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Key Points:

- We retrieved total columns of CFC–12 in 1951, using historical solar absorption spectra
- We show the evolution of atmospheric CFC–12 from 1950 to 2024 using different measurement and model results
- The surface volume mixing ratio from the historical spectra is larger than the emission-based forward model estimates but within error bars

Correspondence to:
J. Makkor,
makkor@iup.physik.uni-bremen.de

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Author Contributions:
Conceptualization: Jamal Makkor
Data curation: Jamal Makkor, Irene Pardo Cantos, Emmanuel Mahieu
Formal analysis: Jamal Makkor
Funding acquisition: Justus Notholt
Investigation: Jamal Makkor
Methodology: Jamal Makkor
Project administration: Justus Notholt
Resources: Mathias Palm
Software: Mathias Palm
Supervision: Mathias Palm, Matthias Buschmann, Emmanuel Mahieu, Martyn P. Chipperfield, Justus Notholt
Validation: Jamal Makkor
Visualization: Jamal Makkor
Writing – original draft: Jamal Makkor
Writing – review & editing: Jamal Makkor, Mathias Palm, Irene Pardo Cantos, Matthias Buschmann, Emmanuel Mahieu, Zihao Wang, Martyn P. Chipperfield, Justus Notholt

First Measurements of CFC-12 in 1951 at Jungfraujoch and Comparison to Current Measurements and Atmospheric Models

Jamal Makkor[1], Mathias Palm[1], Irene Pardo Cantos[2], Matthias Buschmann[1], Emmanuel Mahieu[2], Zihao Wang[3], Martyn P. Chipperfield[3], and Justus Notholt[1]

[1]Institute of Environmental Physics (IUP), University of Bremen, Bremen, Germany, [2]Department of Astrophysics, Geophysics and Oceanography, UR SPHERES, University of Liège, Liège, Belgium, [3]School of Earth and Environment, University of Leeds, Leeds, UK

Abstract Chlorofluorocarbons (CFCs) have played a major role in the depletion of stratospheric ozone. Understanding historical trends in emissions and atmospheric concentrations is crucial for quantifying their impact. The first measurements of atmospheric CFCs were performed in-situ by Lovelock in 1970. We have analyzed historical 1951 solar absorption infrared spectra, recorded at Jungfraujoch, to retrieve the CFC– 12 surface mole fraction. We compare to routine solar absorption measurements starting at Jungfraujoch in 1986 and emission-based forward models. The surface mole fraction derived from the historical spectra is (26.1 ± 18.5) pptv compared to (9.2 ± 0.2) pptv from a reconstructed history model, and (7.00 ± 0.28) pptv from the Advanced Global Atmospheric Gases Experiment 12-Box model. The 1951 measurement and model values agree within error bars although the models may be biased low due to unreported emissions. Our result represents the earliest atmospheric CFC measurement, predating Lovelock's detection by over two decades.

Plain Language Summary This paper presents the first measurement of CFC– 12 surface mole fraction obtained at Jungfraujoch in 1951. The study was performed using digitized paper-based solar absorption spectra produced by a Pfund-type grating spectrometer. The surface mole fraction was calculated using modern retrieval methods, and compared with model predictions and measurements obtained at the same site over the last four decades. An analysis of errors is presented and compared with the reconstructed history and AGAGE model. The comparison gives a surface mole fraction three times higher than the one predicted by the model. However, the model result and the reconstructed history lie within uncertainty of measurement. Our result represents the earliest atmospheric CFC measurement, two decades earlier than the first in-situ measurements.

1. Introduction

The compound $CCl_2 F_2$, more commonly referred to as CFC– 12 or Freon-12™, was first synthesized by Thomas Midgley (Midgley & Henne, 1930) and is one of the most important atmospheric ozone-depleting substances (ODSs) regulated by the Montreal Protocol. It has an ozone depletion potential of 1.0 and contributes around 1,000 pptv of current stratospheric chlorine loading (WMO, 2022). It is also a potent greenhouse gas (GHG) with a Global Warming Potential relative to CO_2 of 10,900 over a 100-year horizon, one of the highest of the regulated gases (The Kigali Amendment, 2016).

CFC– 12 was used for many decades due to its chemical non-reactivity and stability as a refrigerant and as a propellant. Most of the reported production and emissions of CFC– 12 (and other regulated ODS) were compiled by the Chemical Manufacturers Association (CMA, 1980). In 2016, the global emissions of CFC– 12 were estimated to be approximately (33 ± 21) $\mathrm{Gg\,yr^{-1}}$, while in 2020, these emissions were estimated to have reduced to around (25 ± 20) $\mathrm{Gg\,yr^{-1}}$ (WMO, 2022).

In July and August of 1970, James Lovelock discovered trace amounts of a similar chlorofluorocarbon, $CCl_3 F$ (CFC– 11) and SF_6, using a new and very sensitive Electron Capture Detector (ECD) device when studying tropospheric haze over Ireland. Lovelock also tried to measure CFC– 12 in the atmosphere. However, this was not possible due to its relatively low rate of reaction with thermal electrons in the ECD (Lovelock, 1971). Later, Molina and Rowland (1974) proposed that CFCs would dissociate in the stratosphere when exposed to ultraviolet radiation, freeing chlorine, and causing a catalytic reaction cycle that destroys stratospheric ozone. This discovery was one prime motivation for the Montreal Protocol (MP), which proposed a gradual phase-out of these gases (United Nations Treaty Collection, 1989). The Atmospheric Lifetime Experiment started measuring multiple gases including CFC– 11 and CFC– 12 in 1978 based on theoretical work of Cunnold et al. (1978) using ECD-based chromatographs.

Following a continued increase in its atmospheric abundance, the first slowing in the growth rate of CFC– 12 was reported by Engel et al. (1998) based on in-situ balloon measurements. The subsequent global decline in CFC– 12, albeit slow due to the relatively long lifetime of CFC– 12 of more than 100 years, has contributed to the slow recovery of the ozone layer (WMO, 2022). This global picture of declining emissions of the major CFCs suffered a setback due to non-compliant production of CFC– 11 from 2012, which was reported by Montzka et al. (2018) and later confirmed using Fourier Transform Infrared (FTIR) observations at Jungfraujoch and Lauder (Pardo Cantos et al., 2022). However, CFC– 11 emissions now seem to have returned to values consistent with expectations (Montzka et al., 2021).

In this work, we present the retrieval of CFC– 12 from historical (1951) solar infrared absorption spectra from a Pfund-type grating spectrometer together with FTIR spectra from both a home-made (since 1986) and a commercial instrument (Bruker, since the mid-1990s) from the International Scientific Station at Jungfraujoch, as well as an estimation of the surface mole fraction of this gas. The retrieved CFC– 12 mole fractions are compared to reconstructed history estimation of CFC– 12 in 1951 as well as the AGAGE 12-Box Model (Rigby et al., 2013). The digitization and calibration of the historical spectra has been published by Makkor et al. (2024a).

2. Atmospheric Measurements at Jungfraujoch and Models Used

2.1. Atmospheric Measurements at Jungfraujoch

2.1.1. Grating Measurements at Jungfraujoch

In 1949, Professor Migeotte and his team built and used a Pfund-type infrared grating spectrometer with a 1-m focal length, which was equipped with a PerkinElmer thermopile detector, to record the solar spectrum at Jungfraujoch (46.55°N, 7.98°E, 3.58 km above sea level) (Migeotte, 1949). The recorded spectra were saved on paper rolls using an electronically guided pen. Altogether, these paper spectra covered a wavenumber range from 421 to 3571 cm^{-1} and contained handwritten atmospheric metadata such as surface temperature and humidity (Migeotte et al., 1956). These spectra from 1950 to 1951 have now been scanned, digitized and calibrated to the proper wavenumber range, and saved in a machine readable format (Makkor et al., 2024a). Overall 108 historical spectra were available, and three cover the spectral region of CFC– 12. An example of the resulting digitized spectrum covering the retrieved CFC– 12 region is shown in Figure 1a.

2.1.2. FTIR Measurements at Jungfraujoch

The first modern instrument that allowed routine measurements of broadband atmospheric spectra at Jungfraujoch was a redesign of an earlier Connes-type Fourier Transform Infrared (FTIR) spectrometer (Zander et al., 2008). By changing from a step-scan mode to a continuous scan mode, the scan speed increased by 100-fold. In addition to this, the instrument's optical pathlength was doubled reaching a resolution of 0.005 cm^{-1}. These changes allowed the start of recording atmospheric spectra regularly until the instrument was retired in 2008. The University of Liège team deployed a Bruker IFS 120HR instrument in 1989, achieving an ultimate spectral resolution of 0.001 cm^{-1}, and recorded spectra alongside the home-made FTIR spectrometer starting from 1995. The home-made instrument operated at standard 0.0061 cm^{-1} resolution, corresponding to maximum optical path difference (maxOPD) of 81.97 cm. The 120HR operated at either 0.0061 or 0.004 cm^{-1} resolutions, that is, with corresponding max OPD of 81.97 and 125 cm, respectively. More information about all three instruments used in the present work is shown in Table 1.

2.2. Reconstructed History of CFC– 12 and AGAGE Model

The first model-reconstructed history of CFC– 11 and CFC– 12 were performed by Walker et al. (2000) from a two-box atmospheric model using estimates of annual atmospheric halocarbon release, following the work of Bullister and Weiss (1983). These estimates extend from 1935 to 1998 for CFC– 12.

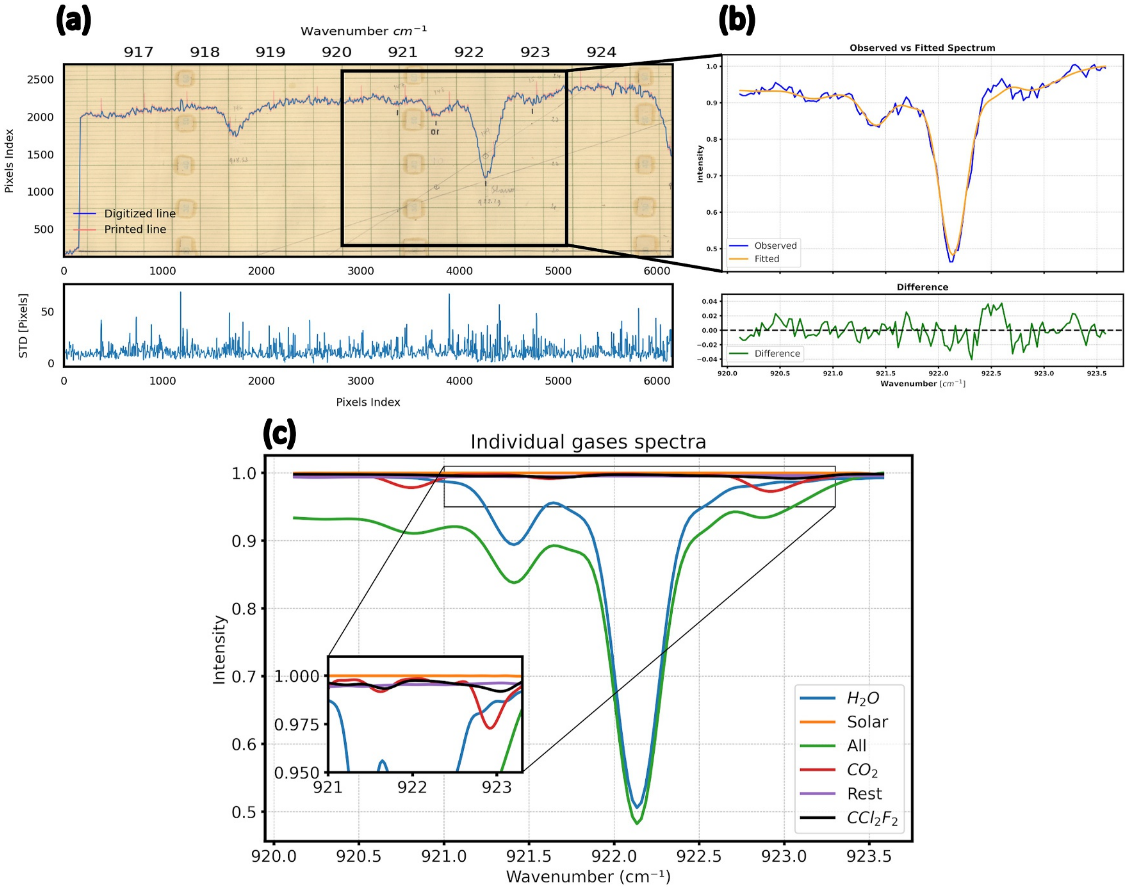

Figure 1. (a) Example spectrum from which the CFC– 12 surface volume mixing ratio (VMR) value was retrieved. This spectrum was digitized and calibrated using the procedure described in Makkor et al. (2024a). The lower panel shows the standard digitization deviation of a 9.9 pixel average. The black rectangle shows the retrieval region used for the historical spectrum (a). (b) Fitting of a grating spectrum compared to the forward model spectrum. This retrieval gives a CFC– 12 surface VMR of 26.1 pptv. The lower panel shows the difference between the fitted and the observed spectrum. An optimal resolution of 0.277 cm^{-1} and a triangular apodization were used. (c) Fitted absorption for individual gases. CFC– 12 absorption although weak is still present even on spectra from 1951 with an absorption strength of about 1%. The small zoomed-in window allows a closer look at the CFC– 12 feature (black). The retrieval was performed using Tikhonov regularization facilitated by SFIT4 spectral fit routines.

The 12-Box AGAGE model we used is a simplified advection-convection model developed by the AGAGE group that uses emission estimates to calculate the atmospheric mole fractions of multiple gases such as CFC– 11, CFC– 12 and others (Rigby et al., 2013). The emissions for this model have been calculated up to the year 2024 using the approach provided by Bullister and Weiss (1983) and Lickley et al. (2020), which employs the so-called Bayesian melding method developed by Poole and Raftery (2000). This technique enables the estimation of

Table 1
Summary of Characteristics of the Historical Grating Instrument, the Home-Made, and the Bruker FTIR Instruments

Instrument	Pfund-type grating	Home-made FTIR	Bruker 120HR FTIR
Operation years	1950–1951	1986–2008	1995–2024
Instrument type	Grating	FTIR	FTIR
Detector	Thermocouple	MCT (HgCdTE)	MCT (HgCdTE)
S/N	40–80	660 (mean)	800 (mean)
Retrieval windows	[920.1–923.6 cm^{-1}]	[920.1–923.6 cm^{-1}] and [1,160–1,163 cm^{-1}]	[920.1–923.6 cm^{-1}] and [1,160–1,163 cm^{-1}]
Degrees of freedom (DOFs)	~1	1.87	1.87
Number of spectra	3	>1,700	>8,600

emissions by leveraging information from both observed concentrations and the mechanistic simulation model of the bank, emissions, and concentrations. CFC– 12 (as well as CFC– 11) production data have been reported since 1975 by the CMA and the Alternative Fluorocarbons Environmental Acceptability Study (AFEAS), covering most major global producers. However, these reports exclude significant production from non-reporting companies, particularly in the former Soviet Union and Eastern Europe. Emission estimates incorporating these unreported sources were later provided by McCarthy et al. (1977) who estimated the total world annual production and subsequent world atmospheric emission from 1930 onwards. Both the AGAGE model and the reconstructed history cover the years from 1950 to 2024.

3. Instrumental and Retrieval Parameters

3.1. Retrieval Theory

The inverse model follows the optimal estimation or Tikhonov regularization formalism proposed by Rodgers (2000). It is a semi-empirical method of inverse calculation of the state of the atmosphere. The optimal estimation method (following Bayesian statistics) constricts the unknown state of the atmosphere to a gas a priori state vector $\mathbf{x_a}$,

$$\hat{\mathbf{x}} = \mathbf{x_a} + \mathbf{A}(\mathbf{x_t} - \mathbf{x_a}) + \boldsymbol{\epsilon} \tag{1}$$

where $\hat{\mathbf{x}}$ represents the retrieved state, $\mathbf{x_t}$ is the true state of the atmosphere and $\mathbf{A}$ represents the averaging kernel matrix, which provides an assessment of the sensitivity of the retrieval over a given altitude range for a smooth profile. The retrieval requires an a priori profile that is usually constructed to represent the general state of the atmosphere (layers, temperature, pressure and gas profiles). The tool used to perform the retrievals is SFIT4 (currently at version v1.0.21). It is the successor of SFIT1 and SFIT2, which were originally developed over time at NASA Langley, NIWA Lauder NZ and the University of Denver, and is now maintained by the National Center for Atmospheric Research (NCAR) and the University of Bremen, Germany (Hannigan et al., 2024). It is often used within the solar absorption infrared community of the Network for the Detection of Atmospheric Composition Change (See NDACC; ndacc.org and De Mazière et al. (2018)).

3.1.1. The Spectroscopy

The molecular absorption database used in this work combines the 2020 version of HITRAN (Gordon et al., 2022) and the ATM20 line-by-line and pseudoline lists provided by Geoff Toon (See Toon et al. (2016)) and can be found at https://mark4sun.jpl.nasa.gov/pseudo.html (last accessed 30.09.2025), where for each gas, the line position, the strength and other parameters are compiled into a line-list that is then used to calculate the simulated spectrum based on radiative transfer theory. In this work CFC– 12 from the historical spectra is retrieved from the microwindow 1 (MW1) [920.1–923.6 cm^{-1}] and the FTIR spectra from both the aforementioned and the microwindow 2 (MW2) [1,160–1,163 cm^{-1}] (Mahieu et al., 2008).

3.1.2. Instrumental Parameters

The instrumental line shape (ILS) of the grating spectrometer depends mostly on the grating and the entrance and exit slit widths. Since the authors have access only to the paper spectra, no information is available on the grating and slit widths used. Unfortunately, the spectrometer has been dismantled and disposed of. In general, the ILS of a grating spectrometer can best be described by a sinc square function. In order to determine the resolution we retrieved O_3-lines assuming different resolutions. Since the half width of the O_3-lines are very narrow, the resolution is mainly determined by the spectrometer and not the spectral shapes of the lines. The results with the lowest Root Mean Square (RMS) gave the resolution of the grating spectrometer. The value for the retrieved resolution and the sinc-square ILS have then been used for the retrieval of CFC– 12.

SFIT4 requires the ILS in the interferogram domain. A $sinc^2$ function in the spectral domain corresponds to a triangular apodization in the interferogram domain (Griffiths, 2006). The overall resolution of the Pfund-type grating spectrometer was usually between 0.1 and 0.4 cm^{-1} depending on the wavenumber range and the grating used. However, in the retrieval, it must be considered that the resolution of a grating spectrometer is wavelength dependent. The FTIR spectra from Jungfraujoch are much lower in noise and higher in resolution than the grating-based ones. The apodization function in the interferogram domain used is a boxcar function, corresponding to a sinc-function in the spectral domain. The MaxOPD for the home-made is 81.97 and 125 cm for the Bruker FTS 120HR. The pressure, temperature and a priori water vapor profiles are obtained from the National Centers for Environmental Prediction reanalysis (NCEP; Kalnay et al., 1996) and are extended above 55 km using data from the Whole Atmosphere Community Climate Model version 7 (WACCMv7) (Gettelman et al., 2019).

4. Results

4.1. Estimation of CFC– 12 Surface Mole Fraction in 1951

The MW1 was used to retrieve CFC– 12 from the digitized historical spectra (see Figure 1a). This microwindow is normally significantly influenced by water vapor, making it inappropriate for ground-based retrievals at sea level but suitable for sites located at higher altitudes like Jungfraujoch (3.58 km above sea level) where this influence is less critical. MW1 and MW2 showed the best agreement and minimum intra-day variability in the total columns when adopting 300 and 65 for the Tikhonov regularization parameter, respectively. These parameters were obtained by considering the respective monochromatic point-spacings of the home-made and 120HR spectra, as instructed by Sussmann et al. (2009).

In MW1 the spectral bands of CO_2 and CFC– 12 overlap, which requires a careful retrieval of CO_2 to get CFC– 12 correct. Figure 1b shows the measured and calculated spectra with a relatively good fit, albeit with high noise. When using the optimal estimation method to perform a retrieval using the historical spectra, we constrained the a priori profile with a Tikhonov regularization parameter of 1,000, which is a much higher value compared to the FTIR one (due to the higher noise), resulting in a largely scaled retrieval with a degree of freedom around 1. Given the low resolution of the historical spectra, performing a profile retrieval is not meaningful. The a priori volume mixing ratio (VMR) is derived from current measurements. The retrieval process is primarily influenced by the tropospheric VMR profile, which remains relatively constant throughout the atmosphere. It can be assumed that the current shape of the tropospheric VMR profile aligns with those from 1951, as chemical reactions exert minimal influence in the troposphere for such a long-lived and well-mixed target gas.

Figure 1c shows all the retrieved gases alongside CFC– 12. The main contributions in this spectral interval come from H_2O and CO_2, but there is also a small and quantifiable contribution from CFC– 12 in this spectrum (black curve in Figure 1c). This is not surprising since the production of CFC– 12 started in the 1930s, and the compound was subsequently widely adopted by various industries as a foam agent and propellant. The early emissions of CFC– 12 mostly came from the United States and various European countries. The CFC– 12 feature can be observed in the less noisy spectrum shown in Figure 1c, with an absorption of below 1%. The retrieval of CFC– 12 from MW2 using the grating spectra was not possible due to significant influence from the noise.

4.2. Error Analysis

4.2.1. Error Estimation of Spectra From 1951

Quantifying the sources of errors in the Pfund-type instrument from the 1950s involves considering two main categories of errors: those originating from the instrument itself and those arising from the paper spectra after processing (which includes digitization and calibration). One source of random error associated with the instrument, the zero transmission level offset, accounts for approximately 3% of the error (Zander et al., 1994). The resulting spectra have two error sources: a digitization error of around 1.55% and a wavenumber shift error of about 1%. The largest source of error comes from the retrieval itself. This error was calculated using Rodgers formalism for retrieval error using formulas 2–5

$$\mathbf{x}-\mathbf{x_a}=(\mathbf{A}-\mathbf{I_n})(\mathbf{x}-\mathbf{x_a}) \qquad \text{(Smoothing error)} \tag{2}$$

$$+\mathbf{G_y}\mathbf{K_b}\left(\mathbf{b}-\hat{\mathbf{b}}\right) \qquad \text{(Model parameter error)} \tag{3}$$

$$+\mathbf{G_y}\boldsymbol{\Delta}\mathbf{f}\left(\mathbf{x},\mathbf{b},\hat{\mathbf{b}}'\right) \qquad \text{(Forward model error)} \tag{4}$$

$$+\mathbf{G_y}\boldsymbol{\epsilon} \qquad \text{(Measurement noise)} \tag{5}$$

Table 2

Error Summary of the Retrieved CFC– 12 Mole Fractions From the Historical 1951 Grating Data and the Modern FTIR Spectra

	Digitized 1951 grating spectrum	Bruker FTIR (1996–2024) spectra
	Random (%)	
Zero level offset	3.0	0.2
Temperature	0.72	1.34
Solar zenith angle	0.11	0.7
Phase function	–	0.28
Telluric species interference	35.6	0.02
Measurement	21.7	0.34
Digitization/Calibration	2.55	–
Resolution bias	1.0	–
Total random	48.3	1.64
	Systematic (%)	
Zero level offset	3.0	0.2
Spectroscopy (ATM20)	2.0	2.0
Temperature	4.8	1.0
Interfering species	21.5	–
Solar zenith angle	1.19	0.21
Phase function	–	0.28
Total systematic	21.6	2.31

where the smoothing error comes from the estimate of the state coming from the averaging kernel matrix, which is a representation of the expected state to the true state. The latter cannot really be known, which means that the exact value of the error is not possible to calculate. However, the statistics of the error can be meaningfully represented. The model parameter error is relatively simple to calculate as long as the individual parameter errors are evaluated correctly, and the model is sufficiently linearized. Forward modeling error accuracy relies heavily on the understanding of the underlying physics of the retrieval. If the confidence in the latter is sufficient and the equations are not overly complicated then this error can be very accurate. On the other hand, if the opposite is true, then this error is harder to evaluate. This error is usually taken as systematic for simplicity's sake. Finally, the measurement noise is the simplest to calculate since it is usually random, unbiased and correlated, with a known covariance matrix (The error methodology is discussed in details in Rodgers (2000)).

The total random error is about 48.3% (retrieval, digitization and instrumental errors, etc.) and total systematic error of about 21.6% (see Table 2). The resolution of the historical spectra is not well known, but it is between 0.1 and 0.4 cm^{-1}. Multiple retrievals were therefore performed for different resolutions. The resolution of 0.277 cm^{-1}, which has the lowest calculated RMS was used in the retrieval. Additionally, the bias arising from the low resolution and triangular apodization when using the grating spectra was analyzed. To achieve this, high-resolution FTIR spectra from the Jungfraujoch site were artificially lowered to resolutions of 0.1, 0.25 and 0.4 cm^{-1} (minimum, average and maximum resolutions) by truncating the Fourier transform of the high-resolution spectrum using the Bruker OPUS software (OPUS - Spectroscopy Software, 2020). Subsequently, CFC– 12 total columns were retrieved using these resolution values, then compared to the original values from the high-resolution FTIR spectra. The triangular apodization was also applied to the lowered resolution FTIR spectra. The three lower resolutions analyzed correspond to relative differences in CFC– 12 total columns of 0.65%, 1.0%, and 2.5%, respectively.

4.2.2. Error Estimation of Jungfraujoch Spectra

The largest source of error for the FTIR spectra is from temperature with a random and systematic error of 2.34% (in total). The random smoothing error ‘$\mathbf{x}_t - \mathbf{x}_a$‘ is calculated from WACCM covariance matrix. The uncertainty coming from the solar zenith calculation is about 0.1° for Jungfraujoch. The resulting errors from the historical spectra and the FTIR spectra are shown in Table 2. Additionally, only the errors from the Bruker FTIR are presented, as the retrievals from both FTIR instruments show very similar error results.

4.3. The Full Trend of CFC– 12

Figure 2 shows the long-term trend of CFC– 12 from 1951 to 2024 using various data sets and model results. The reconstructed historical model values represent the assumed CFC VMRs for the selected period between 1950 and 1960 (represented in the region of interest by the blue markers in Figure 2) from estimates of annual industrial production and emissions (Walker et al., 2000). The calculated CFC– 12 surface mole fraction for 1951 is (9.2 ± 0.2) pptv for the Northern Hemisphere. This reconstructed historical value has never been validated using actual measurements, because no measurements existed. The surface mole fraction we derived for 1951 of (26.1 ± 18.5) pptv from the historical spectra is three times larger than the reconstructed historical estimate for the Northern Hemisphere. These differences can be explained by inaccurate emissions in 1951, but the uncertainty of the measurement from the historical instrument needs to also be considered. The surface mole fraction of CFC– 12 from the historical grating measurement was taken from the value given by SFIT4 at the surface during the retrieval of the total column (which has a value of $(3.36 \pm 1.58) \times 10^{14}$ molecule/cm^2). The grating mole fractions are calculated for moist air, while the FTIR ones are calculated for dry air using H_2O total columns and very accurate surface pressure measurements (which are not available for the historical spectra), according to the methodology outlined in Barthlott et al. (2015). The difference between dry air and moist air is negligibly small due to the higher altitude of the site (Lejeune et al., 2017; Mahieu et al., 2014). The dry air mole fractions from the FTIR measurements were then plotted, and their trend fitted using a Dynamic Linear Model facilitated by the tool provided by Hachmeister et al. (2024). Additionally, the whole time series was complemented with the 12-Box AGAGE model with a CFC– 12 VMR value of (7.00 ± 0.28) pptv for 1951 to give a complete picture of the evolution of CFC– 12 over the past decades and to account for the missing data between the 1950s and the start of FTIR measurements at Jungfraujoch. The observed annual cycle is caused by the seasonal variability in the tropopause height. This feature can also be found for many trace gases with VMR-profiles decreasing in the stratosphere, in the measurements and simulations (like CH_4, N_2O).

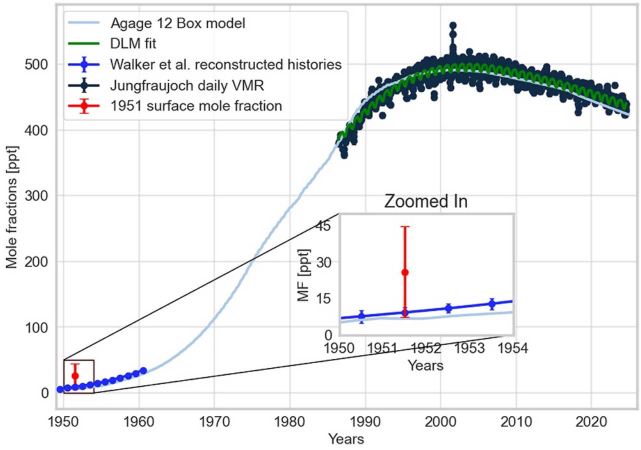

Figure 2. Atmospheric surface CFC– 12 mole fraction (pptv) from 1950 to 2024. The measurement value in 1951 is retrieved in this work from solar measurements at Jungfraujoch in the same time period. It is compared to a 2-Box model reconstructed history and 12-Box model from AGAGE. The retrieved mole fraction from FTIR measurements at Jungfraujoch are also represented and fitted using a Dynamic Linear Model (DLM).

5. Conclusions

A CFC– 12 surface mole fraction of (26.1 ± 18.5) pptv for 1951 was derived from a grating spectrometer observation obtained at Jungfraujoch. Using results from a home-made FTIR-spectrometer (from 1986 to 2008) and from a commercial FTIR-spectrometer (from the mid-1990s to 2024), the interannual trend for the period 1951–2024 has been presented. The result for 1951 has been compared to estimates from reconstructed history and the AGAGE 12-Box model. The estimated error includes the preprocessing error (digitization and calibration) of the historical paper spectra, the error inherent to the instrument (finite S/N ratio) as well as the retrieval error. The largest error source comes from the retrieval, due to the low signal-to-noise ratio of the historical spectra for a weak absorption. The reconstructed history and the AGAGE 12-Box model estimates of CFC– 12 for the Northern Hemisphere in 1951 of about (9.2 ± 0.2) pptv and (7.00 ± 0.28) pptv, respectively, are about three times lower than the retrieved surface mole fraction from the historical grating instrument, but the error bars overlap. We note, however, that these modeled mole fractions could be biased low due to erroneous emission estimates in the 1950s. The historical measurement has allowed us to retrieve the earliest atmospheric surface mole fraction of CFC– 12, predating previous earliest values by over two decades. The historical spectra also cover other spectral regions, allowing the future retrieval of other trace gas concentrations in 1950–1951.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The FTIR measurements are regularly provided and updated by the GIRPAS team and can be freely downloaded from https://www-air.larc.nasa.gov/pub/NDACC/PUBLIC/stations/jungfraujoch/hdf/ftir/ (last accessed 17/12/2025). The digitized grating spectra can be freely downloaded via Makkor et al. (2024b) (last accessed 17/12/2025). SFIT4 retrieval program and related tools can be freely downloaded under https://wiki.ucar.edu/spaces/sfit4/pages/217711301/Infrared+Working+Group+Retrieval+Code+SFIT (last accessed 17/12/2025). The Error calculation is performed using the same tools provided alongside SFIT4 and are written in python (see link above).

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