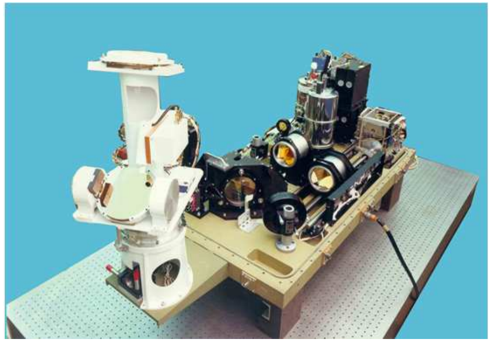

MkIV/JPL Site Report

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Not a primary NDACC site, but dataset is still potentially useful

MkIV is now 31 years old, still with original KBr beamsplitter/compensator.

Instrument covers entire 650-5650 cm^{-1} region simultaneously (no filters) at 0.005 cm^{-1} resolution (117 cm MOPD) for ground-based obs.

~1100 days of ground observations, 23 balloon flights, and 30+ aircraft flights.

Ground-based dataset has many interruptions due to balloon/aircraft campaigns

NDACC-IRWG / TCCON meeting June 2015

New MkIV ground-based dataset

A single file covering 30 years, 12 measurement locations, 26 gases

Re-analysis covers 1985 to 2014 time period with ~1100 observation days

3300+ observation (HgCdTe + InSb spectral pairs) covering 650 to 5650 cm^{-1}

12 measurement locations from 78S to 68N are included in single file

All data measured with same instrument (BS, detectors, etc) and analyzed with the same GGG/TCCON methodology (I2S, GFIT, ATM15 linelist, etc)

Profile scaling retrievals of 26 gases: H_2O, CO_2, O_3, N_2O, CO, CH_4, NO, NO_2, NH_3, HNO_3, HCL, HF, OCS, H_2CO, $ClNO_3$, HCN, CCl_2F_2 COF_2, C_2H_6, C_2H_6, N_2, $CHClF_2$, HCOOH, HDO, SF_6, C_3H_8

Dataset submitted to NDACC archive. Also available from: http://mark4sun.jpl.nasa.gov/ground.html

MkIV ground-based dataset

mark4sun.jpl.nasa.gov/ground.html

JPL

Ground-Based Observations

Between balloon and aircraft campaigns, the MkIV instrument is used to make ground-based observations. Although these measurements lack the vertic observations can nevertheless be made much more frequently - MkIV has averaged over 50 days of observation per year recently. Ground-based observations Earth's atmosphere is changing, which is the main purpose of NDACC.

MkIV Ground-based Vertical Column Abundances

Individual Column Abundances: (85 columns, 3939 rows) m4_avg_1985_2014.vav
Individual Column Abundances: (Ames-1001 format) m4_avg_1985_2014.vav.ames — Column observations
Daily Average Column Abundances: (85 cols, 1027 rows) m4_avg_1985_2014.vad — Daily Averages
List of windows: (242 rows) all_mols_mir_1985_2014.gnd
Window-to-window biases: m4_avg_1985_2014.vav.cew

Observation Locations (sorted by latitude)

Location	Key	Nobs	Latitude (deg.)	Longitude (deg.)	Altitude (km)
Esrange, Sweden	ESN	160	+67.889	+21.085	0.271
Ft Wainwright, Fairbanks, Alaska	FAI	124	+64.830	-147.614	0.182
Lynn Lake, Manitoba, Canada	LYL	20	+56.858	-101.066	0.354
Mt. Barcroft, California	MTB	1369	+37.584	-118.235	3.801
ARC, Mountain View, California	ARC	7	+37.430	-122.080	0.010
Daggett, California	DAG	33	+34.856	-116.790	0.626
Ft Sumner, New Mexico	FTS	172	+34.480	-104.220	1.260
TMF, Wrightwood, California	TMF	475	+34.382	-117.678	2.257
JPL B183, Pasadena, California	JPL	758	+34.199	-118.174	0.345
JPL Mesa, Pasadena, California	JPL	20	+34.205	-118.171	0.460
NSBF, Palestine, Texas	PAL	4	+31.780	-95.700	0.100
McMurdo, Antarctica	MCM	37	-77.847	+166.728	0.100

Nobs = Number of Observations; +ve Latitude = N; +ve Longitude = E

MkIV dataset is unique in the sense that the same instrument and analysis method has been applied to 12 different locations, minimizing site-to-site biases.

Site Report Conclusions

MkIV task funded thru 2016. Primary task is balloon flights, ground-based secondary

Successful balloon flight in Sep 2014. Next flight planned for September 2016.

Instrument continues to make high quality ground-based observations from JPL.

57 ground-based observation days in 2014 (despite balloon campaign).

Variety of measurement locations (12) provides a better evaluation of global models than could be achieved by a single fixed site, but detracts from trend detection.

MkIV data also useful for spectroscopy and window evaluation due to the wide simultaneous spectral coverage and diversity of measurement conditions (pressure, temperature, latitude).

Can NDACC measure Propane (C_3H_8) ?

Used MkIV ground-based spectra, together with GFIT code, to see whether propane could be measured.

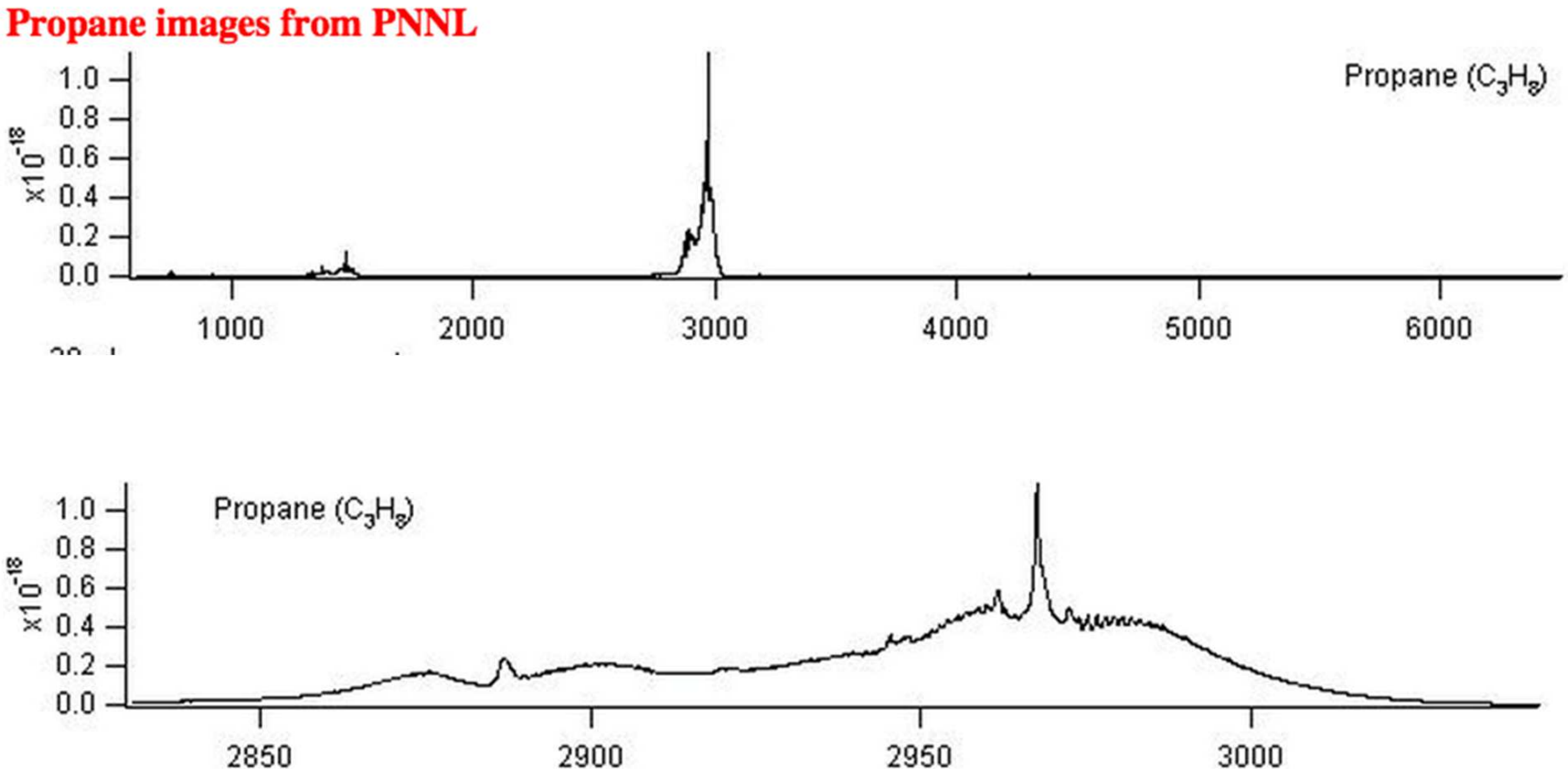
C_3H_8 spectroscopy: pseudo-line-list (PLL) based on lab measurements of Harrison & Bernath [2010]. PLL available from: http://mark4sun.jpl.nasa.gov/pseudo.html
http://mark4sun.jpl.nasa.gov/data/spec/Pseudo/c3h8_pll_2560_3280.pdf

Other gases use 2015 version of atm.101 linelist (based on HITRAN 2012), except for C_2H_6 for which another PLL is used.

Main spectroscopic difficulties:

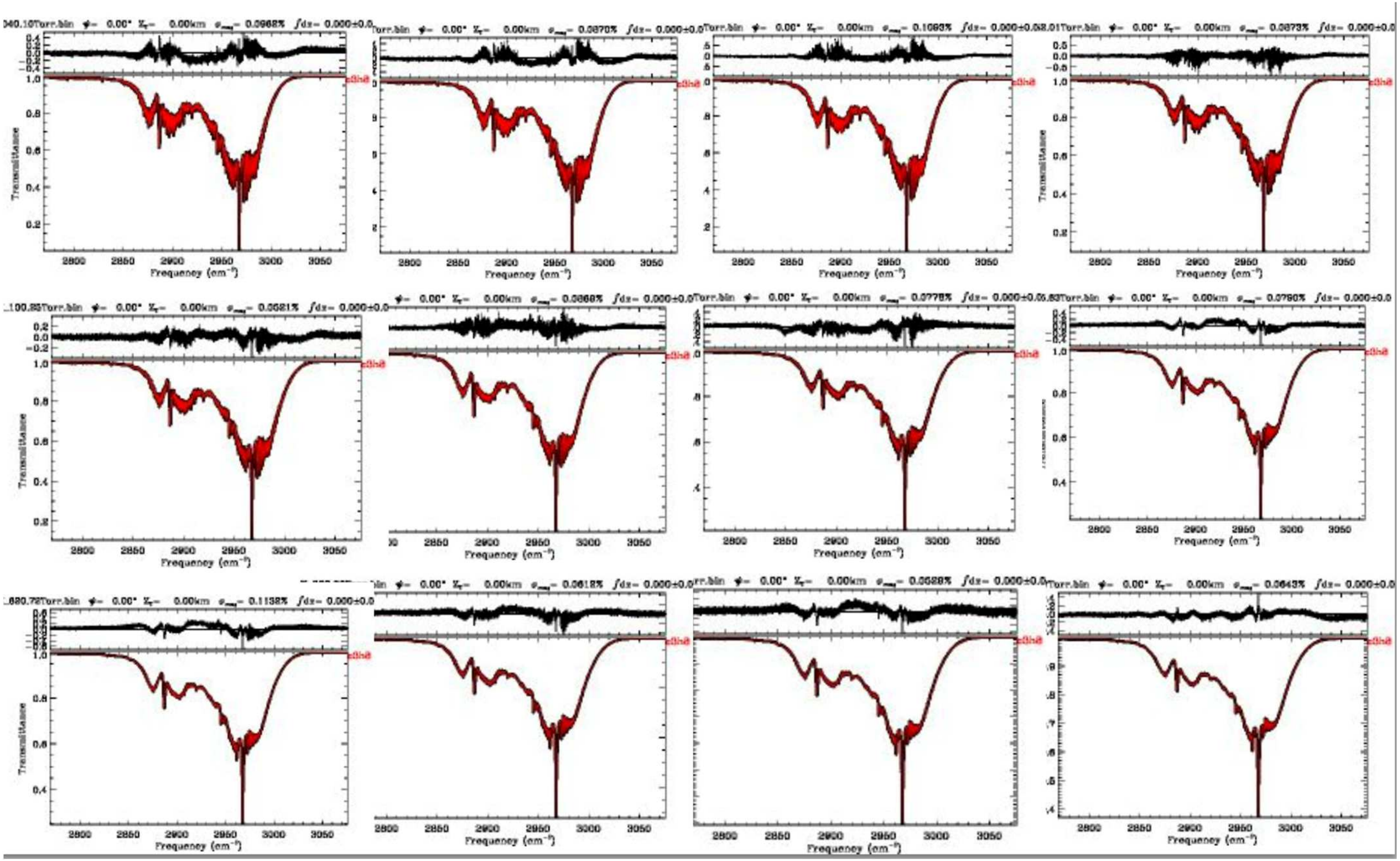
- strongest C_3H_8 absorption (unresolved Q-branch) is weak, featureless, and overlapped by much stronger absorption from H_2O, and CH_4
- absorption from HDO, C_2H_6 and solar lines is comparable with that from C_3H_8
- possible additional missing molecules with overlapping CH-stretch absorptions

PNNL Propane spectra

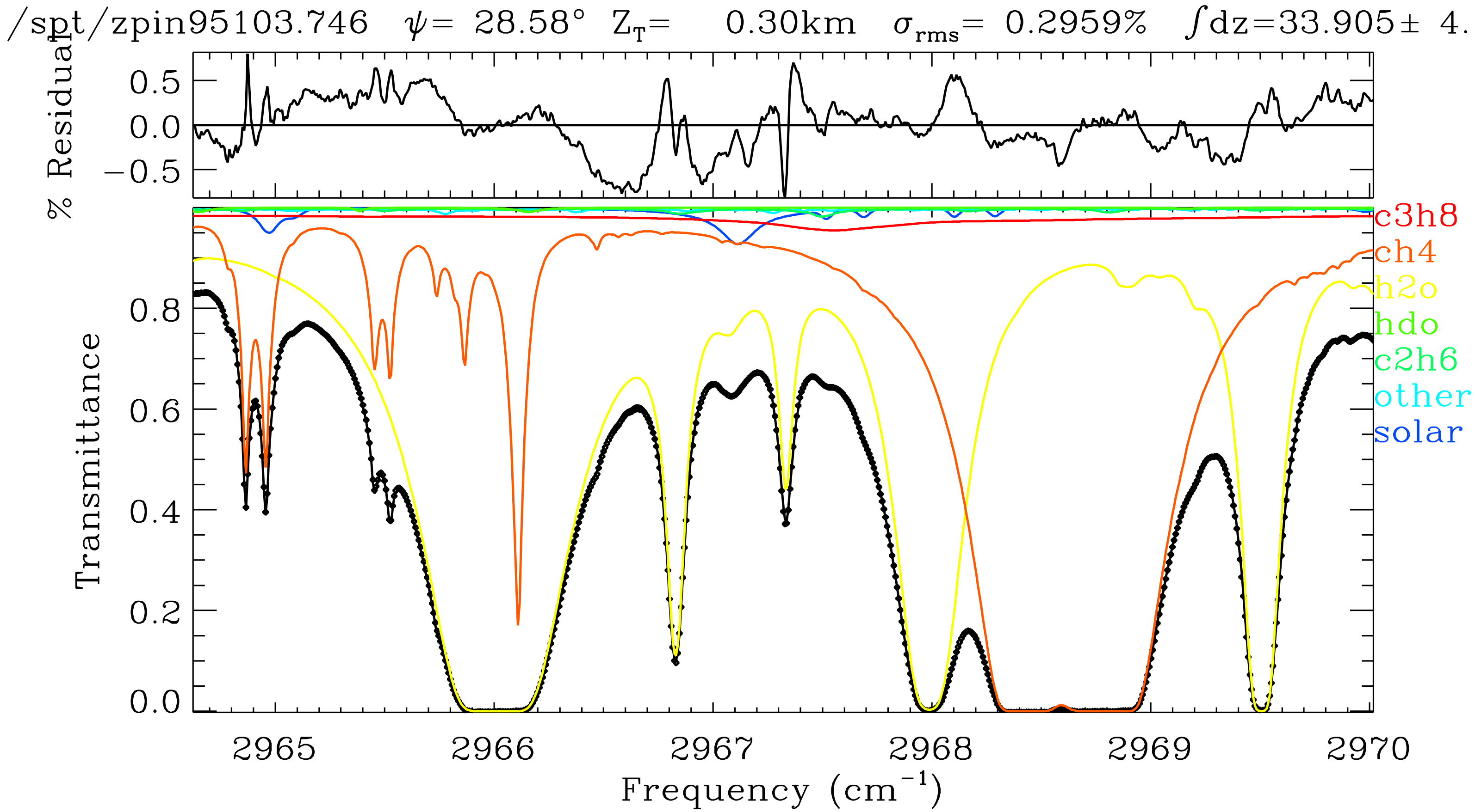


C-H stretch absorption band Q-branch at 2967 cm^{-1} is strongest and most distinctive feature

Fitting Harrison's lab C_3H_8 spectra with PLL

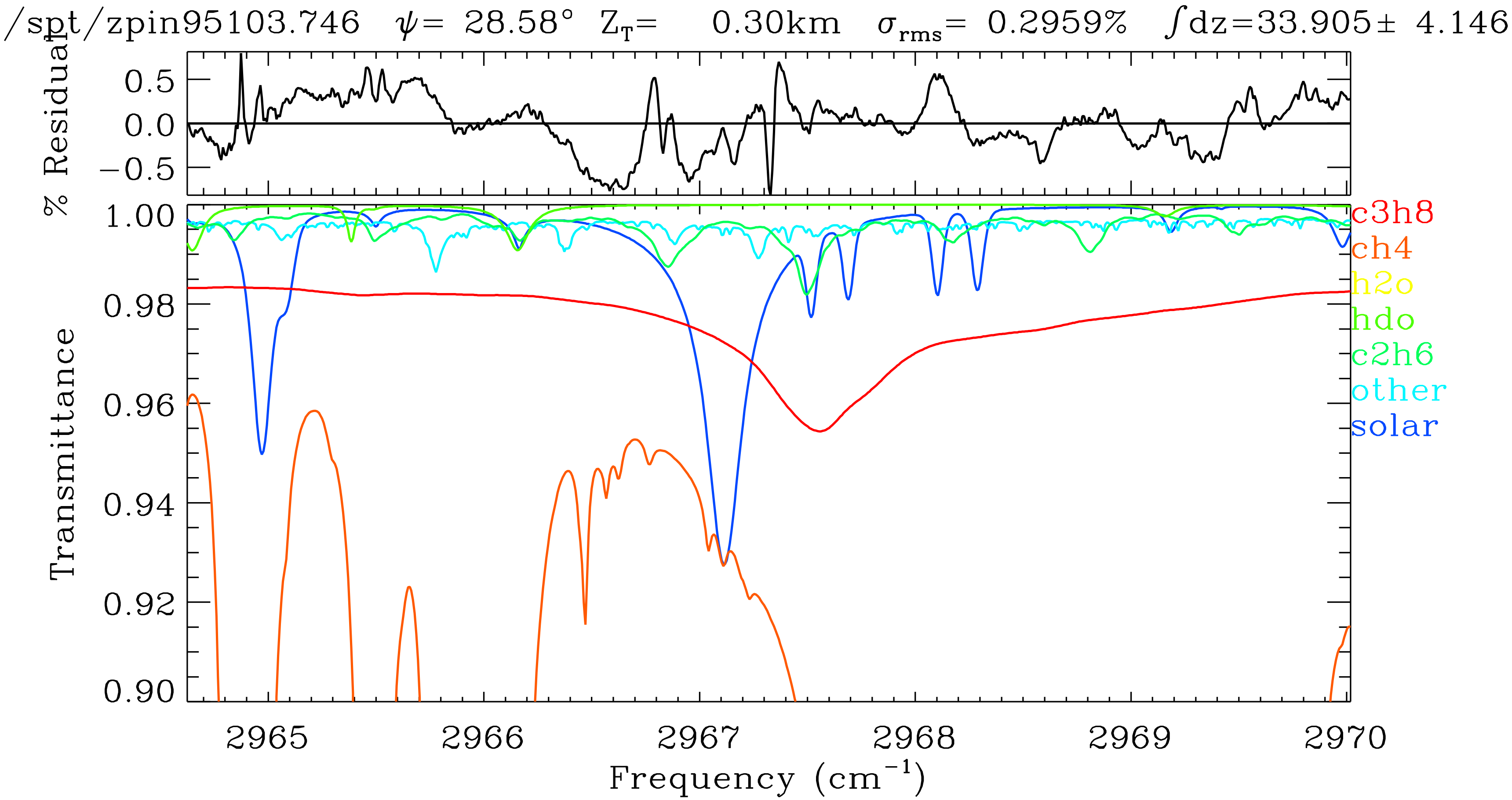


Example of ground-based MkIV Spectral fit



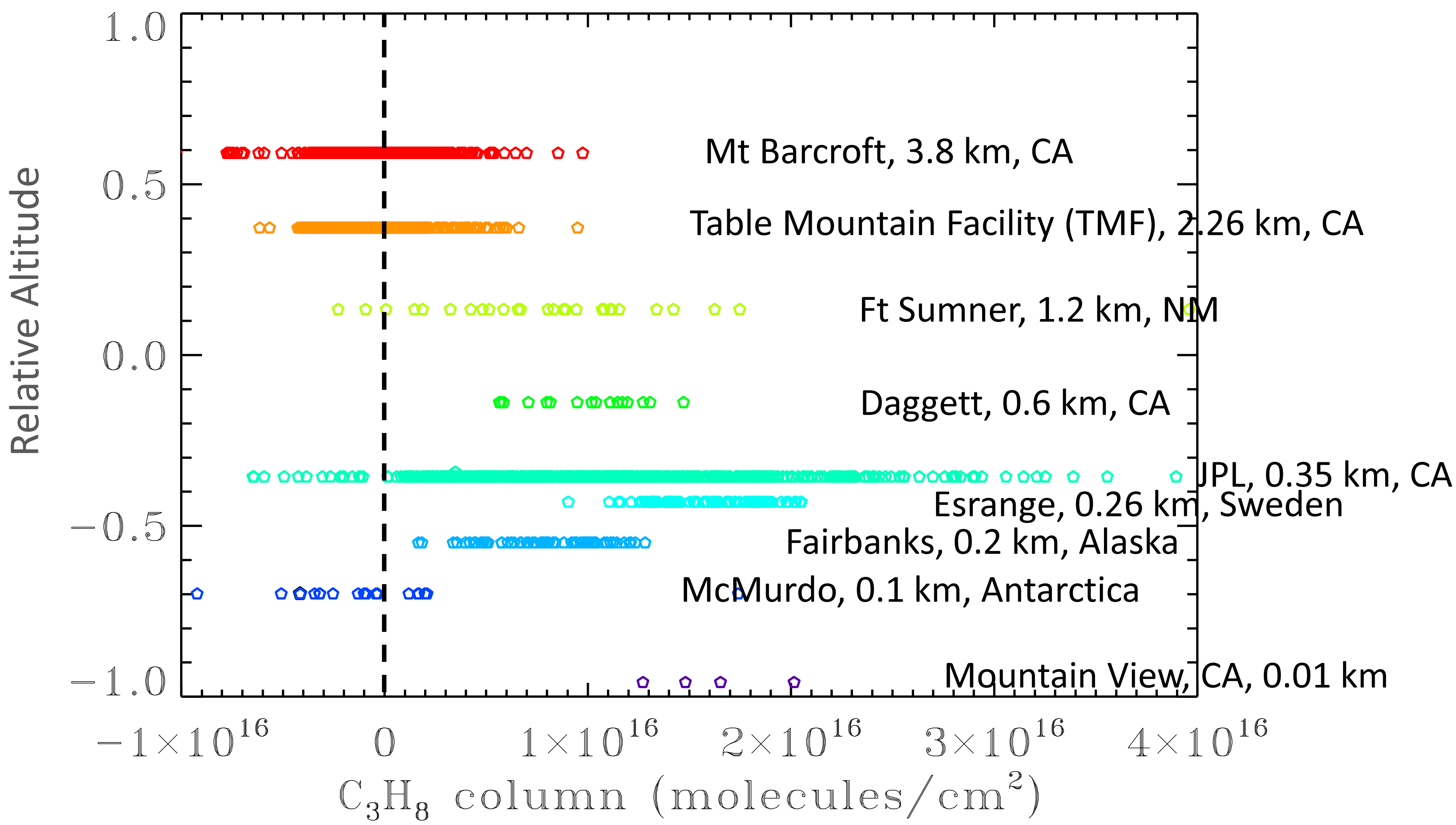
Fit to spectrum from JPL, April 13, 1995, with 3.4E+15 molecules/cm^2 of C_3H_8 retrieved.
C_3H_8 absorption (red) was 4% deep, but still dwarfed by the H_2O, CH_4 and solar features.
Anti-symmetric residual about H_2O line at 2966 cm^{-1} is persistent (neglect of line-mixing?)
Fitted window: 2967.32 5.40 20 1 1 0 cl ct fs so zo : c3h8 ch4 h2o hdo c2h6

Example of MkIV spectral fit: zoomed

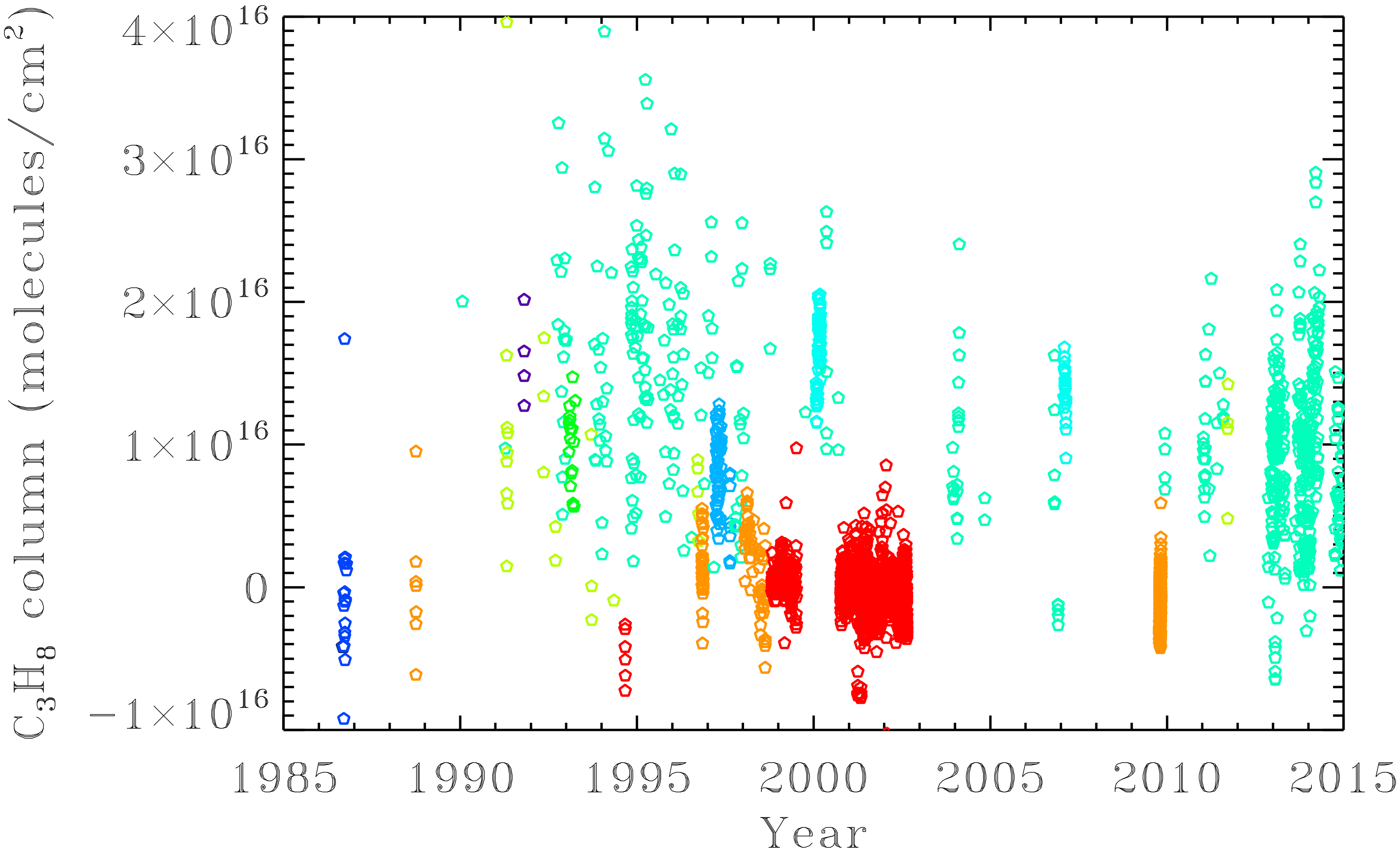


This case (April 13, 1995) represents one of the largest C_3H_8 column amounts. Although the peak absolute C_3H_8 absorption is 4%, its spectral variation is only 2% . Unfitted gases are labeled “other” and include O_3, CH_3OH, H_2CO, CH_3Cl.

Retrieved MkIV C_3H_8 column versus site altitude



Time series of MkIV C_3H_8 columns



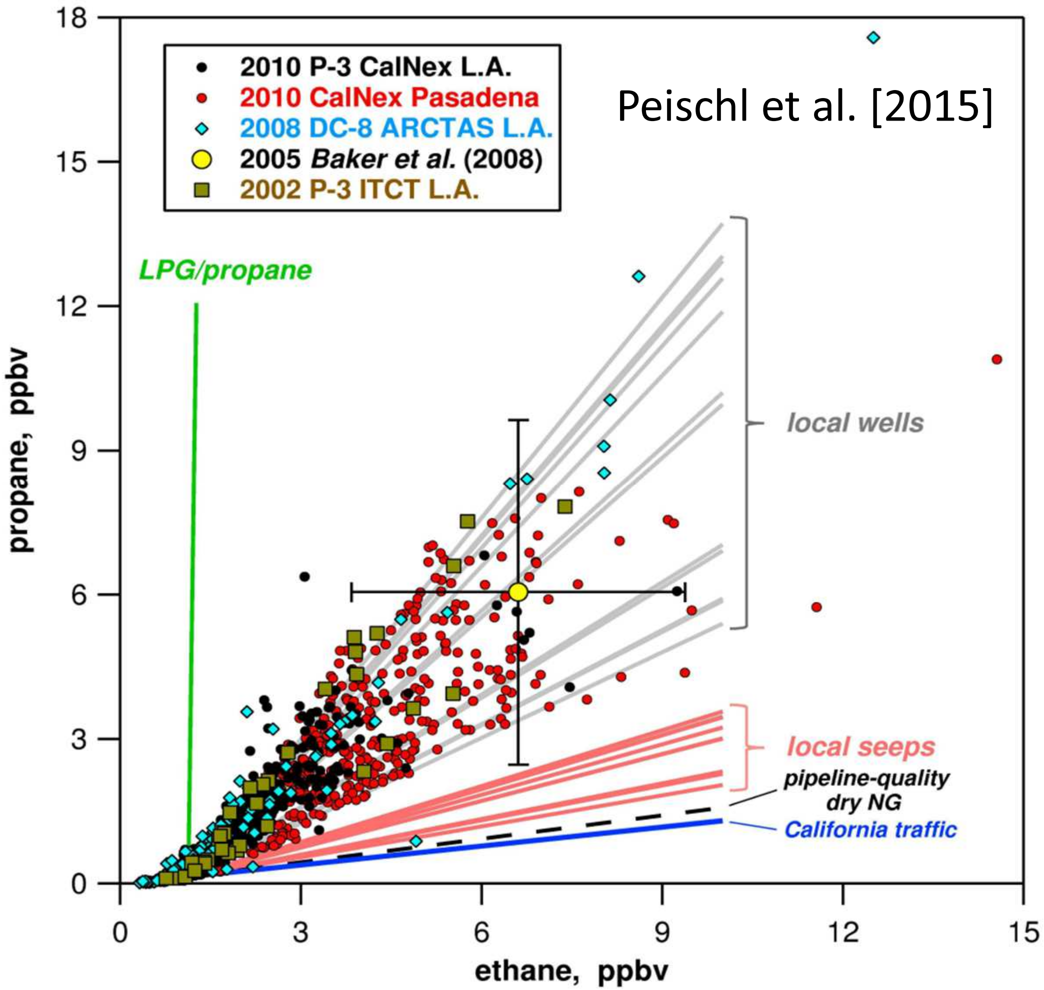
Comparison with in situ measurements

Figure (right) from Peischl [2015] shows in situ measurements of C_3H_8 over the Los Angeles basin, ranging from 0-7 ppb, with a mean value of around 2 ppb, occasionally 8 ppb.

MkIV C_3H_8 column measurements above JPL average 9E+15 molec/cm^2. Assuming that this is contained mostly within a 2 km thick PBL of 250 mbar pressure-thickness, this corresponds to 2.5 ppb in the PBL.

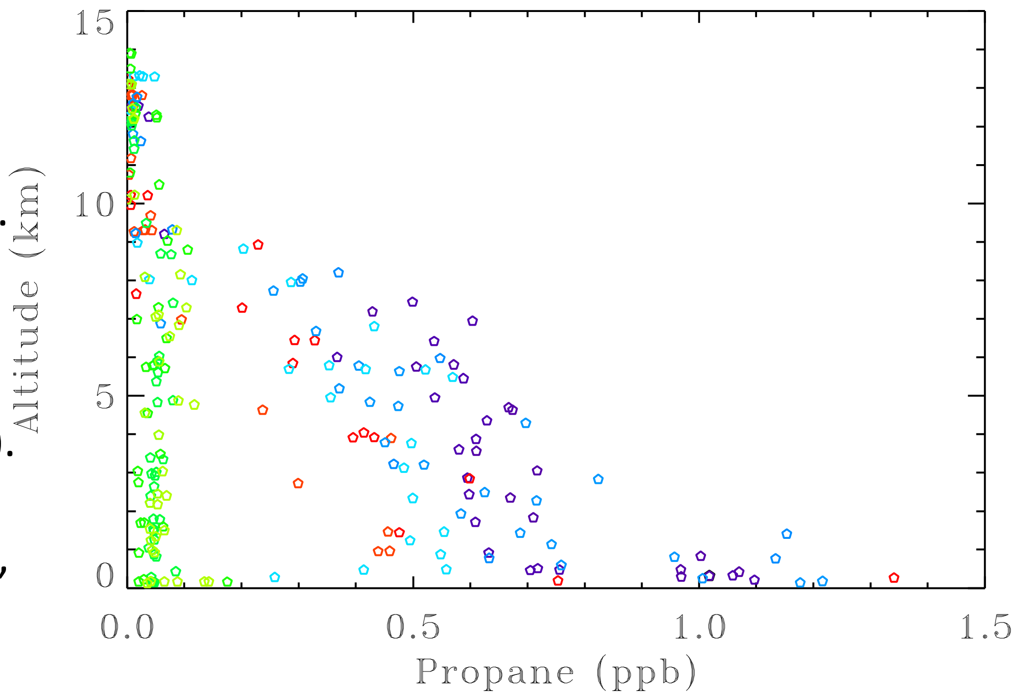
Appears to be reasonable consistency between MkIV column and in situ measurements over Los Angeles.

What about non-polluted sites?



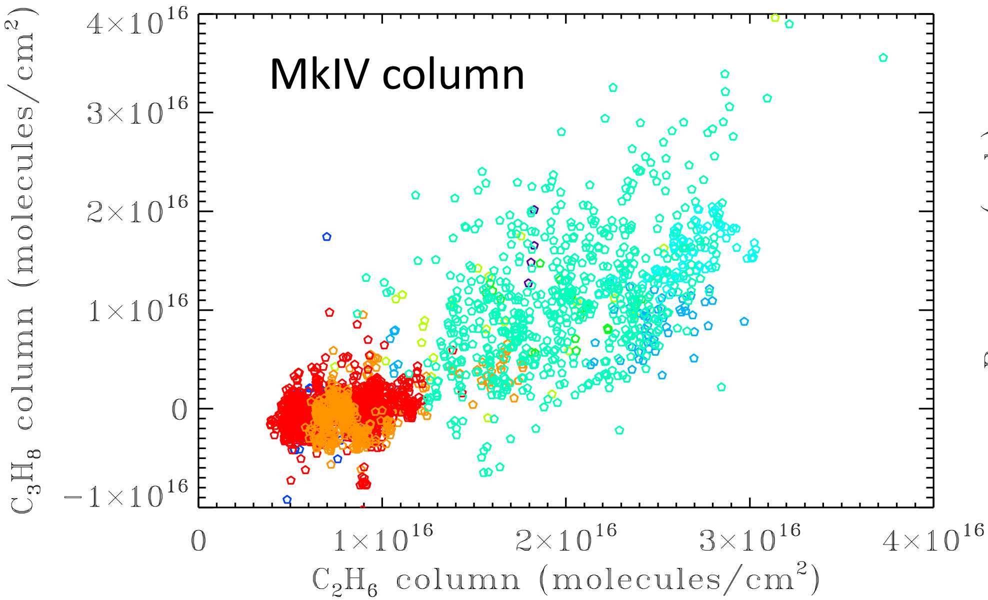
Comparison with HIPPO airborne in situ measurements measured 60-72N

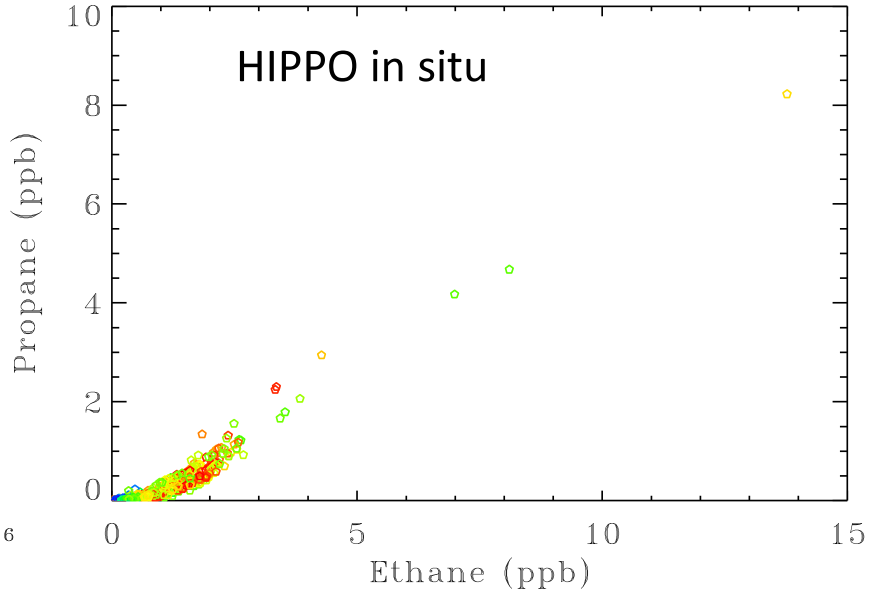
- In winter (purple) and spring (blue) C_3H_8 averages 0.7 ppb over the 0-8 km altitude range, which spans 1000 to 400 mbar, corresponds to a column of 8E+15.
- MkIV measured columns over Esrange (67N) averaged 15E+15. Perhaps the European sector of the Arctic is more polluted than the Alaskan sector (HIPPO).
- In summer (green) C_3H_8 vmrs < 0.1 ppm at all altitudes, implying column < 2E+15, contradicting MkIV summer obs from Fairbanks which average 8E+15.



MkIV measured consistently large C_3H_8 columns were at Esrange, Sweden (67N) in winter/spring, and at Fairbanks, Alaska (65N) in summer. Pollutants are known to build up during the Arctic winter due to proximity to sources and lack of OH destruction. More problematic is the summertime columns over Fairbanks, which average 8E+15.

$C_3H_8 - C_2H_6$ correlation





Since direct comparisons are unavailable, perhaps use C3H8/C2H6 correlation for validation

Good correlation between C_3H_8 and C_2H_6:
$C_3H_8 = 0.6 * (C_2H_6 - 7E+15)$
for all data gradient is steeper for JPL, less steep for Fairbanks & Esrange (blue).

In situ gradient similar to MkIV (0.6) for polluted cases, and smaller for less polluted cases.

Propane Summary/Conclusions

Liquid Petroleum Gas (LPG = Propane + butane)) is replacing kerosene as a heating source due to its clean burning. Leaks of LPG would therefore enhance propane relative to ethane.

MkIV ground-based measurements have been analyzed to determine C_3H_8 column amounts. In places where C_3H_8 is large (e.g. LA basin) there appears to be reasonable consistency between MkIV column measurements and in situ measurements.

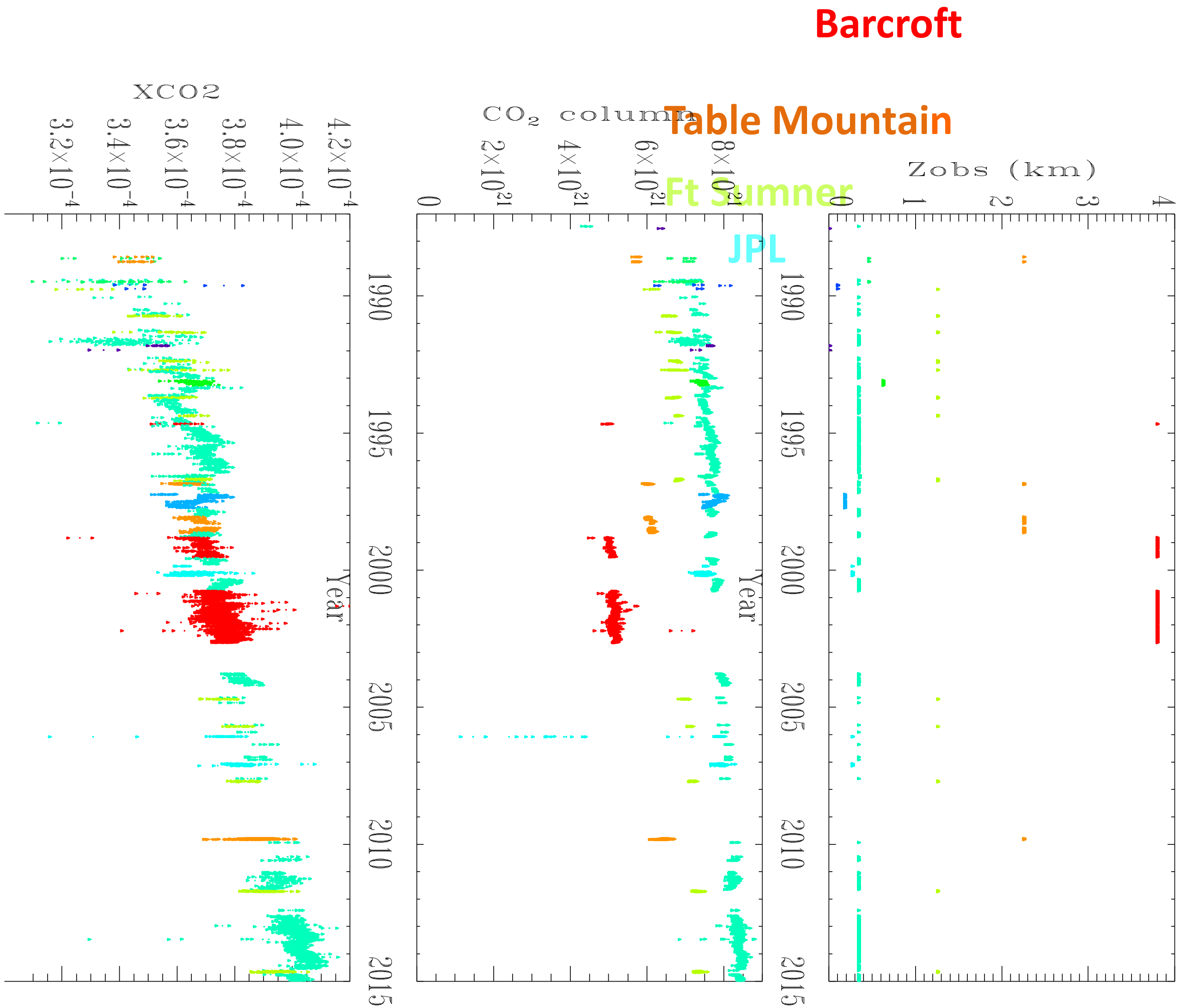
In places where in situ C_3H_8 is small (most notably Fairbanks in summer), the MkIV column measurements seems to over-estimate the column amount (unless Fairbanks is a strong local source of propane from LPG).

Or perhaps there is a spectroscopic issue in which other gases with C-H stretch absorptions are missing from linelist.

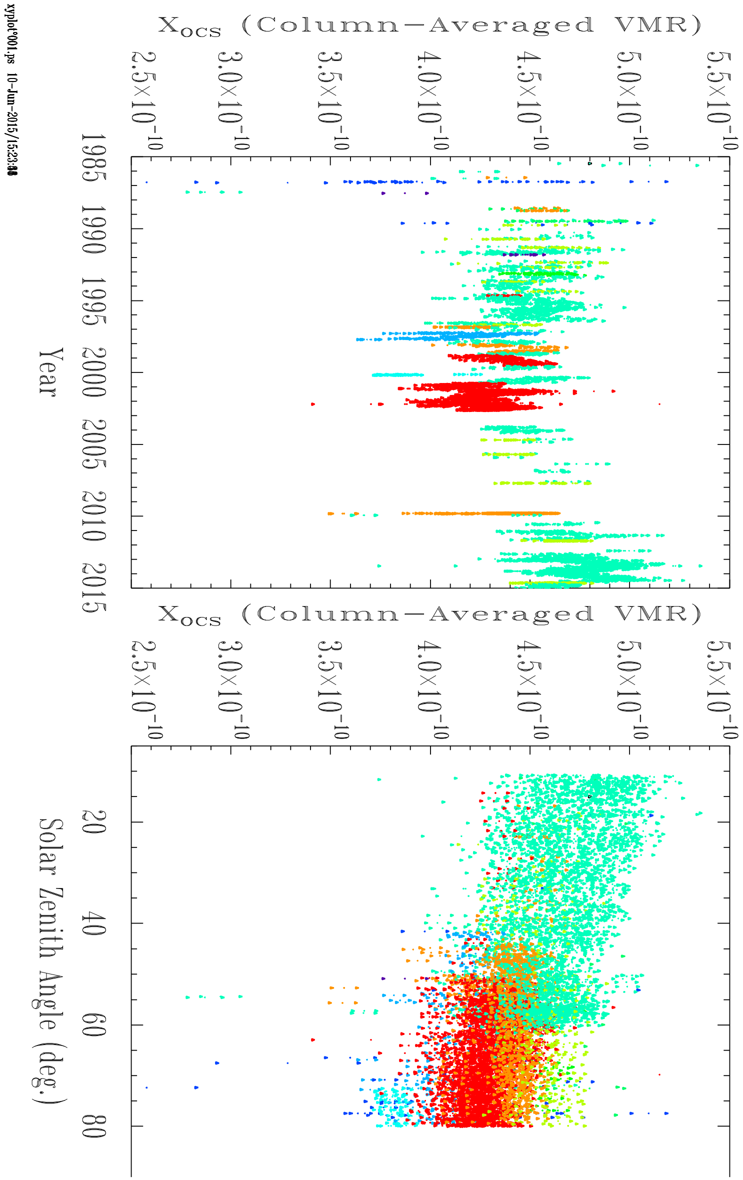
Or perhaps inadequacies in our ability to fit the interfering H_2O and CH_4 absorptions (e.g. neglect of LM) is causing a high bias in the retrieved C_3H_8 column, which is relatively small under polluted conditions (LA basin) but large under clean conditions (Fairbanks).

Yes, NDACC can measure propane in polluted locations with large C_3H_8 columns. Otherwise, it is currently difficult.

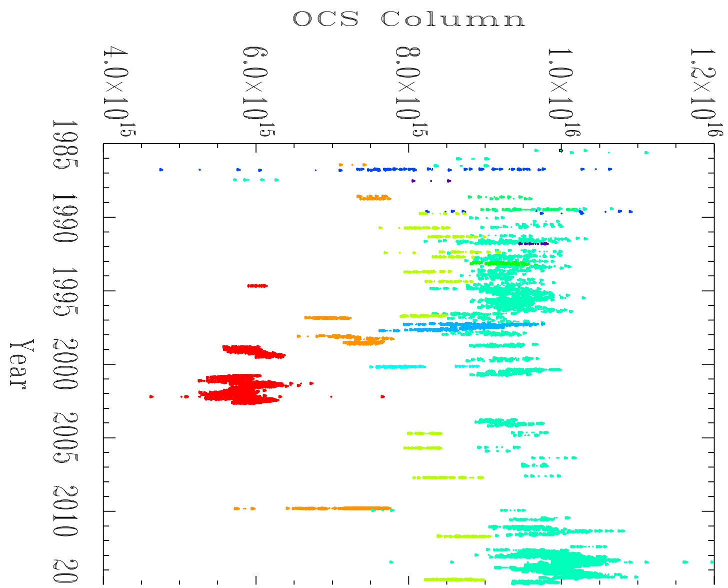
MkIV CO_2 Columns



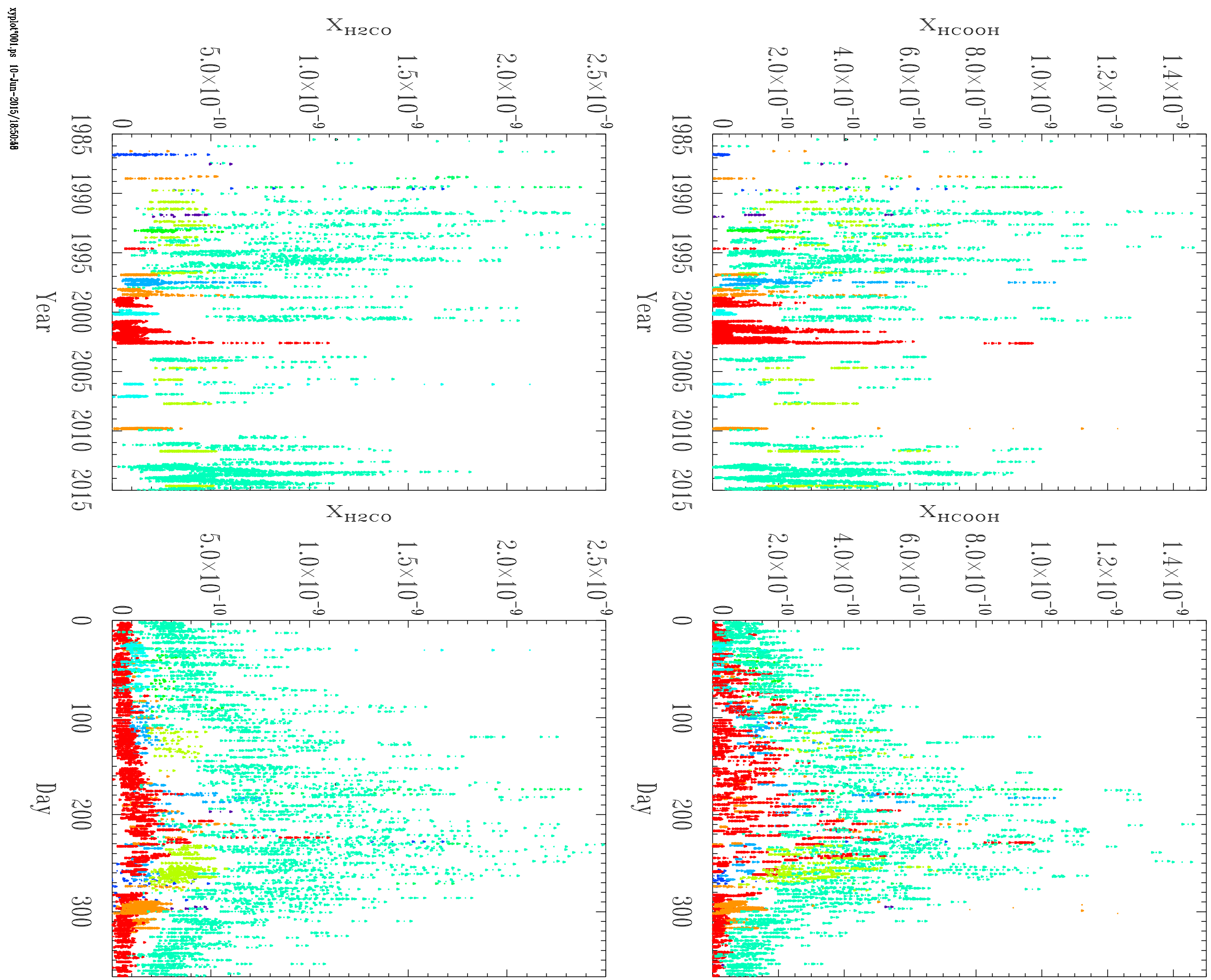
OCS



OCS exhibits a springtime maximum and autumn minimum.
Note also the large springtime variability compared with summer
Low values in polar winter vortices



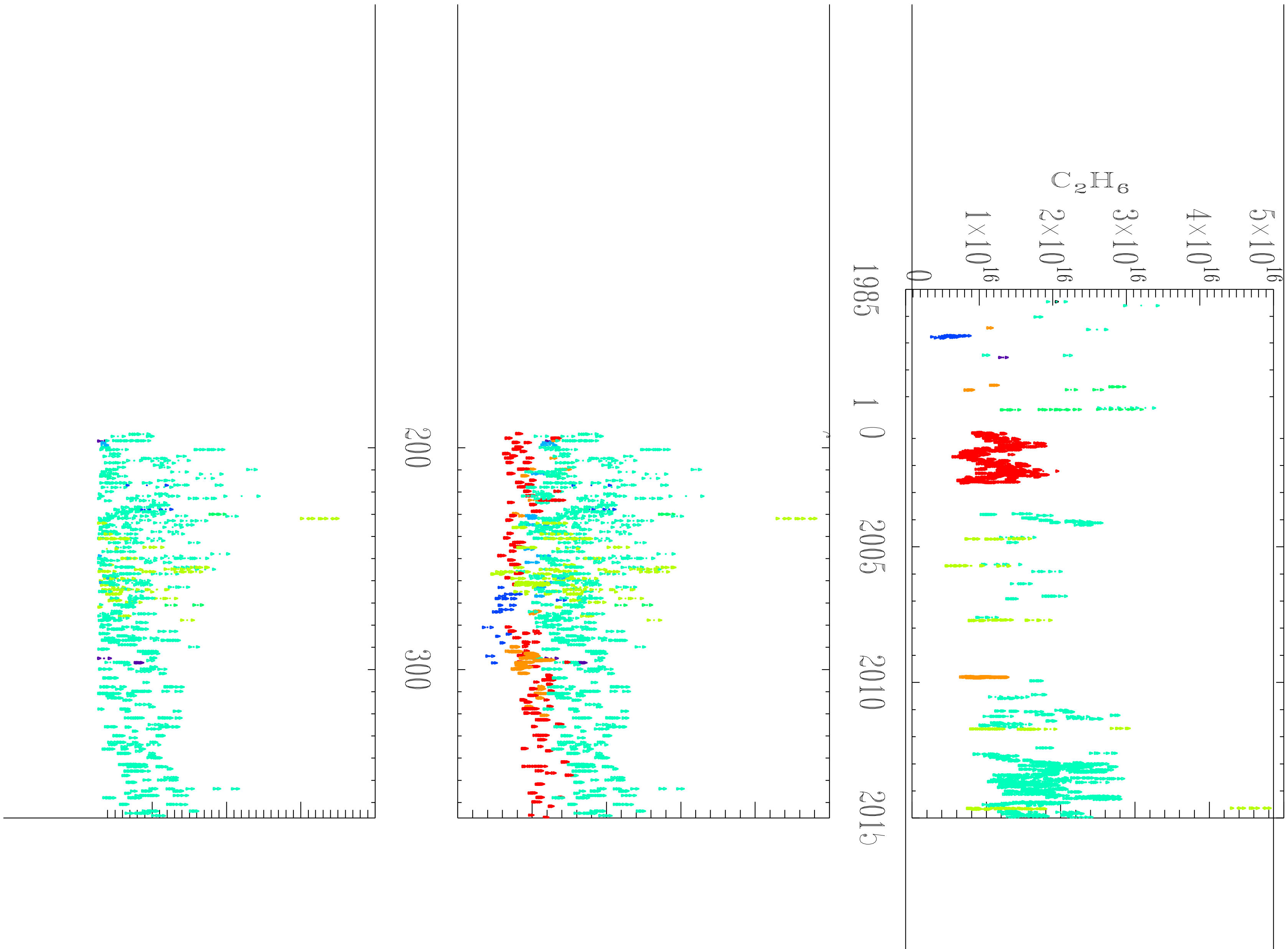
HCOOH and H_2CO



HCOOH – H_2CO Correlation

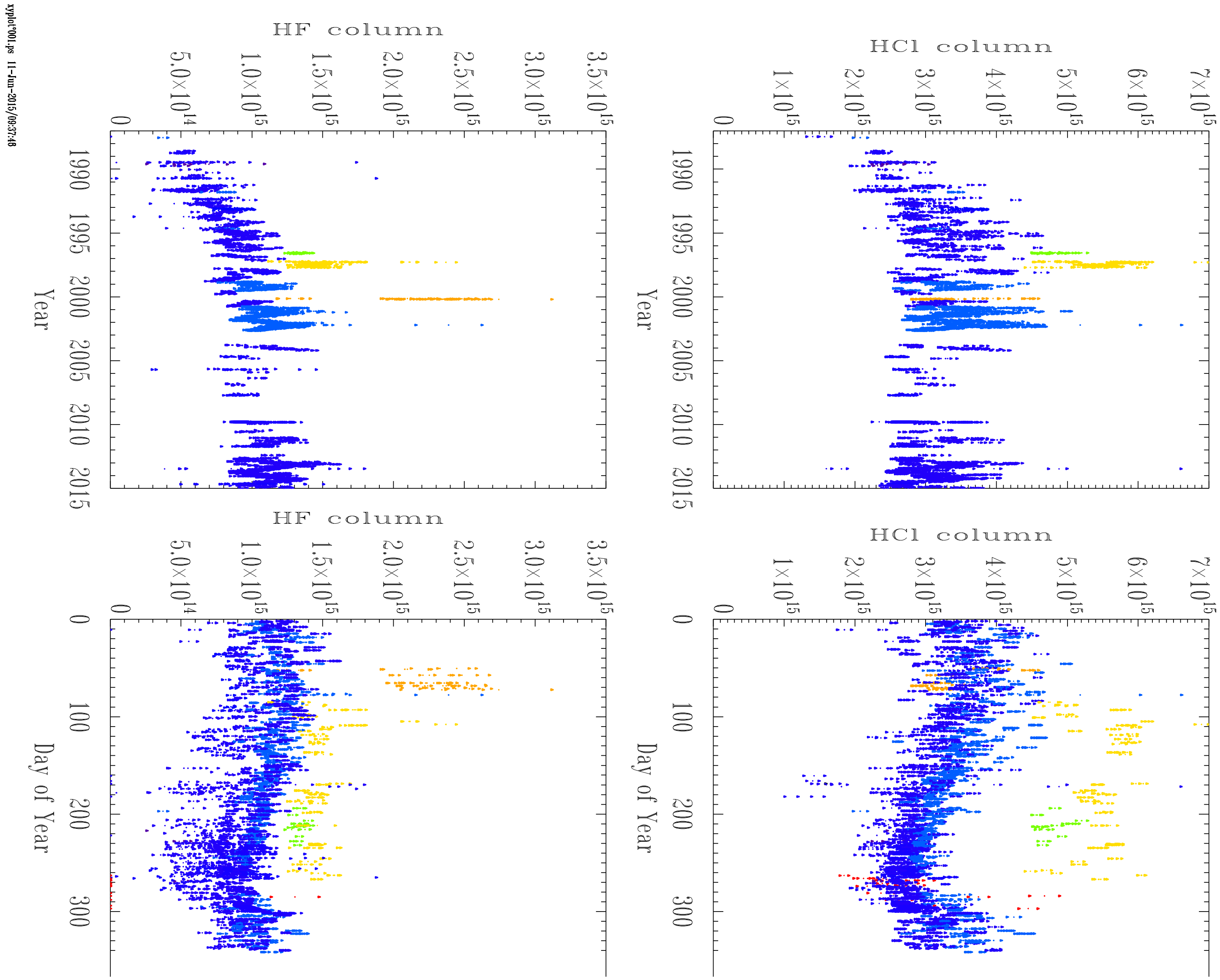
Surprising that these two gases correlate well given their different lifetimes.
Different slope to correlation at clean (high) and dirty (low) sites.

C_2H_6 column



C2H6
0
1×10^16
2×10^16
3×10^16
4×10^16
5×10^16
1985
2005
2010
2015
200
300

HCl and HF (color-coded by latitude)



HCl/HF Ratio