Update to IRWG-wide OCS analysis

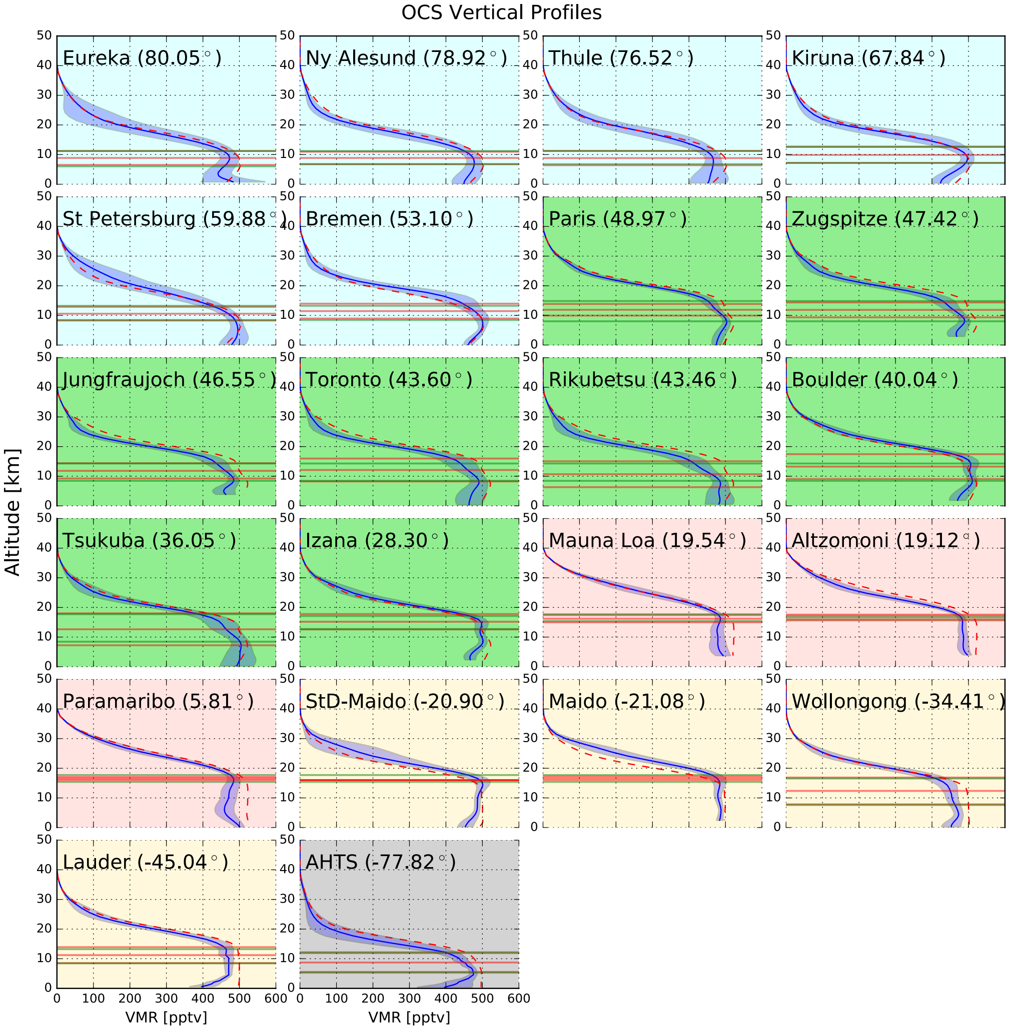
J Hannigan & Ivan Ortega

E Mahieu, N Jones, S Conway, M, Palm – preliminary testing

F Hase, M Rettinger – Conversion to PROFFIT

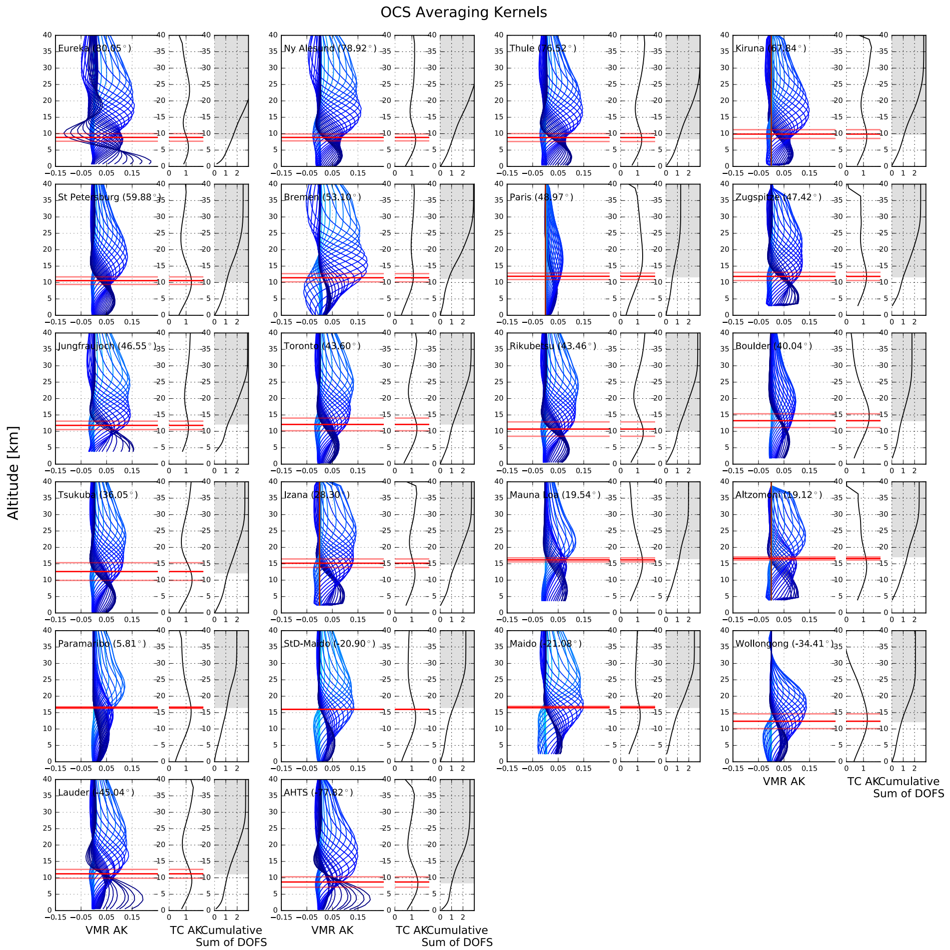
M Makarova – Recent sensitivity testing

All Profile Data



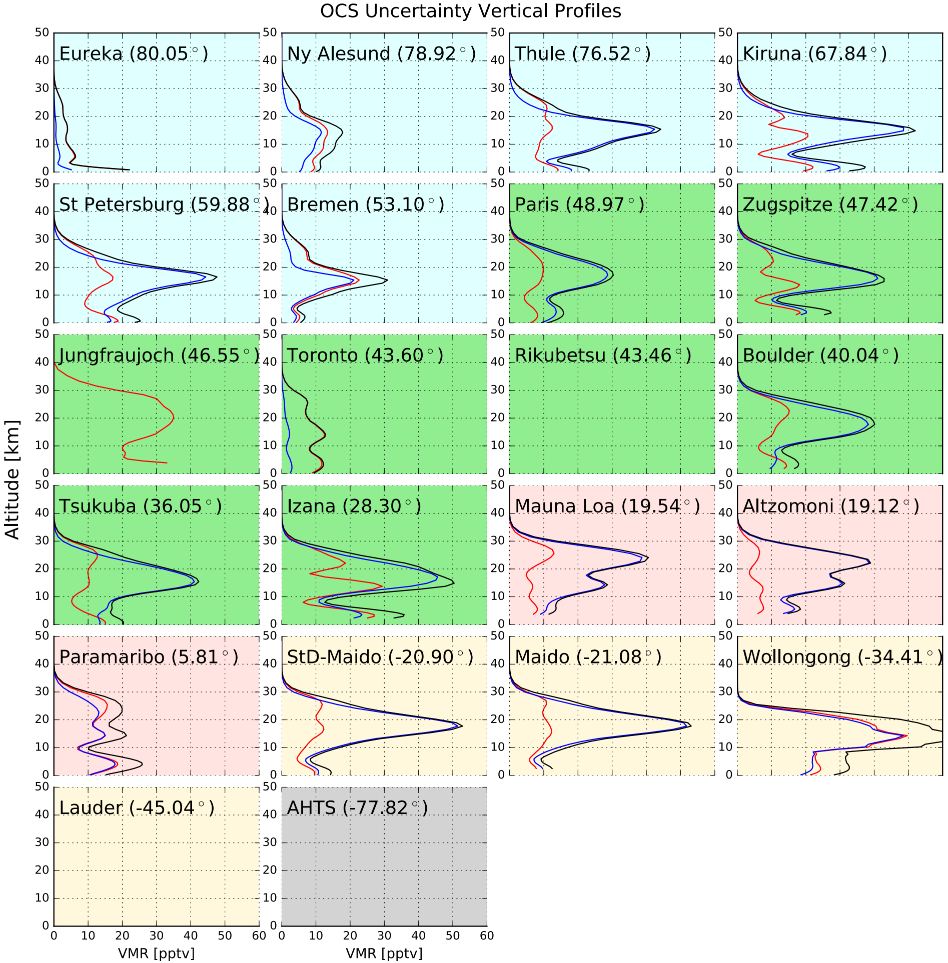
Current Averaging Kernels

- Paris site overly constrained?
- Eureka under constrained in lower levels
- Lauder, Arrival Heights similar but also some constraint variant in troposphere
- Likely small effects…



Uncertainties from HDF

- Not all sites submitted uncertainties yet
- Most have a maximum in absolute uncertainty in lower stratosphere
- Legend:
    - Red – random
    - Blue – systematic
    - Black - Combined



NCEP Tropopause height (TPH) - Binned

The TPH is latitude dependent. A 10 deg binned latitude has been identified to calculate the 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

To avoid any seasonal cycle variability affecting differently across sites the mean TPH ± 2·STD is used to define the altitude range where partial columns are calculated

Site	Mean TPH [km]	STD [km]	Binned Lat [∘]	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

Trend analysis

(1) Apply a linear least squares fit $y = f(x - x_{min})$ to data where f is given by Fourier series + drift.

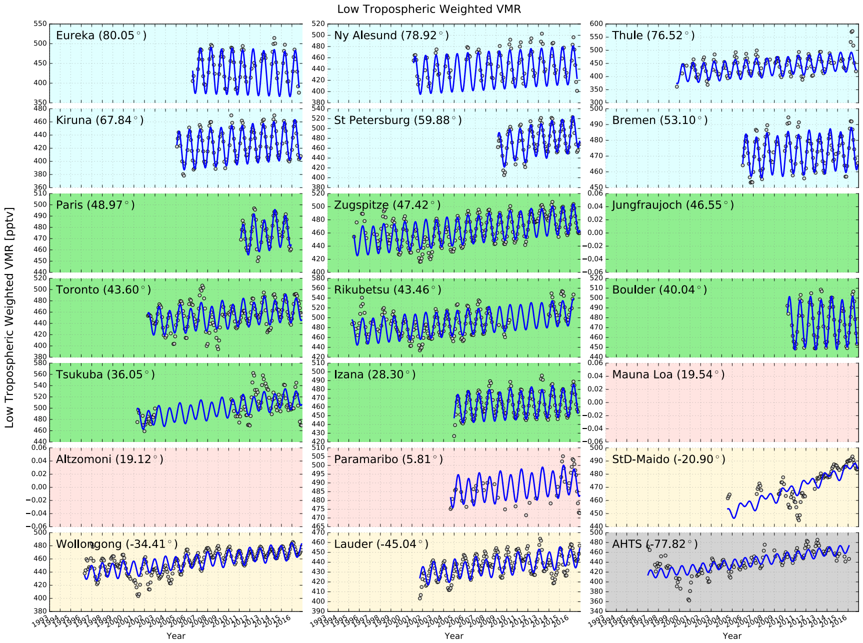
$$f_{Drift} = mx + a_0$$
$$f_{Fourier} = a_0 + \sum_{n=1}^{N} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{N} b_n \sin\left(\frac{n\pi x}{L}\right)$$
$$f(x) = f_{Drift} + f_{Fourier}$$
$$f(x) = mx + a_0 + \sum_{n=1}^{N} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{N} b_n \sin\left(\frac{n\pi x}{L}\right)$$
$$x = t - x_{min}$$
$$N = 2$$

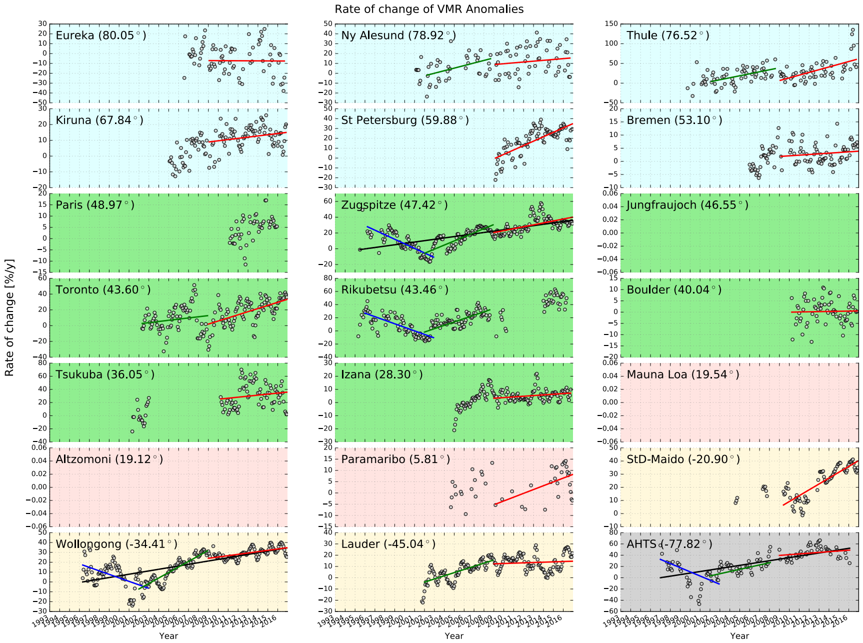
(2) Calculate Anomalies: Data - $f_{Fourier}$

(3) For sites with long-term measurements estimate inflection points using the following approach:

$$f_{Drift} = m_1 x + m_2 x^2 + m_3 x^3 + m_4 x^4 + m_5 x^5 + a_0$$
$$f_{Fourier} = a_0 + \sum_{n=1}^{N} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{N} b_n \sin\left(\frac{n\pi x}{L}\right)$$
$$f(x) = f_{Drift} + f_{Fourier}$$
$$x = t - x_{min}$$
$$N = 2$$

Low Troposphere surface – 4km

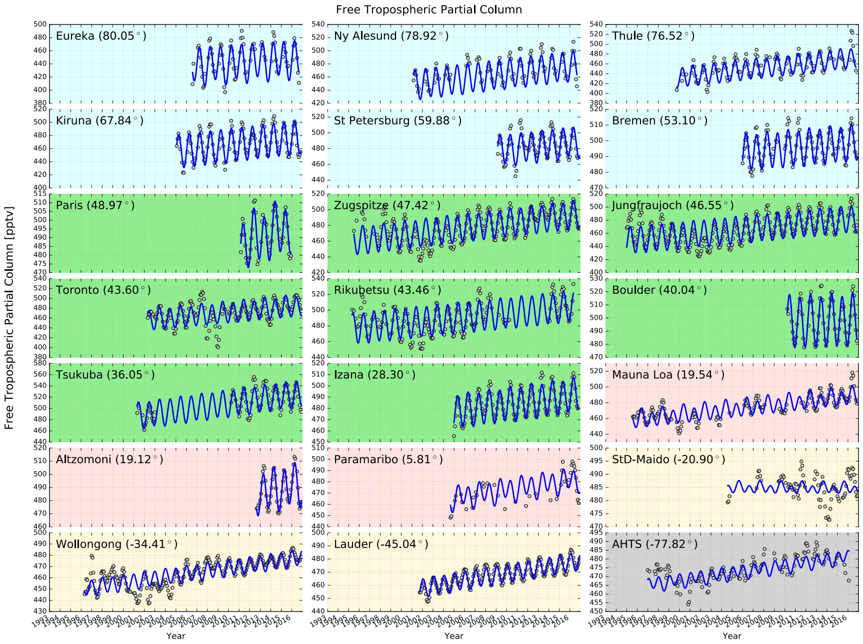


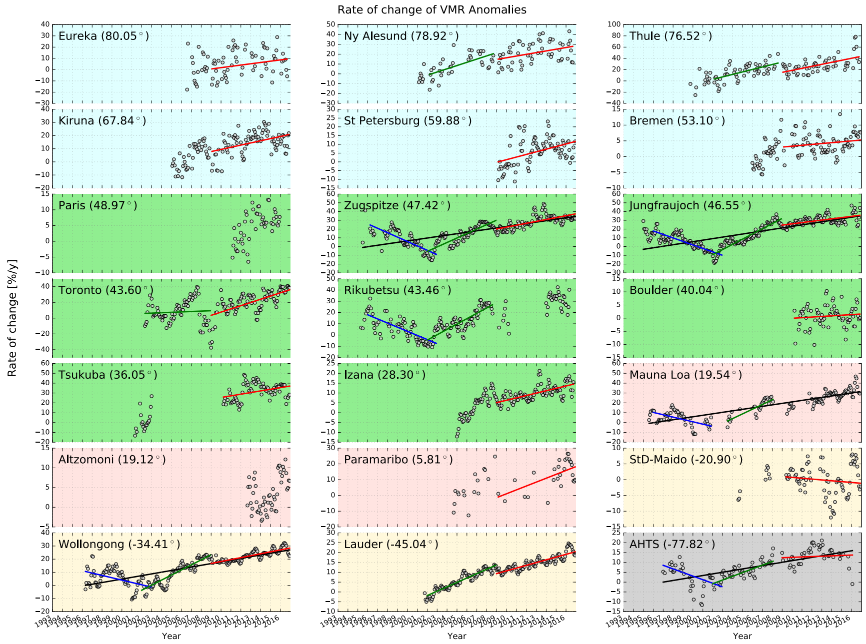


- Monthly Mean
- Partial column

- Anomalies + segmented linear trends

Free Troposphere 4km – Lower TP boundary

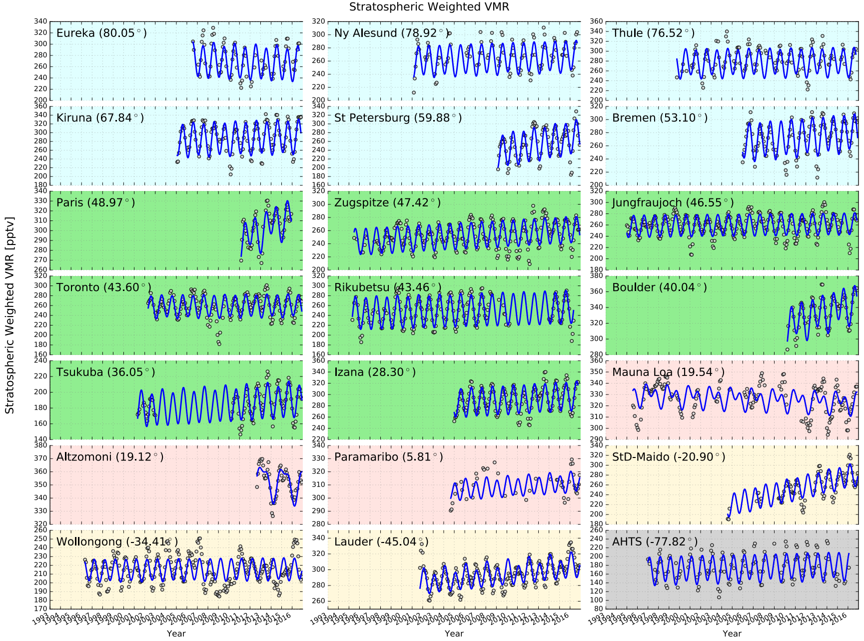


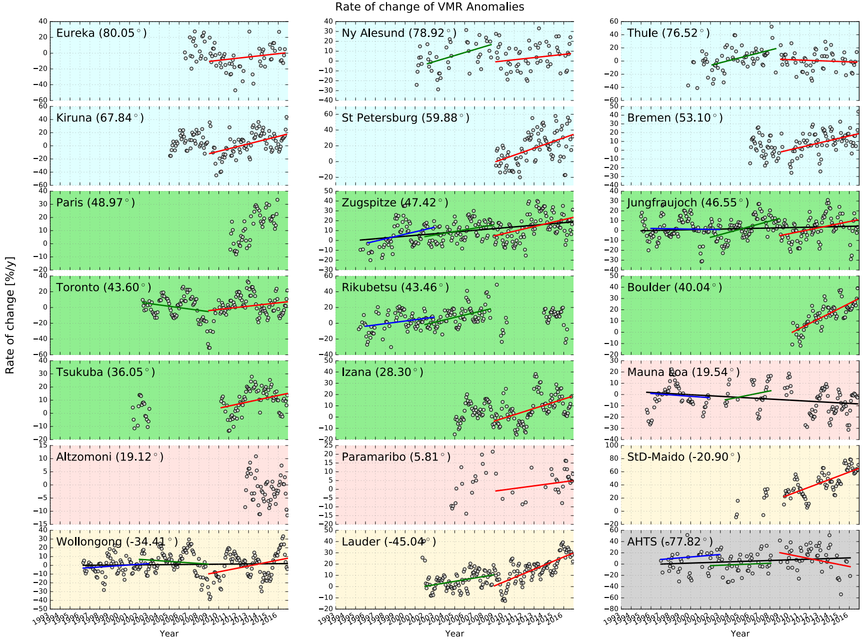


- Monthly Mean
- Partial column

- Anomalies + segmented linear trends

Stratosphere



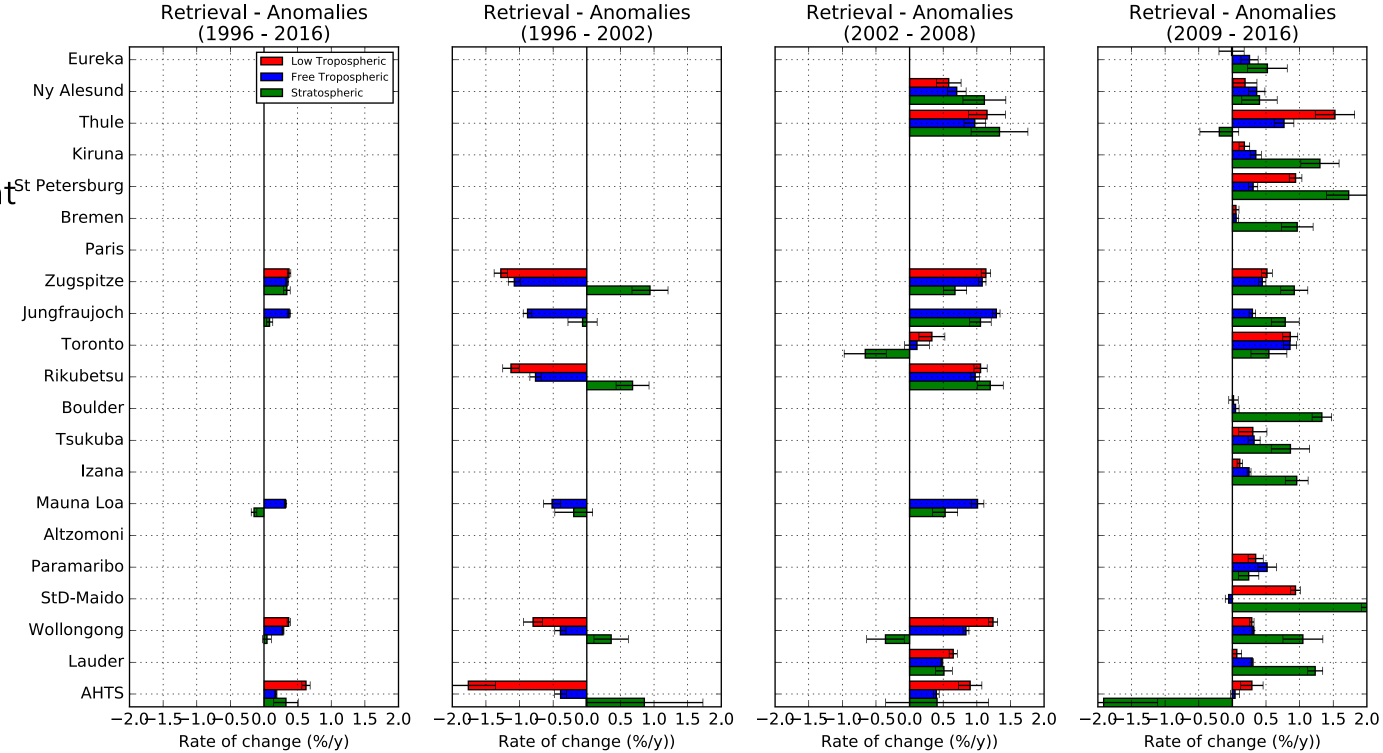


- Monthly Mean
- Partial column

- Anomalies + segmented linear trends

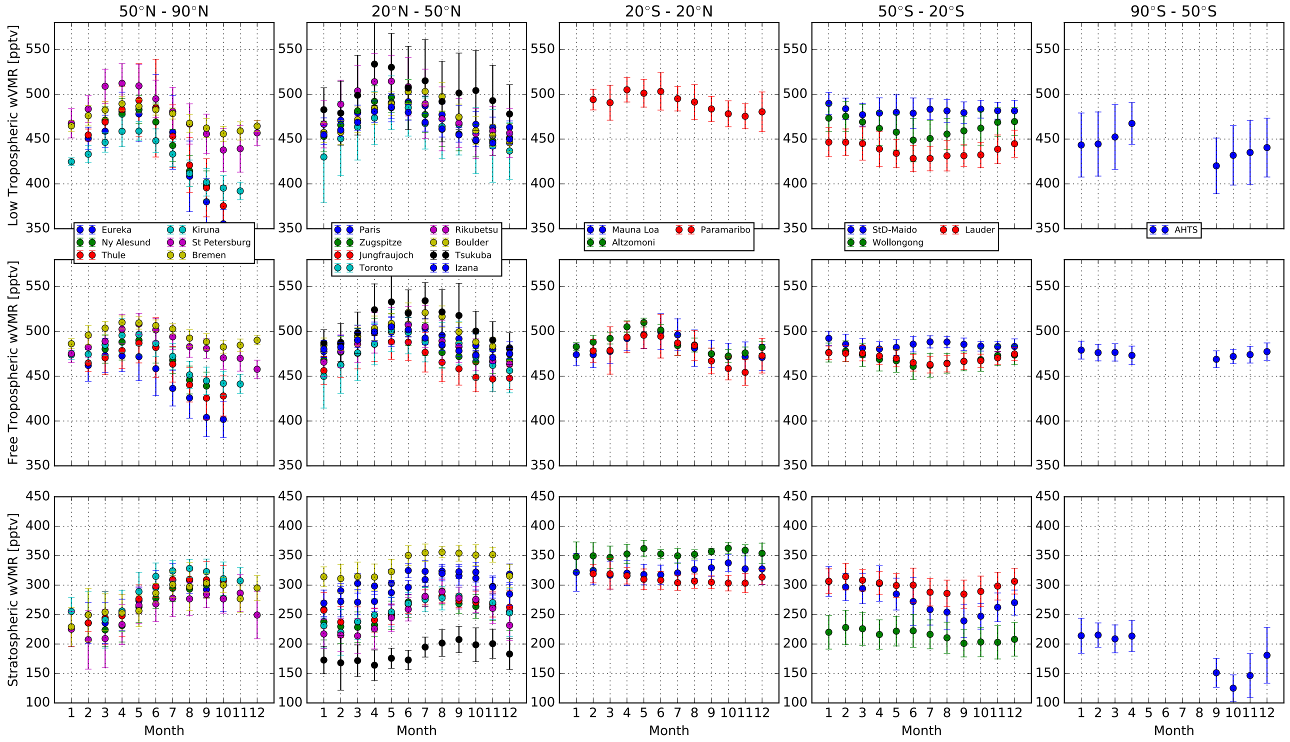
Revised Trends

- Included only sites / years that span period
- Revised tropopause height definition



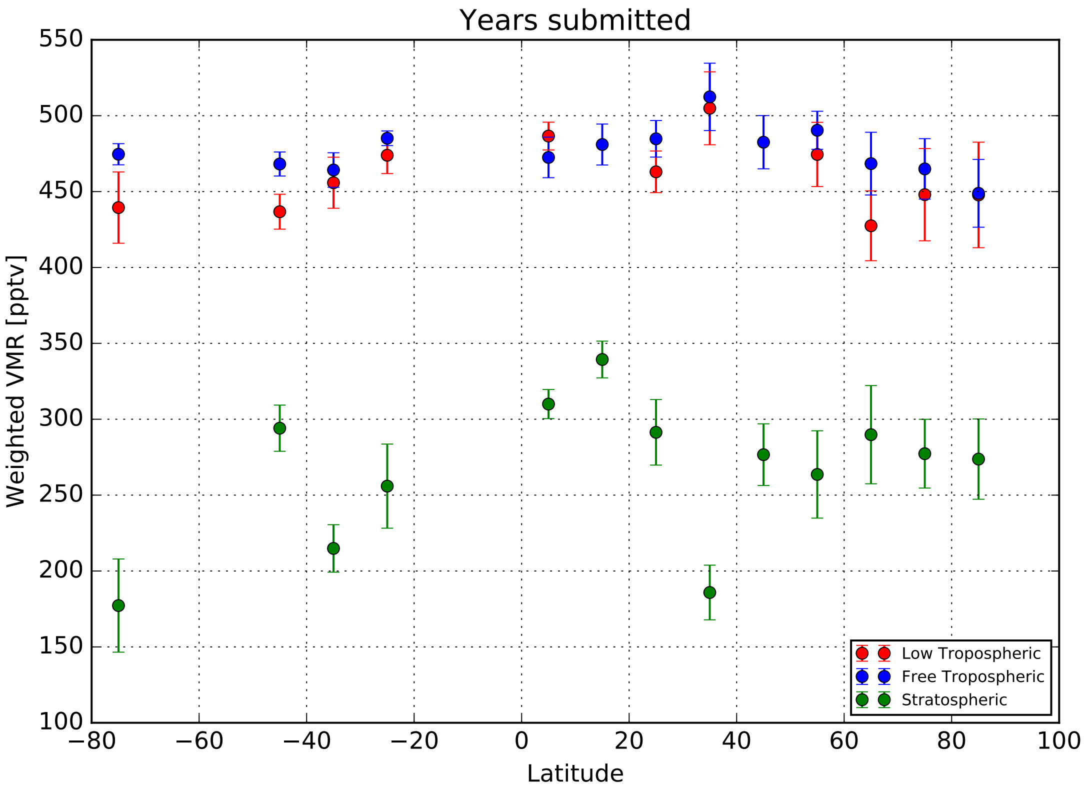
Annual Cycle

- All sites
- Binned by a priori Latitude range



Mean VMR

- Mean weighted VMR for all data
- Binned by 10° latitude bands



end

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2017

Purpose

- SSiRC
    - 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

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

So this effort follows on from recent studies:

- Legeune et al – detailed reanalysis of retrieval strategy for a single IRWG station
- Wang et al - total column & tropospheric focus at selected IRWG stations
- Kremser et al – Troposphere & stratosphere, Southern Hemisphere focus
- Krysztofiak, et al – global/latitudinal analysis NDACC, MKIV and SPIRALE

Kremser, S., et al., (2015), Positive trends in Southern Hemisphere carbonyl sulfide, GRL

Lejeune, B., et al., (2017), Optimized approach to retrieve information on atmospheric carbonyl sulfide (OCS) above the Jungfraujoch station and change in its abundance since 1995, JQSRT

Wang, Y., et al., (2016), Towards understanding the variability in biospheric CO_2 fluxes: using FTIR spectrometry and a chemical transport model to investigate the sources and sinks of carbonyl sulfide and its link to CO2, ACP

Krysztofiak, G., et al., (2015). Carbonyl Sulphide (OCS) Variability with Latitude in the Atmosphere. Atmosphere-Ocean, 53(1):89–101.

Sources/Sinks Atm Chem

- 6 year tropospheric lifetime (Ulshöfer and Andreae, 1997)

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

- Oceanic source
  - Direct OCS, DMS, CS_2
  - Oxidation of CS_2 ~ lifetime of 6 days
  - Oxidation DMS ~ lifetime <1 - days

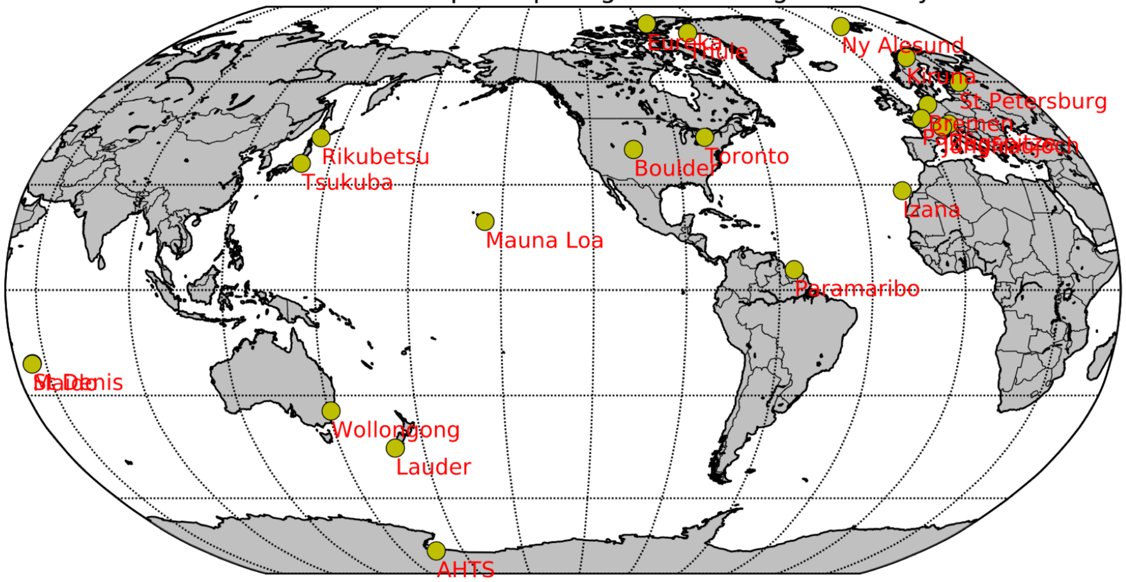
- Terrestrial Sinks
  - Photosynthetic uptake
  - Soil uptake

- 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

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

IRWG sites

IRWG-NDACC Sites participating in the OCS global study



NADCC/IRWG + affiliated sites total 22 sites so far

Common Retrieval Parameters

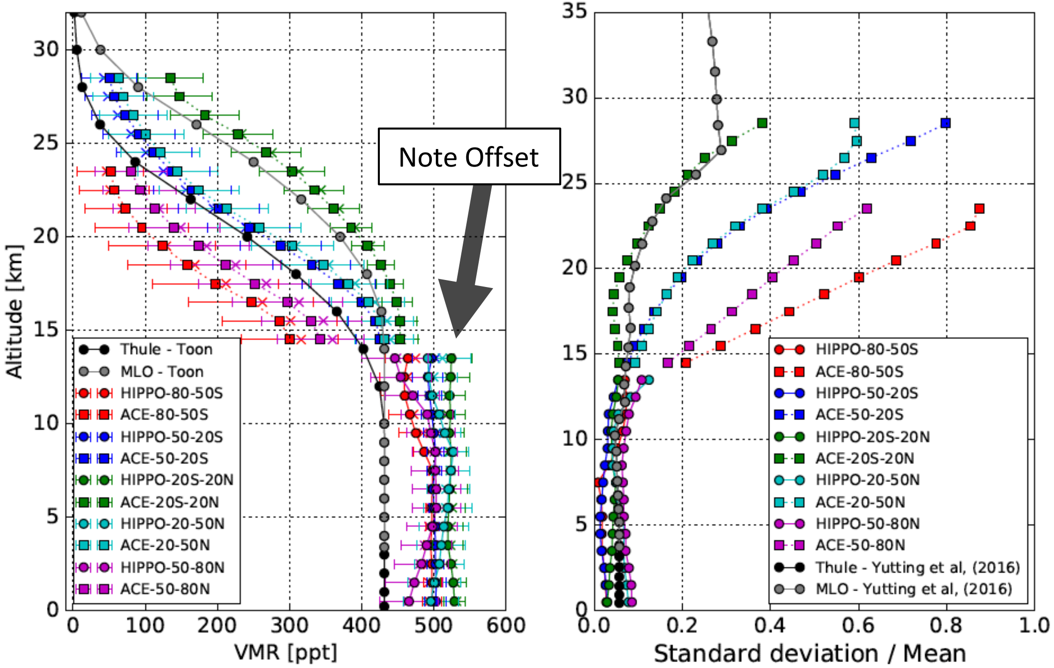
- Use 4.8μ OCS features & follow investigation by Legeune et al for interfering species and linelist
- HITRAN12 but not hot band line (too weak to have an effect)
  - ATM16 not significantly different from HIT12
  - O3 may yet be a limiting issue for residuals
  - Background CO_2, needs to be reviewed
- To account for the layer thickness and its influence please weight the Sa by (Sa/sqrt(thickness)) *(Must do this)*
- We used a Gaussian inter-correlation with a half-width length of 4 km for the off diagonal elements of the covariance matrix
- Uncertainties, needed soon

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…

Global Profiles / Variance 1/2

Smooth mean profiles obtained during
1. HIPPO quality assured RF + 4 missions spanning seasons 2009 – 2011
2. ACE-FTS all profiles from 2004 – 2013 v3.5

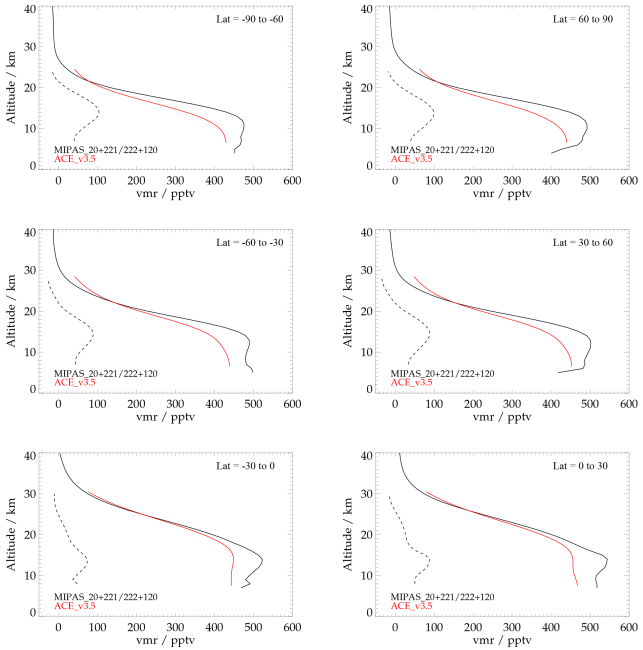


Intermediate smoothed, reduced and binned a priori and Sa from two global datasets.

Global Profiles / Variance 2/3

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

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

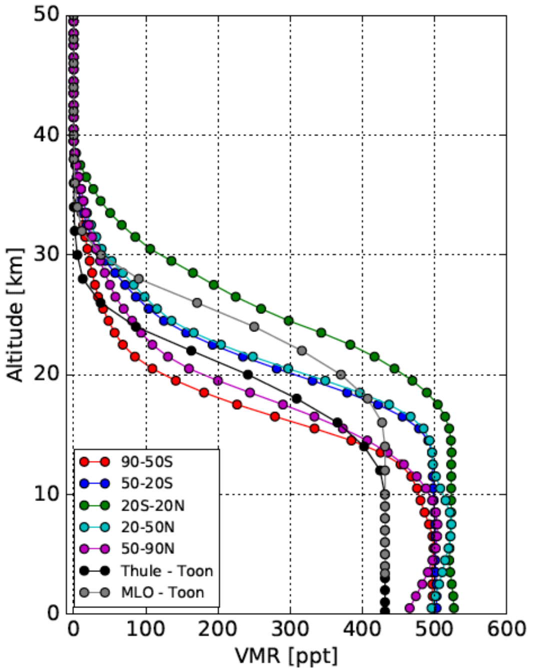


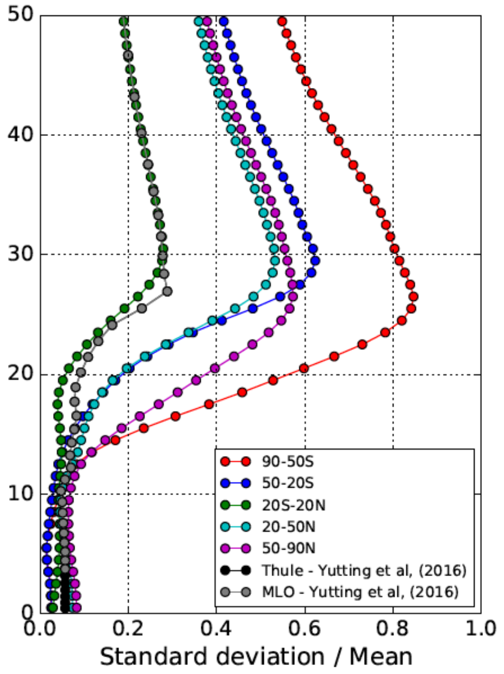
Coincident profiles averaged over 6 latitude bands.
Between Feb 2004 – Apr 2012

Glatthor, et al., (2017), Global carbonyl sulfide (OCS) measured by MIPAS/Envisat during 2002-2012, ACP

Global Profiles / Variance 3/3

Vertical profiles have been extended up to 120 km





Final smoothed reduced and co-joined a priori and Sa from two global datasets.

All OCS Profiles

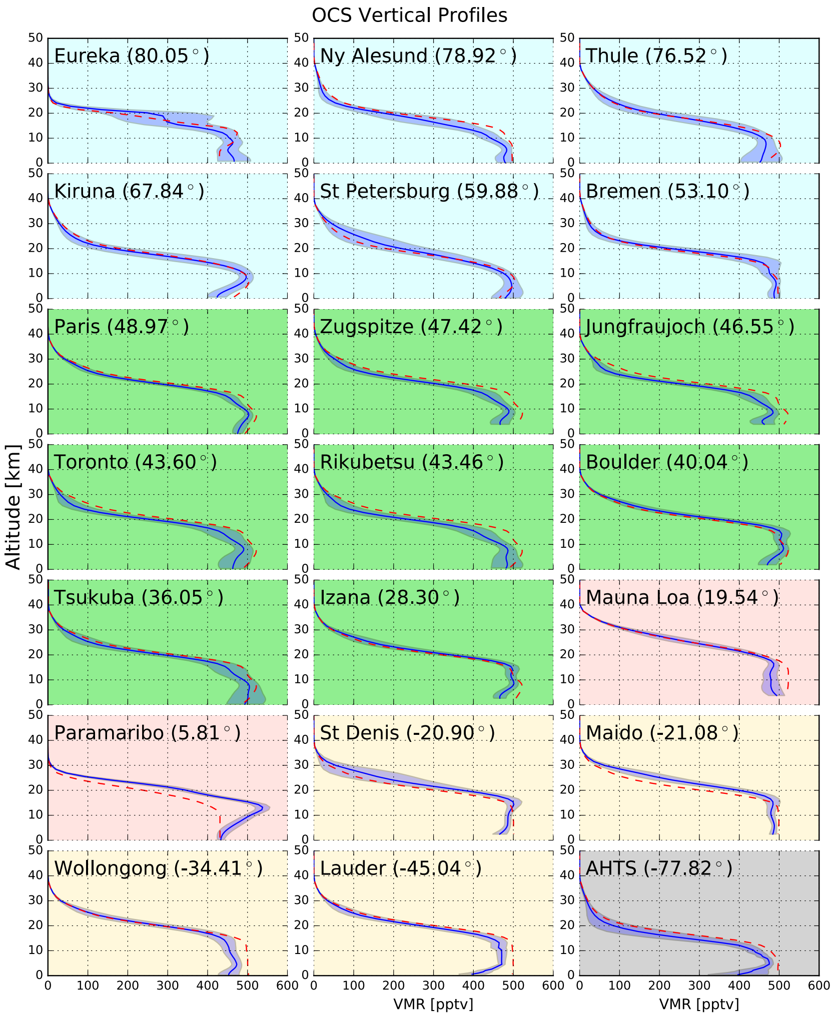
Snapshot of all profiles to date

Panels color coded by latitude bands
(same a priori & Sa)
Blue: 50 – 90 N
Green: 20 – 50 N
Orange: 20S – 20N
Yellow: 20 – 50S
Grey: 50 – 90S

A priori: Red dashed
Mean retrieved all data: Solid blue
±1σ of retrieved profile: Shaded blue

Large troposphere variability TOR, RIK, TKU

Note: a priori to be revised for :
Eureka, Ny Alesund, Bremen, Paramaribo



ALL Kernels

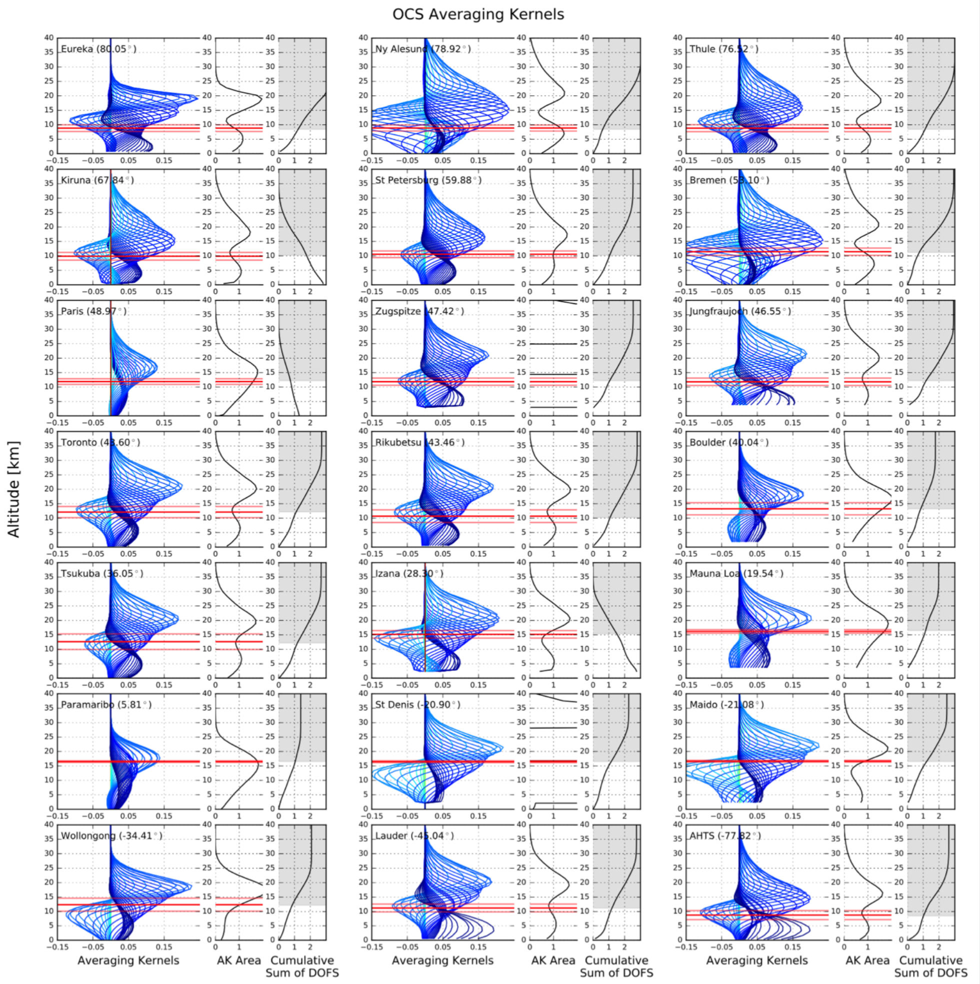
Left panel:
All Kernels:
Blue
NCEP TH ± 1σ:
Red

Middle panel:
AK area:
Black

Right Panel:
Cumulative DOFS: Black

- Most AK Area show
  - 2 peaks: TAB, BRE, JFJ,
  - but not all PRS, WLG, MLO, 1pk
- PROFFIT show a drop in sensitivity at surface
- AK for ZUG, St Denis (error in file/reading)

Note:
- PROFFIT cum. DOFS not summed properly in plots
- a priori to be revised for :
  - EUR, NYA, BRE, PAR



DOFS

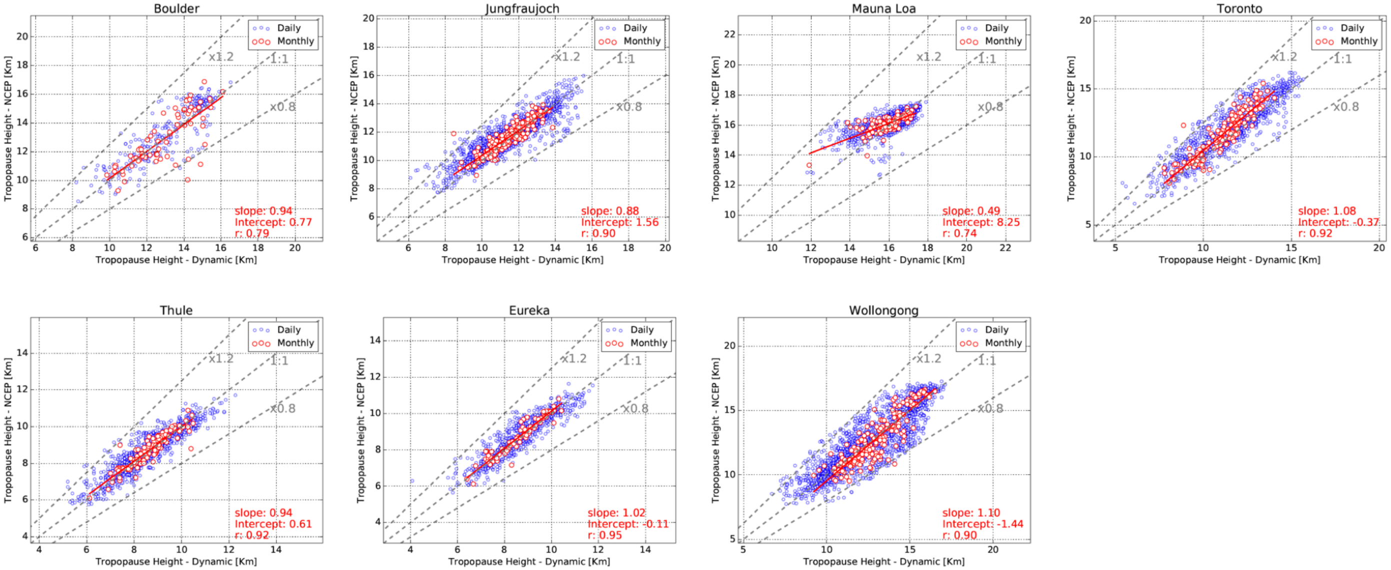
Preliminary accumulation of DOFS for selected sites

Site	Mean Tropopause Height [km]	Total DOF	DOF above the mean tropopause
Eureka	8.75 ± 1.20	3.1	1.9
Thule	8.72 ± 1.26	3.0	1.9
Jungfraujoch	11.62 ± 1.50	2.9	1.8
Toronto	11.45 ± 1.89	2.7	1.7
Boulder	13.02 ± 1.92	1.8	0.9
Mauna Loa	16.09 ± 1.00	2.0	0.8
Wollongong	12.66 ± 2.23	2.1	1.2

Table should be ‘consistent’ for hallmark of representative global retrieval

Tropopause Heights 1/2

Comparison of tropopause height derived (NCEP Vs Dynamical)



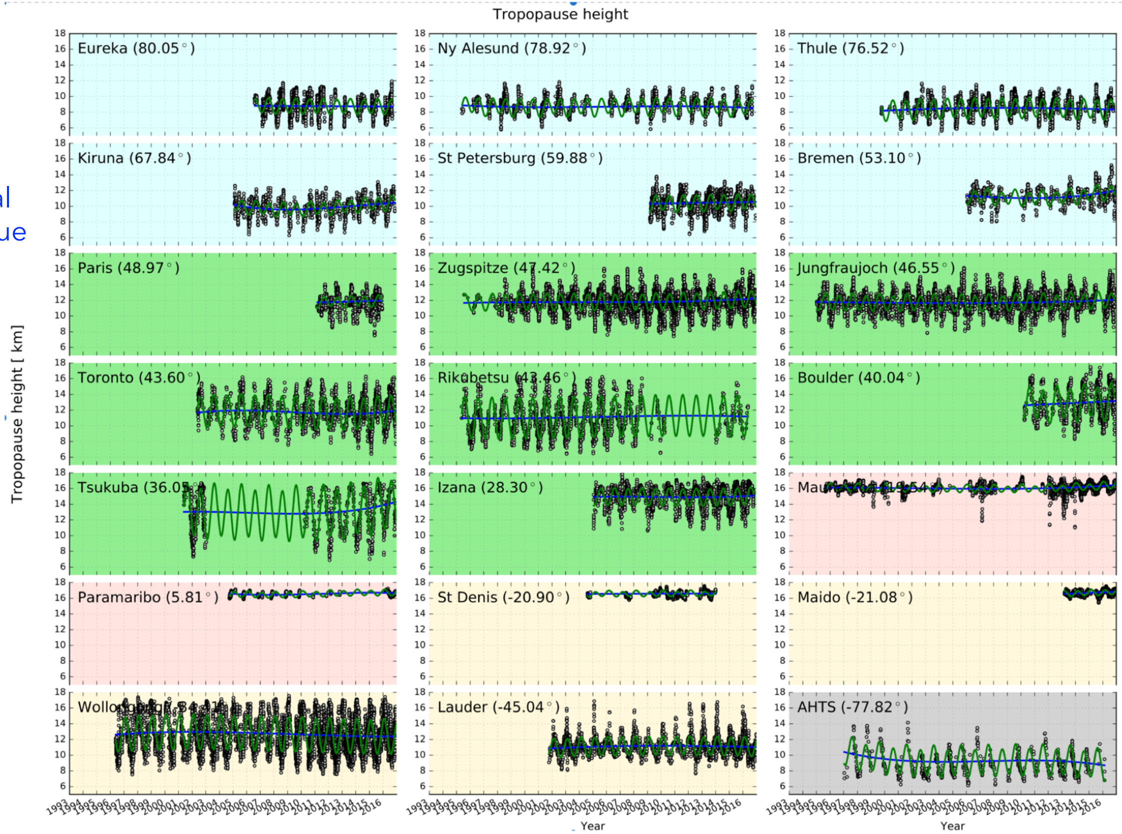
Tropopause Height defined by dynamical tropopause height (DTH) M. von Hobe
Here compared with NCEP TH data product for selected sites

Tropopause Heights 2/2

NCEP Tropopause Heights for Retrieved data dates

Same Altitude scale for all sites

3rd order polynomial + annual cycle in blue



1993 2017

Time Series – Total Columns

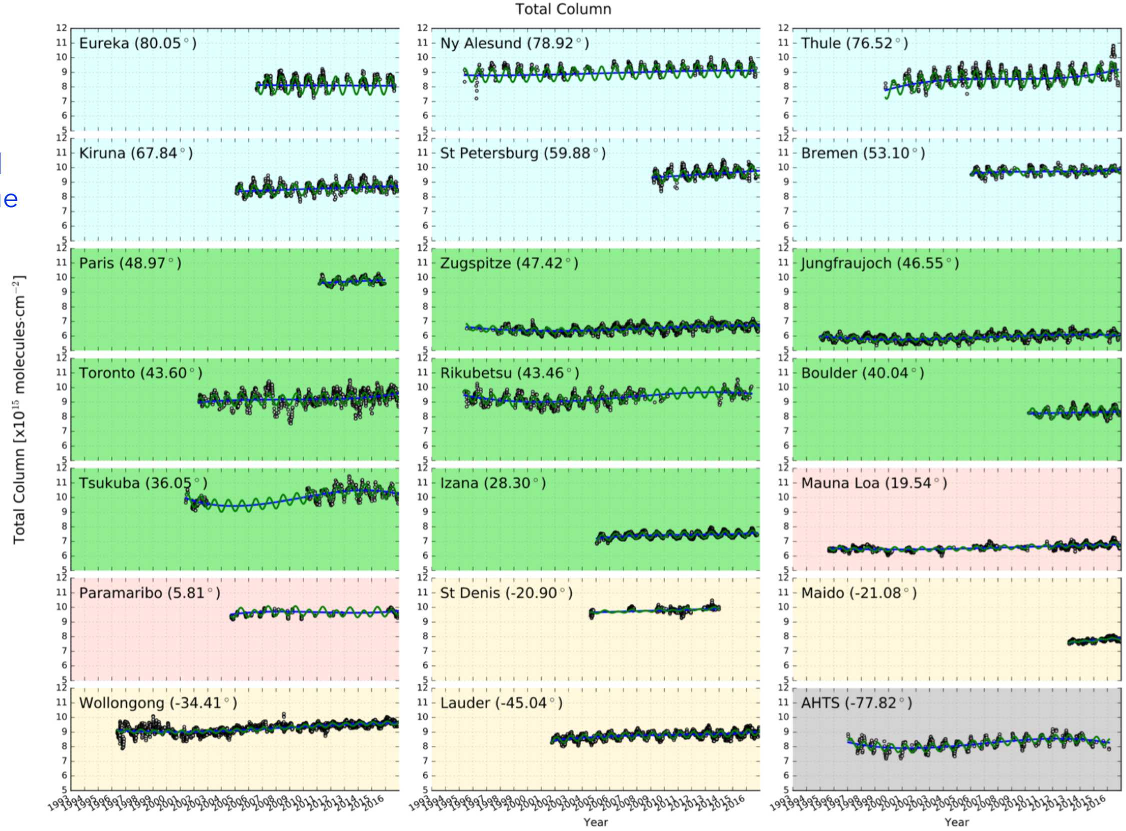
Same abundance scale for all sites

3rd order polynomial + annual cycle in blue

Gaps in TKU, RIK, MLO

Possibly combine:

- TKU & RIK?
- STD & MDO

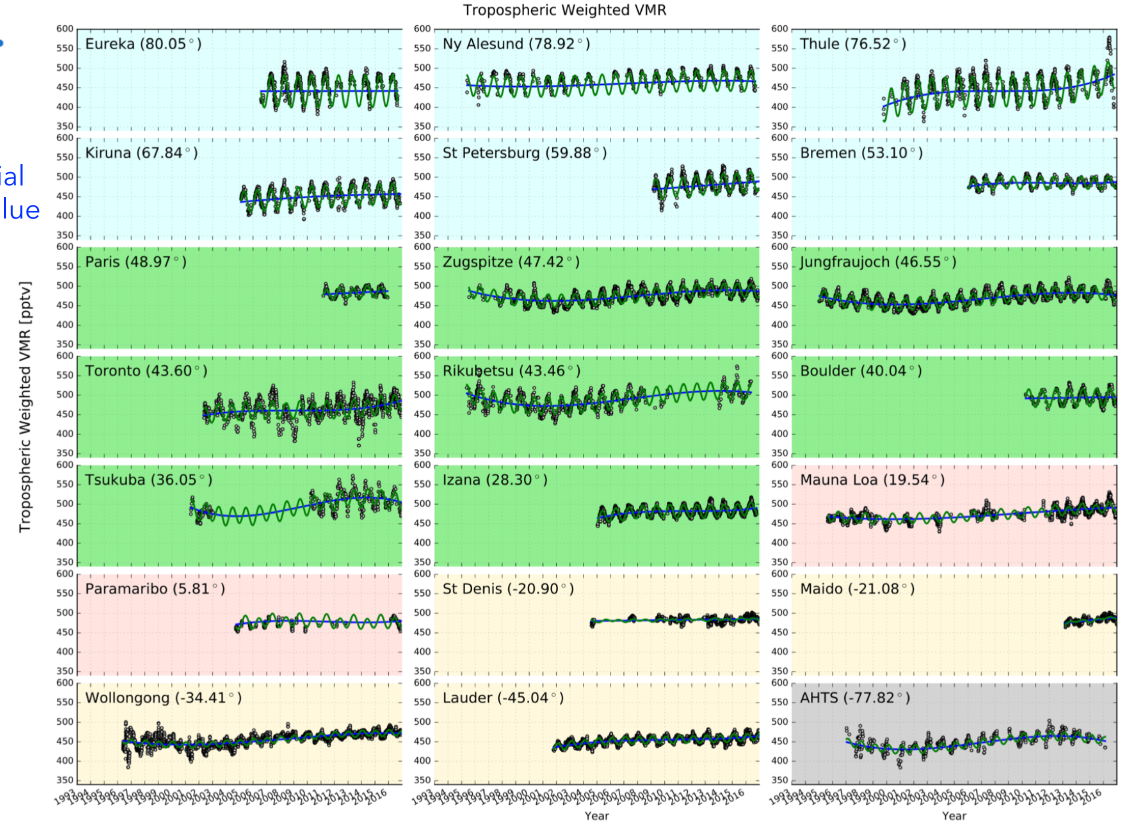


1993 2017

Time Series – Troposphere Weighted Mean VMR

- Same mixing ratio scale for all sites

3rd order polynomial + annual cycle in blue



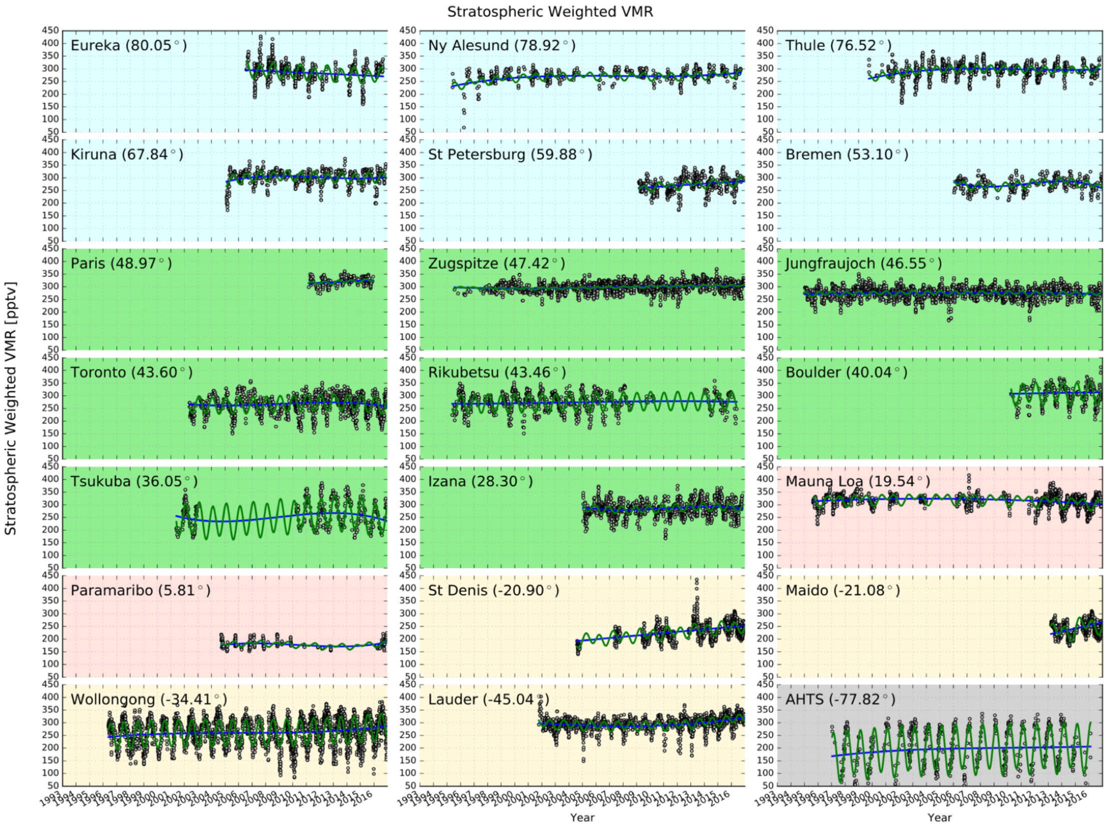
1993 2017

Time Series – Stratospheric Weighted Mean VMR

Concern about tropsophere and/or tropopause effect on stratospheric columns.

We tested defining the lower boundary of the stratospheric layer at NCEP TH +0, +2, +4, +6km –

- Not a convincing difference
- May require visiting on a site by site basis
- Or apply a regression e.g. Kremser et al.



1993 2017

Mean Weighted VMR

Mean weighted VMR by site (latitude) and by trend period after Legeune et al. (approx).

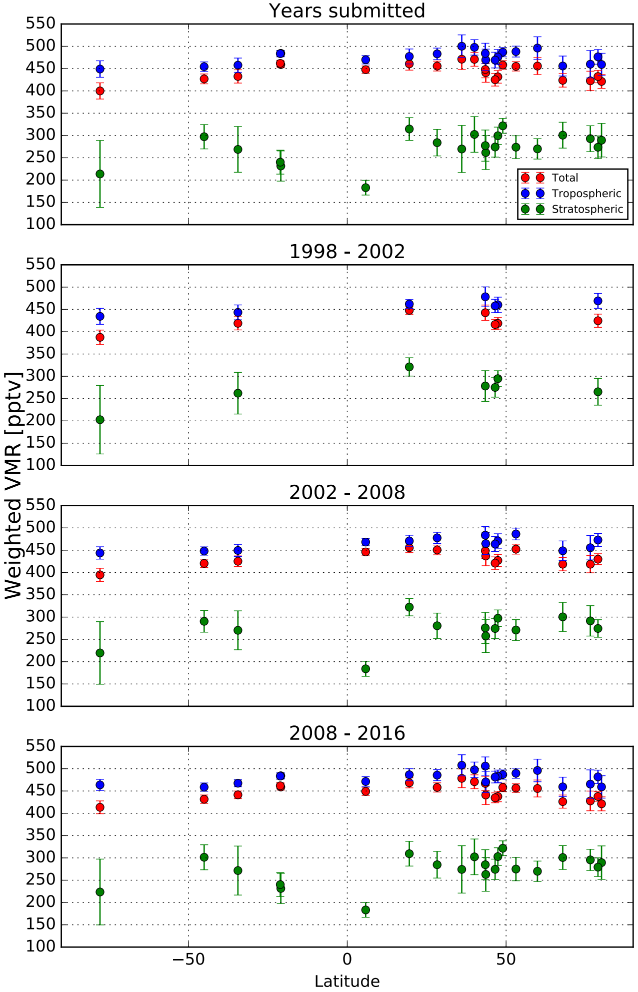
Top is all years, then 1998-2002, 2002-2008, 2008-2016
Note that different sites have varying series density.

Highest in N. mid-latitudes,

Drawdown (if this is correct) at 40-50°N clearly seen [Montzka et al 2007]

Fall off at both poles

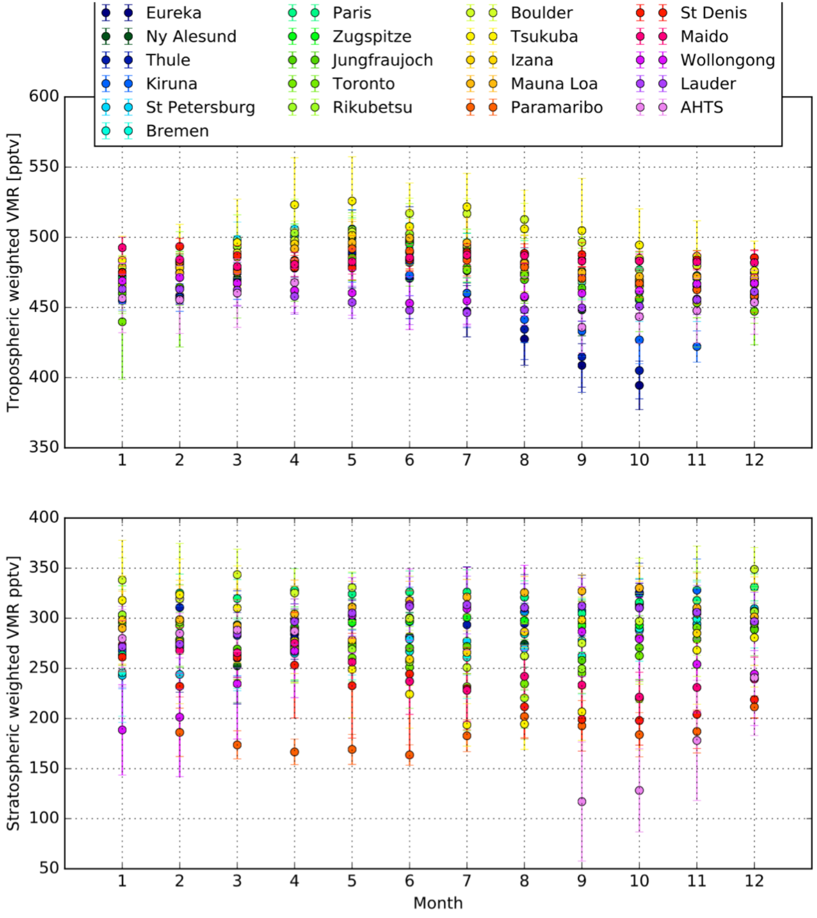
PAR (tropics) clearly a different regime from say MLO … ADDIS?



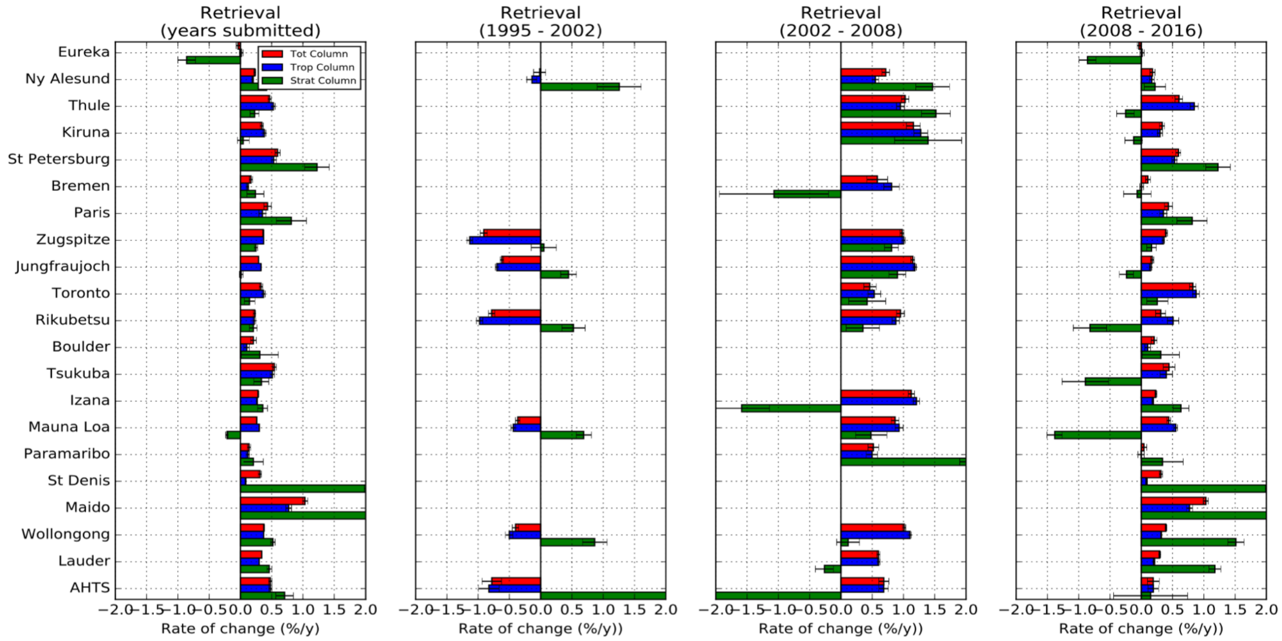
Mean Seasonal Cycle

- For all data
- Column averaged mixing ratio

- Examine phases of cycles for sites (lat)



Current Summary of linear trends in 4 time periods



- For all sites all years negligible to positive in trop & total column
- Though 1995-2002 these were negative & stratosphere was positive
- Largest pos. trend in lower atm mid 2000's, mixed but more positive in strat.
- Most recent positive for all in lower atm 0-1%/y, large positive in SH, mixed in NH

Conclusions to Date & Next Steps

- Network wide retrievals still in process
  - Need to revise a priori & Sa for some sites. (EUR, U Bremen sites) (PROFFIT at surface)
  - Line parameters still may be updated. (O_3?)
  - Some background retrieval species may be revisited (CO_2)

- Analyze
  - Annual cycles by latitude
  - Annual cycle phase

- Can we parse the troposphere?
  - Clearly the chemistry is hemisphere, latitude, ocean/land surface, temperature, solar flux, anthropogenic sources dependent
  - UTLS profiles from ACE, MIPAS but much less data from 2-10km (NOAA flask sample flights – limited geographical coverage)

- Respond to groups with this summary & attempt to improve / explain DOFS & AK consistency
  - Ask for your patience if reanalysis is requested
  - Error analysis will be needed

end

(2) Calculate Anomalies: Data - $f_{Fourier}$

(3) For sites with long-term measurements estimate inflection points using the following approach:

$$f_{Drift} = m_1 x + m_2 x^2 + m_3 x^3 + m_4 x^4 + m_5 x^5 + a_0$$

$$f_{Fourier} = a_0 + \sum_{n=1}^{N} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{N} b_n \sin\left(\frac{n\pi x}{L}\right)$$

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

$$x = t - x_{min}$$

$$N = 2$$

Comparison of OCS trends with previous studies

Jungfraujoch

	1995 – 2016	1995-2002	2002-2008	2008-2016
Total column (%yr^{-1})				
Lejeune et al (2016)	0.31 ± 0.03	-0.62 ± 0.08	1.21 ± 0.10	0.23 ±0.10
This work	0.29 ± 0.01	-0.62 ± 0.03	1.15 ± 0.04	0.17 ± 0.04
Tropospheric Column (%yr^{-1})				
Lejeune et al (2016)	0.32 ± 0.03	-0.89 ± 0.08	1.34 ± 0.08	-0.04 ± 0.08
This work*	0.33 ± 0.04	-0.72 ±0.15	1.18 ± 0.78	0.15 ± 0.14
Stratospheric Column (%yr^{-1})				
Lejeune et al (2016)	0.20 ± 0.06			
This work	0.08 ± 0.10	0.03 ± 0.41	1.00 ± 0.46	0.13 ± 0.38

Lejeune et al (2016) used data from 1995 – 2015. They calculated the tropospheric partial column between 3.6 – 8.9 km and the stratospheric partial columns between 13.8 – 19.5 km.

*Using the NCEP tropopause + 2.0km

Comparison of OCS trends with previous studies

Wollongong

	2002-2008	2008-2016
Total column (%yr^{-1})		
Kremser et al (2015)	1.13 ± 0.04 (2001-2009)	0.84 ± 0.08 (2010-2014)
This work	1.01 ± 0.03	0.33 ± 0.03
Tropospheric Column (%yr^{-1})		
Kremser et al (2015)	0.99 ± 0.04 (2001-2009)	0.51 ± 0.11 (2010-2014)
This work	1.10 ± 0.10	0.21 ± 0.12
Stratospheric Column (%yr^{-1})		
Kremser et al (2015)	0.11 ± 0.02 (2001-2008)	0.13 ± 0.04 (2009-2014)
This work	-0.07 ± 0.62	1.24 ± 0.76

Kremser et al (2015) used data from 2001– 2014. Tropospheric columns were calculated from the surface to 12.5 km. Stratospheric columns comprise the OCS column concentrations above this mean tropopause level.

Comparison of OCS trends with previous studies

Lauder

	2002-2008	2008-2016
Total column (%yr^{-1})		
Kremser et al (2015)	0.68 ± 0.04 (2001-2009)	0.57 ± 0.07 (2010-2015)
This work	0.60 ± 0.03	0.30 ± 0.02
Tropospheric Column (%yr^{-1})		
Kremser et al (2015)	0.47 ± 0.04 (2001-2008)	0.51 ± 0.11 (2012-2015)
This work	0.60 ± 0.10	0.20 ± 0.07
Stratospheric Column (%yr^{-1})		
Kremser et al (2015)	0.21 ± 0.02 (2001-2008)	0.13 ± 0.05 (2010-2015)
This work	0.19 ± 0.44	1.00 ± 0.29

Kremser et al (2015) used data from 2001– 2015. Tropospheric columns were calculated from the surface to 10.9 km. Stratospheric columns comprise the OCS column concentrations above this mean tropopause level.

Comparison of OCS trends with previous studies

Arrival Heights

	2002-2008	2008-2016
Total column (%yr^{-1})		
Kremser et al (2015)	0.69 ± 0.10 (2001-2008)	0.55 ± 0.45 (2012-2015)
This work	0.62 ± 0.09	0.20 ± 0.10
Tropospheric Column (%yr^{-1})		
Kremser et al (2015)	0.66 ± 0.12 (2001-2007)	0.22 ± 0.14 (2007-2014)
This work	0.72 ± 0.28	0.21 ± 0.22
Stratospheric Column (%yr^{-1})		
Kremser et al (2015)	0.13 ± 0.05 (2001-2012)	-0.06 ± 0.29 (2012-2015)
This work	-0.44 ± 1.17	0.03 ± 1.03

Kremser et al (2015) used data from 2001– 2015. Tropospheric columns were calculated from the surface to 9.2 km. Stratospheric columns comprise the OCS column concentrations above this mean tropopause level.

Site	Latitude [∘]	Longitude [∘]	Altitude [masl]	Years submitted	Trend of years submitted molec·cm^{2}·yr^{-1}[x10^{15}]/ %yr^{-1}	1995 – 2002 molec·cm^{2}·yr^{-1}[x10^{15}]/ %yr^{-1}	2002 – 2008 molec·cm^{2}·yr^{-1}[x10^{15}]/ %yr^{-1}	2008 – 2016 molec·cm^{2}·yr^{-1}[x10^{15}]/ %yr^{-1}
Eureka	80.05	273.58	610	2006-2016				
Thule	76.52	291.23	225	1999-2016				
St Petersburg	59.88	29.83	20	2009-2016				
Jungfraujoch	46.55	7.98	3580	1995-2016				
Toronto	43.60	280.60	174	2002-2016				
Rikubetsu	43.46	143.77	200	1995-2016				
Boulder	40.04	254.76	1612	2010-2016				
Tsukuba	36.05	140.12	31	2001-2016				
Mauna Loa	19.54	204.43	3396	1995-2016				
Wollongong	-34.41	150.88	30	1996-2013				
Lauder	-45.04	169.68	370	2001-2016				
Arrival Heights	-78.82	166.65	200	1997-2016				