



Multi-decadal trend of HFC-23 from FTIR observations at the NDACC Jungfraujoch station: Persistent increase and comparison with *in situ* AGAGE observations, TOMCAT model simulations, and ACE-FTS satellite data

Florentin Hiault¹, Emmanuel Mahieu¹, Pierre-Henri Lefebvre¹, Martyn P. Chipperfield^{2,3}, Zihao Wang², Martin K. Vollmer⁴, Jeremy J. Harrison^{5,6}, and Diana Roos⁷

¹Department of Astrophysics, Geophysics and Oceanography, UR SPHERES, Université de Liège, Liège, 4000, Belgium

²School of Earth, Environment and Sustainability, University of Leeds, Leeds, UK

³National Centre for Earth Observation, University of Leeds, Leeds, UK

⁴Laboratory for Air Pollution and Environmental Technology, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

⁵School of Physics and Astronomy, University of Leicester, Leicester, UK

⁶National Centre for Earth Observation, University of Leicester, Leicester, UK

⁷Laboratory Gas Analysis, METAS, Federal Institute of Metrology METAS, Bern, Switzerland

Correspondence: Florentin Hiault (Florentin.Hiault@uliege.be)

Abstract. The gradual phase-out of stratospheric ozone-depleting substances (ODS), including chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), has led to the widespread adoption of hydrofluorocarbons (HFCs). HFC-23 (CHF_3) ranks third among HFCs in radiative forcing contribution. As a potent greenhouse gas (GHG), it falls under the Kyoto Protocol and the Montreal Protocol's Kigali Amendment (2016), justifying careful monitoring. HFC-23 is not intentionally manufactured; its atmospheric release stems primarily from HCFC-22 production. This study presents the multi-decadal trend of HFC-23 derived from a newly developed retrieval methodology applied to high-resolution solar absorption spectra recorded by ground-based Fourier Transform InfraRed (FTIR) instruments. Measurements obtained at the Jungfraujoch high-altitude research station (Switzerland) within the Network for the Detection of Atmospheric Composition Change (NDACC) were combined across three successive FTIR instruments to produce a continuous and consistent time series from 1986 to 2024, including the earliest detected occurrence of HFC-23 at the site. The FTIR time series was compared with two independent observation datasets, surface *in situ* measurements from the Advanced Global Atmospheric Gases Experiment (AGAGE) network at Jungfraujoch and satellite retrievals from the Atmospheric Chemistry Experiment - Fourier Transform Spectrometer (ACE-FTS, L2 v5.3), as well as simulations from the TOMCAT global three-dimensional chemical transport model. The resulting annual relative trends (2008–2023) are $3.52 \pm 0.37 \text{ \%}.\text{yr}^{-1}$ (FTIR), $3.52 \pm 0.15 \text{ \%}.\text{yr}^{-1}$ (AGAGE), $3.66 \pm 0.22 \text{ \%}.\text{yr}^{-1}$ (ACE-FTS) and $3.53 \pm 0.11 \text{ \%}.\text{yr}^{-1}$ (model). The consistency among these datasets supports the validity of our retrieval strategy. This methodology can be applied at additional NDACC sites, enabling broader spatial coverage for monitoring this compound using ground-based FTIR instrumentation.



1 Introduction

In 1973, Lovelock et al. (1973) provided the first evidence of the global presence of CFC-11 (trichlorofluoromethane), identifying its primary sources in the Northern Hemisphere. By comparing emission estimates with atmospheric concentration measurements, it was demonstrated that CFC-11 is highly stable in the troposphere. CFC-11 belongs to the chlorofluorocarbons (CFCs), a family of synthetic compounds first developed in the 1930s, for which no natural sources have been identified. These compounds were predominantly used as propellants in aerosol cans, as refrigerants in cooling and air conditioning systems, and as blowing agents in the production of expanded foams. The following year, in 1974, Molina and Rowland suggested the critical role that CFCs could play in stratospheric ozone depletion (Molina and Rowland, 1974).

These initial discoveries prompted the United Nations Environment Programme (UNEP) Council, in 1977, to define a global action plan aimed at protecting the ozone layer (Secretariat, 2000). Following these UN-led efforts, UNEP presented a first draft of the "Global Convention on the Ozone Layer" in 1981, which was subsequently adopted on March 22, 1985, as the Vienna Convention for the Protection of the Ozone Layer (<https://ozone.unep.org/treaties/vienna-convention>). In the same year, Farman et al. (1985) reported the first observation of the Antarctic ozone hole.

This discovery intensified the negotiations initiated under the Vienna convention, leading to the Montreal Protocol on Substances that Deplete the Ozone Layer in 1987. This international treaty gradually phased out CFCs and other ozone-depleting substances (ODSs), thereby initiating the conditions for a progressive recovery of the ozone layer. Consequently, industry developed hydrochlorofluorocarbons (HCFCs) as transitional substitutes, characterized by reduced ozone depletion potentials (ODPs).

These were later followed and progressively replaced by hydrofluorocarbons (HFCs), a second family of CFC substitutes including trifluoromethane (HFC-23, CHF_3). Containing neither chlorine nor bromine, HFCs exhibit negligible ODPs (WMO, 2022). However, while posing no direct threat to the ozone layer, HFCs are potent greenhouse gases due to strong infrared absorption, contributing significantly to Earth's radiative forcing. Due to their high global warming potentials (GWPs), HFCs were included under the 1997 Kyoto Protocol. This agreement, however, established no binding emission limits. This regulatory gap was ultimately addressed by the 2016 Kigali Amendment to the Montreal Protocol, mandating a global phasedown of long-lived HFCs with an 80–85% reduction in consumption by 2040, subject to further adjustments. Implementation began for developed countries in 2019, extending to most developing countries with a baseline freeze on HFC use initiated in 2024 (WMO, 2018). In recent years, consumption and emissions of CFCs have declined (e.g., Makkor et al., 2026), while those of HCFCs have stabilized, as confirmed, e.g., for HCFC-22 (Zhou et al., 2024). In contrast, consumption and emissions of most HFCs continue to rise, driven by their use as replacements in refrigeration, foam blowing, air conditioning, as firefighting agents and propellants (Liang et al., 2022). Consequently, the global atmospheric abundance of major HFCs continues to steadily increase. This rise has amplified their cumulative radiative forcing, which reached $44.1 \pm 0.6 \text{ mW m}^{-2}$ in 2020, an increase of approximately 30% relative to 2016 (Liang et al., 2022). Among these compounds, HFC-23 is the third-largest contributor, after HFC-134a (44%) and HFC-125 (18%) accounting for 15% of this forcing (Liang et al., 2022). The total



top-down HFC emissions grew to 1.22 ± 0.05 Gt CO₂-equivalent terms (CO₂-eq) yr⁻¹ in 2020 (100-year GWP, GWP₁₀₀), representing a 19% increase since 2016. HFC-23 comprised 20% of this total (Liang et al., 2022).

This observation-based emission total is substantially higher than the aggregate summation as reported by Annex I countries to the United Nations Framework Convention on Climate Change (UNFCCC). The divergence between top-down atmospheric
55 estimates and bottom-up national inventories has grown since the early 2000s, indicating substantial contributions from un-reported sources (Liang et al., 2022). Among the long-lived HFCs contributing to this burden, HFC-23 is particularly potent. Indeed, it has a total atmospheric lifetime of 228 years and a GWP₁₀₀ of 14,700 (Liang et al., 2022). Its primary atmospheric sink is reaction with the hydroxyl radical (OH) in the troposphere. Stratospheric loss via reaction with OH and electronically excited atomic oxygen (O(¹D)) can also occur, slightly influencing the lifetime of HFC-23. Although dissolution into the ocean
60 is a potential sink, its impact on the total atmospheric lifetime of HFC-23 is negligible (Yvon-Lewis and Butler, 2002).

HFC-23 is not intentionally manufactured but is primarily emitted as a by-product during the production of HCFC-22 (CHClF₂) (Oram et al., 1998; Miller et al., 2010; Miller and Kuijpers, 2011; Simmonds et al., 2018; Stanley et al., 2020; Rust et al., 2024). Secondary emissions occur during the synthesis of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) from HCFC-22 (Sung et al., 2006; Ebnesajjad, 2015). Minor sources include its application in halon-1301 synthesis, semi-
65 conductor plasma etching/cleaning, low-temperature refrigeration, and specialty fire suppression. Additionally, photolysis of trifluoroacetaldehyde (CF₃CHO) at 254 nm in the stratosphere represents a potential atmospheric source of HFC-23 (Sulbaek Andersen et al., 2023). HFC-23 atmospheric abundances are continuously monitored through surface networks such as AGAGE and NOAA, as well as by satellite-based instruments (ACE-FTS) (WMO, 2022). In 2022, the atmospheric abundance of HFC-23 reached 35.9 ± 0.9 ppt, continuing its long-term upward trend from 28.9 ± 0.7 ppt in 2016 (<http://agage.mit.edu/>).
70 The associated radiative forcing in 2022 was 6.9 mW m^{-2} (Montzka et al., 2024). Its annual growth rate exhibited notable variability: after slowing from 1.1 ppt.yr^{-1} (2014–2016) to 0.9 ppt.yr^{-1} , it reversed to 1.3 ppt.yr^{-1} in 2018–2019 (Montzka et al., 2018; Stanley et al., 2020), before slowing again to an average of 1.13 ppt.yr^{-1} during 2019–2022 (Montzka et al., 2024). Global top-down emissions peaked at $17.3 \pm 0.8 \text{ Gg yr}^{-1}$ in 2019 and subsequently decreased to $13.9 \pm 0.8 \text{ Gg yr}^{-1}$ in 2022 (Montzka et al., 2024).

75 This study presents the multi-decadal trend of HFC-23 above the NDACC Jungfraujoch station. Its determination was possible thanks to the development of a retrieval strategy for HFC-23 from ground-based Fourier Transform InfraRed (FTIR) solar absorption spectra. This approach was applied to derive a continuous time series spanning 1986–2024. The retrieved total columns (dry-air mole fractions) are compared with surface measurements from the Advanced Global Atmospheric Gases Experiment (AGAGE), satellite observations from the Atmospheric Chemistry Experiment Fourier Transform Spectrometer
80 (ACE-FTS), and simulations from the TOMCAT 3D chemical transport model for January 2008 to December 2024. The paper is organized as follows. Section 2 describes the datasets used. Section 3 details the retrieval methodology. Section 4 presents the trend analysis and intercomparison results. Finally, Section 5 summarizes the main findings.



2 Observation methods and data sources

2.1 NDACC FTIR measurements at Jungfraujoch station

85 This study relies on FTIR measurements acquired under clear-sky conditions at the Jungfraujoch station (46.55°N, 7.98°E),
located in the Swiss Alps at 3580 m above mean sea level. This site is positioned between the Mönch (4107 m) and Jungfrau
(4158 m) peaks, and it benefits from exceptionally dry conditions compared to most NDACC locations (Mahieu et al., 2021).
The University of Liège has initiated a spectroscopic monitoring programme there that has been ongoing since the early
1950s. Routine high-resolution FTIR observations began in 1984 (Zander et al., 2008). They have later been integrated into the
90 NDACC network (De Mazière et al., 2018). For this work, the analyzed data originate from infrared solar absorption spectra
recorded using three successive instruments: a homemade spectrometer, a Bruker IFS-120HR and, more recently, a Bruker
IFS-125HR. These instruments have been in routine operation since 1984, the early 1990s and September 2024, respectively.
All instruments were equipped with a HgCdTe (MCT) detector, allowing them to cover the 700–1400 cm⁻¹ spectral range,
typically with maximum optical path differences (OPD) of 82 cm, or also 125 cm for the two Bruker spectrometers.

95 2.2 AGAGE *in situ* observations at Jungfraujoch

Independent *in situ* HFC-23 measurements at Jungfraujoch are conducted using a preconcentration gas chromatograph–mass
spectrometer (GC–MS) system (Miller et al., 2008; Arnold et al., 2012). Additional high-precision HFC-23 observations are
available from the AGAGE network (Prinn et al., 2000). HFC-23 was first measured following the upgrade to a Medusa GC–
MS system in 2008 (Miller et al., 2008). In this system, 2 L air samples are preconcentrated at –160 °C, thermally desorbed
100 at 100 °C, cryofocused, and injected into the GC–MS. Each analysis requires about 70 minutes. To correct for instrumental
drift, a calibration standard is analyzed after every two ambient air samples. All measurements are reported on the SIO-07
calibration scale, with a precision of 0.6% and an accuracy of 3% (Miller et al., 2010; Prinn et al., 2000). For this study, annual
means were calculated from background-filtered measurements deemed representative of broad atmospheric regions following
the statistical filtering algorithm described by O’Doherty et al. (2001).

105 2.3 ACE-FTS retrievals

The primary instrument aboard the Canadian SCISAT satellite is the Atmospheric Chemistry Experiment Fourier Transform
Spectrometer (ACE-FTS) (Bernath et al., 2005; Lachance et al., 2013). Launched into a low-Earth orbit in August 2003, the
satellite has measured vertical profiles of atmospheric pressure, temperature, and trace gas abundances since February 2004
(Fernando et al., 2019). ACE-FTS operates on the solar occultation principle, functioning as a Fourier transform spectrometer
110 (FTS) that records up to 30 occultations daily during sunrise and sunset events. Each occultation consists of a series of infrared
transmittance spectra measured at different altitudes. The geographical locations of these occultations are determined by the
satellite’s orbital geometry relative to the Sun (Bernath et al., 2005; Lachance et al., 2013). The instrument operates across
the 750–4400 cm⁻¹ spectral band at a resolution of 0.02 cm⁻¹ (Boone et al., 2023). Its signal-to-noise ratio (SNR) ranges



from approximately 100:1 to 400:1 (Boone et al., 2023). Atmospheric profiles are retrieved from 150 km down to the cloud
115 tops. These profiles have an average vertical resolution of 3 km. Under clear-sky conditions, the lower measurement limit
is 5 km (Bernath et al., 2005; Lachance et al., 2013). Twenty-two micro-windows (MW) are used for the HFC-23 retrievals
(Dodangodage et al., 2025b). This study employs HFC-23 abundances from the ACE-FTS Level 2 version 5.3 research product
(Dodangodage et al., 2025b). Spectroscopic data for version 5 were taken from HITRAN 2020 (Gordon et al., 2022). The
selected data used here correspond to altitudes between 6.5 km and 12.5 km (Fernando et al., 2019) and are restricted to the
120 mid-latitude band (40–55°N) surrounding the Jungfraujoch station. A comprehensive overview of the ACE-FTS version 5
retrieval characteristics is provided by Boone et al. (2023).

2.4 TOMCAT model simulations

The interpretation of the Jungfraujoch measurements was guided by simulations from the TOMCAT/SLIMCAT (hereafter
TOMCAT) three-dimensional chemical transport model (CTM) (Chipperfield, 2006). The simulation analyzed here focuses on
125 the 2000–2025 period and uses a horizontal grid of $2.8^\circ \times 2.8^\circ$ with 32 hybrid σ - p vertical levels from the surface to approxi-
mately 60 km. Meteorological drivers are provided by the ECMWF ERA5/5.1 reanalysis (Hersbach et al., 2020). A chemistry
scheme with a detailed stratosphere and simplified troposphere is incorporated (Chrysanthou et al., 2025), which interactively
calculates hydroxyl radical (OH) concentrations and photolysis rates—key processes governing the atmospheric chemical loss
of HFCs. Surface fluxes of long-lived source gases are represented through prescribed lower boundary conditions. Specifically,
130 global monthly mean surface volume mixing ratios (VMRs) for CFCs and HCFCs were obtained from the Scientific Assess-
ment of Ozone Depletion (2022) (WMO, 2022), while those for HFCs, including HFC-23, were sourced from the NOAA
Annual Greenhouse Gas Index (<https://gml.noaa.gov/aggi/aggi.html>). This dataset provides annual mean global mean surface
mole fractions for the major HFCs but data for HFC-23 (not observed by NOAA) is actually obtained from AGAGE observa-
tions. The TOMCAT run interpolates the annual mean values linearly in time to obtain smoothly varying global surface values.
135 TOMCAT therefore does not capture the fine-scale spatial or short-term temporal variability at the surface for HFC-23. The
model simulates the vertical profile shape of HFC-23 based on large-scale atmospheric transport and the explicitly calculated
chemical loss. For direct comparison of the observations, the model output was sampled daily at 00:00 Universal Time (UT)
at the geographic coordinates of the Jungfraujoch station. The column calculation accounts for the difference in altitude of the
site in the low resolution model output with smoothed surface orography.

140 3 HFC-23 retrievals

3.1 Retrieval Strategy

The retrieval of HFC-23 at the Jungfraujoch station benefits from the site's dry conditions, leading to significantly reduced
interference from water vapour absorptions in the infrared. The retrieval strategy builds upon a method previously validated
at two other NDACC sites (Takeda et al., 2021). Spectral analysis is performed within the microwindow $1138.5\text{--}1160\text{ cm}^{-1}$,



145 which is consistent with the ACE-FTS retrieval approach (Dodangodage et al., 2025b) and established in previous work by Mahieu et al. (2021) and Takeda et al. (2021). To ensure sufficient information content, retrievals were conducted only for observations with an apparent solar zenith angle (SZA) yielding a degree of freedom for signal (DOFS) of at least one. The resulting HFC-23 columns were corrected for apparent SZA dependence (see Appendix), and statistical outlier filtering was applied using the median absolute deviation (MAD) method (Sheese et al., 2015). No filtering based on H₂O total columns was
150 required, as no dependence was observed.

Retrievals were performed using the Optimal Estimation Method (OEM) (Rodgers, 2000) as implemented in the SFIT-4 v1.0.21.RV (research version) algorithm. The atmospheric profile was discretized into 41 layers from 3.58 km to 120 km, with layer thickness increasing from 0.65 km at the surface to 14 km at the top of the atmosphere. For HFC-23 column retrieval, OEM regularization was preferred over Tikhonov regularization. The diagonal elements of the *a priori* covariance matrix, S_a ,
155 were set to 27.5% per km from 3.58 km to 36.34 km and 40% per km from 36.34 km to 120 km. Off-diagonal elements were modelled with an exponential-shape correlation using an interlayer correlation half-width of 2 km. A signal-to-noise ratio of 200 was adopted for all inversions.

The following molecules were treated as interferences in the HFC-23 retrieval: PAN, H₂O, HDO, N₂O, O₃, CCl₂F₂ (CFC-12), CH₄, CHClF₂ (HCFC-22), and CHF₂CF₃ (HFC-125, a species added in the 1.0.21.RV version of SFIT-4). This selection
160 aligns with the ACE retrieval methodology (Dodangodage et al., 2025b). Spectroscopic parameters were taken from the 2024 ATM line list, which is distributed in HITRAN format and incorporates empirical updates to HITRAN spectroscopy based on atmospheric FTIR observations (Toon et al., 2016). Depending on the retrieval window and species considered, the underlying spectroscopic parameters may originate from different HITRAN releases. For our HFC-23 retrieval window, the N₂O spectroscopy is based on HITRAN 2004 (Toth, 2000), whereas the O₃ spectroscopy follows HITRAN 2008. Empirical pseudo-
165 line lists (EPPL) produced by G.C. Toon (CalTech: <https://www.caltech.edu/>) were used for unresolved features. For HFC-23 itself, we employed the 2020 EPPL. This list is based on laboratory cross-section datasets from Gohar et al. (2004) (Gohar et al., 2004), Sharpe et al. (2004) (Sharpe et al., 2004), Chung et al. (2005) (Kyoung Chung, 2005), and Harrison (2013) (Harrison, 2013) (https://mark4sun.jpl.nasa.gov/data/spec/Pseudo/CHF3_PLL_Update.pdf) and covers 1104.9 to 1425 cm⁻¹ at a line spacing of 0.004 cm⁻¹ (80,051 lines). *A priori* profiles for trace gases except water vapour, HFC-23 and HFC-125 were
170 based on the Whole Atmosphere Community Climate Model (WACCM) (Ortega et al., 2025). Specifically, we used the updated WACCM6 version (Gettelman et al., 2019), which incorporates improvements in physical, chemical, and aerosol parameterizations relative to WACCM version 4, providing climatological mean profiles spanning 1980–2040. In contrast, *a priori* water vapour profiles were based on the ERA-Interim (Dee et al., 2011) and ERA5 (Hersbach et al., 2020) meteorological reanalyses. To ensure full vertical coverage, these reanalysis data were merged with climatological monthly means from WACCM6 for the
175 uppermost atmospheric layers. To define the *a priori* HFC-23 profile, we used the vertical distribution from ACE-FTS data by calculating the mean profile over the period 2007–2010 (Dodangodage et al., 2025b), covering the altitude range from 5.5 km to 25.5 km. A constant *a priori* profile was assumed from the lower limit of the ACE-FTS HFC-23 profile (5.5 km) for the lower troposphere, and from its upper limit (25.5 km) for the middle stratosphere. To construct the HFC-125 *a priori* profile, the mean vertical distribution was also calculated from ACE-FTS observations spanning 2007 to 2010 (Dodangodage et al.,



2025a). The resulting profile is constrained to the 12.5–25.5 km altitude range, with the profile value held constant below the lower limit and above the upper limit.

We used pressure and temperature profiles from the National Centers for Environmental Prediction (NCEP; <https://www.weather.gov/ncep/>). For the Jungfraujoch station, the profiles were computed daily and interpolated onto discrete vertical layers, assuming constant temperature, pressure, and mixing ratios of the target gases and interfering species within each layer. The associated uncertainty in the NCEP temperature fields was propagated into the total uncertainty budget (see Section 3.2).

Figure 1 shows a simulation of the 1138.5 to 1160.0 cm^{-1} spectral window, as retrieved for a spectrum recorded with the Bruker IFS-125HR instrument on 3 March 2025, with an RMS of 0.18%. Panel A shows the fitting residuals (observed – calculated). The observed spectrum (obs) is displayed in black, while the simulated spectrum (fit) is shown in red (Panel B). The main interfering species— H_2O , O_3 , CCl_2F_2 , N_2O , CH_4 , CHClF_2 , HDO , PAN, and HFC-125— are plotted using the colour key depicted in the legend (Panel B). The primary interference within the measurement window is ozone (dark green in Panel B). Panel C shows the absorption of the target gas, HFC-23, which, in the present case, contributes for a maximum depth (absorption) close to 2.5% (dependent on the solar height and time period) to the total signal. Given its weak absorption, it is essential that the contributions from the other chemical species are well characterized and adjusted in the retrieval. The spectrum was recorded with a maximum optical path difference (OPD) of 82 cm at a solar zenith angle of 77.4° , an instrumental resolution of 0.0110 cm^{-1} defined here as $0.9/\text{OPD}$.

3.2 Measurement uncertainty analysis

The main sources of uncertainty affecting the HFC-23 retrieval were quantified for 2012 and are listed in Table 1. The total retrieval uncertainty consists of random and systematic uncertainty components. The uncertainty budget contributions were evaluated using the formalism and equations presented in Section 2.2 of Zhou et al. (2018). The smoothing uncertainty contribution was quantified using Equation (3.16) of Rodgers (2000). The contribution of temperature uncertainties to both components of the uncertainty budget was evaluated using altitude-dependent uncertainties derived from NCEP temperature profiles. Random (systematic) temperature uncertainties of 2 (1) K in the lower and middle troposphere, 4 (1) K in the upper troposphere, 2 (2) K in the tropopause region, 3 (2) K in the lower stratosphere, 6 (4) K in the middle stratosphere, and 1 (5) K in the upper stratosphere were adopted.

The random component of the error covariance matrix was generated using the relative standard deviation (RSD) affecting HFC-23 measurements as obtained from ACE-FTS v5.3 (Dodangodage et al., 2025b) for each level of a grid between 5.5 and 24.5 km altitude (1 km spacing; latitude 40° – 55°N). The uncertainty associated with the solar zenith angle (SZA) was set at $\pm 0.1\%$ (Pardo Cantos et al., 2024). The resulting total random uncertainty for the HFC-23 retrieval was estimated to be $8.7 \pm 1.9\%$. As shown in Table 1, the random uncertainty is dominated by temperature uncertainties and measurement noise.

The systematic uncertainty component affecting the HFC-23 retrieval was evaluated by calculating the annual average of the TOMCAT model data for the years 2020, 2021, and 2022. Subsequently, the relative difference between the TOMCAT and ACE-FTS v5.3 profiles was evaluated (Dodangodage et al., 2025b). Based on this comparison, a systematic uncertainty contribution of 3% was assigned to each layer of the grid. In addition, the correlation width of the HFC-23 profile was set at 2

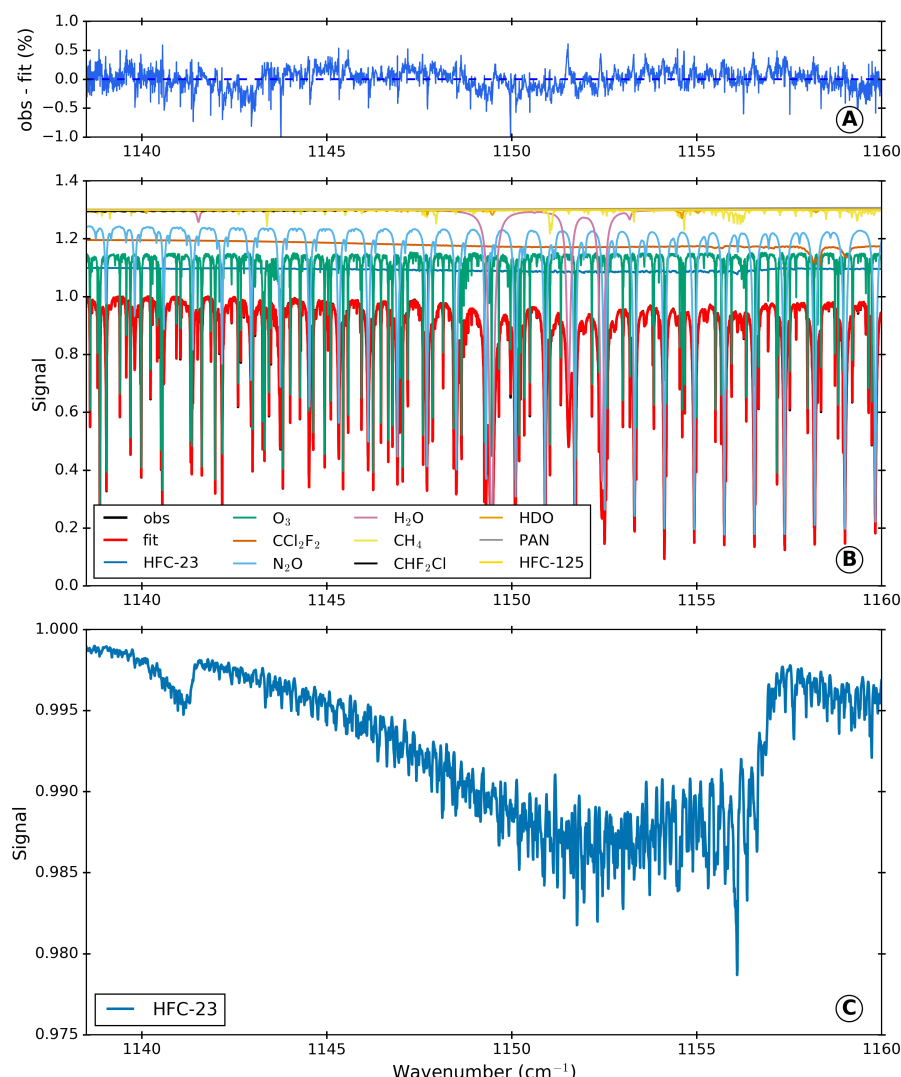


Figure 1. Simulations of the 1138.5-1160.0 cm⁻¹ spectral window from a spectrum recorded with the Bruker IFS-125HR FTIR instrument at Jungfraujoch station. The root-mean-square of the residuals (RMS) is 0.18% (panel A). The main interfering species (H₂O, O₃, CCl₂F₂, N₂O, CH₄, CHCl₂F, HDO, PAN, and HFC-125) are shifted vertically for clarity (panel B). Note the difference in vertical scale in panel C, where the HFC-23 absorption is greatly amplified.

km. The systematic uncertainty for the solar zenith angle (SZA) was estimated at $\pm 0.03\%$ in accordance with Pardo Cantos et al. (2024). The relative systematic uncertainties assigned to the HFC-23 spectroscopic parameters were 5% for both the temperature and pressure broadening coefficients (G. C. Toon, CalTech: <https://www.caltech.edu/>). The original EPLL assumed a 15% uncertainty for pseudoline intensities. Based on the improved spectroscopic constraints reported by Berezkin et al. (2025), this uncertainty was reduced to 5% in the present study. This estimate is considered conservative and likely represents



Table 1. Mean relative uncertainties (%) derived for the 2012 spectra for the HFC-23 total column retrievals at the Jungfraujoch station.

Uncertainty type and source	Relative uncertainty (%)	
	Mean	Standard deviation
Random components		
Measurement	4.0	1.5
Temperature	7.5	1.6
SZA	0.6	0.3
Interfering species	1.4	0.4
Smoothing	1.9	1.0
Retrieval parameters	0.05	0.02
Total random	8.7	1.9
Systematic components		
HFC-23 line intensity	4.7	0.2
Temperature	6.3	1.5
SZA	0.2	0.1
Total systematic	7.9	1.1

an upper bound on the residual spectroscopic uncertainty. The total systematic uncertainty was estimated to be $7.9 \pm 1.1\%$. As shown in Table 1, the systematic uncertainty budget is primarily dominated by the assumed atmospheric temperature profile and, to a lesser extent, by the HFC-23 spectroscopic parameters.

The mean layer averaging kernels characterize the retrieval's information content by weighting the contributions of the *a priori* and true atmospheric state to the retrieved vertical profile (Rodgers, 2000). Figure 2 shows the mean layer averaging kernels (left) and the first two eigenvectors (right) from Jungfraujoch solar absorption spectra (January 2008 to December 2009). The total column averaging kernel (thick black line, scaled by 0.1) spans 3.58 km to 40 km; coloured lines denote individual layer kernels, referenced to the vertical colour bar. The DOFS quantify the independent information available from the retrieval. The mean DOFS over this measurement period is about 1.0, corresponding to eigenvalues $\lambda_1 = 0.865$ and $\lambda_2 = 0.129$. This indicates that the retrieval is dominated by one independent piece of information—the total column—with only minor sensitivity to vertical structure. Consequently, the retrieved column is well constrained, while the vertical profile is poorly resolved.

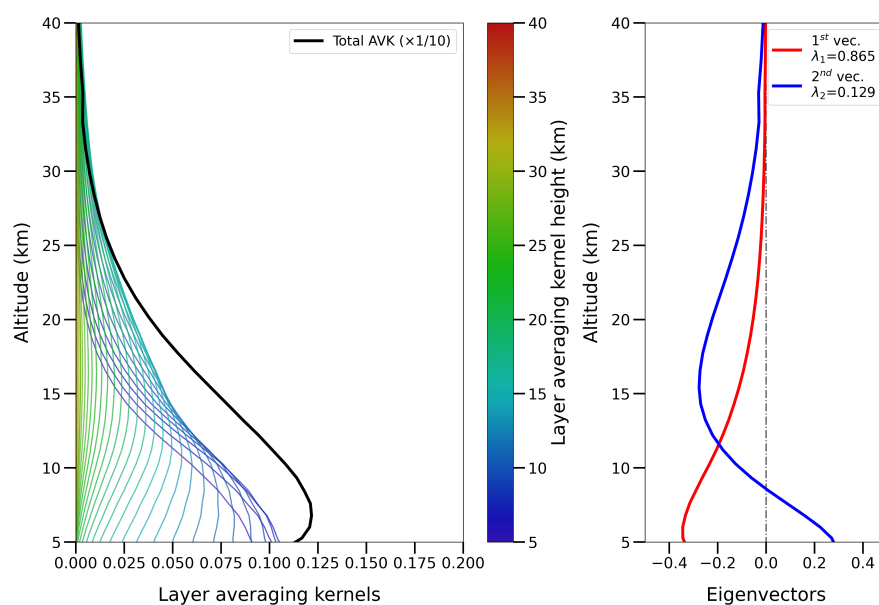


Figure 2. Mean layer averaging kernels and first two eigenvectors for Jungfraujoch spectra (January 2008–December 2009). On the left, mean averaging kernels for each atmospheric layer, with individual kernels indicated by colour bar ticks. On the right, first two eigenvectors with corresponding eigenvalues ($\lambda_1 = 0.865$, $\lambda_2 = 0.129$).



4 Results and discussion

4.1 The long-term HFC-23 time series above the Jungfraujoch station

Fig. 3 shows the FTIR time series of HFC-23 monthly mean total columns (in molec.cm⁻²) from June 1986 to December 2024. The red dashed line represents the linear trend. The statistical filters applied are detailed in Section 3. After applying
235 these filters, 4272 spectra were retained (9358 spectra fitted), representing 342 monthly averages.

A nonlinearity-related inconsistency was observed between the 120HR and 125HR spectra, traced to the MCT detectors. To address this, an interferogram-based correction was applied to the 2024 125HR spectra using the BRUKER OPUS software. Following this nonlinearity correction, the monthly average RSD decreased from 1.6% to 1.1%. Nevertheless, this correction improves only the fit of the zero level. An envelope effect arising from the instrumental response of the detector and the optical
240 filter still persists. To quantify this effect, we compared observations acquired using the same instrumental configuration (i.e. the same detector and optical filter), with and without the nonlinearity correction applied. Using this approach, we estimated a bias of 2.5%, which quantifies the envelope effect. We emphasize the limitation of this estimate, noting that the bias calculation was performed using a sample of only three daily averages. Future observations are necessary to refine this value. Thus, to harmonize the entire time series, a scale-down factor of -2.5% was applied to observations from the "homemade" and the
245 120HR spectrometer instruments.

A figure showing the data recorded by each instrument is provided in the Appendix. The various instrument datasets exhibit different levels of precision over time. Specifically, data from the "homemade" spectrometer (1986–1999) show a mean monthly RSD of 28.2%, whereas data from the IFS-120HR (1996–2024) and IFS-125HR (2024) yield values of 7.2% and 1.1%, respectively. Owing to the exceptional temporal extent of the time series, we find that HFC-23 concentrations become
250 detectable in our observations from 1986 onwards, within the associated uncertainty.

The linear trend associated with this FTIR time series, and its 95% confidence interval uncertainty level were estimated using the wild bootstrap autoregressive method (AWB) proposed by Friedrich et al. (2020b). Further information on this method can be found in Friedrich et al. (2020a). The relative trend was calculated as the absolute linear slope normalized by the mean of the time series over the 1986–2024 period. For the FTIR data, this yields an absolute trend of $1.17 \pm 0.03 \times 10^{13}$ molec.cm⁻²,
255 i.e., 5.07 ± 0.13 % yr⁻¹, quantifying the steady increase in HFC-23 atmospheric concentrations.

While the linear trend indicates a sustained increase, previous studies have suggested potential changes in the growth rate. Specifically, results from the studies by Montzka et al. (2018) and Stanley et al. (2020) highlighted a notable change in the annual growth rate of HFC-23. Specifically, after slowing from 1.1 ppt.yr⁻¹ (2014–2016) to 0.9 ppt.yr⁻¹, it reversed to 1.3 ppt.yr⁻¹ in 2018–2019. We therefore carried out a kernel fit to test this behaviour, along with its corresponding uncertainty
260 using the AWB method described in Friedrich et al. (2020a, b). For our time series, the results did not match to those studies, neither in terms of break point location nor in terms of the associated large uncertainty.

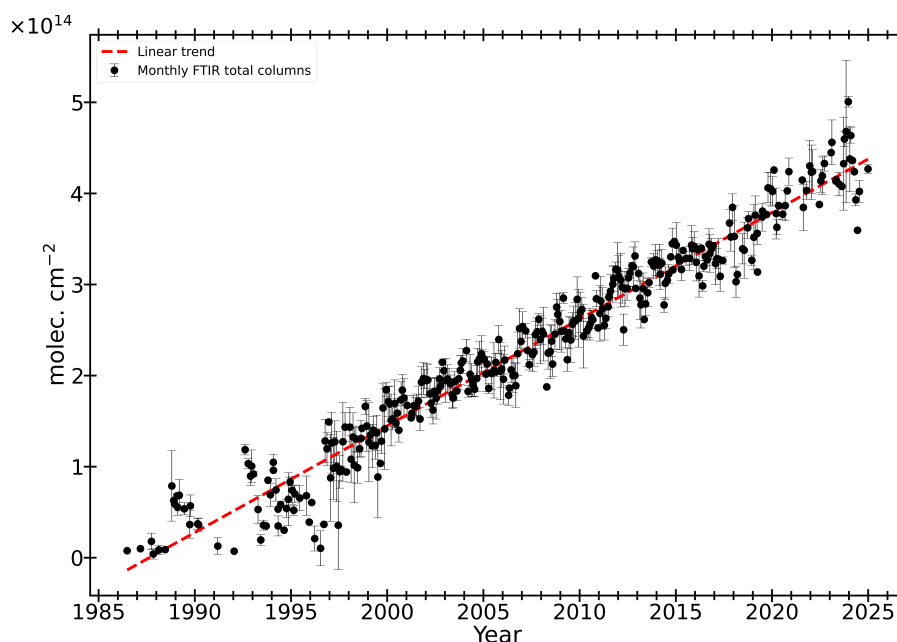


Figure 3. The multidecadal FTIR time series of HFC-23 vertical column abundances above Jungfraujoch (in molecules cm^{-2}). Black dots indicate monthly means, with vertical bars representing ± 1 standard deviation. The red dashed line shows the trend when using a linear function.

4.2 Comparisons to independent datasets

Fig. 4 presents an intercomparison of annual mean mole fractions derived from FTIR remote sensing (NDACC, ACE-FTS), *in situ* (AGAGE), and model (TOMCAT) datasets from January 2008 to December 2023. The specific characteristics and any statistical filtering applied to these datasets are described in Section 2. To enable an easier comparison between datasets, we converted the FTIR Jungfraujoch and TOMCAT model data, originally expressed as total columns, into dry-air mole fractions (xHFC-23). This conversion was performed by dividing the HFC-23 total columns by the dry-air column pressure (DPC), following the approaches of Barthlott et al. (2015) and Pardo Cantos et al. (2022). The water vapour column used in this conversion was obtained via a dedicated retrieval strategy, as described in Sussmann et al. (2009) while the surface pressure values were obtained from MeteoSwiss. The intra-annual variability of HFC-23, expressed as the mean RSD of values within each year, is 6.4% for the FTIR total column at Jungfraujoch, 19.1% for the ACE upper-tropospheric data, 0.7% for the AGAGE surface baseline, and 1.3% for the TOMCAT model. The higher RSD for ACE reflects the sparse and irregular sampling of the upper troposphere by solar occultation measurements, while the FTIR total column is smoothed by integration over the entire atmospheric column. The dashed lines, colour-coded to match the data symbols, represent the linear trends. All atmospheric mole fractions are expressed in parts per trillion (ppt).



The ACE-FTS observations sample a higher altitude region of the atmosphere than the Jungfraujoch FTIR measurements. To assess the representativeness of the ACE-FTS observations relative to the ground-based measurements, TOMCAT was used as a transfer standard. The simulated HFC-23 profile exhibits only weak vertical gradients throughout the lower troposphere and the lower part of the ACE-FTS sampling range. Relative to the model level closest to Jungfraujoch (~ 3.8 km), mean scaling factors are 0.9999 ± 0.0001 at ~ 6.5 km, 0.9985 ± 0.0006 at ~ 8.5 km, and 0.9925 ± 0.0025 at ~ 10.5 km, indicating that HFC-23 is nearly well mixed over this altitude range. To account for the atmospheric layer located below the lowest ACE-FTS retrieval altitude, a model-derived partial-column correction was calculated between the Jungfraujoch model level (~ 3.8 km) and the lower boundary of the ACE-FTS retrieval range (~ 6.1 km):

$$C_{\text{JFJ}_{\text{model}}-\text{ACE}} = \frac{1}{g} \sum_i \chi_i \Delta p_i \quad (1)$$

where χ_i is the HFC-23 volume mixing ratio in model layer i , Δp_i is the corresponding pressure thickness, and g is the acceleration due to gravity. The pressure difference between these two levels corresponds to $26.4 \pm 0.02\%$ of the atmospheric mass above Jungfraujoch. Given the near-uniform vertical distribution of HFC-23 between the Jungfraujoch model level and the lower ACE-FTS retrieval altitude, the estimated correction is governed primarily by the pressure distribution rather than by variations in HFC-23 abundance. The small differences in modelled HFC-23 mixing ratios between Jungfraujoch and the ACE-FTS sampling region indicate that altitude-dependent sampling effects are negligible. This supports the use of TOMCAT as a transfer standard for comparisons between the FTIR and ACE-FTS datasets.

Analysis of the mean offsets between datasets reveals varying degrees of agreement. To facilitate comparison, we normalized the annual mean HFC-23 mole fractions to the AGAGE surface baseline (AGAGE = 100). Relative to AGAGE, the mean values are 95 for TOMCAT, 89 for ACE-FTS, and 79 for the FTIR total column at Jungfraujoch. These offsets indicate that AGAGE surface measurements are systematically higher than the other datasets, with the largest difference observed for FTIR (21% lower), followed by ACE (11% lower) and TOMCAT (5% lower).

Although systematic offsets are observed between the FTIR and AGAGE datasets, differences between annual mean values alone do not necessarily imply a discrepancy. The significance of the observed FTIR–AGAGE offset was therefore assessed by accounting for the uncertainties associated with both datasets. Since a complete FTIR uncertainty budget was available only for 2012, this analysis was restricted to that year. To assess the consistency between the FTIR and AGAGE observations, the annual mean xHFC-23 values were compared while accounting for the uncertainties associated with each measurement technique. Let A and B denote the annual mean xHFC-23 derived from the FTIR and AGAGE datasets, respectively. The associated expanded uncertainties are denoted by $U(A)$ and $U(B)$, and are expressed at the same confidence level (coverage factor $k=2$). The difference between the two annual mean estimates is defined as:

$$\Delta = B - A. \quad (2)$$

Assuming that the uncertainty contributions associated with the two measurement systems are independent, the combined expanded uncertainty of the difference is given by:

$$U_{\Delta} = \sqrt{U(A)^2 + U(B)^2}. \quad (3)$$



The FTIR and AGAGE annual mean values are considered to be statistically consistent when the absolute difference between the two estimates does not exceed the combined expanded uncertainty:

$$|\Delta| \leq U_{\Delta}. \quad (4)$$

This criterion provides a quantitative assessment of the agreement between the two independent measurement techniques by determining whether the observed difference can be explained by their respective uncertainty budgets. For the FTIR observations, the expanded uncertainty was derived from the combined systematic and random retrieval uncertainties. For AGAGE, the expanded uncertainty was obtained by combining in quadrature the calibration-scale accuracy (3%, $k=2$), the uncertainty associated with the propagation of the calibration scale through the AGAGE standard hierarchy, and the measurement precision (0.6%) (Miller et al., 2010; Prinn et al., 2000). All uncertainties were expressed as expanded uncertainties ($k=2$). For 2012, the annual mean xHFC-23 derived from FTIR (22.4 ± 5.3 ppt, $k=2$) and AGAGE (25.6 ± 1.7 ppt, $k=2$) differ by 3.2 ± 5.6 ppt. Since the observed difference is smaller than the combined expanded uncertainty, the FTIR and AGAGE annual mean values considered in this analysis are in agreement within their respective uncertainties.

The mean offset of 10.1% between ACE-FTS and ground-based FTIR data can be partly attributed to differences in measurement geometry between the Jungfraujoch FTIR instruments (zenith-looking) and those aboard SCISAT (limb-sounding). The comparison may also be affected by differences in vertical sensitivity, since the FTIR retrieval represents a near-total atmospheric column whereas the ACE-FTS dataset was restricted to the 6.5-12.5 km altitude range. Nevertheless, owing to the long atmospheric lifetime and relatively weak vertical gradients of HFC-23, this effect is expected to be small. Furthermore, the EPLL used in this study relies primarily on the laboratory spectra of Harrison (2013) (also used for ACE-FTS retrievals, but as native cross-sections), with an estimated overall systematic error of 3%. Given this common spectroscopic source, differences in the absolute HFC-23 band intensity are unlikely to explain the full 10.08% bias. Even so, residual spectroscopic effects related to the temperature dependence of the empirical pseudo-linelist cannot be entirely excluded, particularly at the lower temperatures. The limitations of the original 2011 pseudo-linelist included a large fraction (37%) of pseudolines with $E'' = 0$ (<https://mark4sun.jpl.nasa.gov/data/spec/Pseudo/Readme.chf3.pdf>), leading G. C. Toon to question the fidelity of its temperature dependence. However, the updated pseudo-linelist used in this study was generated from an expanded laboratory dataset (Section 3.1) and reduced the fraction of pseudolines with $E'' = 0$ to only 0.5% (https://mark4sun.jpl.nasa.gov/data/spec/Pseudo/CHF3_PLL_Update.pdf), indicating a substantial improvement in the representation of temperature-dependent absorption. Furthermore, spectroscopic uncertainties associated with interfering species may contribute to the observed bias. In particular, CCl_2F_2 (CFC-12), N_2O , and O_3 are among the principal interfering species in the retrieval microwindows and therefore constitute plausible sources of systematic error, particularly as their impact differs between limb-viewing and ground-based geometries. Potential differences in the spectroscopic parameters adopted for the ACE-FTS and FTIR retrievals may also contribute to the observed bias. ACE-FTS v5.3 employs HITRAN 2020 spectroscopy (Section 2.3), whereas the FTIR retrievals are based on the 2024 ATM linelist (Subsection 3.1), which incorporates empirical updates to HITRAN spectroscopy derived from atmospheric FTIR observations (Toon et al., 2016).

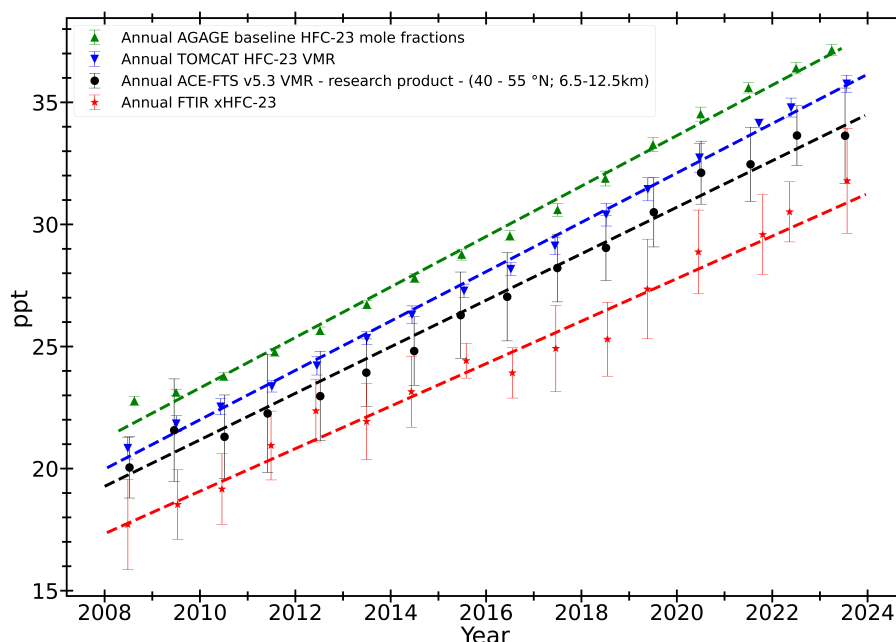


Figure 4. Annual mean atmospheric HFC-23 mole fractions from four datasets. Green upward-pointing triangles show AGAGE Jungfraujoch *in situ* measurements; blue inverted triangles indicate xHFC-23 derived from TOMCAT model simulations; black dots denote ACE-FTS v5.3 (research version) and red stars represent xHFC-23 from Jungfraujoch FTIR measurements. Vertical bars mark ± 1 standard deviation around annual means, while dashed lines show the linear trend for each dataset.

The linear trend values (absolute and relative) are presented in Table 2. These were estimated for the four datasets using the method described in Section 4.1. Relative trends were derived for each dataset by normalizing the absolute linear slope by the mean of the corresponding time series over the 2008–2023 period. The ground-based column-average observations from NDACC FTIR increased by 0.86 ± 0.09 ppt.yr⁻¹, i.e. a relative increase of 3.52 ± 0.37 %.yr⁻¹. The ACE-FTS data shows an increase of 0.98 ± 0.06 ppt.yr⁻¹, equivalent to 3.66 ± 0.22 %.yr⁻¹ in relative terms; while the model and *in situ* data exhibit more pronounced absolute trends than the ground-based FTIR data, with 0.99 ± 0.03 ppt.yr⁻¹ (3.53 ± 0.11 %.yr⁻¹) and 1.04 ± 0.04 ppt.yr⁻¹ (3.52 ± 0.15 %.yr⁻¹), respectively. The relative trends are consistent with each other within the estimated uncertainties. Notably, the absolute trend values derived from ACE-FTS and TOMCAT datasets are nearly identical, though the satellite data demonstrate a higher relative trend value.

As illustrated in Figure 4, the NDACC FTIR data exhibit varying degrees of agreement with the other datasets. Notably, the satellite data display a systematic offset with higher absolute and relative trend values (Table 2). This pattern is similarly observed in the *in situ* measurements except for the relative trends (same value but higher uncertainty for FTIR data), which reflect surface-level values. The TOMCAT model data align closely with the ACE-FTS data across the entire time series, yielding nearly identical relative trend values (as mentioned before). However, the model trend slope shows closer agreement with AGAGE compared to ACE-FTS, which can be attributed to the TOMCAT incorporating annual mean global mean AGAGE *a*



Table 2. Relative and absolute trends of HFC-23 derived from annual data from AGAGE *in situ*, TOMCAT model simulation for the 2008–2023 period, ACE-FTS and NDACC FTIR.

Source	Absolute trend (ppt.yr ⁻¹)	Relative trend (%.yr ⁻¹)
AGAGE <i>in situ</i>	1.04 ± 0.04	3.52 ± 0.15
TOMCAT simulation	0.99 ± 0.03	3.53 ± 0.11
ACE-FTS FTIR	0.98 ± 0.06	3.66 ± 0.22
NDACC FTIR	0.86 ± 0.09	3.52 ± 0.37

priori HFC-23 concentration values as a surface boundary condition. The observed differences between all datasets arise from various sources, including the transport time required for mixing and vertical transport between surface sources and the upper troposphere.

360 Several studies have documented the evolution of atmospheric HFC-23 abundances. For instance, Takeda et al. (2021) provided the first FTIR-retrieved xHFC-23 estimates for two NDACC sites (Rikubetsu, Japan; Syowa, Antarctica, now decommissioned). In this study, the same version of pseudoline spectroscopic parameters for HFC-23 was adopted as in the reference (Takeda et al., 2021) retrieval strategy. However, their strategy does not account for spectral interference from HFC-125. To assess whether this difference affects our ability to compare results, we evaluated the impact of including HFC-125 in the

365 retrieval model using ten years of measurements (2000–2010). The corresponding absolute trends remained unchanged: $(1.00 \pm 0.04) \times 10^{13} \text{ molec.cm}^{-2}.\text{yr}^{-1}$ with and without HFC-125 as interference. The relative trends remained comparable: $4.61 \pm 0.21 \text{ %.yr}^{-1}$ taking HFC-125 into account and $4.85 \pm 0.21 \text{ %.yr}^{-1}$ without. Including or excluding HFC-125 from the retrieval does not alter the trend, indicating that this interference has a negligible effect on the long-term trend, although it may affect the absolute column values. Therefore, our two strategies are comparable. This consistency enables a direct comparison

370 of our results with theirs. Takeda et al. (2021) reported trends of $0.93 \pm 0.11 \text{ ppt.yr}^{-1}$ (2008–2019, Rikubetsu) and $0.82 \pm 0.07 \text{ ppt.yr}^{-1}$ (2007–2016, Syowa). Moreover, they described systematic biases between monthly ground-based FTIR and *in situ* AGAGE measurements, ranging from –15% to –20% at Rikubetsu and –25% at Syowa. A comparison of the Jungfraujoch FTIR and AGAGE datasets performed in this study reveals a mean offset of approximately –21%, indicating that the FTIR-derived HFC-23 mole fractions are systematically lower than the corresponding AGAGE measurements. This offset is

375 of similar magnitude to those reported by Takeda et al. (2021). According to their results, the main sources of systematic error include uncertainties in the HFC-23 spectroscopic parameters (line intensity and lower-state energy) and spectroscopic uncertainties associated with interfering species, notably CH₄, H₂O, and HDO. While these factors may also contribute to the discrepancy observed at Jungfraujoch, the present study does not provide a detailed attribution of the FTIR-AGAGE offset.

We assessed the impact of adding HFC-125 as an interference for HFC-23 retrievals using both the standard and research

380 versions of ACE-FTS v5.3 (2004–2025). We report results from both versions for comparison. The research version (which includes HFC-125 as an interference) showed a higher RSD (22.8%) compared to the standard product (20.8%). Furthermore, higher positive trends were derived from the research version: $0.91 \pm 0.02 \text{ ppt.yr}^{-1}$ ($3.50 \pm 0.08 \text{ %.yr}^{-1}$) compared to 0.76



$\pm 0.01 \text{ ppt.yr}^{-1}$ ($2.90 \pm 0.05 \text{ \%.yr}^{-1}$) for the standard version. These findings are consistent with those of Dodangodage et al. (2025b), who reported an ACE-FTS VMR trend (v5.3, research version) of $1.03 \pm 0.01 \text{ ppt.yr}^{-1}$ (30°S – 30°N latitude band; 9.5–15.5 km) over 2012–2024. Thus, the research version achieves closer agreement with *in situ* AGAGE measurements due to the inclusion of new interferences (notably HFC-125) and the correction of ACE-FTS systematic instrumental effects (channelling).

4.3 Seasonal analysis

Figure 5 presents the seasonal cycle of xHFC-23 derived from the FTIR time series over the 2008–2009 2-year period. The fitted seasonal component reaches its minimum in early June and its maximum in mid-November, yielding a seasonal amplitude of 1.3 ppt (7.6% of the mean abundance for the period under consideration). The TOMCAT simulation reproduces a similar annual cycle (seasonal amplitude of 0.2 ppt), although with an earlier phase, displaying a minimum in April and a maximum in October. In contrast, the AGAGE baseline observations at Jungfraujoch show minimum and maximum amount-of-substance fraction in February and mid-May, respectively.

These differences likely reflect the distinct processes represented by each dataset. In TOMCAT, no seasonal cycle is imposed on the surface HFC-23 mixing ratios, such that the simulated annual variability arises solely from atmospheric transport and seasonally varying chemical loss, primarily through reaction with OH. Conversely, the AGAGE surface measurements are expected to be more sensitive to regional transport patterns and source influences. The FTIR observations, which provide information on the total atmospheric column, integrate signals from a larger fraction of the atmosphere and therefore likely reflect a combination of transport, chemical loss, and emission-related effects. The differing phase of the seasonal cycle among the FTIR, TOMCAT, and AGAGE datasets suggests that both atmospheric processes and source influences contribute to the observed seasonality of xHFC-23.

To assess the potential influence of tropopause height variability on the FTIR retrievals, a sensitivity analysis was performed by shifting the tropopause by approximately $\pm 2 \text{ km}$ and $\pm 4 \text{ km}$. This resulted in peak-to-peak changes in the retrieved HFC-23 total columns of $\sim 0.6\%$ and $\sim 1.3\%$, respectively, indicating a relatively weak sensitivity to tropopause height variations. Furthermore, the vertical gradient change in the *a priori* HFC-23 profile occurs in the lower stratosphere, above the tropopause, such that moderate variations in tropopause height have only a limited influence on the retrieval. These results suggest that tropopause height variability is unlikely to be a major driver of the observed seasonal cycle in xHFC-23. Instead, the seasonality is more likely driven by seasonally varying OH loss and large-scale meridional transport.

5 Conclusions

HFC-23 is a potent, long-lived greenhouse gas unintentionally produced as a byproduct of HCFC-22 synthesis. It is regulated under both the Kyoto Protocol and the Montreal Protocol. We derived a multi-decadal record of HFC-23 above the NDACC Jungfraujoch station. To this end, we developed a new retrieval strategy for HFC-23 which was applied to high-resolution FTIR solar absorption spectra.

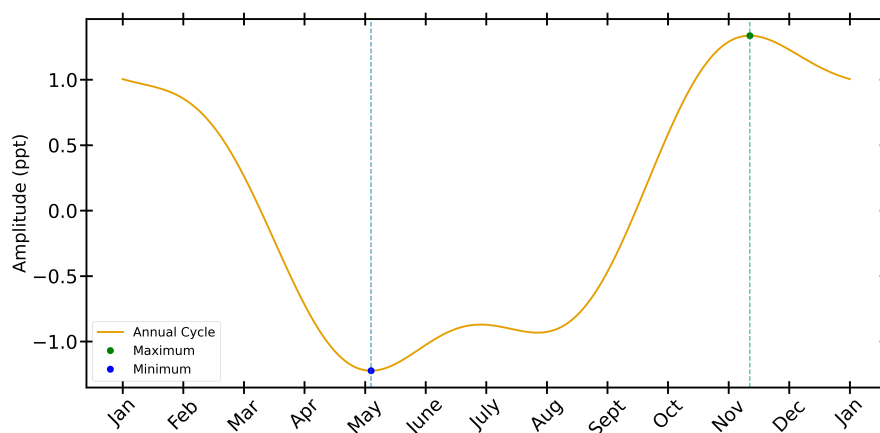


Figure 5. Seasonal cycle of xHFC-23 derived from FTIR observations at Jungfraujoch for the 2008-2009 2-year period.

415 A spectral window between 1138.5 and 1160 cm^{-1} was selected for the retrievals to minimize strong water vapour absorption, based on previous studies (Mahieu et al., 2021; Takeda et al., 2021). Within this window, the maximum absorption depth for HFC-23 is approximately 2.5%, with a mean DOFS of 1.10 (providing one independent piece of information). Although the vertical profile is poorly resolved, the retrieved total column of HFC-23 is well constrained.

We investigated observations from three successive FTIR spectrometers, yielding an unrivaled time series from 1986 to 420 2024. Retrievals from these archived spectra reveal a continuous increase in atmospheric HFC-23 abundance throughout the observation period. Error budget analysis indicates that the main source of systematic uncertainty is the assumed atmospheric temperature profile.

Jungfraujoch FTIR observations were compared with three independent datasets: ACE-FTS satellite measurements, *in situ* observations (AGAGE), and global 3-D model simulations (TOMCAT). Relative linear trends estimated for the 2008–2024 425 period reveal good agreement among datasets. Specifically, Jungfraujoch NDACC FTIR data are in close agreement with ACE-FTS, AGAGE *in situ* observations, and model simulations, with relative trends of $3.52 \pm 0.37\text{ \%.yr}^{-1}$, $3.66 \pm 0.22\text{ \%.yr}^{-1}$, $3.52 \pm 0.15\text{ \%.yr}^{-1}$, and $3.53 \pm 0.10\text{ \%.yr}^{-1}$, respectively.

In 2016, the Kigali Amendment of the Montreal Protocol mandated a phasedown of long-lived HFCs for developed countries starting in 2019, followed by a baseline freeze for developing countries in 2024 (WMO, 2018). Unlike other HFCs subject to 430 phasedown, HFC-23 faces additional destruction requirements: parties must destroy this by-product 'to the extent practicable' when it is produced during HCFC or HFC manufacturing (Secretariat, 2016). However, our results suggest these effects are not yet detectable. Instead, they highlight the steady increase in the global atmospheric abundance of major HFCs (Liang et al., 2022; Pardo Cantos et al., 2024). The 2022 Scientific Assessment of Ozone Depletion (Liang et al., 2022) reports that global observation-based emissions exceed those reported by Annex I countries to the UNFCCC, with a growing gap since the early 435 2000s. To verify the effectiveness of the Kigali Amendment, continuous monitoring of targeted species is essential.



Our retrieval strategy has been validated through intercomparison with independent datasets. The approach could be applied at other NDACC sites equipped with similar FTIR spectrometers (28 in the Northern Hemisphere and 4 in the Southern Hemisphere) to expand global HFC-23 monitoring. Whilst surface networks such as those operated by NOAA and AGAGE provide high-frequency *in situ* measurements, they are inherently limited to near-surface mixing ratios and cannot resolve vertical structure or stratospheric abundances. NDACC column measurements address this limitation by integrating the total atmospheric burden and providing sensitivity to the upper troposphere and lower stratosphere. This upper-atmospheric sensitivity is of particular relevance given that the ACE-FTS satellite instrument is operating well beyond its nominal design lifetime with no immediate successor currently approved (Salawitch et al., 2025). NDACC therefore represents an essential ground-based capability for sustaining long-term time series sensitive to the free atmosphere. Our findings underscore the necessity of robust monitoring frameworks that integrate such column observations to effectively assess the impact of international agreements.

Data availability. The Jungfraujoch FTIR data are available upon request (florentin.hiault@uliege.be and emmanuel.mahieu@uliege.be). The ACE-FTS volume mixing ratio data can be accessed at https://database.scisat.ca/level2/ace_v5.3/display_data.php (registration required). The v5.3 HFC-23 research product is available upon request from the ACE team (mlecours@scisat.ca). The *in situ* AGAGE Jungfraujoch data are available at the AGAGE website (<https://www-air.larc.nasa.gov/missions/agage/data>). TOMCAT-SLIMCAT model simulation is available upon request from Prof. Martyn Chipperfield (M.Chipperfield@leeds.ac.uk).

Appendix A: Supplementary Information

A1 Solar zenith angle dependence

The HFC-23 total columns retrieved with SFIT4 exhibit a dependence on the solar zenith angle (SZA). To correct for this effect, we applied the following linear correction:

$$TC_{\text{corrected}} = TC_{\text{retrieved}} + m \times (78^\circ - \text{SZA}) \quad (\text{A1})$$

where $TC_{\text{retrieved}}$ is the original retrieved HFC-23 total column (in molec. cm^{-2}), m is the slope of the linear regression (in molec. cm^{-2} degree $^{-1}$), and 78° is the reference SZA. This correction ensures that all retrievals are normalized to a common geometry, removing the SZA-induced bias from the time series.

A2 Data recorded by each FTIR instrument since 1986 at the Jungfraujoch station

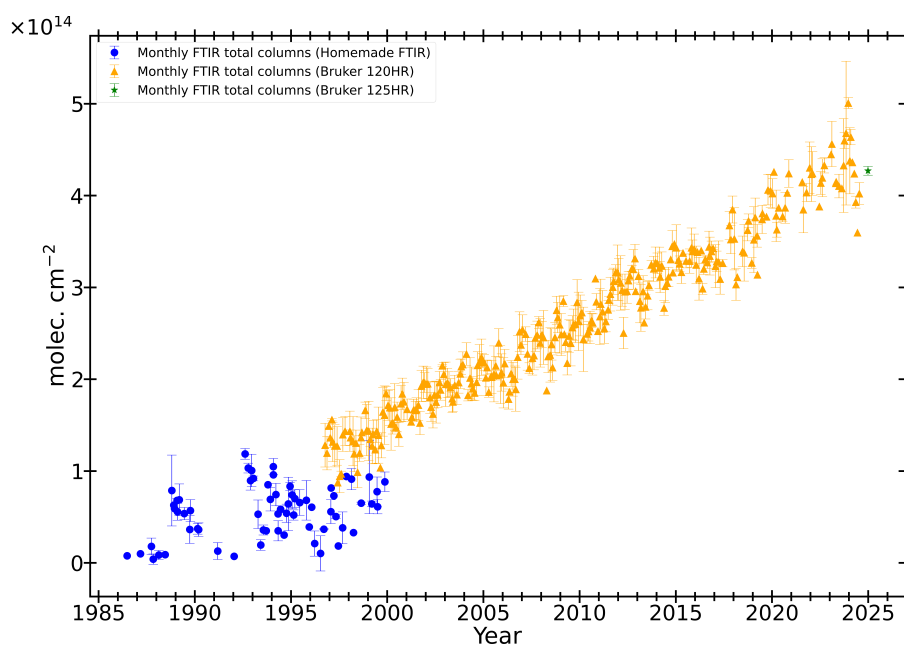


Figure A1. 40-year FTIR time series of HFC-23 vertical column abundances above Jungfraujoch (in molec. cm⁻²). Blue dots, orange upward-pointing triangles, and green star indicate monthly means for the homemade, 120HR, and 125HR instruments, respectively. The vertical error bars represent $\pm 1\sigma$.



460 *Author contributions.* **Florentin Hiault:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Visual-
ization, Writing – original draft. **Emmanuel Mahieu:** Conceptualization, Data curation, Funding acquisition, Investigation, Methodology,
Project administration, Supervision, Writing – review & editing. **Martyn P. Chipperfield:** Data curation, Resources, Validation, Writing –
review & editing. **Zihao Wang:** Data curation, Resources, Writing – investigation - review & editing. **Martin K. Vollmer:** Writing – inves-
tigation - review & editing. **Jeremy J. Harrison:** Writing – investigation - review & editing. **Diana Roos:** Writing – investigation - review
465 & editing. **Pierre-Henri Lefebvre:** Software.

Competing interests. The authors declare the following financial interests/personal relationships which may be considered as potential com-
peting interests: All other authors declare no competing interests.

Acknowledgements. We thank the Atmospheric Chemistry Experiment (ACE) Science Team and the AGAGE community for providing
the data used in this study. The TOMCAT model simulations were performed on the UK ARCHER2 and University of Leeds Aire high-
470 performance computing systems. The ULiège team acknowledges the support of the International Foundation High Altitude Research Sta-
tions Jungfraujoch and Gornergrat (HFSJG, Bern, Switzerland) for maintaining the facilities necessary for the Fourier Transform Infrared
(FTIR) observations at Jungfraujoch. Support from the GAW-GCOS Office of MeteoSwiss is also gratefully acknowledged. EM is a Research
Director with F.R.S.-FNRS. The research infrastructure at Jungfraujoch is maintained by the HFSJG.ch Foundation. We acknowledge the
essential contribution of G.C. Toon for the provision of the ATM compilations and EPLL linelists.
475 The FTIR monitoring program of the University of Liège has been primarily supported by the F.R.S. - FNRS (Brussels, Belgium; grant
n° J.0139.24), the GAW-CH program of MeteoSwiss (Zürich, CH) and the University of Liège. The Atmospheric Chemistry Experiment
(ACE) is funded by the Canadian Space Agency. MPC and ZW were supported by the Natural Environment Research Council (NERC)
project InHALE (NE/X003450/1). JJH was supported by NERC national capability funding for the National Centre for Earth Observation
(grant number NE/Y006216/1). Support was also provided by the SI-haloVOCs project, co-funded by the Federal Office of Meteorology and
480 Climatology MeteoSwiss as part of GCOS-CH. Support for the *in situ* HFC-23 AGAGE measurements was provided by the Swiss National
Programmes HALCLIM and CLIMGASCH (Swiss Federal Office for the Environment, FOEN) and by the International Foundation High
Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG).



References

- Arnold, T., Mühle, J., Salameh, P. K., Harth, C. M., Ivy, D. J., and Weiss, R. F.: Automated Measurement of Nitrogen Trifluoride in Ambient
485 Air, *Analytical Chemistry*, 84, 4798–4804, <https://doi.org/10.1021/ac300373e>, 2012.
- Barthlott, S., Schneider, M., Hase, F., Wiegeler, A., Christner, E., González, Y., Blumenstock, T., Dohe, S., García, O. E., Sepúlveda, E.,
Strong, K., Mendonça, J., Weaver, D., Palm, M., Deutscher, N. M., Warneke, T., Notholt, J., Lejeune, B., Mahieu, E., Jones, N., Griffith,
D. W. T., Velasco, V. A., Smale, D., Robinson, J., Kivi, R., Heikkinen, P., and Raffalski, U.: Using XCO₂ retrievals for assessing the
long-term consistency of NDACC/FTIR data sets, *Atmospheric Measurement Techniques*, 8, 1555–1573, [https://doi.org/10.5194/amt-8-](https://doi.org/10.5194/amt-8-1555-2015)
490 1555-2015, 2015.
- Berezkin, K., Li, G., Lüttschwager, N., Kim, M., Bohlius, H., Ebert, V., Harrison, J., and Domanskaya, A.: Absorption cross sec-
tions of CHF₃ (HFC-23) in synthetic air at 296 K, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 347, 109642,
<https://doi.org/10.1016/j.jqsrt.2025.109642>, 2025.
- Bernath, P. F., McElroy, C. T., Abrams, M. C., Boone, C. D., Butler, M., Camy-Peyret, C., Carleer, M., Clerbaux, C., Coheur, P.-F., Colin, R.,
495 DeCola, P., DeMazière, M., Drummond, J. R., Dufour, D., Evans, W. F. J., Fast, H., Fussen, D., Gilbert, K., Jennings, D. E., Llewellyn,
E. J., Lowe, R. P., Mahieu, E., McConnell, J. C., McHugh, M., McLeod, S. D., Michaud, R., Midwinter, C., Nassar, R., Nichitiu, F.,
Nowlan, C., Rinsland, C. P., Rochon, Y. J., Rowlands, N., Semeniuk, K., Simon, P., Skelton, R., Sloan, J. J., Soucy, M.-A., Strong,
K., Tremblay, P., Turnbull, D., Walker, K. A., Walkty, I., Wardle, D. A., Wehrle, V., Zander, R., and Zou, J.: Atmospheric Chemistry
Experiment (ACE): Mission overview, *Geophysical Research Letters*, 32, L15S01, <https://doi.org/10.1029/2005gl022386>, 2005.
- 500 Boone, C. D., Bernath, P. F., and Lecours, M.: Version 5 retrievals for ACE-FTS and ACE-imagers, *Journal of Quantitative Spectroscopy
and Radiative Transfer*, 310, 108749, <https://doi.org/10.1016/j.jqsrt.2023.108749>, 2023.
- Chipperfield, M. P.: New version of the TOMCAT/SLIMCAT off-line chemical transport model: Intercomparison of stratospheric tracer
experiments, *Quarterly Journal of the Royal Meteorological Society*, 132, 1179–1203, <https://doi.org/10.1256/qj.05.51>, 2006.
- Chrysanthou, A., Dubé, K., Tegtmeier, S., and Chipperfield, M. P.: Hemispheric Asymmetry in Stratospheric Trends of
505 HCl and Ozone: Impact of Chemical Feedback on Ozone Recovery, *Journal of Geophysical Research: Atmospheres*, 130,
<https://doi.org/10.1029/2024jd042161>, 2025.
- De Mazière, M., Thompson, A. M., Kurylo, M. J., Wild, J. D., Bernhard, G., Blumenstock, T., Braathen, G. O., Hannigan, J. W., Lambert,
J.-C., Leblanc, T., McGee, T. J., Nedoluha, G., Petropavlovskikh, I., Seckmeyer, G., Simon, P. C., Steinbrecht, W., and Strahan, S. E.: The
Network for the Detection of Atmospheric Composition Change (NDACC): History, status and perspectives, *Atmospheric Chemistry and
510 Physics*, 18, 4935–4964, <https://doi.org/10.5194/acp-18-4935-2018>, 2018.
- Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmaseda, M. A., Balsamo, G., Bauer,
P., Bechtold, P., Beljaars, A. C. M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., Fuentes, M., Geer, A. J., Haim-
berger, L., Healy, S. B., Hersbach, H., Hólm, E. V., Isaksen, I., Kållberg, P., Köhler, M., Matricardi, M., McNally, A. P., Monge-
Sanz, B. M., Morcrette, J., Park, B., Peubey, C., de Rosnay, P., Tavolato, C., Thépaut, J., and Vitart, F.: The ERA-Interim reanalysis:
515 configuration and performance of the data assimilation system, *Quarterly Journal of the Royal Meteorological Society*, 137, 553–597,
<https://doi.org/10.1002/qj.828>, 2011.
- Dodangodage, R., Bernath, P., Boone, C., Harrison, J., Lecours, M., Schmidt, M., Montzka, S., Vimont, I., and Crotwell, M.: The first satellite
measurements of HFC-125 by the ACE-FTS: Long-term trends and distribution in the Earth’s upper troposphere and lower stratosphere,
Journal of Quantitative Spectroscopy and Radiative Transfer, 330, 109218, <https://doi.org/10.1016/j.jqsrt.2024.109218>, 2025a.



- 520 Dodangodage, R., Bernath, P. F., Boone, C., Lecours, M., and Schmidt, M.: HFC-23 from updated Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS) retrievals, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 338, 109 416, <https://doi.org/10.1016/j.jqsrt.2025.109416>, 2025b.
- Ebnesajjad, S.: Preparation of Tetrafluoroethylene and Other Monomers, in: *Fluoroplastics*, pp. 48–75, William Andrew Publishing, Oxford, 2 edn., 2015.
- 525 Farman, J. C., Gardiner, B. G., and Shanklin, J. D.: Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction, *Nature*, 315, 207–210, <https://doi.org/10.1038/315207a0>, 1985.
- Fernando, A. M., Bernath, P. F., and Boone, C. D.: Trends in atmospheric HFC-23 (CHF₃) and HFC-134a abundances, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 238, 106 540, <https://doi.org/10.1016/j.jqsrt.2019.06.019>, 2019.
- Friedrich, M., Beutner, E., Reuvers, H., Smeekes, S., Urbain, J.-P., Bader, W., Franco, B., Lejeune, B., and Mahieu, E.: A statistical analysis
530 of time trends in atmospheric ethane, *Climatic Change*, 162, 105–125, <https://doi.org/10.1007/s10584-020-02806-2>, 2020a.
- Friedrich, M., Smeekes, S., and Urbain, J.-P.: Autoregressive wild bootstrap inference for nonparametric trends, *Journal of Econometrics*, 214, 81–109, <https://doi.org/10.1016/j.jeconom.2019.05.006>, 2020b.
- Gettelman, A., Mills, M. J., Kinnison, D. E., Garcia, R. R., Smith, A. K., Marsh, D. R., Tilmes, S., Vitt, F., Bardeen, C. G., McInerny, J., Liu, H.-L., Solomon, S. C., Polvani, L. M., Emmons, L. K., Lamarque, J.-F., Richter, J. H., Glanville, A. S., Bacmeister, J. T., Phillips, A. S.,
535 Neale, R. B., Simpson, I. R., DuVivier, A. K., Hodzic, A., and Randel, W. J.: The Whole Atmosphere Community Climate Model Version 6 (WACCM6), *Journal of Geophysical Research: Atmospheres*, 124, 12 380–12 403, <https://doi.org/10.1029/2019jd030943>, 2019.
- Gohar, L. K., Myhre, G., and Shine, K. P.: Updated radiative forcing estimates of four halocarbons, *Journal of Geophysical Research: Atmospheres*, 109, <https://doi.org/10.1029/2003jd004320>, 2004.
- Gordon, I., Rothman, L., Hargreaves, R., Hashemi, R., Karlovets, E., Skinner, F., Conway, E., Hill, C., Kochanov, R., Tan, Y., Wcislo, P.,
540 Finenko, A., Nelson, K., Bernath, P., Birk, M., Boudon, V., Campargue, A., Chance, K., Coustenis, A., Drouin, B., Flaud, J., Gamache, R., Hodges, J., Jacquemart, D., Mlawer, E., Nikitin, A., Perevalov, V., Rotger, M., Tennyson, J., Toon, G., Tran, H., Tyuterev, V., Adkins, E., Baker, A., Barbe, A., Canè, E., Császár, A., Dudaryonok, A., Egorov, O., Fleisher, A., Fleurbaey, H., Foltynowicz, A., Furtenbacher, T., Harrison, J., Hartmann, J., Horneman, V., Huang, X., Karman, T., Karns, J., Kass, S., Kleiner, I., Kofman, V., Kwabia-Tchana, F., Lavrentieva, N., Lee, T., Long, D., Lukashetskaya, A., Lyulin, O., Makhnev, V., Matt, W., Massie, S., Melosso, M., Mikhailenko, S.,
545 Mondelain, D., Müller, H., Naumenko, O., Perrin, A., Polyansky, O., Raddaoui, E., Raston, P., Reed, Z., Rey, M., Richard, C., Tóbiás, R., Sadek, I., Schwenke, D., Starikova, E., Sung, K., Tamassia, F., Tashkun, S., Vander Auwera, J., Vasilenko, I., Vigasin, A., Villanueva, G., Vispoel, B., Wagner, G., Yachmenev, A., and Yurchenko, S.: The HITRAN2020 molecular spectroscopic database, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 277, 107 949, <https://doi.org/10.1016/j.jqsrt.2021.107949>, 2022.
- Harrison, J. J.: Infrared absorption cross sections for trifluoromethane, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 130,
550 359–364, <https://doi.org/10.1016/j.jqsrt.2013.05.026>, 2013.
- Hersbach, H., Bell, B., Berrisford, P., Hirahara, S., Horányi, A., Muñoz-Sabater, J., Nicolas, J., Peubey, C., Radu, R., Schepers, D., Simmons, A., Soci, C., Abdalla, S., Abellan, X., Balsamo, G., Bechtold, P., Biavati, G., Bidlot, J., Bonavita, M., De Chiara, G., Dahlgren, P., Dee, D., Diamantakis, M., Dragani, R., Flemming, J., Forbes, R., Fuentes, M., Geer, A., Haimberger, L., Healy, S., Hogan, R. J., Hólm, E., Janisková, M., Keeley, S., Laloyaux, P., Lopez, P., Lupu, C., Radnoti, G., de Rosnay, P., Rozum, I., Vamborg, F., Villanueva, S., and Thépaut, J.-N.: The ERA5 global reanalysis, *Quarterly Journal of the Royal Meteorological Society*, 146, 1999–2049, <https://doi.org/10.1002/qj.3803>, 2020.



- Kyoung Chung, Y.: Absorption cross-sections off HFC-23 at atmospheric conditions, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 96, 281–287, <https://doi.org/10.1016/j.jqsrt.2005.04.004>, 2005.
- Lachance, R. L., Buijs, H. L., and Soucy, M.-A.: ACE-FTS on SCISAT: 10th year on-orbit anniversary, in: *Infrared Remote Sensing and Instrumentation XXI*, edited by Strojnik Scholl, M. and Páez, G., vol. 8867, p. 88670J, SPIE, <https://doi.org/10.1117/12.2024985>, 2013.
- Liang, Q., Rigby, M., et al.: Chapter 2: Hydrofluorocarbons (HFCs), in: *Scientific Assessment of Ozone Depletion: 2022*, Ozone Research and Monitoring, edited by Organization, W. M., no. 278 in GAW Report, p. 509, WMO, Geneva, Switzerland, 2022.
- Lovelock, J. E., Maggs, R. J., and Wade, R. J.: Halogenated Hydrocarbons in and over the Atlantic, *Nature*, 241, 194–196, <https://doi.org/10.1038/241194a0>, 1973.
- Mahieu, E., Fischer, E. V., Franco, B., Palm, M., Wizenberg, T., Smale, D., Clarisse, L., Clerbaux, C., Coheur, P.-F., Hannigan, J. W., Lutsch, E., Notholt, J., Cantos, I. P., Prignon, M., Servais, C., and Strong, K.: First retrievals of peroxyacetyl nitrate (PAN) from ground-based FTIR solar spectra recorded at remote sites, comparison with model and satellite data, *Elementa: Science of the Anthropocene*, 9, <https://doi.org/10.1525/elementa.2021.00027>, 2021.
- Makkor, J., Palm, M., Pardo Cantos, I., Buschmann, M., Mahieu, E., Wang, Z., Chipperfield, M. P., and Notholt, J.: First Measurements of CFC-12 in 1951 at Jungfraujoch and Comparison to Current Measurements and Atmospheric Models, *Geophysical Research Letters*, 53, <https://doi.org/10.1029/2025gl117453>, 2026.
- Miller, B. R. and Kuijpers, L. J. M.: Projecting future HFC-23 emissions, *Atmospheric Chemistry and Physics*, 11, 13 259–13 267, <https://doi.org/10.5194/acp-11-13259-2011>, 2011.
- Miller, B. R., Weiss, R. F., Salameh, P. K., Tanhua, T., Grealley, B. R., Mühle, J., and Simmonds, P. G.: Medusa: A Sample Preconcentration and GC/MS Detector System for in Situ Measurements of Atmospheric Trace Halocarbons, Hydrocarbons, and Sulfur Compounds, *Analytical Chemistry*, 80, 1536–1545, <https://doi.org/10.1021/ac702084k>, 2008.
- Miller, B. R., Rigby, M., Kuijpers, L. J. M., Krummel, P. B., Steele, L. P., Leist, M., Fraser, P. J., McCulloch, A., Harth, C., Salameh, P., Mühle, J., Weiss, R. F., Prinn, R. G., Wang, R. H. J., O'Doherty, S., Grealley, B. R., and Simmonds, P. G.: HFC-23 (CHF₃) emission trend response to HCFC-22 (CHClF₂) production and recent HFC-23 emission abatement measures, *Atmospheric Chemistry and Physics*, 10, 7875–7890, <https://doi.org/10.5194/acp-10-7875-2010>, 2010.
- Molina, M. J. and Rowland, F. S.: Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone, *Nature*, 249, 810–812, <https://doi.org/10.1038/249810a0>, 1974.
- Montzka, S. A., Velders, G. J. M., Krummel, P. B., Mühle, J., Orkin, V. L., Park, S., Shah, N., Walter-Terrinoni, H., Bernath, P., Boone, C., Hu, L., Kurylo, M. J., Elvidge, E. L., Maione, M., Miller, B. R., O'Doherty, S., Rigby, M., Simpson, I. J., Vollmer, M. K., Weiss, R. F., Kuijpers, L. J. M., and Sturges, W. T.: Hydrofluorocarbons (HFCs), in: *Scientific Assessment of Ozone Depletion: 2018*, edited by Research, G. O. and Project, M., no. 58 in Report, chap. 2, World Meteorological Organization, Geneva, Switzerland, 2018.
- Montzka, S. A., Burkholder, J. B., Carpenter, L. J., Fahey, D. W., Jucks, K. W., and Safari, B.: Report of the Scientific Assessment Panel in Response to Decision XXXV/7: Emissions of HFC-23, Report, Montreal Protocol Scientific Assessment Panel, Nairobi, Kenya, 2024.
- O'Doherty, S., Simmonds, P. G., Cunnold, D. M., Wang, H. J., Sturrock, G. A., Fraser, P. J., Ryall, D., Derwent, R. G., Weiss, R. F., Salameh, P., Miller, B. R., and Prinn, R. G.: In situ chloroform measurements at Advanced Global Atmospheric Gases Experiment atmospheric research stations from 1994 to 1998, *Journal of Geophysical Research: Atmospheres*, 106, 20 429–20 444, <https://doi.org/10.1029/2000jd900792>, 2001.
- Oram, D. E., Sturges, W. T., Penkett, S. A., McCulloch, A., and Fraser, P. J.: Growth of fluoroform (CHF₃, HFC-23) in the background atmosphere, *Geophysical Research Letters*, 25, 35–38, <https://doi.org/10.1029/97gl03483>, 1998.



- 595 Ortega, I., Hannigan, J. W., Baier, B. C., McKain, K., and Smale, D.: Advancing CH₄ and N₂O retrieval strategies for NDACC/IRWG
FTIR observations with the support of airborne in situ measurements, *Atmospheric Measurement Techniques*, 18, 2353–2371,
<https://doi.org/10.5194/amt-18-2353-2025>, 2025.
- Pardo Cantos, I., Mahieu, E., Chipperfield, M. P., Smale, D., Hannigan, J. W., Friedrich, M., Fraser, P., Krummel, P., Prignon, M., Makkor, J.,
Servais, C., and Robinson, J.: Determination and analysis of time series of CFC-11 (CCl₃F) from FTIR solar spectra, in situ observations,
600 and model data in the past 20 years above Jungfraujoch (46°N), Lauder (45°S), and Cape Grim (40°S) stations, *Environmental Science:
Atmospheres*, 2, 1487–1501, <https://doi.org/10.1039/d2ea00060a>, 2022.
- Pardo Cantos, I., Mahieu, E., Chipperfield, M. P., Servais, C., Reimann, S., and Vollmer, M. K.: First HFC-134a retrievals from
ground-based FTIR solar absorption spectra, comparison with TOMCAT model simulations, in-situ AGAGE observations, and
ACE-FTS satellite data for the Jungfraujoch station, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 318, 108938,
605 <https://doi.org/10.1016/j.jqsrt.2024.108938>, 2024.
- Prinn, R. G., Weiss, R. F., Fraser, P. J., Simmonds, P. G., Cunnold, D. M., Alyea, F. N., O'Doherty, S., Salameh, P., Miller, B. R., Huang,
J., Wang, R. H. J., Hartley, D. E., Harth, C., Steele, L. P., Sturrock, G., Midgley, P. M., and McCulloch, A.: A history of chemically
and radiatively important gases in air deduced from ALE/GAGE/AGAGE, *Journal of Geophysical Research: Atmospheres*, 105, 17751–
17792, <https://doi.org/10.1029/2000jd900141>, 2000.
- 610 Rodgers, C. D.: *Inverse Methods for Atmospheric Sounding: Theory and Practice*, Series on Atmospheric, Oceanic and Planetary Physics,
WORLD SCIENTIFIC, ISBN 9789812813718, <https://doi.org/10.1142/3171>, 2000.
- Rust, D., Vollmer, M. K., Henne, S., Frumau, A., van den Bulk, P., Hensen, A., Stanley, K. M., Zenobi, R., Emmenegger, L., and Reimann,
S.: Effective realization of abatement measures can reduce HFC-23 emissions, *Nature*, 633, 96–100, <https://doi.org/10.1038/s41586-024-07833-y>, 2024.
- 615 Salawitch, R. J., Smith, J. B., Selkirk, H., Wargan, K., Chipperfield, M. P., Hossaini, R., Levelt, P. F., Livesey, N. J., McBride, L. A.,
Millán, L. F., Moyer, E., Santee, M. L., Schoeberl, M. R., Solomon, S., Stone, K., and Worden, H. M.: The Imminent Data Desert: The
Future of Stratospheric Monitoring in a Rapidly Changing World, *Bulletin of the American Meteorological Society*, 106, E540–E563,
<https://doi.org/10.1175/bams-d-23-0281.1>, 2025.
- Secretariat, O.: Action on ozone, United Nations Environment Program, Nairobi Kenya, p. 21, 2000.
- 620 Secretariat, O.: Amendment to the Montreal Protocol on Substances that Deplete the Ozone Layer, United Nations Environment Programme,
Nairobi, Kenya, p. 21, 2016.
- Sharpe, S. W., Johnson, T. J., Sams, R. L., Chu, P. M., Rhoderick, G. C., and Johnson, P. A.: Gas-Phase Databases for Quantitative Infrared
Spectroscopy, *Applied Spectroscopy*, 58, 1452–1461, <https://doi.org/10.1366/0003702042641281>, 2004.
- Sheese, P. E., Boone, C. D., and Walker, K. A.: Detecting physically unrealistic outliers in ACE-FTS atmospheric measurements, *Atmo-
spheric Measurement Techniques*, 8, 741–750, <https://doi.org/10.5194/amt-8-741-2015>, 2015.
- 625 Simmonds, P. G., Rigby, M., McCulloch, A., Vollmer, M. K., Henne, S., Mühle, J., O'Doherty, S., Manning, A. J., Krummel, P. B., Fraser,
P. J., Young, D., Weiss, R. F., Salameh, P. K., Harth, C. M., Reimann, S., Trudinger, C. M., Steele, L. P., Wang, R. H. J., Ivy, D. J., Prinn,
R. G., Mitrevski, B., and Etheridge, D. M.: Recent increases in the atmospheric growth rate and emissions of HFC-23 (CHF₃) and the
link to HCFC-22 (CHClF₂) production, *Atmospheric Chemistry and Physics*, 18, 4153–4169, <https://doi.org/10.5194/acp-18-4153-2018>,
630 2018.



- Stanley, K. M., Say, D., Mühle, J., Harth, C. M., Krummel, P. B., Young, D., O'Doherty, S. J., Salameh, P. K., Simmonds, P. G., Weiss, R. F., Prinn, R. G., Fraser, P. J., and Rigby, M.: Increase in global emissions of HFC-23 despite near-total expected reductions, *Nature Communications*, 11, <https://doi.org/10.1038/s41467-019-13899-4>, 2020.
- 635 Sulbaek Andersen, M. P., Madronich, S., Ohide, J. M., Frausig, M., and Nielsen, O. J.: Photolysis of CF₃CHO at 254 nm and potential contribution to the atmospheric abundance of HFC-23, *Atmospheric Environment*, 314, 120087, <https://doi.org/10.1016/j.atmosenv.2023.120087>, 2023.
- Sung, D. J., Moon, D. J., Kim, J., Moon, S., and Hong, S.-I.: Production of TFE by catalytic pyrolysis of chlorodifluoromethane (CHClF₂), vol. 159, pp. 233–236, Elsevier, ISBN 9780444517333, [https://doi.org/10.1016/s0167-2991\(06\)81576-4](https://doi.org/10.1016/s0167-2991(06)81576-4), 2006.
- 640 Sussmann, R., Borsdorff, T., Rettinger, M., Camy-Peyret, C., Demoulin, P., Duchatelet, P., Mahieu, E., and Servais, C.: Technical Note: Harmonized retrieval of column-integrated atmospheric water vapor from the FTIR network – first examples for long-term records and station trends, *Atmospheric Chemistry and Physics*, 9, 8987–8999, <https://doi.org/10.5194/acp-9-8987-2009>, 2009.
- Takeda, M., Nakajima, H., Murata, I., Nagahama, T., Morino, I., Toon, G. C., Weiss, R. F., Mühle, J., Krummel, P. B., Fraser, P. J., and Wang, H.-J.: First ground-based Fourier transform infrared (FTIR) spectrometer observations of HFC-23 at Rikubetsu, Japan, and Syowa Station, Antarctica, *Atmospheric Measurement Techniques*, 14, 5955–5976, <https://doi.org/10.5194/amt-14-5955-2021>, 2021.
- 645 Toon, G. C., Blavier, J.-F., Sung, K., Rothman, L. S., and E. Gordon, I.: HITRAN spectroscopy evaluation using solar occultation FTIR spectra, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 182, 324–336, <https://doi.org/10.1016/j.jqsrt.2016.05.021>, 2016.
- Toth, R. A.: N₂- and air-broadened linewidths and frequency-shifts of N₂O, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 66, 285–304, [https://doi.org/10.1016/s0022-4073\(99\)00167-3](https://doi.org/10.1016/s0022-4073(99)00167-3), 2000.
- 650 WMO: GAW Report No. 58: WMO Global Atmosphere Watch (GAW) Implementation Plan: 2016–2023, Report 58, World Meteorological Organization, Geneva, Switzerland, 2018.
- WMO: Scientific Assessment of Ozone Depletion: 2022, Ozone Research and Monitoring, Report 278, WMO, Geneva, Switzerland, 2022.
- Yvon-Lewis, S. A. and Butler, J. H.: Effect of oceanic uptake on atmospheric lifetimes of selected trace gases, *Journal of Geophysical Research: Atmospheres*, 107, <https://doi.org/10.1029/2001jd001267>, 2002.
- 655 Zander, R., Mahieu, E., Demoulin, P., Duchatelet, P., Roland, G., Servais, C., De Mazière, M., Reimann, S., and Rinsland, C. P.: Our changing atmosphere: Evidence based on long-term infrared solar observations at the Jungfraujoch since 1950, *Science of The Total Environment*, 391, 184–195, <https://doi.org/10.1016/j.scitotenv.2007.10.018>, 2008.
- Zhou, M., Langerock, B., Vigouroux, C., Wang, P., Hermans, C., Stiller, G., Walker, K. A., Dutton, G., Mahieu, E., and De Mazière, M.: Ground-based FTIR retrievals of SF₆ on Reunion Island, *Atmospheric Measurement Techniques*, 11, 651–662, <https://doi.org/10.5194/amt-11-651-2018>, 2018.
- 660 Zhou, M., Langerock, B., Vigouroux, C., Smale, D., Toon, G., Polyakov, A., Hannigan, J. W., Mellqvist, J., Robinson, J., Notholt, J., Strong, K., Mahieu, E., Palm, M., Prignon, M., Jones, N., García, O., Morino, I., Murata, I., Ortega, I., Nagahama, T., Wizenberg, T., Flood, V., Walker, K., and De Mazière, M.: Recent Decreases in the Growth Rate of Atmospheric HCFC-22 Column Derived From the Ground-Based FTIR Harmonized Retrievals at 16 NDACC Sites, *Geophysical Research Letters*, 51, <https://doi.org/10.1029/2024gl112470>, 2024.