

First Atmospheric Measurements and Emission Estimates of HFO-1336mzz(Z)

Dominique Rust^{a,b}, Martin K. Vollmer^{a,}, Stephan Henne^a, Tobias Bühlmann^c, Arnoud Frumau^d, Pim van den Bulk^d, Lukas Emmenegger^a, Renato Zenobi^b, Stefan Reimann^a*

^aLaboratory for Air Pollution/Environmental Technology, Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland

^bDepartment of Chemistry and Applied Biosciences, ETH, Swiss Federal Institute of Technology, Vladimir-Prelog-Weg 3, 8093 Zurich, Switzerland

^cLaboratory for Gas Analysis, METAS, Federal Institute of Metrology, Lindenweg 50, 3003 Bern-Wabern, Switzerland

^dDepartment of Environmental Modelling, Sensing & Analysis, TNO, Organisation for Applied Scientific Research, Westerduinweg 3, 1755LE Petten, the Netherlands

*Corresponding author

E-mail: martin.vollmer@empa.ch

Supporting Information

27 pages (including title page); 2 text sections; 3 tables (Table S1–S3);

10 figures (Figure S1–S10)

Atmospheric Properties

Table S1. Extended listing of the atmospheric properties of HFO-1336mzz(Z) (*cis*-CF₃CH=CHCF₃), HFO-1336mzz(E) (*trans*-CF₃CH=CHCF₃) and mixtures of the isomers.^a

atmospheric lifetime (days)	RE (W m ⁻² ppb ⁻¹)	GWP (100 yr)	GTP (100 yr)	ODP	k (296 K) for reaction with OH radical (cm ³ molecule ⁻¹ s ⁻¹)	k (296 K) for reaction with O ¹ D (cm ³ molecule ⁻¹ s ⁻¹)	k (296 K) for reaction with O ₃ (cm ³ molecule ⁻¹ s ⁻¹)	k (296 K) for reaction with Cl (cm ³ molecule ⁻¹ s ⁻¹)	POCP
HFO-1336mzz(Z)									
22 ¹	0.38 ¹	9 ²	<1 ³	0 ²⁻⁴	(4.91 ± 0.50)E– 13 ^{1,c} ; (5.18 ± 0.46)E–13 ^{1,d}	(5.73 ± 0.50)E–13 ^{1,c}	<6E–21 ¹	(2.59 ± 0.47)E–11 ^{5,e}	3.4 ¹
27 ^{3,5}	0.33 ⁵ ; 0.069 ^{5,b}	8.9 ¹			k(298 K) = (3.80 ± 0.04)E– 13 ^{6,f}	(6.94 ± 1.25)E–13 ^{5,e}	(6.25 ± 0.70)E– 22 ^{5,e}		3.1 ⁴
	0.42 ⁷ ; 0.07 ^{7,b}	2 ^{3,5,7}			(4.21 ± 0.62)E–13 ^{5,e}				
21 ⁶	0.08 ^{3,b}								
HFO-1336mzz(E)									
67 ⁵	0.30 ⁵ ; 0.11 ^{5,b}	7 ⁵	5 ³	0 ³	k(298 K) = (5.86 ± 0.06)E–	(5.61 ± 0.98)E– 13 ^{5,e}	(4.14 ± 0.42)E–22 ^{5,e}	(1.36 ± 0.27)E–11 ^{5,e}	

				13 ^{6,f}	
121 ³	0.19 ^{3,b}	26 ³		(1.72 ± 0.42)E– 13 ^{5,c}	
34 ⁶					
Mixture E/Z-isomers					
24 ^{8,h}	0.32 ^{8,h}	6 ^{8,h}	0 ⁹	k(298 K) = (5.05 ± 0.09)E– 13 ^{6,f,i}	(7.27 ± 0.88)E– 12 ^{8,d,h}
31 ^{9,h}	0.30 ^{9,h}	5 ^{9,h}		(4.82 ± 1.15)E– 13 ^{8,d,h}	
				k(298 K) = (3.7 ± 0.2)E–13 ^{9,h,g}	

^agiven is the radiative efficiency (RE), the global warming potential (GWP) on a 100 year horizon, the global temperature change potential (GTP) on a 100 year horizon, the reaction rate coefficient (k) for different reactions, the ozone-depletion potential (ODP), and the photochemical ozone creation potential (POCP); ^bwith correction factor for lifetime dependent vertical mixing/ adjusted number; ^cpulsed laser photolysis-laser induced fluorescence (PLP-LIF) technique; ^drelative rate-Fourier transform infrared spectroscopy (RR-FTIR) technique; ^ephotoreactor interfaced with FTIR (FTIR smog chamber experiment); ^fflash photolysis resonance fluorescence (FPRF) technique; ^grelative rate technique with gas chromatography coupled to flame ionization detection (GC-FID); ^hmixture of 70% E-isomer and 30% Z-isomer; ⁱindustrial mixture of 71.5% E-isomer and 28.5% Z-isomer; uncertainties at 2-sigma level

Company Information and Market Products

Table S2. Summary of press releases and marketing information found for HFO-1336mzz(Z).

HFO-1336mzz(Z)				
year	company	trade name/ patent	comment	references
2012	Du Pont de Nemours	patent US8287752B2	fire extinguishing	10
2014	DuPont		start of small scale production	11
2015	DuPont	Formacel™ 1100	tested as potential replacement for HCFC-141b (CH ₃ CCl ₂ F) as foam blowing agent	12
end 2015	Chemours & partner Changshu 3F Zhonghao		Announcement on start building full-scale production facility in Changshu, Jiangsu Province, China	13
2016	Chemours	Opteon™ 1100	first field application as foam blowing agent for an insulation closed cell spray polyurethane foam (SPF) in a residential home in Texas	14
mid-2017	Chemours		expected start full-scale production	13
			replacement refrigerant for HFC-245fa (CHF ₂ CH ₂ CF ₃) and HFC-365mfc (CH ₃ CF ₂ CH ₂ CF ₃) in organic Rankine cycles and high-temperature heat pumps	2,15–21
2020	Fumakilla Ltd, Chemours-	patent	pest-controlling agent	22

	Mitsui Fluoroproducts Co Ltd	WO2017/122684		
2020	Arkema France	patent JP2020007561A	blend with HCFO-1233zd ($\text{CF}_3\text{CH}=\text{CHCl}$); for use as refrigerant, heat transfer fluid, foaming agent, solvent and aerosol	23
2021	Chemours	Opteon™ 1100	sold as foam blowing agent	24
2021	Chemours	Opteon™ XP30 (R-514A, a blend of 74.7 wt% HFO-1336mzz(Z) and 25.3 wt% HCC-1130(E) ($\text{CHCl}=\text{CHCl}$))	sold as replacement for HCFC-123 (CF_3CHCl_2) for application in low pressure centrifugal chillers	25,26
2021	Chemours	Opteon™ MZ	sold as refrigerant for application in HTHPs, ORCs, evaporative cooling, and as heat transfer fluid	27
2021	Chemours	Opteon™ SF33	sold for application in metal degreasing, as cleaning and rinsing agent, and as solvent	28
2021	Chemours	1100/1500 Blends	foam blowing	29
2021	Climalife® of the Dehon Group	Novexpans™	advertised/ sold as foam blowing agent for PU foams, replacing the Novexpans™ HFC-365mfc/ HFC-227ea (CF_3CHF_2) (93/7) blend and HFC-245fa	30
2021	Chemours	Opteon™ 1150	announcement on production start of HFO-1336mzz(E) (<i>trans</i> - $\text{CF}_3\text{CH}=\text{CHCF}_3$) in El Dorado, Arkansas, US; assumption of possibility to re-isomerize between the two HFO-1336mzz isomers in the production plants	31

general areas of application/ products: heat transfer fluids (sector of end use: General manufacturing, e.g. machinery, equipment, vehicles, other transport equipment), foam expansion agent (sector of end use: Building and construction work), polymers, carrier fluid or aerosol (product category: semiconductors, sector of end use: Manufacture of computer, electronic and optical products, electrical equipment), cleaning agent (sector of end use: Manufacture of computer, electronic and optical products, electrical equipment), blowing agent (sector of end use: Other), di-electric insulation/ inerting agent	32
	33

Reported Information on or Application of HFO-1336mzz(Z) in Switzerland, Germany, Europe, and Other Countries

In Switzerland, reporting the import, placing on the market and use of HFO-1336mzz(Z) as a foam blowing agent, a solvent and a fire extinguishing agent is not mandatory. The application as a refrigerant in stationary air conditioners has to be reported when exceeding 3 kg. In Germany, the use of 10.1 Mg and 0.5 Mg for the production of integral and polyurethane (PU) foams, respectively, was reported for 2019³⁴. No data were reported for other applications. For 2020, no numbers were reported for HFO-1336mzz(Z)³⁵. In addition, for Germany it is not mandatory to report the import or export of finished goods containing this substance.

The European Chemicals Agency (ECHA)³² currently specifies imports to the European Economic Area of 100 to 1000 Mg yr⁻¹. In European Union (EU) member states, HFC-1336mzz(Z) is subject to reporting under the F-gas regulation in terms of "production, import, export, feedstock use and destruction"³⁶ since 2015. However, up to 2019, the reported usage numbers are marked confidential^{37,38}. A new proposal³⁹ for an update of the current F-gas regulation³⁶ was published in 2022, drafting tightened measures towards the use of low-GWP gases, for which HFOs like HFO-1336mzz(Z) are eligible. Furthermore, the European Commission's RePowerEU plan⁴⁰ set ambitious aims to expand the installation of heat pumps, for which HFO-1336mzz(Z) might also be contrived as candidate with high potential as a low-GWP working fluid. Behringer et al. (2021)³⁷ estimated an increase of demand in Europe (EU-28) of a factor of four between 2020 and 2030, and an increase of emissions by a factor of six between 2020 and 2030. However, in the debate of new Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulations in the EU, the refrigeration and air-conditioning industry was concerned that new alternatives like HFO-1336mzz(Z) could be

affected⁴¹. In 2023, a proposal to restrict per- and polyfluorinated substances (PFASs) was submitted to ECHA⁴², which could also apply to HFO-1336mzz(Z).

In the US, HFO-1336mzz(Z) was exempt from the volatile organic compound (VOC) regulation under the Clean Air Act (CAA) beginning of 2019, because its contribution to ground-level ozone formation was regarded negligible⁴³. Use of HFO-1336mzz(Z) as replacement substance in different applications is expected to increase in the US in the future⁴⁴. Also in Australia, the use of HFO-1336mzz(Z) has been and is expected to increase further, at least in its possible application as cooling agent⁴⁵. In Thailand funds were provided for a project on testing low-GWP foam blowing alternatives, specifically HFO-1336mzz(Z)^{46,47}. Overall, the increasing attention on HFO-1336mzz(Z) is reflected by the increasing number of published studies and granted patents involving HFO-1336mzz(Z)^{44,48}.

Sampling Sites and Analytical Details

Table S3. Details for the different sampling sites for in situ and flask measurements throughout the record of HFO-1336mzz(Z).^a

instrument/ site	time period	coordinates measurement site	geographic altitude (m a.s.l.)	inlet height (m a.g.l.)	description of site
Medusa-12					
Jungfrau-joch	31.01.2019– 31.12.2022	46.5° N, 8.0° E	3580	–15	high-Alpine site
Medusa-20					
Dübendorf	18.05.2018– 21.08.2019	47.4° N, 8.6° E	440	30	rooftop in suburban Zurich
Beromünster	22.08.2019– 28.08.2020	47.2° N, 8.2° E	797	212	tall tower in the center of the Swiss Plateau
Dübendorf	29.08.2020– 03.03.2021	47.4° N, 8.6° E	440	30	rooftop in suburban Zurich
Sottens	04.03.2021– 25.10.2021	46.7° N, 6.7° E	755	120	tall tower in the west of the Swiss Plateau
Cabauw	14.11.2021– 08.08.2022	52.0° N, 4.9° E	–0.7	207	tall tower in central Netherlands
King Sejong ⁴⁹	weekly, 2016–2021	–62.2° N, –58.8° E			flask measuremnts
Cape Grim ⁵⁰	distributed over 1990– 2007	–40.7° N, 144.7° E			flask measuremnts
^a measurement instruments Medusa-12 and Medusa-20; geographic altitudes and inlet heights as above sea level (a.s.l.) and as above ground level (a.g.l.)					

HFO-1336mzz(Z) peak identification on the used Medusa-gas chromatography/mass spectrometry (GC/MS) systems was achieved by measuring diluted samples of high-mole fraction standards made of the pure substance. For detection, mass/charge (m/z) 95 ($[M - CF_3]^+$) was used as the target mass, and m/z 145 ($[M - F]^+$) as the qualifying mass. In 200 mL of a sample at 2.16 ppb mole fraction (equivalent to 19 pmol), the following ions, in units m/z and in the order of decreasing relative abundance (in brackets), were detected: 95 (100%), 145 (56%), 69 (34%), 75 (14%), 164 (12%), 76 (6%), 113 (4%). Chromatographic separation on the two Medusa systems was achieved with a PoraBOND Q column (0.32 mm ID x 25 m; 5 μ m film thickness; Agilent), resulting in symmetric peaks with stable baseline. Depending on column age or column manipulation during maintenance, retention times of HFO-1336mzz(Z) varied over time. Therefore, only approximate time ranges for elution are given. On Medusa-20, HFO-1336mzz(Z) eluted between 1306 s and 1349 s. On Medusa-12, HFO-1336mzz(Z) eluted between 1294 s and 1377 s. On both Medusa systems, HFO-1336mzz(Z) was bracketed by HCFO-1233zdE (*trans*-CF₃CH=CHCl) and furane (C₄H₄O) at slightly lower retention times; and CFC-11 (CCl₃F), dichloromethane (CH₂Cl₂), and carbon disulphide (CS₂) at slightly higher retention times. Chromatograms were integrated by area. An example chromatogram showing the target and qualifier ion is given in Figure S1.

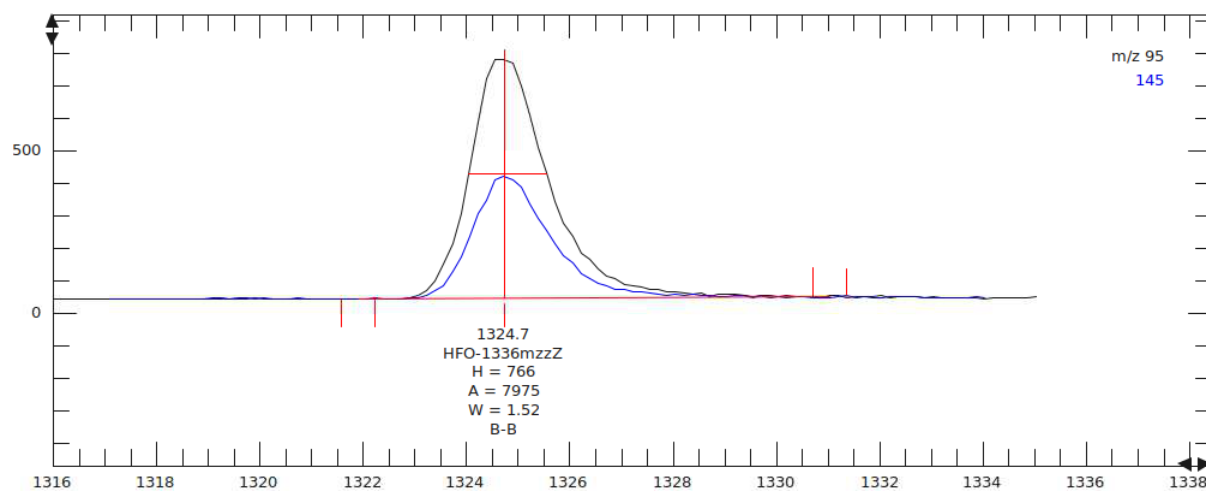


Figure S1. An example chromatogram (x-axis in (s); y-axis in arbitrary units) of HFO-1336mzz(Z) from the analysis of 2 L of a working standard (0.59 ppt) with the Medusa-20 GC-MS instrument. The target ion with mass/charge (m/z) 95 (black line), and the qualifier ion with m/z 145 (blue line) were detected at the retention time of 1324.7 s.

Evaluation of Measured HFO-1336mzz(Z) Records

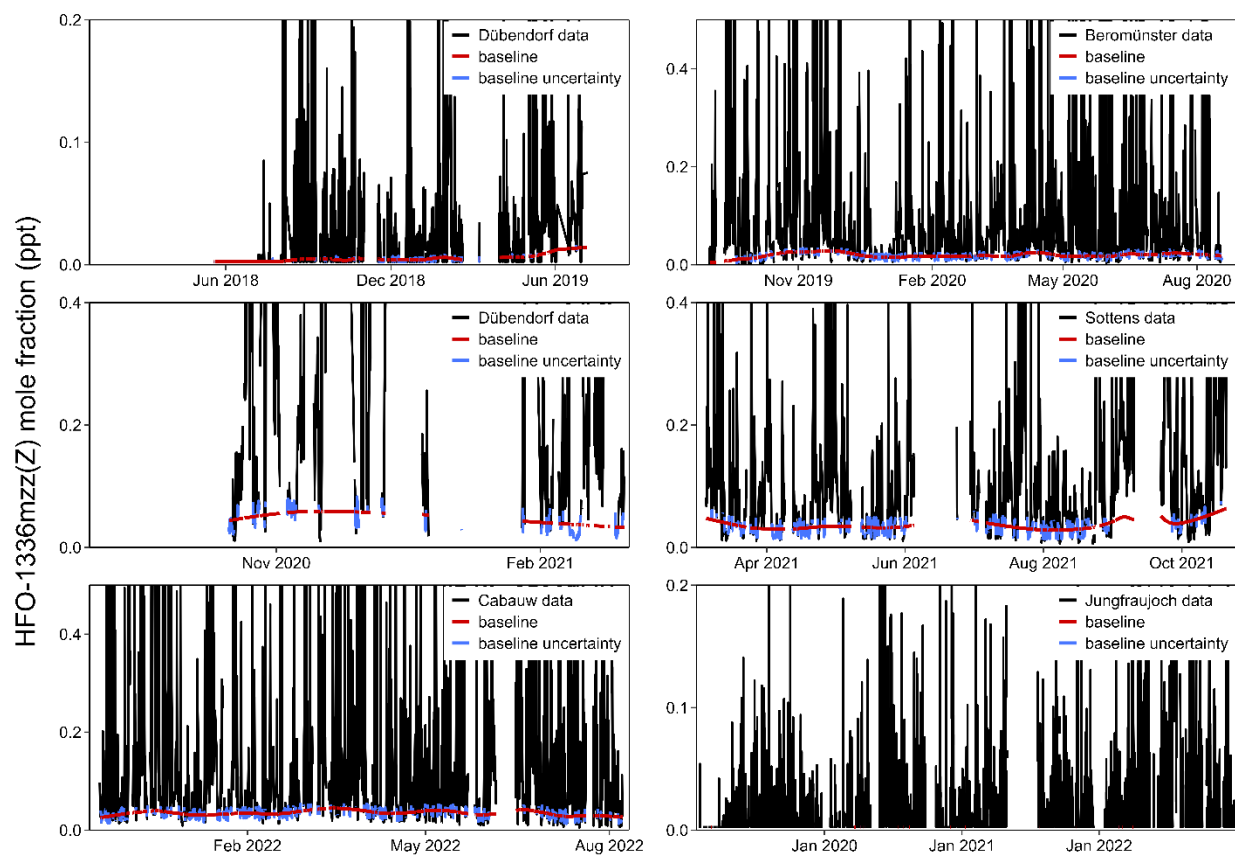


Figure S2. The baselines (red lines) calculated by the "robust extraction of baseline signal" (REBS) method⁵¹ for the HFO-1336mzz(Z) record at each site. The shown baselines were calculated with the REBS bandwidth parameter set to 30 days. Uncertainty bands (blue) were derived with the REBS multiplication factor set to 1.5.

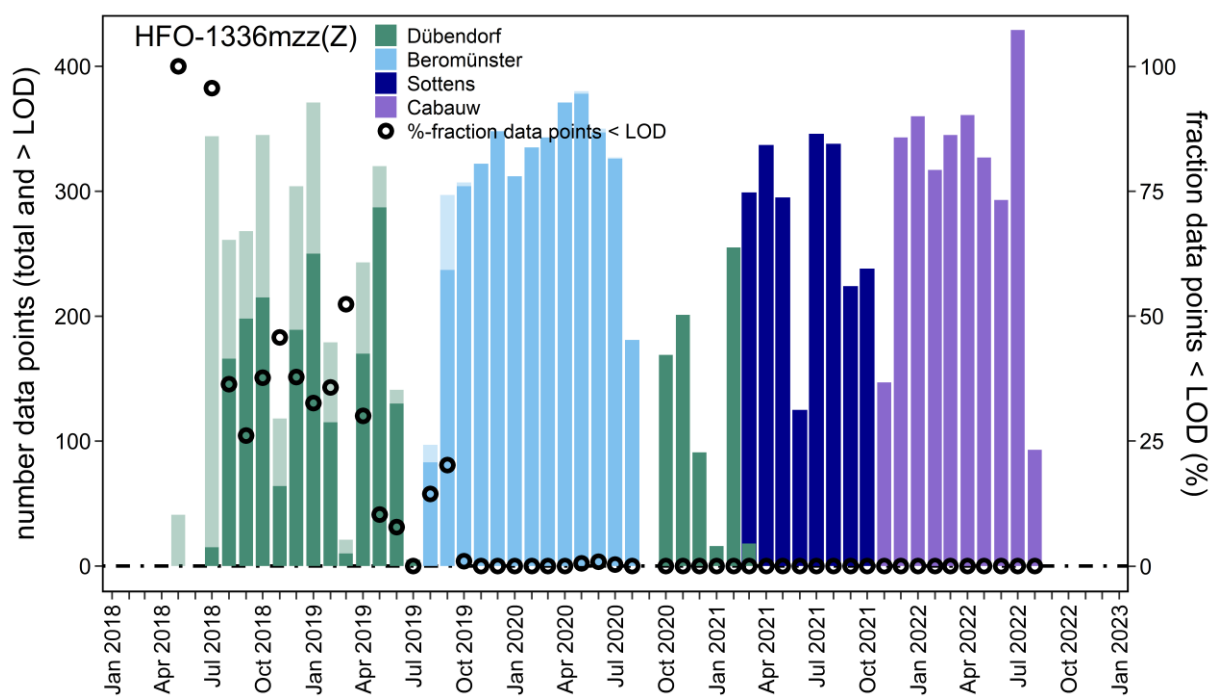


Figure S3. The total number of measurements (transparent bars) and the number of data points above limit of detection (LOD; non-transparent bars) for the HFO-1336mzz(Z) records at Dübendorf, Beromünster, Sottens, and Cabauw, against the monthly percentage of data points below LOD (black points).

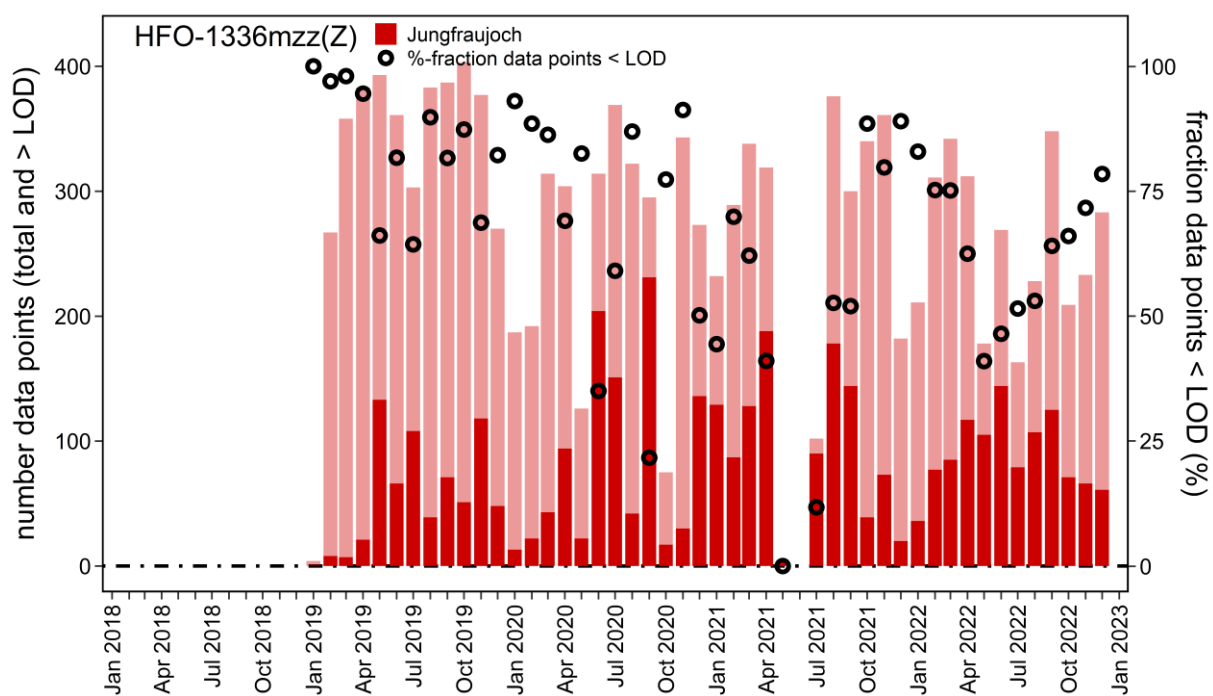


Figure S4. The total number of measurements (transparent bars) and the number of data points above limit of detection (LOD; non-transparent bars) for the Jungfraujoch record, against the monthly percentage of data points below LOD (black points).

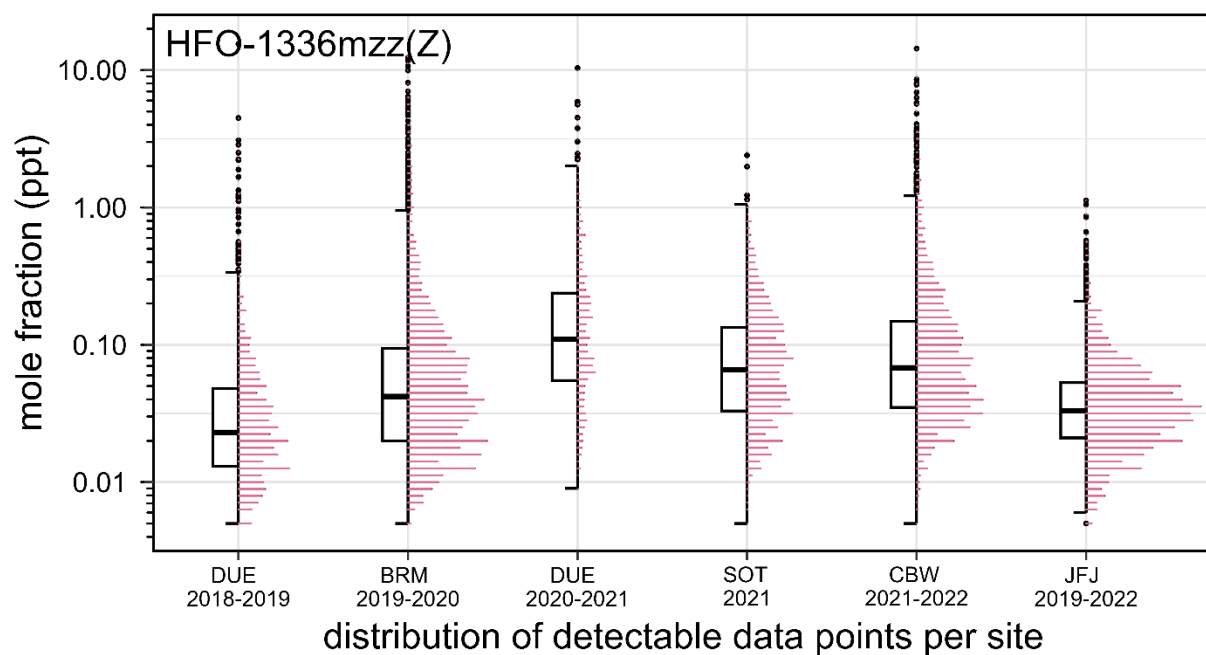


Figure S5. The distribution of detectable data points summarised as boxplot and histogram for the two Dübendorf (DUE) records, i.e. in 2018–2019 and in 2020–2021, for the Beromünster (BRM), the Sottens (SOT), the Cabauw (CBW), and the Jungfraujoch (JFJ) record.

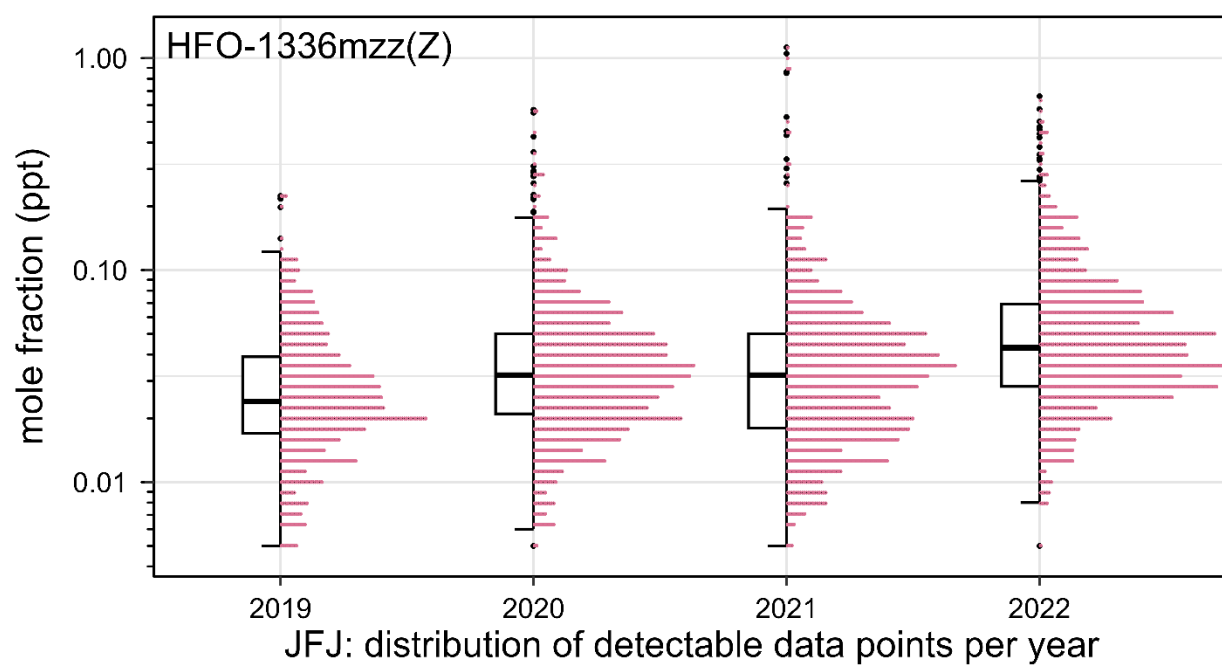


Figure S6. The annual distribution of detectable data points summarised as boxplot and histogram for the Jungfraujoch (JFJ) record.

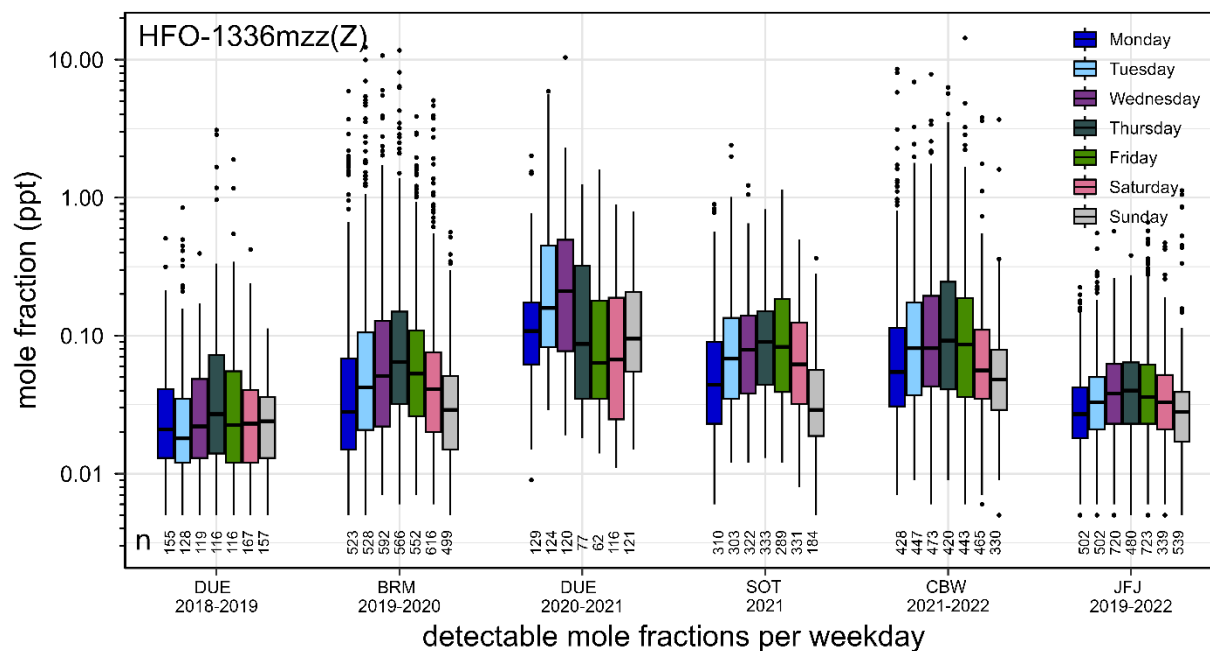


Figure S7. The weekday distribution of the number (n) of detectable mole fractions (above limit of detection, LOD) for the two Dübendorf (DUE) records, i.e. in 2018–2019 and in 2020–2021, for the Beromünster (BRM), the Sottens (SOT), the Cabauw (CBW), and the Jungfrauoch (JFJ) record.

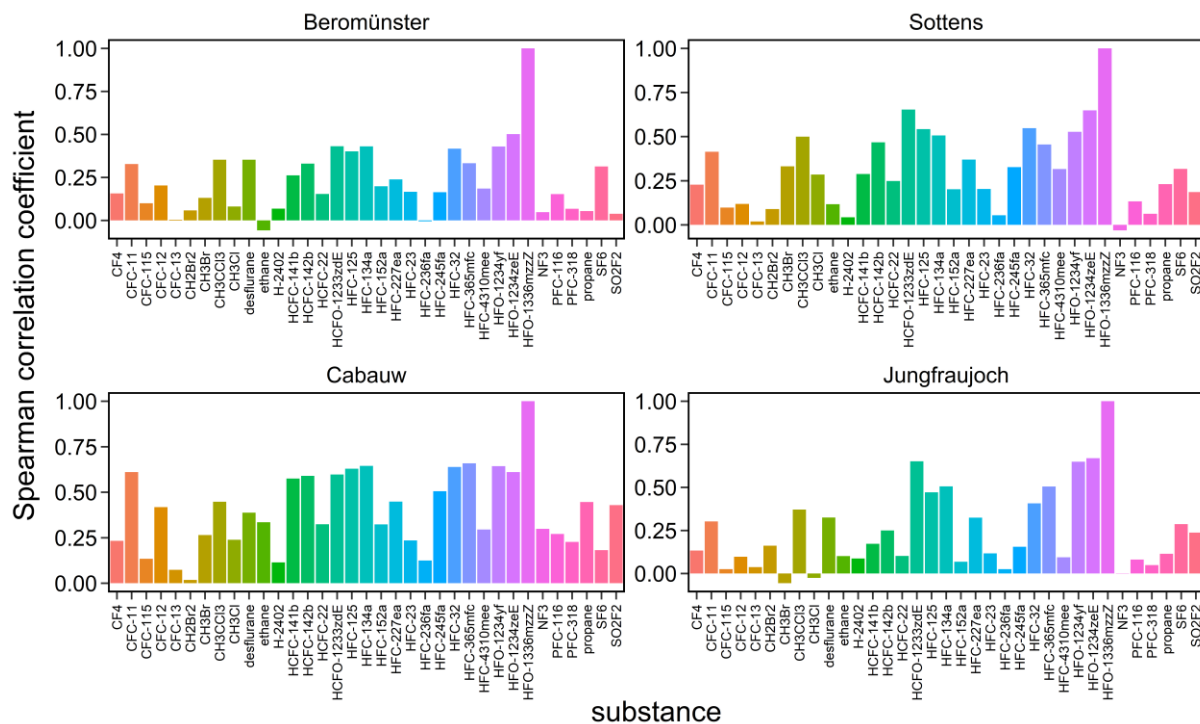


Figure S8. Subset of Spearman correlations between HFO-1336mzz(Z) and other substances measured at Beromünster, Cabauw, Jungfrauoch, and Sottens.

Atmospheric Transport and Inverse Modelling

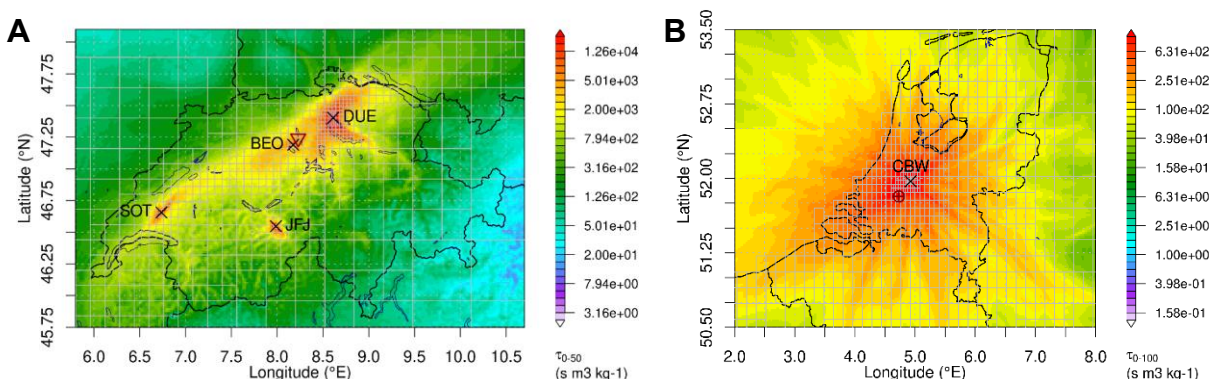


Figure S9. Total source-receptor relationship for (A) sites in Swiss domain and (B) Cabauw; aggregated only for times when valid HFO-1336mzz(Z) observations were available. Observation locations (Dübendorf, DUE; Beromünster, BEO; Sottens, SOT; Jungfraujoch, JFJ; and Cabauw, CBW) are marked with a black cross. Color scales for the two maps differ because units depend on grid resolution, which was different for the Swiss sites and Cabauw. However, in both cases values span four orders of magnitude.

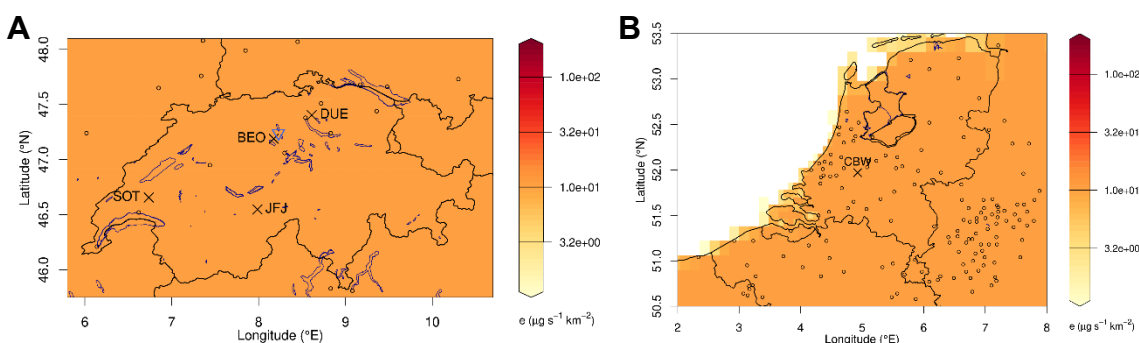


Figure S10. A priori HFO-1336mzz(Z) emission estimate for the (A) Swiss and the (B) Dutch inversion domains. Observation locations (Dübendorf, DUE; Beromünster, BEO; Sottens, SOT; Jungfraujoch, JFJ; and Cabauw, CBW) are marked with a black cross. Cities with a population larger than 50'000 inhabitants are marked by open circles.

REFERENCES

- (1) Baasandorj, M.; Ravishankara, A. R.; Burkholder, J. B. Atmospheric Chemistry of (Z)-CF₃CH=CHCF₃: OH Radical Reaction Rate Coefficient and Global Warming Potential. *J. Phys. Chem. A* **2011**, *115* (38), 10539–10549. <https://doi.org/10.1021/jp206195g>.
- (2) Molés, F.; Navarro-Esbrí, J.; Peris, B.; Mota-Babiloni, A.; Barragán-Cervera, Á.; Kontomaris, K. Low GWP Alternatives to HFC-245fa in Organic Rankine Cycles for Low Temperature Heat Recovery: HCFO-1233zd-E and HFO-1336mzz-Z. *Appl. Therm. Eng.* **2014**, *71* (1), 204–212. <https://doi.org/10.1016/j.applthermaleng.2014.06.055>.
- (3) WMO. *Scientific Assessment of Ozone Depletion: 2022, Global Ozone Research and Monitoring, GAW Report No. 278*; Geneva, Switzerland, 2022; 509 pp.
- (4) Wallington, T. J.; Sulbaek Andersen, M. P.; Nielsen, O. J. Atmospheric Chemistry of Short-Chain Haloolefins: Photochemical Ozone Creation Potentials (POCPs), Global Warming Potentials (GWPs), and Ozone Depletion Potentials (ODPs). *Chemosphere* **2015**, *129*, 135–141. <https://doi.org/10.1016/j.chemosphere.2014.06.092>.
- (5) Østerstrøm, F. F.; Andersen, S. T.; Sølling, T. I.; Nielsen, O. J.; Sulbaek Andersen, M. P. Atmospheric Chemistry of Z- and E-CF₃CH=CHCF₃. *Phys. Chem. Chem. Phys.* **2017**, *19* (1), 735–750. <https://doi.org/10.1039/c6cp07234h>.
- (6) Orkin, V. L.; Poskrebyshv, G. A.; Kurylo, M. J. Rate Constants for the Reactions between OH and Perfluorinated Alkenes. *J. Phys. Chem. A* **2011**, *115* (24), 6568–6574. <https://doi.org/10.1021/jp201663j>.
- (7) Hodnebrog; Etminan, M.; Fuglestad, J. S.; Marston, G.; Myhre, G.; Nielsen, C. J.;

- Shine, K. P.; Wallington, T. J. Global Warming Potentials and Radiative Efficiencies of Halocarbons and Related Compounds: A Comprehensive Review. *Rev. Geophys.* **2013**, *51* (2), 300–378. <https://doi.org/10.1002/rog.20013>.
- (8) Young, C. J.; Hurley, M. D.; Wallington, T. J.; Mabury, S. A. Atmospheric Chemistry of Perfluorobutenes ($\text{CF}_3\text{CF}=\text{CFCF}_3$ and $\text{CF}_3\text{CF}_2\text{CF}=\text{CF}_2$): Kinetics and Mechanisms of Reactions with OH Radicals and Chlorine Atoms, IR Spectra, Global Warming Potentials, and Oxidation. *Atmos. Environ.* **2009**, *43* (24), 3717–3724. <https://doi.org/10.1016/j.atmosenv.2009.04.025>.
- (9) Cometto, P. M.; Taccone, R. A.; Nieto, J. D.; Dalmasso, P. R.; Lane, S. I. Kinetic Study of OH Radical Reactions with $\text{CF}_3\text{CCl}=\text{CCl}_2$, $\text{CF}_3\text{CCl}=\text{CClCF}_3$ and $\text{CF}_3\text{CF}=\text{CFCF}_3$. *ChemPhysChem* **2010**, *11* (18), 4053–4059. <https://doi.org/10.1002/cphc.201000430>.
- (10) Nappa, M. J.; Swearingen, E. N.; Capron Sievert, A. Fire Extinguishing and Fire Suppression Compositions Comprising Unsaturated Fluorocarbons, Patentnumber US8287752B2 to E I Du Pont de Nemours and Company, 2012.
- (11) DuPont. DuPont Develops HFO Foam Expansion Agent with Low Global Warming Potential. *Additives for Polymers*. 2014, p 2. [https://doi.org/10.1016/s0306-3747\(14\)70083-1](https://doi.org/10.1016/s0306-3747(14)70083-1).
- (12) Loh, G.; A Ata, S.; Jovicic, J. Recent Development of Formacel ® 1100 – a Zero ODP and Low GWP Foam Expansion Agent. 2015. https://www.researchgate.net/publication/283089847_Recent_Development_of_Formacel_R_1100_-_a_Zero_ODP_and_Low_GWP_Foam_Expansion_Agent.

- (13) Chemours. <https://investors.chemours.com/news-releases/news-releases-details/2015/Chemours-Breaks-Ground-for-Worlds-First-Full-Scale-Production-of-HFO-1336mzz/default.aspx>, last access 01.02.2023.
- (14) Chemours. <https://www.chemours.com/en/news-media-center/all-news/press-releases/2016/chemours-completes-first-field-application-of-opteon-1100-foam-blowing-agent>, last access 01.02.2023.
- (15) Arpagaus, C.; Bertsch, S. S. Experimental Results of HFO/HCFO Refrigerants in a Laboratory Scale HTHP with up to 150 °C Supply Temperature. *2nd Conference on High Temperature Heat Pumps, September 9, 2019, Copenhagen*. 2019, pp 1–9.
- (16) Arpagaus, C.; Bless, F.; Uhlmann, M.; Büchel, E.; Frei, S.; Schiffmann, J.; Bertsch, S. High Temperature Heat Pump Using HFO and HCFO Refrigerants - System Design, Simulation, and First Experimental Results. *17th International Refrigeration and Air Conditioning Conference*. 2018, pp 1–12.
- (17) Arpagaus, C.; Bless, F.; Uhlmann, M.; Schiffmann, J.; Bertsch, S. S. High Temperature Heat Pumps: Market Overview, State of the Art, Research Status, Refrigerants, and Application Potentials. *Energy* **2018**, *152*, 985–1010.
<https://doi.org/10.1016/j.energy.2018.03.166>.
- (18) Huo, E.; Liu, C.; Xin, L.; Li, X.; Xu, X.; Li, Q.; Wang, S.; Dang, C. Thermal Stability and Decomposition Mechanism of HFO-1336mzz(Z) as an Environmental Friendly Working Fluid: Experimental and Theoretical Study. *Int. J. Energy Res.* **2019**, *43* (9), 4630–4643.
<https://doi.org/10.1002/er.4599>.

- (19) Kontomaris, K. HFO-1336mzz-Z: High Temperature Chemical Stability and Use as A Working Fluid in Organic Rankine Cycles. *International Refrigeration and Air Conditioning Conference*. 2014, pp 1–11.
- (20) Kontomaris, K. K.; Simoni, L. D.; Nilsson, M.; Hamacher, T.; Rislå, H. N. Combined Heat and Power From Low Temperature Heat: HFO-1336mzz(Z) as a Working Fluid for Organic Rankine Cycles. *Proceedings of the 16th International Refrigeration and Air Conditioning Conference*. 2016, pp 1–11.
- (21) Mateu-Royo, C.; Navarro-Esbrí, J.; Mota-Babiloni, A.; Amat-Albuixech, M.; Molés, F. Thermodynamic Analysis of Low GWP Alternatives to HFC-245fa in High-Temperature Heat Pumps: HCFO-1224yd(Z), HCFO-1233zd(E) and HFO-1336mzz(Z). *Appl. Therm. Eng.* **2019**, *152*, 762–777. <https://doi.org/10.1016/j.applthermaleng.2019.02.047>.
- (22) Honda, K.; Amagai, M.; Matsumoto, T.; Yabe, H.; Shiratori, S. Insect Pest Repellent, Patentnumber WO 2017/122684 to Fumakilla Ltd, Chemours-Mitsui Fluoroproducts Co Ltd, 2018.
- (23) Wissam, R.; Laurent, A.; Boutier, J.-C. Composition of Chlorotrifluoropropene and Hexafluoro-Butene, Patentnumber JP2020007561A to Arkema France, 2020.
- (24) Chemours. *OpteonTM 1100 Foam Blowing Agent*, <https://www.opteon.com/en/products/foam-blowing/1100>, last access 01.02.2023.
- (25) Chemours. *OpteonTM XP30 (R-514A) Refrigerant*, <https://www.opteon.com/en/products/refrigerants/xp30>, last access 01.02.2023.
- (26) Majurin, J.; Sorenson, E.; Steinke, D.; Herried, M. Chemical Stability Assessments of R-

- 514A and R-1233zd(E). *ASHRAE Winter Conference, Las Vegas, NV*. 2017.
- [https://www.trane.com/content/dam/Trane/Commercial/global/products-systems/education-training/industry-articles/ASHRAE012017_Chemical Stability Assessments of R-1233zd\(E\) and R-514A.pdf](https://www.trane.com/content/dam/Trane/Commercial/global/products-systems/education-training/industry-articles/ASHRAE012017_Chemical Stability Assessments of R-1233zd(E) and R-514A.pdf).
- (27) Chemours. *Opteon™ MZ Fluid for Thermal Management*,
<https://www.opteon.com/en/products/thermal-management/fluid>, last access 01.02.2023.
- (28) Chemours. *Opteon™ SF33 Specialty Fluid*,
<https://www.opteon.com/en/products/specialty-fluids/sf33>, last access 01.02.2023.
- (29) Chemours. *1100/1500 Blends*, https://www.opteon.com/fr/-/media/files/opteon/opteon-1100-1150-blend-push-bulletin_final.pdf?rev=2a16e845745349bb9e4bd496eed67c57,
 last access 01.02.2023.
- (30) Climalife. <https://de.climalife.dehon.com/novexpans-hfo-1336mzz>, last access 01.02.2023.
- (31) Chemours. <https://www.chemours.com/en/news-media-center/all-news/press-releases/2021/chemours-begins-production-of-opteon-1150-to-meet-escalating-demand-for-low-global-warming-potential>, last access 01.02.2023.
- (32) ECHA. <https://echa.europa.eu/de/substance-information/-/substanceinfo/100.217.885>, last access 01.02.2023.
- (33) ECHA. <https://echa.europa.eu/de/registration-dossier/-/registered-dossier/10030/3/1/4>,
 last access 01.02.2023.
- (34) Destatis. *Erhebung Bestimmter Klimawirksamer Stoffe 2019, Ergebnisbericht Statistisches Bundesamt (DESTATIS)*; 2021. <https://www.destatis.de/DE/Themen/Gesellschaft->

- Umwelt/Umwelt/Klimawirksame-Stoffe/Publikationen/Downloads-Klimawirksame-Stoffe/erhebung-klimawirksamer-stoffe-5324201197004.html.
- (35) Destatis. *Erhebung Bestimmter Klimawirksamer Stoffe 2020, Ergebnisbericht Statistisches Bundesamt (DESTATIS)*; 2022. <https://www.destatis.de/DE/Themen/Gesellschaft-Umwelt/Umwelt/Klimawirksame-Stoffe/Publikationen/Downloads-Klimawirksame-Stoffe/erhebung-klimawirksamer-stoffe-5324201207004.html>.
- (36) EU. Regulation (EU) No 517/2014 of the European Parliament and of the Council of 16 April 2014 on Fluorinated Greenhouse Gases and Repealing Regulation (EC) No 842/2006, Official Journal of the European Union, Policy Document. 2014, pp 1–36. <http://eur-lex.europa.eu/eli/reg/2014/517/oj>.
- (37) Behringer, D.; Heydel, F.; Gschrey, B.; Osterheld, S.; Schwarz, W.; Warncke, K.; Freeling, F.; Nödler, K.; Henne, S.; Reimann, S.; Blepp, M.; Jörß, W.; Liu, R.; Ludig, S.; Rüdener, I.; Gartiser, S. *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*; 2021.
- (38) European Environment Agency. *Fluorinated Greenhouse Gases 2020 - Data Reported by Companies on the Production, Import, Export and Destruction of Fluorinated Greenhouse Gases in the European Union, 2007-2019*; 2020. <https://doi.org/10.2800/08599>.
- (39) European Commission. Proposal for a Regulation of the European Parliament and of the Council on Fluorinated Greenhouse Gases, Amending Directive (EU) 2019/1937 and Repealing Regulation (EU) No 517/2014, Strasbourg, 5.4.2022. 2022, pp 1–75.

- (40) European Commission. REPowerEU Plan, Communication from the Commission to the European Parliament, the European Council, the Council, the European Economic and Social Committee and the Committee of the Regions, Brussels, 18.5.2022. 2022, pp 1–21.
- (41) Top Refrigerants. <https://top-refrigerants.com/de/reach-vorschl%C3%A4ge-k%C3%B6nnen-hfc-und-hfo-k%C3%A4ltemittel-betreffen>, last access 12.01.2023.
- (42) ECHA. <https://echa.europa.eu/de/hot-topics/perfluoroalkyl-chemicals-pfas>, last access 19.02.2023.
- (43) EPA. <https://www.regulations.gov/docket/EPA-HQ-OAR-2017-0175>, last access 01.02.2023.
- (44) Booten, C.; Nicholson, S.; Mann, M.; Abdelaziz, O. *Refrigerants: Market Trends and Supply Chain Assessment*, CEMAC Technical Report NREL/TP-5500-70207; 2020.
- (45) Brodribb, P.; McCann, M.; Dewerson, G. *Cold Hard Facts 2021, Expert Group Report Prepared for the Department of Agriculture, Water and the Environment, Canberra, Australia*; 2021.
- (46) UNEP. <http://www.multilateralfund.org/76/English/1/7650.pdf>, last access 07.03.2023.
- (47) The World Bank. <https://projects.worldbank.org/en/projects-operations/project-detail/P165235>, last access 12.01.2023.
- (48) Giménez-Prades, P.; Navarro-Esbrí, J.; Arpagaus, C.; Fernández-Moreno, A.; Mota-Babiloni, A. Novel Molecules as Working Fluids for Refrigeration, Heat Pump and Organic Rankine Cycle Systems. *Renew. Sustain. Energy Rev.* **2022**, 167. <https://doi.org/10.1016/j.rser.2022.112549>.

- (49) Vollmer, M. K.; Miller, B. R.; Rigby, M.; Reimann, S.; Mühle, J.; Krummel, P. B.; O'Doherty, S.; Kim, J.; Rhee, T. S.; Weiss, R. F.; Fraser, P. J.; Simmonds, P. G.; Salameh, P. K.; Harth, C. M.; Wang, R. H. J.; Steele, L. P.; Young, D.; Lunder, C. R.; Hermansen, O.; Ivy, D.; Arnold, T.; Schmidbauer, N.; Kim, K. R.; Grealley, B. R.; Hill, M.; Leist, M.; Wenger, A.; Prinn, R. G. Atmospheric Histories and Global Emissions of the Anthropogenic Hydrofluorocarbons HFC-365mfc, HFC-245fa, HFC-227ea, and HFC-236fa. *J. Geophys. Res.* **2011**, *116* (8), 1–16. <https://doi.org/10.1029/2010JD015309>.
- (50) Langenfelds, R. L.; Fraser, P. J.; Francey, R. J.; Steele, L. P.; Porter, L. W.; Allison, C. E. The Cape Grim Air Archive: The First Seventeen Years, 1978 - 1995. In *Baseline Atmospheric Program Australia 1994 - 95*; Francey, R. J., Dick, A. L., Derek, N., Eds.; 1996; pp 53–70.
- (51) Ruckstuhl, A. F.; Henne, S.; Reimann, S.; Steinbacher, M.; Vollmer, M. K.; O'Doherty, S.; Buchmann, B.; Hueglin, C. Robust Extraction of Baseline Signal of Atmospheric Trace Species Using Local Regression. *Atmos. Meas. Tech.* **2012**, *5* (11), 2613–2624. <https://doi.org/10.5194/amt-5-2613-2012>.