

Determination and analysis of time series of CFC-11 (CCl₃F) 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

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INTRODUCTION

Trichlorofluoromethane (CFC-11) is the second most important chlorofluorocarbons (CFCs) in the Earth's atmosphere. CFCs are long-lived chemicals which were exclusively produced by the industry and broadly used as aerosol spray propellants, refrigerants, inflating and insulating agents in the production of foam materials, as well as solvents [Fleming et al., 2020]. CFCs are transported into the stratosphere where they are photodissociated by UV radiation, releasing chlorine atoms that catalytically destroy stratospheric ozone [Molina and Rowland, 1974].

The atmospheric concentration of CFC-11 has declined in response to the phase-out of its production by the Montreal Protocol. Nevertheless, this atmospheric concentration decline suffered a slowdown around 2012 due to emissions from non-reported production [Montzka et al., 2018]. Emissions from this illegal CFC-11 production are mainly coming from eastern China [Rigby et al., 2019]. Consequently, this slowdown in the decrease of CFC-11 atmospheric concentrations is expected to produce a delay in stratospheric ozone recovery. Fortunately, a return to reduced emission rates levels, similar to that during 2008–2012 since 2018, has been reported [Montzka et al., 2021] [Park et al., 2021]. Since CFC-11 remains one of the most important ozone-depleting halocarbons, its continuous monitoring is essential.



CFC-11 FTIR, IN SITU SURFACE AND 3-D MODEL TIME SERIES

- FTIR observations at Jungfraujoch:** The High Altitude Research Station Jungfraujoch (46.55°N, 7.98°E) is located on the Northern Swiss Alps, on a saddle between the Mönch and the Jungfrau summits, at 3580 m above mean sea level (a.m.s.l.), thus the station is most of the time in free troposphere conditions. The IR solar absorption spectra used in this study were recorded by a homemade and a Bruker Fourier-Transform Infrared (FTIR) spectrometers, under clear-sky conditions. Since the CFC-11 has a very broad but relatively unstructured absorption in the infrared spectral range, the retrieval spectral window has to be relatively large to encompass the whole feature. Furthermore, it has to be carefully optimised in order to limit the interference by other molecules. For this study, the spectral window was adjusted to 830.0 - 859.3 cm⁻¹; and only the observations with an apparent solar zenith angle (SZA) between 60° and 85° were fitted such as to maximize the CFC-11 absorption depth and information content. The interfering telluric species used in this retrieval strategy were H₂O, CO₂, O₃, OCS, HNO₃, COCl₂, and H₂¹⁸O.
- FTIR observations at Lauder:** Like Jungfraujoch, the Lauder Atmospheric Research Station (45.04°S, 69.68°E, 370 m a.m.s.l.) was a founding site of NDACC. The spectral observations used in this study were recorded with a Bruker 120HR (2000 – 2018) and Bruker 125HR (2018 – 2020). In both instruments, solar spectra are taken on days with cloud-free line of sight to the Sun using solar trackers with active tracking. The observations fitted were those with an apparent SZA between 60° and 89°.
- In situ observations at Cape Grim:** The station, operated by the Australian Bureau of Meteorology, sits atop a 90 m cliff on Tasmania's west coast (40.7°S, 144.7°E) and the ambient air is sampled 36 times per day from a tower at 70 m above the station. The Cape Grim CFC-11 baseline monthly mean data (2001 – 2020) reported in this study are obtained from CSIRO's participation in the global AGAGE program [Prinn et al., 2018]. The data were obtained from a gas chromatographic (GC) instrument incorporating an electron capture detector (ECD) and are calibrated in the Scripps Institution for Oceanography (SIO-05) scale.
- TOMCAT/SLIMCAT model:** TOMCAT/SLIMCAT (hereafter TOMCAT) is a global 3-D off-line chemical transport model [Chipperfield, 2006]. It is used to study a range of chemistry-aerosol-transport issues in the troposphere and stratosphere. The model is usually forced by European Centre for Medium-Range Weather Forecasts (ECMWF) meteorological (re)analyses, although General Circulation Model (GCM) output can also be adopted. For the simulations used in this study, the model was run at horizontal resolution of 2.8° × 2.8° with 60 hybrid σ -pressure levels from the surface to \approx 60 km. The model simulations included three idealised CFC-11 tracers (see Figure 1), as used in Montzka et al., 2021.

FTIR JUNGFRAUJOCH TIME SERIES ANALYSIS

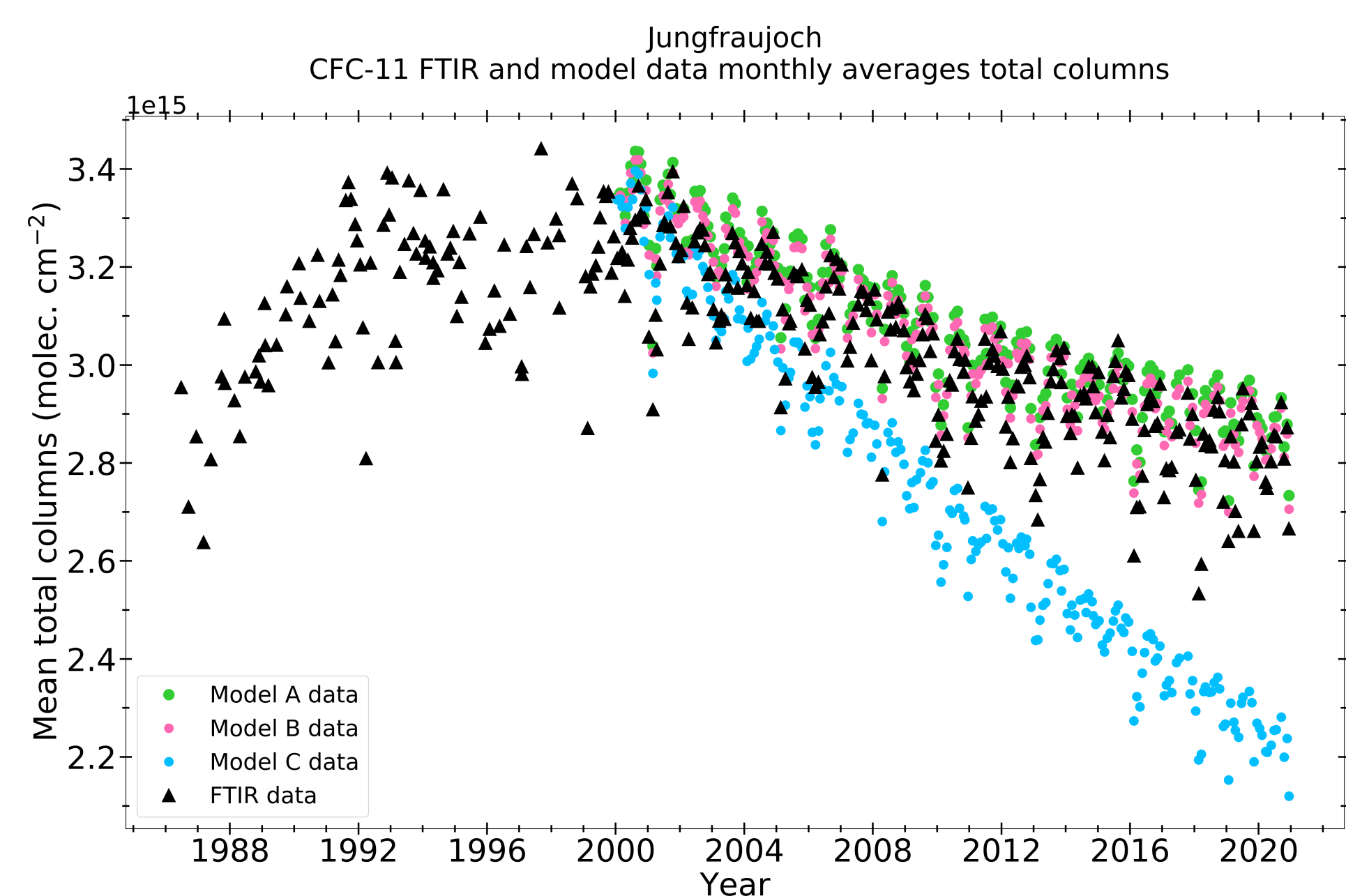


Figure 1: Jungfraujoch FTIR (from June 1986 to December 2020) and TOMCAT (from January 2000 to December 2020) monthly mean total columns. In black, FTIR data; in green, TOMCAT model simulation A: best estimate of historic CFC-11 emissions with realistic distribution at the surface; in pink, TOMCAT model simulation B: same total time-dependent emissions as Tracer A but they were distributed uniformly over the Earth's surface; and in blue, TOMCAT model simulation C: assumed zero CFC-11 emissions after 2000 (simple decay).

TREND ANALYSES

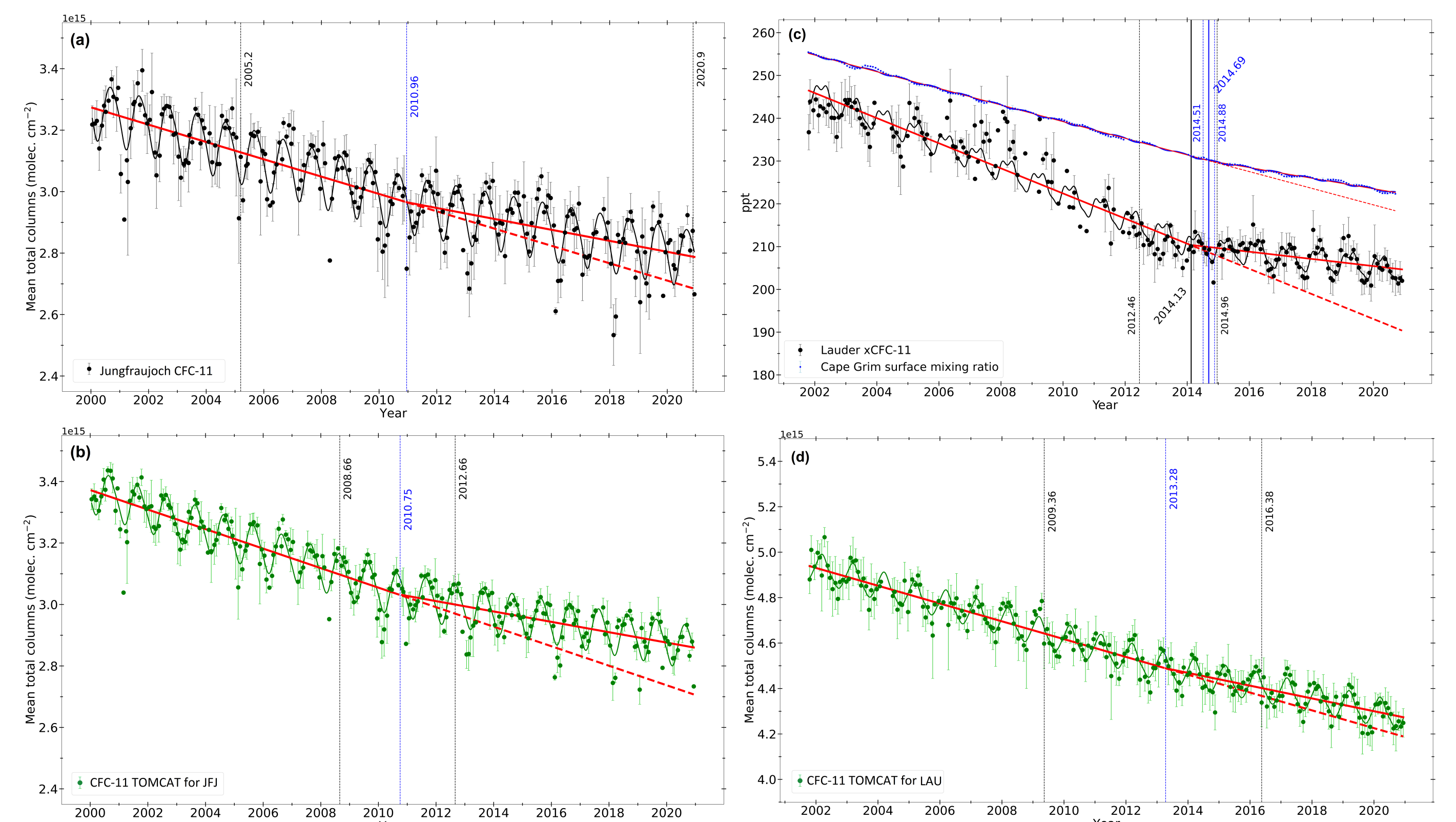


Figure 2: (a) FTIR and (b) TOMCAT monthly time series of CFC-11 total columns above Jungfraujoch. (c) In situ monthly CFC-11 at Cape Grim (in blue) and monthly xCFC-11 FTIR above Lauder (in black). (d) TOMCAT model monthly time series of CFC-11 total columns above Lauder. All vertical bars represent the standard deviation around the monthly means. The "best estimation/realistic" simulation (TOMCAT tracer A) has been chosen here.

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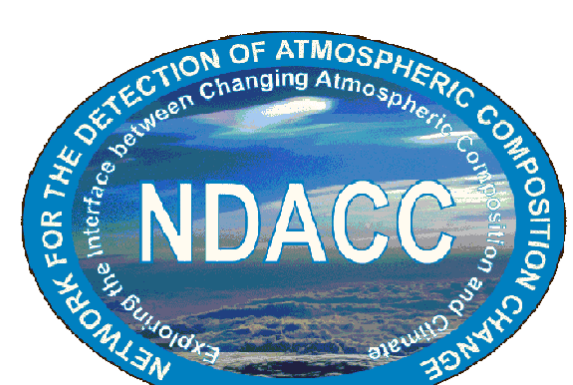
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	Break location 2000 – Break	Break – 2020
CFC-11 FTIR JFJ	2010.96	-0.95±0.13
TOMCAT(A) for JFJ	2010.75	-1.03±0.08
In situ CG	2014.69	-0.82±0.01
xCFC-11 FTIR LAU	2014.13	-1.34±0.08
TOMCAT(A) for LAU	2013.28	-0.86±0.05
CFC-11 ACE (global)	2012.0	-0.8

Table 1: Relative trends (% per year) derived from the Jungfraujoch (JFJ) and Lauder (LAU) FTIR time series, from TOMCAT model and in situ measurements at Cape Grim (CG). We used a 95% confidence interval. Tropospheric CFC-11 trends from the ACE-FTS instrument (60°N to 60°S) are also shown [Chipperfield et al., 2021].

CONCLUSIONS

- First harmonised CFC-11 FTIR Jungfraujoch time series extended back before the 2000s.
- First merged CFC-11 FTIR dataset from Lauder.
- Trend analyses performed using an advanced statistical tool [Friedrich et al., 2020].
- Break point around 2011 for the NH and around 2014 for the SH.
- Undeclared CFC-11 emissions can be detected by FTIR spectrometers.
- FTIR measurements provide complementary monitoring to surface-measurement networks.



Extensive information on this work can be found in the recent open access paper by Pardo Cantos et al. (2022)

