Satellite observations and modelling of stratospheric fluorine

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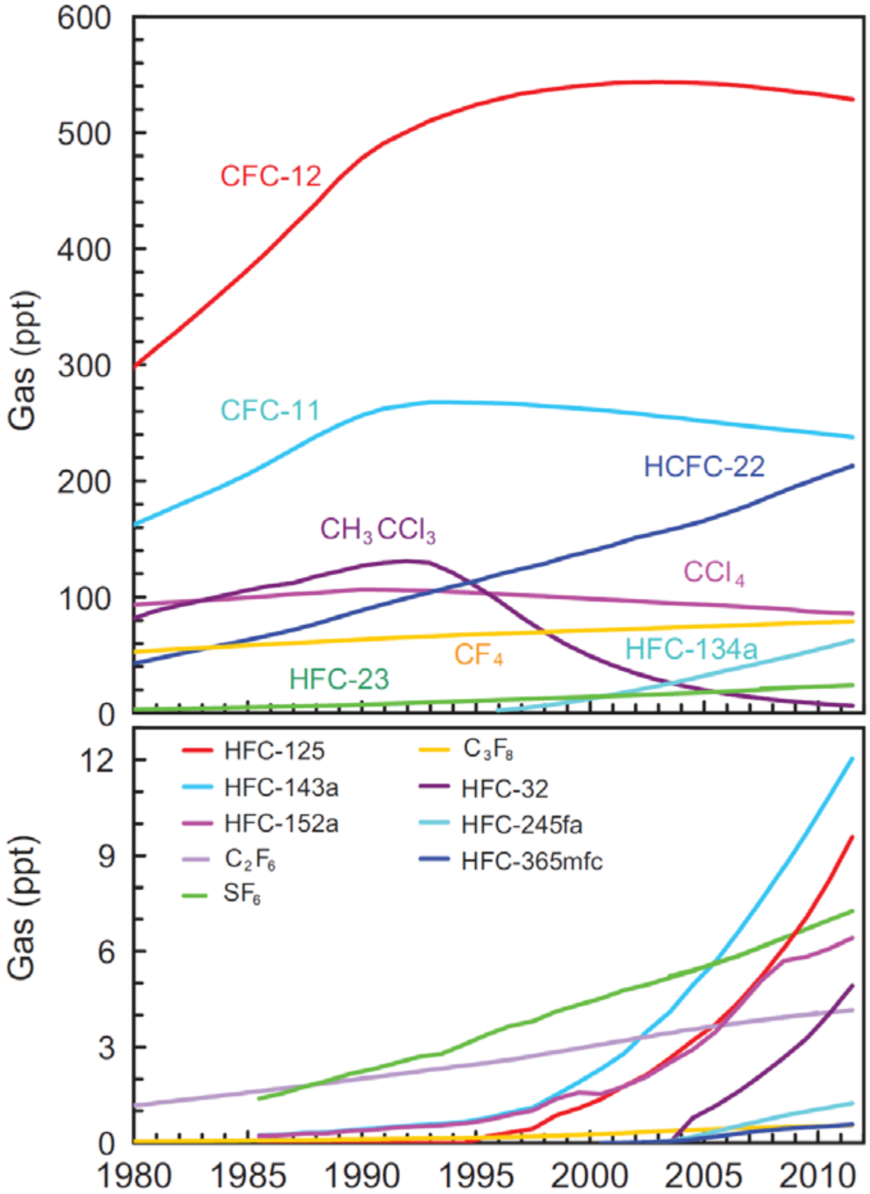


Figure 2.4 | Globally averaged dry-air mole fractions at the Earth's surface of the major halogen-containing well-mixed GHG. These are derived mainly using monthly mean measurements from the AGAGE and NOAA/ESRL/GMD networks. For clarity, only the most abundant chemicals are shown in different compound classes and results from different networks have been combined when both are available.

Halocarbons

- Many are ozone depleting substances
  - Regulated by the Montreal Protocol
- Strong greenhouse gases
- Many are increasing in the atmosphere
- Many have long atmospheric lifetimes

Inorganic Fluorine

- Inorganic fluorine dominates in the stratosphere: HF, COF_2, COClF
- Main sources are CFC-11, CFC-12 and HCFC-22

$$CCl_2F_2\ (CFC\text{-}12) + h\nu \rightarrow CClF_2 + Cl$$

$$CCl_3F\ (CFC\text{-}11) + h\nu \rightarrow CCl_2F + Cl$$

$$CHClF_2\ (HCFC\text{-}22) + OH \rightarrow CClF_2 + H_2O$$

$$CClF_2 + O_2 + M \rightarrow CClF_2O_2 + M$$

$$CClF_2O_2 + NO \rightarrow CClF_2O + NO_2$$

$$CClF_2O + O_2 \rightarrow COF_2 + ClO_2$$

$$CCl_2F + O_2 + M \rightarrow CCl_2FO_2 + M$$

$$CCl_2FO_2 + NO \rightarrow CCl_2FO + NO_2$$

$$CCl_2FO + O_2 \rightarrow COClF + ClO_2$$

Inorganic Fluorine

$$COF_2 + h\nu \rightarrow FCO + F$$

$$COClF + h\nu \rightarrow FCO + Cl$$

$$FCO + O_2 + M \rightarrow FC(O)O_2 + M$$

$$FC(O)O_2 + NO \rightarrow FCO_2 + NO_2$$

$$FCO_2 + h\nu \rightarrow F + CO_2$$

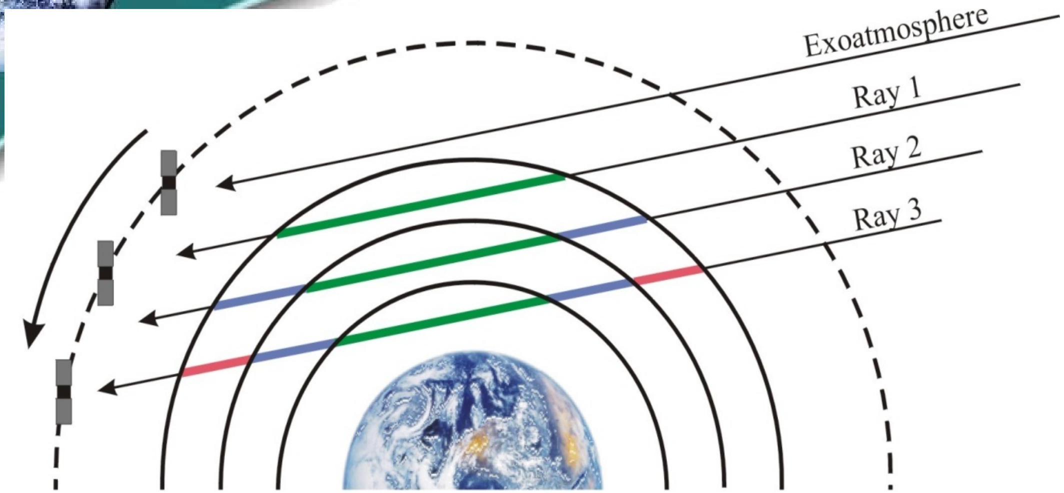
- Secondary loss mechanism via reaction with $O(^1D)$
- F reacts with CH_4, H_2O or H_2 to produce HF, an almost permanent F reservoir.

TOMCAT/SLIMCAT Off-Line 3-D CTM

Off-line 3-D chemical transport model (www.see.leeds.ac.uk/slimcat)

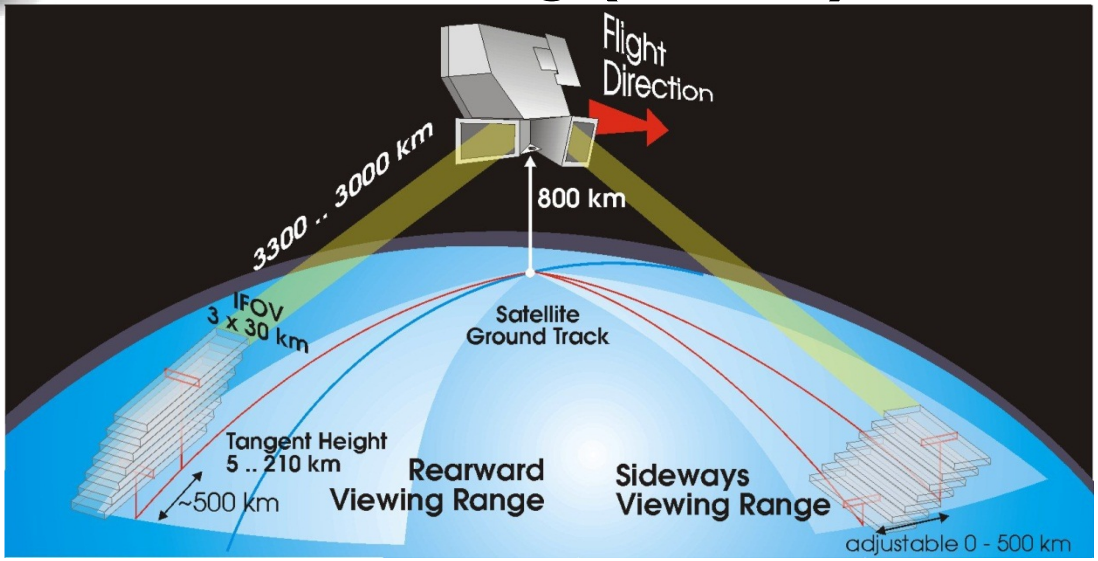
- <u>Vertical coordinate</u> (σ-p - TOMCAT, σ-θ - SLIMCAT). Variable resolution.
- <u>Horizontal winds</u> and <u>temperatures</u> specified from analyses (e.g. ECMWF, UKMO).
- <u>Vertical winds</u> from analysed divergence *or* diagnosed heating rates (in stratosphere).
- <u>Advection</u>: Prather [1986] second-order moments
- <u>Physics</u>: Tiedtke [1989] convection scheme.
  Holtslag and Boville [1993] *or* Louis [1979] PBL schemes.
- <u>Chemistry</u>: Stratosphere: O_x, NO_y, HO_x, Cl_y, Br_y, F_y, CHO_x,
  Source gases: CH_4, N_2O, CFCs, HCFCs, HFCs etc.
- <u>Aerosols</u>: Specified sulphate surface area.
  Polar stratospheric clouds
- <u>COF_2 & HF model runs</u>: 1977– 2013
  5.6^o x 5.6^o. 32 levels from surface to 60 km.

Atmospheric Chemistry Experiment (ACE)



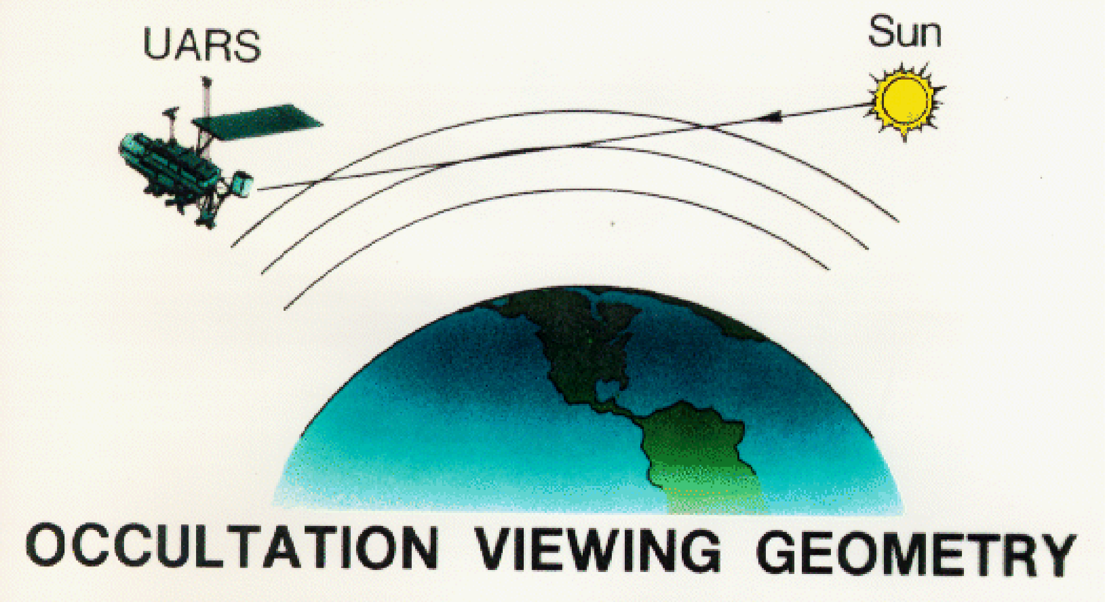
- Fourier transform spectrometer (FTS): 750 to 4400 cm^{-1}
- Records at 0.02 cm^{-1} spectral resolution
- Has been recording atmospheric spectra since 2004
- Uses sun as a radiation source, high S/N
- Long path lengths ~ 300 km (limb sounding)
- Measurements at many altitudes
- ACE detects more trace molecules than any other satellite instrument, including COClF, COF_2, HF
- This work uses the v3.0/v3.5 ACE data product

Michelson Interferometer for Passive Atmospheric Sounding (MIPAS)



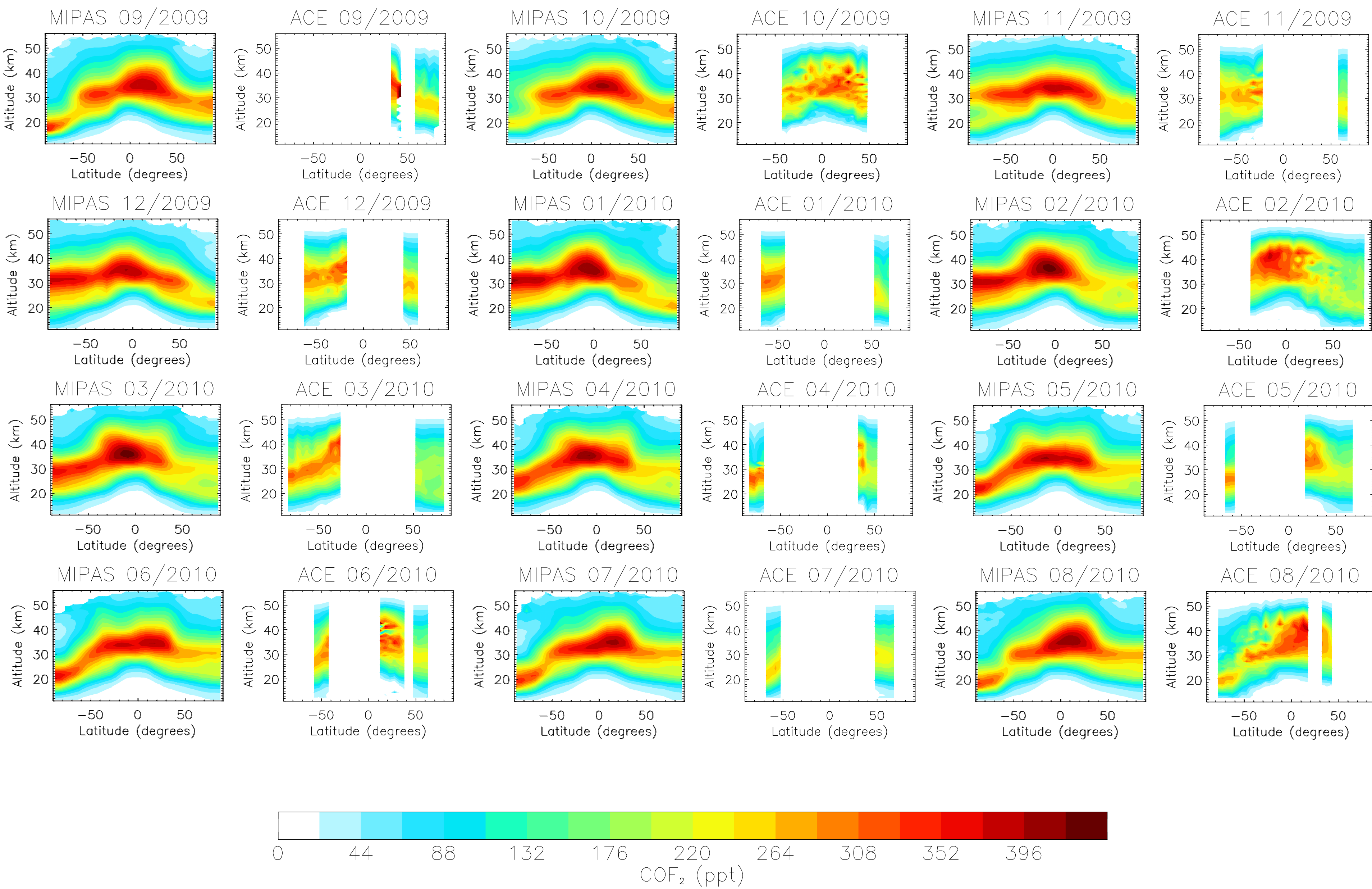
- Fourier transform spectrometer (FTS): 685 to 2410 cm^{-1}
- Recorded initially at 0.025 cm^{-1} spectral resolution, later 0.0625 cm^{-1}
- Detection of limb emission spectra
- Spectra acquired between July 2002 and April 2012
- Measurements at many altitudes
- COF_2 retrievals in this work were performed using v1.3 of the Oxford L2 retrieval algorithm MORSE (MIPAS Orbital Retrieval using Sequential Estimation) with ESA v5 L1B radiance spectra.

Halogen Occultation Experiment (HALOE)

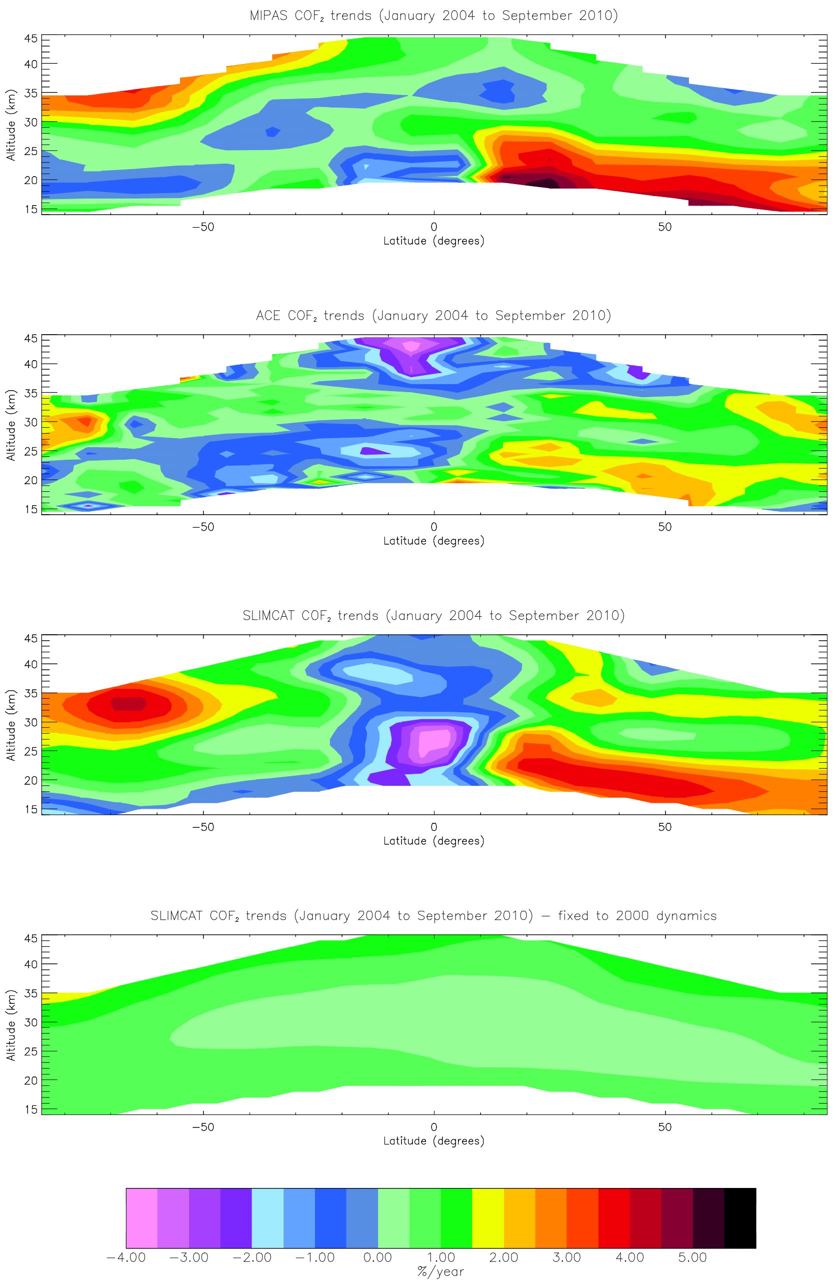


- Gas filter correlation / broadband filter radiometer
- Uses sun as a radiation source, high S/N
- Operational between 1991 and 2005
- Limb sounder – measurements at many altitudes
- HCl, HF, NO, CH_4, H_2O, NO_2, O_3, CO_2
- This work uses the v19 HALOE HF data product

MIPAS – ACE COF_2 zonal means (09/2009 – 08/2010)

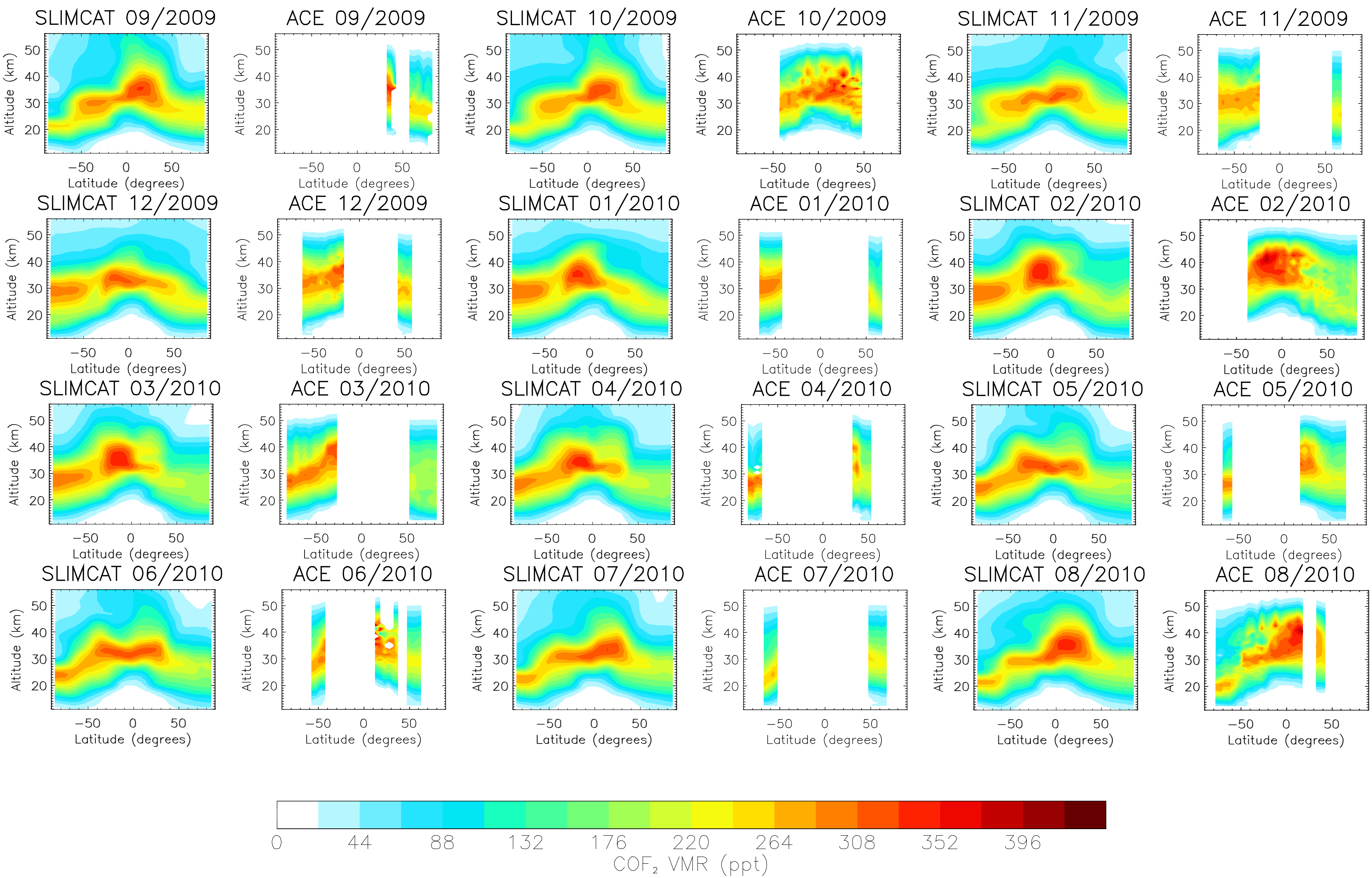


MIPAS – ACE – SLIMCAT COF_2 trends (%/year, 01/2004 – 09/2010)

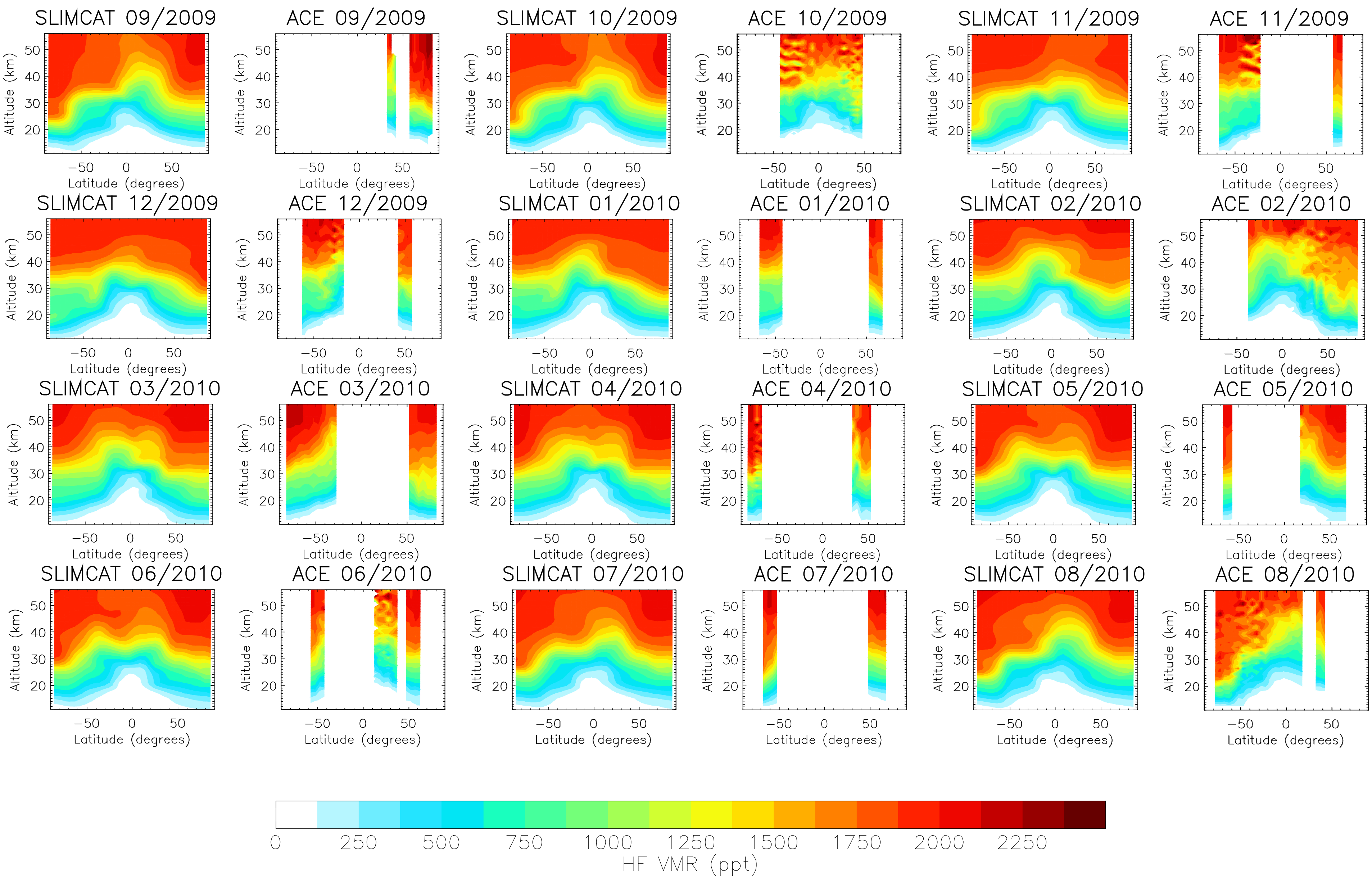


- ACE trends calculated at each altitude in 10° latitude bins from linear regression of percentage anomalies in the monthly COF_2 VMRs
- A SLIMCAT run using fixed dynamics (2000) indicates that the variation in trends is due to changing stratospheric dynamics over the observation period
- Overall VMR-weighted trends:
  - ACE: 0.30 ± 0.44 %/year
  - MIPAS: 0.83 ± 0.34 %/year
  - SLIMCAT: 0.88 %/year

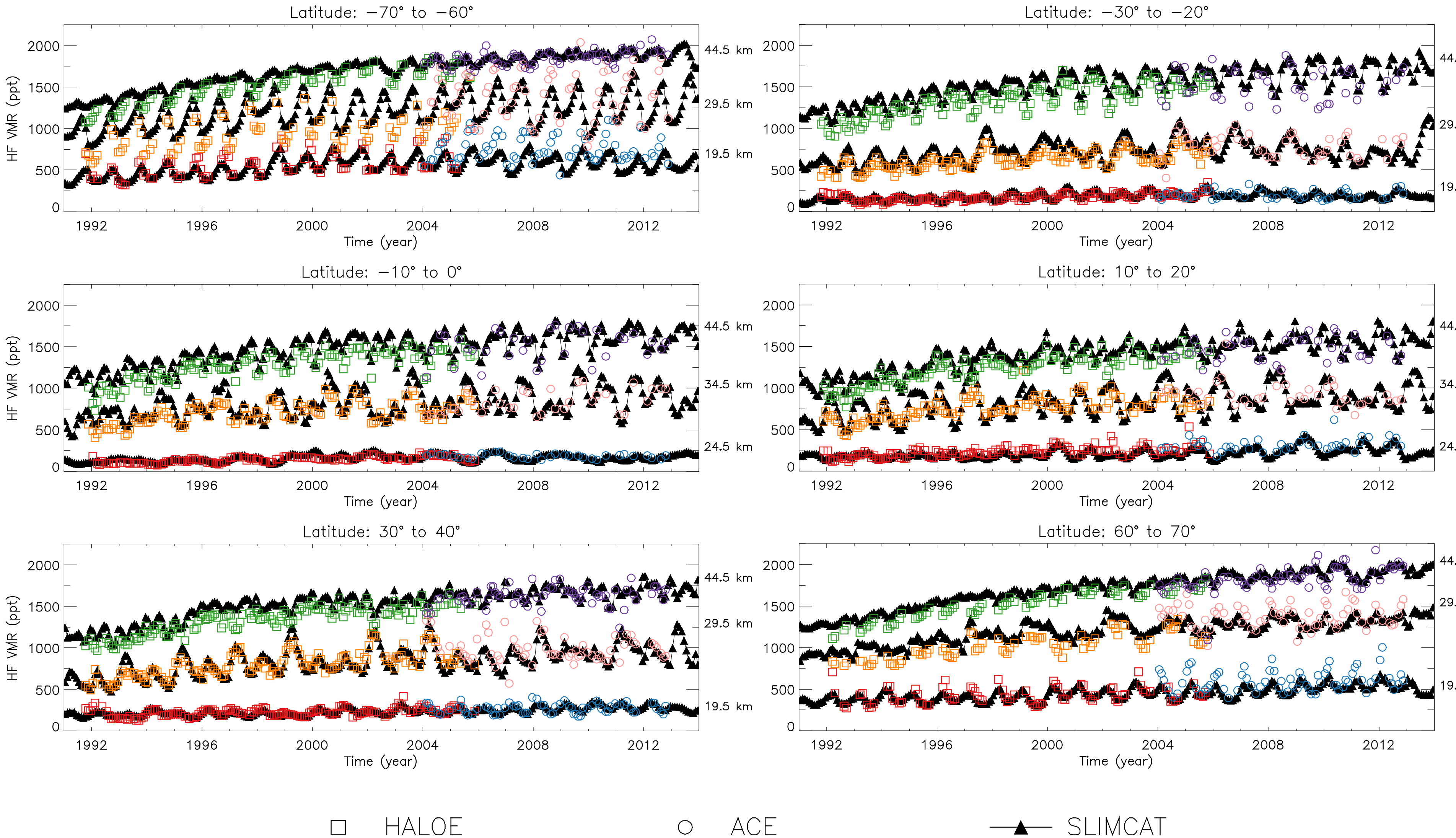
SLIMCAT – ACE COF_2 zonal means (09/2009 – 08/2010)



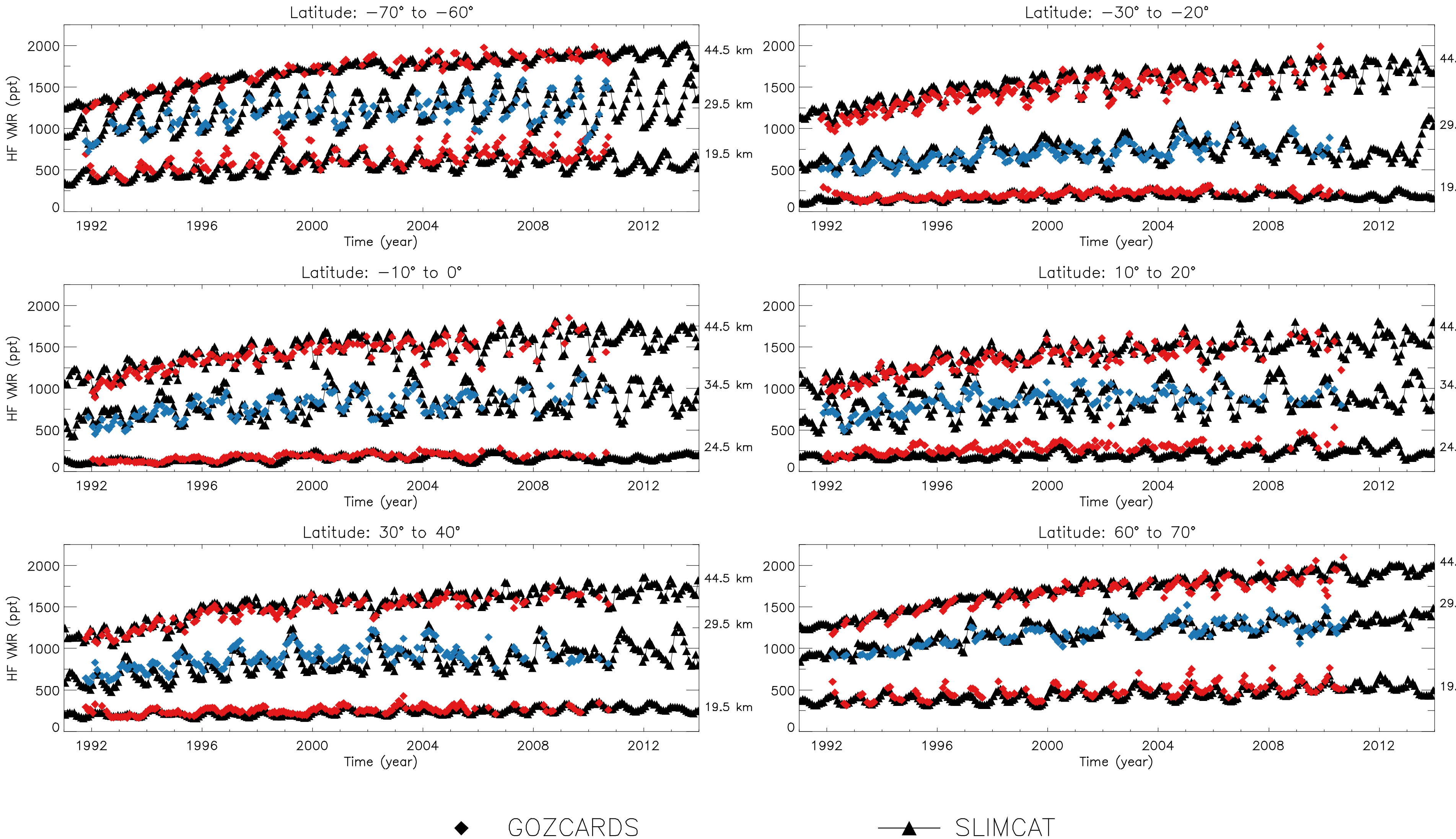
SLIMCAT – ACE HF zonal means (09/2009 – 08/2010)



ACE – HALOE – SLIMCAT time series

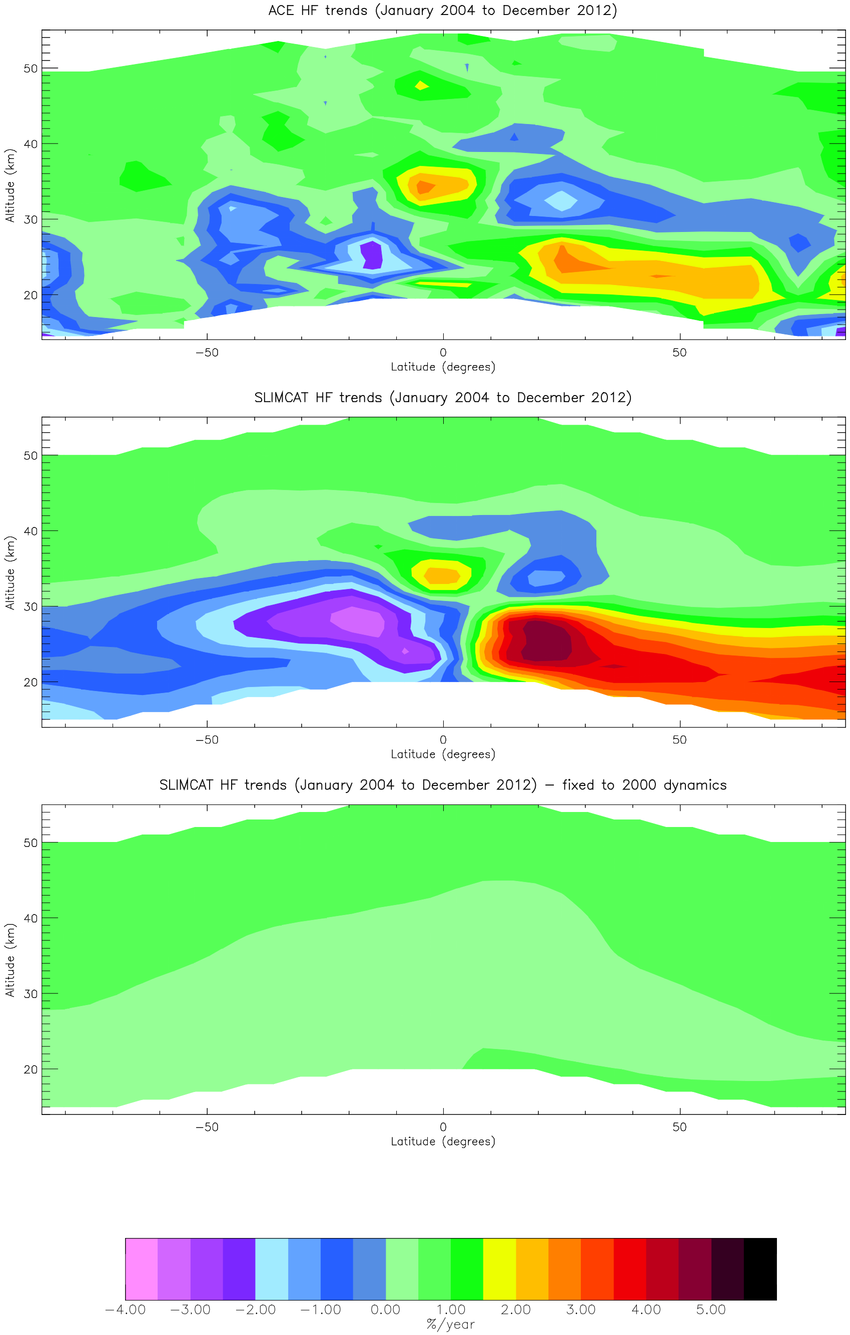


GOZCARDS– SLIMCAT time series



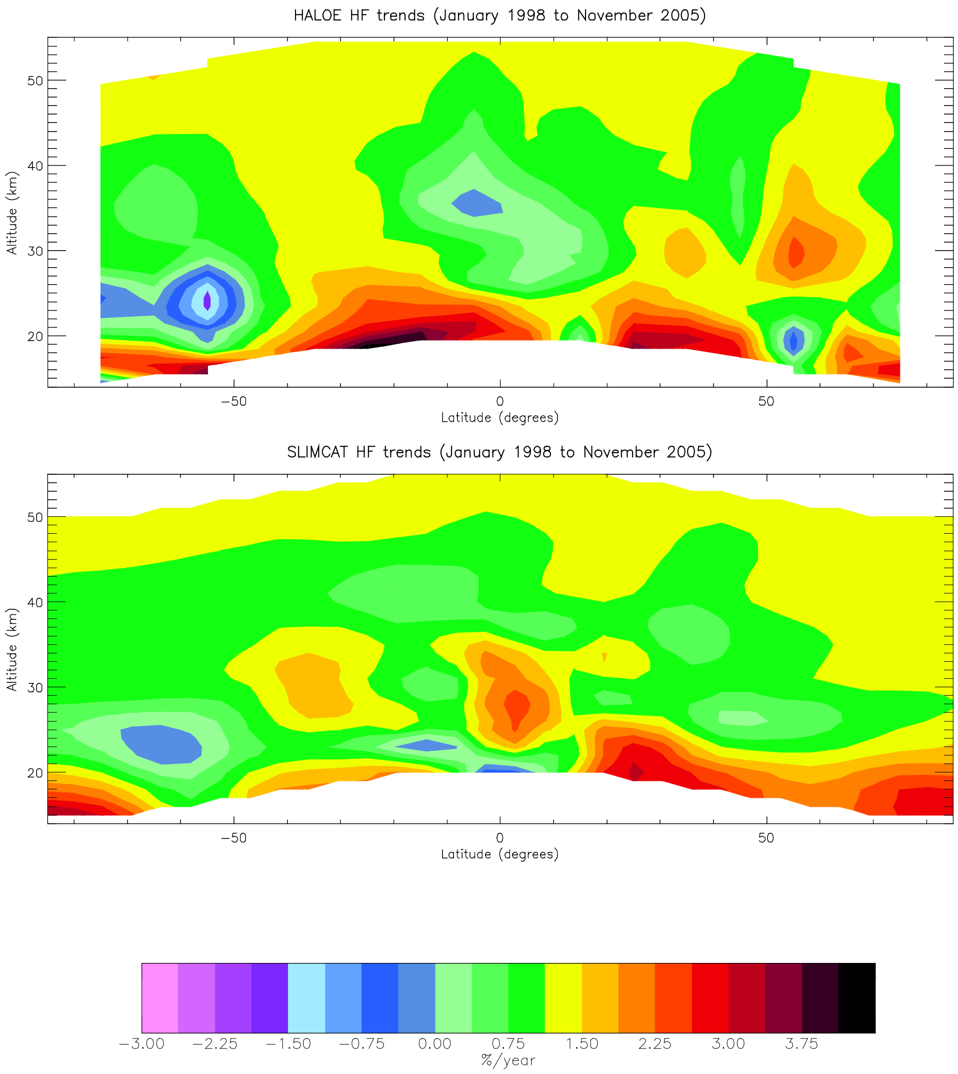
GOZCARDS is a merged v19 HALOE / v2.2 ACE-FTS HF data product

ACE – SLIMCAT HF trends (%/year, 01/2004 – 12/2012)



- ACE trends calculated at each altitude in 10° latitude bins from linear regression of percentage anomalies in the monthly HF VMRs
- A SLIMCAT run using fixed dynamics (2000) indicates that the variation in trends is due to changing stratospheric dynamics over the observation period
- Overall VMR-weighted trends:
  - ACE: 0.52 ± 0.03 %/year
  - SLIMCAT: 0.48 %/year

HALOE – SLIMCAT HF trends (%/year, 01/1998 – 11/2005)



- HALOE trends calculated at each altitude in 10° latitude bins from linear regression of percentage anomalies in the monthly HF VMRs
- Overall VMR-weighted trends:
  - HALOE: 1.12 ± 0.08 %/year
  - SLIMCAT: 1.10 %/year
- BUT overall trends for 10/1991 to 12/1997 do not agree:
  - HALOE: 4.97 ± 0.12 %/year
  - SLIMCAT: 4.01 %/year

Recently published:

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Satellite observations of stratospheric carbonyl fluoride

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Conclusions

- SLIMCAT agrees well with COF_2/HF satellite observations
  - Need improved COF_2 lab spectroscopy to resolve MIPAS bias
- COF_2 is increasing in the atmosphere
  - HCFC-22 concentrations increasing faster than CFC-12 decreasing
- HF is increasing in the atmosphere
- Variation in COF_2 / HF trends with latitude and altitude indicate changing stratospheric dynamics, particularly between 2004 and 2012.
- But what happens after ACE?