# Determination of time series of halogenated gases relevant to the Montreal Protocol using ground-based, satellite and model data

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## Research context

Since the discovery of the involvement of chlorofluorocarbons (CFCs) in the depletion of the stratospheric ozone [1], the Montreal Protocol (1987) has aimed to control the production of CFCs and other ozone-depleting substances (ODS) in order to protect and subsequently restore the ozone layer. Consequently, temporary substitutes for CFCs were developed and produced by industry. The first substitutes were hydrochlorofluorocarbons (HCFCs), which have smaller ozone depletion potentials (ODP) than CFCs since their atmospheric lifetimes are shorter. Nevertheless, HCFCs still contain chlorine atoms and therefore also deplete the stratospheric ozone, requiring them to be banned in turn. Therefore, chlorine-free molecules, i.e. hydrofluorocarbons (HFCs) were introduced to replace both CFCs and HCFCs [2]. The atmospheric concentrations of CFCs have declined in response to the phase-out and banning of their production by the Montreal Protocol and its subsequent amendments, while the HCFCs burden is now leveling off. In contrast, the atmospheric concentrations of HFCs have increased notably in the last two decades. Even if HFCs do not contribute to ozone depletion, they are very powerful greenhouse gases, with high global warming potentials [3]. The Kigali Amendment (2016) to the Montreal Protocol aimed for their phase-out. In my PhD project, I have studied CFC-11 ($CCl_3F$) and HFC-134a ($CH_2FCF_3$), the main substitute for CFC-12. These two molecules are mainly used for mobile and domestic refrigerators, air-conditioning, aerosol propellants and as blowing agents. Consequently, monitoring the atmospheric concentration of these types of molecules is necessary to support the Montreal Protocol and its amendments.

**Figure 1:** Jungfraujoch station, Swiss Alps (3580 m; 46.55°N, 7.98°E).

## CFC-11

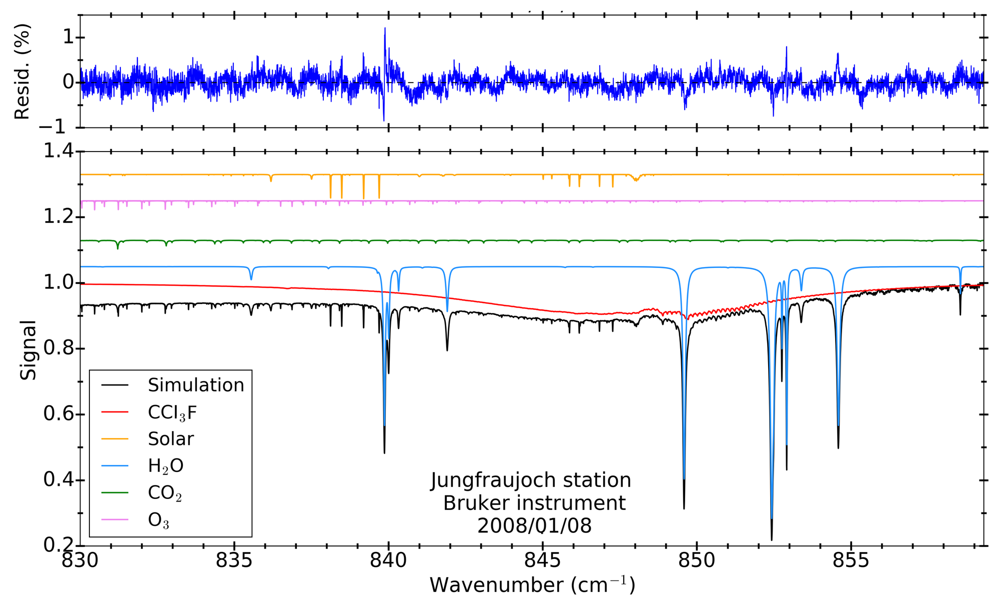


**Figure 2:** Simulations of the 830.0 – 859.3 cm$^{-1}$ spectral window for spectra recorded by the Bruker IFS-120HR FTIR instrument at Jungfraujoch station with an apparent solar zenith angle of 80.3°. The root-mean-square of the fitting residuals (RMS) is 0.20%. Second-order absorbers are not shown. The top panel displays the observed-calculated residuals, in %, from the fit to the spectrum. Figure 2 from Pardo Cantos et al., 2022 [4].

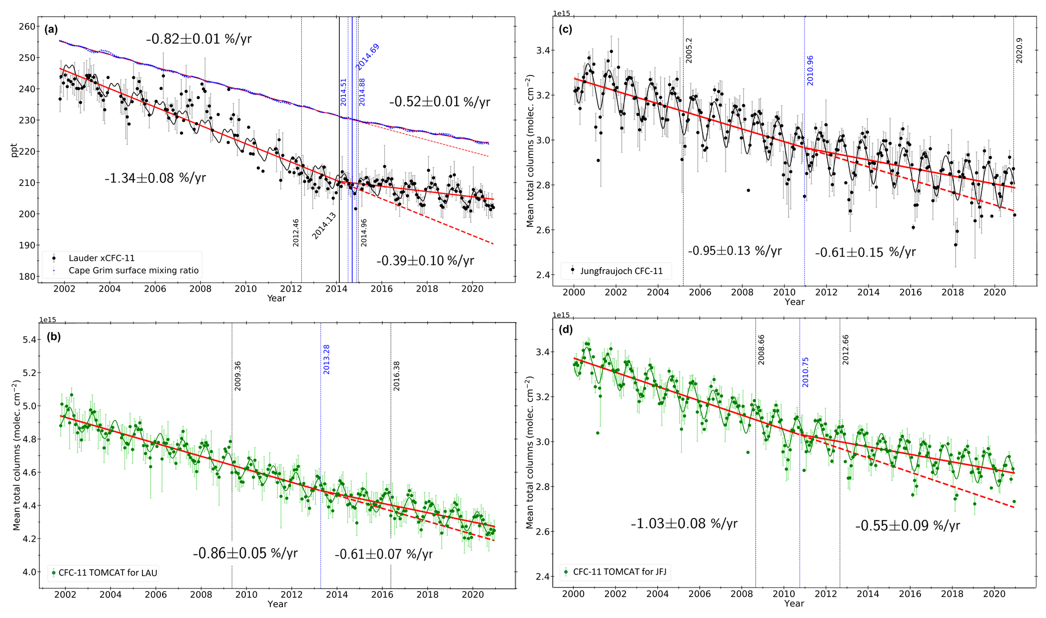

**Figure 3:** Atmospheric CFC-11 monthly means derived from the different datasets. Left: Southern Hemisphere; Right: Northern Hemisphere. The vertical error bars represent one standard deviation. Modified Figures 5 and 6 from Pardo Cantos et al., 2022 [4].

## HFC-134a

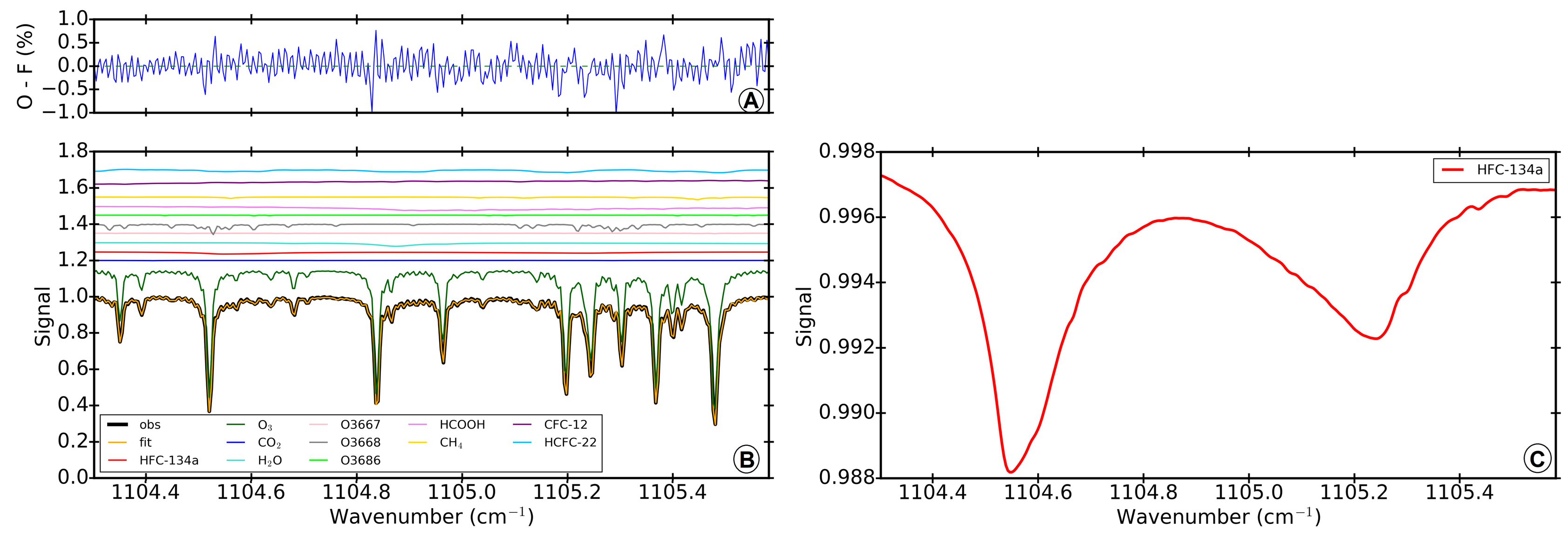


**Figure 4:** Simulations of the 1104.300 – 1105.585 cm$^{-1}$ spectral window for spectra recorded by the Bruker IFS-120HR FTIR instrument at Jungfraujoch station with an apparent solar zenith angle of 77.2°. The RMS of the fitting residuals is 0.27%. Panel A displays the observed-calculated residuals, in %, from the fit to the observed spectrum. Be aware of the scale of the vertical axis in Panel C, where the HFC-134a absorption is magnified.

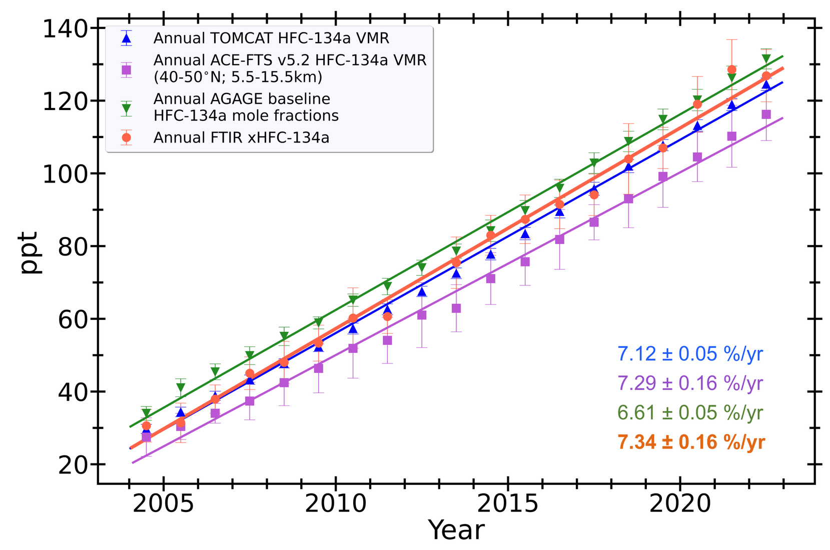


**Figure 5:** Atmospheric HFC-134a annual means derived from the different datasets. The vertical error bars represent one standard deviation.

## Conclusions

- Undeclared CFC-11 emissions can be detected by FTIR spectrometers.
- First harmonised CFC-11 FTIR Jungfraujoch time series extended back before the 2000s and first merged CFC-11 FTIR dataset from Lauder.
- Weak absorption of HFC-134a can be detected by FTIR spectrometers.
- First retrievals of HFC-134a from ground-based FTIR observations. The trends are consistent with other independent datasets.
- FTIR measurements provide complementary monitoring to surface-measurement networks.

## References

[1] Molina, M. J. and Rowland, F. S. (1974) Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone, Nature, 249, 810-812, doi: 10.1038/249810a0.

[2] Harrison, J. J., Chipperfield, M. P., Boone, C. D., Dhomse, S. S. and Bernath, P. F. (2021). Fifteen Years of HFC-134a Satellite Observations: Comparisons With SLIMCAT Calculations. Journal of Geophysical Research: Atmospheres, 126(8), e2020JD033208. doi: 10.1029/2020JD033208.

[3] World Meteorological Organization (WMO). Scientific Assessment of Ozone Depletion: 2022, Ozone Research and Monitoring, GAW Report No. 278, 509 pp.; WMO: Geneva, 2022.

[4] 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. (2022). Determination and analysis of time series of CFC-11 ($CCl_3F$) from FTIR solar spectra, in situ observations, 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(6), 1487-1501. doi: 10.1039/d2ea00060a.

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