

of tracers with a wide range of lifetimes to study UTLS transport

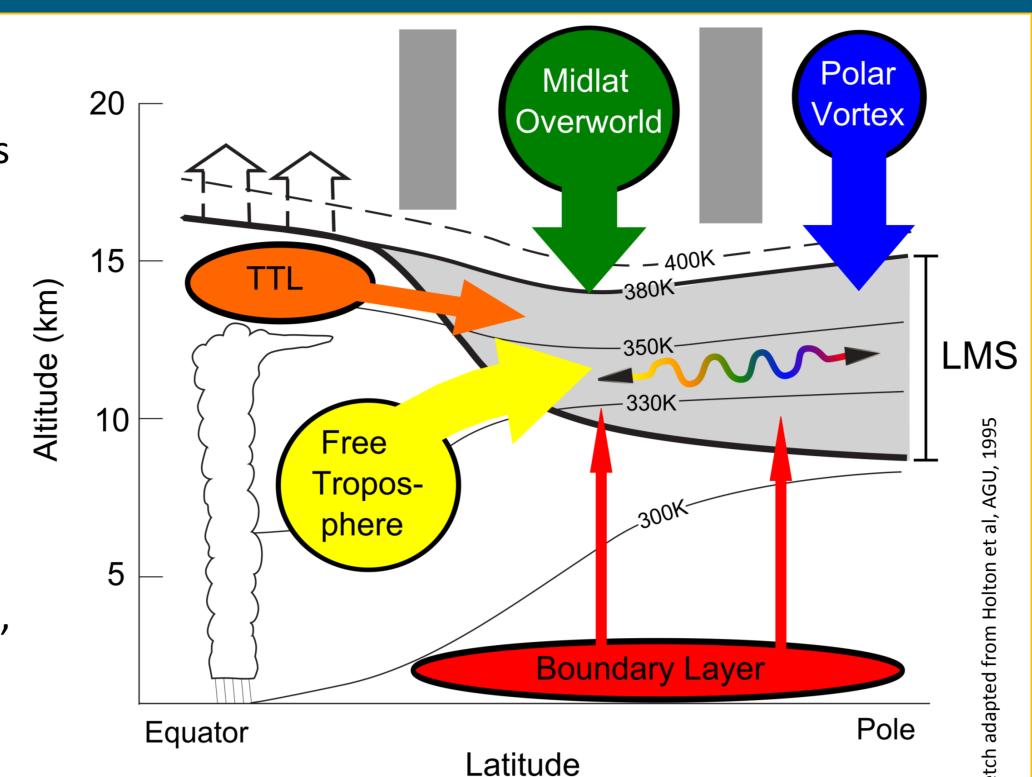
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Motivation

- The upper troposphere/lower stratosphere (UTLS) is a key region in the climate system.
- Radiative forcing is sensitive to the distribution of greenhouse gases (H_2O , CO_2 , CH_4 , O_3) in the UTLS.
- For a stratosphere (LMS) particularly, are determined by transport and mixing of air masses from various regions with widely differing chemical composition.
- Time scales for transport along the various pathways, and for mixing in the LMS, range from days to years.
- Recent observations indicate that transport patterns and transport times may be changing.



Transport pathways into the lowermost stratosphere (LMS)

General objectives

- What is the relative importance of different transport pathways into the lowermost stratosphere (LMS)?
- What are the transport times along these pathways?
- ➤ What are the time scales for mixing within the LMS?

Method: analysis of chemical tracers

Distributions of tracers with a wide range of lifetimes

Pathways and time scales of transport and mixing

New instrument for in situ tracer measurements on board HALO

HAGAR-V (High Altitude Gas AnalyseR-V)

Modernized and extended version of HAGAR instrument on M55 Geophysica

5 channels in 3 modules for in situ tracer measurements:2-Channel GC/ECD-Module

for long-lived tracers
direct sample injection
separation on packed columns
electron capture detection (ECD)

2-Channel GC/MS-Module

 for short- and long-lived tracers

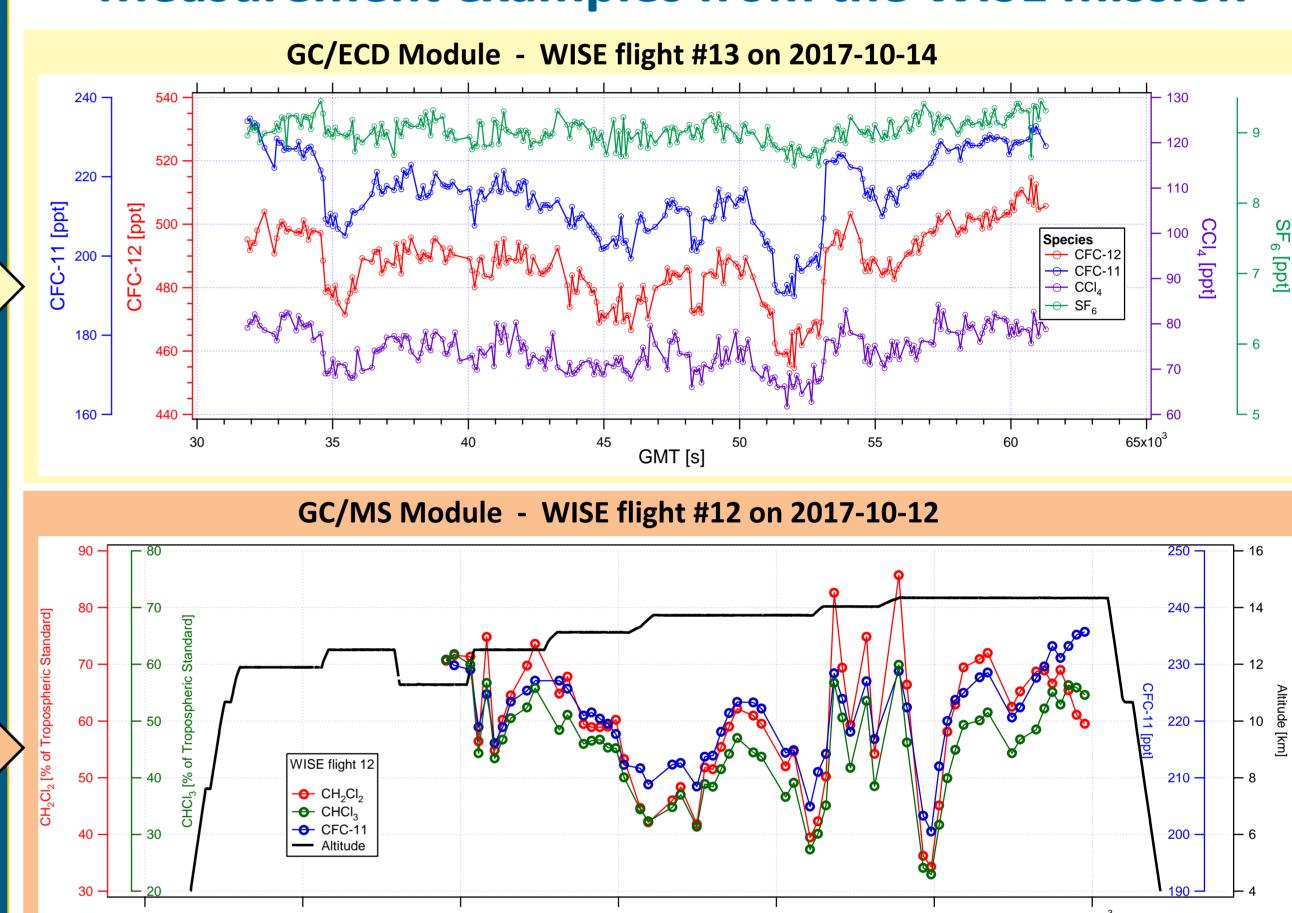
 sample enrichment on cold traps
 separation on capillary columns
 mass spectrometric (MS) detection
 NDIR-Module for CO₂
 Detection: IR-absorption

Total weight: 128.5 kg + 32 kg Rack

Photochemical Contribution to strat. **Target** Time organic chlorine^d resolution lifetime **Species** 3200^a yr 136^b yr CH_4 102^b yr CFC-12 32.1 % 90 s 93^b yr CFC-113 6.8 % 52^b yr 21.6 % CFC-11 44^b yr CCI_{4} 10.4 % 93^b yr CFC-113 6.8 % 52^b yr 21.6 % CFC-11 51^b yr CH₃Cl 16.5 % 180 s 632^c days CH₂Cl₂ 1.4 % (per channel) 601^c days CHCl₃ 0.5 % C_2Cl_4 439^c days 0.1 % 7^c days n-&iso-Butane CO_2 ~ infinite

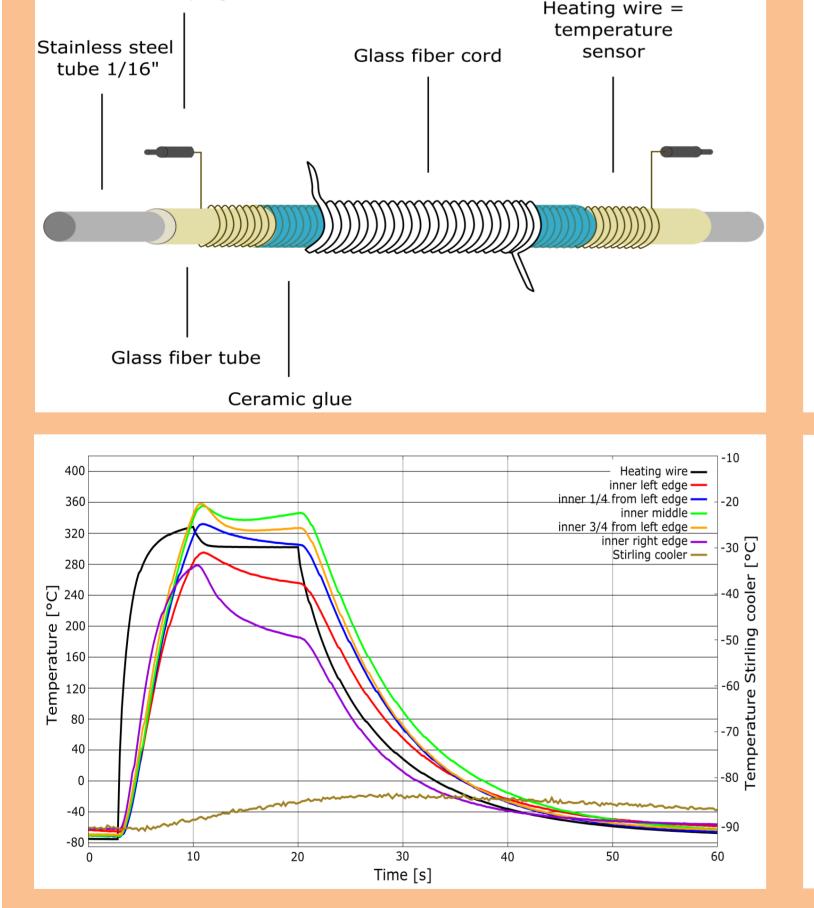
b Stratospheric lifetime, SPARC lifetime assessment report, 2013 c Local lifetime at 15 km, 20°N/S, calculated from photo chemical kinetic data d Calculated from WMO-Scientific Assessment of O₃ Depletion, 2014

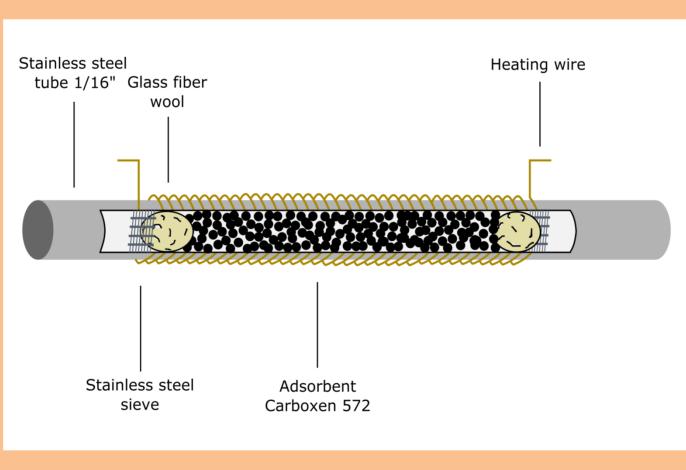
Measurement examples from the WISE mission



- > Measurement of tracers with a wide range of photochemical lifetimes to investigate transport and mixing
- > Species measured by HAGAR-V cover ~90% of the organic chlorine entering the stratosphere

Novel thermal desorption system for GC/MS-Module

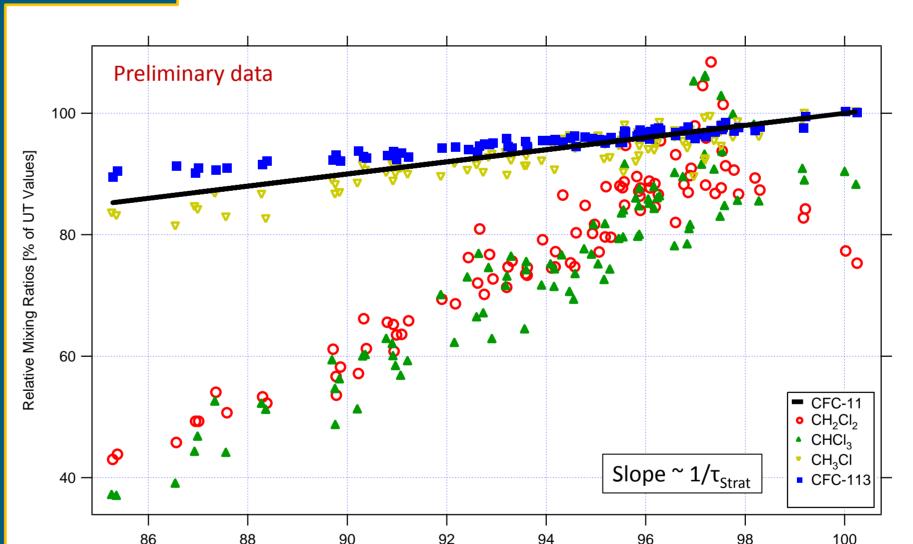




Enrichment & thermal desorption unit for GC/MS-Module

- Per channel one adsorbent filled stainless steel tube is wrapped with a heating wire which at the same time is used as a temperature sensor.
- > The system is thermally coupled to a **stirling cooler**.
- ➤ Heating rates larger than 100K/s are achieved inside the tube, with temperature differences along the tube of ±~50K and a very good reproducibility.
- > Cooling rates inside the tube were determined to be up to

Correlation of short and long-lived tracers



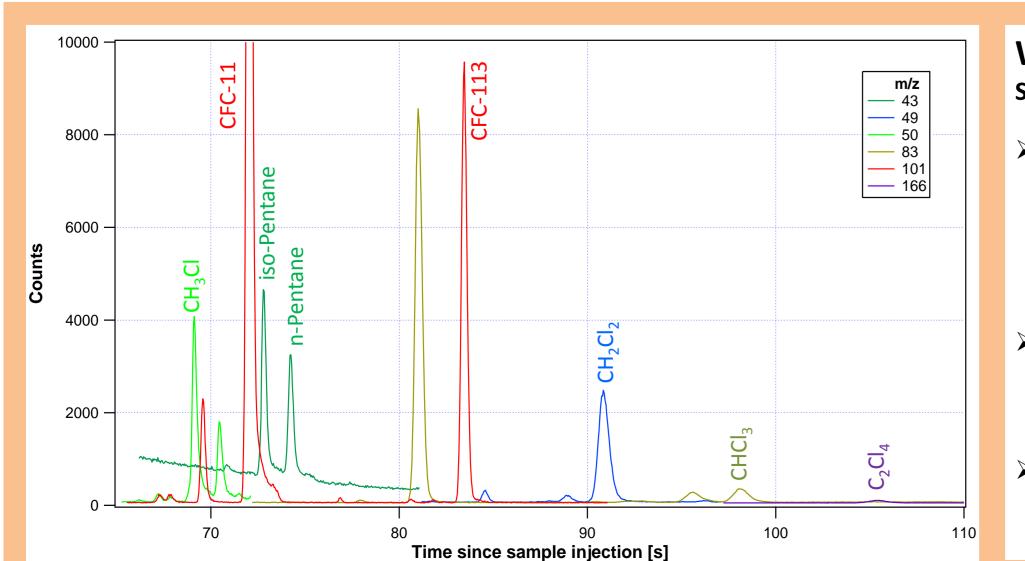
WISE flight #12 on 2017-10-12
Preliminary data from GC/MS-Module

Mixing ratios are plotted in normalized units relative to upper tropospheric values for all species, such that the correlations converge in the upper troposphere at the point 100%:100%.

The slope of each correlation is inversely proportional to the stratospheric lifetime of the respective species.

Correlations of VSLS (Very Short Lived Species) like CH₂Cl₂ and CHCl₃ with long lived tracers (here CFC-11) exhibit **more scatter** than correlations between long lived tracers because **tropospheric sinks of VSLS** induce gradients in the upper troposphere.

Example chromatogram of GC/MS-Module



WISE flight #12 on 2017-10-12 Single injection of one GC/MS channel

- ➤ The species of interest appear within a time window of 40s. The second channel runs countercyclical to use the detector during the waiting time of the first channel.
- Some of the prominent peaks (e.g. at m/z=83, 101, 50) still have to be identified.
- By using the electron ionization mode peaks do not necessarily need to be chromatographically separated.

HAGAR-V measurements during PGS and WISE missions

