Universität Bremen

Retrieval of various trace gases from digitized 1950/51 spectra at Jungfraujoch

Presented by Jamal Makkor

Mathias Palm*, Matthias Buschmann*, Emmanuel Mahieu**, Martyn Chipperfield***, Justus Notholt*

* Institute of environmental physics, Bremen.
** Infrared Group of Atmospheric and Solar Physics, Belgium.
*** School of Earth and Environment, Leeds.

A general overview

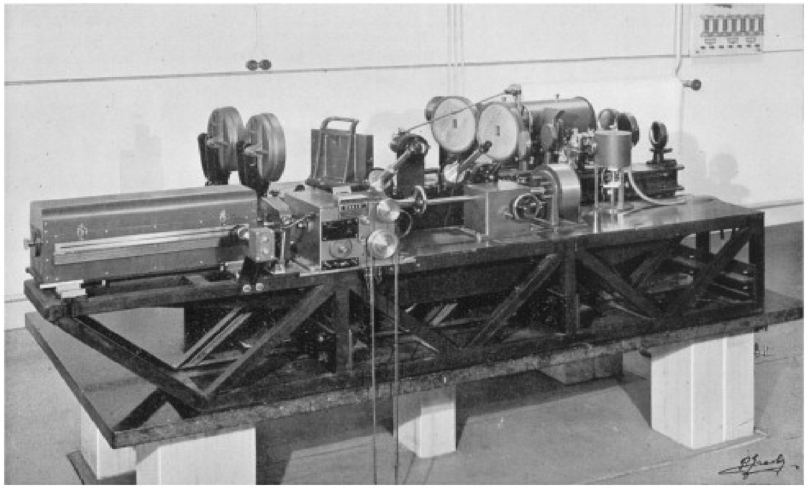
The first Solar measurements at Jungfraujoch

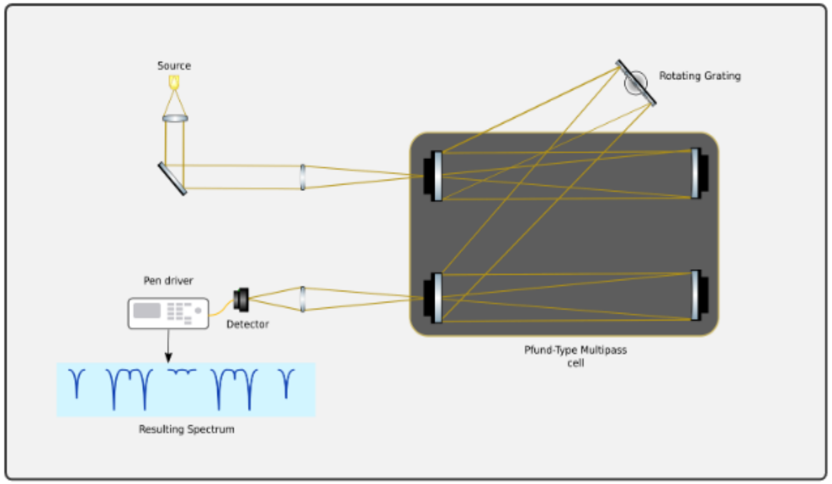
The International Scientific Station at Jungfraujoch (ISSJ) has been a leading scientific station since its inception in 1931 (Nature [1931]).

<u>Grating based measurements</u>

The first-ever instrument to measure the solar spectrum was utilized by Migeotte et al. to create an atmospheric atlas ranging from 2.8 to 23.7 microns (Delbouille, L., Migeotte, M. [1960]).

- The instrument used by Migeotte was a Pfund-Type grating spectrometer
- The spectral resolution and signal-to-noise (S/N) ratio varied respectively from 0.12 to 0.4 cm^{-1} and 40 to 80 (Zander [2008]).





The spectrometer produced paper based spectra using an electric pen

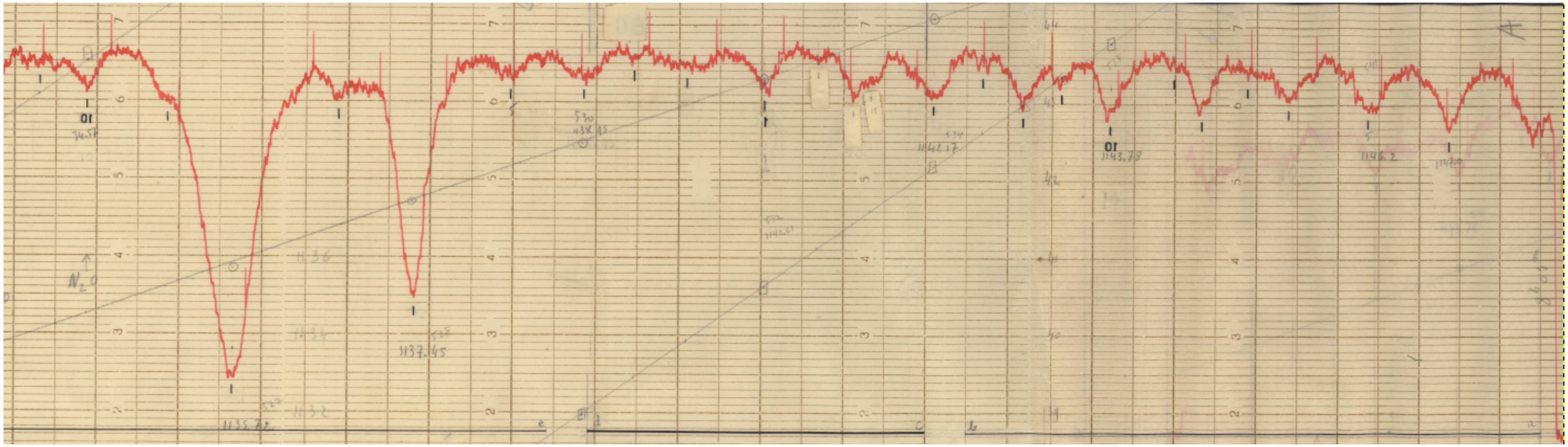
Zander [2008]

The first solar measurements at Jungfraujoch

The Spectra produced by the grating spectrometer

The paper based spectra were printed on high quality paper.
Notes from the scientists running these experiments included:

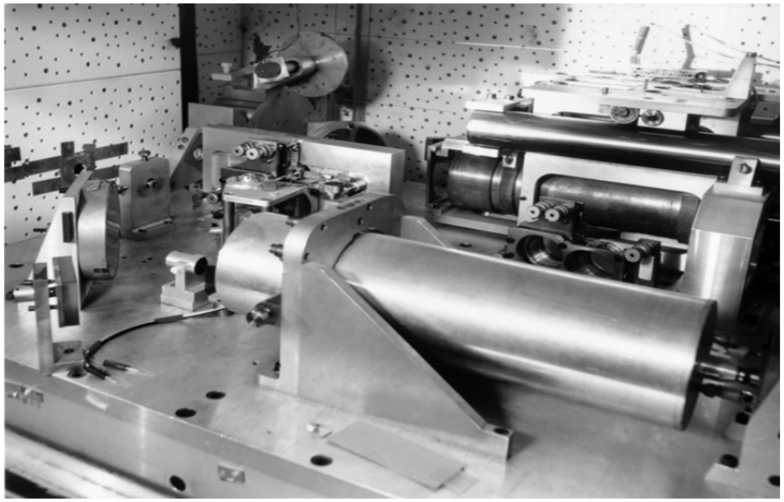
- The date and time of the experiment
- Marking of the zero level
- Humidity and temperature values (not always present).
- The wavenumber range (also not always present).



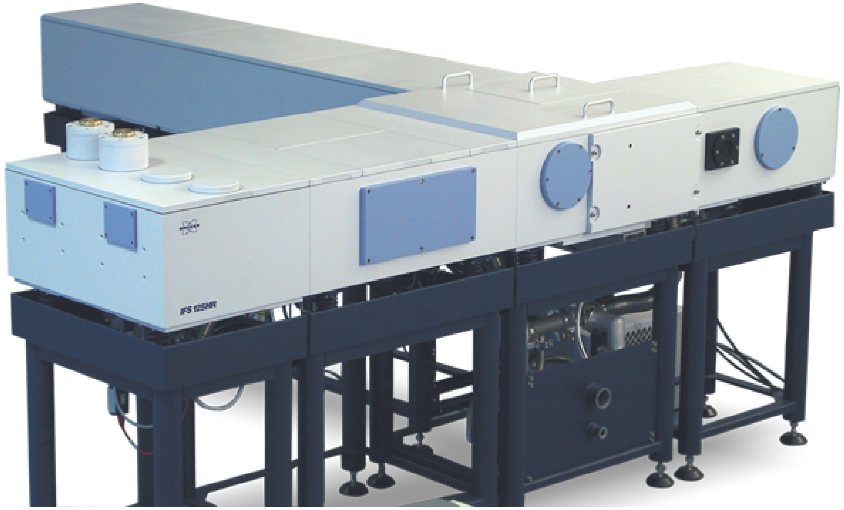
A history of atmospheric measurements at Jungfraujoch

Fourier Transform Infrared (FTIR) based measurements at Jungfraujoch officially began in 1974 with the use of a homemade Connes type FTIR.

- An improved FTIR was then used to start atmospheric measurements in 1984 and continued until its retirement in 2008.
- A Bruker IFS-120 HR model, with a resolution of 0.001cm-1, started measuring alongside the homemade instrument in 1996 and remains operational to this date.



The homemade FTIR with a continuous scanning motor



The commercial Bruker IFS-120 HR model

Methods

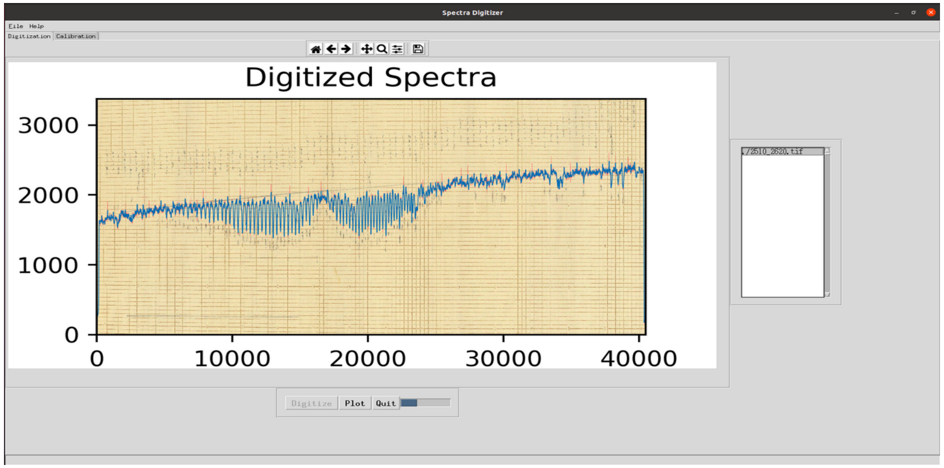
Digitization and calibration of the 1950 spectra

Digitization

The algorithm creates a color mask in the HSV space to specifically identify red pen marks.

Using the color mask, the algorithm selects matching data points and ignores all other image components.

The algorithm extracts the plot data by calculating the mean pixel values for each column in the image.

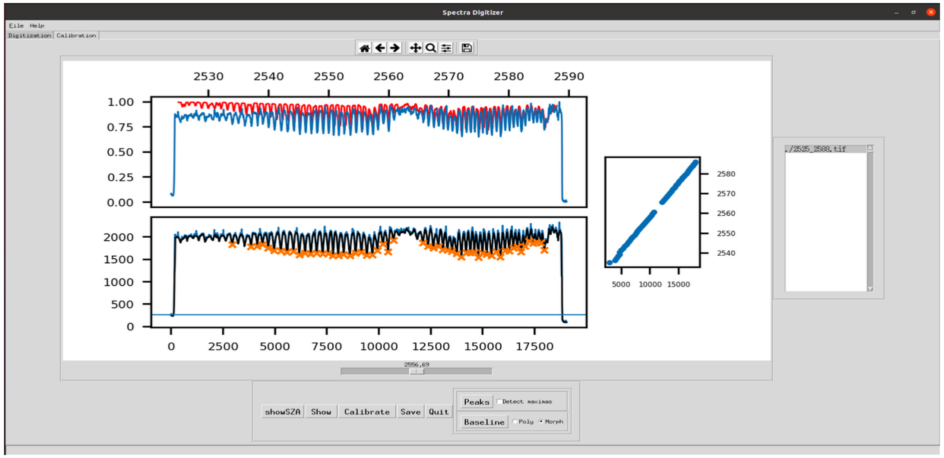


Calibration

A synthetic spectrum is generated using the SFIT4 forward model, which incorporates known spectroscopy from the HITRAN database and specific instrumental parameters.

Peak detection is employed to select calibration points, ensuring an accurate alignment between the digitized spectrum and the synthetic spectrum.

These calibration points are used to perform curve-fitting of the digitized spectrum.



Digitization and calibration of the 1950 spectra

The resulting calibrated spectrum (blue line) is normalized, zero-corrected.

Significant change in the solar zenith angle value (Due to long recording time).

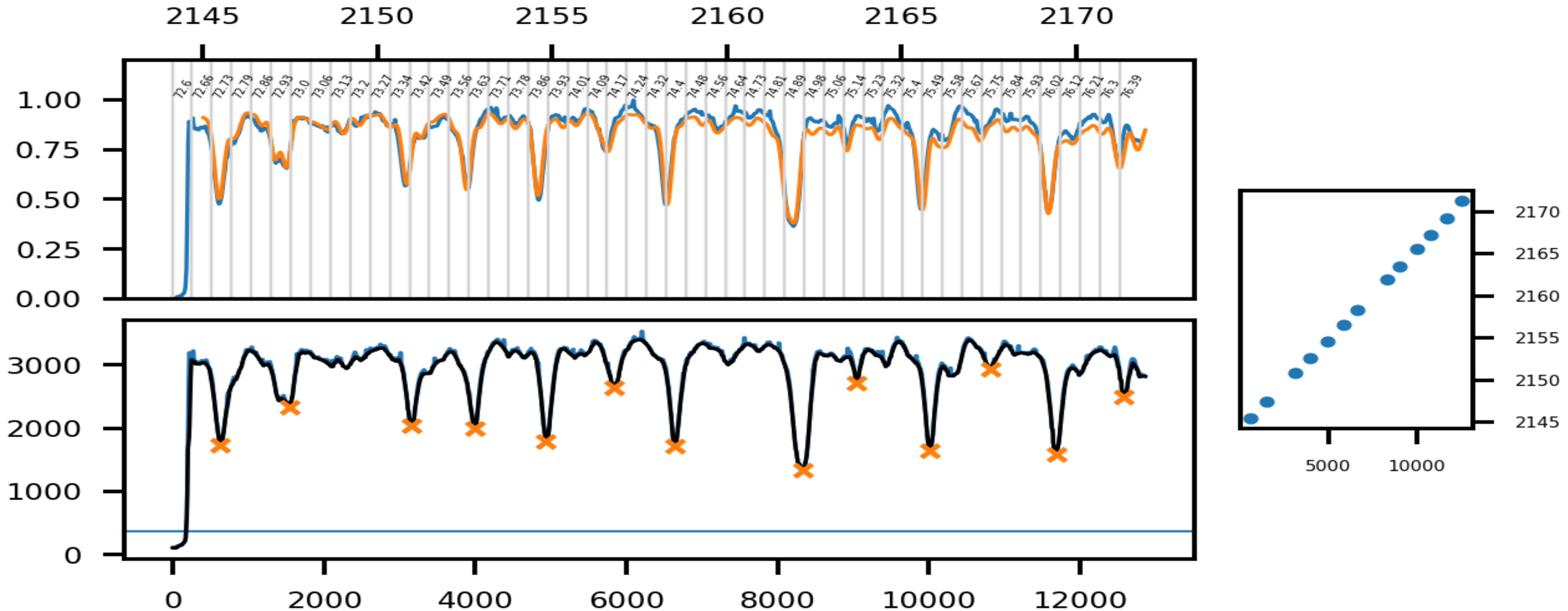


Figure: Digitized (below) and calibrated spectrum (blue line) compared to the simulated spectrum (orange line). Right left shows the calibration points.

Error Sources of the Grating

Inherent limitations

The grating spectrometer had a couple of limitations:

- Very sharp peaks (Like HCl) are not resolvable due to the instrumental properties of the spectrometer.

- The use of the thermocouple detector also contribute to the high level of noise. Most of which come from thermal noise and amplification stage noise.

Possible error sources

Random sources of error:

- Thermal drift inherent to the Thermocouple detector can cause varying levels of noise, subsequently affecting the signal-to-noise ratio (S/N) (Burley, N. A., [1969]).

- mechanical wear and tear over time or paper misalignment can cause distortions in the spectra, resulting in inaccurate retrievals.

Systematic sources of error:

- Instrument misalignment can cause a drop in light intensity received at the detector, thus reducing the signal intensity...

The TOMCAT/SLIMCAT and AGAGE Models

General information about the models

Tomcat Slimcat model

The TOMCAT and SLIMCAT are chemical transport models (CTMs) used extensively for atmospheric chemistry studies for over a decade.

- TOMCAT was first used for studying the polar stratosphere, using hybrid sigma-pressure levels, which were not optimal for these studies.
- SLIMCAT was developed to address these limitations, employing an isentropic vertical coordinate and using diagnosed heating rates for vertical transport. This limited its domain mainly to the stratosphere.

12 Box agage model

- 12box is a global convection–diffusion model developed by AGAGE. It was deployed to study the total trend of CFC-12

The Community Earth System Model (CESM)

The Community Earth System Model

The Community Earth System Model (CESM) is a comprehensive model that combines various independent models for the atmosphere, land, ocean, sea ice, land ice, and river runoff (Neale et al., 2013; Lamarque et al., 2012).

It offers different configurations depending on the choice of components and their coupling. CESM's atmospheric component, known as the Community Atmosphere Model (CAM), can incorporate varying levels of chemical complexity.

The standard CESM model was used to produce CO histories from 1950 to 2008.

Before comparaison with Measurement data, the model needed to be interpolated to appropriate WMO pressure level then smoothed with the averaging kernels of the measurements (Rodgers [2000]) according to the formula.

$$X_S = X_{ap} + A.\left(X_R - X_{ap}\right)$$

Where X_S is the smoothed profile, X_{ap} is the apriori profile, X_R is the profile before smoothing , and A is the seasonally averaged averaged kernels.

Results

Results (CFC 12)

CFC-12 Retrieval strategy

CFC-12, also known as dichlorodifluoromethane, is a chlorofluorocarbon compound commonly used as a refrigerant and propellant.

CFC-12 Retrieval from the old spectra

To retrieve CFC-12 from the grating spectra Tikhonov regularization was used.

- Multiple spectra were tested at both retrieval windows [920.1- 923.8]cm^{-1} and [1159.4 - 1161] cm^{-1}
- A triangular function appropriately represents the instrumental lineshape function of a grating.
- The slope was also fitted when retrieving the total column (TC).
- The retrieval was performed using SFIT4

CFC-12 Retrieval from the recent spectra

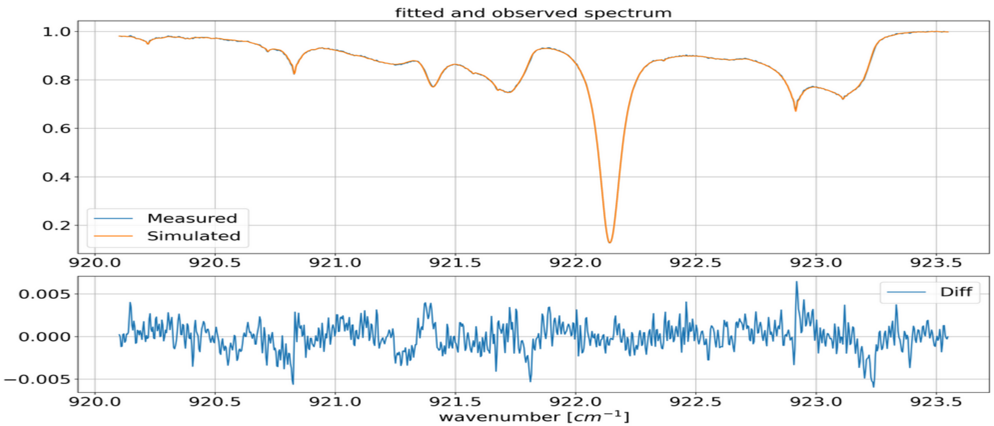
For the recent spectra both windows were also tested but the final spectra were retrieved using the window [1159.4 - 1161] cm^{-1}

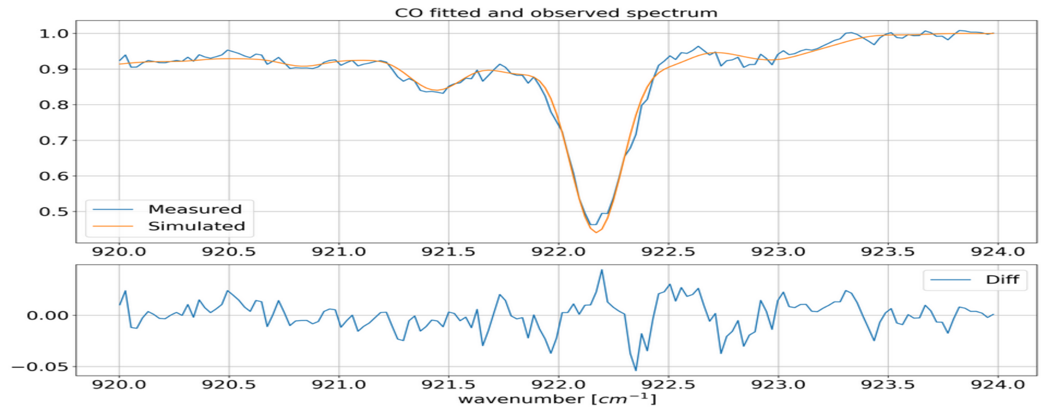
Both HITRAN and ATM19 linelists were tested in the retrieval and ATM19 proved to have a better fitting (particularly for water lines).

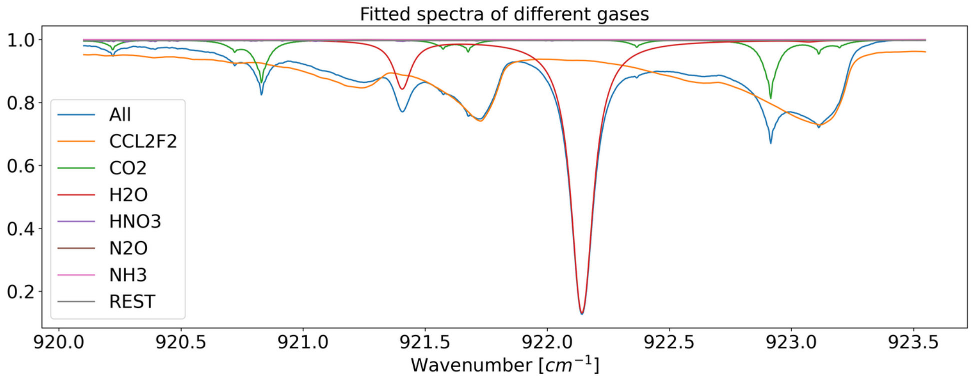
Results (CFC 12)

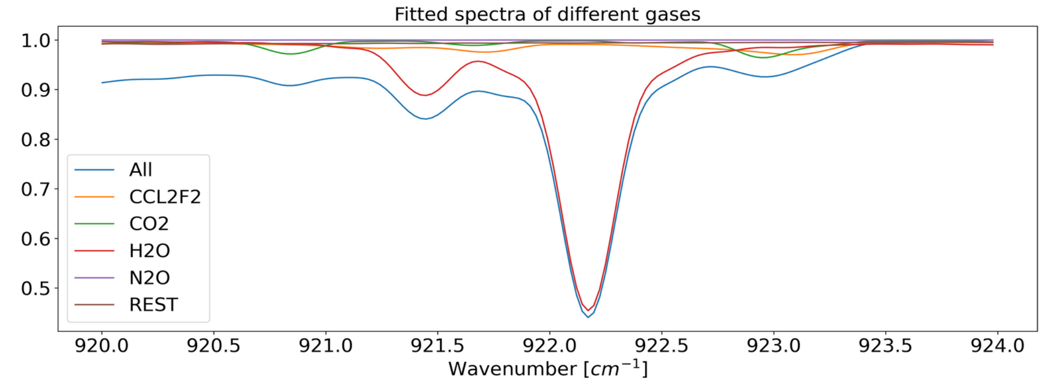
Comparison with both old and recent spectra

Spectral fitting of recent (left figure) and old (right figure) spectra shows both CFC-12 lines.
The upper limit of CFC-12 was detected by gradually increasing the apriori value of the gas until a clear line could be observed which was at 0.76E15 which corresponds of to a calculated VMR of 24.5pptv.







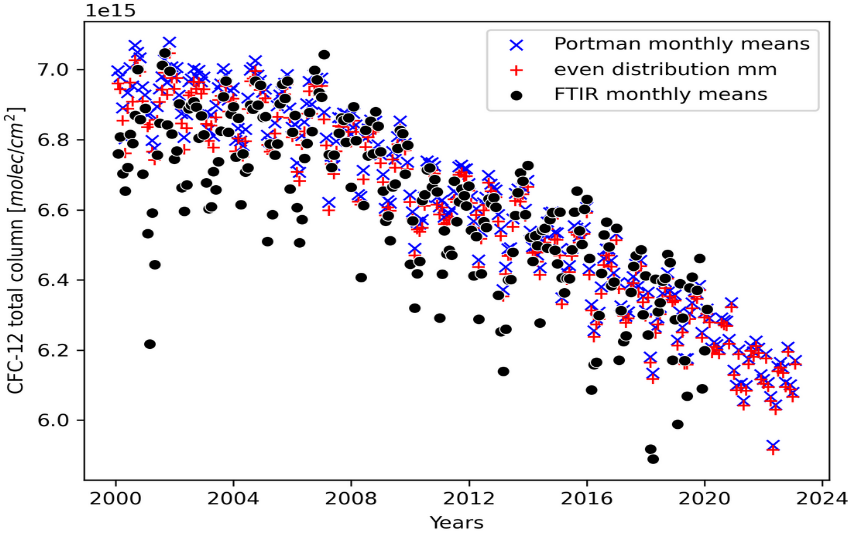


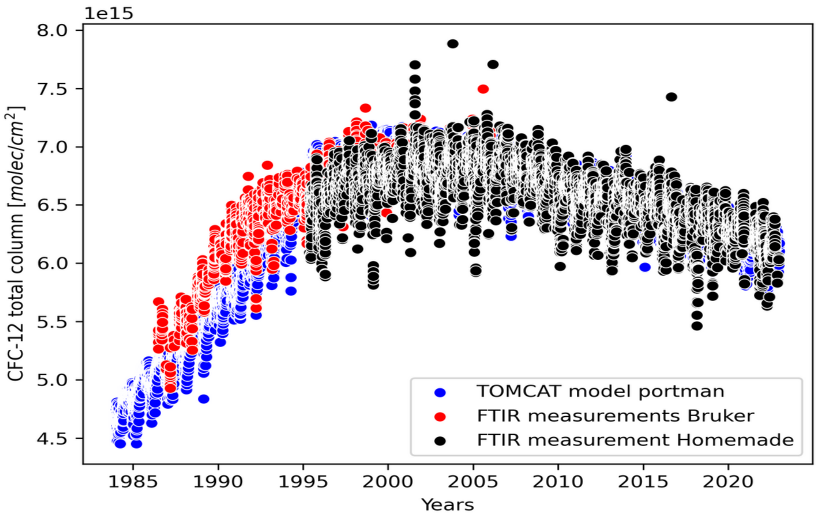
Results (CFC 12)

CFC-12 secular trend

- Using an Idealized run of TOMCAT/SLIMCAT, CFC12 concentrations were calculated using Portman Distribution of emissions (largest contribution of emissions for CFC12/ in the NH). The even distribution assumes equal spread of emissions for both hemispheres.

- The observed seasonal variability could be attributed to the seasonal changes tropospheric height, the inter-hemispheric gradiant influence (Pratheret al., 1987; Prinn et al., 2000).





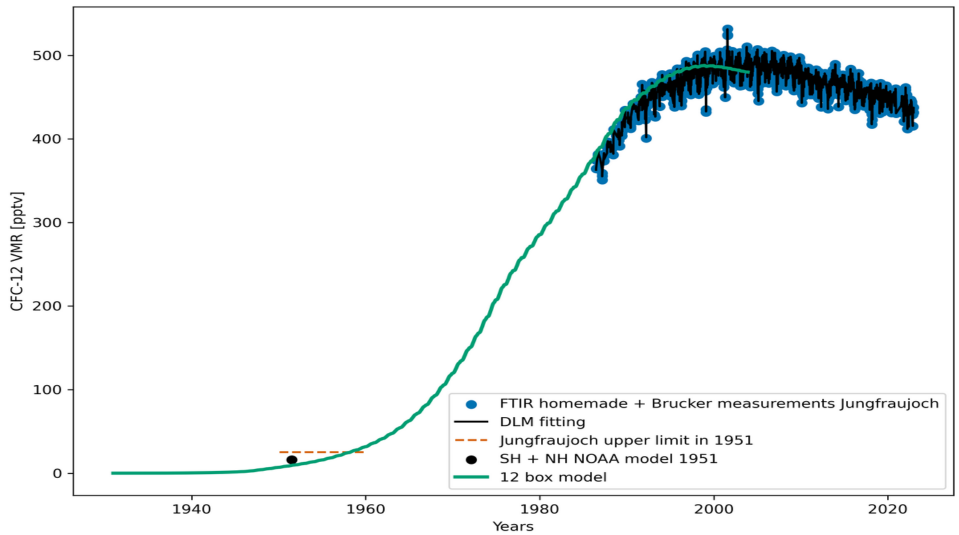
Results (CFC 12)

CFC-12 secular trend

The upper value of CFC-12 using the spectra from Jungfraujoch in 1951 is 24.5ppt compared to 16ppt calculated by (S. J. Walker et al [2000])

(The procedure for converting the total column to dry air mole fractions is described in (Barthlott et al 2005).

To fit the data a new method was applied called Dynamic Linear Models, which offers better fitting of data (Hachmeister .J. et al (Unpublished))



Results (Carbon Monoxide)

Carbon monoxide Retrieval strategy

Carbon monoxide (CO) is an important atmospheric gas with both natural and anthropogenic sources. It is primarily produced by incomplete combustion of fossil fuels, biomass burning, and chemical reactions in the atmosphere.

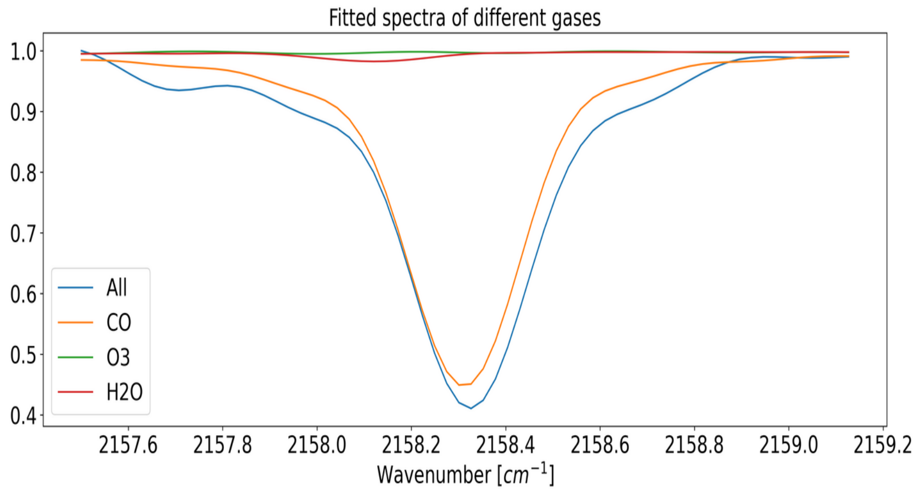
Retrieval strategy

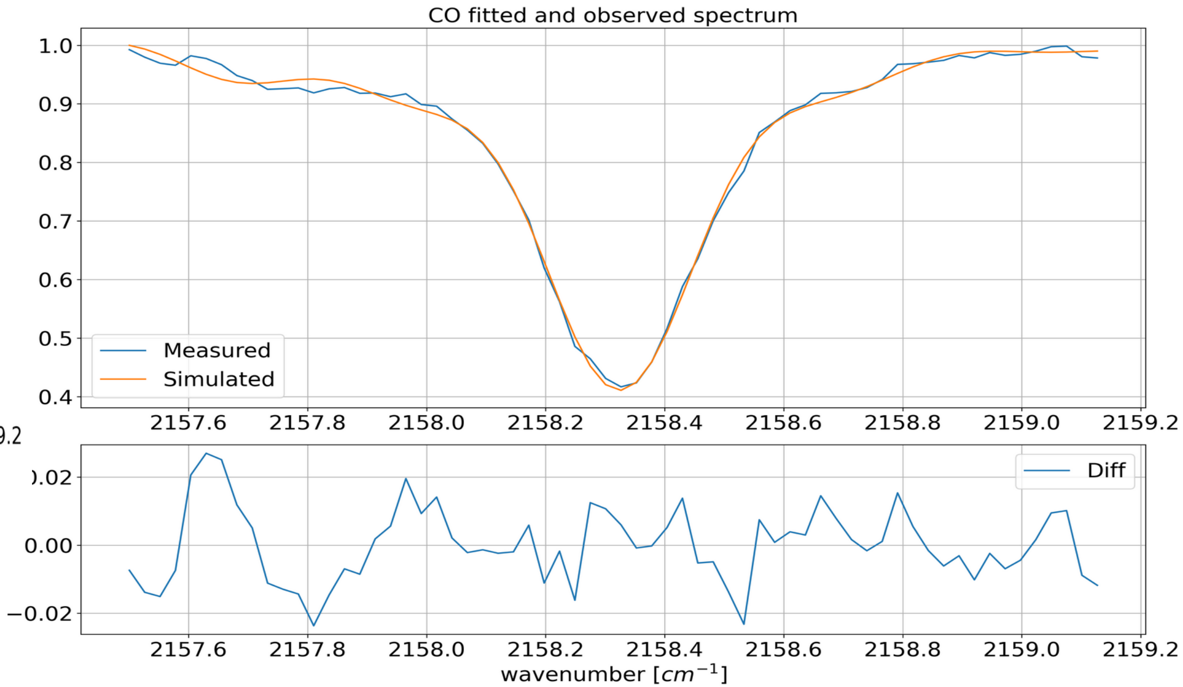
- The wavenumber range is [2157.5, 2159.1]cm^{-1}
- A strong Tikhonov regularization was used to fit the spectra.
- The interfering gases in this region are: O3, CO2 and H2O
- The same instrumental parameters used to retrieve CFC-12 were also used in the case of carbon Monoxide

Results (Carbon Monoxide)

Carbon monoxide Retrieval strategy

Carbon monoxide has a strong absorption line in this spectral window. The fitting using a strong Tikhonov regularization seems to be optimal. Water influence in this region is minimal.

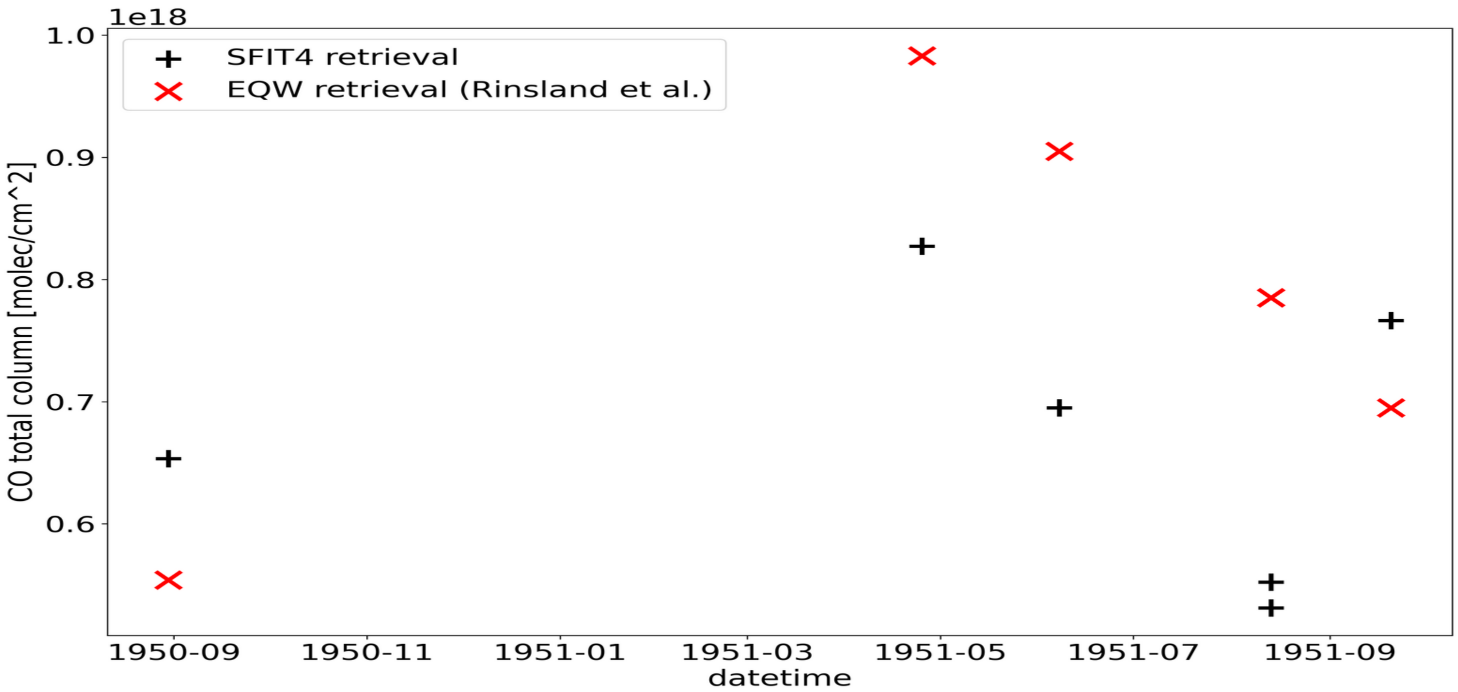




Results (Carbon Monoxide)

Carbon monoxide comparison with equivalent width method

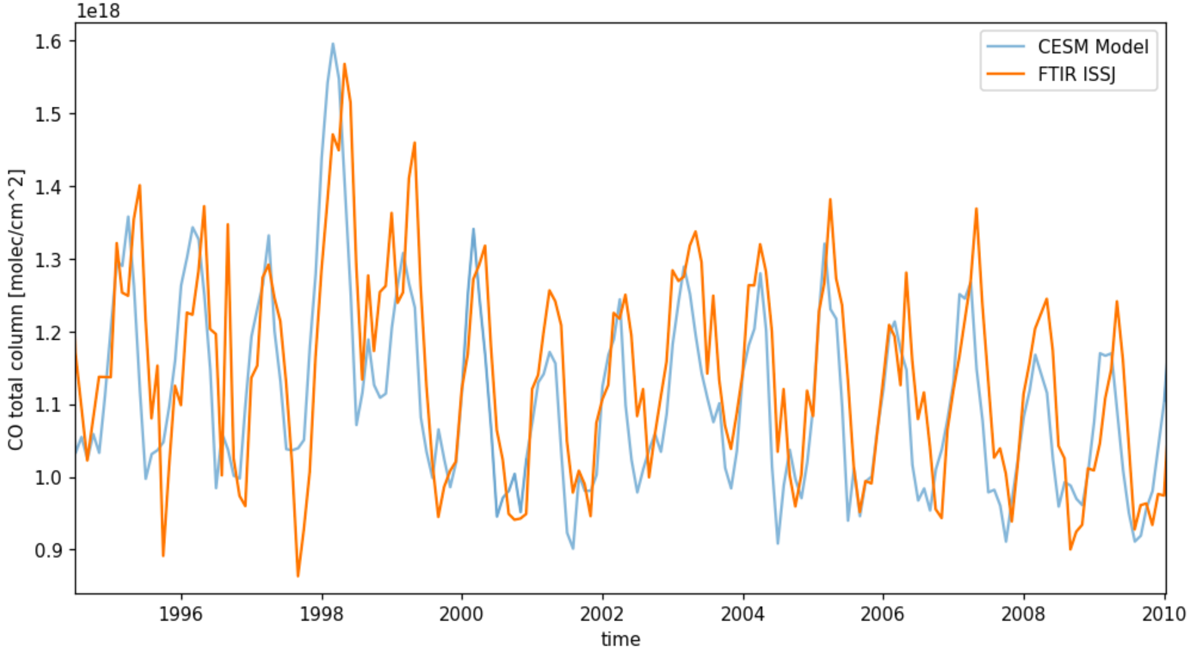
- The equivalent width method is a quantitative technique in spectroscopy that measures the integral of the normalized flux within the width of a spectral feature.
- The values calculated by the recent SFIT4 seem less scattered overall compared to the EQW.



Results (Carbon Monoxide)

Secular trend of Carbon monoxide from 1950 to present

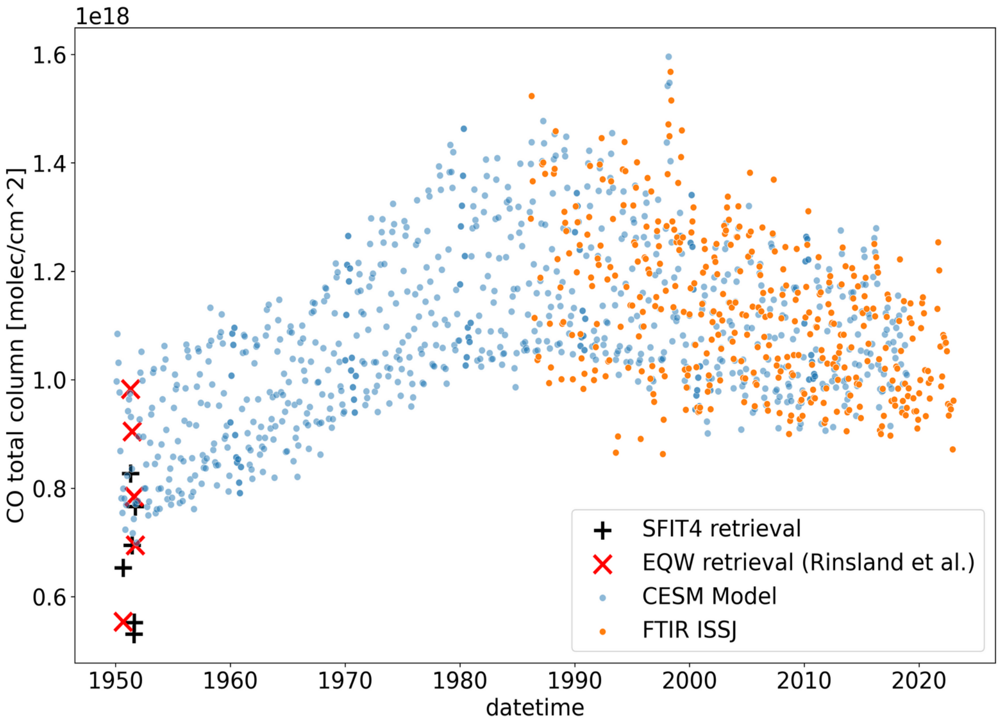
Carbon Monoxide shows a seasonal variability for both FTIR measurements at Jungfraujoch and the CESM model results. The two time series seem to be in agreement throughout the period shown below with matching maximas even at higher peaks like in 1998 (which could be due to the 1998 Florida wildfires (NOAA report [1998]))



Results (Carbon Monoxide)

Secular trend of Carbon monoxide from 1950 to present

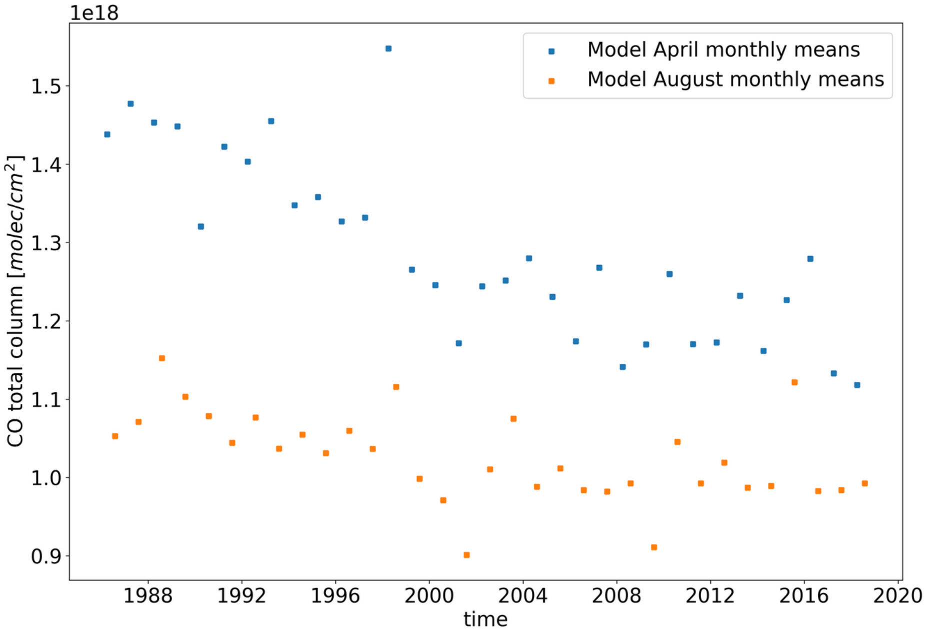
- The CESM model demonstrates a linear increase in CO levels from 1950 to 2008.
- the grating measurements indicate lower CO values during that period. This discrepancy may be attributed to incorrect assumptions regarding earlier emissions values.

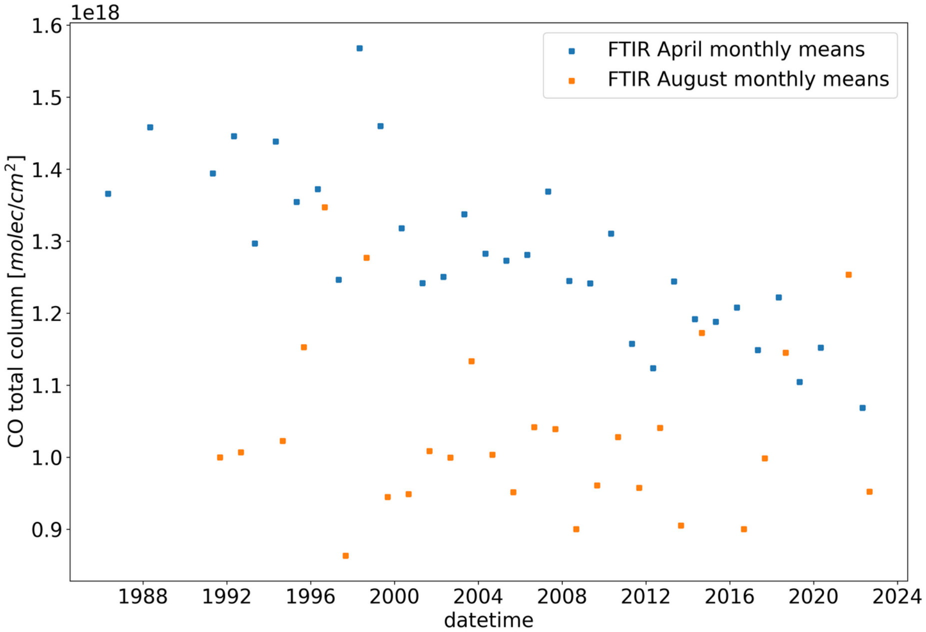


Results (Carbon Monoxide)

Secular trend of Carbon monoxide from 1950 to present

- The CESM model and the FTIR measurements show a decrease in the monthly mean for April
- For the month of August the model shows a general decrease while the FTIR measurements show an apparent increase after 2012





Summary and conclusions

- Spectra from the 1950s, printed on paper using a grating, were digitized to analyze some atmospheric gases.
- Custom software was developed to digitize and calibrate the spectra to the proper wavenumber range.
- Concentrations of CFC-12 and carbon monoxide (CO) were retrieved from the calibrated spectra.
- CFC-12 values from the paper spectra were compared to measurements from homemade and Bruker FTIR instruments, as well as modeled data.
- The initial CFC-12 concentration was around 24.5 pptv, peaked at 520 pptv, and declined due to the phase-out enforced by the Montreal Protocol.
- CO spectra were retrieved from the grating and FTIR instruments, showing a linear increase in carbon monoxide.
- Model calculations of CO in the fifties were overestimated compared to the values from the grating spectra. This discrepancy suggests a possible incorrect assumption about emissions in the CESM model.

Thank you

References

[1931] The Jungfraujoch Scientific Station. (1931). Nature 817–820. https://doi.org/10.1038/128817a0

[1960] Delbouille, L., Migeotte, M. (1960). Infrared Solar Spectroscopy at the Jungfraujoch (Switzerland). https://doi.org/10.1364/JOSA.50.001305

[1949] Migeotte, M. v. The Fundamental Band of Carbon Monoxide at 4.7µ in the Solar Spectrum. https://doi.org/10.1103/PhysRev.75.1108

[2005] M. P. CHIPPERFIELD, New version of the TOMCAT/SLIMCAT off-line chemical transport model: Intercomparison of stratospheric tracer experiments

[1997] Burley, N. A., 1969, "Solute Depletion and Thermo-e.m.f. Drift in Nickel-Base Thermocouple Alloys," J. Inst. Met., 97, pp. 252–254.

Stratospheric influences on the tropospheric seasonal cycles of nitrous

oxide and chlorofluorocarbons, C. D. Nevison and D. E. Kinnison

Reconstructed histories of the annual mean atmospheric mole fractions for the halocarbons CFC-11 CFC-12, CFC-113, and carbon tetrachloride

S. J. Walker, R. F. Weiss, P. K. Salameh

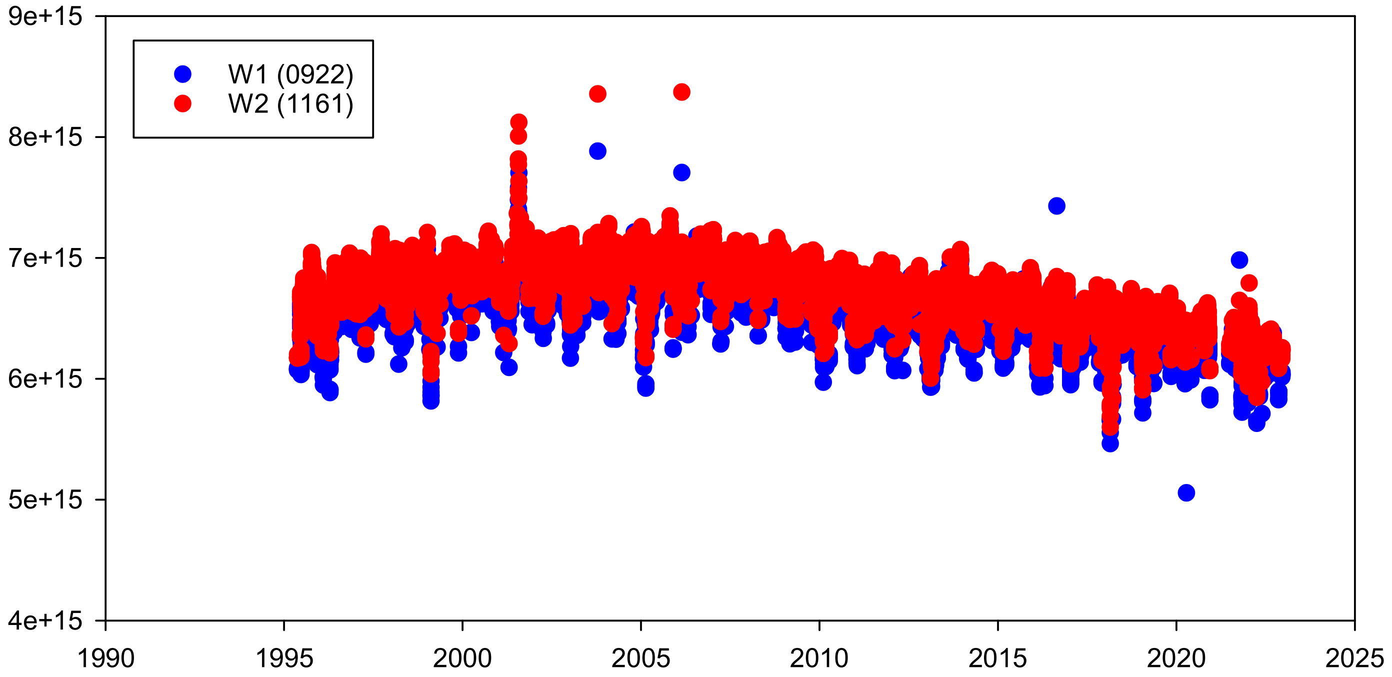
Prinn, R. G., Weiss, R. F., Fraser, P. J., Simmonds, P. G., Cunnold, D. M., Alyea, F. N., O'Doherty, S., Salameh, P., Miller, B. R., Huang, J., Wang, R. H. J., Hartley, D. E., Harth, C., Steele, L. P., Sturrock, G., Midgley, P. M., & McCulloch, A. (2000). A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE.

References

[1998] NOAA National Centers for Environmental Information, Monthly Wildfires Report for Annual 1998, published online January 1999, retrieved on June 7, 2023 from https://www.ncei.noaa.gov/access/monitoring/monthly-report/fire/199813.

Windows Comparaison

Comparison between two retrieval windows
(Bruker)



XCFC-12 calculation

$$\mathrm{DPC} = \frac{P_{\mathrm{s}}}{M_{\mathrm{dryair}} \cdot g(\phi)} - \frac{M_{\mathrm{H_2O}}}{M_{\mathrm{dryair}}} \cdot \mathrm{H_2O_{col}}$$