Status of IRWG CCl_4 Retrievals

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Abstract

Working notes for optimizing CCl_4 retrievals across *IRWG* sites.

There exists a significant difference in the top-down and bottom-up emissions estimates for CCl_4 *of 10-50 [kt / annum]. Our view is that the IRWG can contribute data required to solidify atmospheric trend estimates by verifying free tropospheric values and improve the inverse modeling of source emission rates by providing more sites with profile data and accurate averaging kernels. Current surface measurements are approx. 80ppt with sub ppt precision. Measured inter-hemispheric differences are 1ppt. Precision of the IRWG must be good enough to be useful with these other datasets.*

1 Current Issues with the *IRWG* data

After the initial work to improve the retrievals for the SPARC CCl_4 meeting October 2015 we are left with the following:

Things that *did* work

1. Trends were respectable. We needed to filter data more or less for some sites by SZA and time average.
2. The retrievals used were relatively independent of H_2O variability noted in correlation plots. Using line-mixing aided in removing some unwanted correlation.
3. Using a tight but non-zero variance for fitting curvature seemed to stabilize retrievals.

Things that *need* work

1. Trend should be -1.1 to -1.5 (Assessment 2010), these are at surface.
2. *IRWG* annual cycles were not consistent. Annual cycles are small in surface data and we should expect it to be different. I don't think we know what is the appropriate cycle amplitude at all sites? It is not chemically driven only dynamical transport or winter Arctic stratospheric descent / tropopause height.
3. H_2O interference has implications for cycle and trend.
4. Offset between in situ values and mean tropospheric mixing ratio converted from *IRWG* total columns needs to be within error bars.
5. Errors are not the same across sites but should be close. Obviously they need to be as small as possible to be useful.
6. We need more sites in two key areas:
    (a) East Asia: one or more of the Japanese sites Tsukuba, Rikubetsu, Moshiri.
    (b) Southern Hemisphere: one or more SH sites: Wollongong, Lauder, Arrival Heights.

1.1 Trends

Trends are not bad as they exist. As we improve the retrievals we hope to only improvement and convergence. Trends were calculated with the algorithm developed by Gardiner et al. (2008) and recoded into IDL. The following are the data we have so far. Note that the trend in percent is normalized to the mean of that dataset so normalization from the start would yield a slightly different trend calue. Figures 1 to 4 are what was presented at the SPARC meeting. Note that for Eureka 2014 was missing and is in the all data plots below.

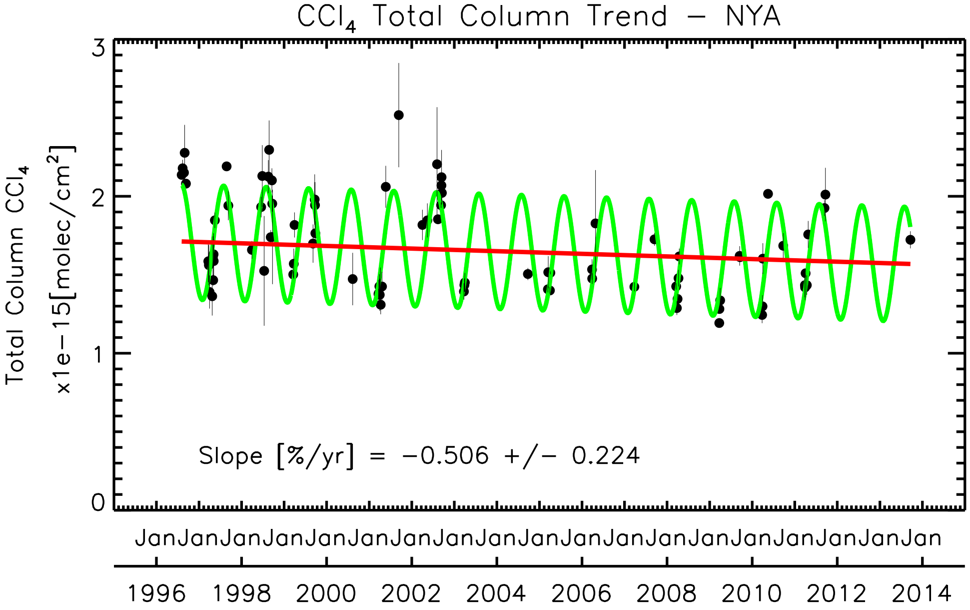

Figure 1: *CCl_4 Trend from Ny Alesund 3 day average.*

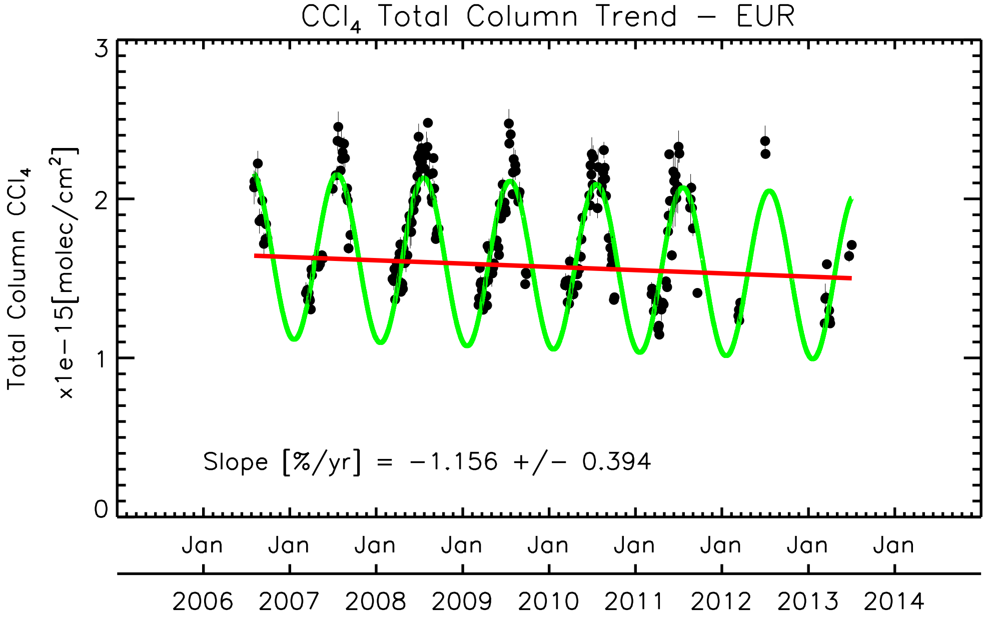

Figure 2: *CCl_4 Trend from Eureka 3 day average.*

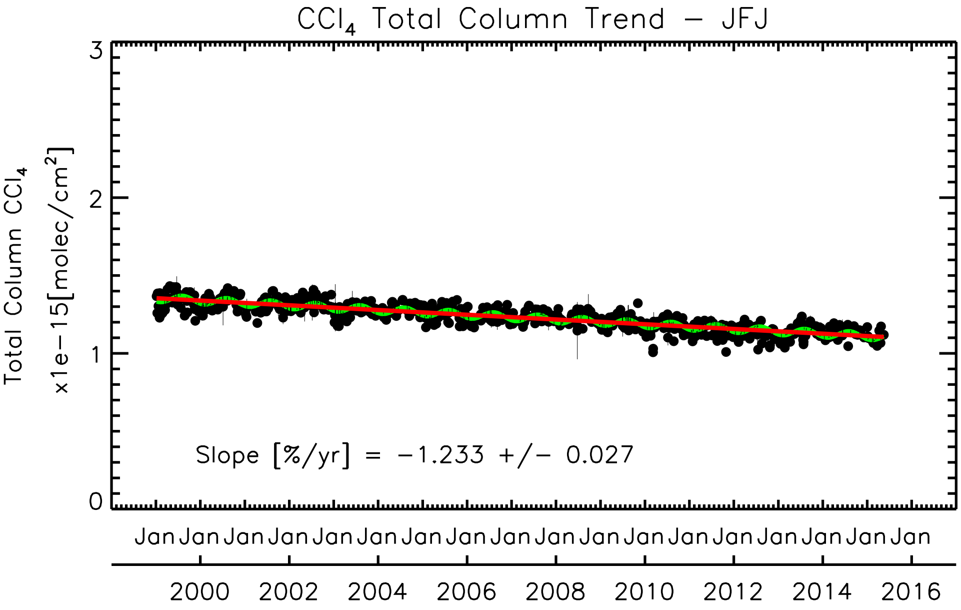

Figure 3: *CCl_4 Trend from Jungfraujoch ? day average.*

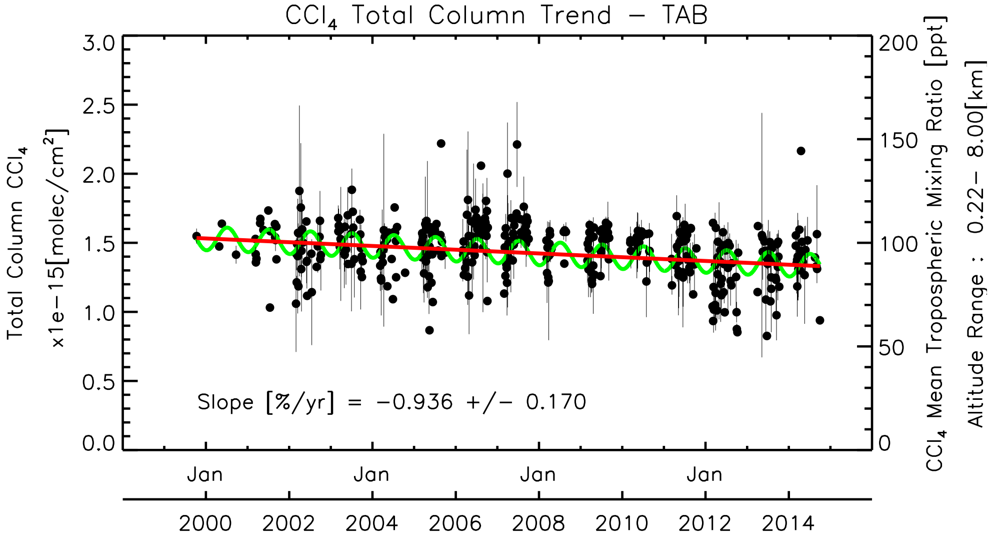

Figure 4: *CCl_4 Trend from Thule 3 day average.*

Note the correlation of the length of the Time series with the trend magnitude. It may well be that the trend magnitude is increasing with time. Figures 5 to **??** are the initial data - no averaging so considered 'all data'.

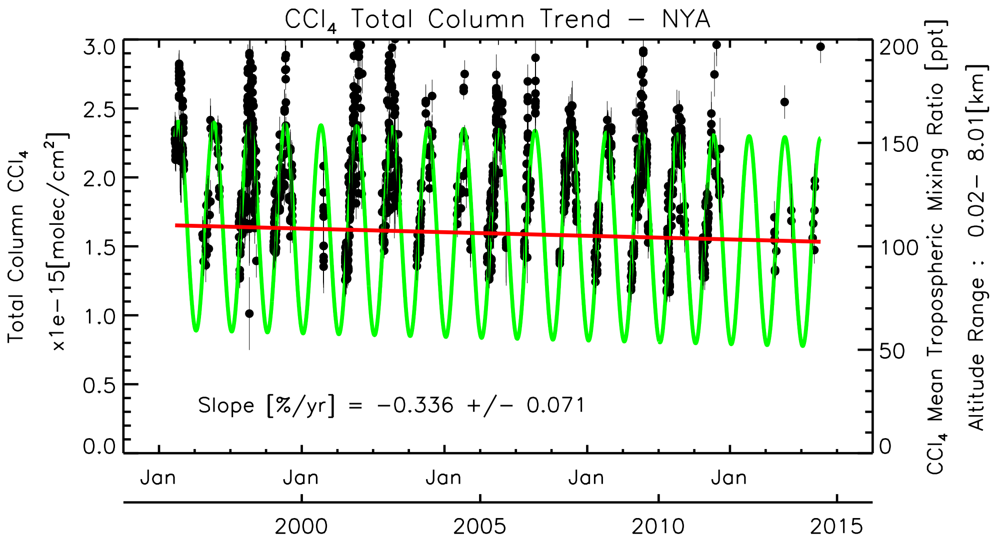

Figure 5: *CCl$_4$ Trend from initial all Ny Alesund data.*

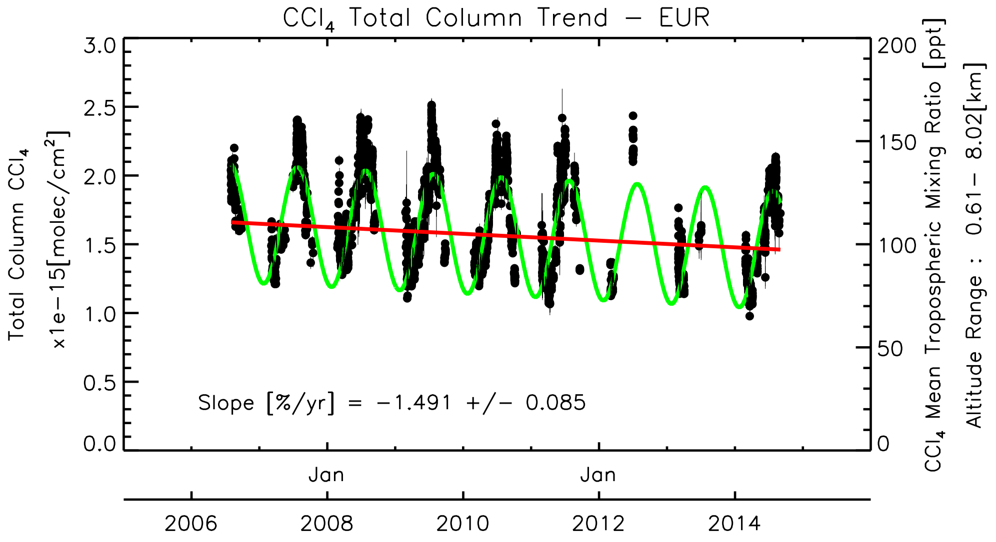

Figure 6: *CCl$_4$ Trend from initial all Eureka.*

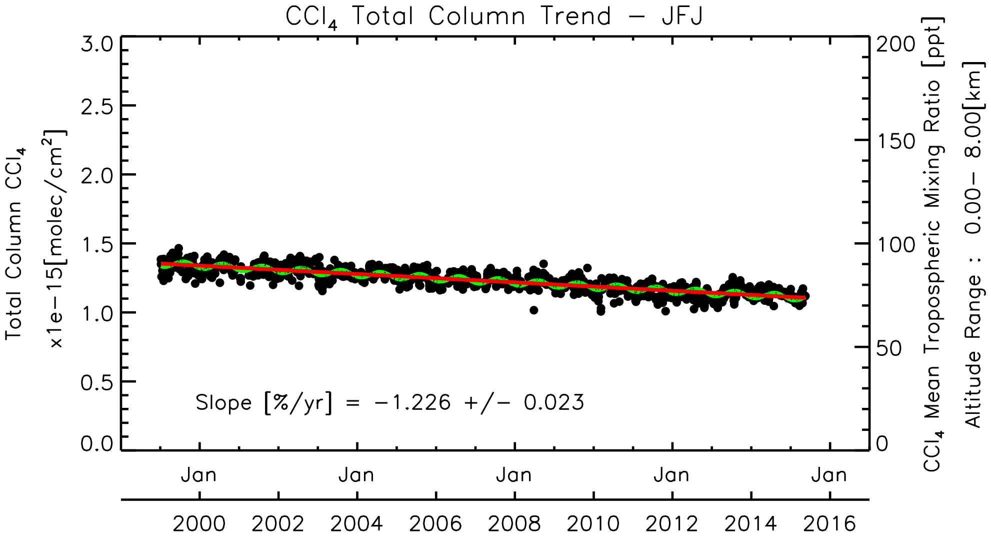

Figure 7: *CCl_4 Trend from pressor normalized Jungfraujoch 1 day average.*

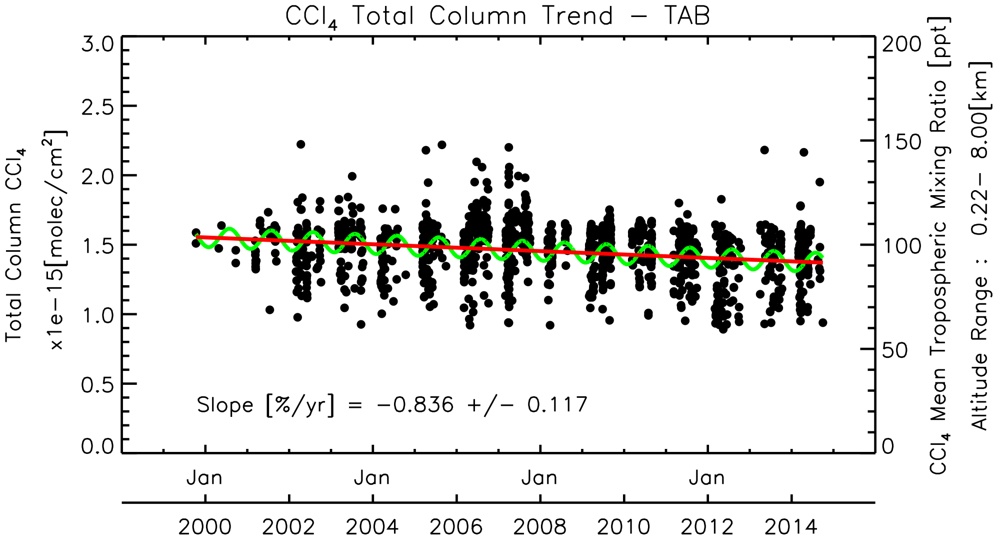

Figure 8: *CCl_4 Trend from initial all Thule data.*

The following are Arrival Heights Fig. 9 all data and Fig. 10 is a 3 day average. Fig. 11 is the initial Wollongong plot.

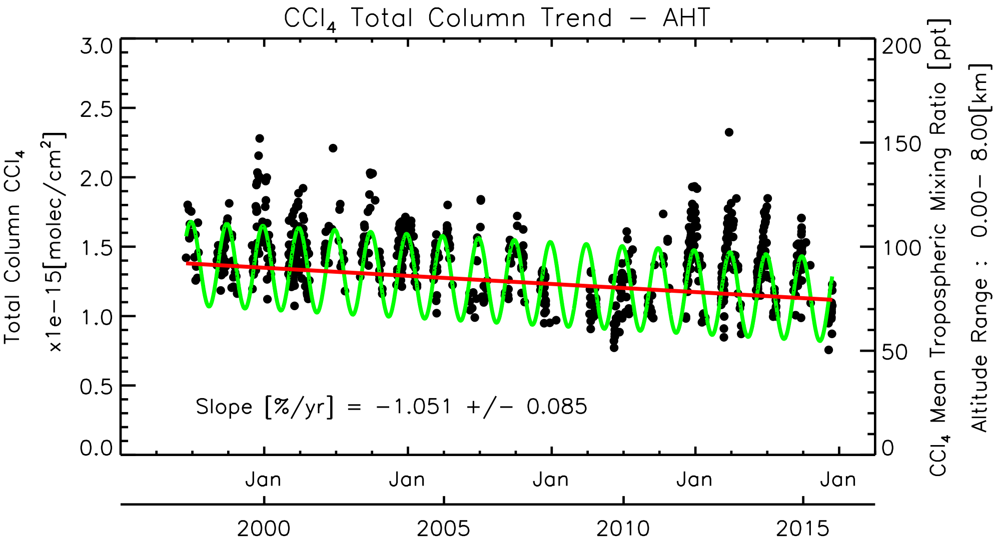

Figure 9: *CCl_4 Trend from Arrival Heights all data version: dofs 0.8.*

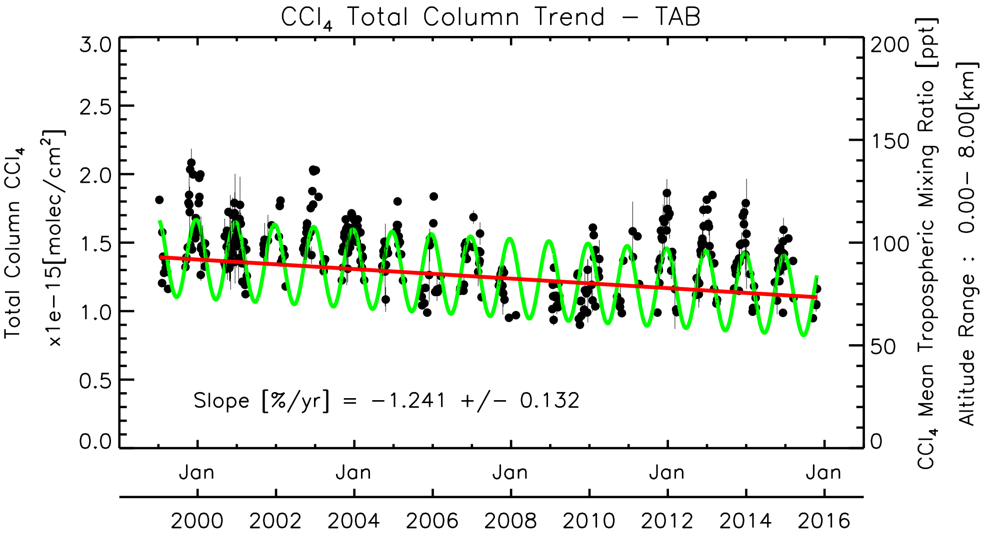

Figure 10: *CCl_4 Trend from Arrival Heights same dataset 3 day average.*

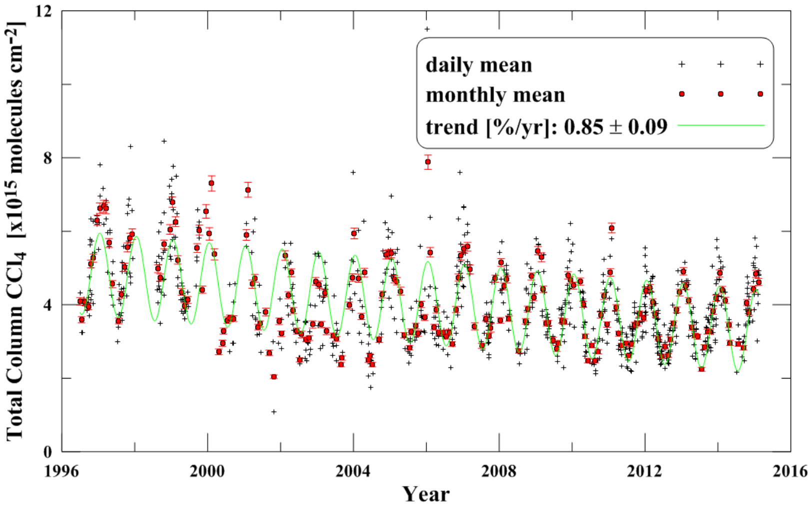

Figure 11: *CCl_4 initial Wollongong plot.*

1.2 Annual Cycle

Annual cycles varied widely from the initial 4 data series (and MLO & LDR which we did not present). We will work with SLIMCAT to get comparable model results for all sites. But we already have the WACCM a priori data and can use this as a first test. We can also use CC_2F_2 retrievals to compare to the CCl_4. We believe these should behave the similarly for all sites given long lifetimes, inert in the troposphere and primarily photolytic destruction in the lower-middle stratosphere. The assumption may more or less valid to the extent of the effect of the rapid fall off in the stratosphere in CCl_4 that is not reproduced in CC_2F_2 (see Fig 12). Also GMI modeled data will be forth coming.

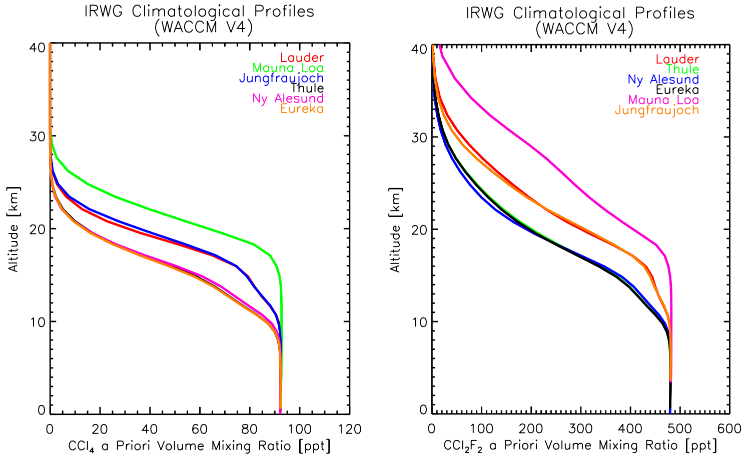

Figure 12: *CCl_4 profiles (left) and CC_2F_2 (right) from the WACCM a priori climatology for several sites (sorry for colors...).*

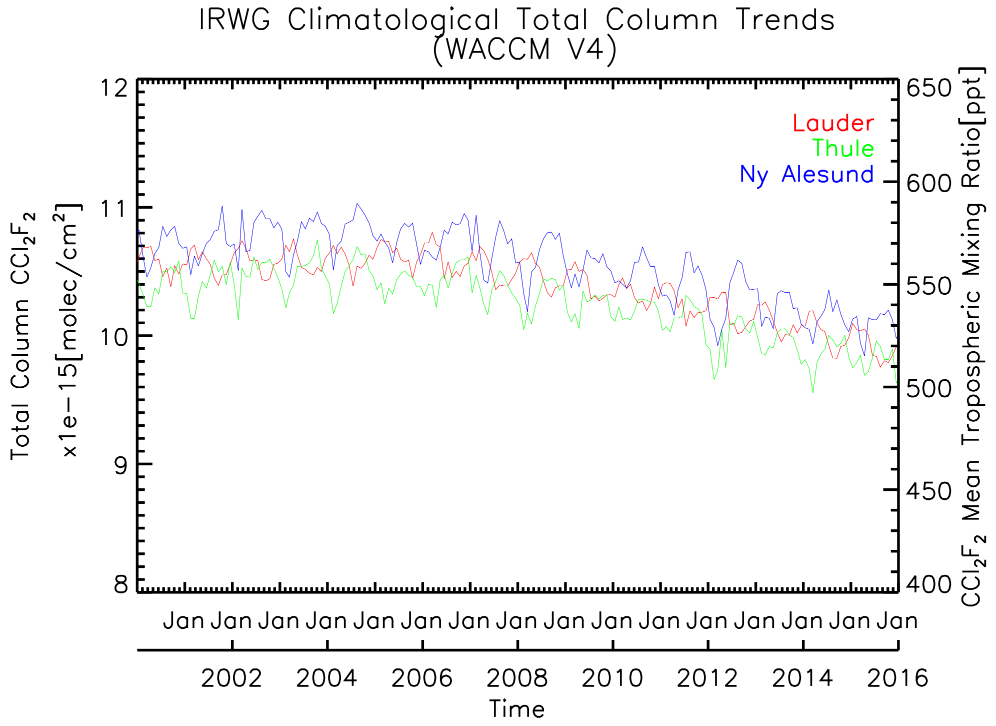

Figure 13: *CC_2F_2 trends for a couple sites from the WACCM a priori climatology.*

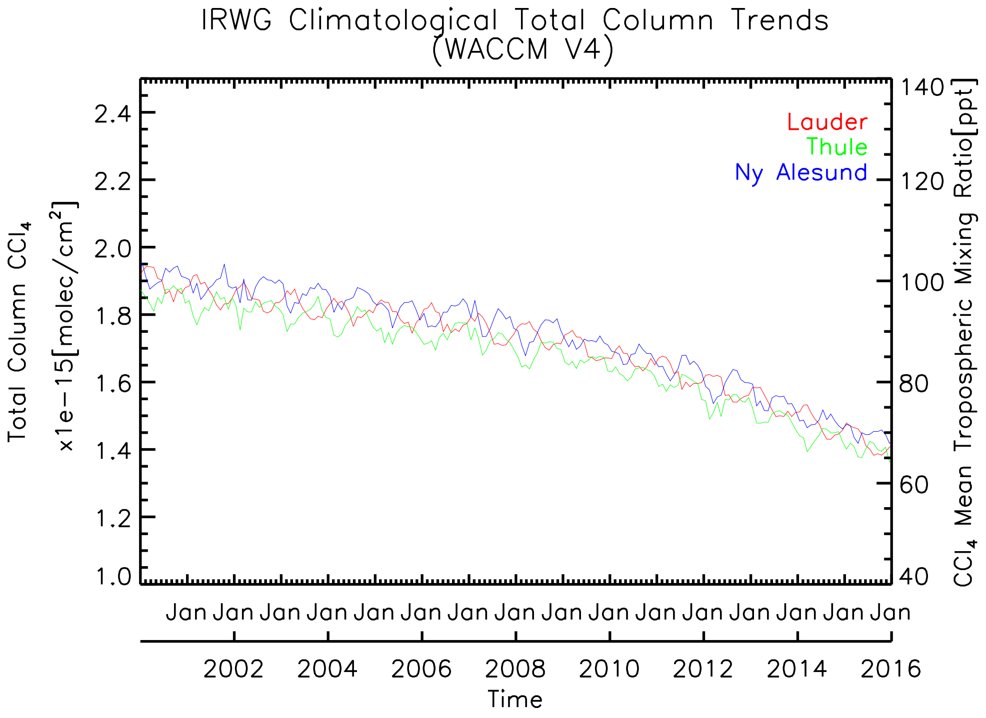

Figure 14: *CCl_4 trends for a couple sites from the WACCM a priori climatology.*

46 Figures 13 and 14 are total column trends integrated from the WACCM V4 (*IRWG* V6) a priori data set.

These are monthly mean columns from the observation site using the WACCM p-T-VMR curves from 1980 - 2020. On the right are scales for a mean mixing ratio from 0 - 10 [km] appropriate for the column range on the left calculated from the average p-T-VMR of the dataset. It may be that we should better fit a 2^{nd} order polynomial rather than a linear trend. The tropospheric mean mixing ratio $\overline{vmr_T}$ is determined by Eqn. (1) where vmr_z and n_z are the mixing ratio and number density at altitude z respectively. This or a similar calculation for xCCl$_4$ can be used.

$$\overline{vmr_T} = \frac{\int_{z=0}^{10km} vmr_z * n_z}{\int_{z=0}^{10km} n_z} \tag{1}$$

Both species show a annual cycle (by eye) of 5% with Lauder data being 6 months out of phase with the Arctic time series. *(we will include the other sites soon).*

Figure 15 shows the Thule data overlaid with the WACCM model monthly sample.

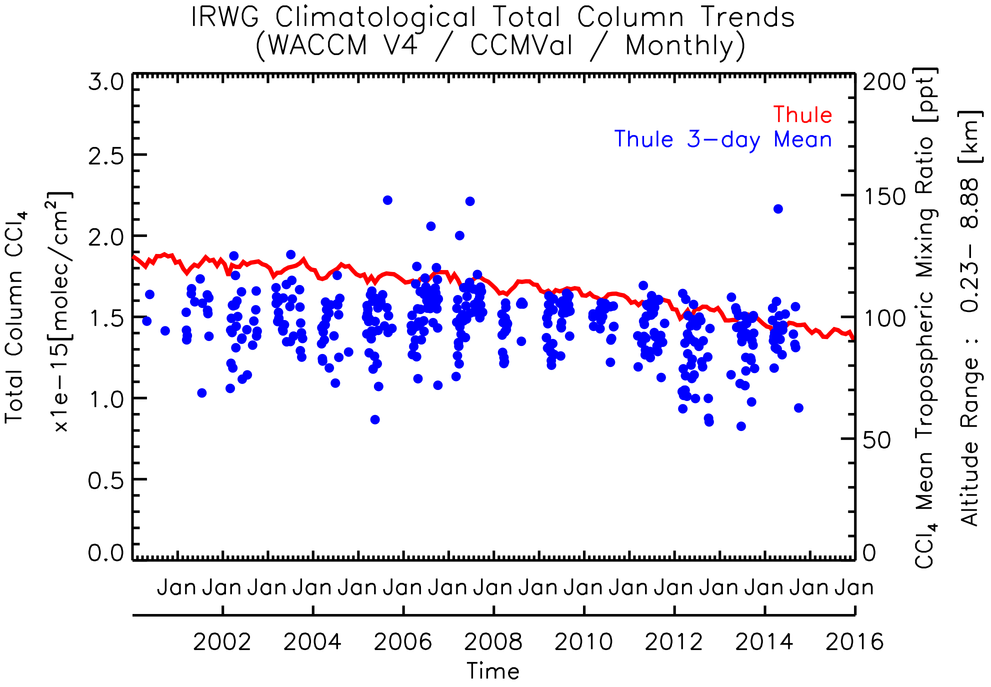

Figure 15: *Thule data overlaid with the WACCM monthly model.*

To evaluate possible bias in the stratospheric component of the two different species Fig 16 shows both ACE zonal retrieved profiles with representative sites for CCl$_4$ at least. ACE looses sensitivity below 7-8 km but above in the lower stratosphere profiles are reasonable close except for maybe Arrival Heights. No screening for polar vortex / descent has been done.

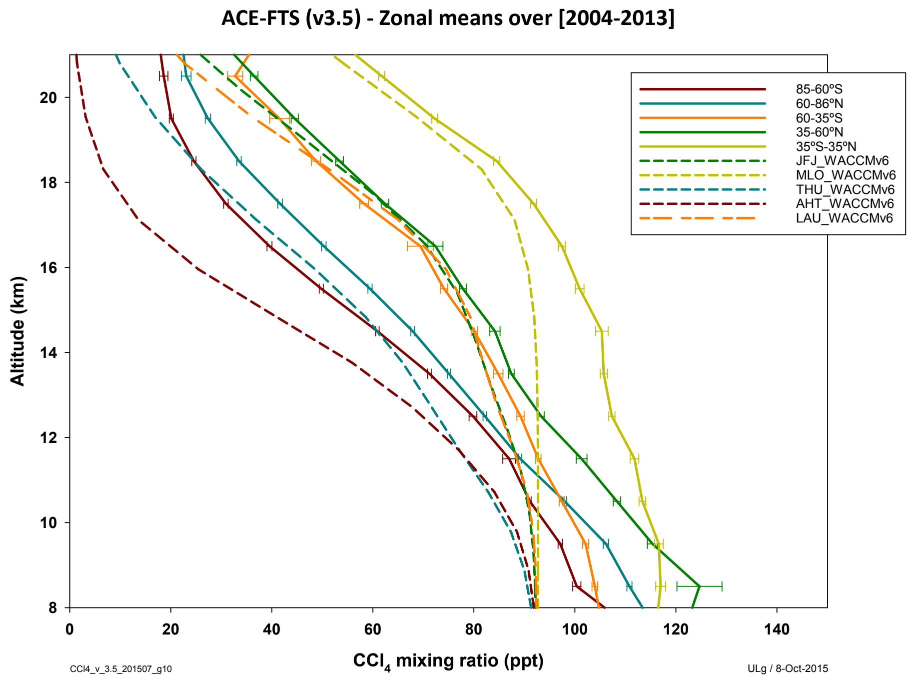

Figure 16: *Zonal mean ACE CCl_4 profiles and WACCM a priori climatology for representative sites.*

1.3 Water Vapor

There is a strong deep and wide H_2O interference directly overlaid with the CCl_4 absorption feature. Care needs to be given to this in all phases of efforts to improve the retrievals. H_2O variability is large 2 orders of magnitude. Fig 17 shows the time series of water vapor total column a priori and retrieved during the CCl_4 retrieval process.

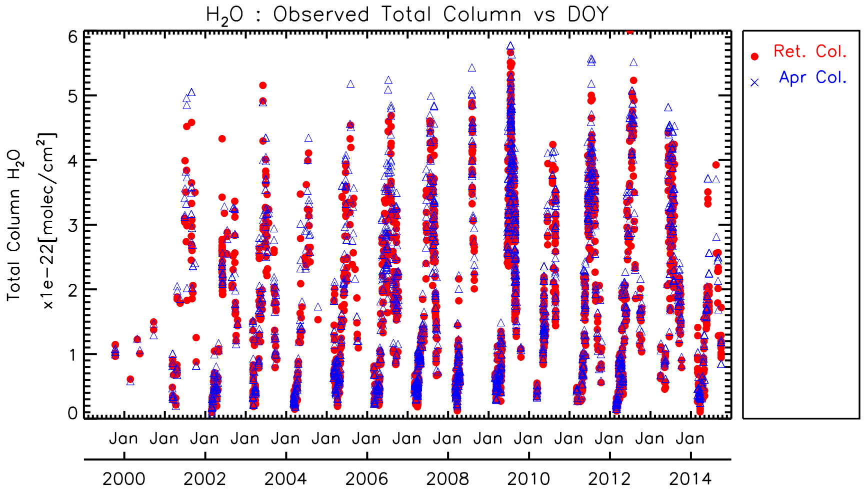

Figure 17: *Time series of water vapor a priori and retrieved during CCl_4 retrieval process from TAB.*

To see this effect we compared independently retrieved H_2O columns with the column retrieved during the CCl_4. Figure 18 shows a correlation plot for TAB and EUR.

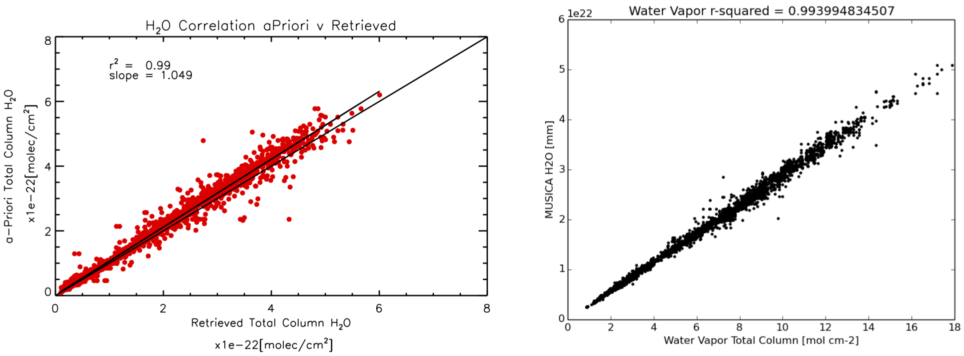

Figure 18: *H_2O retrieval correlations for TAB (left) and EUR (right).*

In the case of TAB this is the a priori H_2O that was pre-retrieved and is the nearest in time after retrieval. For EUR this is MUSICA H_2O for the nearest in time retrieval always less then 1 hour. There is a small bias at TB that needs to be investigated. Similar plot for JFJ also shows general independence from water vapor.

Regarding trends and/or any influence from water vapor Fig 19 shows the time series ratio of the independent to retrieved H_2O column for TAB. Similar plots for JFJ show largely consistent spread of ratios mostly confined to ± 5%.

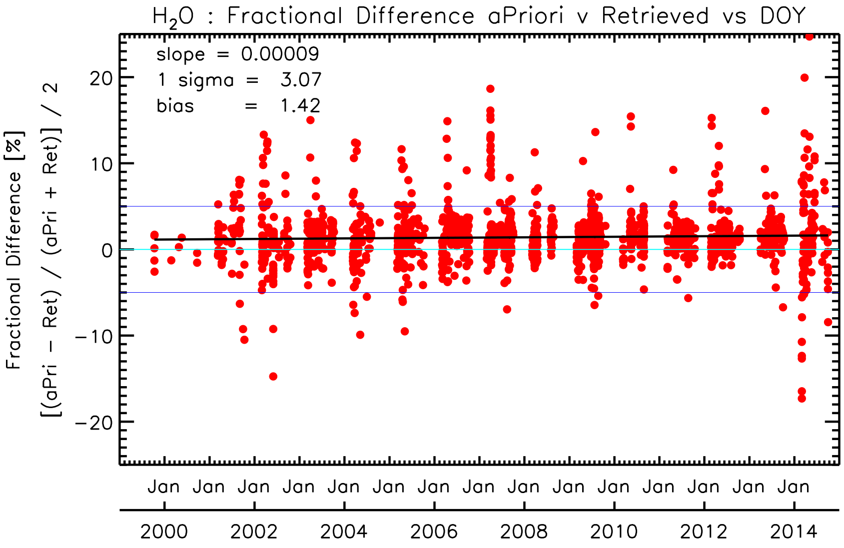

Figure 19: *Time series of the ratio to a priori to CCl_4 retrieved H_2O columns for TAB.*

Correlations with water vapor and linemixing. MP investigated the interplay of the retrieved H_2O and CCl_4 columns with and without employing linemixing for CO_2. This illustrates the need to account for linemixing and also resolve interference correlations.

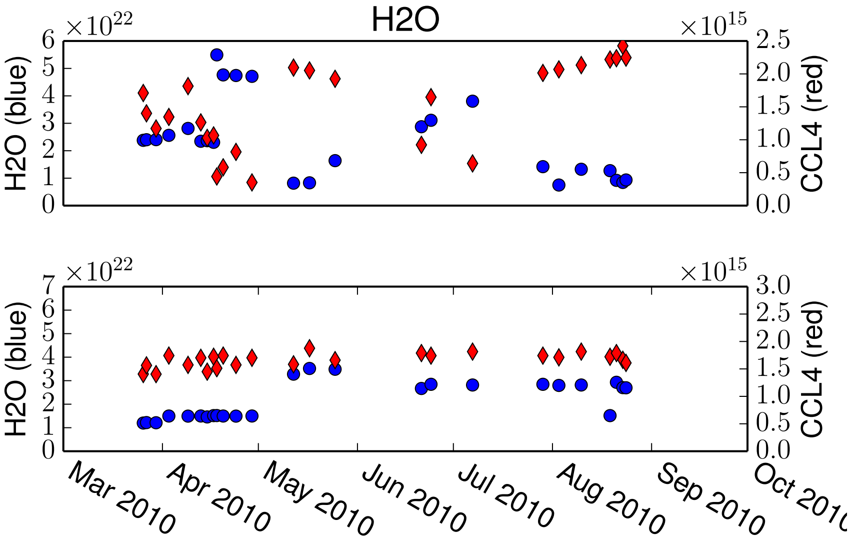

Figure 20: *Test on the effect on CCl_4 and its correlation with H_2O retrieved columns when not employing CO_2 linemixing calculations in the forward model (top) and when employing linemixing (bottom). This is for one year of NYA spectra.*

1.4 Calculated Tropospheric Offset

There is a difference between what in situ measurements provide and our conversion from column to a mean tropospheric value. This may come to adopting an appropriate calculation methodology or possibly revised line parameters from new cross-section data. This latter option TBD in the next 6 months. This *should* be below our error bars. We can test this with comparisons of $\overline{vmr}_T$ or $xCCl_4$ with in situ measurements. This can be done at JFJ and MLO for finite timeseries.

1.5 Errors

We need to explore the space of error sources with SFIT4. Apply appropriate S_b values. This *should* reconcile with JFJ estimates in **?**.

2 Components to Next Address

Plan to build on the tests we have done to converge on a useful retrieval for *IRWG* sites and SPARC science.

Retrieval Components

1. It appears the choice of $\mathbf{S_a}$ and possibly other retrieval parameters will effect the annual cycle (inferred by the large difference between TAB and the other Arctic sites). The cycle ought to be similar to CC_2F_2, as its long lived, inert in troposphere falls off in stratosphere similarly etc. So we should retrieve CC_2F_2 with a similar $\mathbf{S_a}$, SNR, interferences etc. and compare.

   (a) Manu to send a binput as a starting place.

2. Come to agreement on choice and amplitude of errors on parameters. We need to test these to determine the largest / most important. Some large ones are H_2O interference, other gas interference (maybe PAN see below), line parameters (creation of cross-sections and the conversion to pseudolines), zero offset, possibly shifts, smoothing, then usual ones temperature, SZA, measurement.

3. It would be nice to use the same linemixing code. Possibly de-weight $\mathbf{S_e}$ where the fit is poor.
   (a) Mathias to test JFJ spectra with SFIT4.

4. We must be sure all other HITRAN lines are same.
   (a) MLO, TAB, EUR use *IRWG* standard HIT08
   (b) At JFJ it is HIT00 (CO_2) and HIT04 for others
   (c) Maybe try Geoff's ATM list?

5. We all use NCEP p-T from the NDACC site.
   (a) If some other is used it must be shown it is always the same.

6. We use as close as is possible the same $\mathbf{S_a}$ for a given gas (CCl_4 or interfering) at all sites. Same for choice of column or profile retrieval for interfering species

7. Sigma values of other retrieved parameters should be the same (phase, curvature etc.)

8. Use WACCM apriori profiles.
   (a) Pre retrieve H_2O.

9. We think H_2O is the driver for difficulties retrieving at sea level.
   (a) Nicholas will explore with WLG retrievals

Further Details

1. New cross section data for CCl_4 may be available sometime in the not too distant future.

2. This retrieval is at/near the limit of detection, near the combined fall off of *IRWG* filter 6 and the MCT detector. It seems very susceptible to changes in detector, filter, instrument stability etc.
   (a) MLO: We will continue to look MLO data but especially early data may not be useful.
   (b) LDR: We would like to use this even if only the 120HR era. We hope some time can be spent here.
   (c) For both these sites averaging data may help get some useful data points. In looking for 10+ year trends one value / month is more than adequate.

3. Still need to acquire spectroscopy error values for interfering species from HIT08.

4. PAN - Thomas von Claremon (MIPAS) and Jeremy Harrison (ACE) believe this may interfere. (of course they have limb spectra). It is a very broad feature. I did not think it would in our spectra since we could never see it when looking directly.
    (a) But we can test, likely we need some high *SNR* spectra to make it worthwhile..

3 Evaluations

We need to systematically evaluate many components. Being careful to use appropriate equivalent $\mathbf{S_a}$ for each site (ie altitude grid).

Path Forward

1. Pick two years to focus on as a group optimizing parameters & a strategy we can all use that gives good results for both CCl_4 and CC_2F_2, 2009, 2010.
2. Look at only SZA 50-90°.
3. SNR, ideally we use the actual noise value. If not, it ought to be appropriate to your site and not over or under constrain the retrieval.
    (a) Will need to test for trend and annual cycle of any possible over / under fitting.
    (b) Test de-weighting at the still poorly fit q branch.
    (c) Test de-weighting of the H_2O line cores.
        i. We noted that Jeremy Harrison (ACE) was only fitting segments of this 15 wavenumber range avoiding LM and H_2O.
4. Error: use diurnal variation to test noise levels & compare with OE estimates.

4 Appendix

Contacts:

References

Gardiner, T., Forbes, A., de Mazière, M., Vigouroux, C., Mahieu, E., Demoulin, P., Velazco, V., Notholt, J., Blumenstock, T., Hase, F., Kramer, I., Sussmann, R., Stremme, W., Mellqvist, J., Strandberg, A., Ellingsen, K., Gauss, M., 2008. Trend analysis of greenhouse gases over europe measured by a network of ground-based remote ftir instruments. Atmospheric Chemistry and Physics 8 (22), 6719–6727.
URL `http://www.atmos-chem-phys.net/8/6719/2008/`

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