the analysis. However, research has shown that this approach produces poor estimates of statistics (e.g. averages, correlation coefficients, regression slopes, hypothesis tests) and can lead to misinterpretations (Helsel 2006).

Since the data set of the individual precipitation samples contained left-censored observations (i.e. TFA concentrations < 0.025 µg/L), results were represented using so-called censored boxplots. In a censored boxplot the horizontal line depicts the DL. The percentiles below the DL were estimated using the "regression on order statistics" (ROS) method (Helsel 2011). ROS is a so-called imputation procedure, in which the censored data points (i.e. values below the DL) are filled in based on a probability plot of the uncensored data points (i.e. values above the DL), thus avoiding arbitrary substitution or deletion of censored data (Helsel 2005). The ROS method was also used for a better estimate of average trifluoroacetate concentrations of the individual precipitation samples.

4.5 Results

4.5.1 Trifluoroacetate in precipitation

In 17 cases, two consecutive sample tubes were incorrectly labeled with an identical sample number. For these 34 samples of the total of 2,419 individual samples, the measured TFA concentration could not definitively be assigned to the correct precipitation amount. Therefore, statistical parameters were determined for a best-case flux scenario (i.e., assigning the lower of the two concentrations to the higher of the two precipitation amounts) and a worst-case flux scenario (i.e., assigning the higher of the two concentrations to the higher of the two precipitation amounts). Thus, the best-case scenario represents the minimum amount of wet-deposited trifluoroacetate and vice-versa. Due to the negligible differences between the scenarios, only the results of one (i.e., the best-case flux) scenario are discussed in the following. A graphical and tabular presentation of the results of the worst-case scenario can be found in Annex A.10.3.

4.5.1.1 Results of the analysis of monthly (volume-equivalent) composite samples

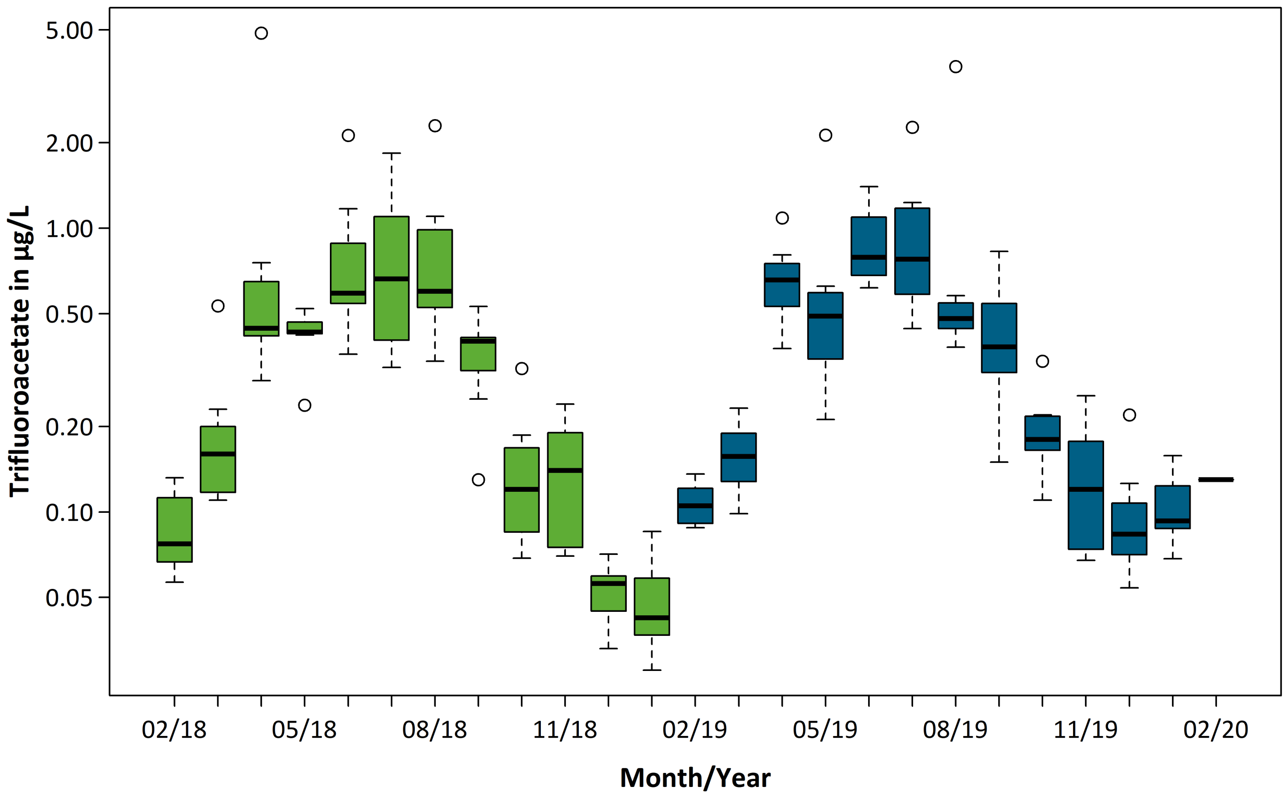
Volume-equivalent trifluoroacetate concentrations in µg/L

In the following, the concentrations of trifluoroacetate of the monthly (volume-equivalent) composite samples from 7 measuring stations (n = 168) are shown. For this purpose, the concentrations were grouped by the attributes time (month and year) (Figure 27 and Table 31) and location (measuring station) (Figure 28 and Table 32).

When grouping the trifluoroacetate concentration data of monthly composite samples by time a pronounced seasonality in the TFA concentration becomes apparent (Figure 27 and Table 31): The lowest trifluoroacetate concentrations were observed in winter (especially in the months December and January), whereas the highest trifluoroacetate concentrations occurred in the summer months (especially June to August). In the spring (March to May) and autumn (September to November) concentrations were in an intermediate position. The difference between the lowest (January 2019: 0.042 µg/L) and the highest median concentration of trifluoroacetate (July 2019: 0.789 µg/L) was 0.747 µg/L. Maximum concentrations during the summer months indicate enhanced trifluoroacetate formation by photochemical degradation of volatile precursors, such as HFCs, HCFCs, and HFOs, in the troposphere. Elevated concentrations in precipitation in summer have already been observed for chlorinated acetic acids (Reimann et al. 1996).

An annual cycle of monthly trifluoroacetate concentrations was observed in both years. Almost identical trifluoroacetate median concentrations were measured in both periods (February 2019 to January 2020: 0.250 µg/L; February 2019 to January 2020: 0.244 µg/L). No trend can be deduced for the individual months either. The highest median concentration was measured in June 2019 (0.789 µg/L) and July 2018 (0.663 µg/L). It is striking that in both years, the media concentration increased sharply from March to April and decreased again in May to values below those in April.

Figure 27: Boxplots of the trifluoroacetate concentration of (volume-equivalent) monthly composite precipitation samples from February 2018 (02/18) to February 2020 (02/20). Data of the site Brocken, where the total amount of atmospherically deposited trifluoroacetate instead of the wet deposited trifluoroacetate was determined, are not included. The best-case scenario is shown. Data is grouped by time (month and year). Note that the boxplot of February 2018 (02/18) does not include data from site Stuttgart, whereas the boxplot of February 2020 (02/20) solely represents data from site Stuttgart. The y-axis is on a binary logarithmic scale. The periods February to January are highlighted in different colors.



Source: Öko-Recherche and TZW Karlsruhe

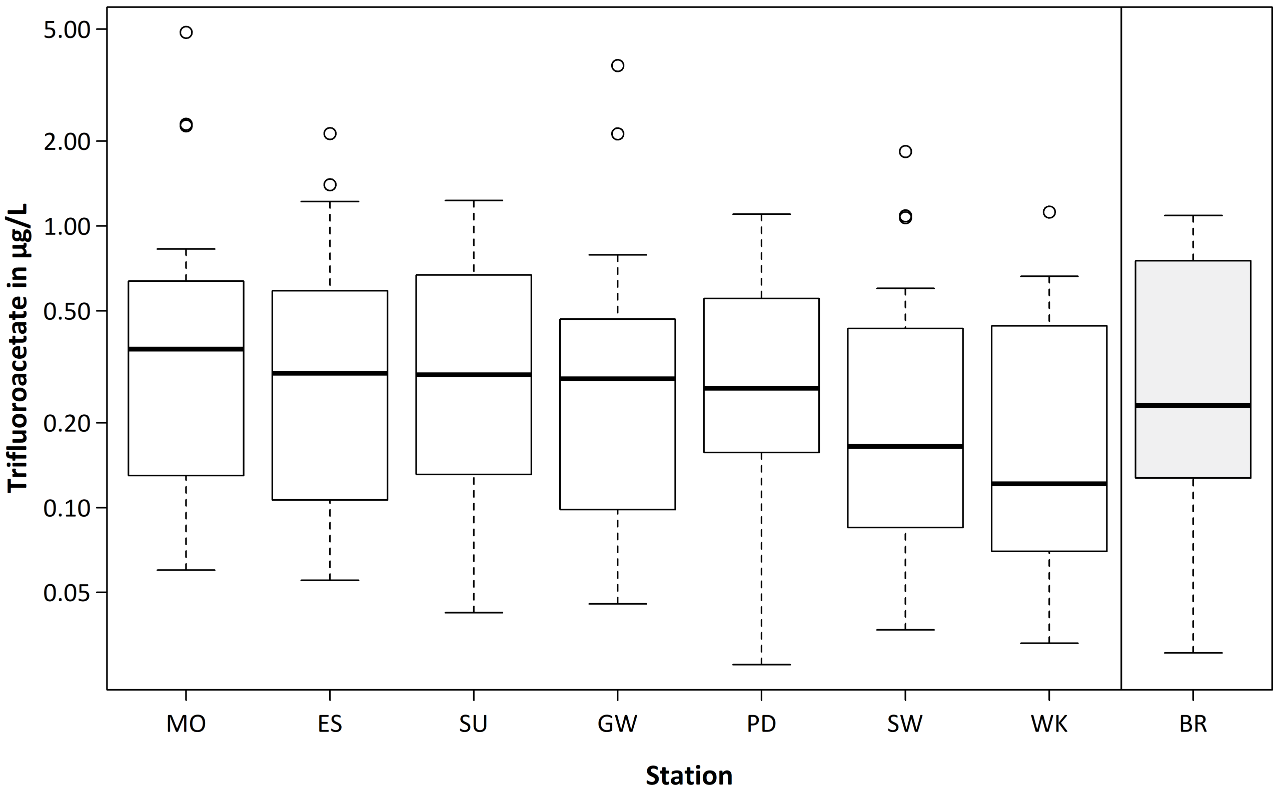
Table 31: Statistical parameters of the trifluoroacetate concentration of (volume-equivalent) monthly composite precipitation samples (MCS) over seven of the eight stations (only wet deposition) per month. The best-case scenario is shown. Data for the Brocken station are not shown as they contain the sum of wet and dry deposition. SD, standard deviation.

Month/Year	Number of MCS	Median (µg/L)	Average (µg/L)	SD (µg/L)	Minimum (µg/L)	Maximum (µg/L)
02/18	6	0.077	0.087	0.029	0.057	0.132
03/18	7	0.160	0.205	0.150	0.110	0.533
04/18	7	0.444	1.105	1.667	0.290	4.870
05/18	7	0.431	0.425	0.090	0.238	0.521
06/18	7	0.590	0.847	0.617	0.360	2.124
07/18	7	0.663	0.833	0.554	0.323	1.840
08/18	7	0.599	0.895	0.669	0.340	2.300
09/18	7	0.400	0.359	0.130	0.130	0.530
10/18	7	0.120	0.145	0.088	0.069	0.320
11/18	7	0.140	0.140	0.069	0.070	0.240
12/18	7	0.056	0.053	0.013	0.033	0.071
01/19	7	0.042	0.049	0.020	0.028	0.085
02/19	7	0.105	0.108	0.020	0.088	0.136
03/19	7	0.157	0.160	0.047	0.099	0.232
04/19	7	0.657	0.669	0.231	0.377	1.087
05/19	7	0.490	0.673	0.658	0.212	2.130
06/19	7	0.789	0.908	0.293	0.617	1.400
07/19	7	0.777	1.001	0.631	0.443	2.270
08/19	7	0.480	0.935	1.225	0.381	3.710
09/19	7	0.382	0.438	0.237	0.150	0.829
10/19	7	0.180	0.199	0.072	0.110	0.340
11/19	7	0.120	0.135	0.075	0.068	0.257
12/19	7	0.083	0.102	0.057	0.054	0.220
01/20	7	0.093	0.106	0.032	0.068	0.158
02/20	1	0.130	-	-	0.130	0.130
02/18 - 01/19	**83**	**0.250**	**0.433**	**0.655**	**0.028**	**4.870**
02/19 - 01/20	**84**	**0.244**	**0.453**	**0.553**	**0.054**	**3.710**

When grouping the trifluoroacetate concentrations of (volume-equivalent) monthly composite samples by location, the difference between the lowest (Wasserkuppe) and the highest trifluoroacetate median concentration (Munich-Oberschleißheim) was 0.243 µg/L (Figure 28 and Table 32). Compared to the data grouped by time, a much smaller variation in the interquartile ranges of the formed groups becomes apparent. This indicates that, at least, for the situation in Germany, the TFA concentration in precipitation depends more on the sampling date than on the sampling location.

In general, median concentrations of trifluoroacetate in precipitation were highest at the sites Munich, Essen, and Stuttgart. While these sites are all located in densely populated areas, the other stations are located in larger distance from urban agglomerations. However, a clear correlation between the proximity of a site to densely populated areas and its median concentrations of trifluoroacetate was not apparent. Greifswald and Potsdam had comparable concentrations of trifluoroacetate in precipitation as Munich-Oberschleißheim, Essen, and Stuttgart. Schleswig and Wasserkuppe also showed a comparable dispersion of the data, while the median concentrations of the two sites over the entire monitoring period were significantly lower than at the other sites. The site Brocken showed similar values to the other stations, although the sampling at this site also included the dry deposition of trifluoroacetate. The highest concentration of a monthly composite sample of 4.87 µg/L was measured at the station Munich-Oberschleißheim in April of 2018.

Figure 28: Boxplots of the trifluoroacetate concentration of (volume-equivalent) monthly composite precipitation samples of studied sites. Data is grouped by the sampling location (site) and sites are plotted in descending median order. Data of the site Brocken, where the total amount of atmospherically deposited trifluoroacetate instead of the wet deposited trifluoroacetate was determined, is included for comparison. The best-case scenario is shown. The y-axis is on a binary logarithmic scale. Note that the boxplot of site Stuttgart includes data from March 2018 to February 2020, whereas boxplots from other sites include data from February 2018 to January 2020.



Source: Öko-Recherche and TZW Karlsruhe

Table 32: Statistical parameters of the trifluoroacetate concentration of (volume-equivalent) monthly composite precipitation samples (MCS) of studied sites. Observation period: February 2018 to January 2020 (site Stuttgart: March 2018 to February 2020). The results of the best-case scenario are shown. Note that at site Brocken, the total amount of atmospherically deposited trifluoroacetate instead of only the wet deposited trifluoroacetate was determined. SD, standard deviation.

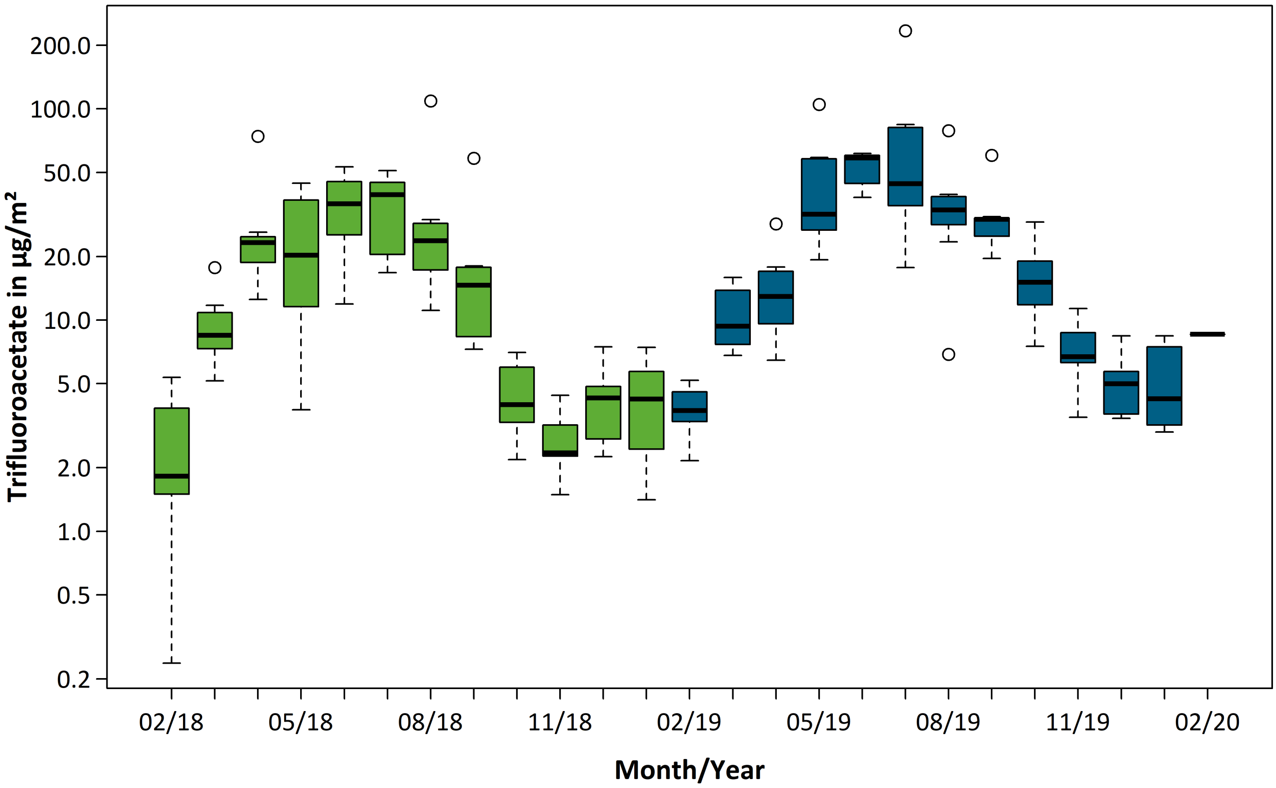
Site	Number of MCS	Median (µg/L)	Average (µg/L)	SD (µg/L)	Minimum (µg/L)	Maximum (µg/L)
Essen	24	0.300	0.483	0.523	0.055	2.130
Greifswald	24	0.286	0.502	0.805	0.046	3.710
Munich	24	0.365	0.688	1.072	0.060	4.870
Potsdam	24	0.265	0.346	0.251	0.028	1.100
Stuttgart	24	0.296	0.411	0.332	0.042	1.230
Schleswig	24	0.165	0.358	0.432	0.037	1.840
Wasserkuppe	24	0.122	0.300	0.316	0.033	1.120
Brocken	*24*	*0.230*	*0.413*	*0.359*	*0.030*	*1.090*

Deposition fluxes of trifluoroacetate in µg/m²

In the following, the mass fluxes of trifluoroacetate (i.e. mass per area, the product of trifluoroacetate concentration (µg/L) and corresponding precipitation sum (mm or L/m^2) per site and month/year) of the (volume-equivalent) monthly composite samples (n = 168) are shown. For this purpose, the fluxes were grouped again by the attributes time (month) (Figure 29) and location (Figure 30).

When grouping the flux data by the sampling month (derived from the monthly averages of trifluoroacetate concentration; Figure 29 and Table 33), an annual cycle, with maximum fluxes in summer and minimum fluxes in winter, becomes again apparent. In the months February 2018, October 2018 to February 2019 as well as December 2018 and January 2020, the median trifluoroacetate concentrations were below 5 µg/m^2. In the summer months (June to July 2018, and May to September 2019), however, the trifluoroacetate inputs all exceeded 25 µg/m^2 per month. The difference between the lowest (February 2018: 1.823 µg/m^2) and the highest median trifluoroacetate flux (June 2019: 58.563 µg/m^2) was 56.740 µg/m^2. In general, an increase in trifluoroacetate flux can be observed when comparing the periods 2018/2019 and 2019/2020. While the median was 8.464 µg/m^2 in the period from February 2018 to January 2019, it was 14.863 µg/m^2 from February to December 2019. However, if one considers the corresponding concentrations of trifluoroacetate in precipitation during these periods (see above), which were almost identical, it becomes clear that the amount of precipitation was the main reason for the higher flux during the second period. With the exception of the Munich-Oberschleißheim site, precipitation was consistently higher at all stations in the period 2019/20 than in the period 2018/19 (see also Figure 31).

Figure 29: Boxplots of the trifluoroacetate wet-deposition flux of (volume-equivalent) monthly composite precipitation samples from February 2018 (02/18) to February 2020 (02/20). Data of the site Brocken, where the total amount of atmospherically deposited trifluoroacetate instead of the wet deposited trifluoroacetate was determined, are not included. The best-case scenario is shown. Data is grouped by time (month and year). Note that the boxplot of February 2018 (02/18) does not include data from site Stuttgart, whereas the boxplot of February 2020 (02/20) solely represents data from site Stuttgart. The y-axis is on a binary logarithmic scale. The periods February to January are highlighted in different colors.



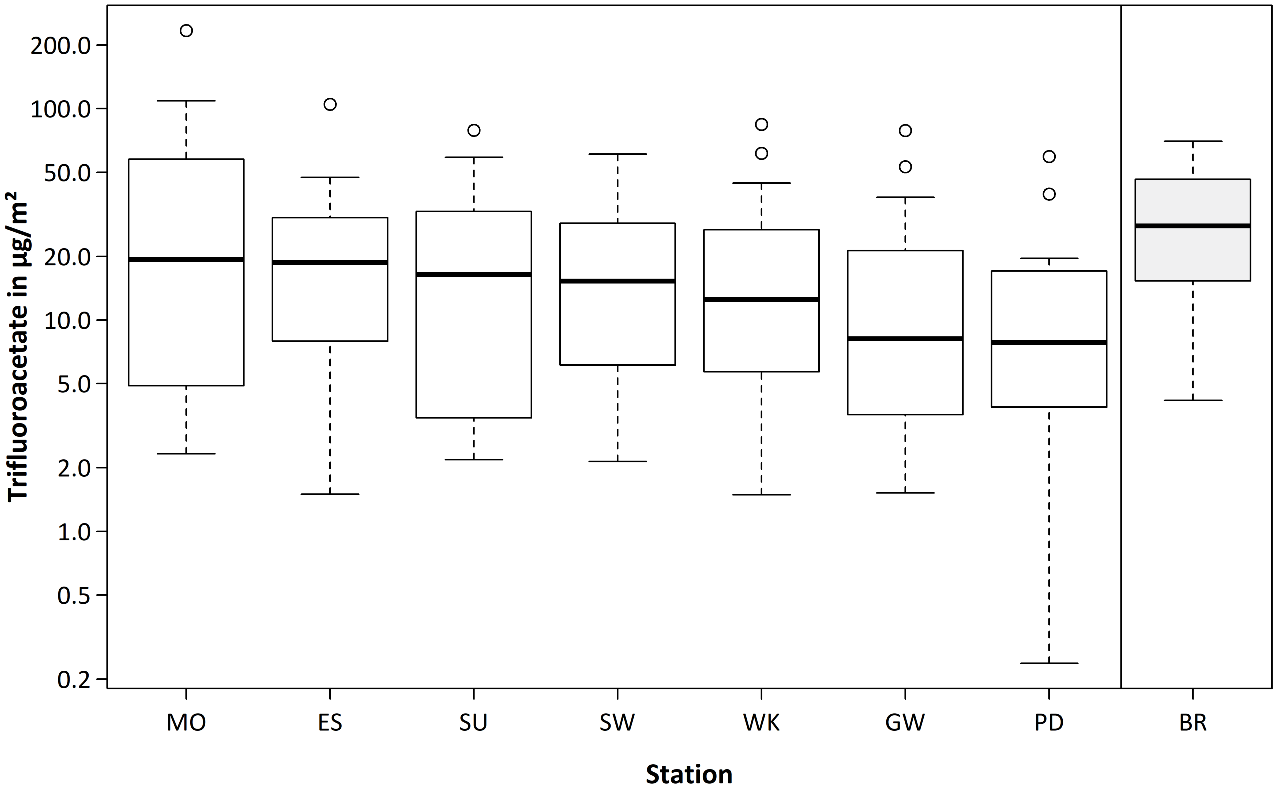
Source: Öko-Recherche and TZW Karlsruhe

Table 33: Statistical parameters of the trifluoroacetate wet-deposition flus of (volume-equivalent) monthly composite precipitation samples (MCS) from February 2018 (02/18) to February 2020 (02/20). Data of the site Brocken, where the total amount of atmospherically deposited trifluoroacetate instead of the wet deposited trifluoroacetate was determined, is not included. The best-case scenario is shown. SD, standard deviation.

Month/Year	Number of MCS	Median (µg/m²)	Average (µg/m²)	SD (µg/m²)	Minimum (µg/m²)	Maximum (µg/m²)
02/18	6	1.823	2.427	1.848	0.238	5.348
03/18	7	8.464	9.671	4.136	5.161	17.734
04/18	7	23.229	28.114	20.724	12.503	74.024
05/18	7	20.252	23.668	16.346	3.760	44.462
06/18	7	35.453	34.511	15.374	11.918	53.103
07/18	7	39.183	33.931	14.326	16.764	50.973
08/18	7	23.715	33.650	33.854	11.110	108.790
09/18	7	14.625	18.938	17.973	7.280	58.391
10/18	7	3.978	4.528	1.799	2.184	7.020
11/18	7	2.352	2.737	0.956	1.491	4.408
12/18	7	4.277	4.166	1.813	2.254	7.476
01/19	7	4.229	4.199	2.215	1.410	7.423
02/19	7	3.728	3.834	1.038	2.158	5.184
03/19	7	9.357	10.730	3.712	6.803	15.904
04/19	7	12.930	14.442	7.371	6.452	28.529
05/19	7	31.673	46.416	30.080	19.282	104.796
06/19	7	58.563	52.422	9.984	38.039	61.488
07/19	7	44.238	75.54	74.047	17.733	234.037
08/19	7	33.185	36.013	21.812	6.878	78.652
09/19	7	29.942	31.485	13.468	19.584	60.268
10/19	7	15.074	16.189	7.307	7.520	29.093
11/19	7	6.708	7.363	2.611	3.469	11.340
12/19	7	4.994	5.063	1.793	3.429	8.418
01/20	7	4.237	5.272	2.405	2.955	8.407
02/20	1	8.56	-	-	-	-
02/18 - 01/19	**83**	**8.464**	**16.884**	**18.998**	**0.238**	**108.790**
02/19 - 02/20	**84**	**14.863**	**25.463**	**31.914**	**2.158**	**234.037**

When grouping the trifluoroacetate fluxes data by the sampling location, the difference between the lowest (Potsdam) and the highest median wet-deposition flux of trifluoroacetate was 11.519 µg/m^2 (Munich-Oberschleissheim) (Figure 30 and Table 34). Similar to the trifluoroacetate concentration data, there was less variation in the median fluxes when grouping the data by location instead of time. The sites Munich-Oberschleißheim, Essen, and Stuttgart showed the highest median wet-deposition fluxes of trifluoroacetate of all studied sites.

Figure 30: Boxplots of the trifluoroacetate wet-deposition flux of (volume-equivalent) monthly composite precipitation samples of studied sites. Data is grouped by the sampling location (site) and sites are plotted in descending median order. Data of the site Brocken, where the total amount of atmospherically deposited trifluoroacetate instead of the wet deposited trifluoroacetate was determined, is included for comparison. The best-case scenario is shown. The y-axis is on a binary logarithmic scale. Note that the boxplot of site Stuttgart includes data from March 2018 to February 2020, whereas boxplots from other sites include data from February 2018 to January 2020.



Source: Öko-Recherche and TZW Karlsruhe

Table 34: Statistical parameters of the trifluoroacetate wet-deposition flux of (volume-equivalent) monthly composite precipitation samples (MCS) of studied sites. Observation period: February 2018 to January 2020 (site Stuttgart: March 2018 to February 2020). The results of the best-case scenario are shown. Note that at site Brocken, the total amount of atmospherically deposited trifluoroacetate instead of only the wet deposited trifluoroacetate was determined. SD, standard deviation.

Site	Number of MCS	Median (µg/m²)	Mean (µg/m²)	SD (µg/m²)	Minimum (µg/m²)	Maximum (µg/m²)
Essen	24	18.66	23.67	24.21	1.50	104.80
Greifswald	24	8.14	13.51	13.86	1.52	53.10
Munich	24	29.51	43.43	56.71	2.33	234.04
Potsdam	24	8.29	12.87	15.03	0.24	59.29
Stuttgart	24	16.44	20.85	20.79	2.18	78.89
Schleswig	24	15.26	20.20	17.45	2.14	60.99
Wasserkuppe	24	12.49	21.07	22.98	1.49	84.34
Brocken	*24*	*27.84*	*31.08*	*19.58*	*4.53*	*64.23*

Comparison of the periods 2018/2019 and 2019/2020

When comparing the median trifluoroacetate concentrations of the different sites for the periods 2018/19 and 2019/20, only minor differences become apparent (Figure 31). At the station level, no systematic differences were apparent. For example, the median trifluoroacetate concentration in 2018/19 was higher at four stations compared to 2019/20, while it was lower at the remaining four stations. For the deposition flux of trifluoroacetate a different picture emerges. In 2019/20, the median deposition flux was 14.86 µg/m^2, while in 2018/19 it was only 8.29 µg/m^2. These dynamics can also be observed at the station level, with the exception of the Munich-Oberschleißheim (MO) site. Here, the median flux of trifluoroacetate in 2019/20 was 15.42 µg/m^2, which is significantly lower than the flux in 2018/19 of 29.56 µg/m^2. Since the trifluoroacetate flux is the product of the trifluoroacetate concentration and the volume of the respective precipitation sample, and since all precipitation events during the studied period were recorded, the precipitation total of the respective periods can be used to explain differences in the fluxes. It has to be noted that 2018 was a year with exceptionally low precipitation in Germany. The average annual precipitation total in Germany for the year 2018 was 586 mm, which is significantly lower than the 2019 average of 735 mm and the long-term average of 771 mm for the period from 1881 to 2019[167]. Less precipitation in 2018/19 in comparison to 2019/20 can be observed at almost all of the studied sites. The only exception is site Munich-Oberschleißheim (MO).

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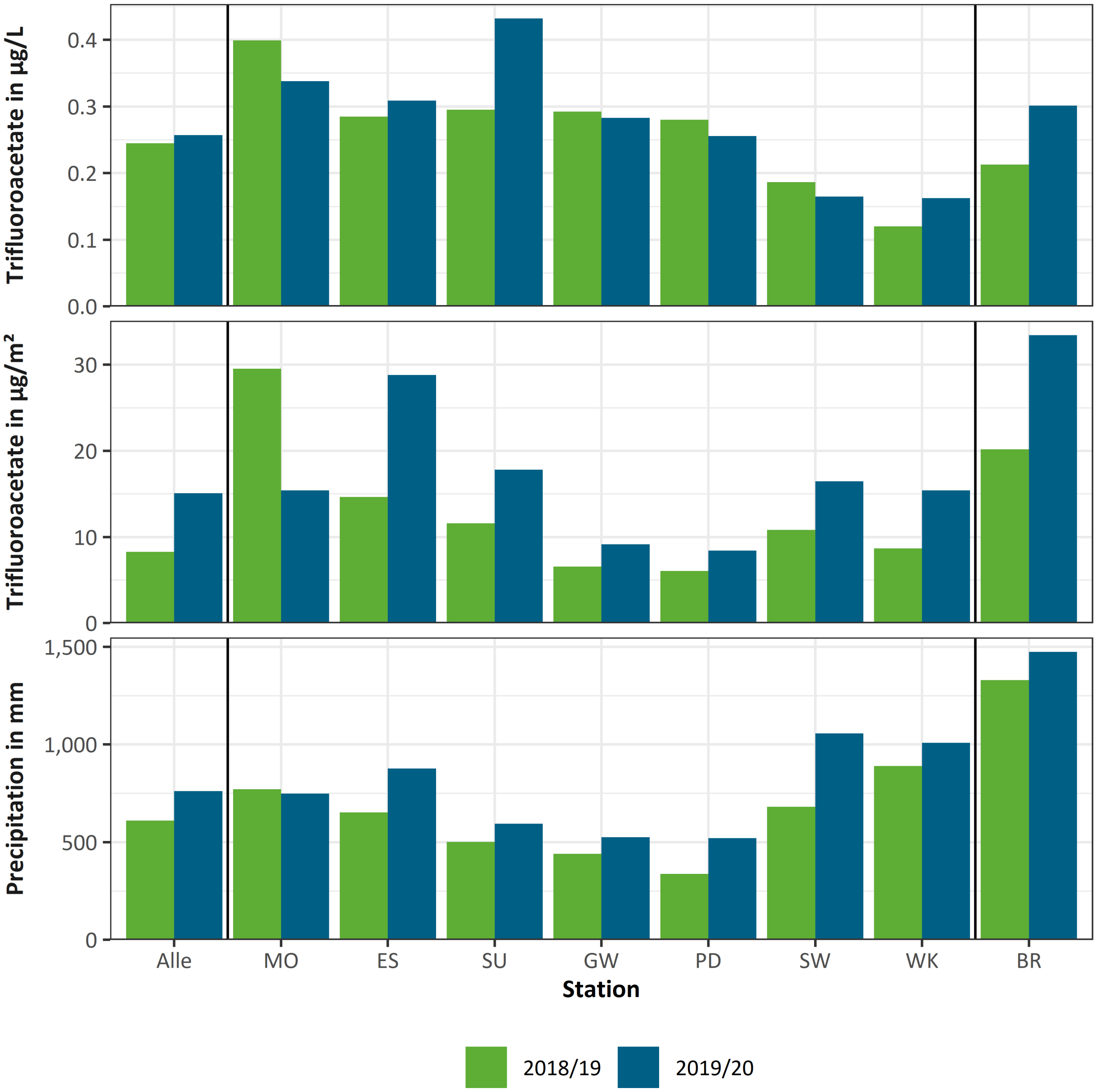
[167] Publicly accessible data of the DWD: https://opendata.dwd.de/climate_environment/CDC/regional_averages_DE/annual/precipitation/regional_averages_rr_year.txt (accessed: 24.03.2020)

Figure 31: Median of the trifluoroacetate concentration (in µg/L) and the trifluoroacetate flux (in µg/m²) of the (volume-equivalent) monthly composite samples, as well as the precipitation total (in mm or L/m²) at the eight investigated stations for the periods February 2018 to January 2019 (2028/19) and February 2019 to January 2020 (2019/20). The best-case scenario is shown. For the Stuttgart site, the periods from March to February of the following year are depicted. The site Brocken is not included in the category "all", since the total amount of atmospherically deposited trifluoroacetate instead of only the wet-deposited trifluoroacetate was determined there.



Source: Öko-Recherche and TZW Karlsruhe

4.5.1.2 Results from the analysis of individual precipitation samples

A total of 1,187 individual samples collected during the first year of observation (February 2018 to January 2019; site Stuttgart: March 2018 to February 2019) were analyzed.

Based on the analysis of the individual samples, the analytical results derived from the analysis of the (volume-equivalent) monthly composite samples, could be validated. As already mentioned, both approaches lead to very similar results (see Figure A 6 to Figure A 9 in Annex A.10.3). This proves that the (volume-equivalent) monthly composite samples had been properly prepared in the laboratory from individual samples.

In approx. 10 % of the cases, 24 h composite samples could not be obtained due to logistical reasons, and multiday composite samples (n = 103), encompassing time periods between 2 and 15 days, were collected instead.

Due to the large differences in the precipitation totals of the respective sites, the precipitation-weighted average trifluoroacetate concentration (C_w; µg/L) is also given in Table 35. This allows for a better comparison of trifluoroacetate concentration levels between different sites and studies. Precipitation-weighted average concentrations were calculated as follows:

$$C_w = \frac{\sum C_{i,j} P_{i,j}}{\sum P_{i,j}}$$

where $C_{i,j}$ and $P_{i,j}$ are the precipitation concentration of trifluoroacetate (in µg/L) and the precipitation amount (in mm), respectively, of sample i and group variable j (j representing either the sampling month or site).

In the case of precipitation-weighted average trifluoroacetate concentrations and fluxes, data points with concentrations below the DL had to be substituted by a fixed value. In the present study, the censored data points were substituted by the DL (0.025 µg/L), thus representing a conservative scenario.

For the sites the Essen, Greifswald, Munich-Oberschleißheim, Potsdam, Stuttgart, Schleswig, and Wasserkuppe (n = 976) it can be assumed that the collected precipitation samples were not substantially influenced by dry-deposited trifluoroacetate and were therefore representative for the amount of wet-deposited trifluoroacetate. This subset of samples is hereafter referred to as “wet deposition (WD) samples”. Samples from the site Brocken (n = 211) contained dry- and wet-deposited trifluoroacetate and therefore represent the total amount of atmospherically deposited trifluoroacetate. As such, the data from the site Brocken is displayed and discussed separately from the WD samples.

Of the 976 analyzed WD samples, 7 % showed a trifluoroacetate concentration below the DL. The highest individual trifluoroacetate concentration observed was 38 µg/L (site Munich-Oberschleißheim; Table 35). The trifluoroacetate concentrations of studied WD samples were mostly in the two- and three-digit ng/L-range.

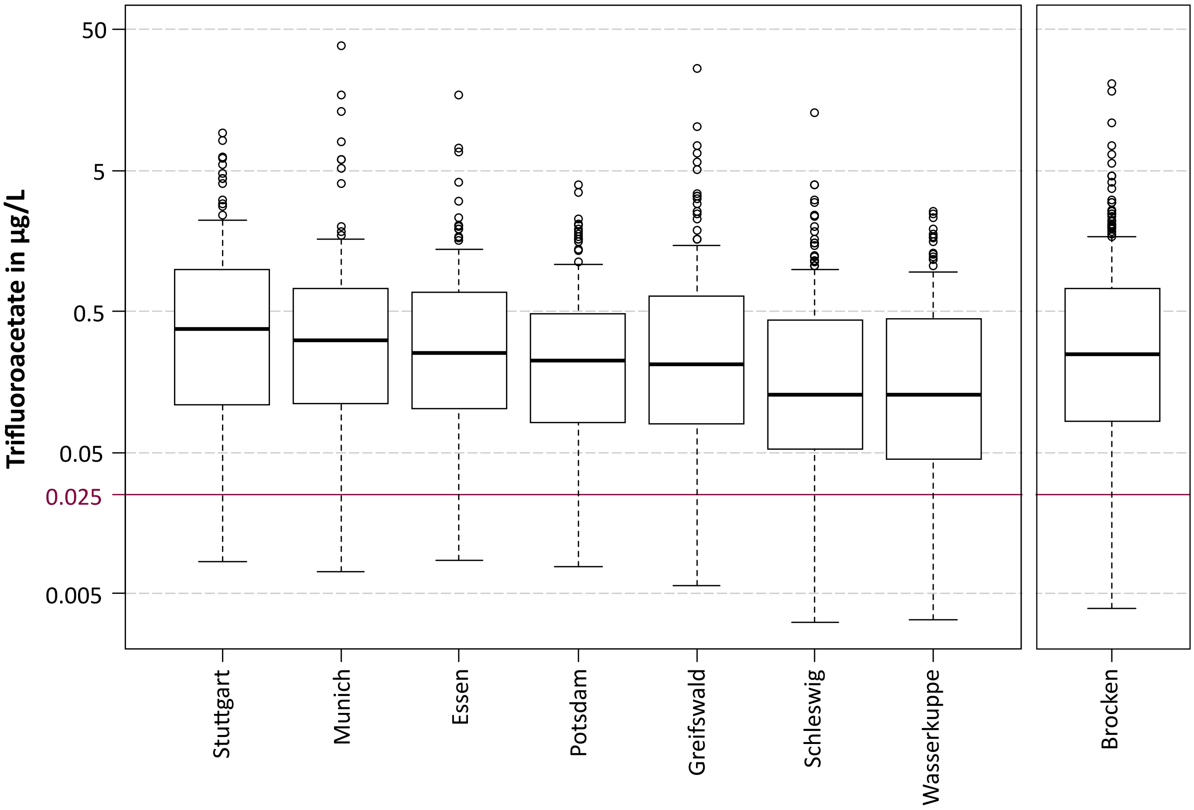
Table 35: Number of samples, total precipitation and statistical parameters of the trifluoroacetate concentration of individual precipitation samples. Detection limit (DL): 0.025 µg/L. The best-case scenario is shown. Observation period: February 2018 to January 2019 (for site Stuttgart: Mach 2018 to February 2019). ROS, regression on order statistics. Concentrations of trifluoroacetate are reported with three significant figures.

Site	No. of samples	Samples <DL	Total precipitation.	Trifluoroacetate concentration			
				Maximum	Median	ROS-estimated average	Precip.-weighted average
		%	mm	µg/L	µg/L	µg/L	µg/L
Essen	149	3.4	653	17.2	0.255	0.692	0.346
Greifswald	147	10.2	440	26.3	0.210	0.883	0.356
Munich	111	3.6	772	38.0	0.310	1.30	0.520
Potsdam	123	4.9	337	3.94	0.227	0.447	0.271
Stuttgart	113	1.8	502	9.16	0.377	1.02	0.393
Schleswig	173	8.1	681	12.8	0.128	0.471	0.284
Wasserkuppe	160	13.8	890	2.58	0.128	0.334	0.186
All	**976**	**7.0**	**-**	**38.0**	**0.210**	**0.703**	**0.335**
Brocken	*211*	*4.7*	*1,130*	*20.6*	*0.248*	*0.895*	*0.256*

Median concentrations at studied sites ranged from 0.128 µg/L to 0.377 µg/L. The median concentration at the Stuttgart site was about three times higher than at sites Schleswig and Wasserkuppe. The median of concentration of all individual WD samples was 0.210 µg/L. The ROS-estimated average at the sites differed more strongly from each other and ranged from 0.334 µg/L (Wasserkuppe) to 1.30 µg/L (Munich-Oberschleißheim) (Table 35). The ROS-estimated average trifluoroacetate concentration of all WD samples was 0.703 µg/L. The precipitation-weighted average is a more reliable measure when comparing trifluoroacetate concentrations from sites with different precipitation totals. The precipitation-weighted average value at the studied WD sites ranged from 0.186 µg/L (Wasserkuppe) to 0.520 µg/L (Munich-Oberschleißheim). The precipitation-weighted average trifluoroacetate concentration of all individual WD samples was 0.335 µg/L (best-case scenario).

Figure 32 depicts censored boxplots of the trifluoroacetate concentration grouped by the sampling location and plotted in descending median order. Data of the site Brocken, where the total amount of atmospherically deposited trifluoroacetate instead of the wet deposited trifluoroacetate was determined, is included for comparison. All boxplots are similarly shaped, demonstrating a similar distribution of measured trifluoroacetate concentration in the precipitation at the studied sites.

Figure 32: Censored boxplots of trifluoroacetate concentrations present in individual precipitation samples grouped by the sampling site. The best-case scenario is shown. Note that the boxplot of site Stuttgart includes data from March 2018 to February 2019, whereas boxplots from other sites include data from February 2018 to January 2019. Sites are plotted in descending median order. The horizontal red line depicts the detection limit. The y-axis is scaled logarithmically.



Source: TZW Karlsruhe

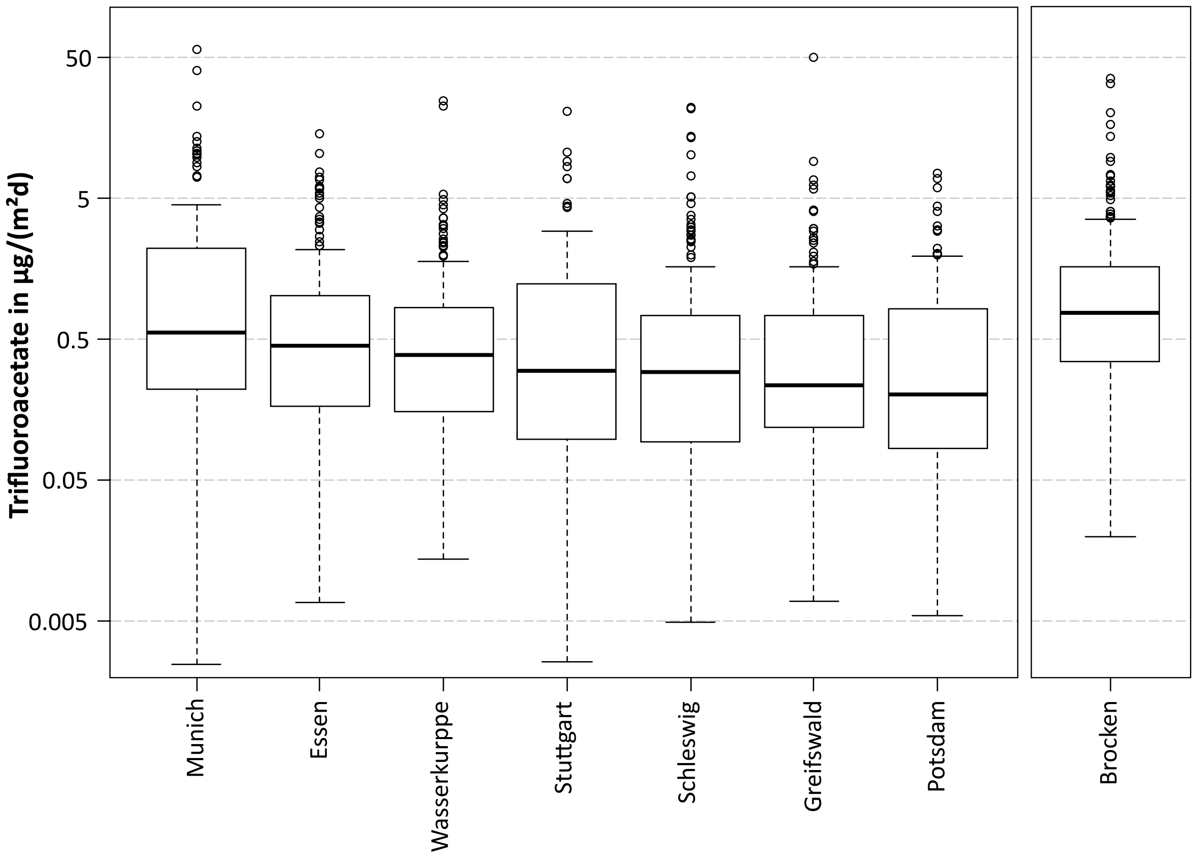
Due to the different sampling duration covered by the collected individual samples (up to 15 days; see explanation above), the trifluoroacetate fluxes were normalized to the duration of a single day by dividing the trifluoroacetate flux of each sample by the sampling duration of the respective sample (in days).

The annual wet deposition trifluoroacetate flux at a sampling site was obtained by taking the sum of the wet deposition trifluoroacetate fluxes of all individual samples from the respective site (observation period: February 2018 to January 2019; for Stuttgart: March 2018 to February 2019). For the site Brocken, total deposition fluxes were determined instead of wet deposition fluxes. The results of the best-case scenario for the daily and yearly fluxes of trifluoroacetate are shown in Table 36 and Figure 33. The results of the worst-case scenario are depicted in Figure A 7 and Table A 9 in Annex A.10.3

Table 36: Statistical parameters of the trifluoroacetate wet-deposition flux of individual precipitation samples of studied sites. Observation period: February 2018 to January 2020 (site Stuttgart: March 2018 to February 2020). The results of the best-case scenario are shown. Note that at site Brocken, the total amount of atmospherically deposited trifluoroacetate instead of only the wet deposited trifluoroacetate was determined. Fluxes of trifluoroacetate are reported with three significant figures.

Site	Maximum µg/(m²d)	Median µg/(m²d)	Average µg/(m²d)	Annual total µg//(m²a)
Essen	14.4	0.452	1.17	226
Greifswald	50.0	0.237	1.07	157
Munich	57.0	0.554	2.96	401
Potsdam	7.46	0.205	0.743	91.4
Stuttgart	20.7	0.302	1.24	197
Schleswig	22.0	0.290	1.12	193
Wasserkuppe	24.3	0.387	1.04	166
All	**57.0**	**0.357**	**1.28**	**-**
Brocken	*35.3*	*0.774*	*1.90*	*340*

Figure 33: Boxplots of trifluoroacetate fluxes of individual precipitation samples grouped by the sampling site. The best-case scenario is shown. Note that the boxplot of site Stuttgart includes data from March 2018 to February 2019, whereas boxplots from other sites include data from February 2018 to January 2019. Sites are plotted in descending median order. The y-axis is scaled logarithmically.



Source: TZW Karlsruhe

The trifluoroacetate median wet-deposition fluxes ranged from 0.205 µg/(m^{2}d) (Potsdam) to 0.554 µg/(m^{2}d) (Munich-Oberschleißheim). The median wet-deposition flux of all WD samples was 0.357 µg/(m^{2}d). The highest wet-deposition flux for a single sample in the observation period was 57.0 µg/(m^{2}d) (Munich-Oberschleißheim). Only at the Potsdam site the maximum measured trifluoroacetate wet-deposition flux was below 10 µg/(m^{2}d). The annual wet deposition of trifluoroacetate at the sites ranged from 91.4 µg/m^2 per year to 401 µg/m^2 per year. Thus, the amount of trifluoroacetate deposited by wet deposition at the Munich-Oberschleißheim site was more than 4 times higher than at the Potsdam site (Table 36).

An average wet deposition of trifluoroacetate for Germany for the sampling period from February 2018 to January 2019 of 190 µg/m^2 or approximately 68 t was estimated by multiplying the precipitation-weighted average concentration of all studied WD samples (0.335 µg/L, Table 36) with the average precipitation total for Germany for this period of 566 mm (DWD 2020).

It should be noted that 2018 was a year with exceptionally low precipitation in Germany. Based on the German multiyear average of 819 mm (climatological standard normal 1981 to 2010), the annual wet deposition flux of trifluoroacetate in Germany is 274 µg/m2 or approximately 98 t.

4.5.2 Results from the analysis of soil and plant samples

The results from the soil analysis are listed in Table 37. The average concentration of trifluoroacetate in soil at the eight sampling sites was 0.97 µg/kg dry weight (DW) or 0.77 µg/kg fresh weight (FW) for the sampling depth from 0 to 30 cm, and 0.49 µg/kg DW or 0.38 µg/kg FW for the sampling depth from 30 to 60 cm. The determined trifluoroacetate contents (FW and DW) are in the same order of magnitude as already detected in topsoils at other locations reported in the literature (see Table 38).

At all sites, higher trifluoroacetate contents were detected in the upper sampling depth. A normalization of the trifluoroacetate results based on the FW did not lead to a significant convergence of the samples from the two sampling depths, i.e. the differences are not due to possibly different water contents in the sampling depths. This changes after normalization to the TOC content of the soil samples, which led to a clear convergence of the results. This indicates that the trifluoroacetate content is associated to the TOC. A possible explanation for this observation could be retention/sorption of atmospherically deposited trifluoroacetate by organic material. The potential relevance of this process could be shown by Richey et al (1997) in batch experiments. However, it cannot be ruled out that the trifluoroacetate left in the soil originated (at least partially) from not yet completely decomposed plant material (i.e., this portion was initially actively accumulated by the living plant and is released to the surrounding medium when the plant is decomposing) and was therefore not retained by sorption. Since only vegetated areas were sampled, a certain proportion of fine roots in the sample is also likely. After standardizing the trifluoroacetate content to the TOC, the higher trifluoroacetate content was detected in the upper depth range for the majority of soils (six out of nine soils). Assuming that the type of TOC is identical at these depths, this could be an indication of an accumulation of trifluoroacetate due to evaporation effects in the upper soil.

Table 37: Trifluoroacetate concentration in soils at studied sites. TOC, total organic carbon of the respective soil sample. DW, dry weight. FW, fresh weight.

Site	Sampling date	Depth range	TOC in %	Trifluoroacetate µg/kg DW	µg/kg FW	µg/kg TOC
Brocken	14.10.2019	0-30 cm	11	0.97	0.77	8.8
		30-60 cm	5.2	0.32	0.24	6.2
Essen	17.10.2019	0-30 cm	1.9	0.7	0.57	37
		30-60 cm	1.1	0.29	0.25	26
Greifswald	15.10.2019	0-30 cm	1.7	0.42	0.35	25
		30-60 cm	1.5	0.31	0.27	21
Munich-Oberschleißheim	16.07.2019	0-30 cm	3.2	0.8	0.69	25
		30-60 cm	1.0	0.2	0.2	20
	24.10.2019	0-30 cm	2.9	0.59	0.49	20
		30-60 cm	0.5	0.31	0.28	62
Potsdam	15.10.2019	0-30 cm	1.3	0.43	0.41	33
		30-60 cm	0.3	<0.2	<0.2	33[a]
Stuttgart	17.07.2019	0-30 cm	1.5	0.64	0.57	43
		30-60 cm	0.5	0.25	0.23	50
Schleswig	16.10.2019	0-30 cm	1.7	1.8	1.4	106
		30-60 cm	0.9	0.51	0.42	57
Wasserkuppe	14.10.2019	0-30 cm	5.5	2.4	1.7	44
		30-60 cm	5.3	2	1.3	38

[a] DL/2 was used for calculations

Table 38: Trifluoroacetate concentration in soils at different locations and times. DW, dry weight. FW, fresh weight. -, no information available.

Sampling site	Sampling time	Sampling depth in cm	Type	Trifluoroacetate in µg/kg	Reference
Germany	2019	0-30	DW	0.42-2.4	This study
			FW	0.35-1.7	
		30-60	DW	<0.2-2	
			FW	<0.2-1.3	
Rastatt/Baden-Baden and Mannheim (Germany)	2017	0-30	DW	0.3-1.1	Sacher et al. (2019)
Great Britain	December 1999	0-10	DW	0.85-7	Scott et al. (2005)
Great Britain (historic samples without replicates)	1956	-	DW	0.35	Scott et al. (2005)
	1944			<0.1	
	1881			0.55	
	1865			0.51	
East-Canada	July 2000	0-10	DW	<0.1-3.3	Scott et al. (2005)
Northern America	2000	-	FW	0.49-2.76	Cahill et al. (1999)
China	Post 2012[a]	-	DW	0.06-2.08	Xie et al. (2019)

[a] Estimated date, since not specified in the study.

The results of the analysis of plant material are listed in Table 39. The sampling location Munich-Oberschleißheim was specifically selected for sampling because of the comparatively high trifluoroacetate concentrations in precipitation. However, the determined concentration range is similar to already published data on trifluoroacetate concentrations of plant material (Cahill et al. 1999, EURL-SRM 2017).

Table 39: Concentrations of trifluoroacetate in plants (sampling site: Munich-Oberschleißheim). DW, dry weight. FW, fresh weight. n, number of replicates.

Plant species	Trifluoroacetate in µg/kg DW		Trifluoroacetate in µg/kg FW	
Crepis capillaris	92	(n=1)	23	(n=1)
Geranium spec.	85	(n=1)	23	(n=1)
Prunella vulgaris	55	(n=1)	16	(n=1)
Achillea millefolium	47 ± 1.4	(n=3)	12 ± 0.37	(n=3)
Epilobium parviflorum	35 ± 1.4	(n=3)	7.3 ± 0.31	(n=3)
Erigeron annuus	120 ± 8.7	(n=3)	39 ± 2.9	(n=3)

The average trifluoroacetate content in precipitation from March to June 2019 - i.e. during the vegetation-relevant months before the sampling of plant material - was 0.45 µg/L. Under the assumption that the soil contained no trifluoroacetate at the beginning of the vegetation period, enrichment factors of 16 to 87 (related to the trifluoroacetate concentration in the precipitation) can be derived from the FW-normalized trifluoroacetate concentrations of the sampled plants. The assumption of a trifluoroacetate-free soil at the beginning of the vegetation period is only an auxiliary number for the calculation of enrichment factors. It is likely that the soil contained trifluoroacetate even during the dormant period.

The analysis of soil and plant material showed that trifluoroacetate is not only detectable in anthropogenic water cycles (Nödler et al. 2019), but can also ubiquitously be found in soils and plants in Germany.

5 Overall evaluation

5.1 Objective

In this concluding chapter the results of the previous chapters, especially the projections of demand and emissions of halogenated refrigerants and blowing agents and the measuring program for the determination of the concentration of trifluoroacetate in rainwater, as well as deposition into the environment, are summarized and discussed. Based on the results obtained so far, the proportion of trifluoroacetic acid (TFA) deposition[168] that can be explained by the emissions of halogenated refrigerants and blowing agents as well as the total TFA input in Germany and Europe (EU-28+) is balanced using atmospheric models and projected for the future. The results of this study are compared with the relevant technical literature to put them into a more general context. The implications of the use of halogenated substitutes with a low global warming potential with respect to the environmental impact of TFA are discussed. Open questions and information gaps are pointed out.

5.2 Estimation of the contribution of atmospheric degradation of HCFCs, HFCs and u-HFC-1234yf to the observed deposition of trifluoroacetic acid (TFA)

In this chapter the contribution of the atmospheric degradation of u-HFC-1234yf and important HCFCs and HFCs to the TFA input observed in Germany is estimated by model calculations. For this purpose, two different approaches were used for the two substances u-HFC-1234yf and HFC-134a, because they have different atmospheric lifetimes. For the short-lived u-HFC-1234yf the contribution was determined using atmospheric transport and chemistry simulation results of the FLEXPART model (Henne et al. 2012). The contributions of the more long-lived HFC-134a were determined using a simple global box model of the troposphere. Both methods are based on continuous concentration measurements at the AGAGE ("Advanced Global Atmospheric Gases Experiment") stations Jungfraujoch (Switzerland) and Mace Head (Ireland) (Prinn et al. 2018).

Both estimates are based on various assumptions, which are discussed below. A further model calculation of a chemical transport model was beyond the possibilities of the present project, but should be aimed for in the future.

5.2.1 Methodology

5.2.1.1 TFA rainwater concentrations from the decomposition of u-HFC-1234yf

In Henne et al. (2012), a spatially highly resolved transport and chemistry model was used to calculate the atmospheric degradation of u-HFC-1234yf and the deposition of TFA, using atmospheric data for the year 2010. The model assumes Europe-wide (EU-28+) emissions of u-HFC-1234yf of 19,000 tons per year, if the refrigerant HFC-134a is completely replaced by u-HFC-1234yf in car air conditioning systems. With this assumption a maximum scenario for the possible TFA input in Europe (EU-28+) was calculated. The simulation results showed the spatial distribution of the atmospheric concentrations of u-HFC-1234yf and TFA, the deposition of TFA (wet and dry deposition separately) and the TFA rainwater concentrations. All results were stored as daily mean values or sums on a regular 3D grid.

In this current project, based on these explicit simulation results of Henne et al. (2012), realistic TFA deposition rates and TFA rainwater concentrations were obtained for the investigation period 2018 without creating new model calculations. For this purpose, two steps were necessary: First, an adjustment of the u-HFC-1234yf emissions to values that are realistic for the new investigation period of

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[168] In this chapter, no distinction is made between trifluoroacetic acid (TFA) and trifluoroacetate, as both substances differ only marginally in their molar masses (<1 %) and the accuracy of the atmosphere models used in the following is much lower in comparison.

2018. Secondly, the interpolation of the simulation results for a whole year at the sites for which rainwater analyses were carried out in this project (see Chapter 4). Because the model time series calculated in Henne et al. (2012) are based on the meteorology for the year 2010 and not on that for the investigation year 2018, the time series cannot be compared directly on a day-to-day basis. However, the frequency distributions, mean and median values can be used for a comparison. When interpreting the results, the fact that the summer of 2018 was particularly dry in Central Europe must be taken into account.

For the first step (emissions adjustment) the u-HFC-1234yf concentration simulations were compared with continuous concentration measurements at the AGAGE stations Jungfraujoch (JFJ), Mace Head (MHD) and the Empa station Dübendorf (DUE) (Vollmer et al. 2015), as well as the Taunus Observatory on the Kleiner Feldberg of the Goethe University Frankfurt am Main (TNS). The u-HFC-1234yf measurements were calibrated against the METAS-2017 scale[169]. The lower detection limit of u-HFC-1234yf was in the ppq range[170]. Measured values below this threshold were set to half the detection limit. The measurements of the station DUE are shown for completeness. This station is located in an urban environment with high emissions of saturated and unsaturated HFCs and HCFCs, which cannot be sufficiently reproduced by the transport model used.

Figure 34 shows the measured and simulated frequency distributions of u-HFC-1234yf at the four sites JFJ, MHD, DUE and TNS based on daily averages. For the measurements, only data for the year 2018 were used (for station TNS only from May 2018 on). The values of the original simulations from 2012 have already been scaled by a factor of 0.068 for the simplified representation (see below for the factor). Figure 35 also shows the monthly mean values and their standard deviations. For the less urban and relatively remote locations JFJ and MHD, the agreement of the scaled simulations with the observations is very satisfactory both in the frequency distribution and in the monthly means. In the case of MHD, there is even a significant (95 % confidence interval) positive correlation between the monthly means of the scaled simulations and the observations (correlation coefficient r = 0.43). As expected, the simulations in DUE strongly underestimate the observed values of u-HFC-1234yf concentrations.

The mean atmospheric concentrations of u-HFC-1234yf are mainly influenced by the emissions of this substance into the atmosphere. A direct linear relationship between concentration and emission of u-HFC-1234yf can be assumed (Henne et al. 2012), since u-HFC-1234yf is not formed in the atmosphere from other substances and, secondly, only a 1st order degradation process[171] takes place. As long as only low concentrations of u-HFC-1234yf are present in the atmosphere, the concentration of the main reaction partner OH will not change significantly. That means, with the factor between observed and simulated concentrations of u-HFC-1234yf, the emissions of u-HFC-1234yf and also the deposition rates of TFA can be directly deduced.

A quantitative comparison between observed and simulated concentrations of u-HFC-1234yf for JFJ, MHD and TNS in fully equipped cars results in a scaling factor between the two annual averages in the range of 0.060 to 0.079 (mean 0.068 ± 0.033). Compared to the maximum scenario of Henne et al. (2012), u-HFC-1234yf emissions of approx. 1,300 ± 600 tons (95 % confidence interval), i.e. approx. 1,300 tons for Europe in 2018 are derived from this. These are lower emissions than those determined for the same year in Chapter 3.4 using the AnaFgas model (approx. 3,000 tonnes). The deviations can be explained on the one hand by the reported relatively large uncertainties in the atmospheric determination. It should also be noted that the MHD and JFJ measuring stations are not fully representative

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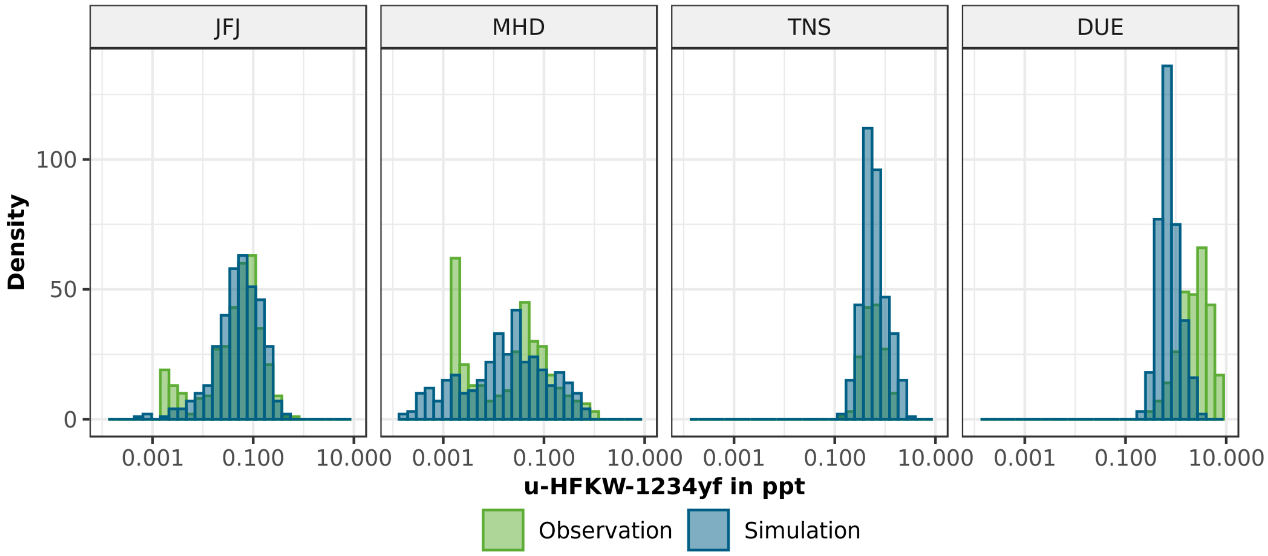
[169] Scale for calibration of the Swiss Federal Institute of Metrology (Metrology and Accreditation Switzerland, METAS).

[170] ppq: parts per quadrillion (10^{-15})

[171] 1st order reactions are elimination reactions in which two groups (atoms, ions, molecules) are split off from a carbon skeleton (Römpp 1995).

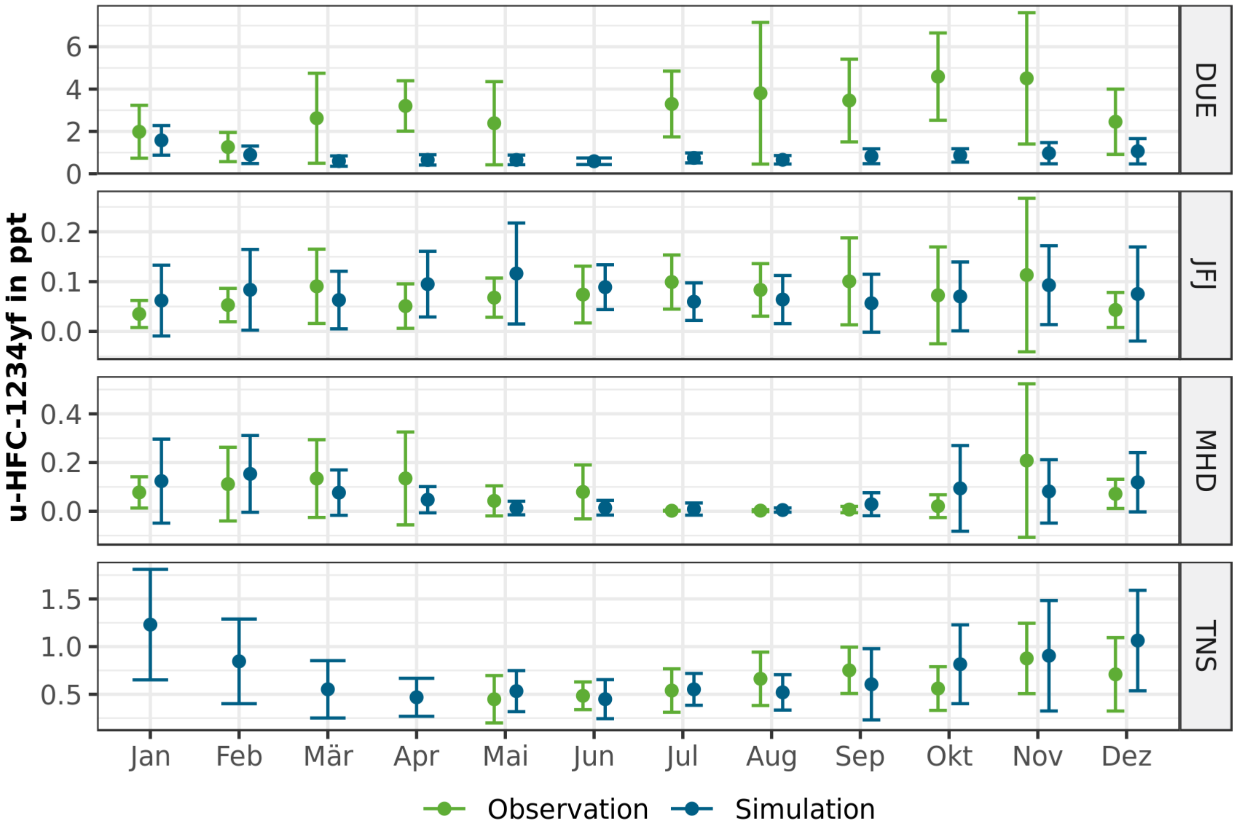
of all European u-HFC-1234yf emissions, as they are relatively remote and located in less urban areas. In addition, due to the delayed market launch and the recent full filling of all new passenger cars with u-HFC-1234yf since 2017, emissions are still in a very dynamic growth phase. Therefore, even small time shifts in the model parameters could lead to large relative deviations. The limits of the AnaFgas gas model itself, from which deviations of the calculated emissions from the real ones can result, are explained in Chapter 3.6.2.

Figure 34: Frequency distribution of the atmospheric concentration of u-HFC-1234yf (in ppt) at the Jungfraujoch (JFJ), Mace Head (MHD), Taunus (TNS) and Dübendorf (DUE) sites: observations and simulations based on Henne et al. (2012) (already scaled with factor 0.068). The x-axis is scaled logarithmically to achieve better comparability. Observations for the year 2018, simulations based on meteorology for 2010.



Source: Own illustration, Empa Zürich

Figure 35: Monthly mean and standard deviation of u-HFC-1234yf concentrations (in ppt) at the Jungfraujoch (JFJ), Mace Head (MHD), Taunus (TNS) and Dübendorf (DUE) sites: observations and simulations based on Henne et al. (2012) (already scaled with factor 0.068). Observations for the year 2018, simulations based on meteorology for 2010.



Source: Own illustration, Empa Zürich

The scaling factor (0.068) obtained from the comparison between observed and simulated concentrations of u-HFC-1234yf (Figure 35) could be used to estimate the TFA deposition and TFA rainwater concentration at the measuring stations of the DWD from the simulations of Henne et al. (2012). For this purpose the simulated quantities were interpolated to the locations of the measurements (bilinear interpolation) and multiplied by the factor mentioned above to account for the lower emissions. Since the error of the scaling factor was approximately ± 50 % (95 % confidence interval), this error range must also be assumed for all further model estimates for the year 2018.

Furthermore, the TFA deposition rates for Europe (EU-28+) simulated by Henne et al. (2012) were re-analysed and applied to the emission projections (see Chapter 3.4). Thus, the expected total deposition loads for different regions resulting from the European u-HFC-1234yf emissions could be determined (see Chapter 5.2.2.5).

5.2.1.2 TFA rainwater concentrations from the decomposition of relevant HCFCs and HFCs

Of the long-lived HFCs with high atmospheric concentrations, HFC-134a contributes significantly to TFA production in the atmosphere (see Chapter 2.7.4). Since HFC-134a has a much longer atmospheric lifetime (approx. 13.4 years, Burkholder et al. 2015) than u-HFC-1234yf (approx. 10.5 days, Nielsen et al. 2007) and no model calculations for the atmospheric degradation process are available, the degradation of HFC-134a and the resulting TFA production and TFA deposition was estimated here with the help of a simple global box model approach. The following assumptions were made:

1. The mean global degradation rate of a substance can be applied approximately also to mid-latitudes.
2. The formed TFA is quickly washed out of the atmosphere and deposited at the place of production.

The first assumption is justified insofar as the average concentrations of the OH radicals mainly responsible for degradation in mid-latitudes correspond approximately to the mean global OH concentration (Spivakovsky et al. 2000). The second assumption can be based on the high-water solubility of TFA. This leads to the fact that formed TFA amounts, as soon as precipitation formation takes place, are completely washed out of the atmosphere and not transported over long distances.

With these assumptions, the degradation rate L_A of a substance *A* in a tropospheric column can be calculated as follows

$$L_A = \frac{C_A}{\tau_A} = \frac{N\chi_A}{\tau_A},$$

where C_A is the column molar density in the unit mol/m² and τ_A is the lifetime in years. The column molar density can be calculated from the average mole fraction χ_A of the substance *A* and *N*, the number of moles of air in the column. *N* is calculated from the standard soil pressure p_s, the acceleration due to gravity *g*, and the average molar mass of air, μ_{air} = 28,96 g/mol according to the formula

$$N = \frac{p_s}{g \cdot \mu_{air}}.$$

The deposited TFA quantity D_{TFA} in the unit g/m² per year is the product of the degradation rate of substance *A*, the substance-specific molar yield γ_A, and the average molar mass of TFA, μ_{TFA} = 114,02 g/mol,

$$D_{TFA} = L_A \cdot \gamma_A \cdot \mu_{TFA}$$

This simple model can be compared with an older global 3D model calculation by Kotamarthi et al. (1998). In their study, the TFA production and TFA deposition from the atmospheric decomposition of HFC-134a, HCFC-123 and HCFC-124 over a period of 20 years was calculated with a chemical transport model. An emission scenario was chosen that allowed the global concentrations to increase linearly over the entire period. The mean concentrations over the whole period were 40, 0.5 and 5 ppt for HFC-134a, HCFC-123 and HCFC-124, respectively. Kotamarthi et al. (1998) assumed TFA molar yields of 33 % for HFC-134a and 100 % for HCFC-123 and HCFC-124. The lifetimes of HFC-134a, HCFC-123 and HCFC-124 were given by Myhre et al. (2013) with 13.4, 1.3 and 5.9 years, respectively.

If these numerical values for all three substances are inserted into the simple box model used in this study, the total TFA deposition for the 20-year period is 1.7 mg/m². This can be compared directly with Figure 12 from Kotamarthi et al. (1998), who calculate values of 1.0 mg/m² to 1.5 mg/m² for the Central European region.

The values calculated with the box model thus correspond very well with the explicit model calculations. In the concentration scenario of Kotamarthi et al. (1998), the shares of the individual substances in the TFA production calculated with the box model were 47 %, 18 % and 35 % for HFC-134a, HCFC-123 and HCFC-124, respectively.

5.2.2 Results

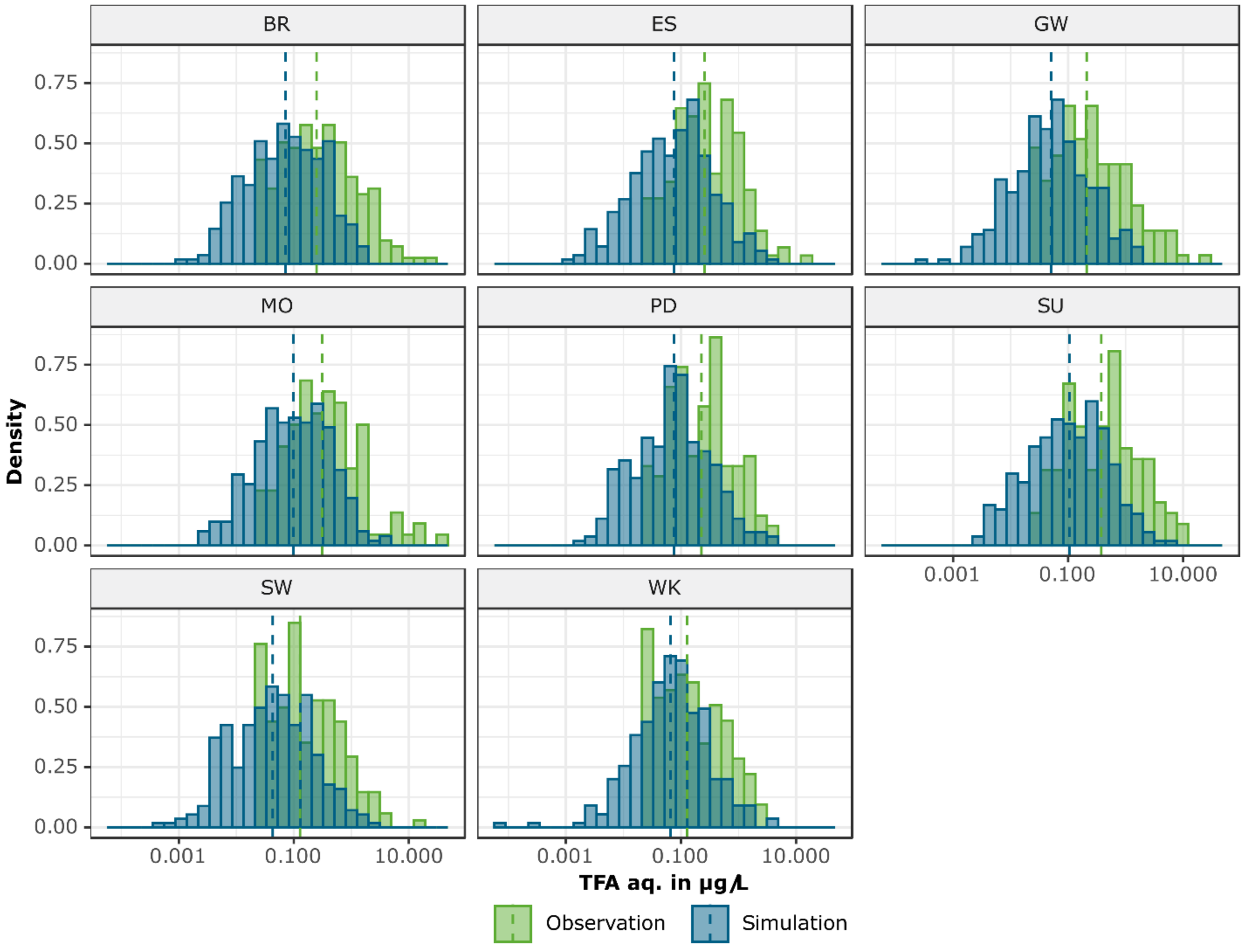
In this chapter, the share of u-HFC-1234yf in the deposition of TFA is discussed followed by the TFA depositions from HFCs resulting from the global box model. Then, the sum of the shares is compared with the total TFA depositions, which were measured at the DWD measuring stations.

5.2.2.1 Share of TFA from the degradation of u-HFC-1234yf at the measuring stations

Figure 36 shows the frequency distributions of the measured and the TFA rainwater concentrations calculated from the u-HFC-1234yf degradation separately for all eight DWD measuring stations. Figure 37 shows the frequency distributions of the TFA wet deposition rates, which were calculated from the measured TFA rainwater concentrations and from the u-HFC-1234yf degradation, also separately for all DWD measuring stations. The shape of the distributions is very similar at all stations and for both parameters. There are differences in the mean values and medians (see also Table 40 and Table 41). From this it can be concluded that the model describes the process of the atmospheric TFA deposition in principle correctly, this however takes place on a clearly lower level. In Figure 36 and Figure 37, the simulated values for the TFA rainwater concentrations from the degradation of u-HFC-1234yf and the following TFA wet deposition rates are always clearly below the measured values.

If we compare the precipitation measured at the stations in 2018 with that from the model calculation (meteorology for the year 2010), it can be seen that in 2018, with the exception of the Brocken station, the precipitation was 40-60 % less than in the model calculation. The smaller dilution could be one of the reasons for higher TFA rainwater concentrations in the measurements. However, less precipitation does not necessarily result in different TFA depositions, since these are probably mainly dependent on the regional TFA formation. In a sunny, dry year the TFA formation could even be increased, because the concentration of OH radicals in the atmosphere is highest. Together with a lower leaching efficiency (fewer precipitation events), however, a similar TFA deposition as in the model year 2010 could result. The comparability of simulated and measured deposition rates is therefore not fundamentally questioned.

Figure 36: Frequency distribution of the daily mean values of the observed TFA rainwater concentration (TFA aq. in µg/L) for the DWD measuring stations and the simulated. The simulated TFA-rainwater concentration contains only on TFA from the decomposition of u-HFC-1234yf. Dashed lines indicate the respective median values. The x-axis is scaled logarithmically.



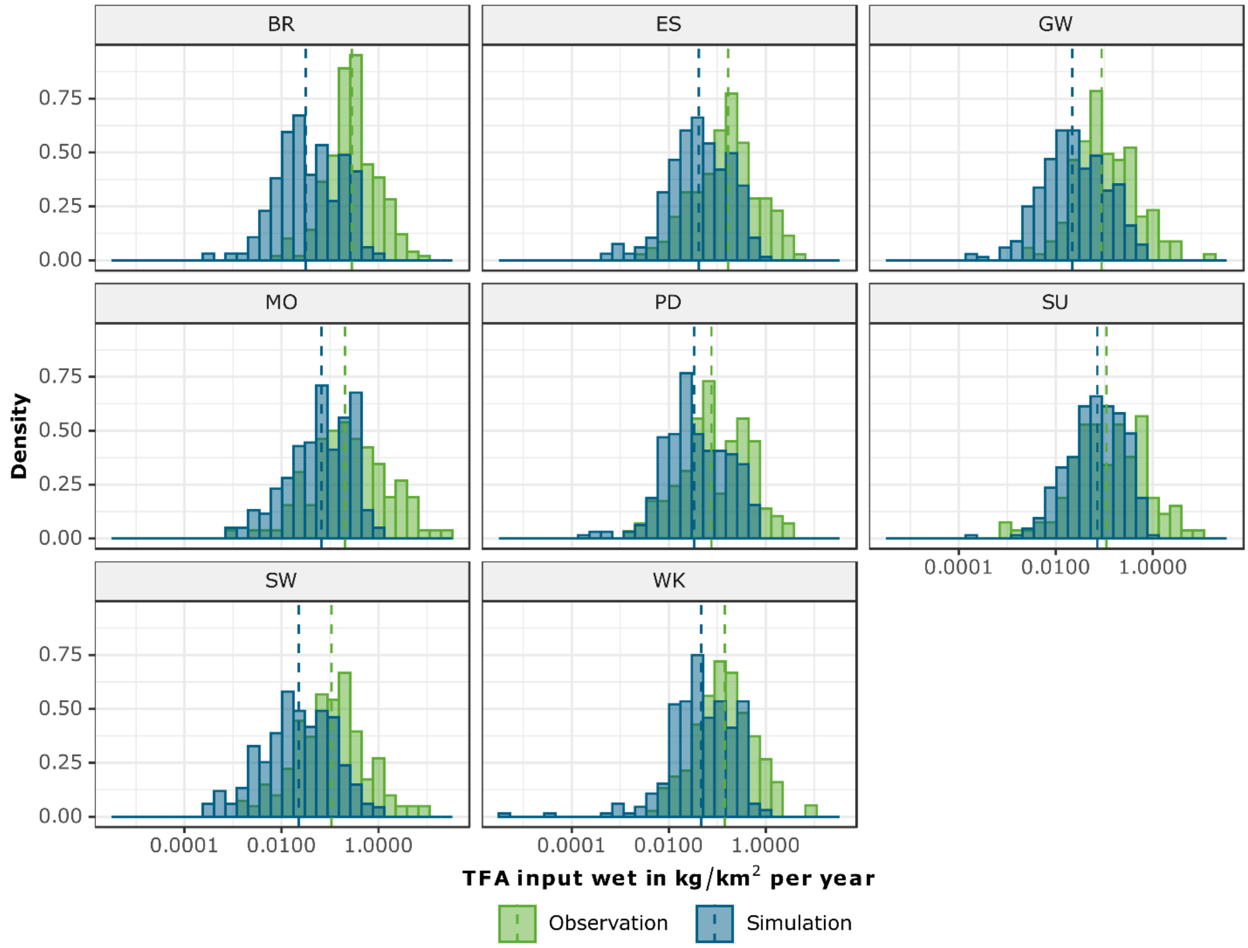
Source: Own illustration, Empa Zürich

Table 40: Statistics of the observed (O) and simulated (S) TFA rainwater concentrations (in µg/L).MV, mean value. SD, standard deviation. MAD, mean absolute deviation from the median ("Median Absolute Deviation").

Station	MV (O)	SD (O)	MV (S)	SD (S)	Median (O)	MAD (O)	Median (S)	MAD (S)
Essen	0.69	1.66	0.18	0.27	0.26	0.27	0.07	0.09
Greifswald	0.89	2.54	0.22	0.42	0.21	0.25	0.08	0.10
Munich	1.30	4.20	0.15	0.28	0.31	0.34	0.05	0.06
Potsdam	0.48	0.67	0.25	0.46	0.23	0.25	0.10	0.12
Stuttgart	1.02	1.65	0.22	0.50	0.38	0.47	0.08	0.09
Schleswig	0.47	1.15	0.29	0.56	0.13	0.15	0.10	0.13
Wasserkuppe	0.34	0.49	0.13	0.25	0.13	0.15	0.04	0.05
Brocken[a]	*0.90*	*2.24*	*0.19*	*0.40*	*0.25*	*0.30*	*0.07*	*0.07*

[a] Values for wet and dry deposition.

Figure 37: Frequency distribution of the daily mean values of the observed wet TFA deposition (input in kg/km² per year) for the DWD monitoring stations and the simulated. The simulated TFA input contains only TFA from the atmospheric degradation of u-HFC-1234yf. Dashed lines indicate the respective median values. The x-axis is scaled logarithmically.



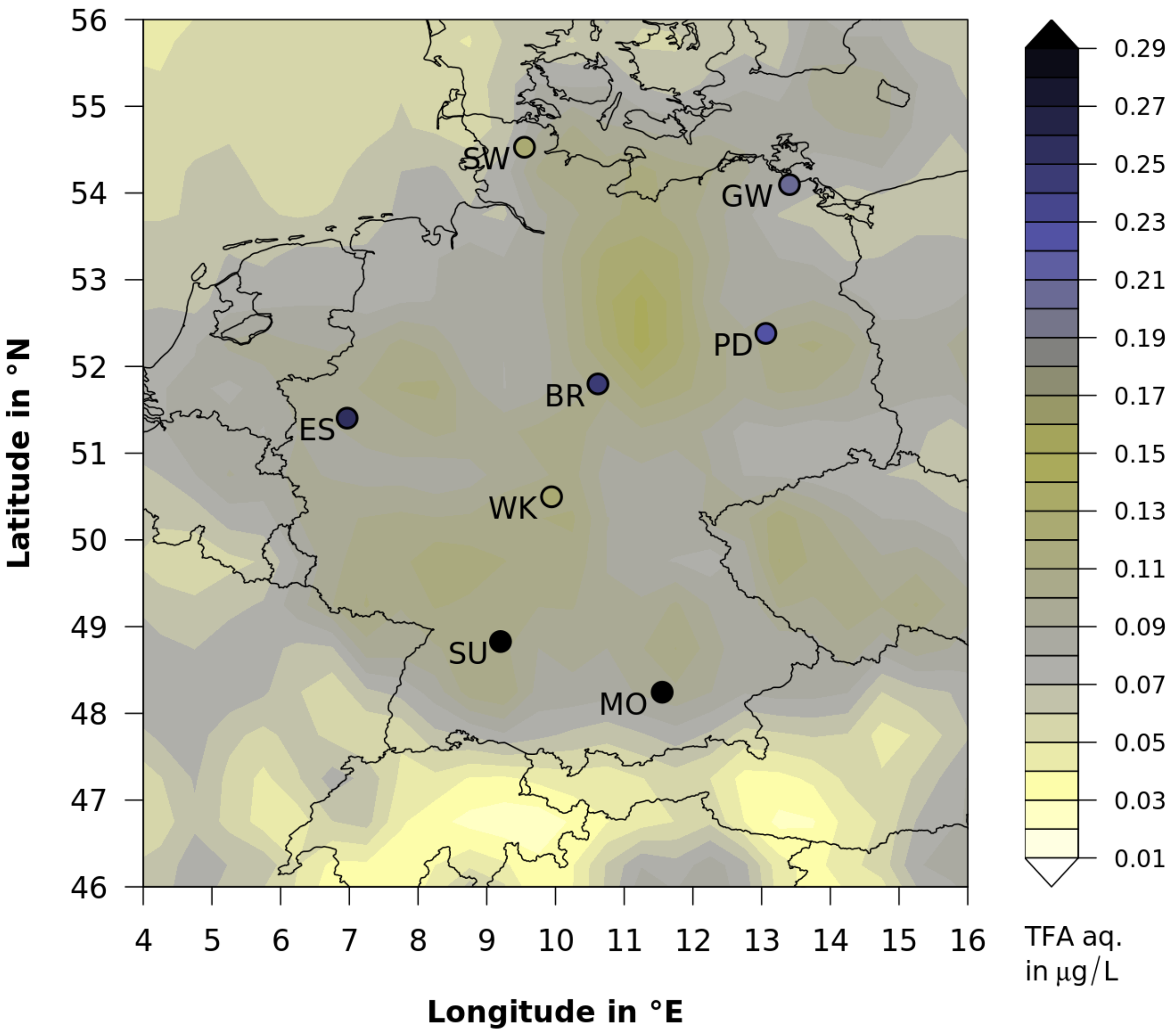
Source: Own illustration, Empa Zürich

5.2.2.2 Spatial distribution of the TFA rainwater concentrations and the TFA deposition from the degradation of u-HFC-1234yf

Figure 38 shows the rainwater concentrations measured directly at the measuring points of the DWD and those simulated from the decomposition of u-HFC-1234yf. The measured TFA rainwater concentrations (coloured symbols) are clearly higher than the values simulated for the degradation of u-HFC-1234yf. Also, the TFA deposition determined for the measuring stations of the DWD from the observed values are higher than the values simulated from the decomposition of u-HFC-1234yf (Figure 39).

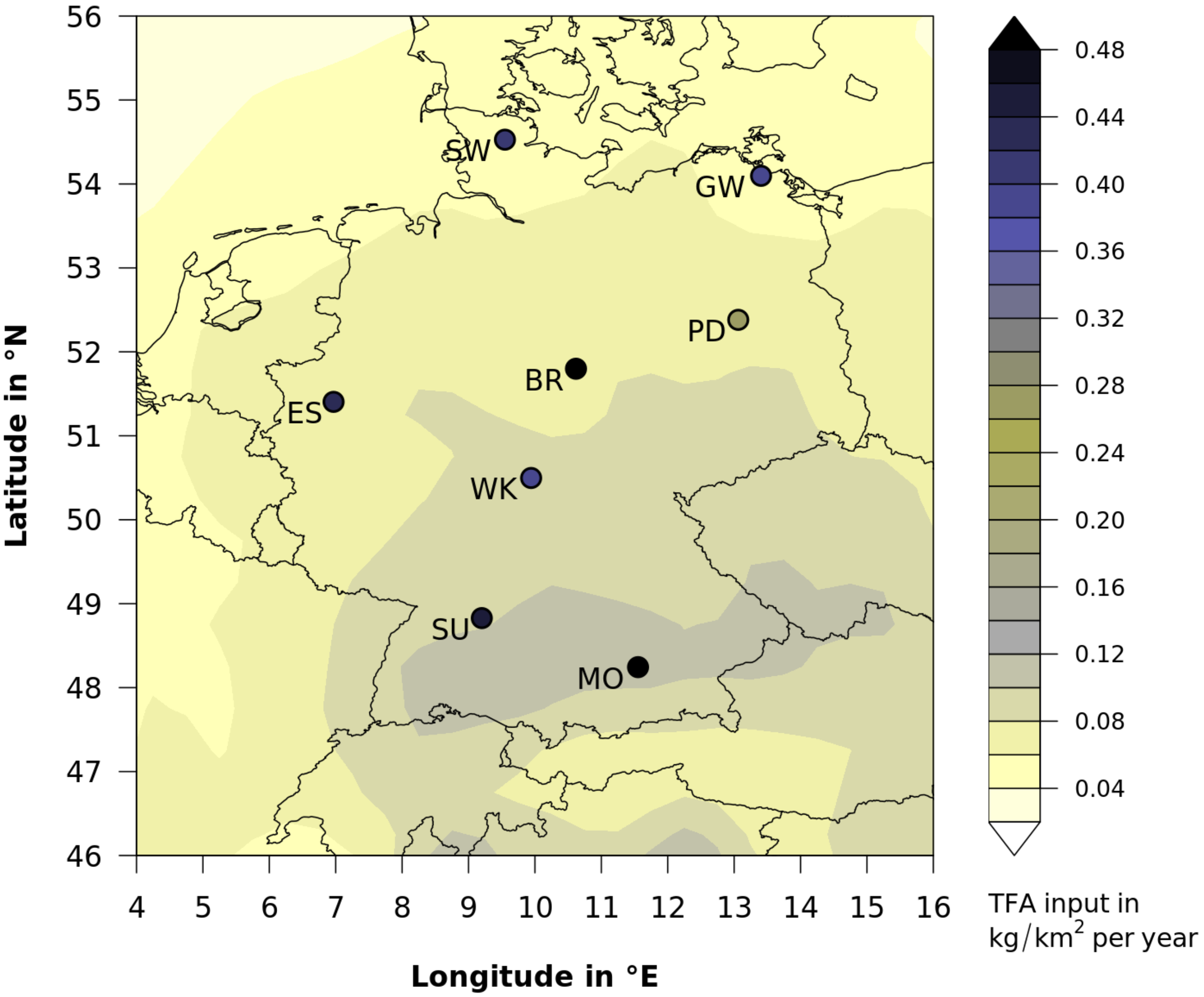
The spatial distribution of the simulated rainwater concentrations (Figure 38) does not show a clear gradient, but shows a more complex pattern, yellow and grey areas for different concentration levels alternate. However, the simulated TFA deposition rates from u-HFC-1234yf (Figure 39) show a clear north-south gradient, with higher deposition in Baden-Württemberg and Bavaria. This means that in the south, the higher precipitation leads to higher deposition.

Figure 38: Spatial distribution of the simulated mean TFA rainwater concentration (TFA aq. in µg/L) from atmospheric u-HFC-1234yf degradation. The colouring of the points corresponds to the measured annual medians at the DWD stations (SW, Schleswig, GW, Greifswald, PD, Potsdam, BR, Brocken, ES, Essen, WK, Wasserkuppe, SU, Stuttgart, MO, Munich-Oberschleißheim).



Source: Own illustration, Empa Zürich

Figure 39: Spatial distribution of the simulated annual sum of wet TFA deposition (input in kg/km² per year) from atmospheric u-HFC-1234yf degradation. The colouring of the points corresponds to the measured annual medians at the DWD stations (SW, Schleswig, GW, Greifswald, PD, Potsdam, BR, Brocken, ES, Essen, WK, Wasserkuppe, SU, Stuttgart, MO, Munich-Oberschleißheim).



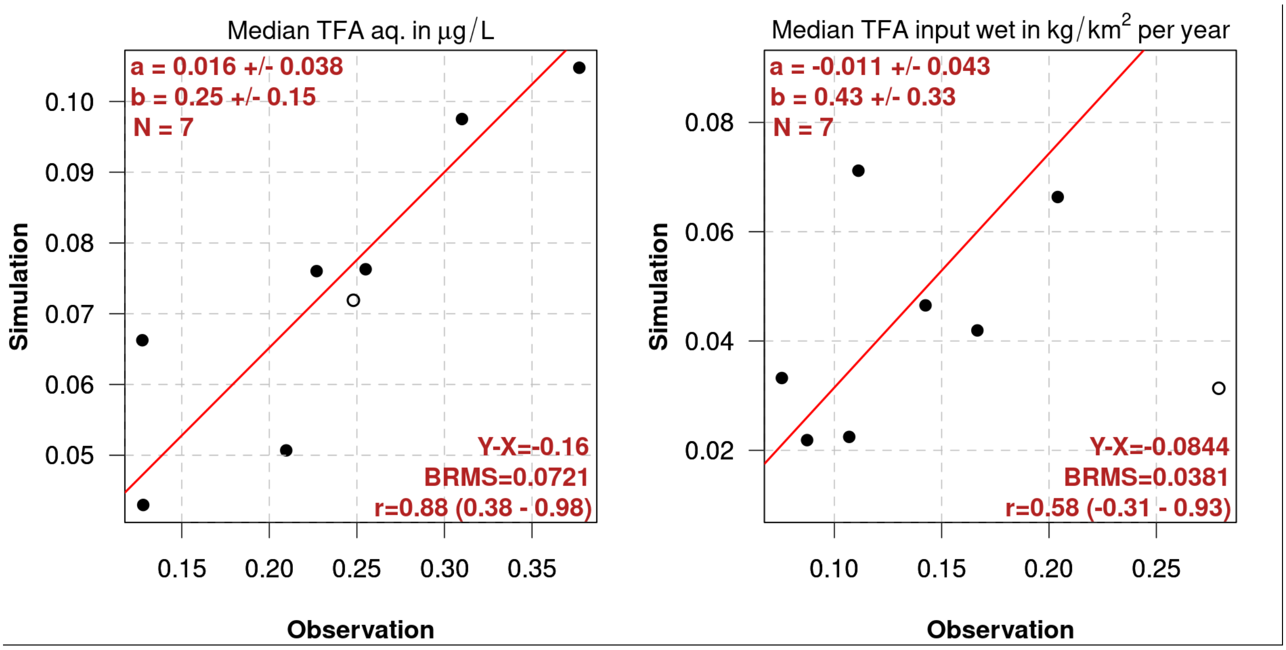
Source: Own illustration, Empa Zürich

5.2.2.3 Regression analysis

Figure 40 shows two regression analyses of the correlations of the observed and simulated medians of the annual values of the TFA rainwater concentration and the wet TFA deposition at the DWD stations. The aim of the analysis is to investigate to what extent the variability of the measured TFA deposition is dominated by the contributions from u-HFC-1234yf degradation, even if the latter were clearly larger than the former. If there is a clear relationship (spatial variability and intensity) between observation and simulation and therefore only a small part of the observed variability remains unexplained, the remaining TFA input could rather be explained by a large-scale source (e.g. long-lived precursors). If the simulation would not explain most of the observed variability, one could rather conclude that more local TFA sources (e.g. direct emissions into the atmosphere or short-lived precursors) play an important role.

Both the TFA rainwater concentrations and the TFA deposition rates show a spatial correlation between model and measurement (the latter, however, not significantly at the 95 % confidence level) (Figure 40). The simulated spatial variability between the sites is smaller than the measured one (for the rainwater concentrations by the factor 4 and for the deposition rates by the factor 2). This means that only a part of the observed variability can be attributed to the variability of TFA deposition from u-HFC-1234yf degradation. Therefore, it cannot be clarified at this point which additional contributions come from local or large-scale sources. However, the existing correlation between measurements and the model suggests that the model correctly reflects the spatial distribution of deposition and, therefore, that TFA sources with a similar spatial distribution as those resulting from u-HFC-1234yf degradation are important (e.g. degradation of precursors with similar lifetimes as u-HFC-1234yf).

Figure 40: Regression analysis between the observed and simulated medians of the yearly residual values (left) of the TFA rainwater concentration (TFA aq. in µg/L) and (right) of the wet TFA deposition (input in kg/km² per year) at the DWD stations. The station BR (open circle) was not used for the regression analysis. a, Axis intercept. b, Slope of the linear regression. N, Number of points. Y-X, Mean difference. BRMS, Bias corrected mean square deviation. r, Correlation coefficient with 95 % confidence interval.



Source: Own illustration, Empa Zürich

5.2.2.4 TFA contribution from the atmospheric decomposition of HCFCs and HFCs

To calculate the TFA contribution from the atmospheric decomposition of HCFCs and HFCs, the box model introduced in Chapter 5.2.1.1 was calculated for 2018 with the following parameters: The atmospheric concentrations of the most important TFA sources (HFC-134a and HCFC-124) were 118 ppt and 1 ppt, respectively, as measured at the station Jungfraujoch. Furthermore, HFC-245fa, HFC-143a, HFC-365mfc, HFC-227ea and HCFC-123 with concentrations of 3.35 ppt, 24.6 ppt, 1.28 ppt, 1.65 ppt and 0.1 ppt, respectively, were considered. For the TFA yield of the degradation of HFC-134a, a value of 15 % was assumed (Wallington et al. 1996), which is smaller than the 33 % used by Kotamarthi et al. (1998). For all other substances, the values in Table 14 were applied. In this case, the box model calculation resulted in an annual deposition rate of 0.062 kg/km² per year.

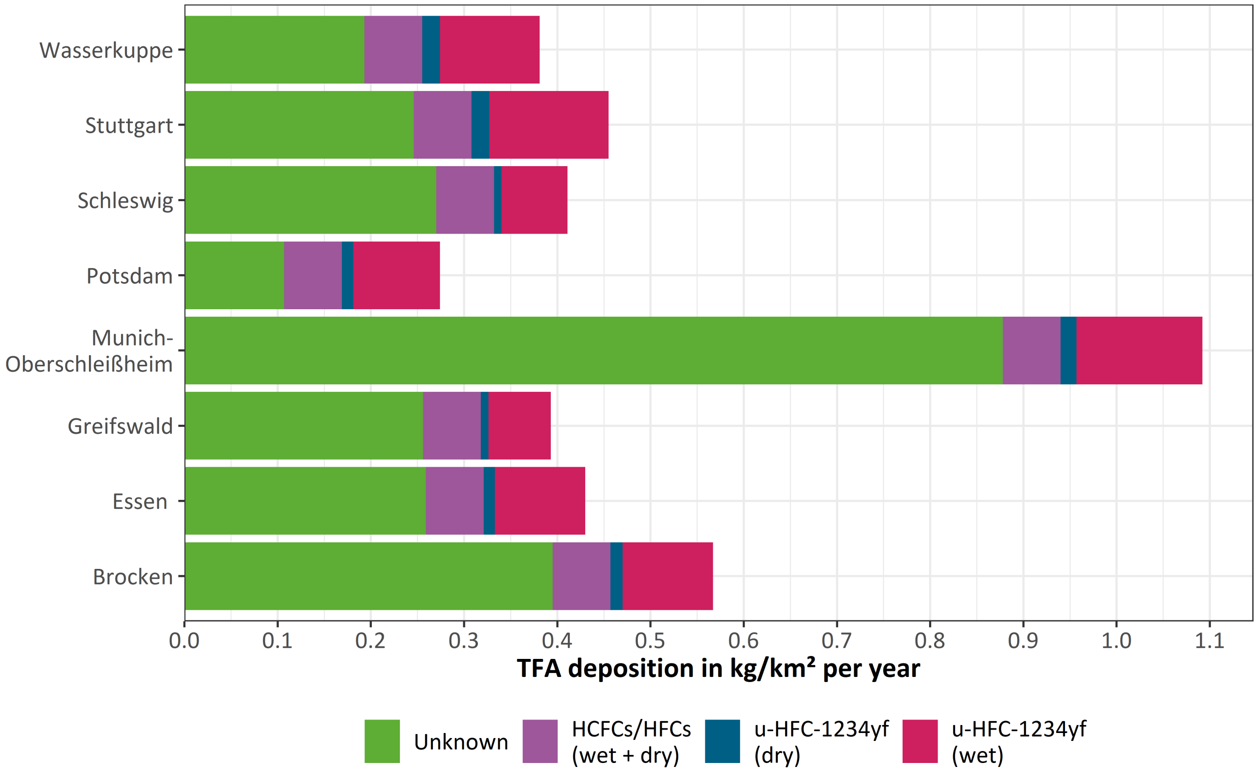
The TFA share caused by HFC-134a is 77 %. This high TFA content of HFC-134a is in contrast to the model calculations of Kotamarthi et al. (1998), in which larger shares of HCFC-123 and HCFC-124 were calculated. However, these refrigerants never reached the market in the high quantities predicted in the 1990s. The strong increase of HCFC-134a in the atmosphere is well illustrated in Figure A 11 in Annex A.11.

From the simulated TFA deposition rates of u-HFC-1234yf and HCFC-/HFC-degradation, their contributions to the measured deposition rates can be calculated. Figure 41, as well as Table 40 and Table 41 summarize the calculated contributions from HCFC-123, HCFC-124, HFC-134a, HFC-245fa, HFC-143a, HFC-365mfc, HFC-227ea and u-HCFC-1234yf. At all measuring sites the share of the annual TFA deposition rate which can be explained by the simulation from the refrigerants is below 50 % of the measured TFA values. The station Potsdam is an exception with 61 % explainable part, but due to very low precipitation it has the lowest measured deposition rate of all eight stations.

In addition to the explicitly simulated wet deposition from u-HFC-1234yf decomposition, the contributions from dry deposition were also included in this calculation, although these should have been largely not recorded in the TFA rainwater measurements. For the explicitly divided contributions from the u-HFC-1234yf decomposition, it can be seen that the contribution of the dry deposition to the total deposition is only about 12 % (Table 41).

The observed TFA deposition rates and rainwater concentrations cannot be explained by the atmospheric degradation processes of the treated halogenated gases alone. Other substances and processes seem to contribute. However, due to the simplified model calculations, this statement is subject to considerable uncertainties.

Figure 41: Estimated contributions to the observed wet TFA deposition at the DWD measuring stations from atmospheric degradation of HFCs (sum of wet and dry deposition), degradation of u-HFC-1234yf (wet and dry deposition) and unexplained fraction (unknown). At the station Brocken the contributions to the observed wet and dry TFA deposition are shown.



Source: Own illustration, Öko-Recherche and Empa Zürich

Table 41: Statistics of observed (O) and simulated (S) wet and dry TFA deposition rates (in kg/km^2 per year). MV, mean value. SD, standard deviation. The figures in brackets for the unknown fraction give the uncertainty due to the simulated u-HFC-1234yf deposition. u-HFC is u-HFC-1234yf, HFC is HCFC/HFC.

Station	MV wet (O)	SD wet (O)	MV wet u-HFC (S)	SD wet u-HFC (S)	MV dry u-HFC (S)	MV HFC[a] (S)	Unknown[b] (uncertainty)
Essen	0.430	0.749	0.097	0.128	0.012	0.062	60 % (48 - 73 %)
Greifswald	0.393	1.573	0.067	0.107	0.008	0.062	65 % (56 - 75 %)
Munich	1.092	2.692	0.135	0.165	0.017	0.062	80 % (73 - 87 %)
Potsdam	0.274	0.463	0.093	0.128	0.012	0.062	39 % (20 - 58 %)
Stuttgart	0.455	0.964	0.128	0.143	0.019	0.062	54 % (38 - 70 %)
Schleswig	0.411	1.082	0.071	0.140	0.008	0.062	66 % (56 - 75 %)
Wasserkuppe	0.381	1.004	0.107	0.139	0.019	0.062	51 % (34 - 67 %)
Brocken	*0.567*[c]	*0.910*[c]	*0.097*	*0.137*	*0.013*	*0.062*	*70 % (60 - 79 %)*

[a] Total HFC deposition (wet and dry)

[b] (MV wet (O) - MV wet u-HFC (S) - MV dry u-HFC (S) - MV HFC (S)) / MV wet (O)

[c] wet + dry deposition

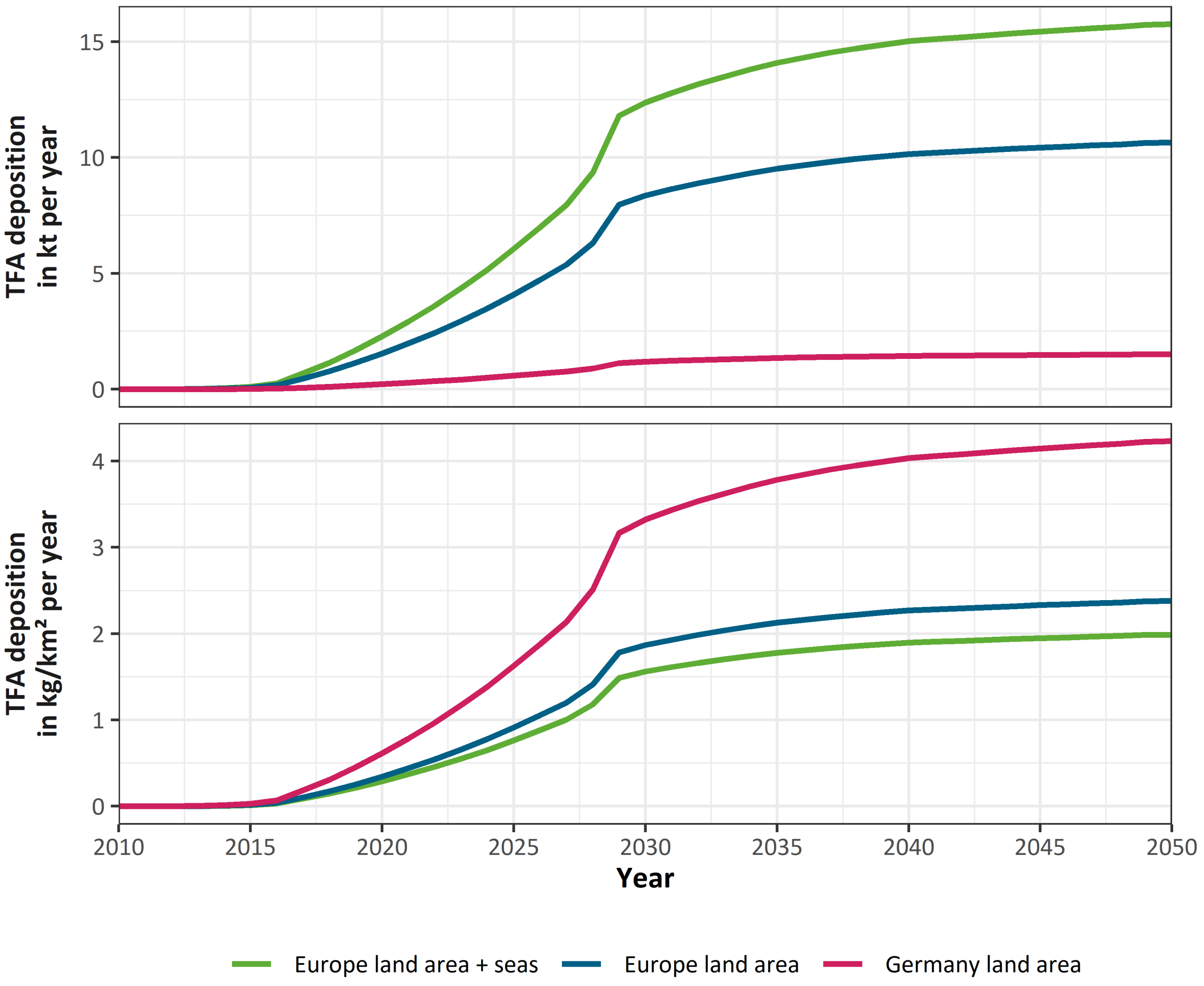
5.2.2.5 Future TFA deposition rates in Germany and Europe

With the help of the projected future HFC and u-HFC emissions in Chapter 3.4, an estimation of the future TFA deposition from their atmospheric degradation shall be given here. As can be seen from Table 26, mainly u-HFC-1234yf will contribute to the TFA production from the group of u-HFCs (98 %). Therefore, the model calculations of Henne et al. (2012) were used again and the deposition rates (wet and dry) determined there were scaled according to the expected u-HFC-1234yf emissions. The total amount of TFA deposited was determined for three regions: Germany, the land area of Europe (EU-28+) and the geographical region including the European states and adjacent seas (west-east extension: 10.0 to 30.0 °East; south-north extension: 35.0 to 65.0 °North) The resulting time series are shown in Figure 42. A comparison between this figure and the TFA production quantities listed in Table 26 and Table 27 shows that only a part of the TFA produced from European u-HFC-1234yf emissions is deposited in Europe again (33 % for EU and surrounding seas and 23 % for the EU land area). This was already found in Henne et al. (2012). Furthermore, the influence of North American u-HFC-1234yf emissions on TFA deposition in Europe was investigated. The share of this imported TFA quantity was comparatively small, so that TFA from European u-HFC-1234yf emissions should make up the majority of the TFA quantity deposited in Europe.

Figure 42 shows as well the expected mean TFA deposition rates for the three regions. For Germany, significantly higher values than in the European average were calculated and average TFA deposition rates of about 4 kg/km^2 per year until the middle of the century must be expected. Compared to the average deposition rates measured in this study, this would be an increase by a factor of 10. On average, a mean TFA deposition rate of 2.5 kg/km^2 per year until 2050 can be expected for Europe.

HFC concentrations in the atmosphere will continue to increase. However, this increase will be strongly dependent on global emissions and therefore cannot be calculated from the emission estimates for Europe in Chapter 3.4 alone. If one assumes that atmospheric HFC concentrations would increase by a factor of 4 to 5 in the next 30 years (as is shown in Figure 2-1 in WMO (2018) for the expected radiative forcing by HFCs and with the assumption that their relative contributions would remain similar), this would result in TFA deposition rates of 0.25 to 0.31 kg/km² per year in Central Europe (calculation analogous to Chapter 5.2.2.4). The TFA deposition expected from the atmospheric degradation of HFCs would thus be almost one order of magnitude smaller than that from the u-HFC-1234yf degradation.

Figure 42: Estimated future TFA deposition (input in kilotons per year) (top) and TFA deposition rates (input in kg/km² per year) (bottom) from the atmospheric depletion of u-HFC-1234yf for Europe (EU-28 + Norway, Switzerland and Turkey) with surrounding seas (Europe land area + seas), the land area of Europe (Europe land area) and of Germany (Germany land area).



Source: Own illustration, Öko-Recherche and Empa Zürich

5.3 Allocation of u-HFC and u-HCFC observations by air mass origin at Taunus Observatory

In the previous chapter, the measured concentrations of u-HFC-1234yf at the AGAGE stations at Jungfraujoch in the Swiss Alps and Mace Head in Ireland, as well as Dübendorf near Zurich and at the Taunus Observatory on the Kleiner Feldberg near Frankfurt am Main were used as comparison to calculate future deposition rates of TFA in Europe. While the concentrations of long-lived HFC-134a are comparable throughout the northern hemisphere (Figure A 11 in Annex A.11), the much shorter-lived u-HFCs and u-HCFCs may show regional concentration variations.

In order to check whether u-HFC-1234yf and u-HFC-1234ze in the vicinity of rainwater measurement stations have similar concentrations as in Switzerland and Ireland, data for the period from May 2018 to May 2019 were compared. For u-HCFC-1233zd, the data basis was not sufficient for an analysis. For the concentrations of u-HFC-1234yf, u-HFC-1234ze and u-HCFC-1233zd measured at the Taunus Observatory, the spatial sectors were determined, from which the corresponding emissions originated.

5.3.1 Methodology

The Taunus Observatory is located on the summit of the Kleiner Feldberg mountain, about 20 km northwest of Frankfurt at an altitude of 825 m. At the station, partly atmospheric background concentrations can be measured, and partly air masses with anthropogenic influences (Schuck et al. 2018). Therefore, the measurements are very well suited to estimate the influence of regional emissions of different gases.

At the Taunus Observatory, automated air sample measurements are regularly performed with a gas chromatography-mass spectrometry (GC-MS) system. The mass spectrometer used is a time-of-flight mass spectrometer (H-TOF, Tofwerk, Thun, Switzerland). To achieve sufficient detection limits, the condensable components are frozen out of 500 mL air on a sample loop and then desorbed into the gas chromatograph. The separation takes place on a GasPro column. The general design and characterization of the GC-MS system and sample preconcentration are described in Obersteiner et al. (2016a) and Obersteiner et al. (2016b).

At the Taunus Observatory, the mixing ratios of u-HFC-1234yf and u-HFC-1234ze were determined from May 2018 to May 2019 with the system outlined above. The u-HCFC-1233zd concentrations were only recorded in the period from March to May 2019, and the data collection was incomplete. Thus, for the period from May 2018 to March 2019, it was possible to determine whether u-HCFC-1233zd was present or not, but without quantification. All measurements were performed against a standard calibrated by Empa (M. Vollmer, private communication). The calibration scales are therefore identical to those of the Empa.

The frequency distribution of the u-HFC and u-HCFC measurements of the University of Frankfurt at the Station Taunus Observatory at Kleiner Feldberg was investigated as a function of air mass origin. For this purpose, backward trajectories were calculated for the last five days before the measurement at Kleiner Feldberg using the HYSPLIT model[172]. The air masses were divided into four different trajectory classes. These sectors are shown in Figure 44. If an air mass remains in a sector at least 50 % of the time, it is assigned to this sector. Air masses that are occurring less than 50 % in one of the sectors are labelled as unclassified.

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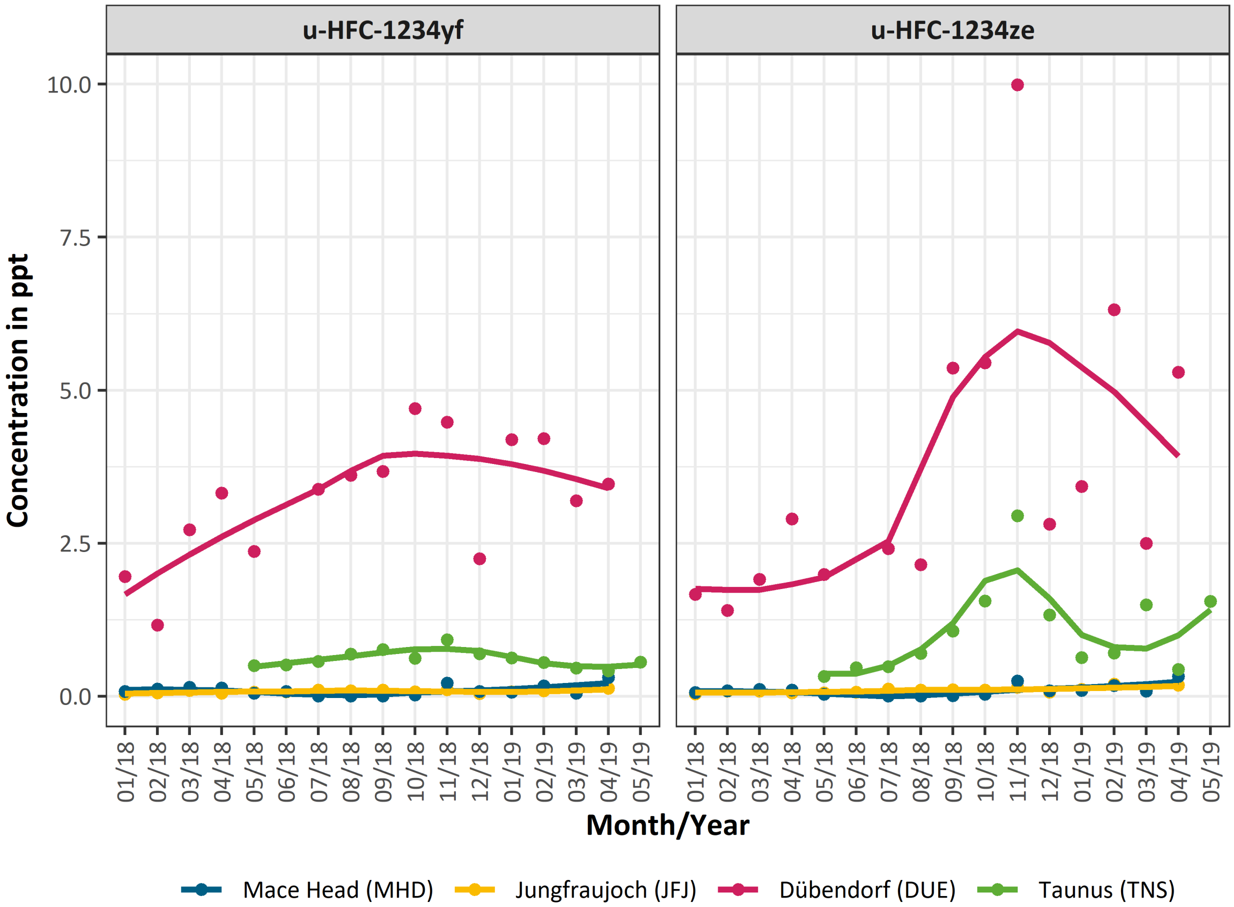
[172] https://www.ready.noaa.gov/HYSPLIT.php (last access: 28.04.2020)

5.3.2 Results

The measured concentrations of u-HFC-1234yf and u-HFC-1234ze at Kleiner Feldberg in Germany were compared with those of the monitoring stations at Dübendorf and Jungfraujoch in Switzerland, and Mace Head in Ireland for the same period of time. These two u-HFCs were measured at Kleiner Feldberg at higher average concentrations than at Mace Head and Jungfraujoch. Dübendorf showed the highest concentrations over the entire period (Figure 43). The special location of the Dübendorf station was already explained in Chapter 5.2.1.1.

The Mace Head and Jungfraujoch stations are located further away from emissions, while the station at Kleiner Feldberg is located in the triangle of the rainwater measuring stations Stuttgart, Essen and Wasserkuppe. It is striking that the concentration of u-HFC-1234ze in the atmosphere rose sharply at all stations, especially in November 2018, and was significantly higher than the concentration of u-HFC-1234yf for the same month. Known sources of u-HFC-1234ze in Europe are the release as propellant in aerosols and the production and use of XPS foam. Without further information, the origin of u-HFC-1234ze cannot be clearly determined.

Figure 43: Concentration of u-HFC-1234yf (left) and u-HFC-1234ze (right) at four different locations in Europe (Mace Head in Ireland, Jungfraujoch and Dübendorf in Switzerland and Taunus Observatory in Germany) from January 2018 (01/18) to May 2019 (05/19). Shown are measuring points and LOESS (locally estimated scatterplot smoothing) regression curves of the measured concentrations.

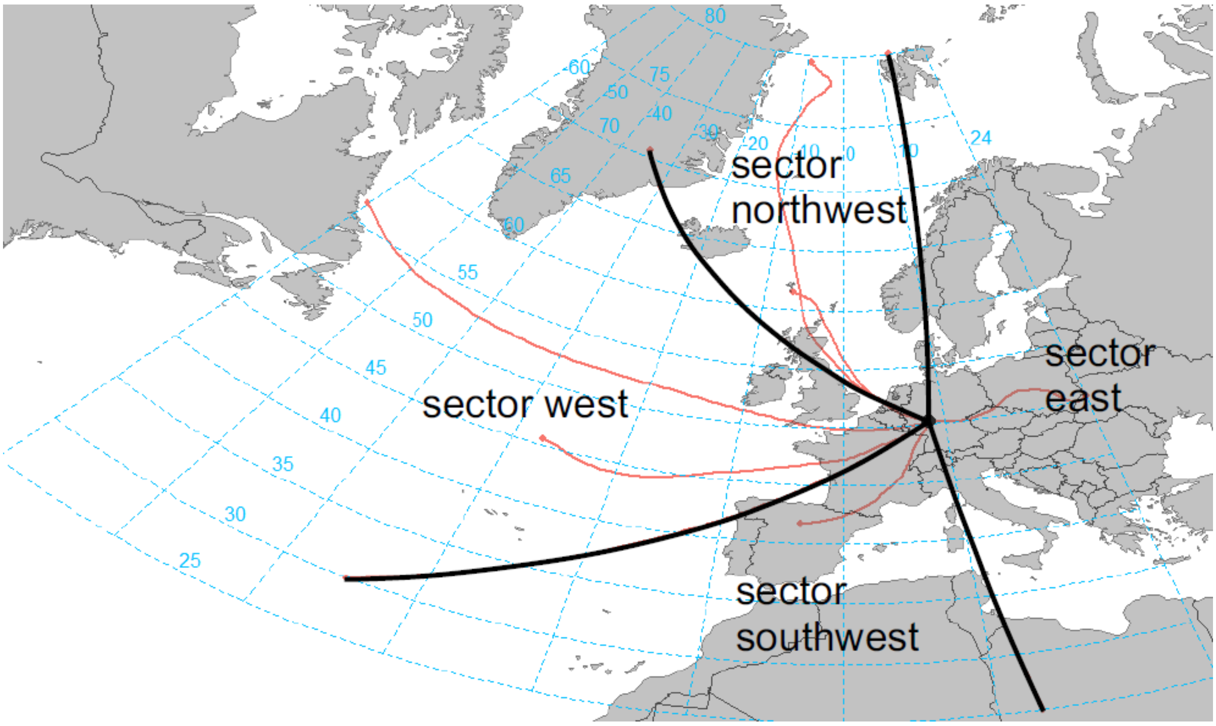


Source: Data from Empa Zurich and Assistant Professor Dr. Andreas Engel (Goethe University Frankfurt), own illustration, Öko-Recherche

The percentage probability to observe u-HFC-1234yf, u-HFC-1234ze and u-HCFC-1233zd at the Taunus Observatory as a function of the air mass sector is listed in Table 42 and shown graphically in Figure 44.

The probability distribution in Table 42 shows that for air masses originating south-west of the Taunus Observatory, the probability of observing u-HFCs and u-HCFCs is highest for all three substances investigated. In this sector, parts of the Rhine-Main area, Central to Southern France and Spain are located. However, the probabilities for the other sectors are not significantly lower. It can therefore be stated that u-HFCs and u-HCFCs can be detected in all air masses observed at the Taunus Observatory with probabilities of 50 % or more.

Figure 44: Classification of air mass sectors for trajectory classification at the Taunus Observatory station at Kleiner Feldberg of the University of Frankfurt. The trajectory classes (sectors) are separated by black lines. The red lines show the backward trajectories of u-HFC-1234yf, u-HFC-1234ze and u-HCFC-1233zd for the last five days since the measurement at Kleiner Feldberg.



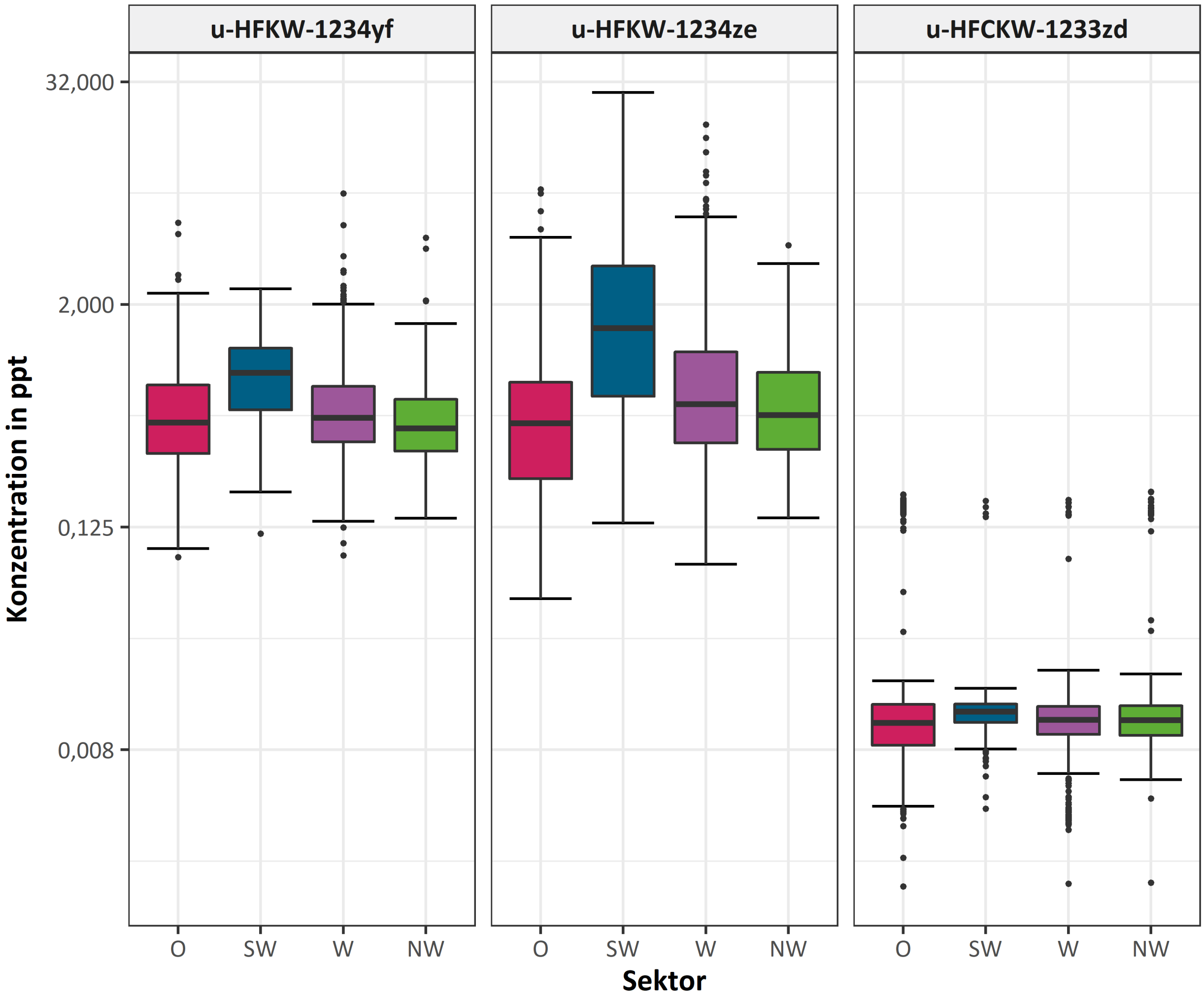
Source: Own illustration, Apl.-Prof. Dr. Andreas Engel (Goethe University Frankfurt)

Table 42: Percentage probability of observing u-HFCs and u-HCFCs at the Taunus Observatory as a function of the air mass sector.

Sector	u-HFC-1234yf	u-HFC-1234ze	u-HCFC-1233zd
Unclassified	79 %	70 %	67 %
East	73 %	54 %	76 %
Southwest	88 %	70 %	83 %
West	76 %	63 %	76 %
Northwest	67 %	48 %	69 %
Total	**75 %**	**60 %**	**75 %**

In a further study, the concentration distributions observed in the different geographical sectors were considered. These are shown in Figure 45. Here, it can be seen again that the highest concentrations of air masses for u-HFC-1234yf, u-HFC-1234ze and u-HCFC-1233zd originated in the southwest of the Taunus Observatory.

Figure 45: Concentration distribution of u-HFC and u-HCFC measured at the Taunus observatory from air masses of different origin in the period from May 2018 to May 2019. E, east. SW, southwest. W, west. NW, northwest. The y-axis is binary logarithmically scaled.



Source: Data from Apl.-Prof. Dr. Andreas Engel (Goethe University Frankfurt), own illustration, Öko-Recherche

At the Taunus observatory, the concentrations of all three investigated substances u-HFC-1234yf, u-HFC-1234ze and u-HCFC-1233zd were above the detection limit in more than 50 % of the cases. The values are particularly frequent and high when there is a southwest air flow, i.e. when the air masses come from the Rhine-Main area or parts of France and Spain. However, u-HFCs and u-HCFCs are also frequently observed for other air mass origins.

Since u-HFCs or u-HCFCs are not produced in Europe (see Chapter 2.4.2), the production of the substances can be excluded as a source of emissions. Remaining sources are the emissions from the production, initial filling, use and destruction of u-HFC- and u-HCFC-containing products. For u-HFC-1234yf, the emissions most likely originate from the initial filling and use of car air conditioning systems, while u-HFC-1234ze(E) emits mainly as a propellant gas during initial filling in XPS foam and the use of aerosols (see Chapter 2.5). The lowest concentrations were measured at the Taunus Observatory for u-HCFC-1233zd(E). This is comparable to Dübendorf, where the mean concentration of u-HCFC-1233zd(E) was also comparatively small at 0.254 ppt. In total, all three u-HFCs and u-HCFCs increased significantly in the atmosphere over the recent years. The concentrations show seasonal variations due to the concentration of OH radicals in the atmosphere with higher concentrations in winter (Reimann et al. 2019).

5.4 Comparison of the trifluoroacetate rainwater measurements with the literature

The detailed individual analysis of all rain events for the period from February 2018 to January 2019[173] resulted in a mean precipitation-weighted concentration of trifluoroacetate in the precipitation in Germany of 0.335 µg/L (Table 43). The total annual trifluoroacetate deposition during this period was 190 g/km^2.[174] This corresponds to a trifluoroacetic acid (TFA) deposition of 192 g/km^2.[175] The non-precipitation-weighted concentration of the individual samples in the period February 2018 to January 2019 was significantly higher at 0.703 µg/L, resulting in a higher deposition of 398 g/km^2.

The monthly composite samples yielded a concentration of 0.330 µg/L for the period February 2018 to January 2019 and 0.398 µg/L for February 2019 to January 2020. This corresponds to a trifluoroacetate deposition of 187 g/km^2 and 276 g/km^2 respectively. If only the summer months May to September are considered, precipitation-weighted trifluoroacetate concentrations of 0.580 µg/L and 0.674 µg/L as well as trifluoroacetate depositions of 131 g/km^2 and 214 g/km^2 result for the year 2018 and 2019.

In the literature, there are studies that have identified trifluoroacetate or TFA in rainwater in various countries (for an overview see Wang et al. (2014) and the "Supporting Information" in Pickard et al. (2020)[176]). These studies have in common that they usually cover only parts of a year at distinct locations. For Europe and neighbouring regions, the number of available studies is modest (Table 43).

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[173] For the seven stations (without the Brocken station) individual analyses were carried out for the period February 2018 to January 2019 with the exception of the Stuttgart station, for which there were no data for February 2018.

[174] Analogous to Berg et al. (2000), the total trifluoroacetate deposition was calculated by multiplying the mean trifluoroacetate concentration (0.335 µg/L = 0.000335 g/m^3) by the total precipitation in Germany from February 2018 to January 2019 (566.4 mm = 203*109 m^3/year, DWD (2020)) and then dividing by the area of Germany (357,582 km^2)

[175] The molar mass of TFA is 114.023 g/mol, whereas that of trifluoroacetate is 113.015 g/mol, as it carries one hydrogen molecule less. 190 g trifluoroacetate therefore correspond to 114.023 g/mol / 113.015 g/mol * 190 g = 192 g

[176] Pickard et al. (2020) give in Table S9 for Guangzhou, China with reference to Chen et al. (2019) annual TFA inputs of 43.8 to 5,480 µg/L. However, this is not correct, because Chen et al. (2019) measured trifluoroacetate and only over a period from May to September 2016 (see also Table 43). However, Pickard et al. (2020) apparently multiplied the trifluoroacetate concentration of 120 ng/L to 16,000 ng/L given in Chen et al. (2019) by 365 to calculate annual values. However, it

Whereas trifluoroacetate itself is measured in the rainwater measurement program in Chapter 4, this is not always the case in other studies. In some studies, the concentration and the deposition of the substance TFA is reported. Since a conversion of TFA concentrations into trifluoroacetate concentrations or trifluoroacetate quantities can be prone to errors, and since molar masses are very similar (the deviation is only small, <1 %), it will be omitted in the following, and instead it will be stated what the measured values of the studies refer to. As the results in Chapter 4.5.1 show, the concentration and deposition for trifluoroacetate have a strong annual variation. In addition, the amount of precipitation over one year plays an important role with regard to the quantities deposited. Therefore, when comparing the results with other studies, the transferability of the results must to be assured.

For Germany and Europe, there are almost no studies available that replicate the concentration and deposition of TFA or trifluoroacetate via precipitation over a whole year at different locations. Although rainwater concentrations have been determined in isolated cases (e.g. by Sydow et al. 2000, Dorgerloh et al. 2019), these results cannot be used for comparison due to the considerable annual variation and the strong variation within sites (see Chapter 4.5.1).

For sites in Germany, only Klein (1997) and Jordan and Frank (1999) have investigated concentrations of trifluoroacetate in precipitation over a whole year. Klein (1997) could detect precipitation-weighted concentrations of trifluoroacetate in Bayreuth for the periods of April 1995 to March 1996 and October 1995 to September 1996 of 0.079 µg/L and 0.106 µg/L, respectively. Compared with the measured values for the period February 2018 to January 2020, this corresponds to an increase in the concentration of trifluoroacetate in the precipitation by a factor of 3 to 5 (Table 43).

Jordan and Frank (1999) determined an average trifluoroacetate concentration in the precipitation of 0.110 µg/L, also in Bayreuth in the period from May 1995 to September 1996. These values are about 3 to 4 times lower than the concentrations recorded at the seven measuring stations in Chapter 4 in the period from February 2018 to January 2020 (Table 43). Since it is uncertain whether the trifluoroacetate concentrations in Jordan and Frank (1999) are precipitation-weighted[177], a comparison with the new precipitation-weighted values recorded in 2018 to 2020 would also be uncertain, so that we will not discuss this here.

The deposited TFA or trifluoroacetate amounts depend on the amount of precipitation. To get statements about the amount of the TFA deposition, the precipitation amount should be included. This also represents a more uniform basis for comparison of the results of different measurements (Wang et al. 2014, Freeling et al. 2020).

Assuming that the concentrations in Bayreuth in 1995/1996 (Klein 1997) were representative for the whole of Germany, the trifluoroacetate deposition in these periods amounted to 54 to 65 g/km² or 19 to 23 tonnes, which would also be about 3 to 5 times lower than the values determined in February 2018 to January 2020. The assumption that the measurements in Bayreuth can be regarded as an average for the whole of Germany is supported by the results in Chapter 4.5.1 which determined only minor differences between the measurement sites.

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can be strongly assumed that measurements over the whole year would have shown a lower concentration. Therefore, it would be more correct to refer the concentration only to the period May to September.

[177] An inquiry with the authors showed that the samples were very probably not precipitation-weighted, which can no longer be proven with 100 % certainty due to the measurements took place long ago.

Table 43: Mean trifluoroacetic acid (TFA) or trifluoroacetate concentration in µg/L and mean TFA or trifluoroacetate input in g/km² and metric tonnes (t) in different regions over various periods of time. mm, mean precipitation sum in mm. MV, measured value. PW, precipitation weighted. SS, single samples for all measuring stations except Brocken. MS, mixed samples for all measuring stations except Brocken. -, data not available.

Region and period	Precipitation	TFA/Trifluoroacetate				PW	Source
	mm	MV	µg/L	g/km²	t		
Germany							
Feb 2019 - Jan 2020[a]	694[b]	acetate	0.398	276	99	yes	this study (MS)
May 2019 - Sep 2019	*318*[b]	*acetate*	*0.674*	*214*	*77*	*yes*	*this study (MS)*
Feb 2018 - Jan 2019[a]	566[b]	acetate	0.330	187	67	yes	this study (MS)
			0.335	190	68	yes	this study (SS)
			0.703	398	142	no	this study (SS)
May 2018 - Sep 2018	*226*[b]	*acetate*	*0.580*	*131*	*47*	*yes*	*this study (MS)*
May 1995 - Sep 1996[c]	628[d]	acetate	0.110	69[e]	25[e]	-	Jordan & Frank (1999)
Oct 1995 - Sep 1996[f]	610[b]	acetate	0.106	65[e]	23[e]	yes	Klein (1997)
Apr 1995 - Mar 1996[f]	679[b]	acetate	0.079	54[e]	19[e]	yes	Klein (1997)
Switzerland							
Jul 1996 - Jun 1997	1,499	acid	0.151	230	9	no	Berg et al. (2000)
			0.116	174[e]	7	yes	
28 cities on the Chinese mainland							
May 2016 - Sep 2016[g]	-	acetate	0.155	337[h]	-	-	Chen et al. (2019)
Guangzhou, South China							
Apr 2007 - Mar 2008[i]	1,500	acid	0.152	229	1.7	yes	Wang et al. (2014)

[a] March to January for Stuttgart station

[b] Precipitation sum for Germany in the corresponding period (DWD 2020)

[c] Measurements were made exclusively at two locations in Bayreuth, northern Bavaria. The exact time period is unclear, since the authors in the method description state rainwater measurements in the Botanical Garden of the University of Bayreuth from May 1995 to June 1996, but in the corresponding figure (Figure 2 in Jordan & Frank (1999)) values from March 1995 to September 1996 are shown. According to the method description, rainwater draining through the tree roofs was additionally sampled in a neighbouring forest area from May 1996 to September 1996, as well as rainwater collected in a felled open area. The mean value of the TFA concentration refers to the concentration in the rainwater samples from the botanical gardens and the open field.

[d] This is the average precipitation sum for Germany in the period May 1995 to September 1996 (DWD 2020). In order to arrive at an annual TFA input (the measurements were carried out over a period of 17 months), the double precipitation amounts for the months in this period were averaged and then the sum was calculated.

[e] Specially calculated value that is not available in the source publication.

[f] Measurements took place exclusively in Bayreuth, Northern Bavaria.

[g] Only 39 precipitation samples were taken, only in four cities more than one sample was taken in the given period, the date of sampling is unknown except for six samples.

[h] Chen et al. (2019) claim to have measured from May to September 2016. This covers 153 days. On average the authors give for this period an entry of TFA over the precipitation of 2.2*103 ng/m² per day. This corresponds to 2.2 g/km² per day. Multiplied with 153 days results in 337 g/km².

[i] The total of 40 measurements were performed at one site (Guangzhou Institute of Geochemistry) and probably only from April to July 2007 and January to March 2008.

Wang et al. (2014) determined a TFA deposition of 229 g/km^2 in Guangzhou, China, from April 2007 to March 2008 (Table 43). Berg et al. (2000) came up with an almost identical deposition of 230 g/km^2, which was determined in the period from July 1996 to June 1997 based on measurements of precipitation (including snow) at six different locations in Switzerland. However, it must be noted that Berg et al. (2000) calculated the annual deposition using the non-precipitation-weighted TFA concentration of 0.151 µg/L. Wang et al. (2014) calculated their deposition using the precipitation-weighted TFA concentration of 0.152 µg/L. If Berg et al. (2000) also use the precipitation-weighted TFA concentration of 0.116 µg/L[178], the annual deposition in Switzerland in the period from 1996 to 1997 is 174 g/km^2.

However, it is critical that Wang et al. (2014) apparently did not measure consistently over the entire period from April 2007 to March 2008. Although it is not mentioned in the text, the months from August up to and including December are missing in the figure on TFA concentration[179]. This circumstance cannot be due to the fact that it has not rained in this period, because the rainy season from April to September is indicated in the text. If one considers the temporal course of the input of TFA over the precipitation in Germany in Chapter 4, it is to be assumed that in these five months significant amounts of TFA are deposited, which were not quantified in Wang et al. (2014). Therefore, the mean TFA concentration in Wang et al. (2014) would be too low and a comparison of concentration and total annual deposition with the data from Berg et al. (2000) and the present study would be misleading.

The mean value of the TFA concentration in precipitation in Berg et al. (2000), on which the calculation of the total annual TFA deposition is based, is also less reliable than the data collected in this study. Berg et al. (2000) determined the TFA concentration in rainwater and snow at six locations in Switzerland, but not all months of the period July 1996 to June 1997 are equally represented. Only in Dübendorf a measurement was taken over the entire period, whereby the months from November 1996 up to and including January 1997 are missing and August 1996 is included in the mean value in a considerably higher number. Four of the remaining five sites were only measured in the period from July to October 1996, often for shorter periods, while the last station, Dübendorf, only included measured values for August to the beginning of October 1996 and May to June 1997. Overall, the calculated mean value of 0.151 µg/L TFA is excessively influenced by the months of August (30 % of all measured values) and September (21 % of all measured values) 1996, while the winter months are completely absent. Based on the measurements in this study (Chapter 3), the accuracy of the mean value from Berg et al. (2000) cannot be determined, because on the one hand the months with the highest expected TFA concentrations are underrepresented (June and July, these account for only 8 and 5 % of the measured values in Berg et al. (2000), respectively) and on the other hand the months with the lowest expected TFA concentration are missing (December, January and February). While the former leads to an underestimation of the mean value, the latter leads to an overestimation. Therefore, it cannot be determined to what extent the mean value in Berg et al. (2000) deviates from a balanced annual mean.

Recent measurements between May and September 2016 in 28 cities on the Chinese mainland showed an average concentration of TFA in rainwater of 0.155 µg/L (Chen et al. 2019). The TFA concentration was thus practically identical to the concentrations measured in Guangzhou in 2007/2008 (Wang et al. 2014) and in Switzerland in 1996/1997 (Berg et al. 2000). In contrast, the mean TFA deposition was significantly higher with 338 g/km^2. On closer inspection, however, Chen et al. (2019) only collected a

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[178] This value was calculated by Wang et al (2014) from the data of Berg et al (2000). In Berg et al. (2000) no precipitation weighted TFA concentration is given.

[179] Figure 2 in Wang et al. (2014)

total of 39 samples in the 28 Chinese cities. The exact date of sampling is also unknown, with the exception of six samples. Only one sample was taken for the majority of the cities, e.g. for Guangzhou. This is surprisingly low at 0.0091 µg/L when compared with the results of the study by Wang et al. (2014), which found an almost 17-fold higher concentration of trifluoroacetate for Guangzhou about eight years earlier. The TFA concentration and the corresponding TFA deposition from Chen et al. (2019) can therefore hardly be used for comparison.

Overall, it is clear that continuous measurement over the entire year at different locations is necessary in order to determine the most accurate estimate of the total annual deposition. So far this has not been done for TFA or trifluoroacetate. The present study therefore allows for the first time to quantify the annual total TFA or trifluoroacetate deposition via the precipitation path for Germany and it is expected to increase. Furthermore, the measurement represents a valid basis for the comparison with future measured values for TFA concentration and deposition.

Wang et al. (2018) estimated the mean annual TFA deposition from mobile air conditioning in Europe (EU-28+) in 2016 at 0.52 kg/km^2, assuming the complete replacement of HFC-134a with u-HFC-1234yf. Similarly, the mean TFA concentration in rainwater was estimated to be 0.62 µg/L. However, according to the projections in Chapter 3 of this study, the complete conversion of air conditioning systems in passenger cars will not be achieved before 2030 at the earliest in the EU-28 (see Chapter 3.4.3.1). Since it is to be assumed that the number of passenger cars in the EU will not show any major growth since the year 2016 (see Figure A 1), the TFA deposition of 0.52 kg/km^2 per year and the mean TFA concentration in rainwater of 0.62 µg/L from Wang et al. (2018) should roughly correspond to the situation in 2030. The same applies to the results of the modelling from Henne et al. (2012). For Europe (EU-28+) they calculated a mean TFA deposition from precipitation of about 0.5 kg/km^2 per year[180]. The TFA concentration was 0.58 µg/L to 0.8 µg/L, depending on the simulation used. If one uses the projected u-HFC-1234yf emission data of this study and the degradation and deposition simulation from Henne et al. (2012) one obtains from 2030 on average European TFA deposition rates from the degradation of u-HFC-1234yf by 2 kg/ km^2 per year (see Chapter 5.2.2.5).

5.5 Development of emissions and deposition of trifluoroacetic acid (TFA)

It can be assumed with very high probability that the deposition of TFA or trifluoroacetate via the precipitation in Europe (EU-28) will increase (Chapters 3.4.3.1 and 5.2.2.5). One of the decisive factors will be the halogenated refrigerants and blowing agents investigated here. As shown in Chapter 3.4.3.1 a strong increase in the demand and thus in the emission of these substances and especially of u-HFC-1234yf can be assumed.

In 2030, the u-HFC-1234yf plays the central role with respect to the TFA quantity formed, especially from mobile (passenger cars) and stationary air conditioning, while the other sectors and gases also contribute significant quantities (Figure 24 in Chapter 3.5). The importance of u-HFC-1234yf is already apparent from 2020 onwards (Table 44). In the following years, u-HFC-1234yf will then clearly become the major source of TFA from the atmospheric degradation of halogenated refrigerants and blowing agents.

This has implications for the European contribution of halogenated refrigerants and blowing agents to global TFA deposition. While for the year 2018 HFC-134a will still be the largest contributor with

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[180] The two simulations used in the study by Henne et al (2012) yielded 0.65 kg/km^2 per year and 0.76 kg/km^2 per year. This refers to the sum of wet and dry deposition. The share of wet deposition was 77 % in the first simulation model and 60 % in the second (Henne et al. 2012). If only the wet deposition is calculated, both simulation models show about 0.5 kg/km^2 per year.

about 60 % and u-HFC-1234yf will account for about 30 %, the ratio is increasingly shifting towards u-HFC-1234yf (Table 44). By 2020, u-HFC-1234yf could contribute approx. 50 % of the TFA amount from the degradation of halogenated refrigerants and blowing agents, while the contribution of HFC-134a and other halogenated refrigerants and blowing agents will strongly decrease in the coming decades until 2050. At the same time, an increase in the total annual amount of TFA from the degradation of halogenated refrigerants and blowing agents can be expected. Compared to 2018, an increase of more than 300 % is expected by 2050.

Table 44: Projected amount of trifluoroacetic acid (TFA) from the atmospheric degradation of halogenated substances emitted in Europe (EU-28) in tonnes for different years from 2018 to 2050 (based on emission data from the modelling in Chapter 3). The TFA totals and the percentage share of the different refrigerants and blowing agents in the total amount are shown. In addition, the percentage increase of the TFA total quantity as well as the individual substances or substance groups in relation to 2018 is shown. "Other" includes all substances projected in Chapter 3 except HFC-134a and u-HFC-1234yf.

Sector	2018	2020	2030	2040	2050
Total TFA quantity in t from EU-28	**11,952**	**14,650**	**40,363**	**47,691**	**49,718**
HFC-134a	60 %	43 %	4 %	2 %	2 %
u-HFC-1234yf	29 %	47 %	93 %	95 %	96 %
Others	11 %	10 %	3 %	2 %	2 %
Increase in relation to 2018		**23 %**	**238 %**	**299 %**	**316 %**
HFC-134a		-11 %	-75 %	-85 %	-88 %
u-HFC-1234yf		98 %	976 %	1,207 %	1,270 %
Others		7 %	-10 %	-13 %	-6 %

5.6 Outlook

The present study allows for the first time to quantify the input of trifluoroacetate via precipitation in Germany. By continuously measuring all precipitation events, the annual course of the trifluoroacetate concentration and the deposition could be mapped and a robust annual mean value could be determined. The analysis carried out here is a basis for comparison with future measuring programs, and thus allows an exact quantification of the increase of TFA or trifluoroacetate in the precipitation and the associated deposition into ground and drinking water. The projections also allow an assessment of the increasing hazard potential of TFA or trifluoroacetate in the environment and show the urgent need for action to protect drinking water as a public good.

It is shown that the trifluoroacetate concentrations in rainwater determined in the measurement program are significantly higher than previously reported in the relevant literature. This applies to both the average and the maximum concentration. The change in the amount of the TFA or trifluoroacetate deposition can only be indicated conditionally due to the lack of data. In the period 2018 to 2020, however, an approximately 4-fold higher deposition was determined in Germany than in the period 1995/1996. On the basis of these new measurement results, significantly higher TFA depositions are predicted for the future until the year 2050 than previously determined in model studies.

A significant portion of the measured trifluoroacetate amount in the precipitation could be explained by the degradation of halogenated refrigerants and blowing agents. Furthermore, due to the higher concentrations of TFA or trifluoroacetate in the precipitation in summer, photochemical degradation is very likely responsible for the measured concentrations. On the basis of the evaluation of the measurement results, it seems unlikely that the predominant part of TFA in the atmosphere is directly introduced into the atmosphere from industrial point sources.

In future, especially sectors in which u-HFC-1234yf is used will have a considerable share in the environmental burden due to the input of highly persistent and highly mobile TFA. Steps to reduce this contamination should be taken at an early stage, since it is not possible to remove TFA from the medium water on a large scale. Furthermore, the unknown TFA sources should be investigated. The literature offers hints in this respect, three further possible sources of TFA have already been identified, namely thermolysis of fluoropolymers, atmospheric oxidation of fluorinated inhalation anaesthetics and photolysis of agrochemicals (Jordan & Frank 1998, Ellis et al. 2001a, Cui et al. 2019). Of these, only the thermolysis of fluoropolymers is considered a potentially relevant contribution. For China, however, this contribution was estimated to be only up to 14 % (Cui et al. 2019). Therefore, there is the possibility that further, so far unknown, anthropogenic TFA sources exist. This should be a main focus in the analysis of the TFA deposition into the environment in the future.

Investigations of ice cores from two Arctic highlands in Canada show that the concentrations of TFA measured therein have been increasing since 1990 (Pickard et al. 2020). Since TFA found in these ice sheets is of atmospheric origin, the authors assume that the TFA sources are most likely HCFCs, HFCs and u-HFCs.

This assumption could now be confirmed by modelling the production capacity of important TFA-forming substances (HFC-134a, HFC-227ea, HCFC-133a, HCFC-123 and HCFC-124). The analysis in this report (Chapter 5.2) showed that on average over all measuring stations about 40 % of the determined amount of trifluoroacetate in the precipitation (Chapter 4) can be explained by u-HFC-1234yf and important HCFCs and HFCs. By now, u-HFC-1234yf already plays a greater role than HCFCs and HFCs (64 % compared to 36 % of the amount that can be explained by known sources). Just as HCFCs and HFCs, as substitutes for CFCs, have significantly contributed to the increase of the TFA and trifluoroacetate concentration in precipitation and thus in groundwater and drinking water, the use of u-HFCs and u-HCFCs as substitutes for HFCs will lead to a much stronger increase of TFA in groundwater and drinking water.

The high persistence of TFA in the environment should be sufficient justification for limiting its input, even if TFA has a low environmental toxicity and shows no bioaccumulation. As Cousins et al. (2019) have demonstrated, the concentration of persistent substances in the environment cannot be regulated in a timely manner. Cousins et al. (2019) bring as an example a fictitious molecule D with a half-life of 2,000 days or 5.5 years[181], which had been emitted dynamically for 10 years (10 mol per hour in each year) and whose emission decreases dynamically in the same way in the following 10 years. Even if the molecule is no longer emitted after 20 years, it does not disappear from the environment until 30 years after emissions were stopped. In contrast to molecule D, TFA has an estimated half-life of about 40,000 years (Lifongo et al. 2010). It can therefore be assumed that TFA remains in the environment for much longer than 30 years after the end of any emission. Therefore, if negative consequences of an increased concentration of TFA in the environment should become apparent in the course of time, it

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[181] In Cousins et al. (2019), this example uses a log K_{OW} of 8 (log K_{OW}, also called P or P_{OW}, “octanol-water partition coefficient”, a measure of the fat and water solubility of a substance). However, for highly persistent substances the log K_{OW} does not play a role for the time it stays in the environment. It only determines the partition into the media air/water (lower log K_{OW}) and soil (higher log K_{OW}). The log K_{OW} of TFA from 0.5 to 0.79 at 25 °C (https://echa.europa.eu/de/brief-profile/-/briefprofile/100.000.846, last access 10.03.2020) means, that TFA is mainly found in the medium air/water.

would certainly not be possible to minimize the pollution of the environment by TFA in an appropriate time period.

5.7 Further need for research

In addition to these direct results, gaps in knowledge were identified in the course of the study, which should be in the focus of future research. There is a clear need for action in the question of the formation potential of TFA during atmospheric degradation of trifluoroacetaldehyde. As an important intermediate product of the degradation of many halogenated refrigerants and blowing agents, especially those with a low global warming potential, this question should be clarified as soon as possible. This is particularly relevant with regard to u-HFC-1234ze(E), as it is claimed, that this substance would not form TFA during atmospheric degradation, but without any reference to relevant sources. In general, the TFA formation rate of the newer u-HFCs and u-HCFCs should be quantified experimentally. With regard to these new substances, it is still necessary to determine the respective emission sources. The u-HFC-1234ze(E) for example shows emission peaks during the winter months (Reimann et al. 2019), whereas the exact origin is unclear. A major knowledge gap, which has existed for many years, is the proportion of trifluoroacetate in precipitation, which cannot be attributed to halogenated refrigerants and blowing agents. Potential sources have been mentioned above, but these are not sufficiently investigated.

The present study quantifies for the first time the current input of TFA or trifluoroacetate into the environment via precipitation. Based on this, a maximum scenario of TFA formation by the future use of halogenated substitutes of HFCs with low global warming potential was modelled. From the current perspective, this represents a possible maximum load on the environment and should serve to assess the hazard potential. It is shown that a replacement of HFCs with u-HFCs and u-HCFCs will lead to a considerable increase of the TFA or trifluoroacetate deposition into ground and drinking water. This pollution is practically irreversible and affects not only the emitting regions but also adjacent countries due to the atmospheric removal of TFA and trifluoroacetate (see Henne et al. 2012). Prevention to keep the ground and drinking water clean is urgently required. Alternatives to halogenated refrigerants and blowing agents, which do not contribute to TFA formation, should be preferred, and promoted. There are commercially solutions for many sectors available that include especially hydrocarbons, ammonia, and CO_2. Although u-HFC-1234yf is established as an industry standard for mobile air conditioning in passenger cars, technologies such as electromobility can pave the way to halogen-free solutions. Other sectors, such as stationary air conditioning and refrigeration applications, are currently transition to low-GWP technologies. To avoid the entry of persistent fluorine compounds, halogen-free solutions should be given preference to.

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A. Annex

A.1 Literature used on biodegradability and environmental toxicity

- ECHA (European Chemicals Agency): http://www.echa.europa.eu
- Note: ECHA explicitly states that "Use of this information is subject to copyright laws and may require the permission of the owner of the information."
- For the five substances trifluoracetic acid, 1,1,1,4,4,4-hexafluorobutene, 2,3,3,3-tetrafluoropropene (or polyhaloalkene), tetrafluoroethene (TFE), (1E)-1-chloro-3,3,3-trifluoropropene and hexafluoropropene, REACH registration dossiers can be found, for three further substances (2,3,3,3-tetrafluoropropene, trans-1,3,3,3-tetrafluoropropene and trans-1-chloro-3,3,3-trifluoropropene) at least information on the classification according to CLP is given.
- TOXNET - Databases on toxicology, hazardous chemicals, environmental health, and toxic releases. Contains, among others, the Hazardous Substances Data Bank (HSDB): http://toxnet.nlm.nih.gov
    1. For trifluoroacetic acid (TFA), tetrafluoroethene (TFE) and hexafluoropropene, HSDB datasets are available.
- US EPA ECOTOX database: http://cfpub.epa.gov/ecotox/quick_query.htm
    2. Only trifluoroacetic acid is covered in the database with the publication of Ulhaq et al. (2013).
- Rigoletto database of the German Environment Agency for the classification of substances that harm bodies of water: https://webrigoletto.uba.de/rigoletto/public/welcome.do. Entries for trifluoracetic acid (Reg. no. 729, WGK 2), 2,3,3,3-tetrafluoropropene (Reg. no. 7910 WGK 1), tetrafluoroethene (Reg. no. 7275, WGK 2) and hexafluoropropene (Reg. no. 7089, WGK 1) can be found.
- GESTIS Substance database, Information system on hazardous substances of the German Social Accident Insurance: http://gestis.itrust.de/
    3. For trifluoracetic acid, 2,3,3,3-tetrafluoropropene, tetrafluoroethene and hexafluoropropene datasets exist but contain no further information on degradation and ecotoxicity.
- OECD Existing Chemicals Database (contains, among others, the OECD Screening Information Dataset, OECD SIDS): https://hpvchemicals.oecd.org/ui/Default.aspx
    4. Only for hexafluoropropene a dataset can be found, but this only contains the information that the substance is the subject of further studies.
- ECETOC JACC Reports (Joint Assessment of Commodity Chemicals): http://www.ecetoc.org/publications/jacc-reports/
    5. Substance reports for tetrafluoroethylene and hexafluoropropylene are available (also for some older CFCs).

A.2 Internet research on niche applications

The following search terms were used for the Internet research, see the table below. The individual available u-HFCs were linked with all main keywords and also subjected to a search.

Table A 1: Search terms for the research on niche applications

Schlagwörter (deutsch)	Key words (Englisch)
HFO (Hydrofluorolefine)	HFO (hydrofluoroolefins)
▶ u-HFKW (ungesättigte HFKW) ▶ Organische Fluorverbindungen ▶ R1234yf ▶ R1234ze(E) ▶ R12336mzz ▶ R1233zd(Z) ▶ R1233zd(E) ▶ R1233xf	▶ R1234yf ▶ R1234ze(E) ▶ R12336mzz ▶ R1233zd(Z) ▶ R1233zd(E) ▶ R1233xf
▶ Aerosole ▶ Sprays ▶ Ausgleichgefäße ▶ Heizungen ▶ Druckausdehnungsgefäße ▶ Treibmittel	▶ aerosols ▶ sprays ▶ condensation chamber ▶ heaters ▶ pressure compensating tanks ▶ propellants/blowing agents
▶ Patente ▶ Produkte ▶ Nischenanwendungen	▶ patents ▶ products ▶ niche applications
Kältesprays, Druckluftsprays, Insektizidsprays, Schmiermittelsprays, Haarsprays, Abwehrsprays (Pfeffersprays), Gefäßfüller/Druckausgleichsbehälter für Heizungen, Rohr-Vereiser, Signalhörner, „Novelties“	cold (coolant) sprays, compressed air sprays, insecticide sprays, lubricant sprays, hair sprays, defence sprays (pepper sprays), vessel fillers / pressure equalisation containers for heaters, pipe freezers, signal horns, "novelties"

In addition, stakeholders were contacted and expert discussions were held in order to obtain real market data on the use of u-HFCs in niche applications.

A.3 Documentation of the expert discussions carried out

A.3.1 Questionnaire template for the expert discussions – industry version

- In your opinion, what u-HFCs and u-HCFCs will be used in the EU as refrigerants and blowing agents in the future?
    - How high do you estimate the potential of u-HFC-1234ze, u-HCFC-1233zd(E) or the mixtures R452A, R448A, R449A etc.?
    2. Do these substances play a different role on the market outside the EU?
- For which u-HFCs and u-HCFCs do you see the greatest potential for the years 2020, 2030 and 2050? Looking at the relevant sectors in turn:
    1. Commercial refrigeration
        - CO_2 systems now dominate
        - Which u-HFC/u-HCFC-mixtures would be possible?
        - Is the situation different for southern Europe?
    2. Transport refrigeration: Mobile air conditioning and refrigeration systems
        - Refrigerated vehicles
            - Which alternatives to R404A exist?
                - R448/R449?
            - Market penetration of CO_2 systems
        - Refrigerated containers
            - Does the demand for CO_2/hydrocarbon systems increase?
            - Alternatives for R134a?
            - Alternatives for R404A?
                - R448/R449?
    3. Industrial refrigeration
        - Which substances, apart from R717, will play a central role in this sector?
            - Will HFC-134a be replaced by u-HFC-1234ze solutions or mixtures?
            - Which substance will the sector switch to if an A1 refrigerant is to be used? Mixtures containing u-HFC-1234yf (e.g. R450A)?
    4. Chillers
        - What market penetration would you assume for Germany and the EU?
        - What role could u-HFC-1234ze(E) play in the future?
            - Estimate for the number of existing devices?
        - What role could u-HCFC-1233zd(E) play? In centrifugal systems?
        - What is your assessment of the market penetration and availability of R513A solutions in chillers?
- Has your company carried out or commissioned research on u-HFCs and u-HCFCs? Do you conduct research on alternatives to u-HFCs and u-HCFCs?
- How high do you estimate the effect of the substance on the environment?
- Do you have recommendations for other experts who are familiar with the topic?

A.3.2 Questionnaire template for the expert discussions – science version

General

- Reaction of HFCs, u-HFCs and u-HCFCs with other compounds (in the atmosphere)
    1. Which reactions are preferred?

Production of u-HFCs and u-HCFCs – synthesis routes

- Are you familiar with the raw materials or by-products used in the manufacture of u-HFCs and u-HCFCs?
    1. HCFCs, HFCs, u-HFCs and u-HCFCs?
- Which minor components can the product contain?
    2. As an example, u-HFC-1225ye in u-HFC-1234yf
    3. Do you know the minor components in u-HFC-1234ze?
- How do you estimate the future availability of the raw materials for the synthesis of HFCs, u-HFCs and u-HCFCs?

Use of u-HFCs and u-HCFCs

- How do you estimate the future market penetration of u-HFCs and u-HCFCs? What potential do you see for unsaturated chlorinated substances?

Destruction of HFCs, u-HFCs and u-HCFCs

- In what kind of process are HFCs, u-HFCs and u-HCFCs destroyed?
- How effective are these processes?
- Which substances and emissions are produced during destruction?
- Which substances can arise in the event of unintentional combustion (e.g. in a fire)?

Atmospheric degradation

- Which intermediate products can arise during atmospheric degradation, especially of u-HFCs and u-HCFCs?
    1. Trifluoroacetyl fluoride (TFF, CF_3CFO)
    2. Trifluoroacetaldehyde (CF_3CHO)
        - Will this be further degraded to TFA?
    3. Trifluoroacetyl chloride (TFAC, CF_3CClO)
- Final degradation products
    2. TFA (trifluoroacetic acid)
        - Do you see this material as a problem from the point of view of environmental protection?
    3. Hydrogen fluoride
        - What happens to this substance in the environment?
    4. Are other/further reactions or degradation pathways possible?
- Chlorine in the compounds:
    5. HCFCs and u-HCFCs: Can the resulting chlorine-containing compounds reach the ozone layer?
- How do HFEs behave in the event of (atmospheric) degradation or destruction?
- Fluoride in the environment– problems?
    6. Toxicity and reactivity?
- Reactivity of the CF_3-group
    7. How do you assess their environmental relevance?
    8. Relevance of the occupation of the carbon atom behind the CF_3-group for the further reaction steps
- Which substances with CF_3-groups could potentially be emitted into the atmosphere and broken down there?

Further questions

- Can you name other experts who should also be interviewed?

A.4 Attended events

Table A 2: List of events attended as part of the project

Date	Title of the event	Meeting place
05.03.2018 - 08.03.2018	Third consultation forum on the EU F-gas Regulation and shecco/3M event "F-gas Regulation: Shaking up the Industry in Europe"	Brussels, Belgium
13.03.2018 - 14.03.2018	Workshop of the German Environment Agency on REACH and PMT criteria	Berlin, Germany
08.07.2018 - 12.07.2018	Conference of the Parties to the Montreal Protocol, OEWG 40	Vienna, Austria
02.09.2018 - 04.09.2018	1st IIR International Conference on the Application of HFO Refrigerants	Birmingham, Great Britain
16.10.2018 - 18.10.2018	Chillventa: International exhibition for refrigeration, AC & ventilation, and heat pumps	Nuremberg, Germany
21.11.2018 - 23.11.2018	Annual Meeting of the German Society of Refrigeration and Air Conditioning, DKV e.V.	Aachen, Germany

A.5 Summary of patented production routes for the manufacture of some u-HFCs and u-HCFCs

The production of u-HFC-1234yf can take place via different reaction paths.

- One of the oldest patents for the manufacture of u-HFC-1234yf was developed for DuPont and expired in the 1970s (Maley 1960). The thermal treatment of equal parts chloromethane (CH_3Cl, HCC-40) and tetrafluoroethene (CF_2=CF_2, TFE), or HCFC-22, which reacts to TFE, leads to the formation of u-HFC-1234yf. With the exception of hydrogen chloride (HCl), no further by-products or intermediate products are mentioned in this patent.
- As a result of a patent from DuPont, it is also possible to manufacture u-HFC-1234yf from HFC-235cb (Nappa et al. 2011). Here, u HFC-1234yf can either be produced directly or via the production of the intermediate products u HCFC-1224yd or HFC-245cb.
- According to another DuPont patent, u-HFC-1234yf can also be produced from u HFC-1225ye, with HFC-245eb being produced in an intermediate step, which is finally converted into u-HFC-1234yf (Rao et al. 2008). HFC-254eb is produced as a by-product in the first reaction and both isomers of u-HFC-1234ze in the second reaction.
- As described in a Honeywell patent, u-HFC-1234yf can, for example, start from u CFC-1113 (CTFE, CF_2=CClF), which is converted into C3H2ClF3 isomers (u-HCFC-1233xd , -xf, -yf and -zd), $C_3H_3Cl_2F_3$ isomers (including HFC-243 and HFC-243db), as well as $C_3H_2Cl_2F_2$ isomers (including u-HCFC-1232, -xc, -xf) (Van Der Puy 2009). In a second reaction, these substances form the target substance u-HFC-1234yf with hydrogen fluoride and (fluorinated) chromium oxide and, as fluorinated by-products, HFC-245fa, C3H2F4 isomers, various other chlorofluoropropenes and other unknown HFCs. With a favorable mixing ratio of the starting materials, 85 % u-HFC-1234yf and 9 % HFC-245fa and 6 % other unknown HFCs and u-HFCs are produced as by-products.
- Another possibility, patented by Honeywell, is to manufacture u-HFC-1234yf directly from u-HCFC-1233xd (CF_3CH=CHCl) or u-HCFC-1233xf (CF_3CCl=CH_2) (Mukhopadhyay et al. 2007,

2009). In a first reaction with hydrogen fluoride, the starting materials are converted to HCFC-244bb ($CF_3CFClCH_3$) and HFC-245eb ($CF_3CF_2CH_3$) in the case of u-HCFC-1233xd. In a second reaction, the conversion to u-HFC-1234yf takes place with the aid of sodium and potassium fluoride. In the case of u HCFC-1233xf, a conversion to HCFC-244bb takes place in a first reaction and conversion to u-HFC-1234yf in a second reaction.

- Hexafluoropropene ($CF_3CF{=}CF_2$, HFP, R1216) can be used as the starting substance for u-HFC-1234yf (Smith et al. 2009). The reaction chain runs through the formation of HFC-236ea (1,1,2,3,3,3-hexafluoropropane), which forms u HFC-1225ye (1,2,3,3,3-pentafluoropropene) through dehydrofluorination in turn reacts via reaction with HF to form HFC-245eb (1,2,3,3,3-pentafluoropropane). A final dehydrofluorination step then gives u HFC-1234yf.
- Arkema holds a patent for the production of u-HFC-1234yf, which uses u-HCKW-1230xa as a starting substance (Pigamo et al. 2011). The reaction with HF forms u HCKW-1233xf, which in turn can react directly to u-HFC-1234yf through fluorination with HF or forms HCFC-244bb, which in turn reacts with HF to form HFC-245cb. The u-HFC-1233xf and HFC-245cb are captured and returned to the reaction to increase the u HFC-1234yf yield.
- Following a Daikin patent, u-HFKW-1234yf can also be manufactured from HCKW-240db (Nose & Komatsu 2014). The u-HFC-1234yf is formed directly by reaction with hydrogen fluoride. The by-products are u-HCFC-1233xf and HFC-245cb, which can be reused to increase the u-HFC-1234yf yield.

The u-HFC-1234ze is produced from the reaction of HFC-245fa with potassium hydroxide (KOH) with the formation of the by-products potassium chloride (KCl) and water (Cottrell et al. 2010). This creates both isomers of u-HFC-1234ze (cis and trans). The target substance u HFC 1234ze (E) is finally isomerized by reaction with a catalyst (e.g. halogenated metal oxides, Lewis acid metal halides or zero-valent metals).

The u-HFC-1336mzz can be produced from HCFC-123, whereby CF3CH = CHCF2Cl is formed as a by-product (Sun et al. 2013). In addition, depending on the process, other by-products may arise (e.g. HFC-236fa, u-HFC-1132a, HFC-143a and HCFC-133a). The u-HCFC-1233zd is produced by the reaction of HFC-240fa with hydrogen fluoride (HF), whereby HF, HCl and other hydrocarbons are produced as by-products (Tung et al. 2005, Cottrell et al. 2013). The resulting HF is captured and fed back into the production process of the u-HCFC-1233zd.

During the production of u-HFC-1123, u-HFC-1132a is produced as a by-product and is contained in the product as a minor component (Tasaka 2016).

A.6 List of product names in niche applications

Table A 3: Niche applications of u-HFCs and u-HCFCs based on an online search.

No.	Company	Product	Use category	Substance	Applications
1	Inventec Performance Chemicals	NovaSpray™ HFO 1234ze	aerosol formulation (propellant)	u-HFC-1234ze(E)	use on electronic assemblies (for the assembly of printed circuit boards and semiconductors); Troubleshooting thermally sensitive electronic components as well as the assembly and disassembly of fitting parts.

No.	Company	Product	Use category	Substance	Applications
2	Inventec Performance Chemicals	NovaSpray™ HFO 1234ze / HFC 134a (90/10)	aerosol formulation (compressed gas)	blend u-HFC-1234ze(E) / HFC-134a	use on electronic assemblies (for the assembly of printed circuit boards and semiconductors).
3	CRC Industries Europe bvba	DRUCKLUFT 67	compressed air	u-HFC-1234ze(E)	precision cleaning
4	Friedrich Huber aeronova GmbH & Co. KG	no product name mentioned	cooling spray	potentially	
5	Purasol	no product name mentioned	cooling spray	potentially	
6	Green Clean	Air + Vacuum GREEN POWER – HI TECH	compressed air spray	u-HFKW-1234ze(E)	dust removal
7	Green Clean	Air + Vacuum GREEN POWER – HI TECH 400 ml	compressed air spray	u-HFKW-1234ze(E)	dust removal
9	Multi Comp.	MC002009 – Freezer Spray, Aerosol, HFO	cooling spray	u-HFKW-1234ze(E)	cleaning
10	ELECTROLUBE	EADH200D - Air Duster, Non-Flammable, HFO, Low GWP, Aerosol, 200 ml	compressed air spray	u-HFKW-1234ze(E)	dust removal of electronic components
11	Multi Comp	MC002008 – Air Duster, Aerosol, Invertible, HFO, 200 ml	compressed air spray	unknown	dust removal of electronic components
12	MG chemicals	G Chemicals 403C Super Cold Spray, HFO-1234ZE, 235 gram Aerosol	cooling spray	u-HFKW-1234ze(E)	For cooling electronic components and locating faults
13	Dr. Smiths	Dr. Smith's® Zinc Oxide Adult Barrier Spray	cosmetic spray barrier spray	u-HFC-1234ze(E)	skin protection product
14	Taerosol Oy	PRF 101/520 ML GREEN NFL	cooling spray	u-HFC-1234ze(E)	fault localization, electronic components

No.	Company	Product	Use category	Substance	Applications
15	Techspray	Eco-Freezer 1583-10S https://www.tech-spray.com/eco-freezer-2	cooling spray	u-HFC-1234ze(E)	
16	Chemtronics	Arctic Blast™ Freeze Spray	cooling spray (ice spray)	u-HFC-1234ze(E)	test circuits, dissipating heat when soldering or desoldering
17	Procter and Gamble Co.	patent for hair mousse spray	cosmetic spray, hair mousse spray	u-HFC-1234ze(E)	hair mousse
18	Klostermann Chemie	tube filler	compressed air spray	u-HFC-1234ze(E)	for checking and supplementing the pressure cushion in expansion vessels in heating and tank technology.
19	Klostermann Chemie	tube filler	compressed air spray	Blend u-HFC-1234ze(E) / HFC-134a / ethylene glycol	for checking and supplementing the pressure cushion in expansion vessels in heating and tank technology.
27	Meier Tobler	Heat pump Carrier 61XWH-ZE	high-temperature heat pumps	u-HFC-1234ze(E)	high-temperature heat pumps
28	MicroCare	ProClean™ EU	compressed air spray	u-HFC-1234ze(E)	dust removal of electronic components
29	MicroCare	Micro Freeze™ EU	cooling spray	u-HFC-1234ze(E)	dust removal of electronic components
30	MicroCare	Big Blast™ EU	compressed air spray	u-HFC-1234ze(E)	dust removal of electronic components
31	Friotherm	Heat pump UNITOP	high-temperature heat pumps	u-HFC-1234ze(E)	high-temperature heat pumps

A.7 List of TFA-forming halogenated refrigerants and blowing agents

Table A 4: Overview of all halogenated substances currently known to us that can form TFA during atmospheric degradation. This also includes commercially insignificant substances. The TFA formation potential is largely determined by the halogenated end products, whereby CF_3CFO (TFF) and CF_3CClO (TFAC) are practically 100 % converted to TFA, CF_3CHO (trifluoroacetaldehyde) up to 10 %.

Substance name	Molar TFA yield	Source	Halogenated final product (Burkholder et al. 2015)[a]
HCFCs			
HCFC-123	94 %	Kotamarthi et al. (1998)	**CF_3CClO**, anorganic chlorine, CF_3CHO
HCFC-124	100 %	Kotamarthi et al. (1998)	**CF_3CFO**, anorganic chlorine
HFCs			
HFC-245eb	up to 100 %	own estimate	CF_3CFO, HC(O)F, $CF_3CHFCFO$
HFC-245fa	up to 10 %	WMO (2010)	**CF_2O**[b], $CF_3C(O)CHF_2$
HFC-134a	7-20 %	Wallington et al. (1996)	**HC(O)F**, CF_3CFO
HFC-143a	up to 10 %	own estimate	**CF_3CHO**
HFC-365mfc	up to 10 %	WMO (2010)	**$CF_3CH_2CF_2CHO$**[c], $F_3COCF_2CH_3$
HFC-227ea	100 %	WMO (2010)	**CF_3CFO,**
HFC-236fa	up to 10 %	WMO (2010)	**$CF_3C(O)CF_3$**[d]
HFC-43-10mee	up to 100%	own estimate [e]	CF_3CFO, CF_3CF_2CFO
u-HFCs			
u-HFC-1234yf	100 %	Hurley et al. (2008)	**CF_3CFO**, HCOCl
u-HFC-1234ze(E)	up to 10 %	WMO (2010)	CF_3CHO, HC(O)F
u-HFC-1336mzz(E and Z)	up to 20 %	Henne et al. (2012a)	CF_3CHO, CF_3CClO
u-HFC-1243zf	up to 10 %	own estimate	CF_3CHO, HCOCl, XCH_2COCF_3
u-HFC-1225zc	up to 100 %	own estimate	CF_3CHO, CF_2O, CF_3COCF_2X, CF_3CClO
u-HFC-1225ye(E and Z)	up to 100 %	own estimate	CF_3CFO, HCFO
u-HFC-1438mzz(E)	up to 100 %	own estimate	CF_3CF_2CHO, CF_3CHO, CF_3CClO, $CF_3CF_2COCHXCF_3$, $CF_3CF_2CHXCOCF_3$
u-HCFCs			
u-HCFC-1233zd(E)	2 %	Sulbaek Andersen et al. (2018)	CF_3CHO, HCOCl, CF_3COCH-ClOH, $CF_3COCHCl_2$
u-HFCKW-1224yd (E and Z)	100 %[f]	own estimate	not mentioned
HCFEs			
HCFE-235da2 (isoflurane)	95 %	Wallington et al. (2002)	CF_2O, CHF_2OCOCF_3[g]

Substance name	Molar TFA yield	Source	Halogenated final product (Burkholder et al. 2015)[a]
HFEs			
HFE-236ea2 (desflurane)	3 %[h]	Sulbaek Andersen et al. (2012b)	CF_2O, CF_3CFO
HFE-347 (sevoflurane)	7 %	Sulbaek Andersen et al. (2012b)	$(CF_3)_2CHOCFO$, $(CF_3)_2COOCH_2F$
HFE-54-11 isomer	100 %	own estimate	$CF_3CHFCF_2OCOCF_2CF_3$, CF_3CHFCF_2OCOH, CF_3CF_2CHO, CF_3CFO, CF_2O
HFE-7500[h]	100 %	Newsted et al. (2002)	not mentioned
unsaturated perfluorinated CFCs			
hexafluoropropene (R1216)	100 %	own estimate	CF_2O, CF_3CFO

[a] The primary end product is printed in bold, if available.

[b] The chlorine-initiated oxidation results in CF_3CHO and CF_2O as the main breakdown products (Chen et al. 1997).

[c] $CF_3CH_2CF_2CHO$ is further oxidised to CF_3CHO and CF_2O (Inoue et al. 2008).

[d] $CF_3C(O)CF_3$ is photolytically degraded to CF_3CO radicals (WMO 2010). Both radicals are broken down to TFA by up to 10 %, so the TFA yield of HFC-236fa, analogous to u-HFC-1336mzz, should, strictly speaking, be up to 20 %. However, since the emissions of HFC-236fa are negligible in terms of quantity, the TFA formation rate from WMO (2010) was retained.

[e] Theoretically, a higher TFA formation rate would be possible here, since the molecule ($CF_3CHFCHFCF_2CF_3$) contains two CF_3-bodies, but there is no further literature on the formation of TFA from HFC-43-10mee, which is based on the information in Burkholder et al. (2015) goes beyond.

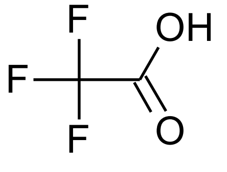
[f] It is not known whether TFF and thus TFA are formed, but u-HCFC-1224yd ($CF_3CF{=}CHCl$) has a CF_3-group and the central carbon atom is fluorinated.

[g] The ester CHF_2OCOCF_3 is practically completely degraded to TFA (Wallington et al. 2002).

[h] Sulbaek Andersen et al. (2012) indicate that 17 % of the breakdown of desflurane takes place via the formation of $CF_3CHFOCF$ radicals, which in turn oxidize to 18 % to TFF (which is completely hydrolyzed to TFA). All other degradation pathways lead to the formation of carbonyl fluoride (CF_2O).

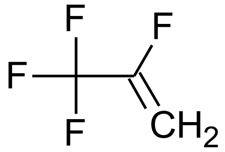
[i] The assessment for HFE-7500 should apply to all representatives of the series (7000, 7100, 7200, 7300 and 7500), since they all carry at least one CF_3-group and the directly adjacent carbon atom is fluorinated.

A.8 Annex on biodegradability and ecotoxicity

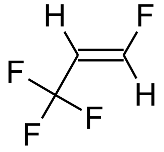
Trifluoroacetic acid		CAS 76-05-1	Source
	synonyms: TFA EU production / import: 1,000 - 10,000 t/a molecular formula: $C_2HF_3O_2$ water miscibility: miscible with water vapour pressure: 130 hPa at 20°C		ECHA ECHA Wiki[a] Wiki[a] Wiki[a]
Test system			
fish acute *Danio rerio*	OECD 203	LC_{50} (96 h) > 1200 mg Na-TFA/L NOEC = 1200 mg Na-TFA/L (= 999 mg TFA/L)	ECHA, Boutonnet et al. (1999)
fish embryo acute toxicity (FET) test *Danio rerio*	OECD 236	EC_{50} (6 d after fertilization) = 700 mg/L	Ulhaq et al. (2013)

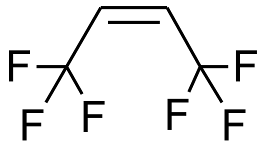
crustacea acute *Daphnia magna*	OECD 202	LC$_{50}$ (48 h) > 1200 mg Na-TFA/L (= 999 mg TFA/L)	ECHA, Boutonnet et al. (1999)
crustacea chronic *Daphnia magna*	OECD 211	NOEC (21 d) for reproductive rate and survival >= 100 mg Na-TFA /L (>= 25 mg TFA/L)	ECHA
algae *Raphidocelis subcapitata*	OECD 201	Na-TFA was studied ErC$_{50}$ (72 h) = 11.4 mg TFA/L ErC$_{10}$ (72 h) = 0.18 mg TFA/L	ECHA
Raphidocelis subcapitata		EC$_{50}$ (72 h) = 4.8 mg Na-TFA/L NOEC (72 h) = 0.12 mg Na-TFA/L	Boutonnet et al. (1999)
Raphidocelis subcapitata	OECD 201	ErC$_{50}$ (72 h) = 237 mg/L ErC$_{10}$ = 5.6 mg/L NOEC = 2.5 mg/L	ECHA, Chabot 2017
cyanobacteria *Anabaena flos-aquae*		EC$_{50}$ (72 h) = 2,400 mg Na-TFA/L NOEC (72 h) = 600 mg Na-TFA/L	Boutonnet et al. (1999)
bacteria Activated sludge	OECD 209	EC$_{20}$ (3 h) / EC$_{50}$ (3 h) > 1000 mg Na-TFA/L (=832 mg TFA/L)	ECHA
aquatic plants *Lemna gibba*		EC$_{50}$ (72 h) = 11,000 mg Na-TFA/L NOEC (72 h) = 300 mg Na-TFA/L	Boutonnet et al. (1999)
Hydrolysis and biological degradation behaviour			
hydrolysis		not relevant	
photolysis	xenon lamp > 300 nm	formation of 92 µmol/L CO$_2$ after 42 min. correspond with a degradation of 0.92 %.	ECHA
degradation	OECD 301 D	no degradation of the ammonia salt of TFA after 28 d in a Closed Bottle Test.	ECHA
		degradation of TFA in the atmosphere by photolytically created OH radicals: calculated half-life 31 d	HSDB
Potential for bioaccumulation			
mesocosm-experiment	Benthic freshwater microbio-zoenosis	after addition of 2-[^{14}C]TFA (43 µg/L) small but statistically significant enrichment over time of approx. a factor 20 within 2.5 years from 1.15 x 10^{13} to 2.22 x 10^{12} µg/cell/day.	ECHA
Risk assessment and safety information			
classification GHS	harmonised classification as Corr. 1A (H314), Acute Tox. 4 (H332) and Aquatic Chronic 3 (H412)		ECHA

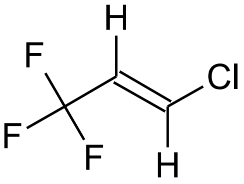
[a] https://de.wikipedia.org/wiki/Trifluoressigs%C3%A4ure (last access: 25.05.2018)

2,3,3,3-Tetrafluoropropene		CAS 754-12-1	Source
	u-HFC-1234yf, R1234yf, HFO-1234yf		
	Synonyms: 2,3,3,3-tetrafluoroprop-1-ene, polyhaloalkene		ECHA
	EU production / import: 1,000 - 10,000 t/a		ECHA
	Molecular formular: $C_3H_2F_4$		ECHA
	Water miscibility: 198.2 - 1540 mg/L at 24 - 25°C, pH 7		ECHA
	Vapour pressure: 580 kPa at 20°C		
Test system			
fish acute	OECD 203	LC_{50} (4 d) = 33 mg/L LC_0 (4 d) = 197 mg/L	ECHA
fish chronic *Cyprinus carpio*	OECD 215	fish juvenile growth test (semistatic): no mortality at highest concentration (22 mg/L) observed. NOEC growth = 2.7 mg/L	ECHA
crustacea acute	OECD 202	EC_{50} (48 h) = 65 mg/L NOEC (48 h) = 34 mg/L	ECHA
crustacea chronic *Daphnia magna*	OECD 211	reproduction toxicity NOEC (21 d) 15.2 mg/L (max. conc.)	ECHA
Algae	OECD 201	EC_{50} (72 h) 2.5 - 100 mg/L NOEC (72 h) 2.5 - 75 mg/L	ECHA
bacteria activated sludge	OECD 209	EC_{50} (3 h) was above the concentration achieved by blowing the substance through at 25 ml / min.	ECHA
Hydrolysis and biological degradation behaviour			
hydrolysis		not relevant	ECHA
photolysis		exposure based waiving	ECHA
degradation		no degradation in 28 d under test conditions	ECHA
Potential for bioaccumulation			
		Log Pow = 2 at 25 °C and pH 7	ECHA
Other characteristics of danger			
		extremely flammable	ECHA
Risk assessment and safety information			
classification GHS	aggregated classification by notifier in Flam. Gas 1 (H220) and H280 (contains gas under pressure; can explode if heated).		ECHA

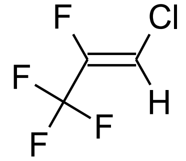
Note: There are two entries in the ECHA database under CAS 754-12-1: 2,3,3,3-tetrafluoroprop-1-ene and polyhaloalkene. The documented studies on polyhaloalkenes were carried out with 2,3,3,3-tetrafluoropropenes. If no methods are listed, the data situation is rare and the information could also come from QSAR assessments.

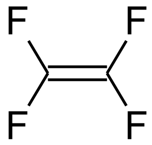
Trans-1,3,3,3-tetrafluoropropene		CAS 1645-83-6 / 29118-24-9	Source
	u-HFC-1234ze(E), R1234ze(E), HFO-1234ze(E) synonyms: 1,3,3,3-tetrafluoroprop-1-ene molecular formula: $C_3H_2F_4$		ECHA Pubchem
Test system			
fish acute	OECD 203	LC0 (4 days) > 117 mg/L	ECHA
crustacea acute	OECD 202	EC50 (48 h) > 160 mg/L	ECHA
algae	OECD 201	EC50 (72 h) > 170 mg/L NOEC (72 h) > 170 mg/L EC10 (72 h) > 170 mg/L	ECHA
Hydrolysis and biological degradation behaviour			
degradation		no aerobic degradation after 28 d	ECHA
Other characteristics of danger			
		extremely flammable	ECHA
Risk assessment and safety information			
classification GHS	aggregated classification by notifier in Flam. Gas 1 (H220) and H280 (contains gas under pressure; may explode if heated), Skin Irrit. 2 (H315), Eye Irrit. 2 (H319) and specific target organ toxicity STOT SE 3: May cause respiratory irritation (H335).		ECHA

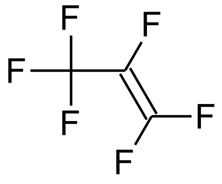
Cis-1,1,1,4,4,4-hexafluorobutene		CAS 692-49-9	Source
	u-HFC-1336mzz(Z), R1336mzz(Z), HFO-1336mzz(Z) synonyms: (2Z)-1,1,1,4,4,4-hexafluorobut-2-ene EU production / import: 10-100 t/a molecular formular: $C_4H_2F_6$ water miscibility: 763 – 895 mg/L at 0 - 50°C, pH 7 vapour pressure: 60.435 kPa at 20°C		ECHA ECHA ECHA ECHA ECHA
Test system			
fish acute *Oryzias latipes*	OECD 203	LC_{50} (96 h) = 76.1 mg/L (semistatic)	ECHA
fish chronic *Gobiocypris rarus*	OECD 210	fish, early-life stage test NOEC (35 d) = 10 mg/L (hatching, survival, behaviour, malformations), semistatic	ECHA
crustacea acute *Daphnia magna*	OECD 202	EC_{50} (48 h) = 22.5 mg/L	ECHA
crustacea chronic *Daphnia magna*	OECD 211	NOEC (Reproduktion) = 10 mg/L semistatic	ECHA
algae *Raphidocelis subcapitata*	OECD 201	ErC_{50} (72 hours) >23.7 mg/L NOEC (72 hours) = 6.92 mg/L.	ECHA
bacteria activated sludge	OECD 209	EC_{50} (3 h) > 1,000 mg/L.	ECHA
Hydrolysis and biological degradation behaviour			
hydrolysis	OECD 211	< 10% hydrolyse after 5 d at 50 °C and pH 4, 7 and 9	ECHA
photolysis			
degradation	OECD 301 D	no degradation (0 %) in 28 d	ECHA
Potential for bioaccumulation			
		Log P_{ow} = 2.3 at 30 °C and pH 6.1	ECHA
Risk assessment and safety information			
classification GHS	no classification into hazard classes notified.		ECHA

Trans-1-chloro-3,3,3-trifluoropropene		CAS 2730-43-0 / 102687-65-0	Source
	u-HCFC-1233zd(E), R1233zd(E), HCFO-1233zd(E) synonyms: 1-chloro-3,3,3-trifluorpropene, (1E)-1-chloro-3,3,3-trifluoropropo-1-ene EU production / import: 100 - 1,000 t/a molecular formular: $C_3H_2F_4$ water miscibility: 1.9 g/L at 20 °C and pH 7.5 – 7.6 vapour pressure: 106.5 kPa at 19.9 °C		ECHA ECHA ECHA Fleets 2017 ECHA ECHA
Test system			
fish acute *Oncorhynchus mykiss*	OECD 203	LC_{50} (96 h) = 38 mg/L (static)	ECHA
crustacea *Daphnia magna*	OECD 202	EC_{50} (48 h) = 82 mg/L (static)	ECHA
algae *Raphidocelis subcapitata*	OECD 201	EC_{50} (72 h) > 215 mg/L NOEC (72 h) = 115 mg/L	ECHA
Hydrolysis and biological degradation behaviour			
hydrolysis		not relevant	ECHA
photolysis		half-life in the atmosphere by reaction with OH radicals 26 days.	ECHA
degradation	OECD 301 D	no degradation in closed bottle test within 28 d.	ECHA
Potential for bioaccumulation			
		Log Pow = 2.2 at 25 °C and pH 7.4	ECHA
Risk assessment and safety information			
classification GHS	trans-isomer: aggregated classification by notifier in H280 (contains gas under pressure; may explode if heated), Skin Irrit. 2 (H315), Eye Irrit. 2 (H319) and specific target organ toxicity STOT SE 3: May cause respiratory irritation (H335). 1E isomer: Aggregated classification by notifier in H280 and Aquatic Chronic 3 (H412).		ECHA

Note: The ECHA database contains different entries / CAS numbers for the trans or (1E) isomer. The degradation and ecotoxicity data refer to the 1E isomer.

Cis-1-chloro-2,3,3,3-tetrafluoropropene	CAS 3110-38-1	Source
	u-HCFC-1224yd(Z), R1224yd(Z), HFO-1224yd(Z) synonyms: 1-chloro-2,3,3,3-tetrafluoropropene	 ECHA
Risk assessment and safety information		
classification GHS	aggregated classification by notifier in Skin Irrit. 2 (H315), Eye Irrit. 2 (H319) and specific target organ toxicity STOT SE 3: May cause respiratory irritation (H335).	ECHA

Tetrafluoroethene (TFE)	CAS 116-14-3		Source
	synonyms: tetrafluoroethylene EU production / import: 10,000 - 100,000 t/a molecular formular: C_2F_4 water miscibility: 110 g/L at 28°C vapour pressure: 32,395 hPa at 24.3°C		ECHA ECHA ECHA ECHA ECHA
Test system			
fish acute	ECOSAR v1.00a	LC_{50} (96 h) 379 mg/L (QSAR estimate) LC_{50} (96 h) 646 mg/L (QSAR estimate)	ECHA ECETOC (2003)
crustacea acute	ECOSAR v1.00a	LC_{50} (48 h) 190 mg/L (QSAR estimate) LC_{50} (48 h) 646 mg/L (QSAR estimate)	ECHA ECETOC (2003)
algae	ECOSAR v1.00a	LC_{50} (96 h) 64 mg/L (QSAR estimate) LC_{50} (96 h) 381 mg/L (QSAR estimate)	ECHA ECETOC (2003)
Hydrolysis and biological degradation behaviour			
hydrolysis		not relevant	ECHA
photolysis		photodegradation in the atmosphere via OH radicals to hydrogen fluoride (HF), half-life in atmosphere 17 / 0.7 d (Acerboni et al. 1999).	ECHA HSDB
degradation	BIOWIN v4.10	not easily degradable (QSAR assessment) no experimental data available	ECHA HSDB
Potential for bioaccumulation			
	EPISUIT	low potential for bioaccumulation QSAR BCF-estimate 4.9 OSAR BCF estimate fish: BCF = 3	ECETOC (2003) HSDB
Other characteristics of danger			
		potentially carcinogenic for humans (group 2B).	HSDB
Risk assessment and safety information			
classification GHS	aggregated classification by notifier in Skin Irrit. 2 (H315), Eye Irrit. 2 (H319) and specific target organ toxicity STOT SE 3: May cause respiratory irritation (H335).		

Hexafluoropropene		CAS 116-15-4	Source
	synonyms: hexafluoroprop-1-ene EU production / import: 10,000 - 100,000 t/a molecular formula: C_3F_6 water miscibility 82 mg/L at 28°C vapour pressure: 587,952 Pa at 25°C		ECHA ECHA ECHA ECHA ECHA
Test system			
fish acute	ECOSAR v1.00a	LC_{50} (96 h) 128 mg/L (QSAR estimate) LC_{50} (96 h) 86 mg/L (QSAR estimate)	ECHA ECETOC (2005)
crustacea acute	ECOSAR v1.00a	LC_{50} (48 h) 72 mg/L (QSAR estimate) LC_{50} (48 h) 93 mg/L (QSAR estimate)	ECHA ECETOC (2005)
algae	ECOSAR v1.00a	LC_{50} (72 h) 33,4 mg/L (QSAR estimate) LC_{50} (72 h) 58 mg/L (QSAR estimate)	ECHA ECETOC (2005)
bacteria		exposure based waiving	ECHA
Hydrolysis and biological degradation behaviour			
hydrolysis		not relevant	
photolysis		reacts with OH radicals to form carbonyl fluoride and trifluoroacetyl fluoride. Half-life in the atmosphere 6.2 d (Acerboni et al. 2001) Reaction in the atmosphere with photochemically produced OH radicals and ozone results in half-lives of 21 or 95 d.	ECHA HSDB
degradation		QSAR- estimate. No significant degradation. No experimental data available	ECHA ECETOC (2005)
Potential for bioaccumulation			
		due to the volatility and the log K_{ow} <3.0, low bioaccumulation potential expected. BCF values estimated by various methods are between 2.0 and 8.6 low bioaccumulation: estimate BCF = 24.	ECHA ECETOC (2005) HSDB
Risk assessment and safety information			
classification GHS	harmonized classification in Acute Tox. 4 (H332) and specific target organ toxicity STOT SE 3: May cause respiratory irritation (H335).		ECHA

A.9 Annex to the projections in Chapter 3

Table A 5: Stock shares of different refrigerants and their alternatives in different sectors in Germany from 2010 to 2016 in percent. Source: Warncke et al. (2017). -, No data available.

Sector	Refrigerant used	2010	2011	2012	2013	2014	2015	2016
Passenger cars								
	HFC-134a	100 %	100 %	100 %	99.8 %	99.4 %	98.6 %	94.4 %
	alternatives	0 %	0 %	0 %	0.2 %	0.6 %	1.4 %	5.6 %
	u-HFC-1234yf	0 %	0 %	0 %	0.2 %	0.6 %	1.4 %	5.6 %
Supermarket								
	HCFC-22	6 %	0 %	0 %	0 %	0%	0%	0 %
	R404A	75 %	79 %	81 %	82 %	79 %	75 %	68.3%
	R407C	2 %	1 %	1 %	0 %	0 %	0 %	0 %
	HFC-134a	11 %	11 %	10 %	11 %	11 %	12 %	13.4 %
	R422 (retrofit)	5 %	6 %	3 %	1 %	0 %	0 %	0 %
	alternatives							
	R410A	0 %	0 %	0 %	0 %	1 %	1 %	3.4 %
	R744 (CO_2)	2 %	3 %	4 %	6 %	9 %	12 %	14.4 %
	R449A	0 %	0 %	0 %	0 %	0 %	1 %	1.9 %
	R448A	0 %	0 %	0 %	0 %	0 %	0 %	0.4 %
Discounter								
	R404A	54 %	54 %	53 %	52 %	51 %	48%	44.3 %
	HFC-134a	45 %	45 %	45 %	46 %	46 %	48%	48.8 %
	alternatives							
	R410A	0 %	0 %	0 %	0 %	1 %	1 %	1.2 %
	R744 (CO_2)	1 %	1 %	1 %	2 %	3 %	4 %	5.2 %
	R290	0 %	0 %	0 %	0 %	0 %	0 %	0.5 %
Movable room air conditioning								
	HCFC-22	9 %	4 %	2 %	1 %	0 %	0 %	0 %
	R407C	71 %	72 %	70 %	68 %	64 %	56.3 %	49.8 %
	R410A	15 %	19 %	23 %	27 %	31 %	43.7 %	50 %
	alternatives							
	HFC-32	0 %	0 %	0 %	0 %	0 %	0 %	0.2 %
	hydrocarbons	5 %	5 %	5 %	5 %	5 %	5 %	-

Table A 6: Assumptions on the market penetration of refrigerants and propellants in the various areas of application up to 2050 in the EU-28 in percent in the AnaFgas model. For standardized mixtures (e.g. R450A / R513A) the mean GWP for both mixtures is given.

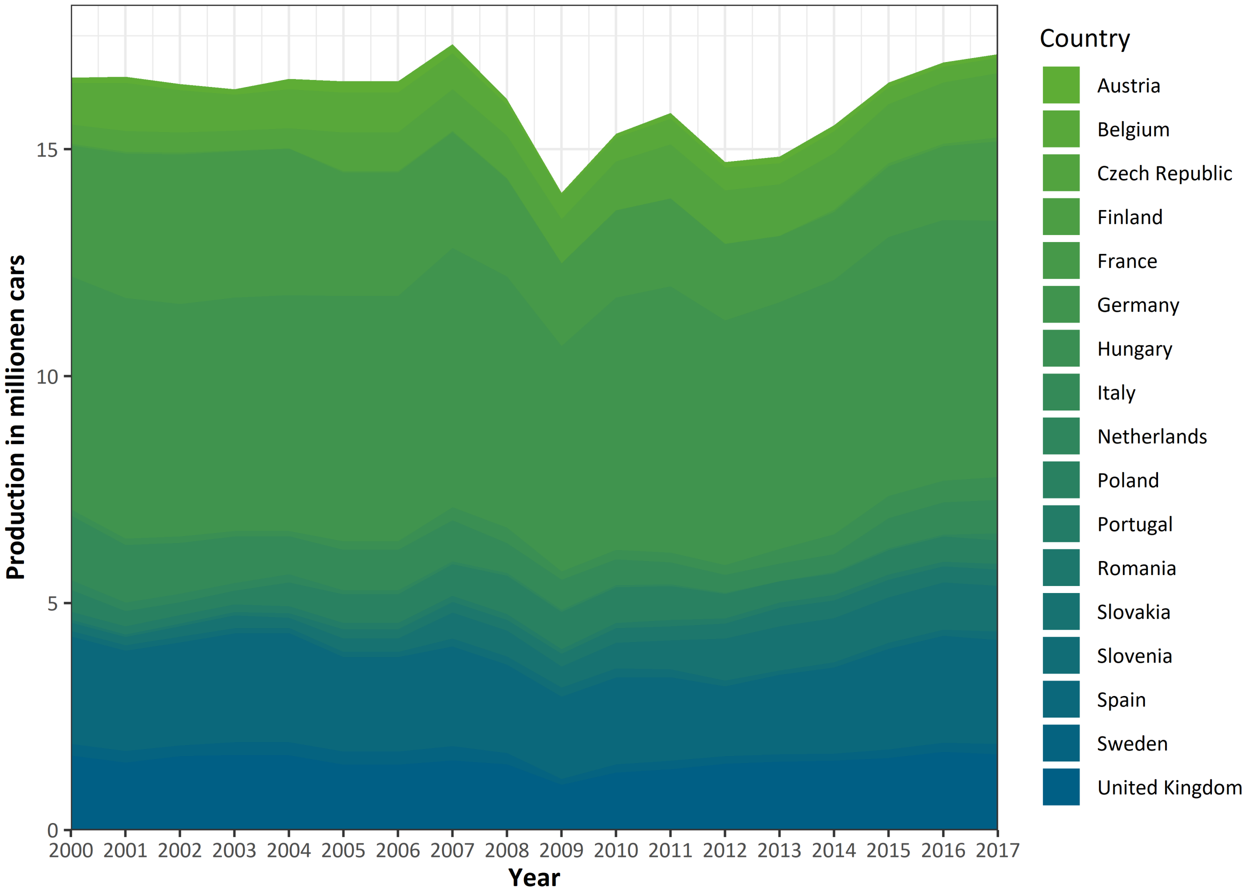
Area of application	Refrigerant / blowing agent and possible low-GWP alternatives	GWP	Year				
			2018	2019	2020	2030	2050
Domestic refrigeration							
	R600a (isobutane)	3	**100**	**100**	**100**	**100**	**100**
Commercial refrigeration							
Hermetic (plug-in) units							
	HFC-134a	1,430	**70**	**45**	**20**	**0**	**0**
	R455A/R454C	148	**0**	**25**	**50**	**70**	**70**
	R290 (propane) direct	3	**30**	**30**	**30**	**30**	**30**
Centralized systems							
	R404A (80 % share) and HFC-134a (20 % share)	3,922 and 1,380	**53**	**20**	**5**	**0**	**0**
	R448A/R449A	1,392	**30**	**30**	**20**	**5**	**0**
	R513A (also in cascade)	631	**0**	**10**	**15**	**20**	**15**
	u-HFC-1234ze + R744 (CO_2) cascade (subcritical)	7 and 1	**0**	**5**	**5**	**5**	**5**
	hydrocarbons	3-6	**2**	**5**	**5**	**10**	**10**
	R744 (CO_2) (transcritical)	1	**15**	**20**	**35**	**40**	**40**
	other systems/technologies	-	**0**	**10**	**15**	**20**	**30**
Condensing units							
	R404A	3,922	**30**	**0**	**0**	**0**	**0**
	HFC-134a	1,430	**70**	**25**	**10**	**0**	**0**
	R448A/R449A	1,392	**0**	**15**	**15**	**10**	**0**
	R513A	631	**0**	**30**	**15**	**5**	**0**
	R454C/R455A	148	**0**	**5**	**15**	**20**	**25**
	u-HFC-1234ze	7	**0**	**5**	**10**	**20**	**25**
	R290 (propane)	3	**0**	**10**	**15**	**20**	**20**
	R744 (CO_2)	1	**0**	**10**	**20**	**25**	**30**
Industrial refrigeration							
	R404A	3,922	**25**	**0**	**0**	**0**	**0**
	R134a	1,430	**30**	**20**	**5**	**0**	**0**
	R450A/R513A	618	**5**	**25**	**30**	**10**	**0**
	u-HFC-1234ze	7	**0**	**10**	**15**	**20**	**20**
	hydrocarbons	3-6	**0**	**0**	**5**	**10**	**10**
	R717 (NH_3)	0	**40**	**45**	**45**	**60**	**70**

Area of application	Refrigerant / blowing agent and possible low-GWP alternatives	GWP	Year				
			2018	2019	2020	2030	2050
Transport refrigeration							
Trucks, trailer and container							
	R404A	3,922	**15**	**5**	**0**	**0**	**0**
	R452A	2,140	**65**	**70**	**0**	**0**	**0**
	HFC-134a	1,430	**20**	**5**	**0**	**0**	**0**
	R513A	631	**0**	**20**	**50**	**20**	**0**
	R454C/R455A	148	**0**	**0**	**50**	**70**	**90**
	R744 (CO_2)	1	**0**	**0**	**0**	**10**	**10**
Vans <3.5 tonnes							
	R404A	3,922	**20**	**0**	**0**	**0**	**0**
	R452A	2,140	**20**	**40**	**10**	**0**	**0**
	HFC-134a	1,430	**60**	**30**	**0**	**0**	**0**
	R513A	631	**0**	**20**	**40**	**5**	**0**
	R454C/R455A	148	**0**	**10**	**50**	**90**	**90**
	R744 (CO_2)	1	**0**	**0**	**0**	**5**	**10**
Stationary air conditioning							
Mobile room air conditioners							
	R410A	2,088	**75**	**30**	**0**	**0**	**0**
	HFC-32	675	**15**	**30**	**20**	**0**	**0**
	R454C/R455A	148	**0**	**30**	**70**	**90**	**90**
	R290 (propane) direct	1	**10**	**10**	**10**	**10**	**10**
Single-split air conditioners							
	R410A	2,088	**70**	**20**	**0**	**0**	**0**
	HFC-32	675	**30**	**35**	**15**	**0**	**0**
	R454C/R455A	148	**0**	**45**	**85**	**100**	**100**
Multi-split air conditioners / variable refrigerant flow (VRF)							
	R410A	2,088	**85**	**35**	**0**	**0**	**0**
	R466A	733	**0**	**5**	**5**	**5**	**5**
	HFC-32	675	**15**	**15**	**20**	**0**	**0**
	R454C/R455A	148	**0**	**45**	**75**	**95**	**95**
Heat pumps							
	R410A	2,088	**48**	**35**	**5**	**0**	**0**
	R407C	1,774	**40**	**20**	**0**	**0**	**0**
	HFC-134a	1,430	**10**	**0**	**0**	**0**	**0**
	HFC-32	675	**0**	**20**	**35**	**5**	**5**
	R513A	631	**0**	**5**	**5**	**5**	**5**
	R454C/R455A	148	**0**	**10**	**45**	**80**	**80**

Area of application	Refrigerant / blowing agent and possible low-GWP alternatives	GWP	Year				
			2018	2019	2020	2030	2050
	R600a (isopentane)	3	**2**	**5**	**10**	**10**	**10**
Mobile air conditioning							
Passenger cars							
	u-HFC-1234yf	4	**100**	**99**	**95**	**90**	**80**
	R744 (CO_2)	1	**0**	**1**	**5**	**10**	**20**
Commercial vehicles							
	HFC-134a	1,430	**80**	**80**	**10**	**0**	**0**
	u-HFC-1234yf	4	**20**	**20**	**80**	**90**	**90**
	R744 (CO_2)	1	**0**	**0**	**10**	**10**	**10**
Buses							
	HFC-134a	1,430	**99**	**80**	**10**	**0**	**0**
	R513A	631	**1**	**20**	**80**	**80**	**80**
	R744 (CO_2)	1	**0**	**0**	**10**	**20**	**20**
Trains							
	HFC-134a	1,430	**99**	**90**	**10**	**0**	**0**
	R513A	631	**0**	**5**	**60**	**50**	**50**
	R744 (CO_2)	1	**0**	**0**	**20**	**30**	**30**
	R729 (air)	0	**1**	**5**	**10**	**20**	**20**
Chiller							
Displacement compressor							
	high-GWP gases (R407C, R404A, HFC-134a)	1,430-3,922	**80**	**50**	**0**	**0**	**0**
	R466A	733	**0**	**10**	**15**	**5**	**0**
	R454C/R455A	148	**0**	**13**	**45**	**45**	**45**
	u-HFC-1234ze	7	**0**	**2**	**10**	**20**	**20**
	R717 (NH_3)	0	**20**	**25**	**25**	**25**	**30**
	R718 (H_2O)	0	**0**	**0**	**5**	**5**	**5**
Centrifugal compressor							
	high-GWP gases (R410A and HFC-134a)	2,088 and 1,430	**75**	**30**	**0**	**0**	**0**
	u-HFC-1234ze	7	**12,5**	**35**	**50**	**50**	**50**
	u-HCFC-1233zd	4,5	**12,5**	**35**	**50**	**50**	**50**
Foam blowing agents							
PU foam							
	High-GWP gases (HFC-134a, HFC-245fa, HFC-365mfc)	794-1,430	**99**	**90**	**75**	**0**	**0**

Area of application	Refrigerant / blowing agent and possible low-GWP alternatives	GWP	Year 2018	2019	2020	2030	2050
	u-HCFC-1233zd	4,5	**0,5**	**5**	**25**	**50**	**50**
	u-HFC-1336mzz	9	**0,5**	**5**	**25**	**50**	**50**
One-component foam							
	HFC-134a	1,430	**1**	**1**	**1**	**1**	**1**
	hydrocarbons	3-6	**99**	**99**	**99**	**99**	**99**
XPS foam							
	HFC-134a	1,430	**40**	**0**	**0**	**0**	**0**
	HFC-152a	124	**50**	**20**	**10**	**0**	**0**
	u-HFC-1234ze	7	**10**	**80**	**90**	**100**	**100**
Propellants							
Technical aerosols							
	u-HFC-1234ze	7	**100**	**100**	**100**	**100**	**100**
Metered dose inhalers (MDIs)							
	HFC-227ea	3,220	**12**	**12**	**12**	**12**	**12**
	HFC-134a	1,430	**88**	**88**	**88**	**88**	**88**
Others							
Solvents							
	HFC-43-10mee	1,640	**-**	**-**	**-**	**-**	**-**
Fire extinguishing agents							
	HFC-227ea	3,220	**10**	**5**	**3**	**0**	**0**
	fluoroketone	-	**90**	**95**	**98**	**100**	**100**
Semiconductor industry							
	HFC-23	14,800	**3**	**3**	**3**	**3**	**3**
	SF_6 and CFCs	-	**97**	**97**	**97**	**97**	**97**
Emissions from the production of halogenated hydrocarbons							
	HFC-23	14,800	**31**	**31**	**31**	**31**	**31**
	HFC-143a	4,470	**9**	**9**	**9**	**9**	**9**
	HFC-125	3,500	**18**	**18**	**18**	**18**	**18**
	HFC-227ea	3,220	**1**	**1**	**1**	**1**	**1**
	HFC-134a	1,430	**13**	**13**	**13**	**13**	**13**
	HFC-365mfc	794	**1**	**1**	**1**	**1**	**1**
	HFC-32	675	**9**	**9**	**9**	**9**	**9**
	SF_6 and CFCs	-	**18**	**18**	**18**	**18**	**18**

Figure A 1: Production quantities of cars in 17 important EU Member States for the years 1999 to 2017.



Source: Data from the statistics of the "Organization Internationale des Constructeurs d'Automobiles" (OICA, International Association of Automobile Manufacturers), own illustration, Öko-Recherche

A.10 Annex to the results of the precipitation analysis from Chapter 4

A.10.1 Materials for rainwater sampling

Table A 7: Material that was made available to each DWD station involved in the measurement program.

Items	Number
Centrifuge tube (polypropylene, 15 mL nominal volume) with screw cap (polypropylene)	500–600 pieces
Waterproof pen	1 piece
Sampling protocol	25 pieces
Small shipping boxes (largest possible maxi letter)	25 pieces
Self-adhesive stamps at 2.60 Euros each	25 pieces
Packaging tape	1 role
All-purpose freezer bags	>25 pieces
Address label TZW-Karlsruhe	25 pieces

A.10.2 Sampling protocol for collecting rainwater samples

“In the event of precipitation, we would like to ask you to homogenize the collected rainwater by shaking it briefly and to fill one of the tubes with approx. 10 mL of the precipitation.

Please close the tube tightly again and label it with the 8-digit sample code. The sample code consists of the abbreviation of your measuring station, the year, month, and the serial number within a month. For example, the first sample in March 2018 at the Stuttgart station receives the code SU180301. You can take the codes from the template for the sample documentation. In addition, we would like to ask you to document the amount of precipitation that has fallen during the sampled event. We need the amount of precipitation i.a. for creating volume-equivalent monthly mixed samples from the individual samples you have collected.

At the end of the respective collection month, please send the collected samples of the month together with the documentation of the corresponding precipitation amounts to the address below. The shipping material and other sampling vessels will be sent to you in February.

To ensure this, a sample of the deionized water should also be taken in the first month. To do this, take one of the tubes and fill it with deionized water (approx. 10 mL). Please label it with ION, station abbreviation and the year and month of the sampling. Example for Stuttgart in March 2018: SUION1803.

In addition, please take a sample of the drinking water on site in the first month. To do this, take one of the tubes and fill it (approx. 10 mL) after the drinking water has run for approx. 10 seconds. Please label it with TW, station abbreviation and the year and month of the sampling. Example for Stuttgart in March 2018: SUTW1803.

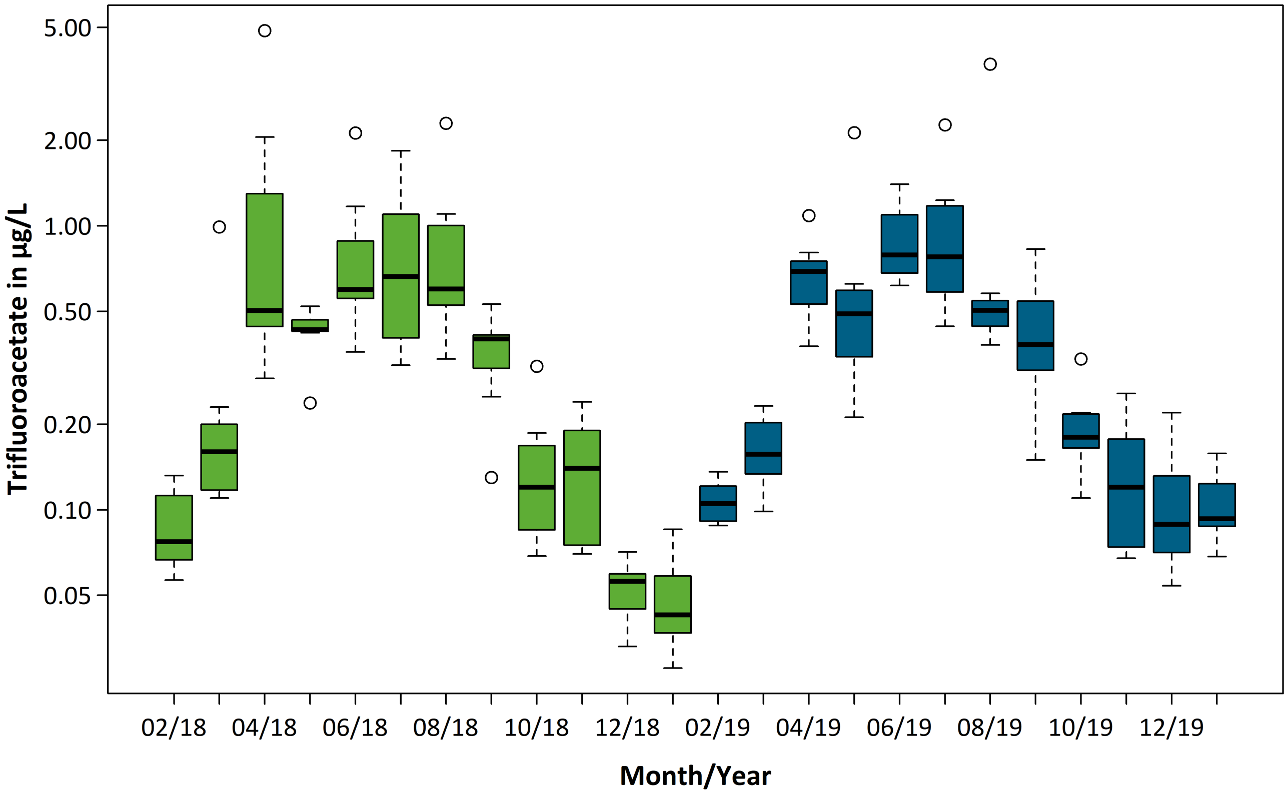
Sampling should start on February 1st, 2018 if possible (or upon receipt of the materials, should this be the case after February 1st) and be carried out continuously until March 1st, 2020. Samples are taken from the collecting container of one of the two precipitation collecting trays to change samples (generally 09:00 UTC in routine operation, 06:00 UTC intensive operation).

If you have a refrigerator on site, the samples should be kept in this until they are sent. If there is no refrigerator, please store the samples in a cool and shady place.

After taking the sample and before shipping, please ensure that the sample containers are well closed."

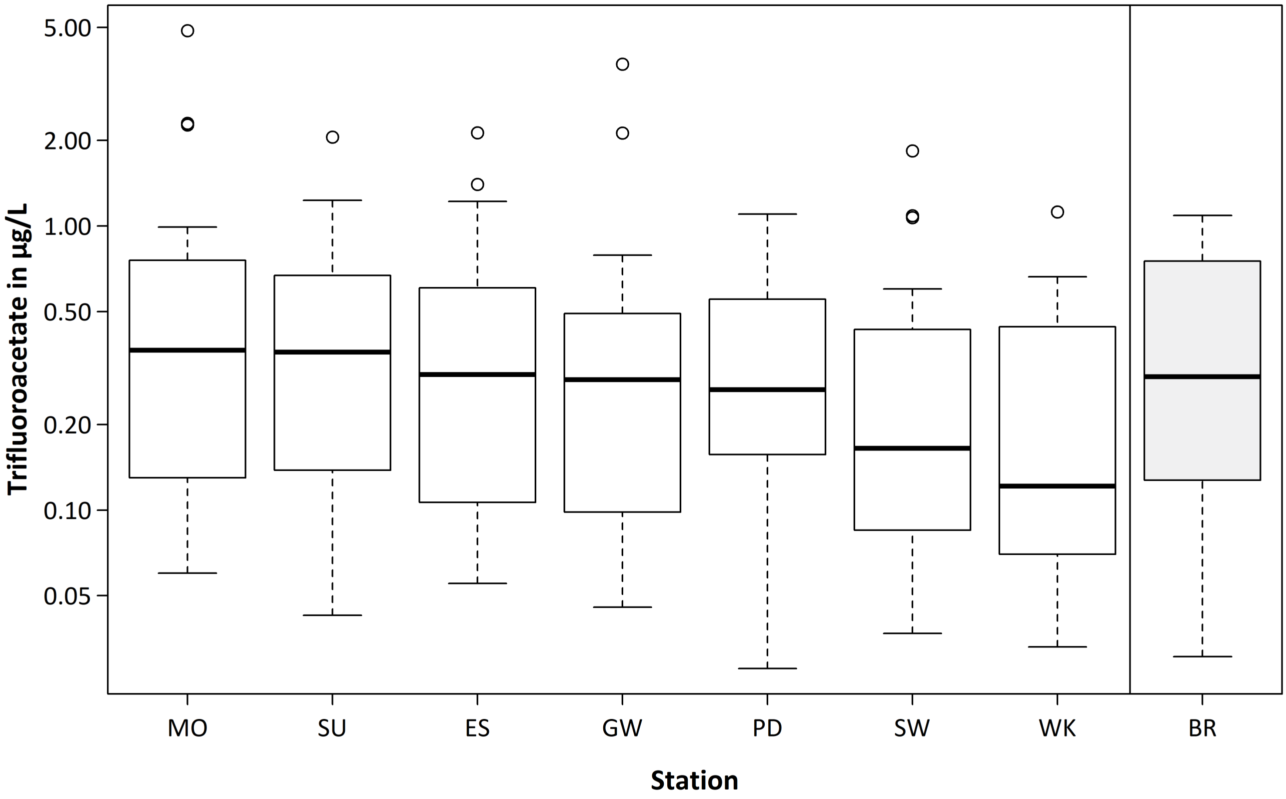
A.10.3 Analysis results

Figure A 2: Box plots of the precipitation-weighted trifluoroacetate concentrations of the volume-equivalent monthly mixed samples of the precipitation from February 2018 (02/18) to January 2020 from seven of the eight measuring stations. Data for the Brocken station are not shown because, in contrast to the results of the other stations, they contain the sums of wet and dry deposition. The worst-case scenario is shown. Grouping of data based on time (month and year). The Stuttgart station is not included in 02/18. The y-axis is scaled binary logarithmically. The periods from February to January are highlighted in different colors.



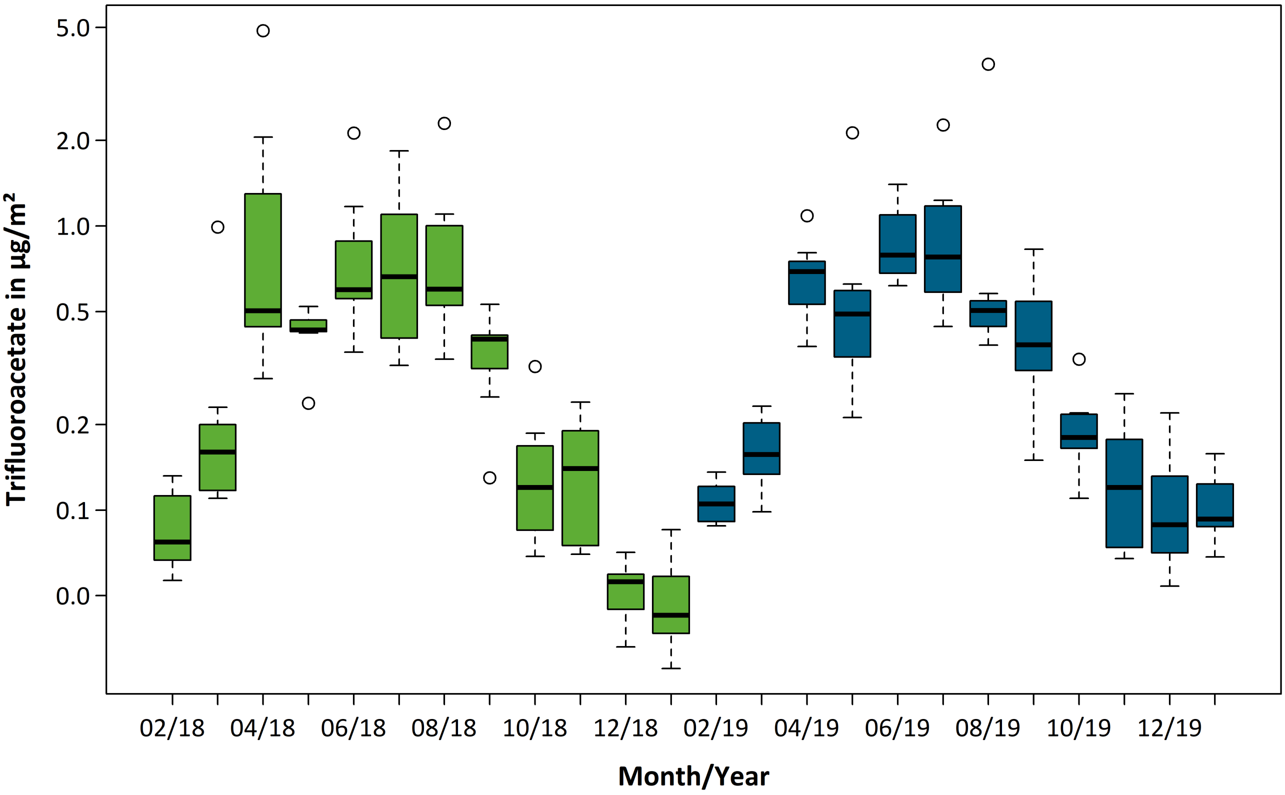
Source: own illustration, Öko-Recherche and TZW Karlsruhe

Figure A 3: Box plots of the trifluoroacetate concentrations of the volume-equivalent monthly mixed samples of the precipitation from February 2018 to January 2020 (for the Stuttgart station from March 2018 to January 2020). The worst-case scenario is shown. Grouping of the data based on the location (measuring station). Order of the measuring stations according to the descending median concentration. The y-axis is scaled binary logarithmically. At the Brocken (BR) station, wet and dry deposition were recorded together, at all other stations only wet deposition.



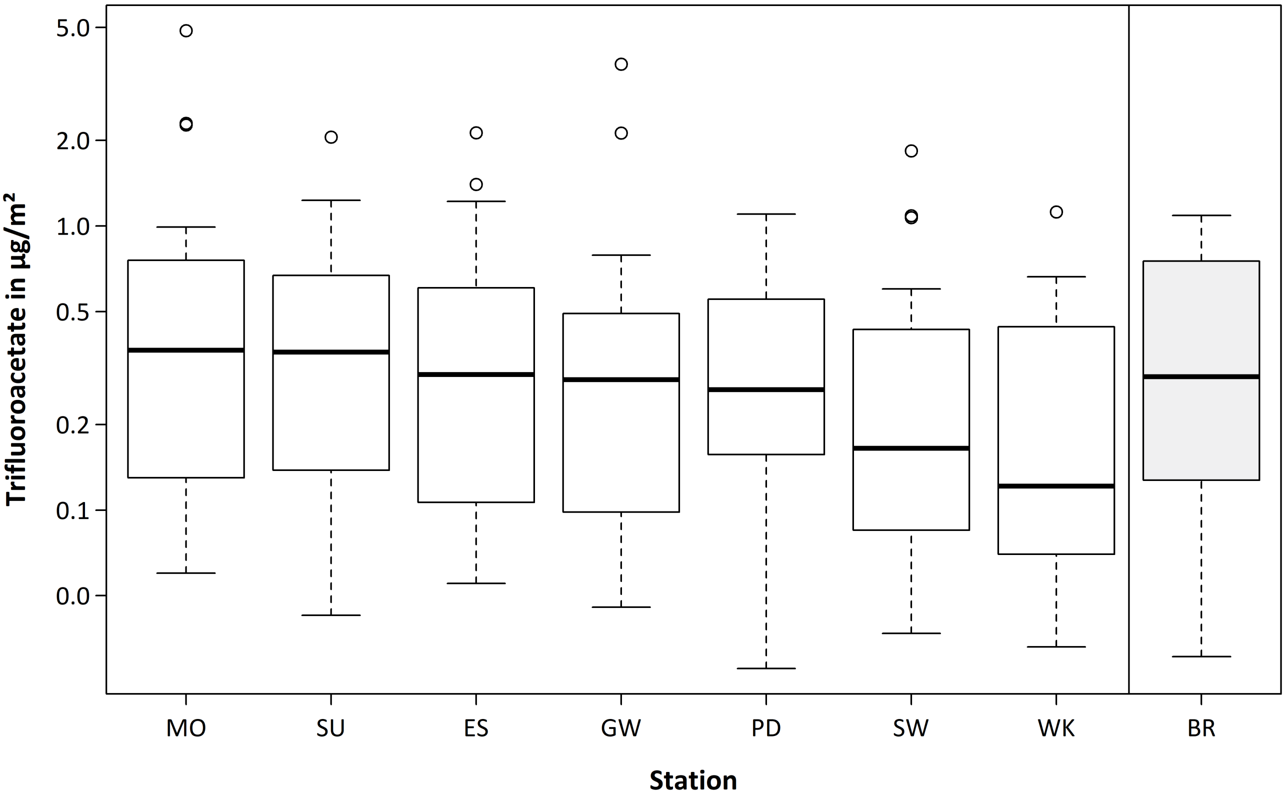
Source: own illustration, Öko-Recherche and TZW Karlsruhe

Figure A 4: Box plots of the trifluoroacetate deposition via precipitation from February 2018 (02/18) to January 2020 (analysis of the volume-equivalent monthly mixed samples) of all 7 measuring stations, exclusively measuring the wet deposition. The worst-case scenario is shown. Grouping of data based on time (month and year). Station Stuttgart not included in 02/18. Data for the Brocken station are not shown, as they include the sum of wet and dry deposition. The y-axis is scaled binary logarithmically. The periods from February to January are highlighted in color.



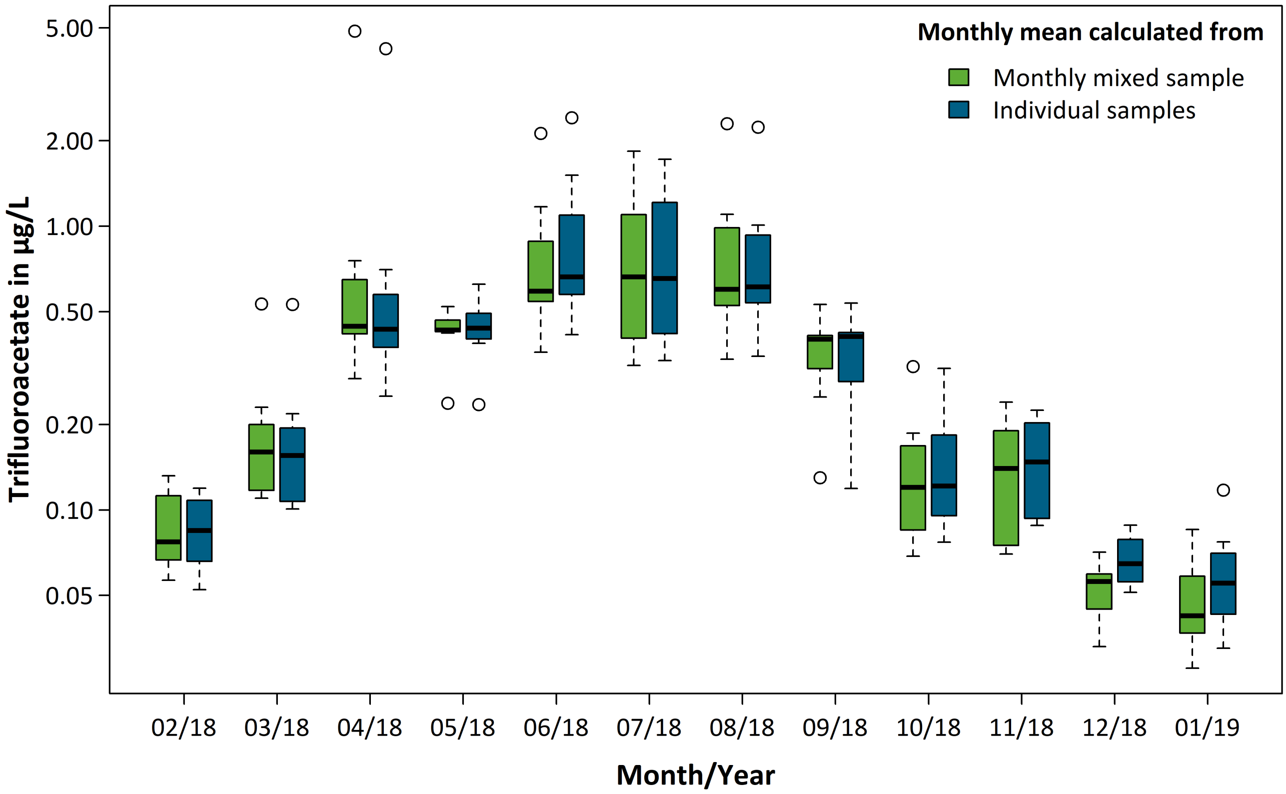
Source: own illustration, Öko-Recherche and TZW Karlsruhe

Figure A 5: Box plots of the trifluoroacetate deposition via precipitation (analysis of the volume-equivalent monthly mixed samples) from February 2018 to January 2020 (for Stuttgart station: from March 2018 to January 2020). The worst-case scenario is shown. Grouping of the data based on the location (measuring station); Order of the measuring stations according to descending median entry. The y-axis is scaled binary logarithmically. Wet and dry deposition were recorded together at the Brocken (BR) station, only wet deposition at all other stations.



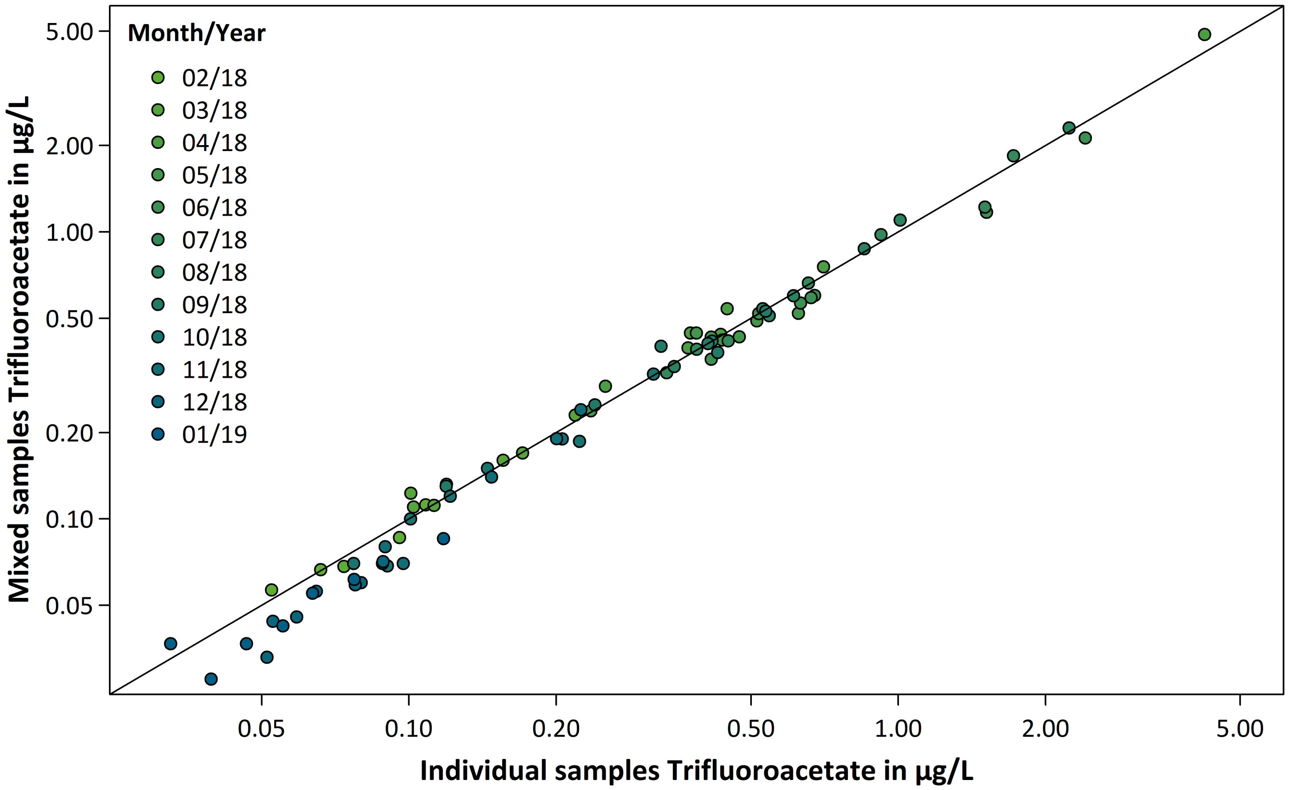
Source: own illustration, Öko-Recherche and TZW Karlsruhe

Figure A 6: Monthly mean values of the trifluoroacetate concentration in rainwater over all measuring stations in the course of the year, measured using two analyzes, volume-equivalent monthly mixed values in the period February 2018 (02/18) to January 2019 (01/19) and based on the individual samples (best-case Scenario) for the same period. The y-axis is scaled binary logarithmically.



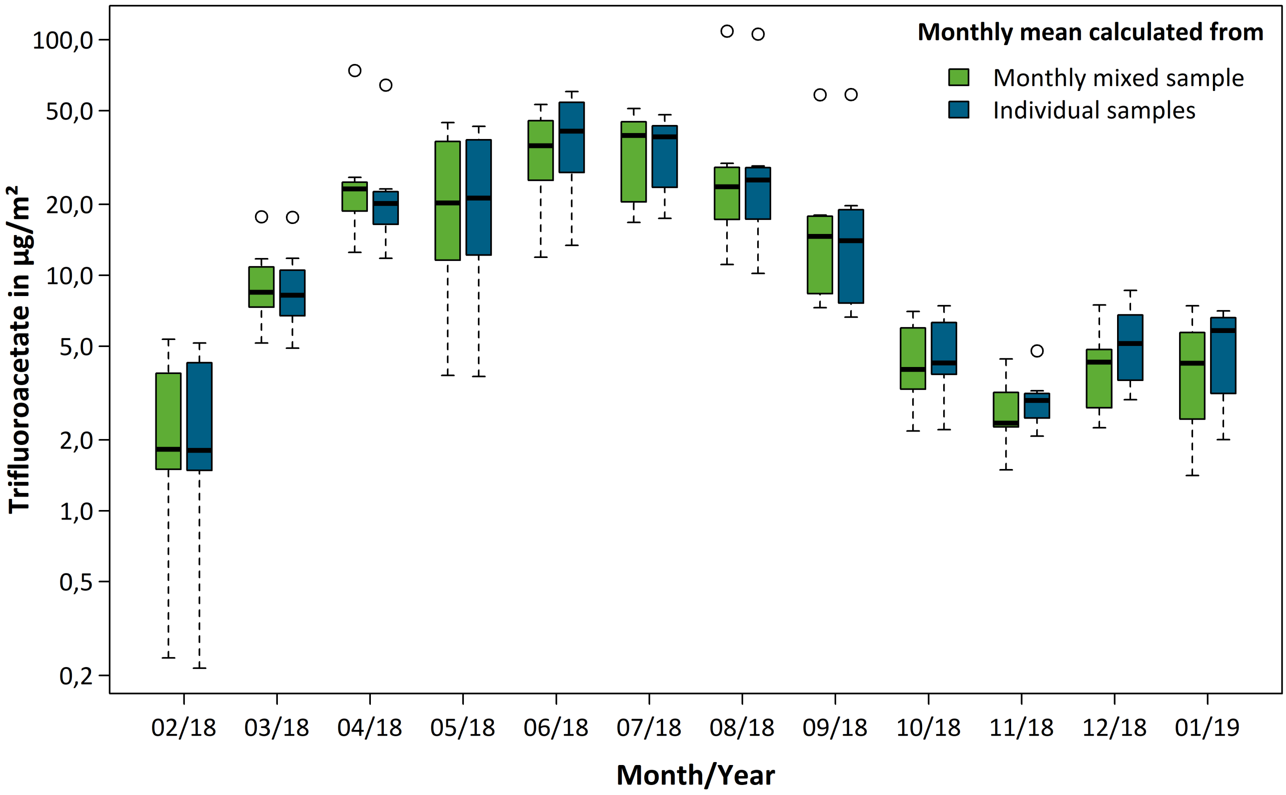
Source: own illustration, Öko-Recherche and TZW Karlsruhe

Figure A 7: Monthly mean values of the trifluoroacetate concentration in rainwater over all measuring stations in the course of the year, measured using two analyzes, volume-equivalent monthly mixed values in the period February 2018 (02/18) to January 2019 (01/19) and based on the individual samples (best-case Scenario) for the same period. The x- and y-axes are scaled binary logarithmically. Points on the line are identical.



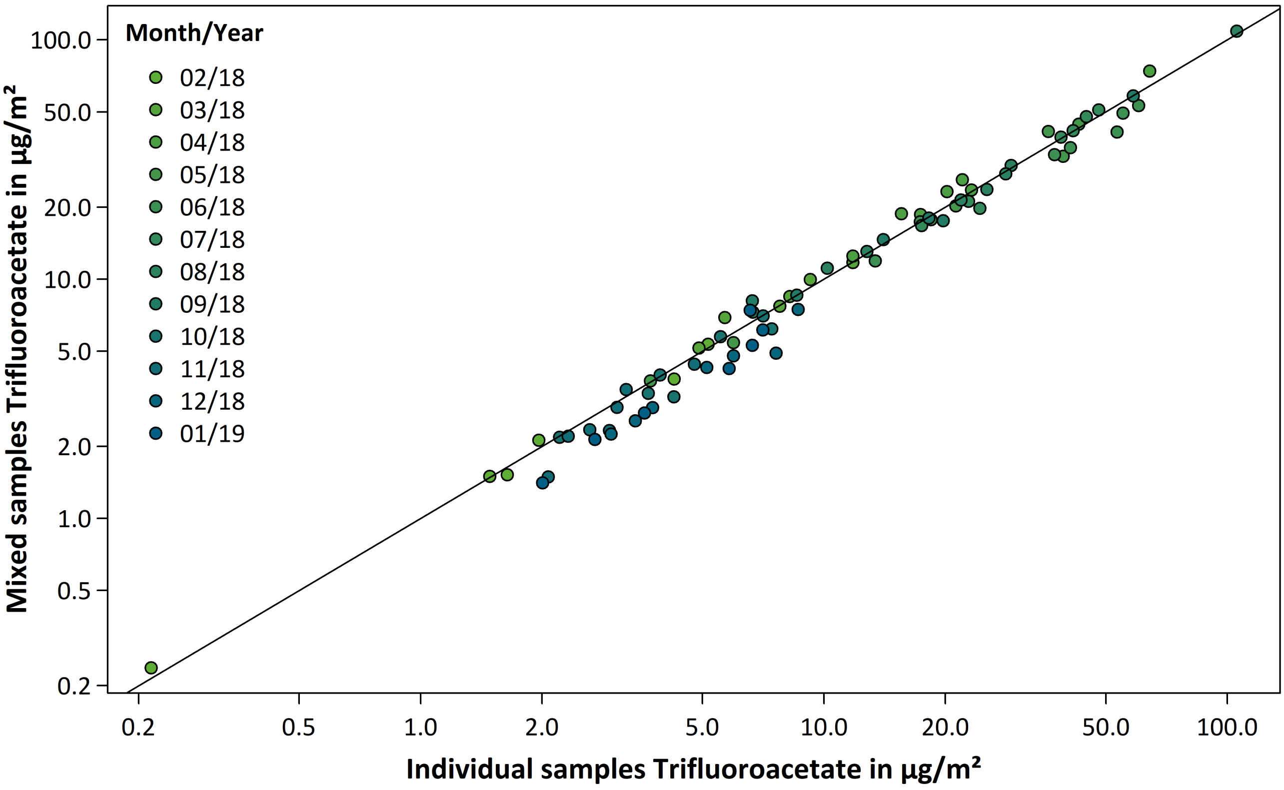
Source: own illustration, Öko-Recherche and TZW Karlsruhe

Figure A 8: Monthly mean values of the trifluoroacetate deposition from the rainwater over all measuring stations in the course of the year, measured on the basis of two analyzes, volume-equivalent monthly mixed samples in the period February 2018 (02/18) to January 2019 (19/01) and on the basis of the individual samples (best-case Scenario) for the same period. The y-axis is scaled binary logarithmically.



Source: own illustration, Öko-Recherche and TZW Karlsruhe

Figure A 9: Monthly mean values of the trifluoroacetate deposition from the rainwater over all measuring stations in the course of the year, measured on the basis of two analyzes, volume-equivalent monthly mixed samples in the period February 2018 (02/18) to January 2019 (19/01) and on the basis of the individual samples (best-case Scenario) for the same period. The x and y axes are scaled binary logarithmically. Points on the line are identical.



Source: own illustration, Öko-Recherche and TZW Karlsruhe

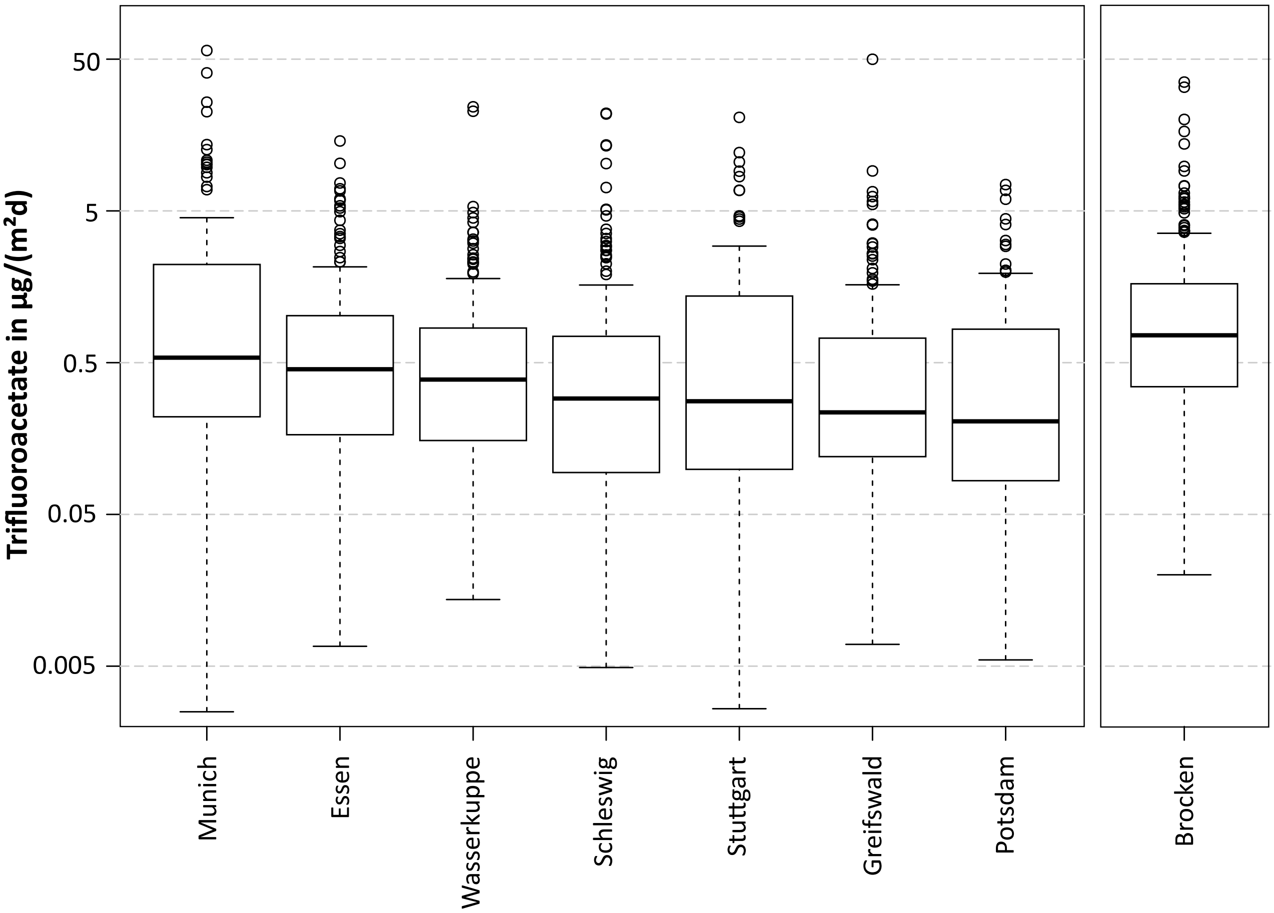
Table A 8: Overview of sample size, annual precipitation, as well as a summary of the trifluoroacetate concentrations of the individual measurements at the locations examined. Detection limit (DL): 0.025 µg/L. The worst-case scenario is shown. Investigation period: February 2018 to January 2019 (for the Stuttgart station: March 2018 to February 2019). Concentrations with three significant digits each.

Station	Number of samples	Share of samples <DL	Total precipitation	Trifluoroacetate concentration			
				Maximum	Median	ROS-estimated mean	Precipitation-weighted mean
		%	mm	µg/L	µg/L	µg/L	µg/L (best-case)
Essen	149	3.4	653	17.2	0.255	0.692	0.347
Greifswald	147	10.2	440	26.3	0.210	0.875	0.364
Munich	111	3.6	772	38.0	0.310	1.30	0.544
Potsdam	123	4.9	337	3.94	0.227	0.447	0.271
Stuttgart	113	1.8	502	9.16	0.377	1.02	0.456
Schleswig	173	8.1	681	12.8	0.128	0.471	0.284
Wasserkuppe	160	13.8	890	2.58	0.128	0.334	0.186
all	**976**	**7.0**	**-**	**38.0**	**0.210**	**0.702**	**0.348**
Brocken	*211*	*4.7*	*1.130*	*20.6*	*0.248*	*0.895*	*0.258*

Table A 9: Summary of the trifluoroacetate flux (individual sample analysis) at the investigated locations. The worst-case scenario is shown. Study period: February 2018 to January 2019 (for the Stuttgart station: March 2018 to February 2019). Entries with three significant digits each.

Station	Maximum µg/(m²d) (worst-case)	Median µg/(m²d) (worst-case)	Mean µg/(m²d) (worst-case)	Annual total µg/(m²a) (worst-case)
Essen	14.4	0.452	1.17	226
Greifswald	50.0	0.235	1.09	160
Munich	57.0	0.540	3.10	420
Potsdam	7.46	0.205	0.743	91.4
Stuttgart	20.7	0.279	1.35	229
Schleswig	22.0	0.290	1.12	193
Wasserkuppe	24.3	0.387	1.04	166
all	**57.0**	**0.353**	**1.31**	**-**
Brocken	*35.3*	*0.758*	*1.92*	*343*

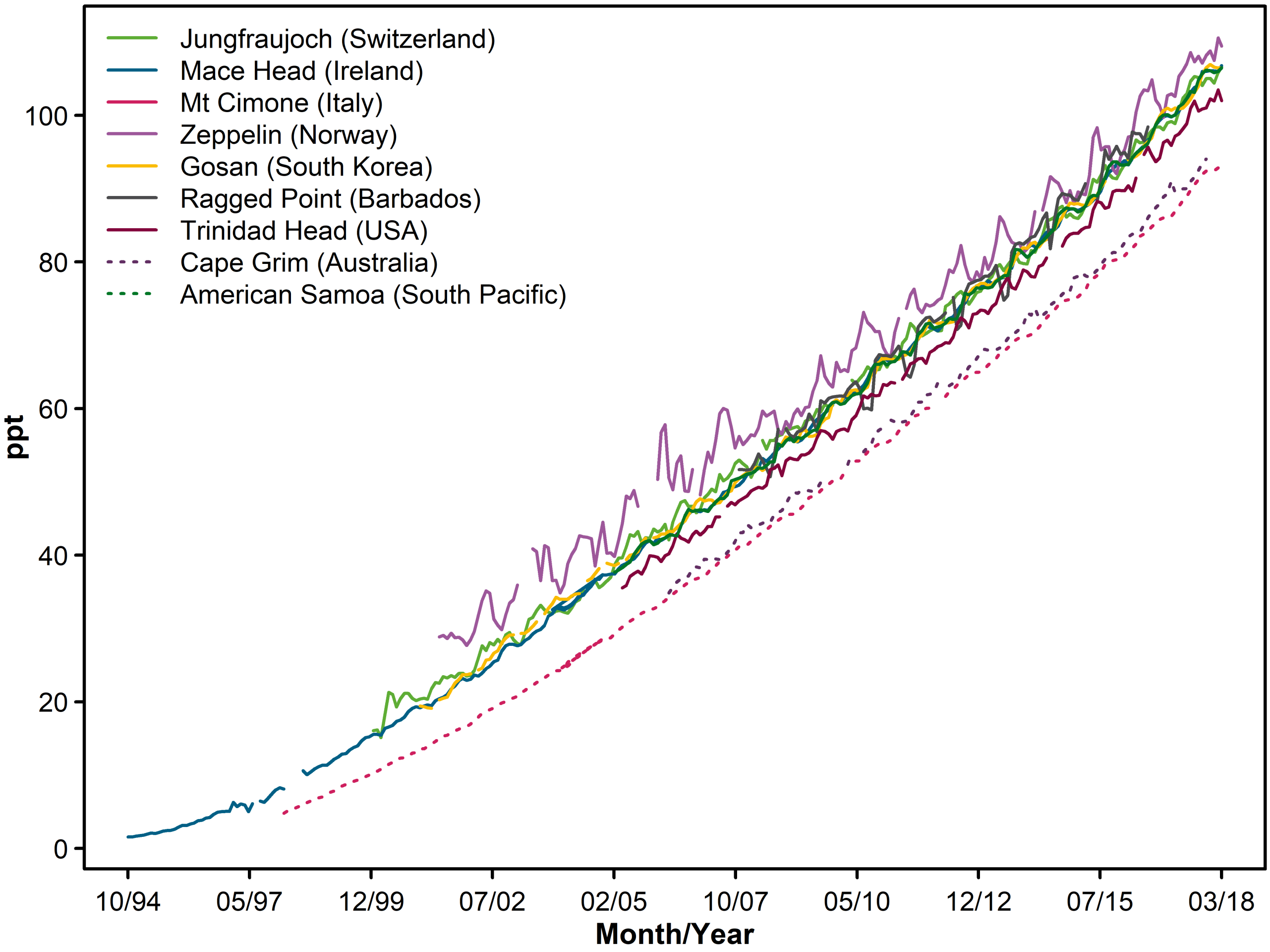
Figure A 10: Boxplots of trifluoroacetate flux of individual precipitation samples grouped by the sampling site. The worst-case scenario is shown. Note that the boxplot of site Stuttgart includes data from March 2018 to February 2019, whereas boxplots from other sites include data from February 2018 to January 2019. Sites are plotted in descending median order. The y-axis is on a logarithmic scale.



Source: own illustration, TZW Karlsruhe

A.11 Concentration of HFC-134a in the atmosphere

Figure A 11: Concentrations of HFC-134a in the atmosphere in ppt in the period from October 1994 (10/94) to March 2018 (03/18). Stations in the northern hemisphere are shown with solid lines, stations in the southern hemisphere with dotted lines.



Source: Data from the AGAGE network (https://agage.mit.edu/data/agage-data), own illustration, Öko-Recherche