Global Trends in Carbonyl Sulfide from 22 NDACC Stations

J Hannigan,

I Ortega, S Bahramvash Shams

& All IRWG Teams

ACOM Seminar, 17 May 2021, Boulder CO

Outline

- Motivation
- Previous Measurements
- NDACC & Observation Stations
    - Infrared Instrumentation
    - Retrievals & Information Content
- Total and Partial Column data
- Regression with Dynamical Proxies and N_2O
- Latitudinal Distribution
- Annual Cycles
- Conclusions

Motivation

- SSiRC - Stratospheric Sulfur and its Role in Climate / SPARC Stratosphere-troposphere Processes And their Role in Climate

  - Study: “The measured stratospheric sulfur burden.” led by T Deshler
    - Review of all stratospheric measurements of sulfur contain species & aerosols.
    - Determine / Quantify / Estimate
      - Total burden, global distribution, changes / trends
      - Sources & sinks

➢ Request to IRWG was for stratospheric trends of OCS mean VMR / partial columns.

From the IR remote-sensing community, this effort follows on from recent studies:

- Lejeune et. al., 2017, JQSRT – Detailed reanalysis of retrieval strategy for a single IRWG station
- Wang et. al., 2016, ACP - Total column & tropospheric focus at selected IRWG stations relating to plant respiration
- Kremser et. al., 2015, GRL – Troposphere & stratosphere trends, Southern Hemisphere focus
- Krysztofiak, et. al., 2015, Atmos-Ocean – Global & latitudinal analysis using NDACC, MKIV and SPIRALE

OCS Sources, Sinks and Atmospheric Lifetime Estimates

- Oceanic sources
  - Direct OCS, DMS, CS_2
  - Oxidation of CS_2 ~ lifetime of 6 days
  - Oxidation DMS ~ lifetime <1 - days
- Terrestrial Sources
  - Biomass burning
  - Volcanoes

- Terrestrial Sinks (Excellent review: Whelan et al., BioGeoSci, 2018)
  - Photosynthetic uptake
  - Soil uptake

- Anthropogenic sources
  - "However, the budget suggests that more than a third of OCS arises from anthropogenic activities. Some 70% of the CS2 comes from human activities and almost all of the thiophenes." [Lee & Brimblecombe, 2016]
    - Paper / pulp production, biomass burning, rayon manufacture
  - Recent inventory (Zumkehr et. al., 2018) shows upward trend since 2002 + inflection ~ 2008 and increasing until 2012

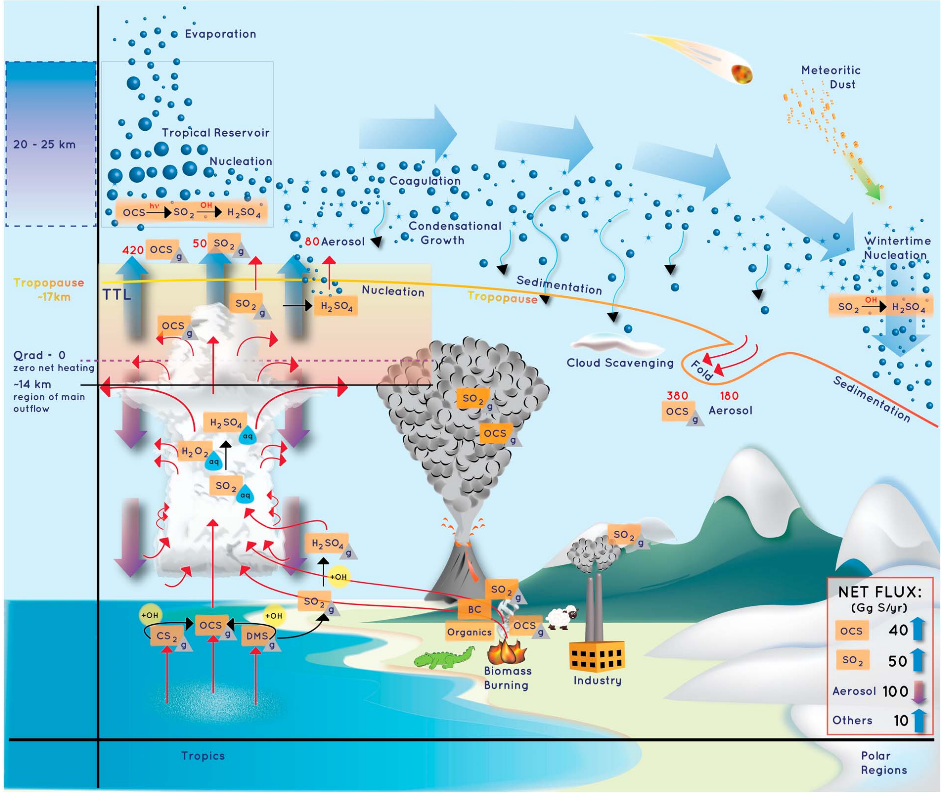
- ~2.7 to 6y tropospheric lifetime (Ulshöfer and Andreae, 1997, Montzka et al., 2006)

- Stratospheric lifetime : 68 ± 20 y at N. polar latitudes & 58 ± 14 y for tropical lat., [Krysztofiak et al., 2015]

- In short …OCS atmospheric budget clearly time dependent & not completely understood… exacerbated in a warming ocean and changing land use environment.

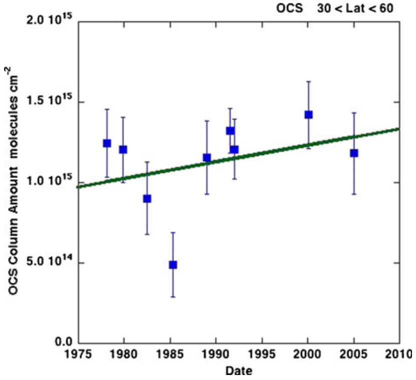
Schematic OCS and Stratospheric Aerosol

- S. Kremser (Rev. Geo., 2016) outlines the complicated movement of net Sulphur species from the surface sources to maintain the stratosphere aerosol layer.
- Modeled based study (Sheng et. al., 2016) shows a transport to the stratosphere via OCS of ~420 Gg S/yr and losses in part to the troposphere yielding a net flux via OCS of ~40 Gg S/yr
- Estimates of between 56 – 70% of the aerosol burden is maintained by OCS transported from the troposphere. The aerosol layer relies on a sustained concentration of OCS in the upper troposphere.



Kremser et al., 2016, Rev. Geophys., 54(2):278–335. (Fig. 1)
Sheng, et. al., 2015, JGR, 120(1):256–276.

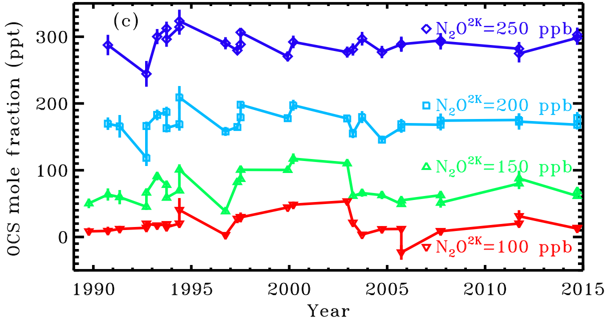
Previous Work : OCS Stratospheric Trends



Multiple airborne missions flown between 1978 – 2005 over northern mid-latitudes 30 – 60°N using the same EOCOM interferometer instrument. The trend in the column above 200hPa was 0.77±0.80%/year.

1978 - 2005
30 – 60°N
0.77±0.80%/year above 200hPa

Coffey & Hannigan JAC, 2011



Multiple balloon flights of the JPL MKIV interferometer flown between 1990 – 2015 in N mid-latitudes 33 – 68°N. These are interpolated to de-trended N2O (at .25%/y) isopleths (red ~21km and blue ~30km at mid-latitudes).
"The MkIV balloon measurements show no significant trend at the N_2O = 250 ppb isopleth."

1990-2015
33 – 68°N
no significant trend at N_2O = 250 ppb

Toon, et. al., ACP 2018

Satellite:

MIPAS: (2002-2012)
"…no significant trends in the upper troposphere. "
Northern Hemisphere, up to -65ppt/decade
weak positive trend in SH up to ~20ppt/decade.

Glatthor et. al., ACP 2017

ACE FTS: (2002-2004)
– no trends determined

Barkley et al, GRL, 2008

Ground Based:

NDACC Jungfraujoch, (1995-2015)
Net positive trends, varies

Lejeune, et. al., JQSRT 2016, 1995

NDACC S.Hemisphere, (2002-2016)

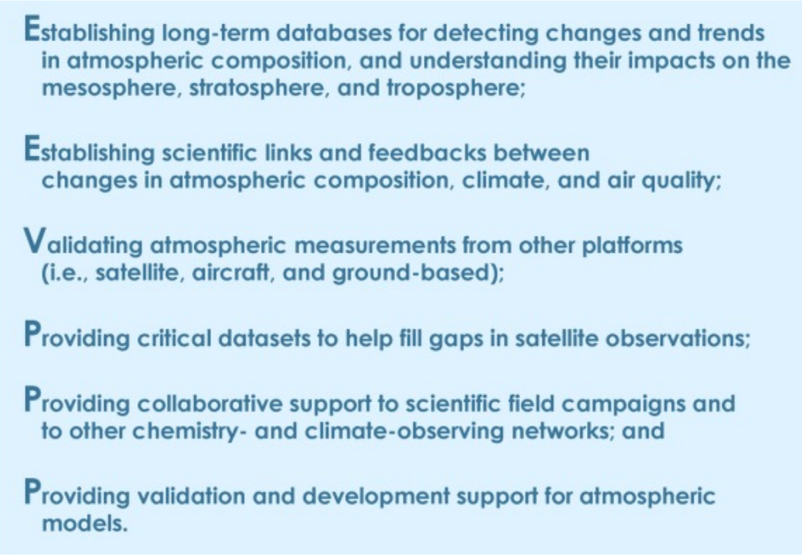
Wollongong:	Net positive, varies
Lauder:	Net positive, varies
Arrival Heights:	Net positive, varies

Kremser et. al., GRL, 2015

Network for the Detection of Atmospheric Composition Change

Active NDACC Stations

Goals & Results



Establishing long-term databases for detecting changes and trends in atmospheric composition, and understanding their impacts on the mesosphere, stratosphere, and troposphere;

Establishing scientific links and feedbacks between changes in atmospheric composition, climate, and air quality;

Validating atmospheric measurements from other platforms (i.e., satellite, aircraft, and ground-based);

Providing critical datasets to help fill gaps in satellite observations;

Providing collaborative support to scientific field campaigns and to other chemistry- and climate-observing networks; and

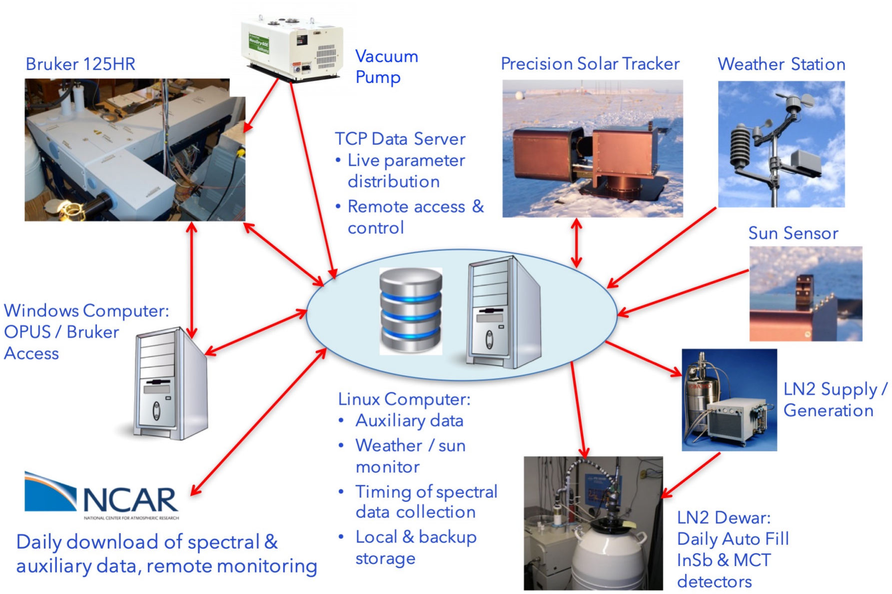
Providing validation and development support for atmospheric models.

- More then 70 remote-sensing stations are/have delivered data to DHF. *Data is publicly available*.
- Instrument Working Groups: UV-Vis, Microwave, Brewer & Dobson, Infrared, Spectral UV, LIDAR, Aerosol & Water Vapor Sondes,
- Integration Working Groups: Satellite, Theory, Water Vapor

www.ndacc.org

Network for the Detection of Atmospheric Composition Change / IRWG

Components of the Autonomous FTIR system



Bruker 125HR

Vacuum Pump

Precision Solar Tracker

Weather Station

TCP Data Server
- Live parameter distribution
- Remote access & control

Sun Sensor

Windows Computer: OPUS / Bruker Access

Linux Computer:
- Auxiliary data
- Weather / sun monitor
- Timing of spectral data collection
- Local & backup storage

LN2 Supply / Generation

NCAR

Daily download of spectral & auxiliary data, remote monitoring

LN2 Dewar: Daily Auto Fill InSb & MCT detectors

- Some stations are local and operated manually,
- Some are distant and operated manually via remote control,
- Some operated autonomously.

	Required by IRWG		**Measured**		**Episodic/Some Sites**
	Species	**DOFS**	**Species**	**DOFS**	**Species**
1	C_2H_6	< 2	CCl_3F (CFC-11)	1*	SO_2
2	HCN	< 2.5	CH_3D	~1	CH_3OH
3	CH_4	2.5 - 3.5	$CHClF_2$ (HCFC-22)	1*	ClO
4	$ClONO_2$	1*	CO_2	2 - 3.5	C_2H_4
5	CO	2.5 - 4	COF_2	< 2	CCl_4
6	HCl	2.5 - 4	H_2CO	1	CF_4
7	HF	2.5 - 3.5	H_2O	< 3	CH_3OH
8	HNO_3	2.5 - 4	CCl_2F_2 (CFC-12)	1*	
9	N_2O	3 - 5	HDO	< 3	
10	O_3	3 - 5	N_2	~1	
11			NO	~1	
12			NO_2	< 2	
13			O_2	~1	
14			OCS	~2.5	
15			SF_6	1*	
16			HCOOH	~1	
17			C_2H_2	~1	
18			NH_3	~1	

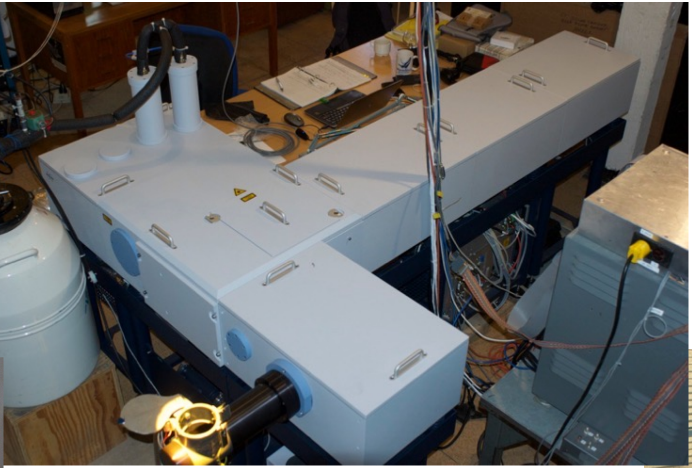
List of gases that are or might be measured by ground based FTS. 'Measured' are those that can be measured routinely at a typical NDACC/IRWG site. 'Episodic' are gases that may be measured during episodic events or at some sites with unique optical configuration or just not routinely. 'Possible' are gases that are currently at or below the detection limit of the technique.

*Retrieval information limited by spectroscopy

Species measured by high-resolution ground-based solar FTS in mid-IR, approx. DOFS from present analysis techniques

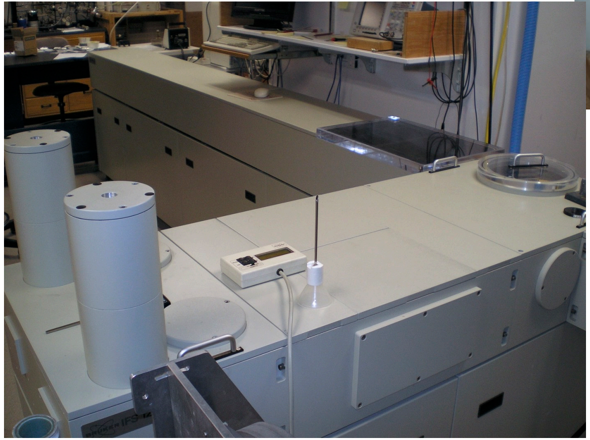
Optical Techniques Project: Observation sites

TAB, Thule Greenland:	76.53°N, 291.26°E, 225 m.a.s.l	Start 1999
BLD, Boulder, Colorado,	40.04°N, 254.76°E, 1612 m.a.s.l	Start 2010
MLO, Mauna Loa Observatory, Hawaii:	19.54°N, 204.43°E, 3396 m.a.s.l	Start 1991



Thule

Mauna Loa



Boulder

Network for the Detection of Atmospheric Composition Change / IRWG

FTIR Instrument stations contributing to this OCS project.

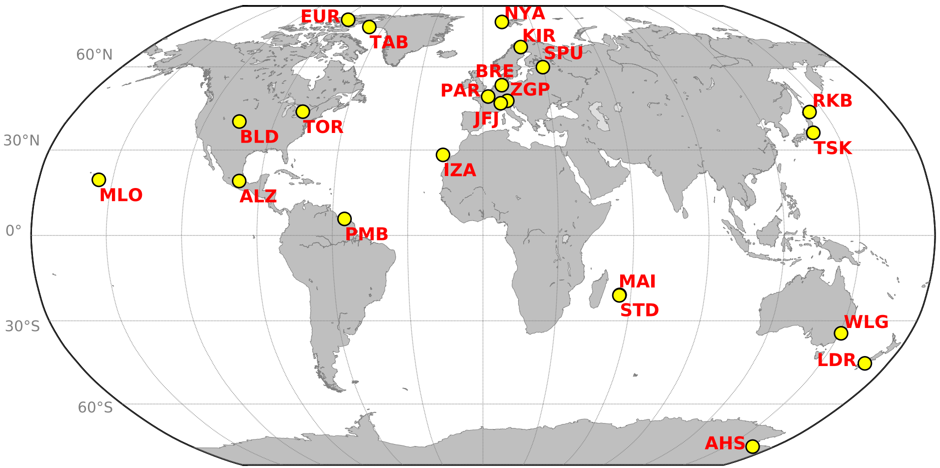


Table 1: Stations contributing to OCS analysis.

Station	*Location*	*N. Lat.*	*E. Lon.*	*masl*	*Managing Inst.*
EUR	Eureka	80.05	273.58	610	U. Toronto
NYA	Ny Alesund	78.90	11.90	20	U. Bremen
TAB	Thule	76.53	291.26	225	NCAR
KIR	Kiruna	67.84	20.41	420	KIT-ASF
STP	St Petersburg	59.88	29.83	20	U. St. Petersburg
BRE	Bremen	53.10	8.90	27	U Bremen
PAR	Paris	48.97	2.37	60	LERMA
ZUG	Zugspitze	47.42	10.98	2964	KIT-IFU
JFJ	Jungfraujoch	46.55	7.98	3580	U. Leige
TAO	Toronto	43.66	280.60	174	U. Toronto
RIK	Rikubetsu	43.46	143.77	380	U. Nagoya
BLD	Boulder	40.04	254.76	1612	NCAR
TSK	Tsukuba	36.05	140.12	31	NEIS
IZN	Izana	28.30	343.52	2370	KIT-ASF
MLO	Mauna Loa	19.54	204.43	3396	NCAR
ALZ	Altzomoni	19.12	261.35	4010	UNAM
PAR	Paramaribo	5.81	304.79	7	U Bremen
RMA	Reunion Is. Maido	-21.07	55.38	2160	BIRA
RSD	Reunion Is. St. Denis	-21.09	55.48	50	BIRA
WLG	Wollongong	-34.41	150.88	30	U Wollongong
LDR	Lauder	-45.05	169.67	370	NIWA
AHT	Arrival Hts.	-78.83	166.66	200	NIWA

Consistent Global Retrieval 1/7 : Initial Retrieval Parameters

Consistency Requirements:

- Latitudinally dependent a priori & covariance
- Same forward model data: spectroscopy, spectral range, fitting parameters: interfering species, backgrounds, uncertainties for error budgets.

- Use 4.8μ OCS features & follow investigation by Lejeune et. al. for interfering species and spectroscopic line-list
- HITRAN12 but not hot band line (too weak to have an effect)
  - ATM16 not significantly different from HIT12
  - O_3 is the limiting issue for residuals (!)
- To account for the variable layer thickness, Sa is weighted by the by (1/sqrt(thickness))
- Gaussian inter-correlation with a half-width length of 4 km for the off diagonal elements of the a priori covariance
- Uncertainties required

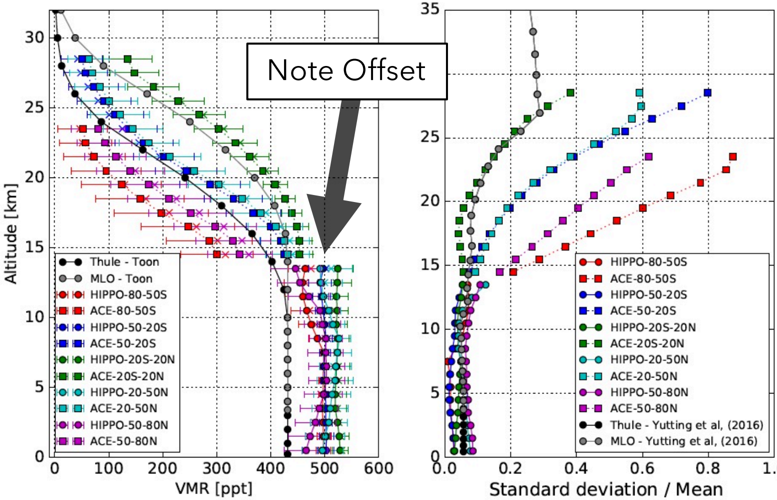
Micro-windows [cm^{-1}]	Column Gas	Profile Gas
2030.75 – 2031.06 (Optional)	CO_2	O_3
2047.85 – 2048.24		OCS, O_3
2049.77 – 2050.18	$^{16}O^{12}C^{18}O$, CO_2	OCS, O_3, CO
2051.18 – 2051.46	$H_2{}^{16}O$	OCS, O_3
2054.33 – 2054.67	$H_2{}^{18}O$, $H_2{}^{16}O$	OCS, O_3

- Require globally consistent a priori & Sa WACCM not available, maybe another model or…

Consistent Global Retrieval 2/7 : a priori Profiles & Variance

Employ measured profiles that have wide latitudinal coverage obtained from:

1. HIPPO Aircraft Mission: quality assured RF + 4 missions spanning seasons 2009 – 2011.
2. ACE-FTS: v3.5, all profiles from 2004 – 2013 v3.5

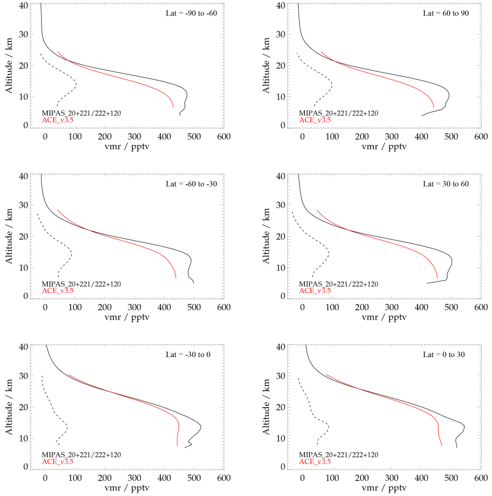


Note Offset

Intermediate smoothed, reduced and binned a priori and Sa from two global datasets.

Several comparisons to ACE OCS noted ACE concentrations in upper troposphere/lower stratosphere were low 10-15%:

- Velazco, 2011, MKIV (4.8μ)
- Krysztofiak, 2014, SPIRALE (4.8μ)
- Glatthor, 2017, MIPAS (11.6μ) comparison on right

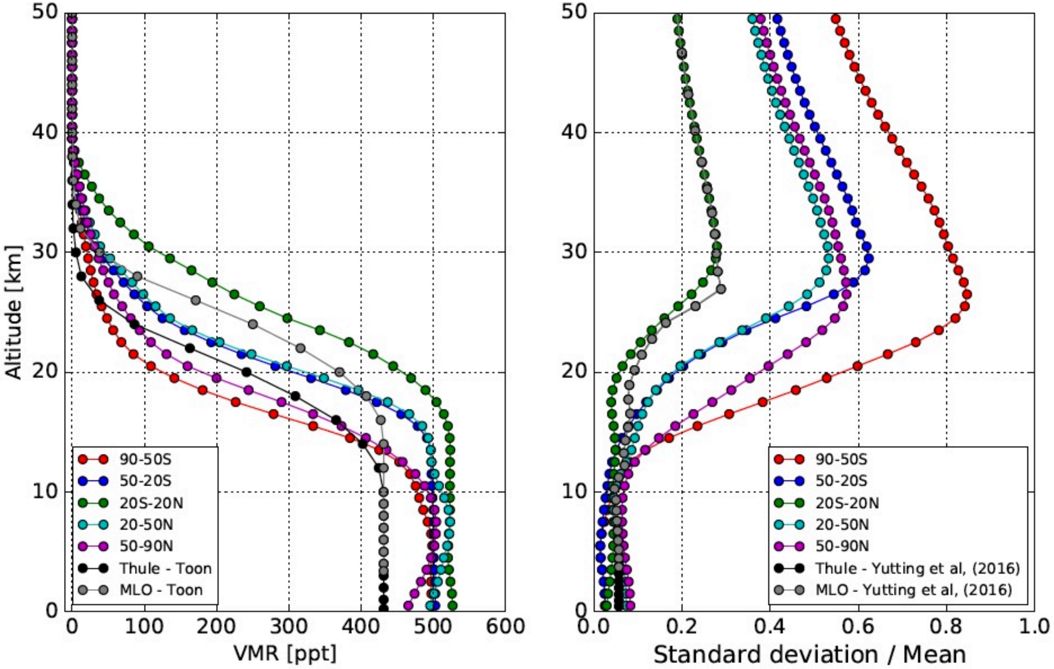


Coincident profiles averaged over 6 latitude bands.
Between Feb 2004 – Apr 2012

Wofsy, S. C. (2011). Phil. Trans. R. S.of London A: Math., Phys. and Engin. Sci.
Boone, et. al., (2013), "ACE at 10: A Solar Occultation Anthology", A. Deepak Publishing

Consistent Global Retrieval 3/7 : a priori Profiles & Variance

- Final, smoothed, reduced and co-joined a priori and standard deviations from the two global datasets binned into 5 latitude regimes.
- Vertical profiles have been extended up to 120 km per IRWG standard retrieval processing.
- Black & grey curves are from previous work for comparison (Toon et. al., 2016)
- Full covariance matrix includes Gaussian interlayer correlation of 4km width.



Consistent Global Retrieval 4/7 : Example Spectral Fit

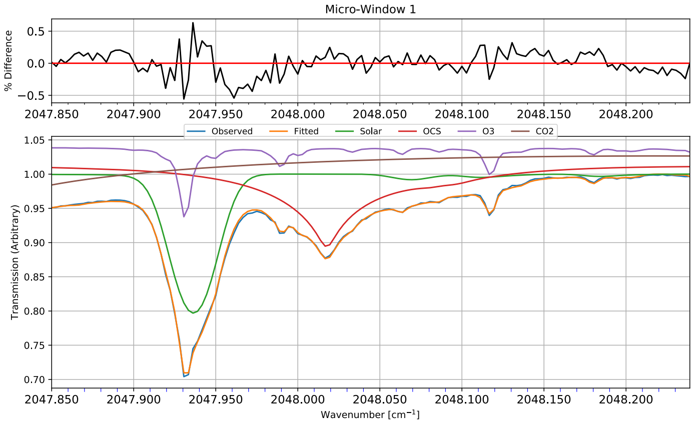
Example of a NLLS fit of observed spectra in the 4.8μ region.

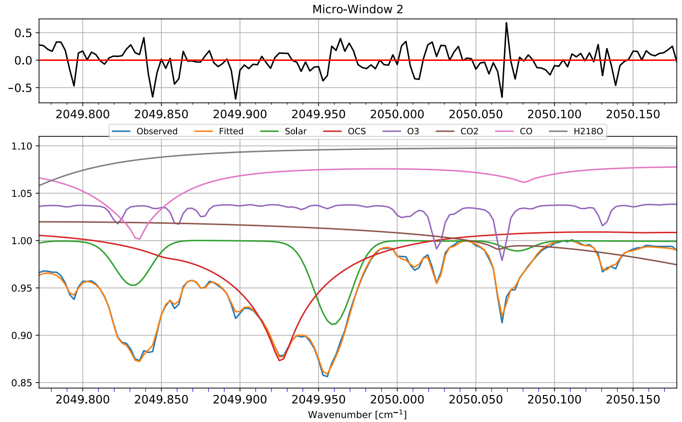
4 spectral windows:
0.25 - 0.4 cm^{-1} wide around a single discrete OCS absorption feature.

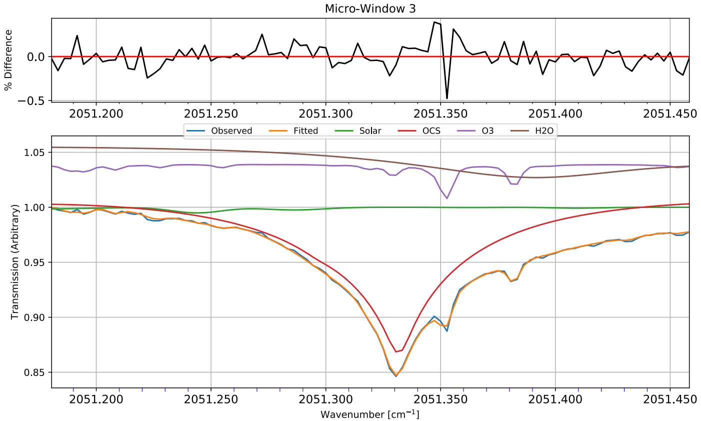
Upper Panels
Residual (Observed – fit)

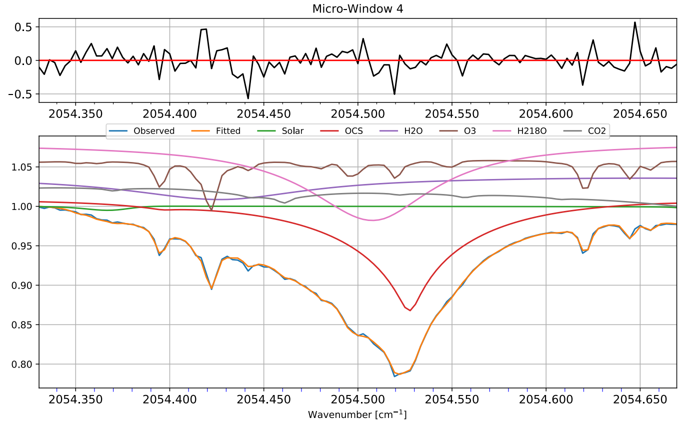
Lower Panels
Teal – Observed
Orange – Retrieved
Red – OCS

+ interfering species
(Offset for clarity)









Consistent Global Retrieval 5/7 : Optimal Estimation Implementation

The Jacobian is the sensitivity of forward model to the state vector (**x** –mixing ratio profile + some fit parameters.) :

$$\mathbf{K} = \partial \mathbf{y} / \partial \mathbf{x}$$

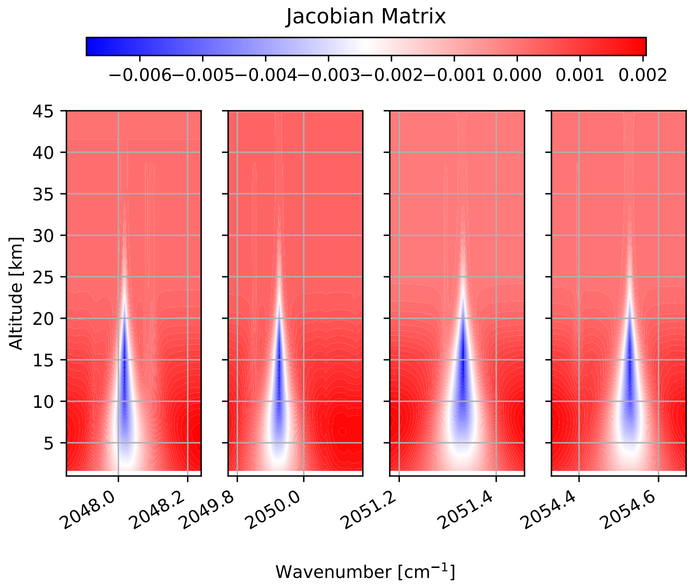
The Gain is the sensitivity of retrieval to the measurement. It includes the a priori knowledge of the state vector $\mathbf{S}_a$ and the noise of the measurement $\mathbf{S}_\varepsilon$:

$$\mathbf{G} = \partial \hat{\mathbf{x}} / \partial \mathbf{y}$$
$$= (\mathbf{K}^T \mathbf{S}_\varepsilon^{-1} \mathbf{K} + \mathbf{S}_a^{-1})^{-1} \mathbf{K}^T \mathbf{S}_\varepsilon^{-1}$$

The Averaging Kernels characterizes the retrieved state to the 'true' state.

$$\mathbf{A} = \partial \hat{\mathbf{x}} / \partial \mathbf{x}$$
$$= \mathbf{G}\mathbf{K} = (\mathbf{K}^T \mathbf{S}_\varepsilon^{-1} \mathbf{K} + \mathbf{S}_a^{-1})^{-1} \mathbf{K}^T \mathbf{S}_\varepsilon^{-1} \mathbf{K}$$

512 Spectral elements to fit
151 State vector components



Jacobian example from a Boulder retrieval

- Four spectral windows with each OCS feature vs altitude
- Note the pressure broadened width diminishing with altitude to the Doppler line core between 20-30km,
- This illustrates the observation's fundamental vertical sensitivity,
- And qualitatively high dependence on spectral SNR.

Consistent Global Retrieval 6/7 : Information Content

Averaging kernels (AK) characterize the vertical sensitivity

Comparing across a network reveals the homogeneity of the total dataset

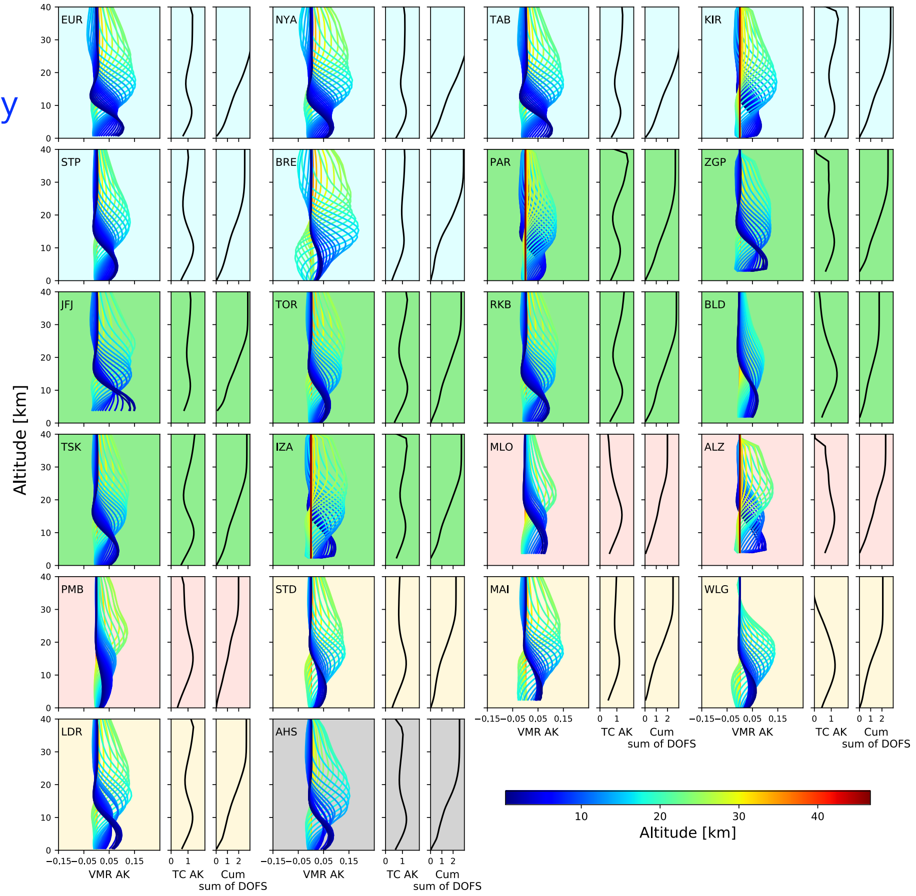
Expected differences:

- Observation site Latitude (tropopause height)
- Observation site Altitude
- Differences in the mixing ratio profile

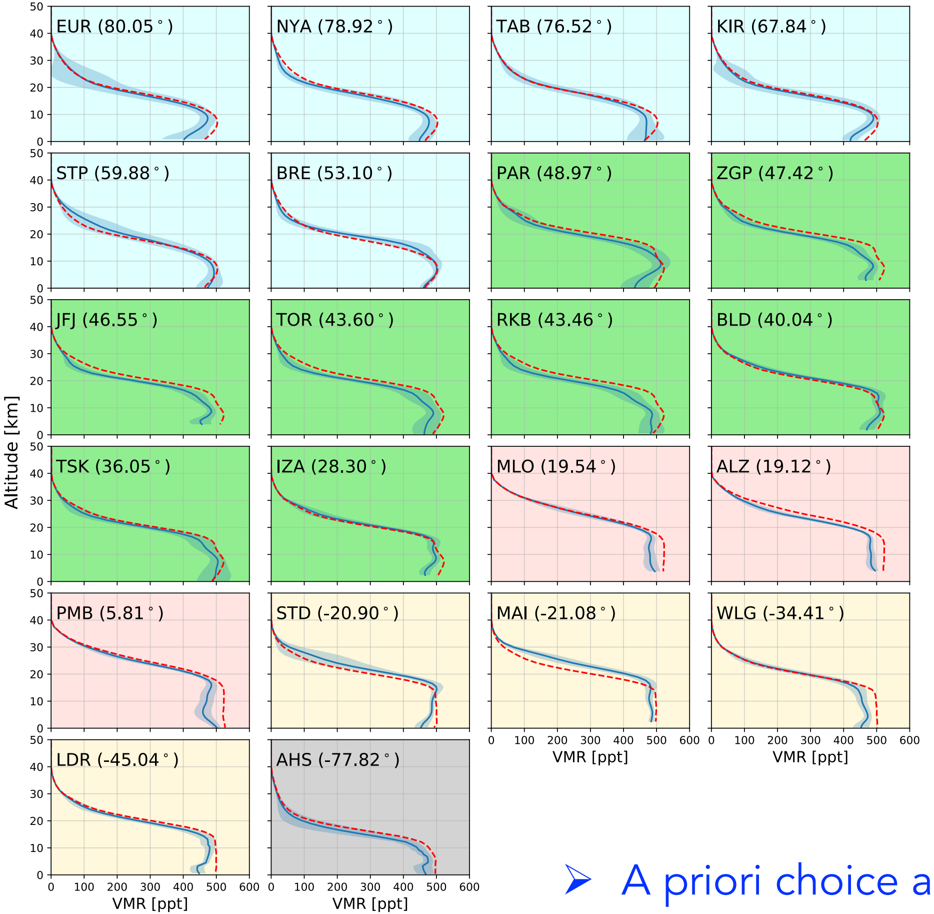
Degrees of Freedom for Signal (DOFS)

Trace of the AK determines the information content from the retrieval.

Selected Sites	Total DOFS
Eureka	3.1
Thule	3.0
Jungfraujoch	2.9
Toronto	2.7
Boulder	2.2
Mauna Loa	2.0
Wollongong	2.1



Consistent Global Retrieval 7/7 : Retrieved Vertical Profiles



Dashed red curve – a priori derived from HIPPO & ACE-FTS for five latitude bands.

Blue curve – Mean retrieved profile & ± 1 std. dev. in shaded area.

Arctic - most stratospheric profiles: a priori ~ retrieved, most tropospheric profiles similar or retrieved is lower. Large variability at TAB.

N mid-lat. – Stratospheric & tropospheric retrieved slightly lower or ~ a priori

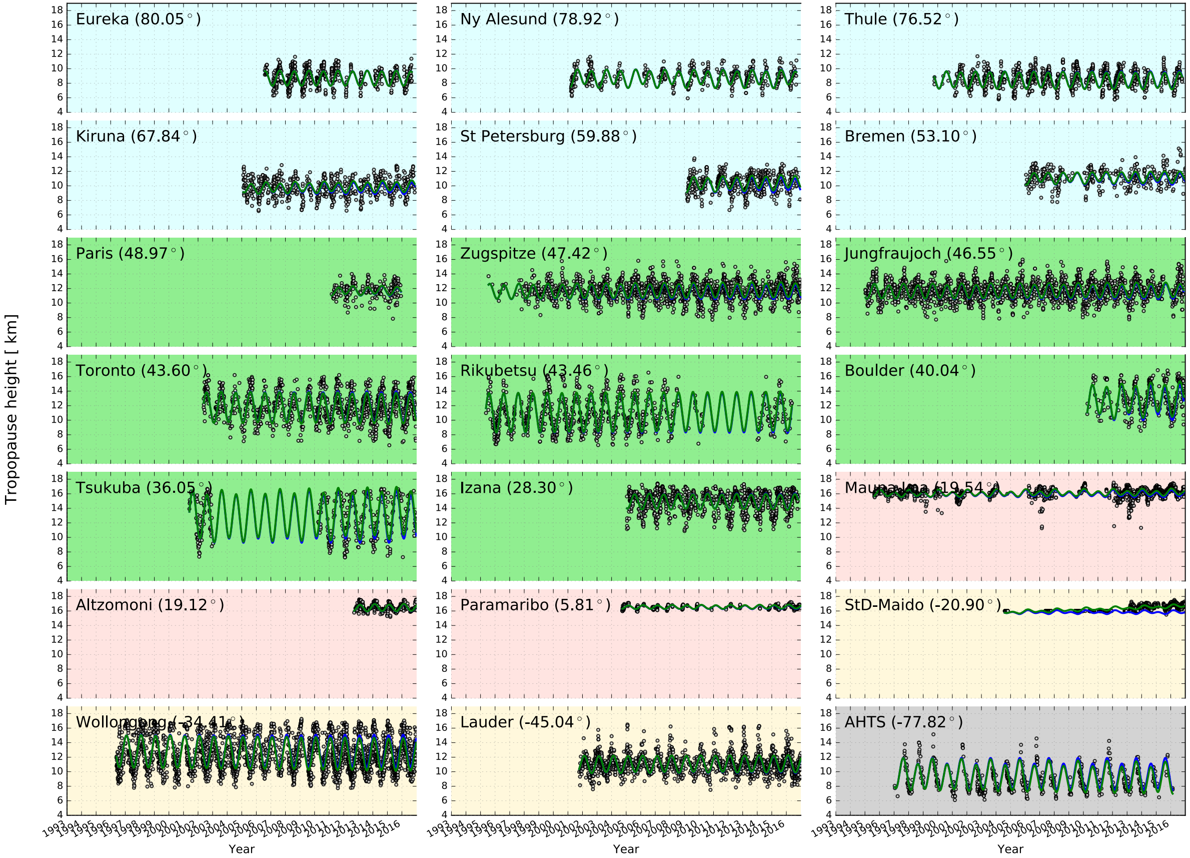
Sub-Tropics tropospheric retrieved notably lower.

S mid-lat. – stratosphere retrieved higher or similar, troposphere retrieved similar or lower

- ➢ A priori choice appears reasonable & without obvious bias

NCEP Tropopause Height (TPH) 1/2

- Attempt to diminish the effect of tropopause height seasonal variation on free tropospheric and stratospheric partial columns regimes.
- Analyze trend and amplitude of NCEP TPH at each station.
  - Same NCEP physical model as temperature, pressure and altitude data used for retrievals.
- Black circles: NCEP TPH
- Green lines: Fitted annual cycle with trend
- Blue lines: Fitted annual cycle



NCEP Tropopause Height (TPH) 2/2 : Zonally Binned

- The TPH is latitude dependent.
  - A 10° zonal band has been identified to calculate the TPH mean and standard deviation.

- Below are the three defined regions:
  - - Low Trop:
    - Surface to 4 km
  - - Free Trop:
    - 4 km to (Mean TPH - 2·STD)
  - - Stratosphere:
    - (Mean TPH + 2 · STD) to 40 km

Site	Mean TPH [km]	STD [km]	Binned Lat. [deg]	Binned TPH [km]
Eureka	8.8	1.2	70 - 80	8.8 ± 1.2
Ny Alesund	8.9	1.1		
Thule	8.7	1.2		
Kiruna	9.8	1.3	60 - 70	9.8 ± 1.3
St Petersburg	10.5	1.2	50 - 60	10.9 ± 1.2
Bremen	11.2	1.2		
Paris	11.7	1.0	40 - 50	11.6 ± 1.6
Zugspitze	11.7	1.3		
Jungfraujoch	11.7	1.3		
Toronto	10.7	2.2		
Rikubetsu	12.0	2.0		
Boulder	13.2	2.0	30 - 40	12.9 ± 2.4
Tsukuba	12.6	2.7		
Izana	15.0	1.3	20 - 30	15.0 ± 1.3
Mauna Loa	16.1	0.6	-25 - 20	16.5 ± 0.4
Altzomoni	16.6	0.5		
Paramaribo	16.5	0.3		
St Denis	16.7	0.3		
Maido	16.7	0.3		
Wollongong	12.3	2.3	-40 – (-25)	12.3 ± 2.3
Lauder	11.1	1.3	-50 – (-45)	11.1 ± 1.3
Arrival Heights	8.8	1.7	< - 50	8.8 ± 1.7

Trends Analysis 1/4

1) To determine annual cycle apply a least squares fit $y = f(x - x_o)$ to data where f is given by a polynomial + annually based Fourier terms

$$f_{poly} = a_0 + \sum_{n=1}^{N} m_i x^i$$

$$f_{Fourier} = \sum_{n=1}^{N} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{N} b_n \sin\left(\frac{n\pi x}{L}\right)$$

$$f(x) = f_{poly} + f_{Fourier}$$

$$x = t - x_o$$

$$N = 5$$

2) Calculate Anomalies as : P_{OCS} - $f_{Fourier}$ where P_{OCS} is the wVMR for the atmospheric layer

3) Later, to best fit the inflections in total column anomaly data we use a higher order polynomial :

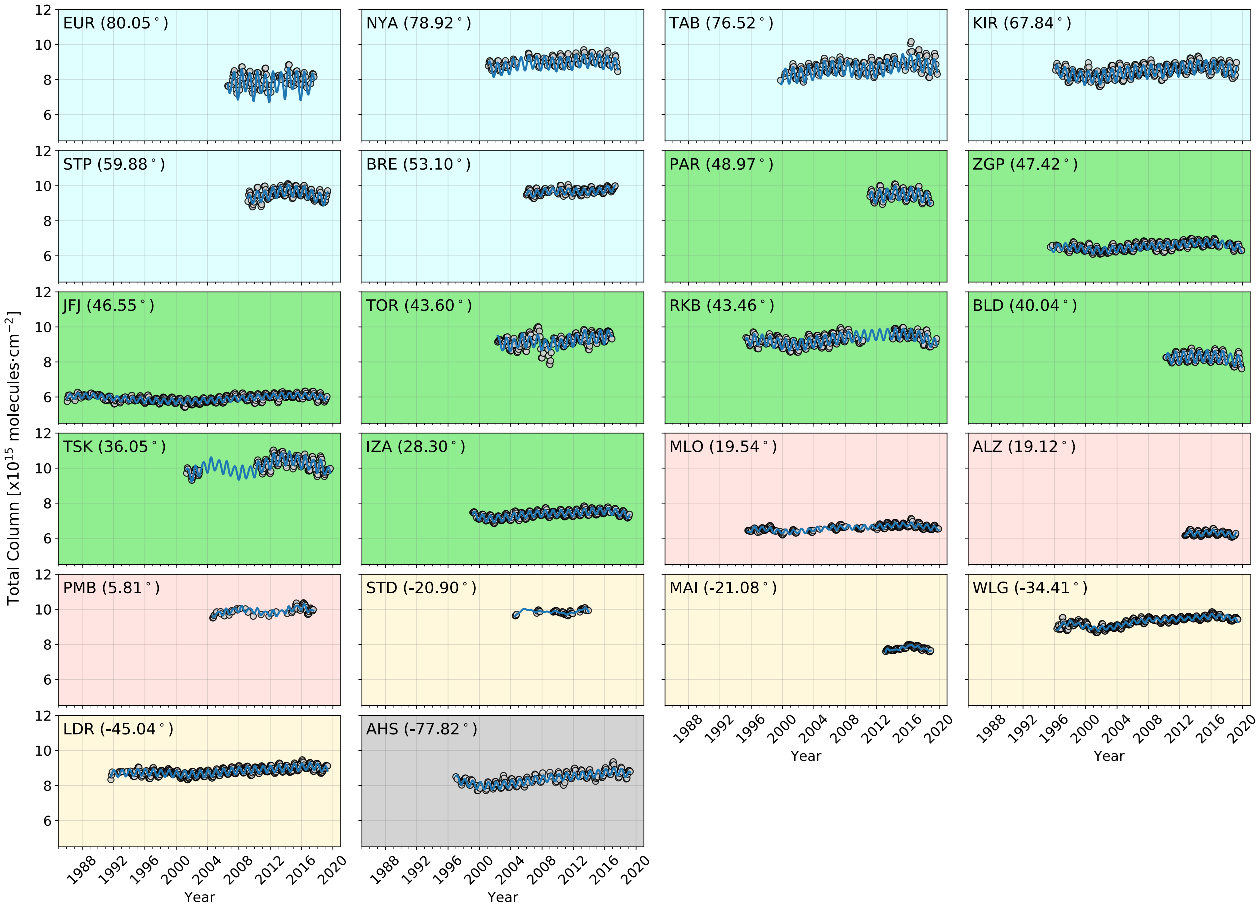
$$f_{poly} = a_0 + \sum_{n=1}^{N} m_i x^i$$

$$x = t - x_o$$

$$N = 7$$

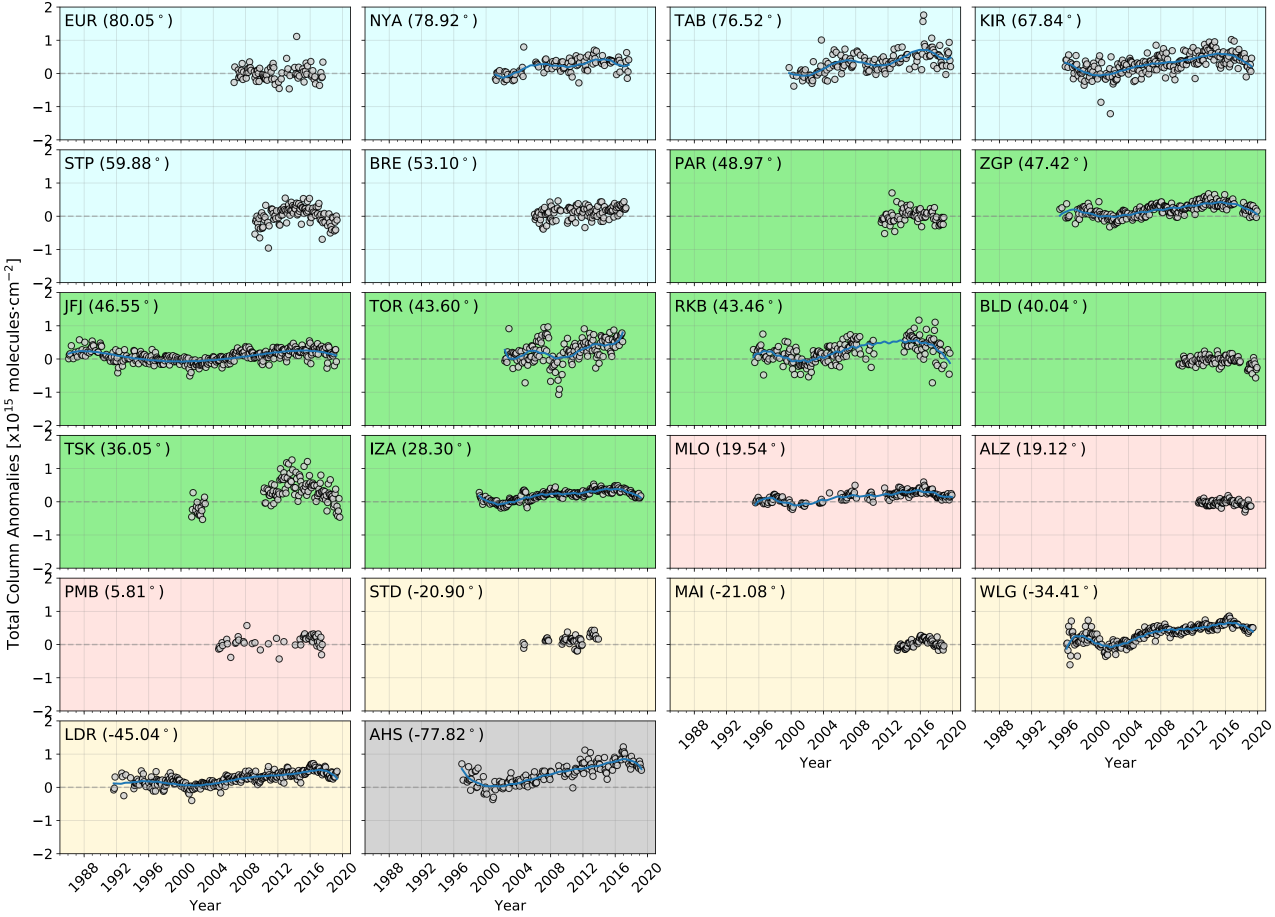
Time Series 1/5 : Total Columns

- Start dates vary for all sites from 1985 to 2012
- Same abundance scale for all sites: x10^{15} molecules/cm^2
- All data are represented as monthly mean values.
- Polynomial + Fourier terms (1) for annual cycle in blue
- Note gaps in STD, TSK, RKB, MLO
- Sr Denis (STD) (seal level) and Maïdo (MAI) (~2km) are both on Île de la Réunion and are combined into one time series.



Time Series 2/5 : Total Column Anomalies

- Total column anomalies:
  = (total column) - $f_{Fourier}$
- Same abundance scale for all sites: x10^{15} molecules/cm^2
- Ubiquitous inflections
  - We look at longest term records NYA, TAB, KIR, ZGP, JFJ, RKB, IZA, MLO, LDR, AHS
  - Often decreasing to ~2000-2002
  - Change at ~ 2008-2009
  - Again ~2018
  - In 2018 nearly all sites show start of a decrease.
- This observation not reflected in all stations e.g. STP, TSK

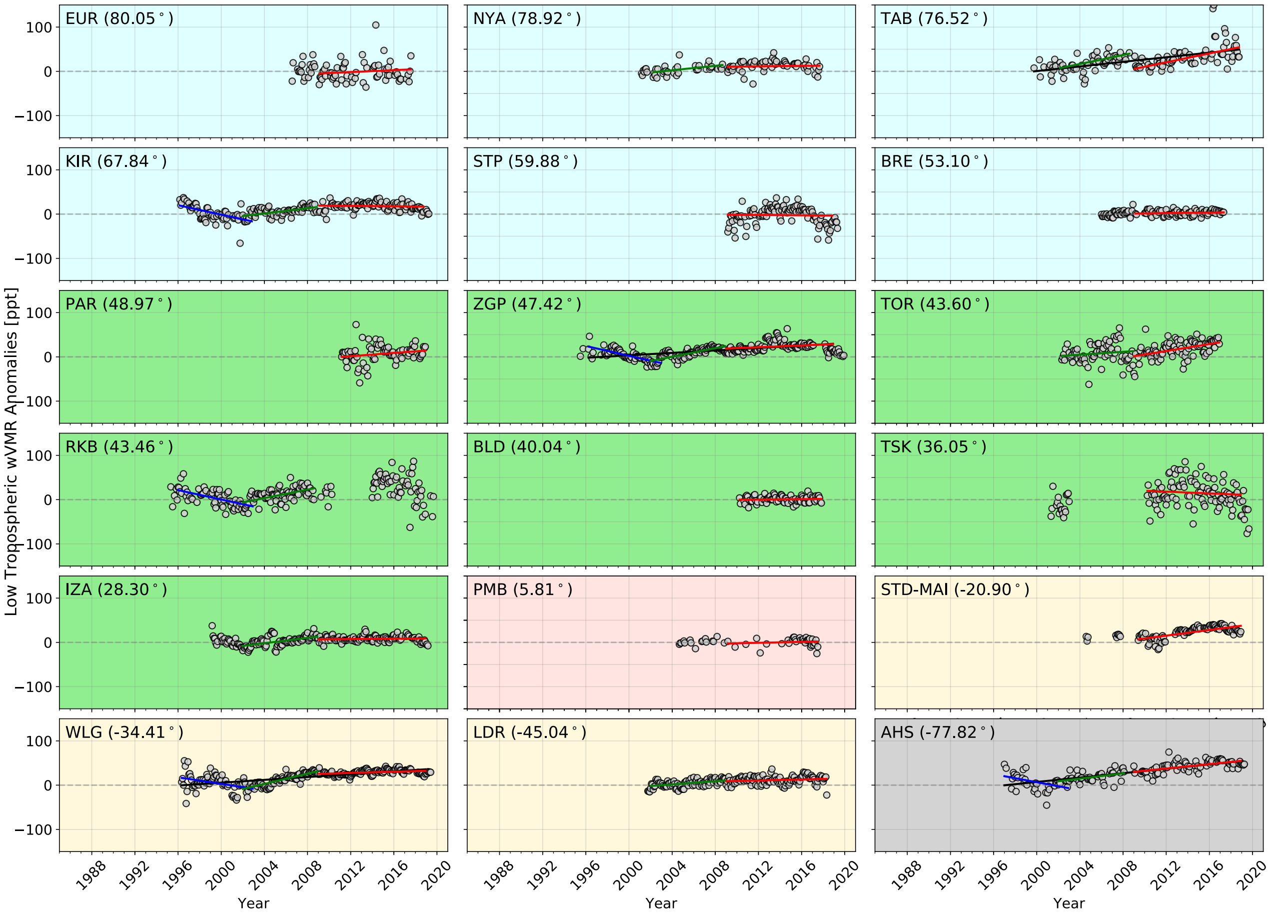


Time Series 3/5 : Lower Troposphere Weighted Mean VMR Anomalies

- Lower troposphere layer weighted mean VMR from surface to ~4km.

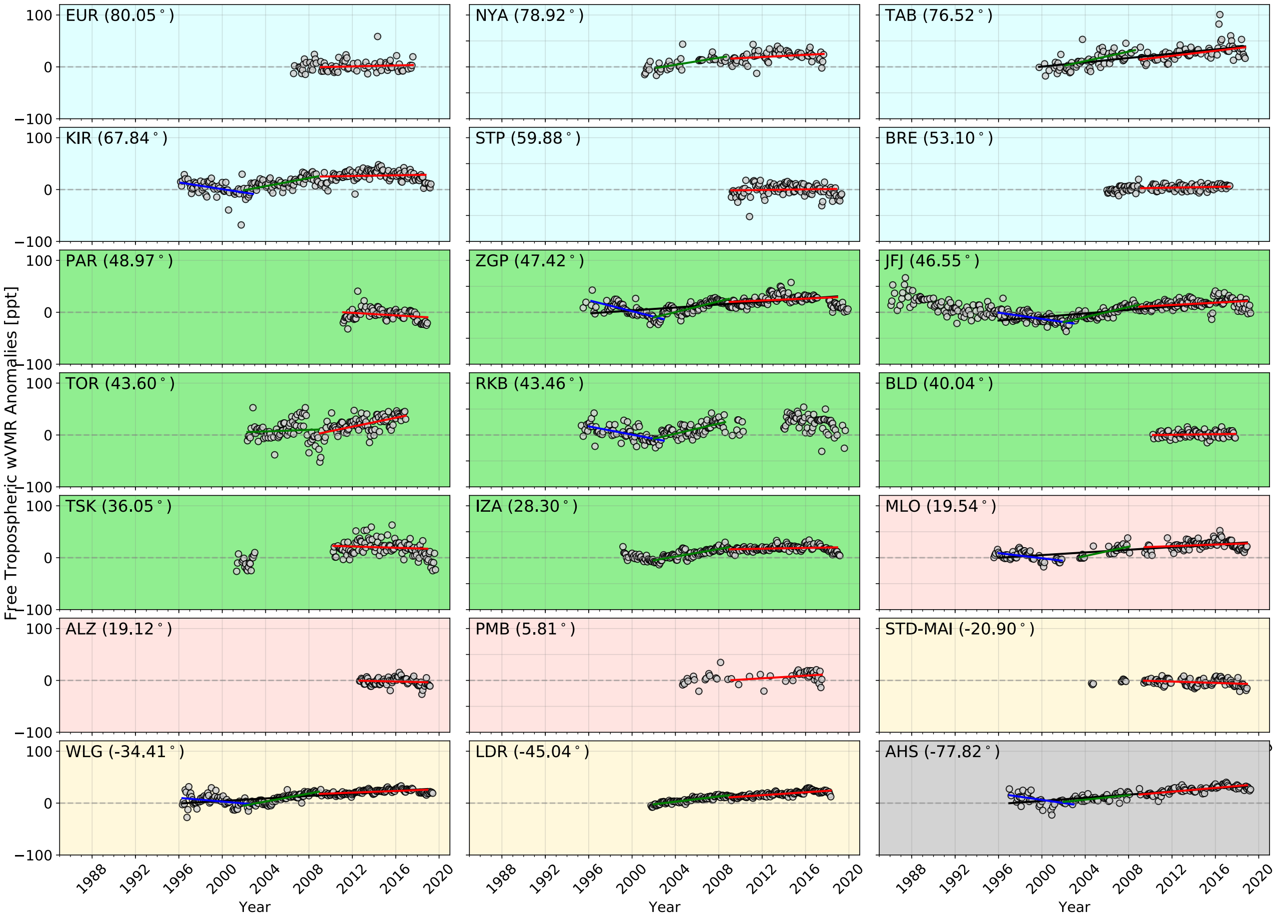
$$wVMR = \frac{\sum_{z=1}^{n} x_z \cdot K_z}{\sum_{z=1}^{n} K_z}$$

- x_z vmr in layer z, K_z is the airmass in layer z
- Anomalies in [ppt]
- Determined linear slopes shown in
  - -2002: blue,
  - 2002-2008: green,
  - 2008-2019: red,
  - 1996–2019: black.



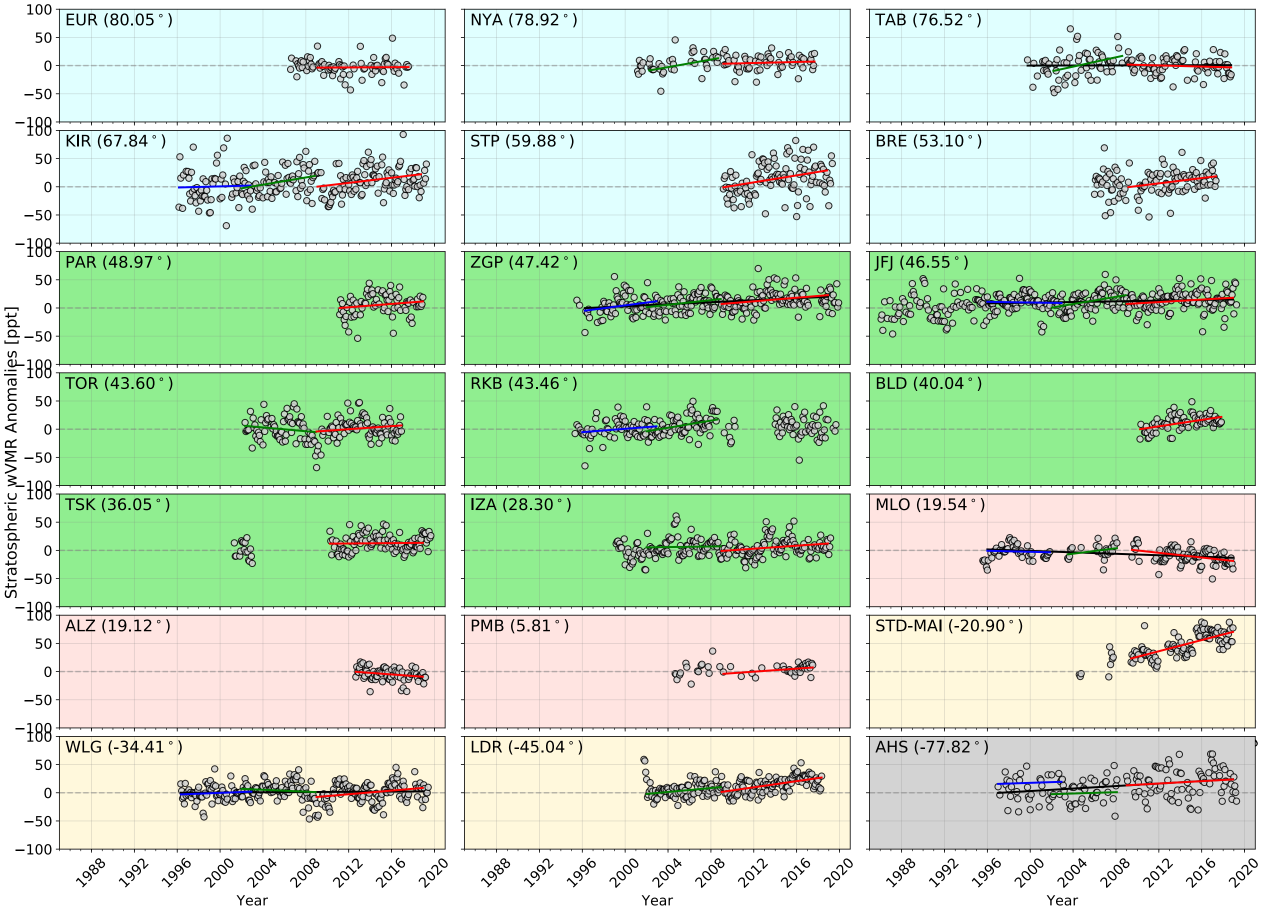
Time Series 4/5 : Free Troposphere Weighted Mean VMR Anomalies

- Free troposphere layer weighted mean VMR from ~4km to 2std. Dev. – mean tropopause for that latitude band.
- Anomalies in [ppt]
- Determine linear slopes shown in
  - -2002: blue,
  - 2002-2008: green,
  - 2008-2019: red,
  - 1996 – 2019: black.



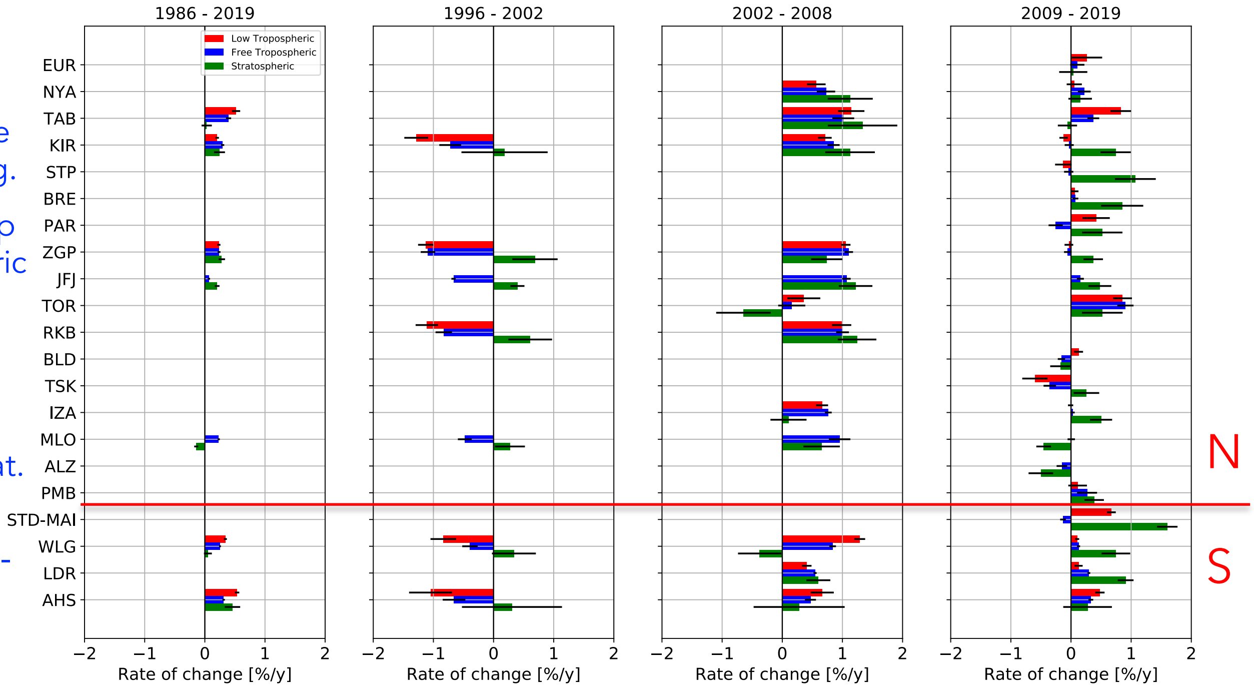
Time Series 5/5 : Stratospheric Weighted Mean VMR Anomalies

- Stratosphere layer weighted mean VMR from mean troposphere + 2 Std. Dev. for that latitude band to 40km. (effective top of atmosphere)
- Anomalies in [ppt]
- Determine linear slopes shown in
  - -2002: blue,
  - 2002-2008: green,
  - 2008-2019: red,
  - 1996 – 2019: black.



Trend Analysis 2/4 : Summary of Long term and Segmented Trends

- Longest term data sets trends near 0 or positive up to ~0.6%/y – except MLO stratosphere.
- During 1996-2002, globally, troposphere decreasing while stratosphere increasing.
- During 2002-2008 near global growth up to over 1%/y except notably stratospheric TOR & WLG
- Most recent trends 2009-2016
  - Lower tropospheric growth in Arctic,
  - Generally high growth in N & S. mid-lat. Stratosphere
  - Low or negative trends in lower N mid-latitudes.
  - Negative trends ~0.5%/y ALZ & PMB
  - Moderate – low growth S. H.
  - TAB – Large positive troposphere recent trend influenced by high 2016 springtime observations.



1986 - 2019 Column is All Data: JFJ 1986, TAB 2000, KIR 1996, ZGP 1995, MLO 1995, WLG 1996, AHS 1997

Trend Analysis 3/4 : N_2O as Dynamical Variability Proxy

(4) To fit the long term stratospheric anomaly time series accounting for dynamical variability as represented in stratospheric N_2O:

$$f_{N_2O} = a_0 + m_1 x + b_0 P_{N_2O}$$

$$x = t - x_o$$

Where P_{N_2O} is the stratospheric partial column measured coincident with OCS & processed similarly as the OCS time series.

N_2O is a standard NDACC product and archived at the DHF.

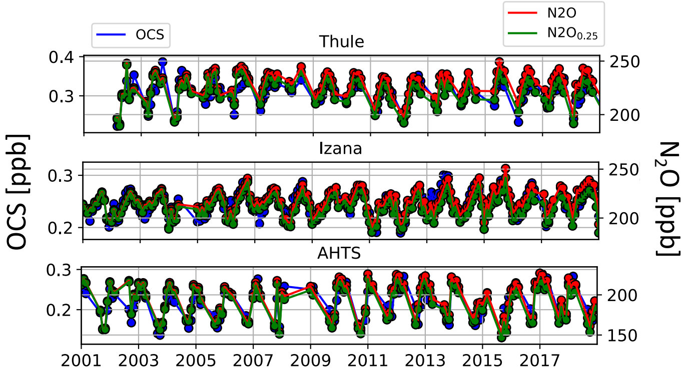
Since N_2O is expected to be increasing at ~0.25%/y, P_{N_2O} is decreased at this rate rendering m_1 the linear trend of OCS after fitting.

Test with stations that begin at latest in 2001: TAB, KIR, ZGP, JFJ, IZA, MLO, WLG, LDR, AHS. 76°N to 78°S

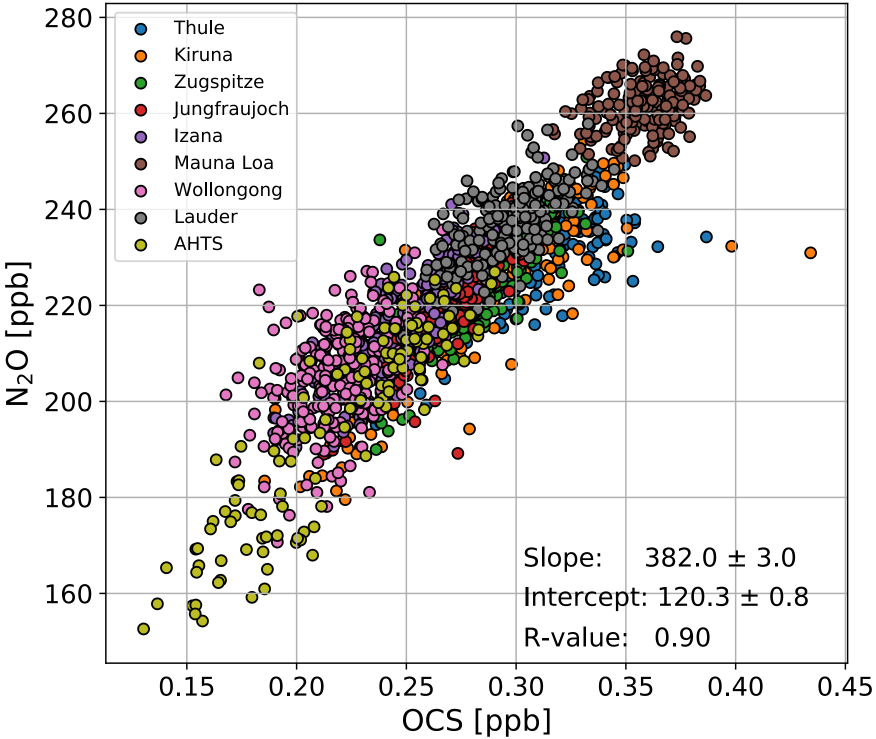
Toon et al., 2018, ACP, 18(3):1923– 1944.
Stolarski et al., 2018, ACP, 18(8):5691–5697.

Stratospheric Trends : N_2O as Dynamical Variability Proxy

- Correlation of stratospheric mean VMR. Annual cycle not excluded.
- High correlation R = 0.9 for all data
- Latitudinal range infer a large range in lower stratospheric N_2O and OCS concentrations.

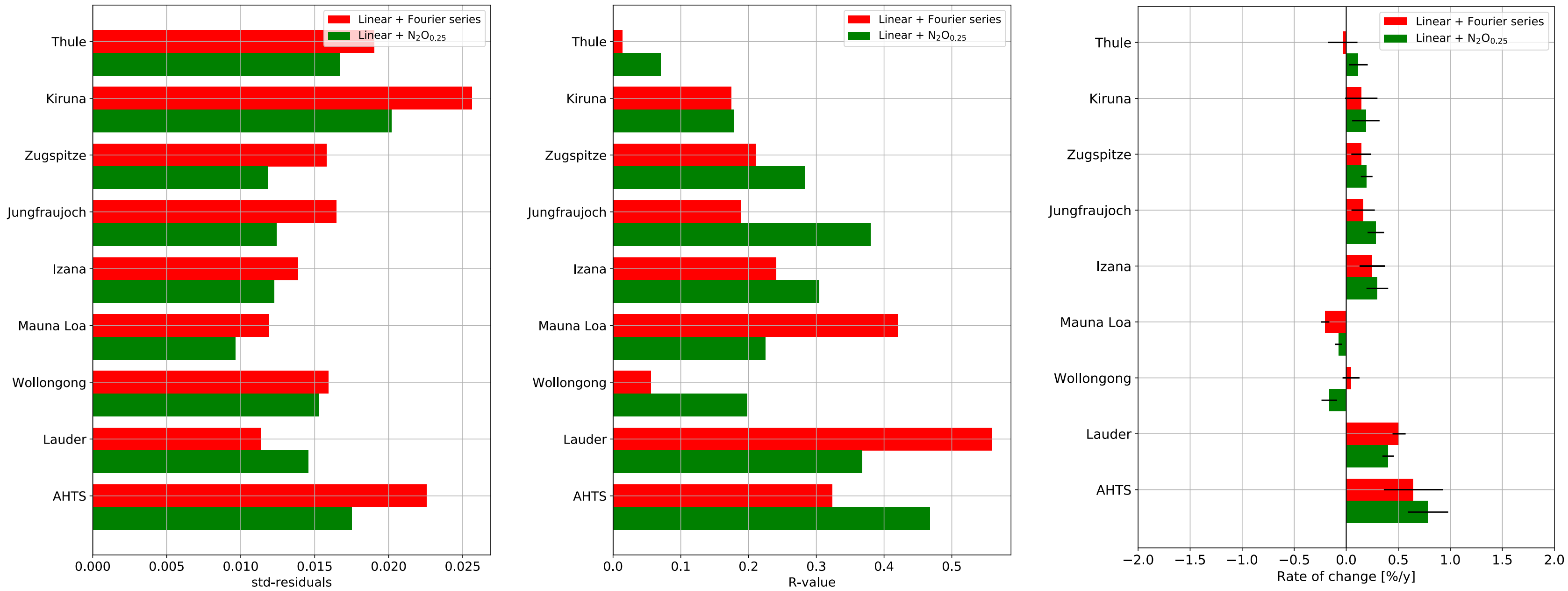


- Examples for 3 stations, OCS, N_2O and N_2O detrended by 0.25%/y



Stratospheric Trends : N_2O as Dynamical Variability Proxy

Comparisons of trend fit (left, middle) & linear trends (right) with previous regression using Fourier terms.



- Residuals all lower with N_2O proxy except notably LDR.
- R value increases with N_2O proxy except notably LDR and MLO.
- Long term stratospheric trends become more positive except LDR & WLG. And overlap within uncertainty range, except MLO and WLG. WLG trends actually reverse sign.

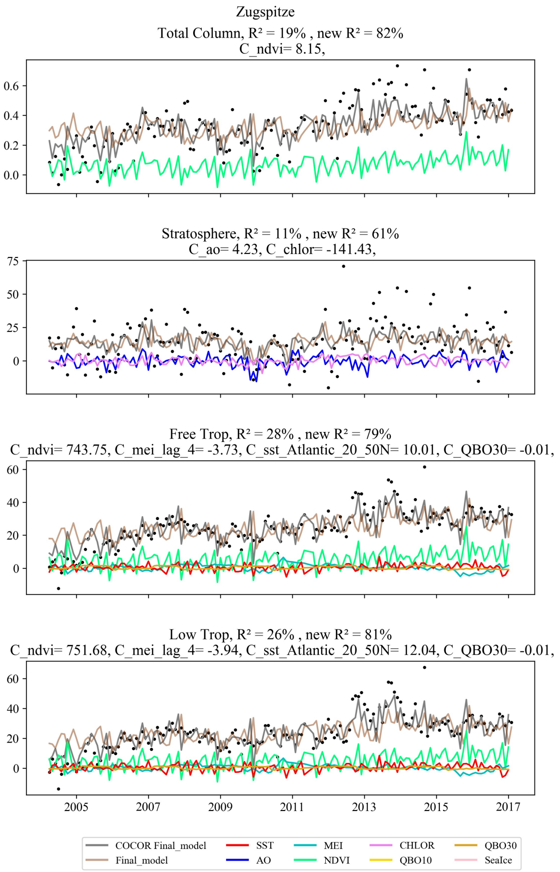
Trend Analysis 4/4 : *Step-wise Multiple Linear Regression*

Proxies

- Arctic Oscillation
- Multivariate ENSO Index (MEI)
  - Using lag time of 0 to 4 months
- Sea Surface Temperature
- Normalized Difference Vegetation Index
- Chlorophyll index
- QBO
  - At 30 & 10 hpa
- Sea ice extent

Cochrane-Orcutt algorithm applied to account for auto-correlation

Ex: Zugspitze in Central Europe



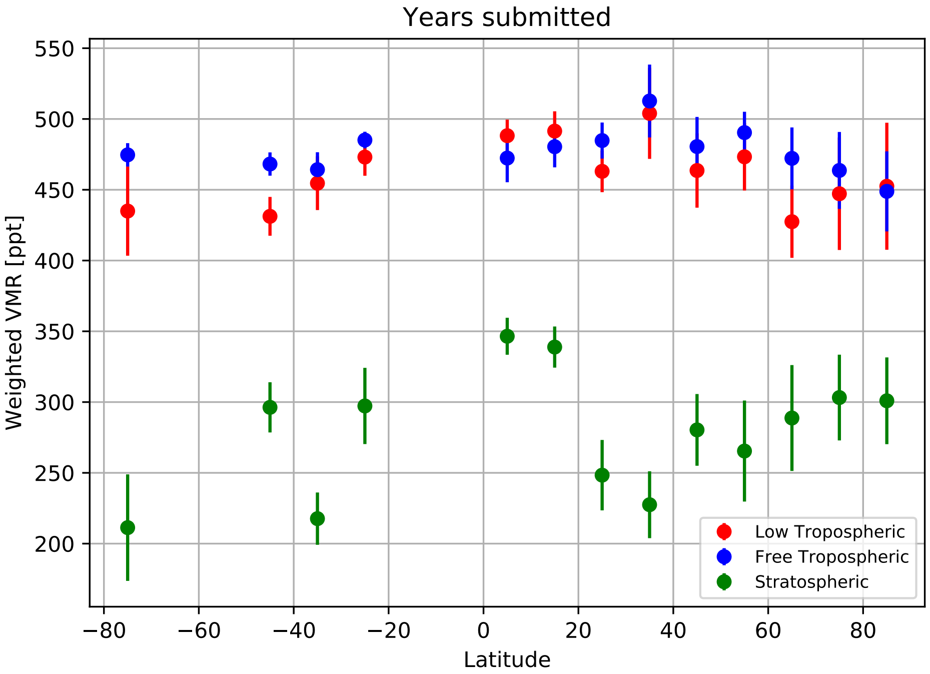
Zugspitze				
Name	R2	Slope	Std_err	P_value
Low	Trop			
ndvi	0.16	751.682091	61.43282	0
mei_lag_4	0.19	-3.9425154	0.98685	0
sst_Atlantic_20_50N	0.24	12.0356292	4.11548	0.00029
QBO30	0.26	-0.0086227	0.00489	0.00175
Free	Trop			
ndvi	0.18	743.753184	57.89566	0
mei_lag_4	0.22	-3.7261877	0.93003	0
sst_Atlantic_20_50N	0.26	10.0131006	3.87852	0.00054
QBO30	0.28	-0.009091	0.00461	0.0003
Stratosphere				
ao	0.07	4.22770336	1.60342	0.01076
chlor	0.11	-141.42822	77.93521	0.01215
Total	Column			
ndvi	0.19	8.15192018	0.84927	0

Global Mean Weighted VMR: Zonal means

Mean weighted VMR by station and altitude.

Note that different sites have varying timeseries length!

- Mean values within 10° zonal bins,
- Highest values seen in N. mid-latitudes (TSK, BLD),
- N mid-latitude drawdown at 40-50°N clearly seen as also seen in in situ data [Montzka et al 2007],
- Fall off at high N. latitudes in troposphere not reflected in the South. – Increase in Stratosphere,
- Low stratospheric values at 20-40° latitude bin seen in both hemispheres.

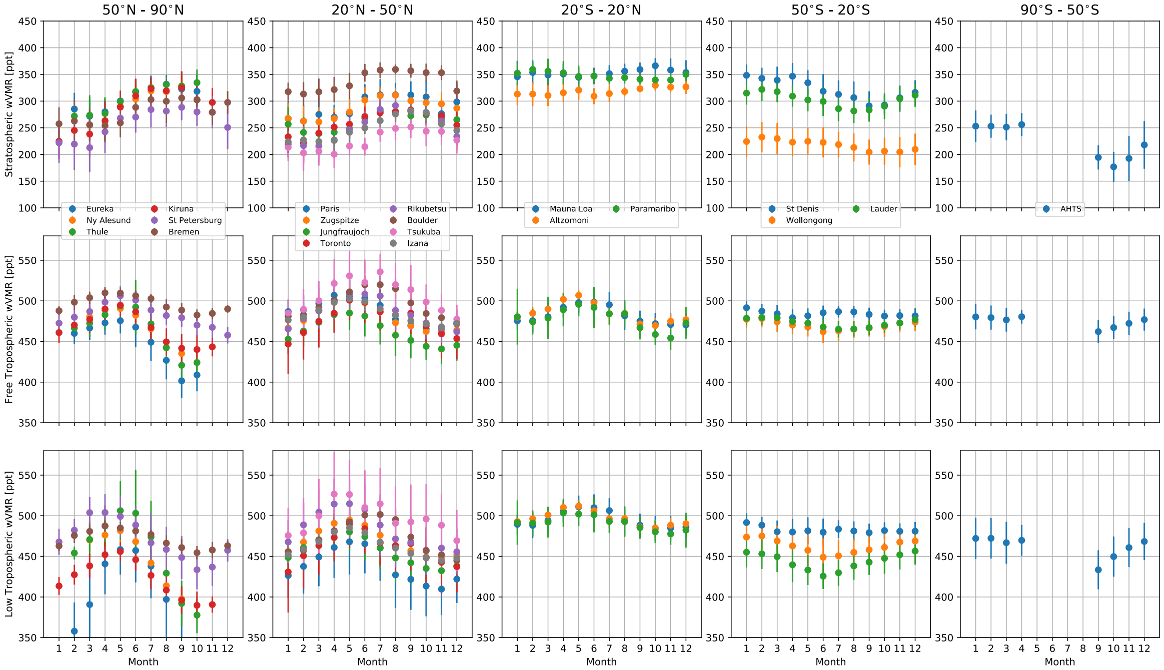


Global Mean Weighted VMR : Annual Cycles

Mean weighted VMR by station, latitude and altitude.

All Data: Note that different sites have varying timeseries length!

- 50 - 90°N : stratosphere peak in autumn
  - At same time Troposphere minimum,
  - FT drawdown less at lower latitude sites STP & BRE.
  - EUR sees lowest spring values ~360ppt
- 20 - 50°N : broad "peak" summer-autumn
  - FT May-Jul, lowest autumn at JFJ
  - LT Apr-May, lowest, autumn at PAR
- 20°S – 20°N : minimal stratospheric annual cycle
  - FT peaks May, LT Apr-Jun



Top : Stratosphere, Middle: free Troposphere, Bottom: lower Troposphere

- 20 – 50°S : Stratosphere: similar broad summer/autumn peak,
  - FT: Distinct minima in WLG & LDR not evident at MAI
- 50 - 90°S broad stratospheric peak autumn
  - Then increasing in spring

Conclusions & Continued Work

i. Developed a global homogeneous long term (up to 35y) vertically resolved OCS dataset.
    i. Determined trends in 3 altitude regimes lower and free troposphere and stratosphere
    ii. Inferred stratospheric lifetimes in 5 zonal bands from 80°N to 80°S

ii. Trends globally, are <u>not</u> linear, but in general increasing. Inflections in trends appear at a wide range of latitudes. Generally ~2002, ~2008 and (apparently) 2018-2019.
    i. That many trends are increasing, is counter to most previous studies.
    ii. Pursue trend variations by station / latitude

iii. Trends <u>generally</u> don't follow dynamical proxies in regression analysis nor proxies: Chlorophyll and SST that may effect some sources and sinks, at least as we can represent them. This leads us to look toward other sources and sinks.
    i. What proxies can represent trends, what sources and sinks are represented.
    ii. Anthropogenic sources are a leading target.
    iii. Also target lower troposphere.

iv. The incorporation of N_2O as a dynamical proxy generally appears appropriate and improves trend fit statistics at the 9 longest term sites. Stratospheric trends became more positive but within error bars except MLO and WLG.
    i. 0.2 – 0.75%/y increasing North to South again excluding MLO & WLG.

v. After 2018 a start to another downturn appears be occurring at a wide range of latitudes.

Infra-red Working Group Teams

Station Lead	***Institution***	***Station(s)***
Kim Strong	Univ Toronto,	Toronto, Canada, Eureka, Canada
Justus Notholt	Univ. Bremen	Ny Alesund, Bremen, Germany Paramaribo, Surinam
Thomas Blumenstock	IMK-Karksruhe	Kiruna, Sweden
Johan Mellqvist	Chalmers Univ.	Harestua, Norway
Maria Makarova	Univ. of St Petersburg	Peterhof, Russia
Ralf Sussmann	IMK-Alpin	Zugspitze, Germany
Emmanuel Mahieu	Univ Liege	Jungfraujoch, Switzerland
Tomoo Nagahama	Nagoya Univ.	Rikubetsu, Japan
Yao Veng TE	Sorbonne Université	Paris, France
Isao Murata, Isamu Morino	Tohoku Univ., NIES	Tsukuba, Japan
Mathias Schneider	IMK-Karlsruhe	Izana, Spain
Michel Grutter de la Mora	UNAM	Altzomoni, Mexico
Martine de Mazière	BIRA	St. Denis, Maïdo, Île de la Réunion
Nicholas Jones	Univ. Wollongong	Wollongong, Australia
Dan Smale	NIWA-Lauder	Lauder, New Zealand, Arrival Heights, Antarctica

This work would not be possible without the long standing commitment of many international and independent collaborators.

Thank You!

end

Stratospheric Lifetime

Determined by ratio with N_2O & N_2O lifetime:

$$\frac{\tau_{OCS}}{\tau_{N_2O}} = A \cdot \frac{wVMR_{OCS}}{wVMR_{N_2O}}$$

$T_{n2o} = 117 \pm 20$ y

Wide latitude coverage with this dataset…

High N. latitudes (85y) found to be longer then most previous values but within uncertainties (barely).

Mid latitudes tend to be lower.

Southern hemisphere especially AHS (78°S) fairly long lifetime.

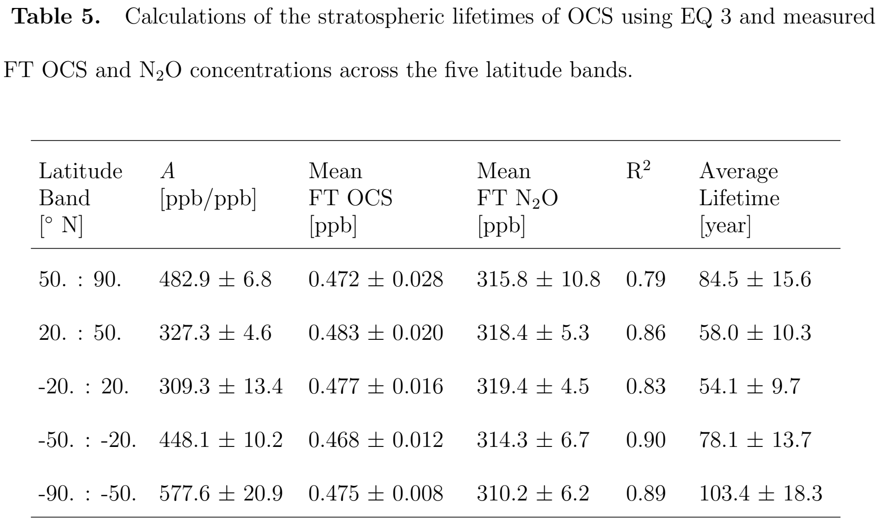


Table 5. Calculations of the stratospheric lifetimes of OCS using EQ 3 and measured FT OCS and N_2O concentrations across the five latitude bands.

Latitude Band [° N]	*A* [ppb/ppb]	Mean FT OCS [ppb]	Mean FT N_2O [ppb]	R^2	Average Lifetime [year]
50. : 90.	482.9 ± 6.8	0.472 ± 0.028	315.8 ± 10.8	0.79	84.5 ± 15.6
20. : 50.	327.3 ± 4.6	0.483 ± 0.020	318.4 ± 5.3	0.86	58.0 ± 10.3
-20. : 20.	309.3 ± 13.4	0.477 ± 0.016	319.4 ± 4.5	0.83	54.1 ± 9.7
-50. : -20.	448.1 ± 10.2	0.468 ± 0.012	314.3 ± 6.7	0.90	78.1 ± 13.7
-90. : -50.	577.6 ± 20.9	0.475 ± 0.008	310.2 ± 6.2	0.89	103.4 ± 18.3

Plumb, R. A. and Ko, M. K. W. (1992). JGR: Atmos., 97(D9):10145–10156.