climate change initiative

LONG-LIVED GREENHOUSE GAS PRODUCTS PERFORMANCES

WP 3500: The atmospheric lifetimes of OLLGHGs

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Lifetimes of halogenated species

Why are we interested in the lifetimes of these species?

- To predict future abundances
- To infer emissions
- To calculate global warming potentials (GWPs) or ozone-depletion potentials (ODPs)

SPARC assessment

- 2013 SPARC assessment of atmospheric lifetimes for ozone-depleting substances, their replacements, and related species
  - Included ACE-FTS analysis from Brown et al. (2013)
- “Best” lifetimes were taken as weighted averages of lifetimes calculated from observations and models
  - Questions still remain about the optimum lifetimes
- While models are able to calculate lifetimes of all relevant gases (given suitable photochemical data), the observation-based estimates are limited to the availability of data and the suitability of different methods.

Some recent lifetime work

- Study by Lickley et al. (2021) indicates that the lifetimes of CFC-11, CFC-12, and CFC-113 are likely shorter than currently recommended values
  - This is important because it suggests that best estimates of inferred emissions, e.g. from banks, are larger than recent evaluations
- Prather et al. (2023) used MLS data (2005–2021) to calculate that the atmospheric lifetime of N_2O is decreasing at a rate of -2.1 ± 1.2 %/decade.
  - Arises from an enhanced Brewer-Dobson Circulation
  - N_2O abundances in the middle tropical stratosphere, where N_2O is photochemically destroyed, are increasing at a faster rate than the bulk N_2O in the lower atmosphere.
- Bourguet et al. (2025) semi-empirically estimated the lifetimes of CFC-11, CFC-12, and CCl_4 using mass balance in the stratosphere.

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In this work package we will

- Determine the stratospheric lifetimes of selected key species utilising ACE-FTS v5.2 data and the method of Volk et al. (1997)
- Investigate the variability in lifetimes for different atmospheric regions over the ACE-FTS time period (almost 20 years);
- Investigate whether there is any evidence for a decrease in the atmospheric lifetime of species such as CFC-12 (which has a similar lifetime and loss region as N_2O), and determine any implication on future abundances and ozone recovery

Volk's Method 1

Stratospheric lifetimes based on correlations with age-of-air at the extratropical tropopause

$$\tau = -\frac{M_a \bar{\sigma}}{M_u C \left.\frac{d\chi}{d\Gamma}\right|_{\Gamma=0}}$$

Note that in the extratropics, transport across the tropopause is extremely slow, meaning that the correlation of the species at the tropopause will be a function of lifetime and not atmospheric transport.

- M_a is the total dry air mass of the atmosphere
- M_u is the mass of the atmosphere above the tropopause
- $\bar{\sigma}$ is the average atmospheric mixing ratio of the species
- Γ is the age-of-air
- C is a correction factor

Volk's Method 1

The correction factor *C* is defined as

$$C = \frac{\left.\frac{d\sigma}{d\Gamma}\right|_{\Gamma=0}}{\left.\frac{d\chi}{d\Gamma}\right|_{\Gamma=0}}$$

Here we use the notation χ to represent the transient volume mixing ratio (VMR) of a species, and σ its steady-state VMR.

where

$$\left.\frac{d\sigma}{d\Gamma}\right|_{\Gamma=0} = \frac{\left(\left.\frac{d\chi}{d\Gamma}\right|_{\Gamma=0} + \gamma_0\sigma_0\right)}{(1 - 2\gamma_0\Lambda)},$$

$$\chi_0(t') = \chi_0(t)\left[1 + b(t' - t) + c(t' - t)^2\right],$$

$$\gamma_0 = b - 2\Lambda c.$$

Volk's Method 2

Relative stratospheric lifetimes using tracer-tracer correlations at the extratropical tropopause

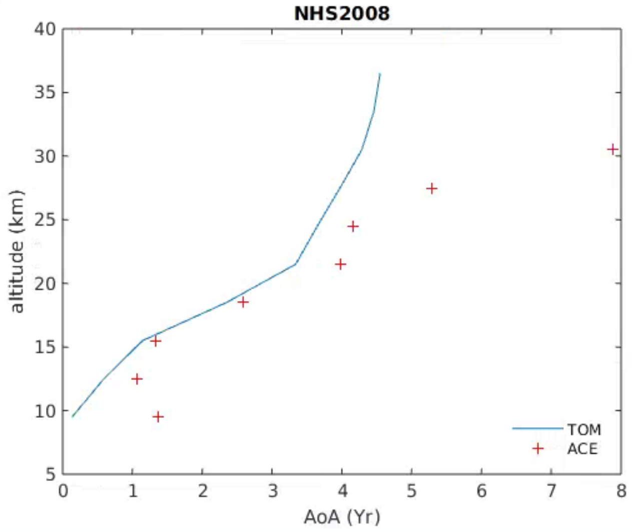
$$\frac{\tau_a}{\tau_b} = \frac{\overline{\sigma_a}}{\overline{\sigma_b}} \bigg/ \frac{d\sigma_a}{d\sigma_b}$$

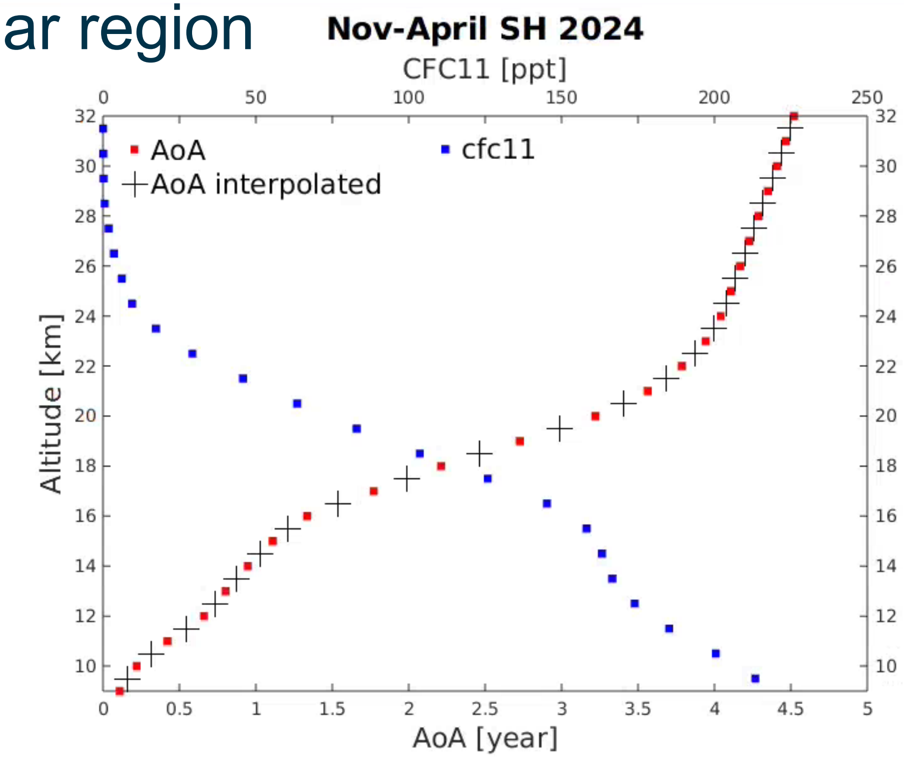
where

$$\frac{d\sigma_a}{d\sigma_b} = \frac{\left.\frac{d\chi_a}{d\chi_b}\frac{d\chi_b}{d\Gamma}\right|_{\Gamma=0} + \gamma_{0_a}\sigma_{0_a}}{\left.\frac{d\chi_b}{d\Gamma}\right|_{\Gamma=0} + \gamma_{0_b}\sigma_{0_b}} \frac{1 - 2\gamma_{0_b}\Lambda}{1 - 2\gamma_{0_a}\Lambda}.$$

Age-of-air data

- We investigated using the ACE-derived age-of-air from Saunders et al. (2025)
  - 10° latitude bins and 3 km altitude bins
  - However, the data are not ideal in the 0-2 year region
    - "kink" in the data near the tropopause
    - occasional missing values





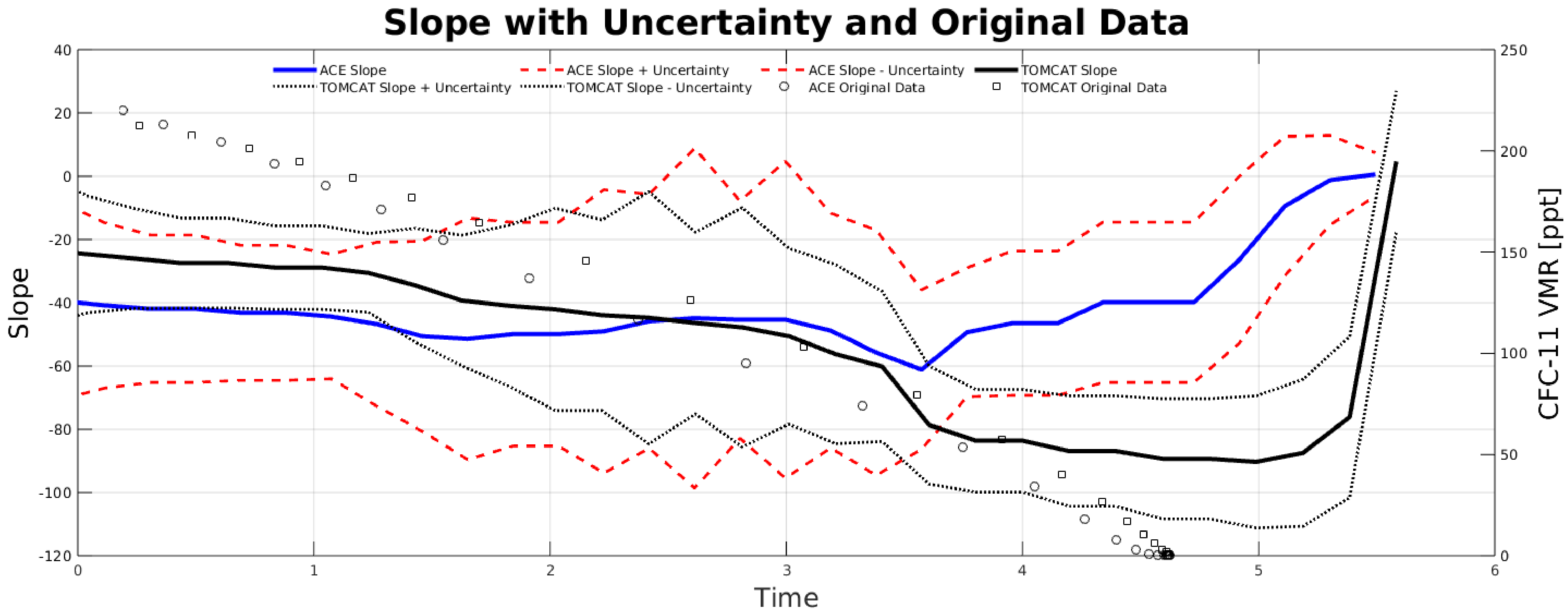
Solution: use TOMCAT age-of-air

Preliminary results – slope calculations

- The slope $\left(\frac{d\chi}{d\Gamma}\Big|_{\Gamma=0}\right)$ calculations were performed using linear least squares fitting with uncertainties applied to both x and y axes.
- Slopes were calculated at each data point from a rolling window over a two-year period. A quadratic function was then used to fit these slopes and enable extrapolation to the tropopause, where Γ=0.
- Correction terms (*C*) are taken from Volk et al. (1997).
- Each year of ACE data was divided into four bins, Northern Hemisphere Winter (NHW), Northern Hemisphere Summer (NHS), Southern Hemisphere Winter (SHW) and Southern Hemisphere Summer (SHS) between 30° N/S to 70° N/S.
- CFC mixing ratios averaged onto the ACE 1-km altitude grid.
- For TOMCAT, data were interpolated to match the ACE bins/altitude grid

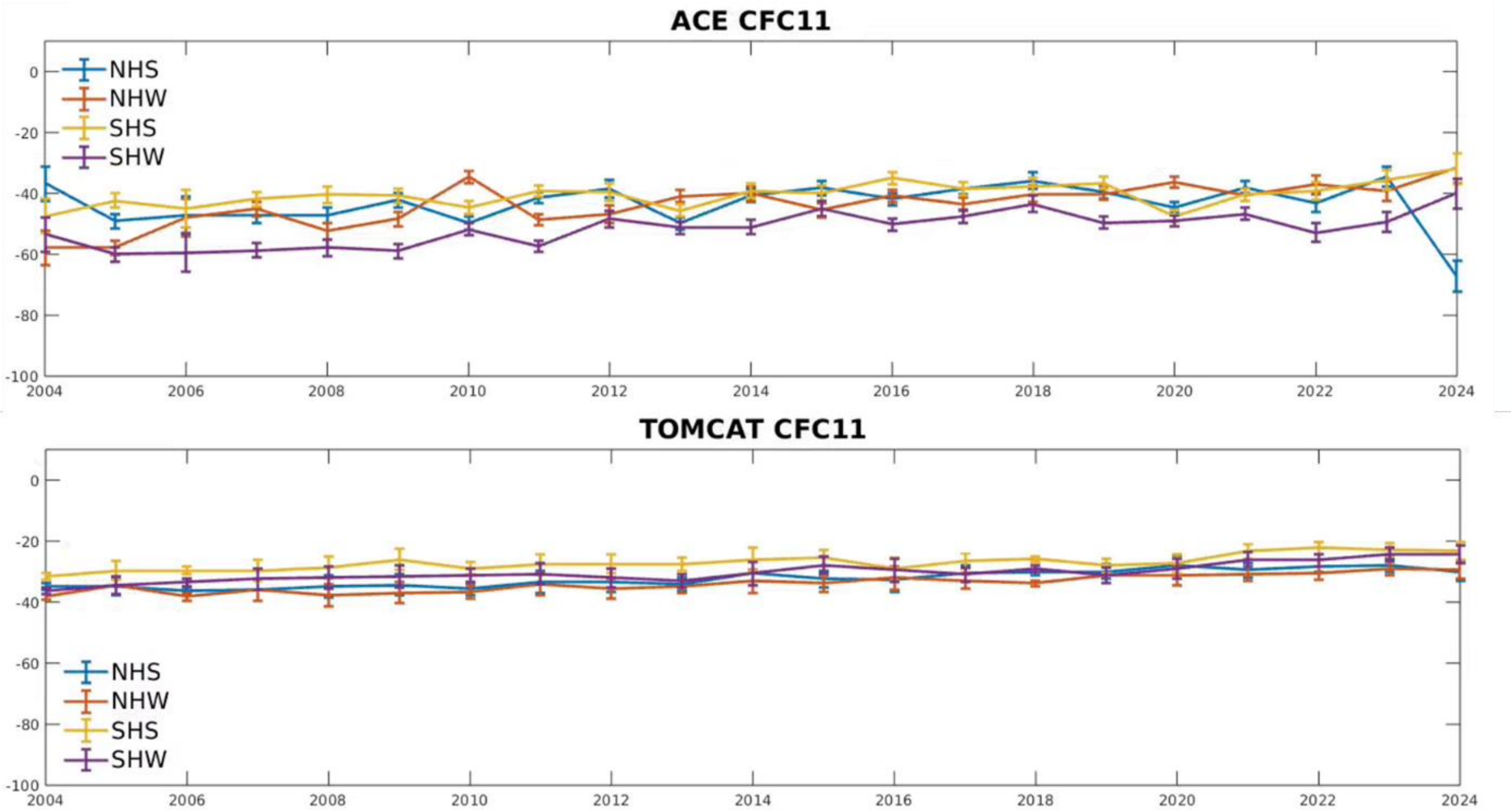
Preliminary results – slope calculations

- Slopes (units ppt/year) for ACE-FTS and TOMCAT CFC-11 for SHW 2024



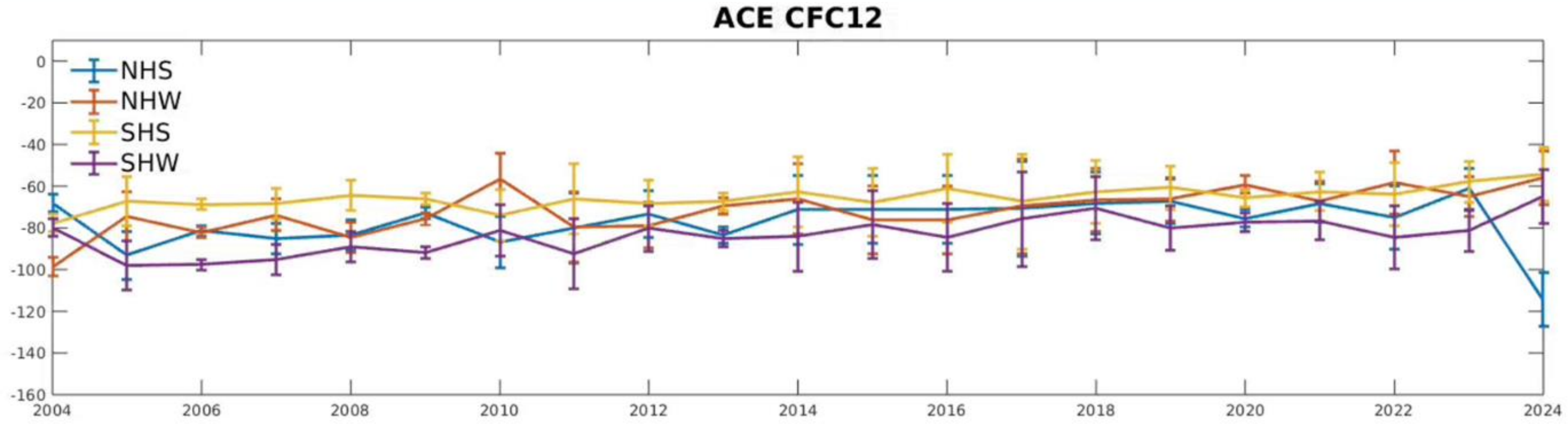
Preliminary results – slope calculations

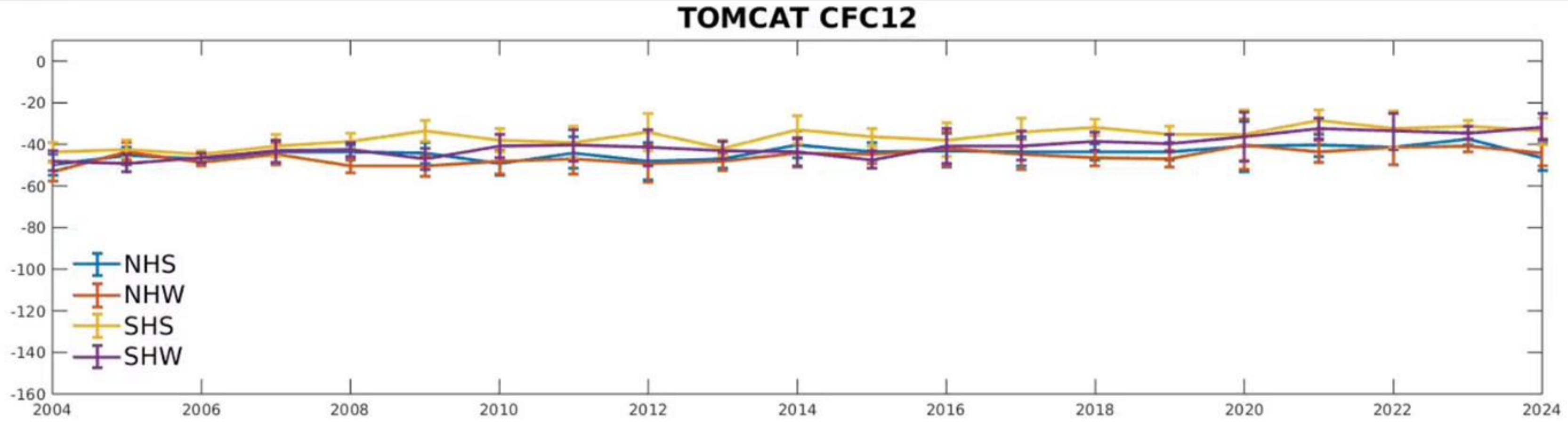
- Slope (units ppt/year) time series for ACE-FTS and TOMCAT CFC-11



Preliminary results – slope calculations

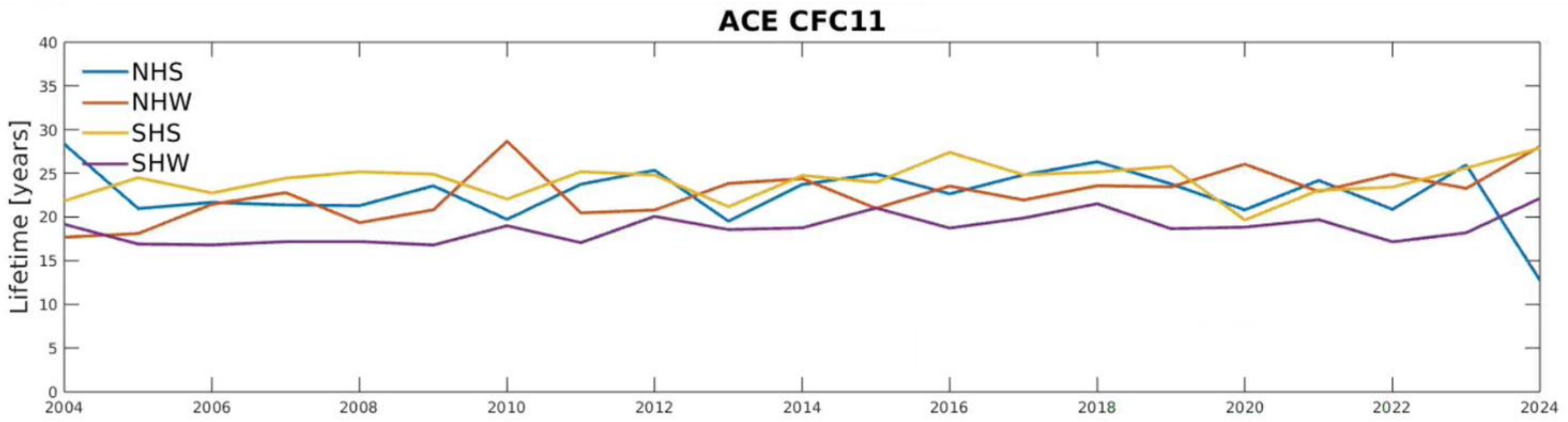
- Slope (units ppt/year) time series for ACE-FTS and TOMCAT CFC-12

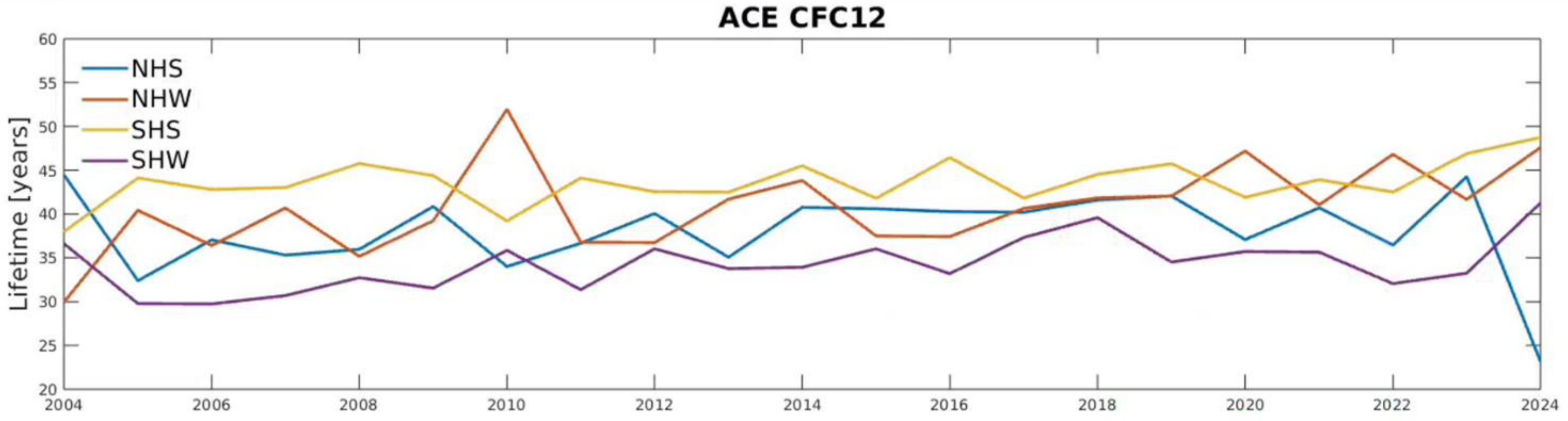




Preliminary results – lifetimes

- Lifetime (year) time series for ACE-FTS CFC-11 and CFC-12





Preliminary results – lifetime comparisons

	WMO (2003)	SPARC	Rigby et al. (2013)	Lickley et al. (2020)	Bourguet et al. (2025)	ACE-FTS* (this work)	TOMCAT* (this work)
CFC-11	45	52	52	54.0	50	22	40
CFC-12	100	102	112	93.2	86	39	74

Preliminary conclusions

- ACE and TOMCAT slopes are quite different
  - We need to investigate the reasons for this
- Preliminary ACE lifetimes are too low
  - Using values of *C* from Volk et al. (1997)
- No evidence for a decreasing CFC-11 or CFC-12 trend between 2004 and 2024
  - Perhaps the ACE data are not precise enough to infer such a trend
- In theory TOMCAT data should be able to test fully the Volk equations
  - Can compare to the model lifetime calculated directly from the atmospheric burden and loss rates
- There is still a lot to do!

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