# Update about the HCFC-22 FTIR harmonized study

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# Motivation

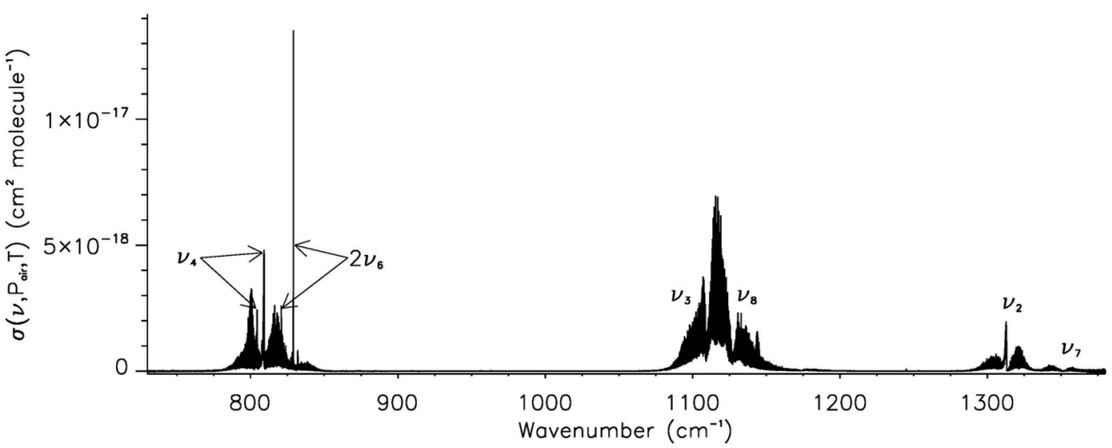
- **There is a renewed interest in CFC and H(C)FC measurements for spotting emission sources (https://library.wmo.int/index.php?lvl=notice_display&id=21919), as CFC and HCFC are important long-lifetime GHGs and ODSs.**

- **After the Montreal Protocol, CFC-11 and CFC-12 both started decreasing in 1990s and 2000s, resp., while HCFC-22 is continuously increasing.**

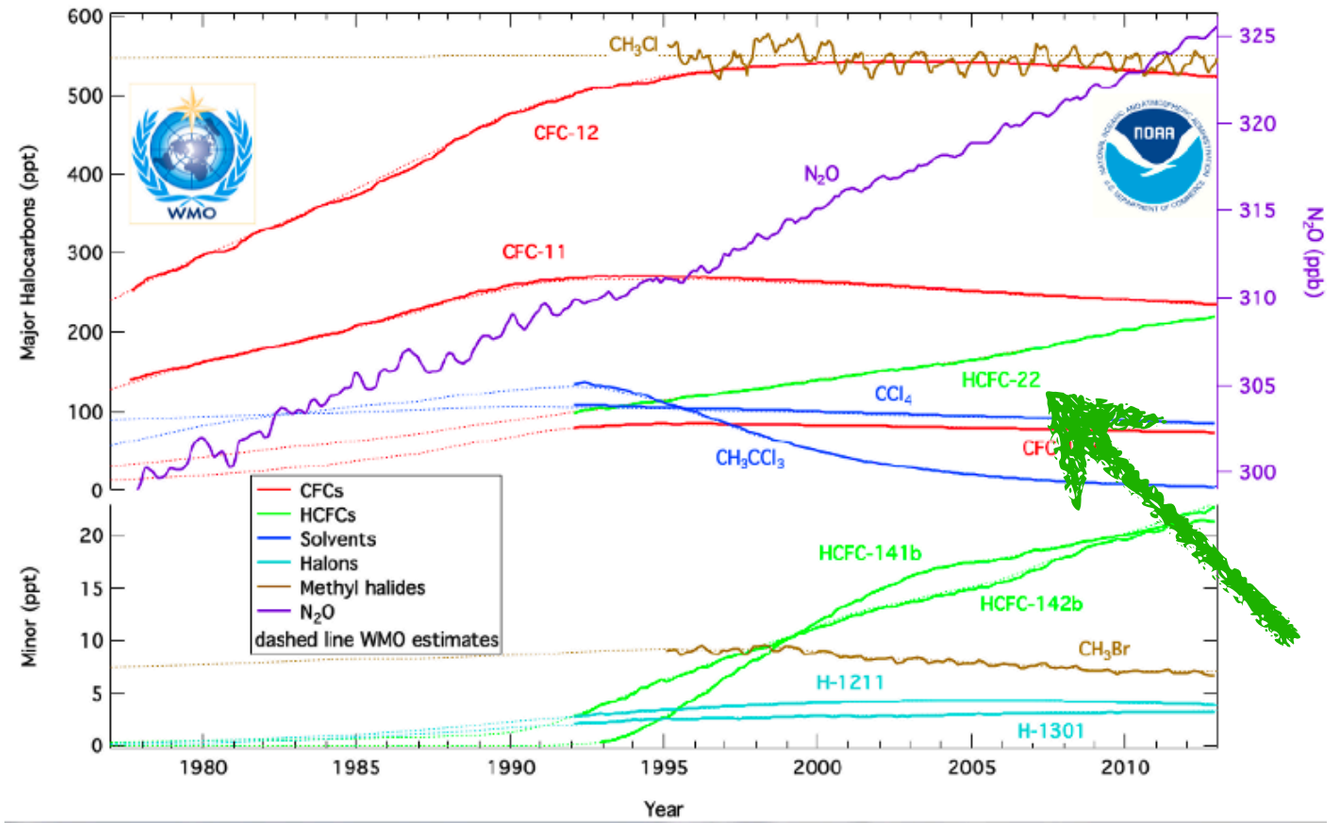
- **In NDACC IRWG, CFC-11, CFC-12, HCFCs are not standard species. We currently only have one site (St. Petersburg) providing the HCFC-22 data in the NDACC archive.**

- **Several groups have related studies regarding CFC-11, CFC-12, HCFCs during the past decades. The relatively isolated absorption line in the mid infrared region allow us to derive the HCFC-22 from the observed spectra at Mountain site (JFJ), urban site (St. Petersburg) and relatively humid site (Reunion St-Denis).**

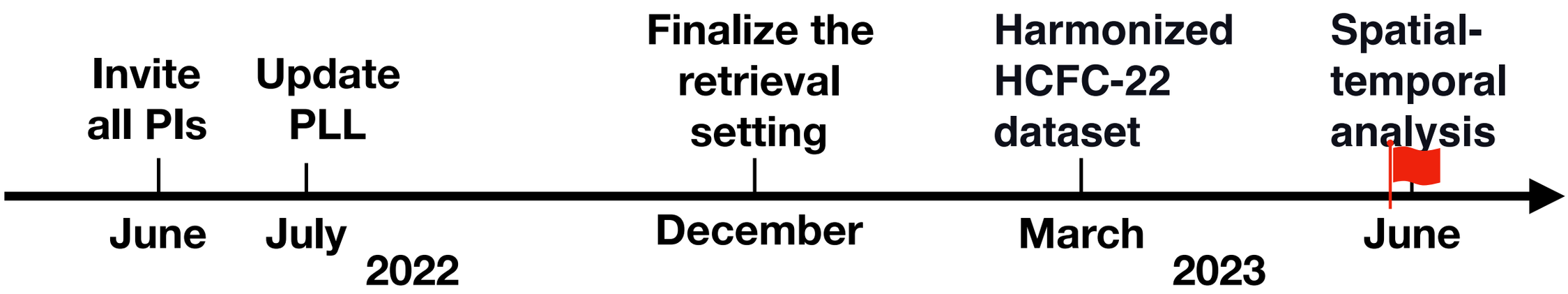
- **The target of this study: providing an NDACC-IRWG harmonized HCFC-22 product and investigate the spatial-temporal variation of HCFC-22 globally.**




HCFC-22 absorption cross section (Harrison, 2016)



# Time schedule and current status

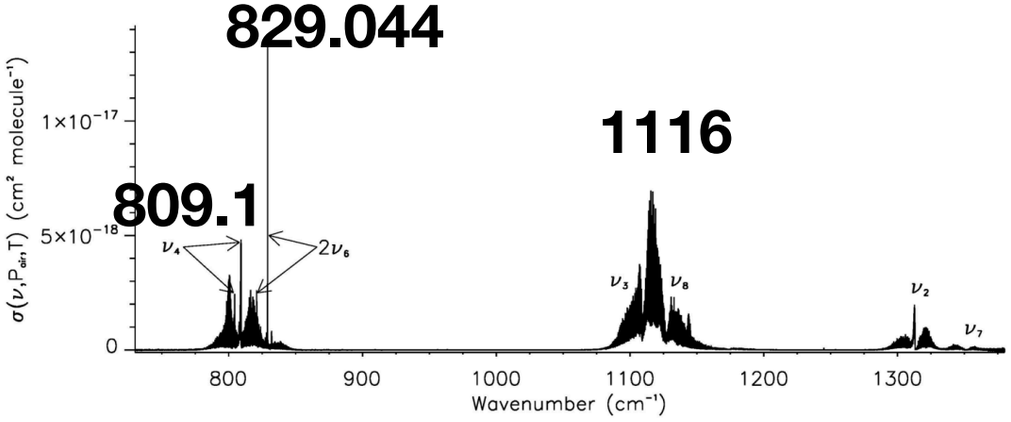


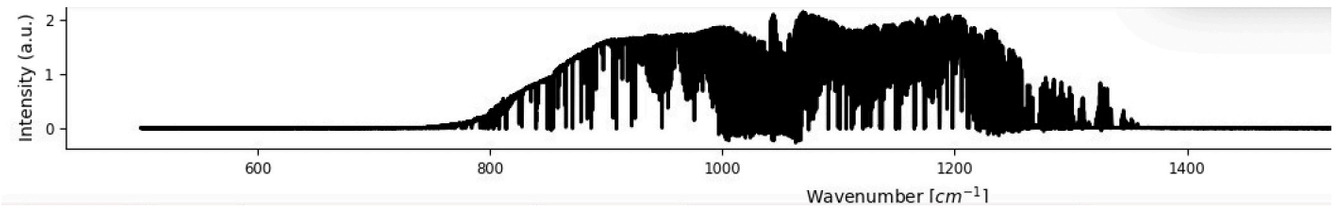

| |
|---|
| 2022-06. Initialized the NDACC FTIR HCFC-22 harmonized study |
| 2022-09-13. Geoff published the new PLL for HCFC-22 |
| 2022-11-22. Finalized the tests based on Reunion data; and send the example retrieval strategy to the community |
| Up to June 2023. We have received tests and results from many groups (thanks!) |

# Retrieval strategy - windows & spectroscopy

**C.C. Toon provides two PLL versions for HCFC-22 (1994 and 2022)**

- **Tested several windows with both PLL versions around 809, 829 and 1116 cm-1 (3 windows).**
- **The fitting residuals (RMSE) and retrieval results (DOF, TC, ERR) using 829 window are very similar from both PLL, with a slightly better RMSE using the new version**
- **The retrieved TCs from 809 and 1116 windows are more close to the TC derived from the 829 window when using the PLL 2022 version as compared to the PLL 1994 version.**
- **We suggest to use the HCFC-22 PLL 2022 version**




| Windows | RMSE | DOF | TC | Sys/Ran |
|---|---|---|---|---|
| 809.0-809.25 | 0,189 | 1.003 | 5.63 | 11.1/26.3 |
| 828.75 - 829.4 | 0,127 | 1.10 | 4.29 | 7.3/7.3 |
| 1115.5-1116.1 | 0,162 | 1.027 | 4.25 | 8.0/14.9 |
| 828.75 - 829.4<br>1115.5-1116.1 | 0,148 | 1.123 | 4.28 | 7.3/3.6 |

# Spectroscopy- interfering species (H2O, O3, CO2 )

**The spectroscopy choices for interfering species ?**

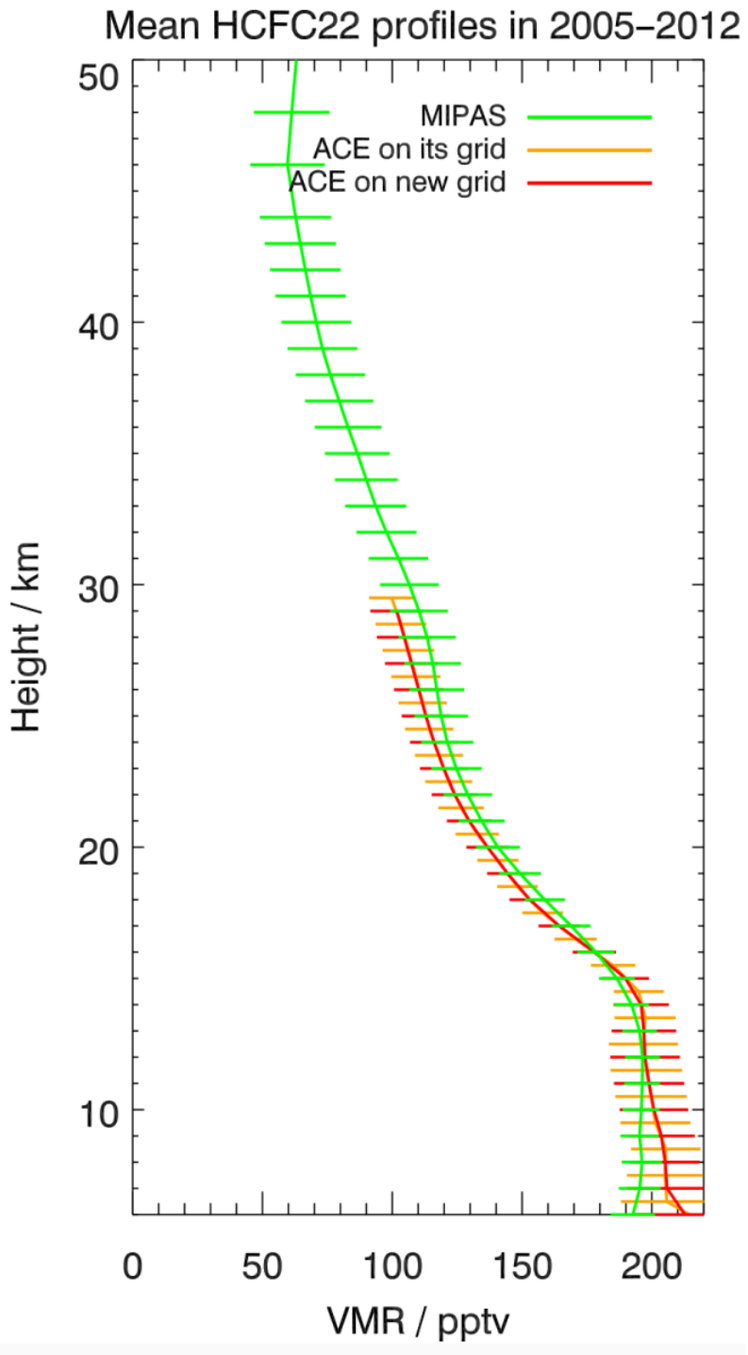
**I took several spectra (~10) at Maido**
**And look at the mean RMSE, TC and DOF**

Retrieval windows
828.75 - 829.4
1115.5-1116.1

| HCFC-22 | PLL2022 | PLL 2022 | PLL 2022 | PLL 2022 |
|---|---|---|---|---|
| CO2 | ATM2020 | ATM2020 | HITRAN2020 | HITRAN2020 |
| H2O | ATM2020 | HITRAN2020 | HITRAN2020 | HITRAN2020 |
| O3 | ATM2020 | ATM2020 | ATM2020 | HITRAN2020 |
| RMSE | 0,14833 | 0,14783 | 0,14780 | 0,14789 |
| TC | 4.289 | 4.287 | 4.286 | 4.2855 |

**Best choice!**

# Retrieval strategy - regularization




**Chirkov et al., 2016**

**We prefer to use the Tik regularization as the absorption line is relatively weak**

Polyakov (2021) tested with both OE and TiK regularization, and they found that the retrieved vertical profiles are more stable with TiK

SNR is user defined, either from the spectra or fixed

# Retrieval strategy - uncertainty estimation

## Parameter sb

| One parameter | |
|---|---|
| sb.lineTAir.CHF2CL.systematic | = 0.01 |
| sb.linePAir.CHF2CL.systematic | = 0.05 |
| sb.sza.random | =0.03 |
| sb.sza.random.unit | ="degrees" |
| sb.sza.systematic | =0.03 |
| sb.sza.systematic.unit | ="degrees" |
| sb.band.zshift.random | =0.0015 #used to be 0.01 |
| sb.band.zshift.systematic | =0.0015 #similar |
| sb.omega.random | =0.001 |
| sb.omega.systematic | =0.001 |
| sb.slope.random | =0.001 |
| sb.slope.systematic | =0.001 |
| sb.curvature.random | =0.001 |
| sb.curvature.systematic | =0.001 |
| sb.solshft.random | =0.0000008 |
| sb.solshft.systematic | =0.0000002 |
| sb.solstrnth.random | =0.01 |
| sb.solstrnth.systematic | =0.01 |
| sb.phase.random | = 0.001 |
| sb.phase.systematic | = 0.001 |
| sb.wshift.random | = 0.001 |
| sb.wshift.systematic | = 0.001 |
| sb.apod_fcn.random | =0.05 |
| sb.apod_fcn.systematic | =0.05 |
| sb.phase_fcn.random | =0.05 |
| sb.phase_fcn.systematic | =0.05 |
| sb.max_opd.systematic | =0. |
| sb.max_opd.random | =0. |

| PROFILE |
|---|
| **sb.profile.temperature.correlation.width = 2** |
| **sb.profile.temperature.random = 2 2 4 4 2 3 6 1 ## unit K** |
| **sb.profile.temperature.systematic = 1 1 1 2 2 2 4 5** |
| **sb.profile.H2O.grid = -0.020 1 6 10 13 25 40 120** |
| **sb.profile.H2O.correlation.width = 4** |
| **sb.profile.H2O.random = 0.10 0.30 0.60 0.50 0.30 0.10 0.10 0.10 #relative units** |
| **sb.profile.H2O.systematic = 0.10 0.4 0.20 0.20 0.20 0.20 0.20 0.20** |
| **sb.profile.CHF2CL.grid =-0.020 4 6 10 13 25 40 120 #coarse grid in km** |
| **sb.profile.CHF2CL.correlation.width =4 #in km, see sfit4 correlation def** |
| **sb.profile.CHF2CL.random = 0.38 0.38 0.38 0.39 0.39 0.40 0.41 0.45 #relative units** |
| **sb.profile.CHF2CL.systematic = 0.05 0.05 0.05 0.07 0.08 0.10 0.10 0.10 #relative units** |

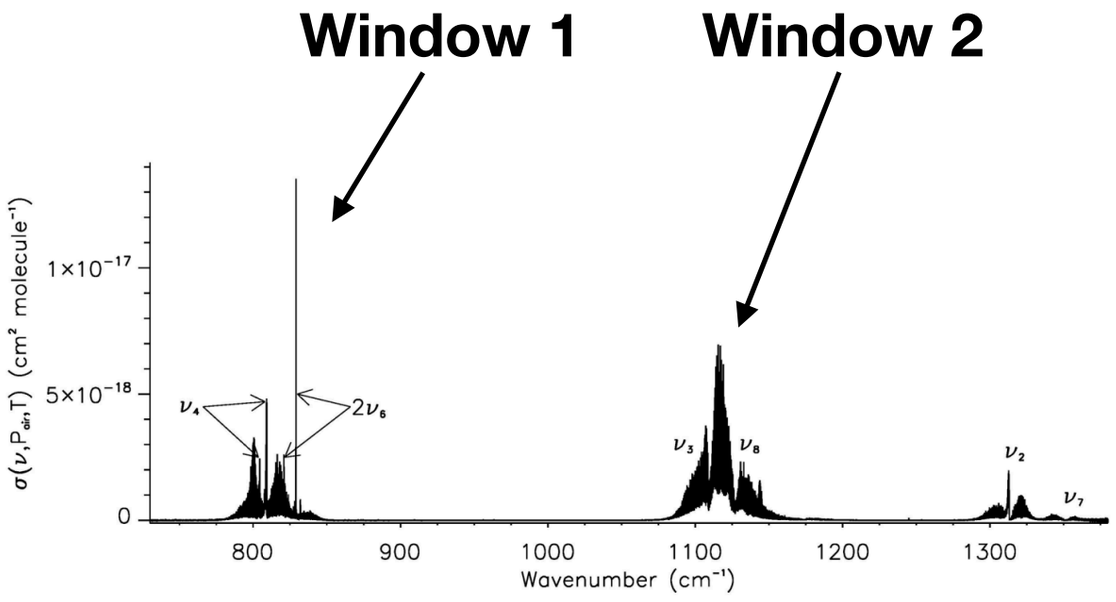
# Sites [15.5+(1)/23]

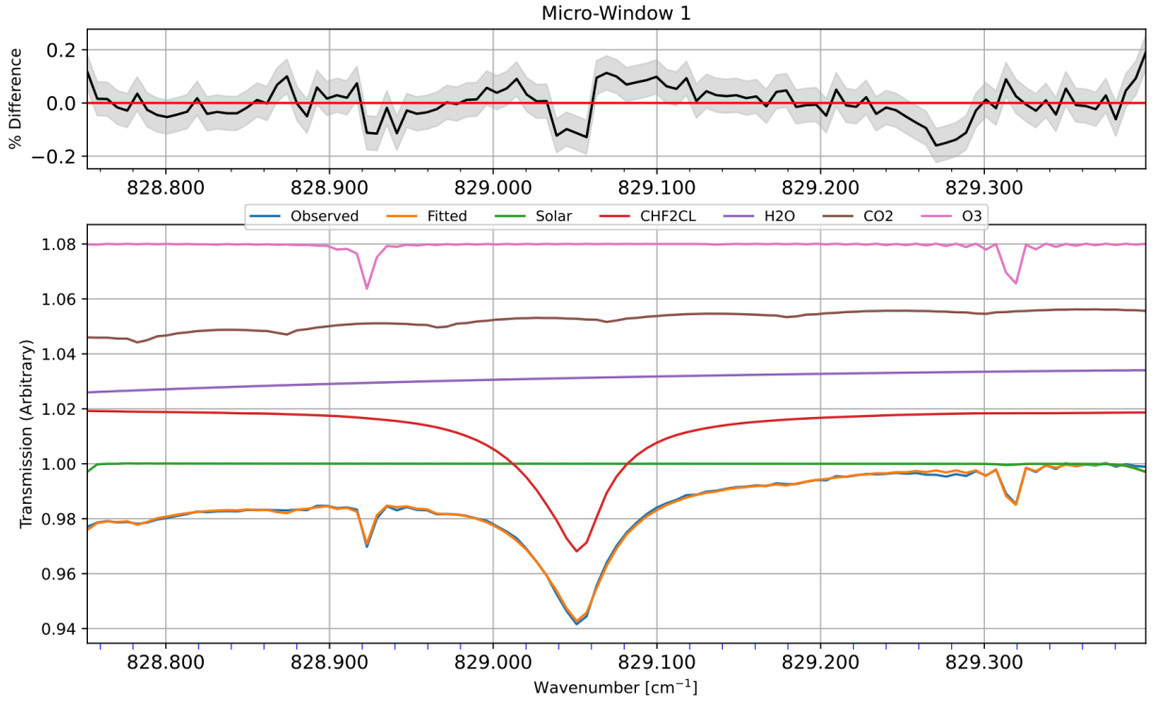
| site | lat | PI/contact | MCT spectra time coverage | Already have the GEOMS HDF file (Yes/No) |
|---|---|---|---|---|
| Thule | 77N | Jim/Ivan | 1999 - now | Yes |
| St.Petersburg | 60N | Maria/Alexander | 2009 - now | Yes |
| Rikubetsu | 43N | Tomoo/Isamu | 1995/05-2009/12, 2014/01-now | (almost ready) |
| Boulder | 40N | Jim/Ivan | 2010 - now | Yes |
| Tsukuba | 36N | Isao/Isamu | 1999 - now | Yes |
| JPL | 34N | Geoff | - | No |
| Izana | 28N | Omaira | 1999 - now | Not in HDF yet (but we have TC data) |
| Altzomoni | 19N | Michel | - | No |
| Mauna Loa | 19N | Jim/Ivan | - | No |
| St-Denis | 21S | Martine/Minq | 2009-2011 | Yes |
| Maido | 21S | Martine/Minq | 2013 - now | Yes |
| Wollongong | 34S | Nicholas | 1996 - now | Yes |
| Lauder | 45S | Dan | ~1993 - now | Yes |
| Arrival Height | 78S | Dan | 1996 - now | Yes |
| Ny Alesund | 78N | Mathias | 1995-now | Yes |
| Paramaribo | 8N | Mathias | 2004 - 2010 | No |
| Palau | 9N | Mathias/Justus | 2022 - 2023 | No |
| Bremen | 53N | Mathias | 2004 - now | Yes |
| JFJ | 46N | Manu/Maxime | ~1990-now | Yes |
| Harestua | 60N | Johan/Maxime | 1994(best case) /2008 - now | Yes |
| Toronto | 44N | Kim/Victoria | 2002 - now | Yes |
| Eureka | 80N | Kim/Tyler | 2006 - March 2020 | Yes |

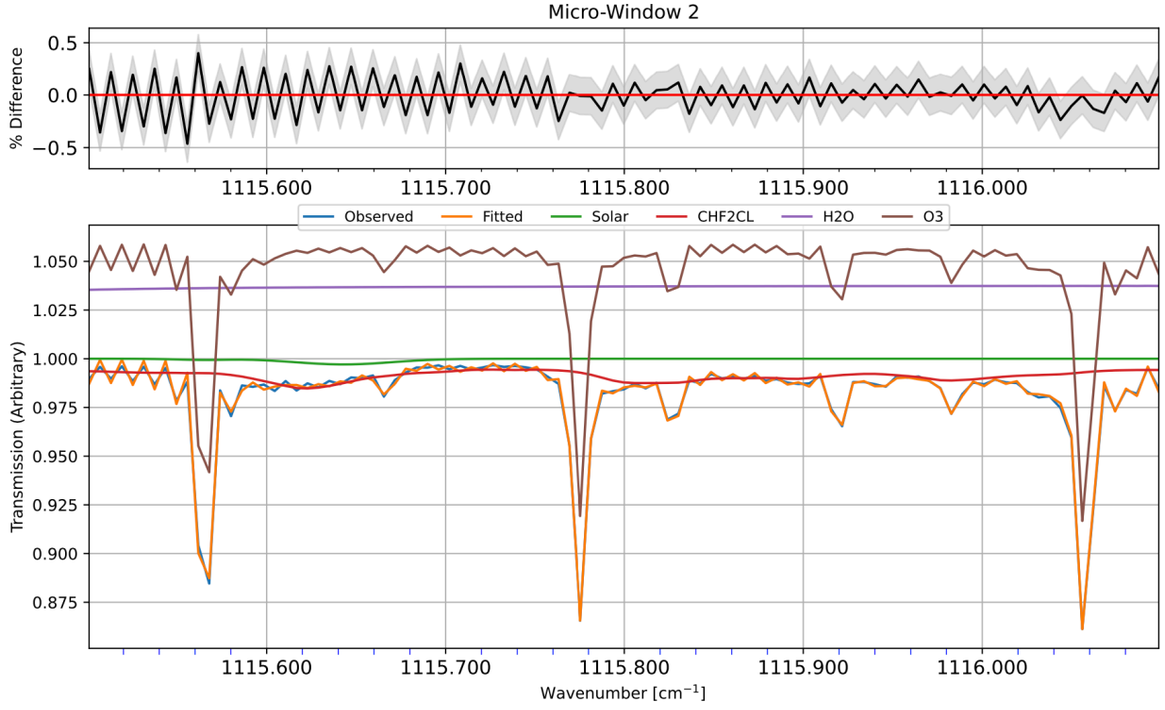
# Retrieval strategy/settings/parameters

| site | lat | Retrieval windows | DOF | Retrieval uncertainty (sys/ran) | Notes |
|---|---|---|---|---|---|
| Thule | 77N | 829 cm-1 | 1.050±0.057 | 7.3/3.5% | Nan values in random error<br>HCFC22 instead of CHF2Cl |
| St.Petersburg | 60N | 829 cm-1 | 1.062±0.079 | 7.9/7.4% | HCFC22 + VOLUMN.DRY |
| Rikubetsu | 43N | | | | |
| Boulder | 40N | 829 cm-1+1116cm-1 | 1.013±0.016 | 7.4/6.7% | HCFC22 |
| Tsukuba | 36N | 829 cm-1+1116cm-1 | 1.042±0.037 | 7.5/8.0% | CHF2CL |
| JPL | 34N | | | | |
| Izana | 28N | 829 cm-1+1116cm-1 | 1.085±0.055 | -/- | |
| Altzomoni | 19N | | | | |
| Mauna Loa | 19N | | | | |
| St-Denis | 21S | 829 cm-1+1116cm-1 | 1.091±0.053 | 7.9/5.3% | CHF2Cl |
| Maido | 21S | 829 cm-1+1116cm-1 | 1.086±0.043 | 7.4/3.6 % | CHF2Cl |
| Wollongong | 34S | 829 cm-1+1116cm-1 | 1.082±0.063 | 6.6/4.4% | CHF2Cl |
| Lauder | 45S | 829 cm-1 | 1.148±0.114 | -/- | CHF2CL + VOLUMN.DRY |
| Arrival Height | 78S | 829 cm-1 | 1.061±0.078 | -/- | CHF2CL + VOLUMN.DRY |
| Ny Alesund | 78N | 829 cm-1 | 1.089±0.075 | 1.2/3.8% | CHF2CL |
| Paramaribo | 8N | | | | |
| Palau | 9N | | | | |
| Bremen | 53N | 829 cm-1 | 1.067±0.084 | 1.2/4.2% | CHF2CL |
| JFJ | 46N | 829 cm-1 | 1.401±0.167 | 5.3/3.7% | CHF2CL |
| Harestua | 60N | 829 cm-1 | 1.267±0.208 | 7.2/3.2% | CHF2CL |
| Toronto | 44N | 829 cm-1 | 1.025±0.035 | 7.4/7.8% | VOLUMN.DRY |
| Eureka | 80N | 829 cm-1 | 1.101±0.129 | 7.3/4.6% | VOLUMN.DRY |
| All | | | 1.013 - 1.401 | ~7.5% / 3.2-8.0% | Not consistent |

# Retrieval windows and spectral residual

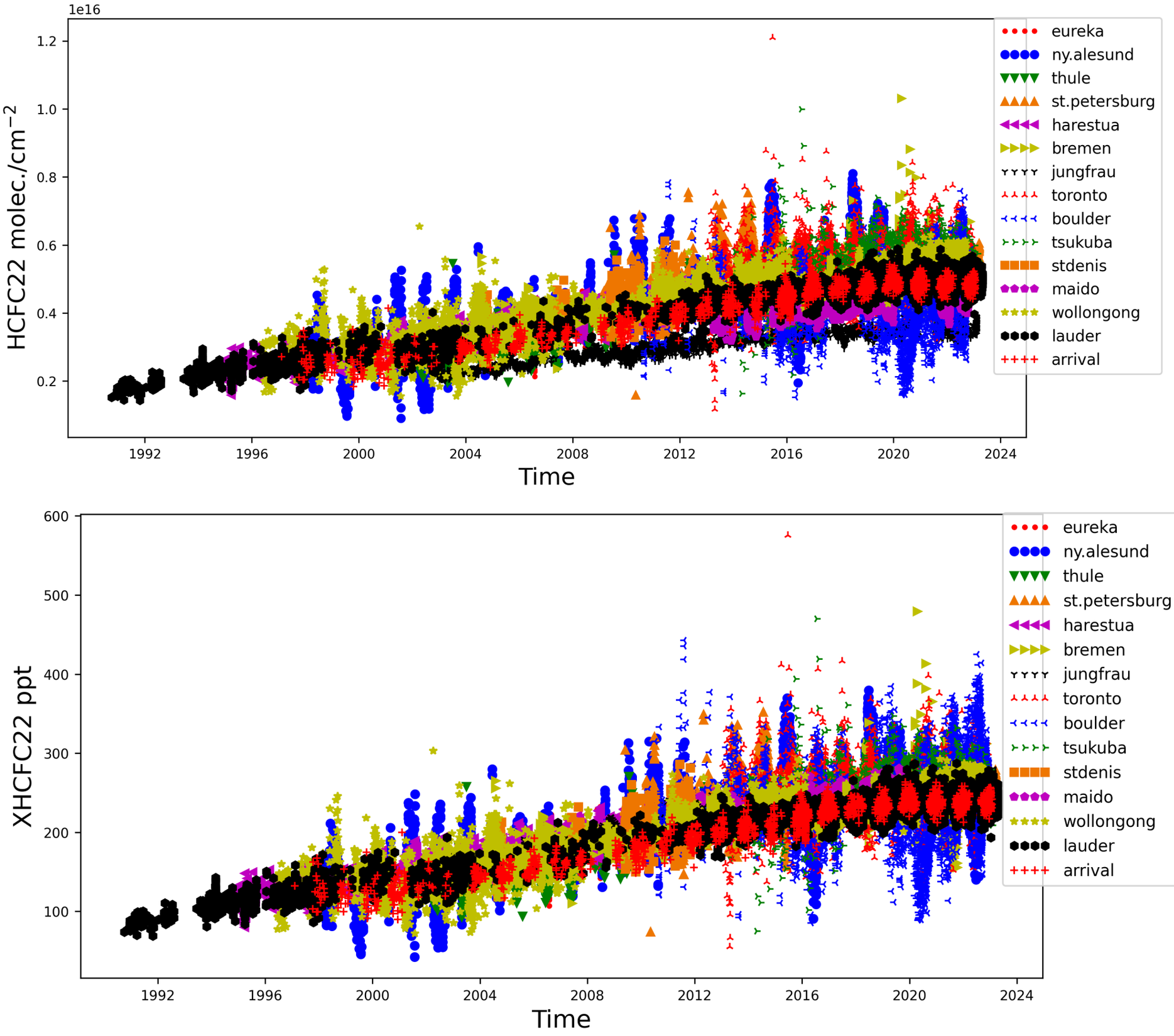


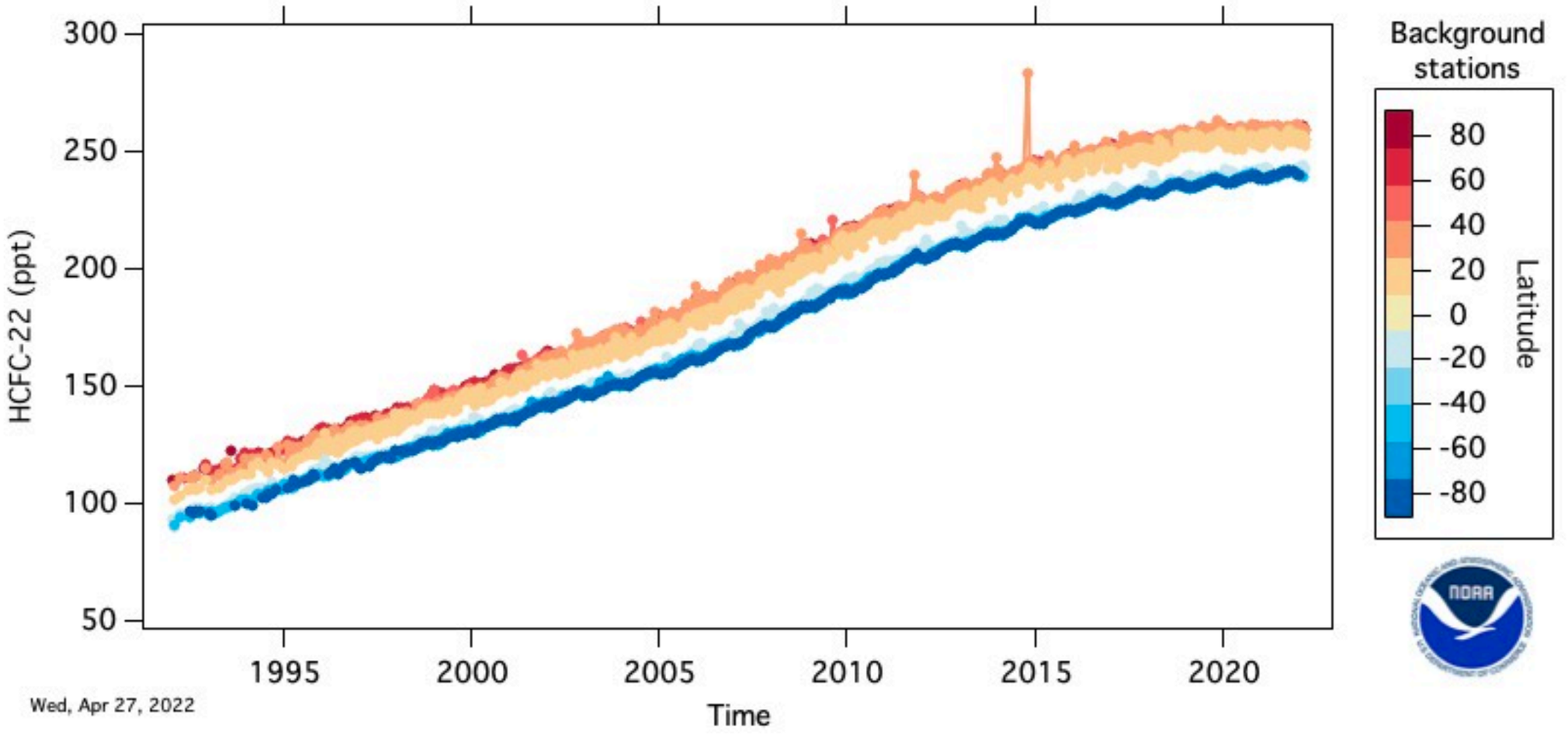




**Fitting residual @ Tsukuba (Isao Murata; imurata@tohoku.ac.jp)**

# Overview HCFC-22 total column

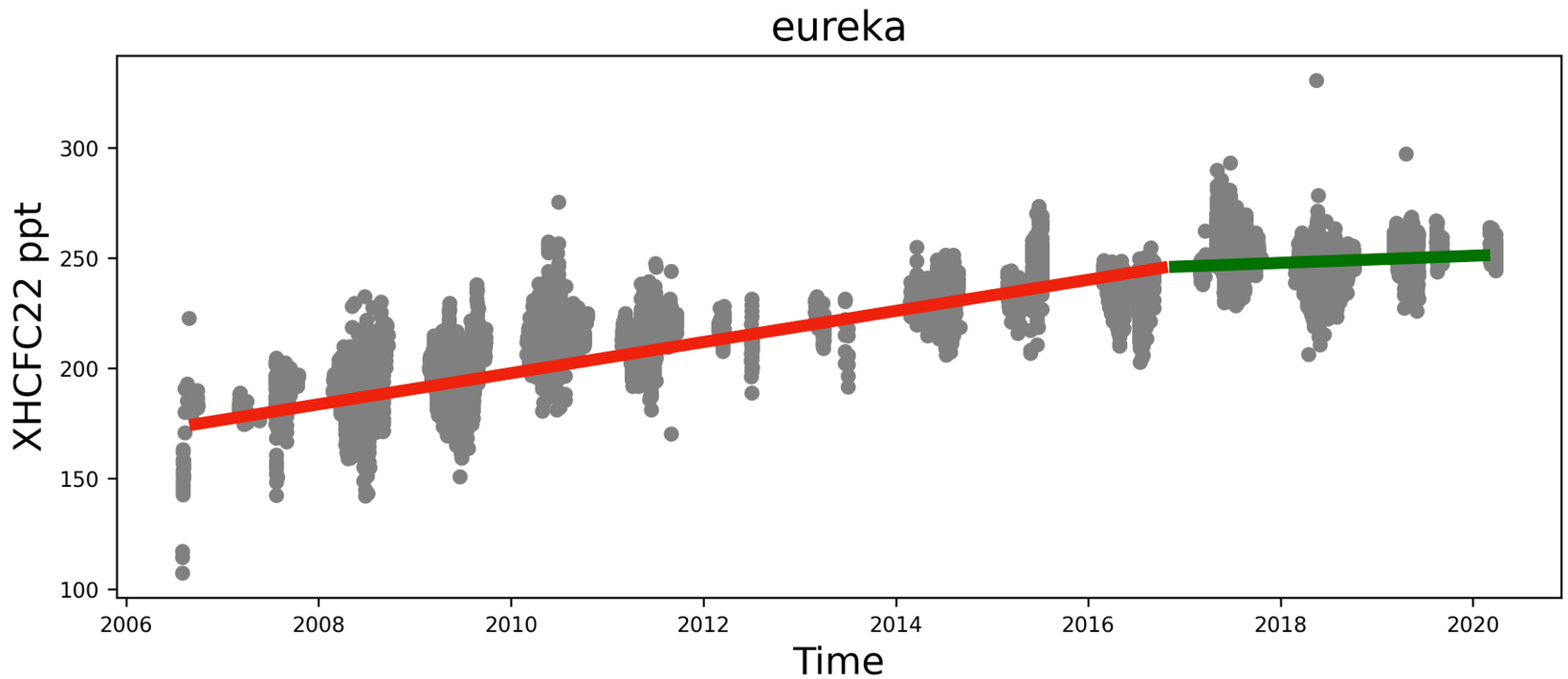


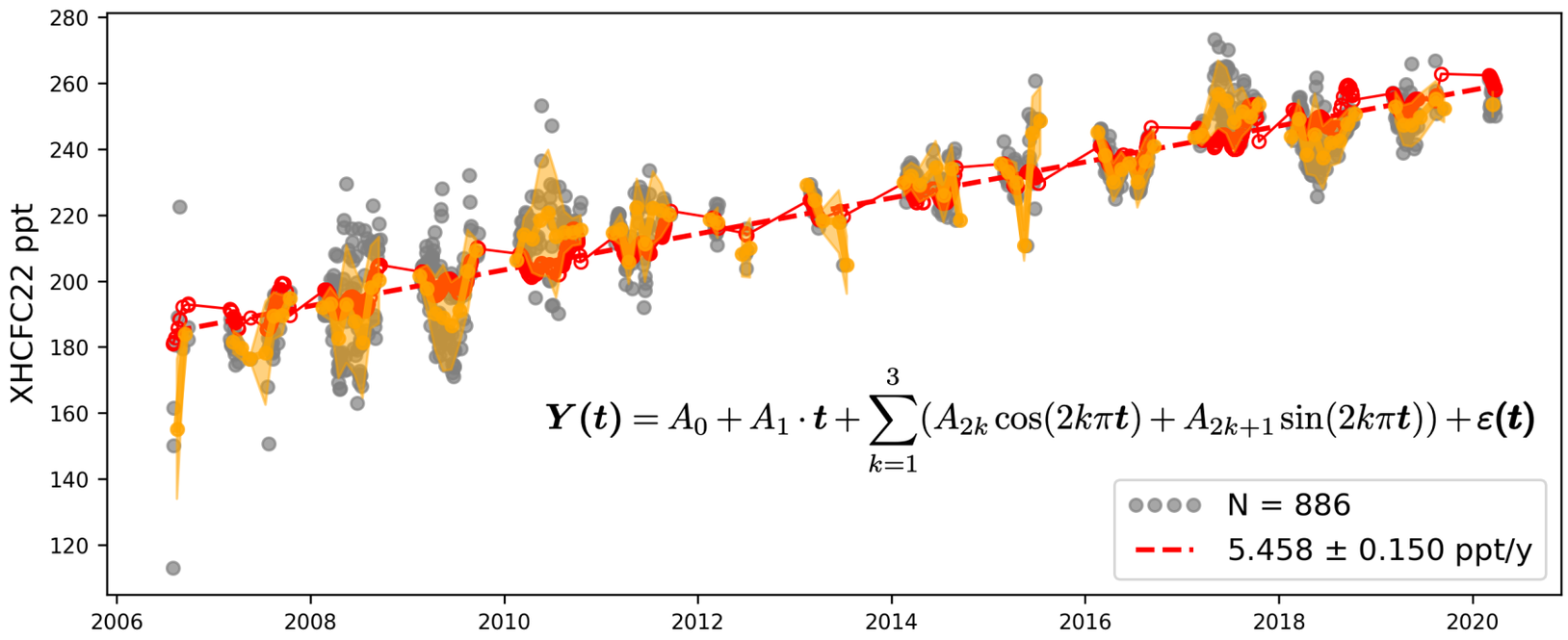
# Overview HCFC-22 from the NOAA in situ measurements



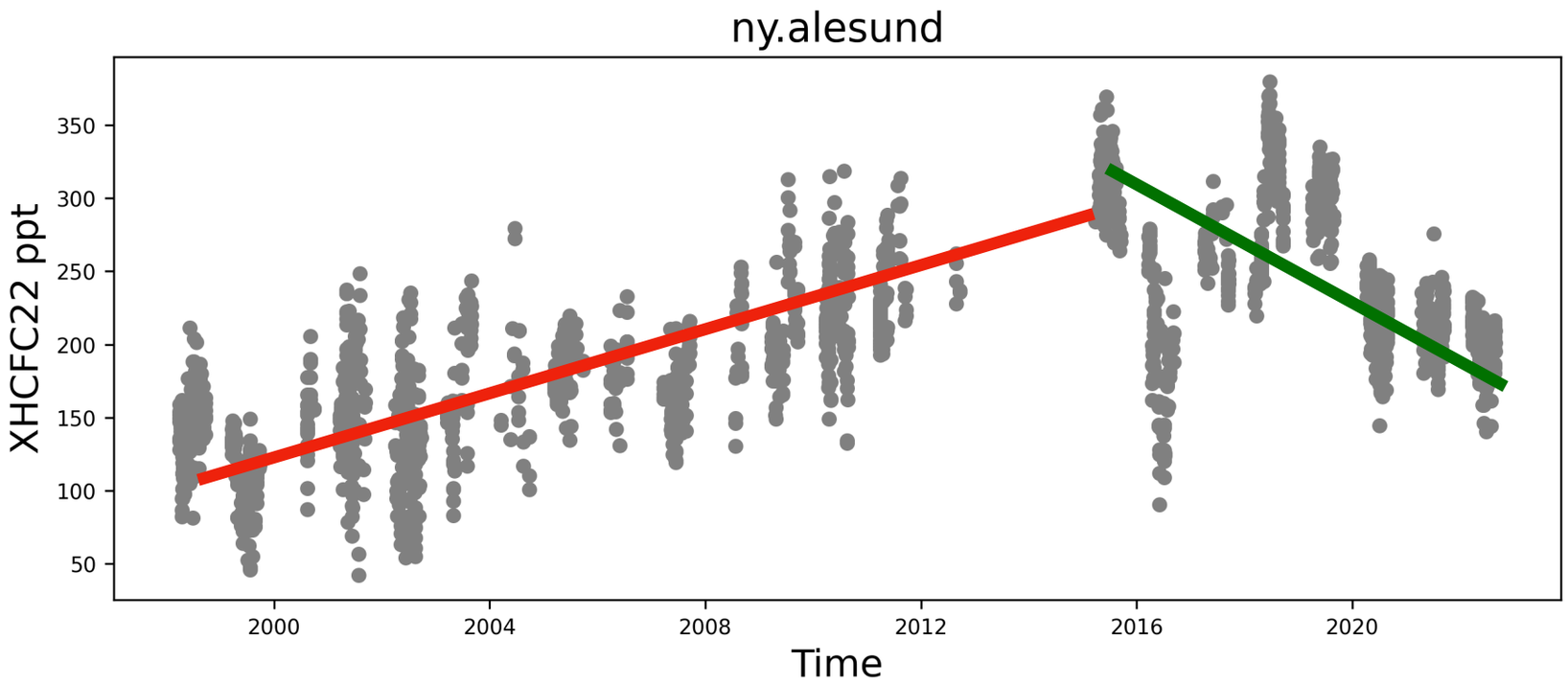

- **HCFC-22 average mole fraction in NH is about 10-15 ppt larger than that in SH**
- **The annual growth of HCFC-22 is decreasing in the recent years (~2016)**

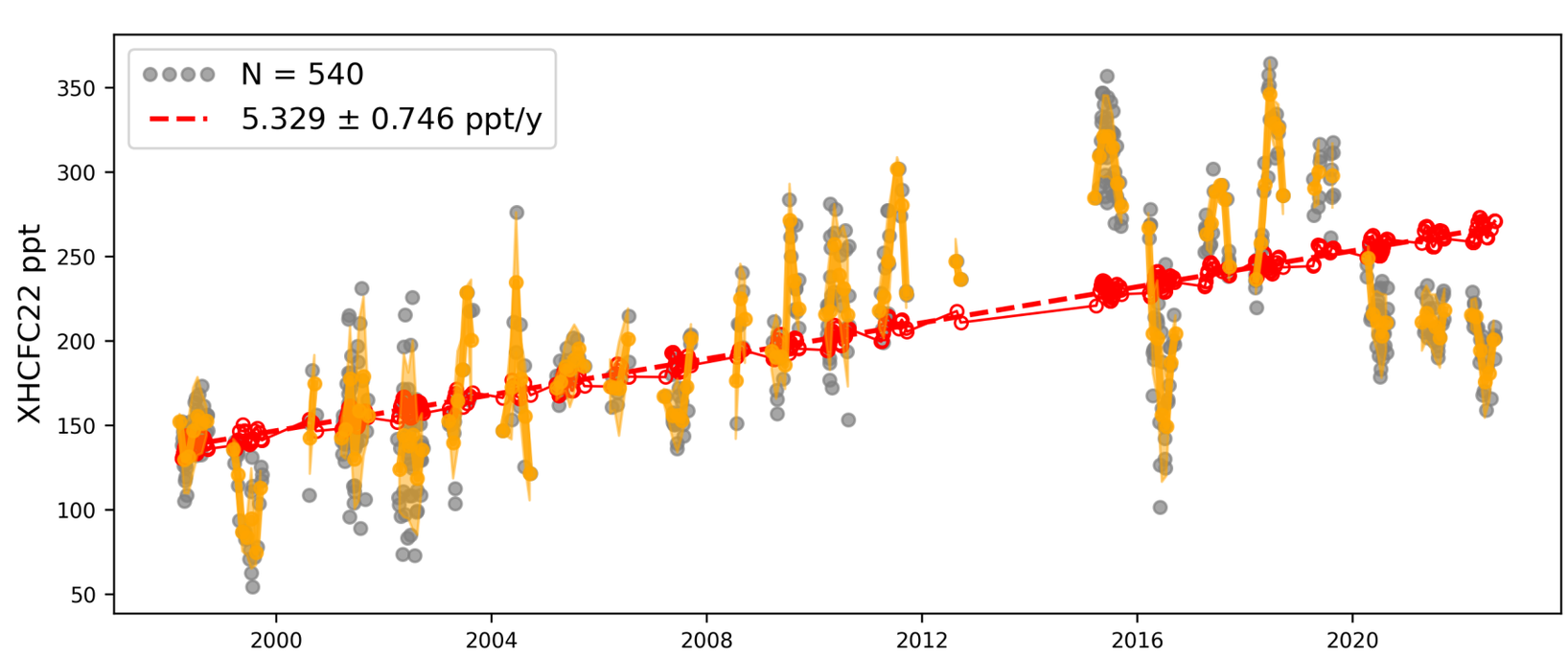
# Eureka


eureka
XHCFC22 ppt
Time
100
150
200
250
300
2006
2008
2010
2012
2014
2016
2018
2020

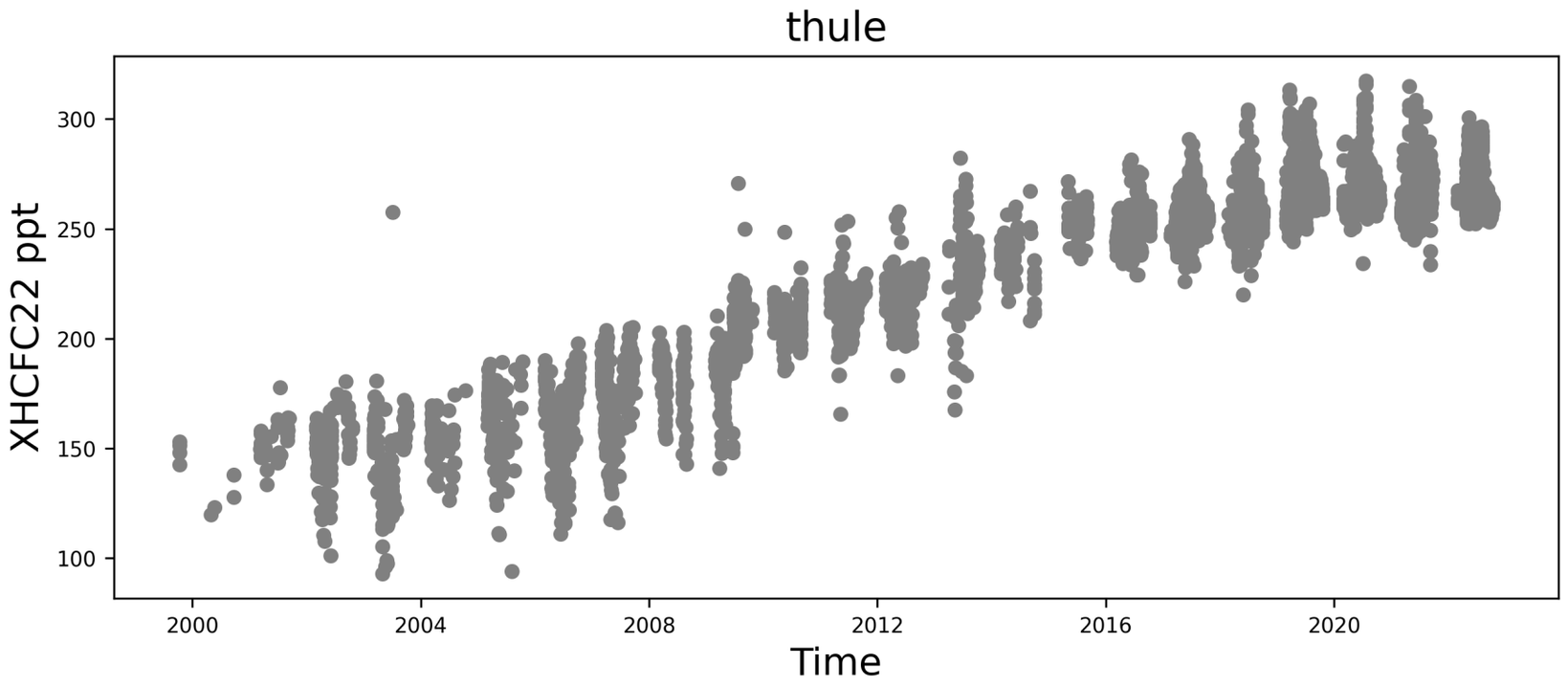

XHCFC22 ppt
120
140
160
180
200
220
240
260
280
2006
2008
2010
2012
2014
2016
2018
2020
$\boldsymbol{Y(t)} = A_0 + A_1 \cdot \boldsymbol{t} + \sum_{k=1}^{3} (A_{2k} \cos(2k\pi \boldsymbol{t}) + A_{2k+1} \sin(2k\pi \boldsymbol{t})) + \boldsymbol{\varepsilon(t)}$
N = 886
5.458 ± 0.150 ppt/y

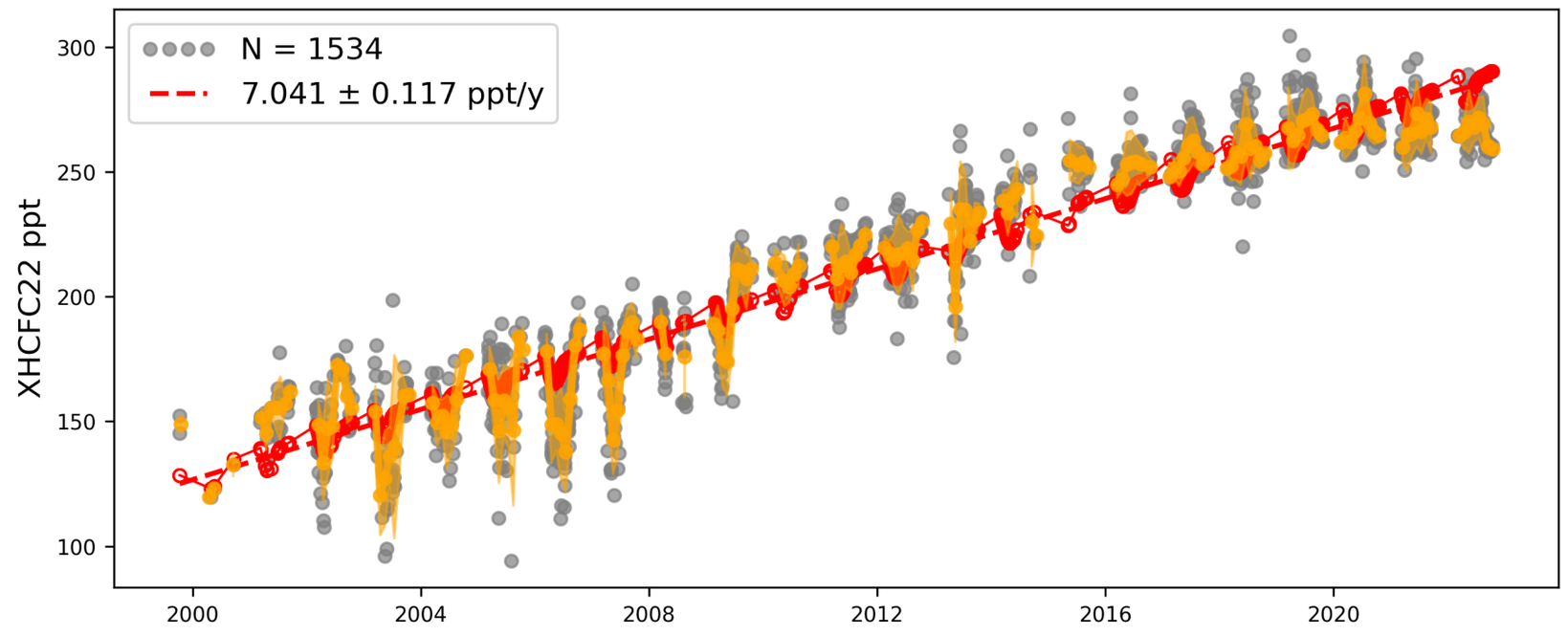
# Ny-Alesund


ny.alesund
XHCFC22 ppt
350
300
250
200
150
100
50
2000
2004
2008
2012
2016
2020
Time

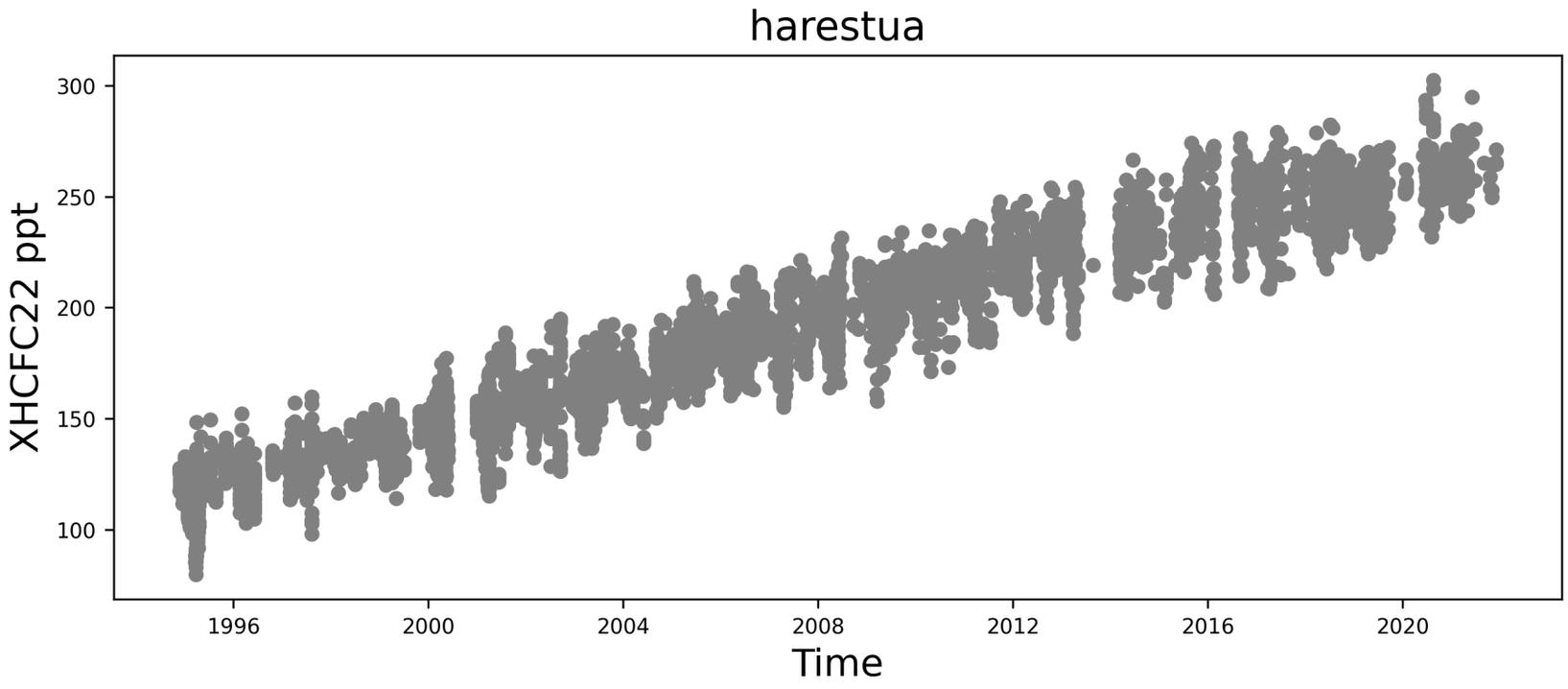

N = 540
5.329 ± 0.746 ppt/y
XHCFC22 ppt
350
300
250
200
150
100
50
2000
2004
2008
2012
2016
2020

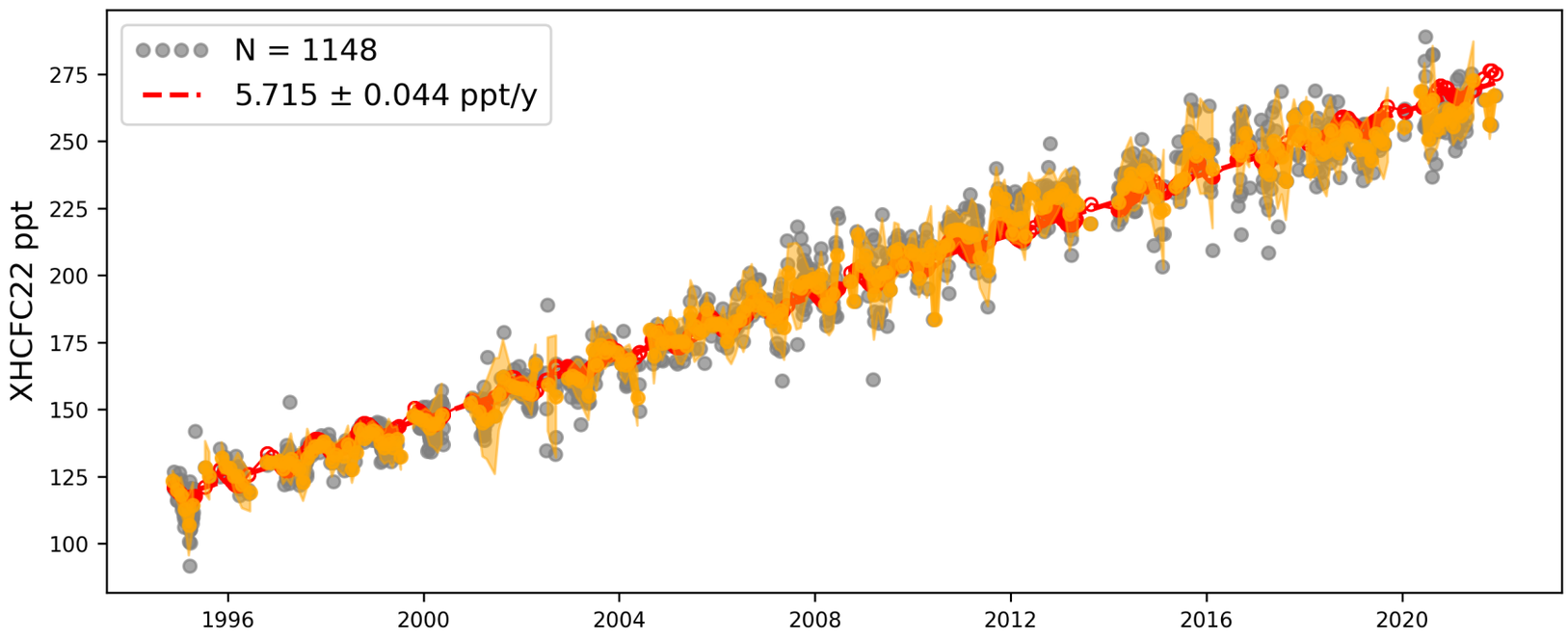
# Thule


thule
XHCFC22 ppt
300
250
200
150
100
2000
2004
2008
2012
2016
2020
Time

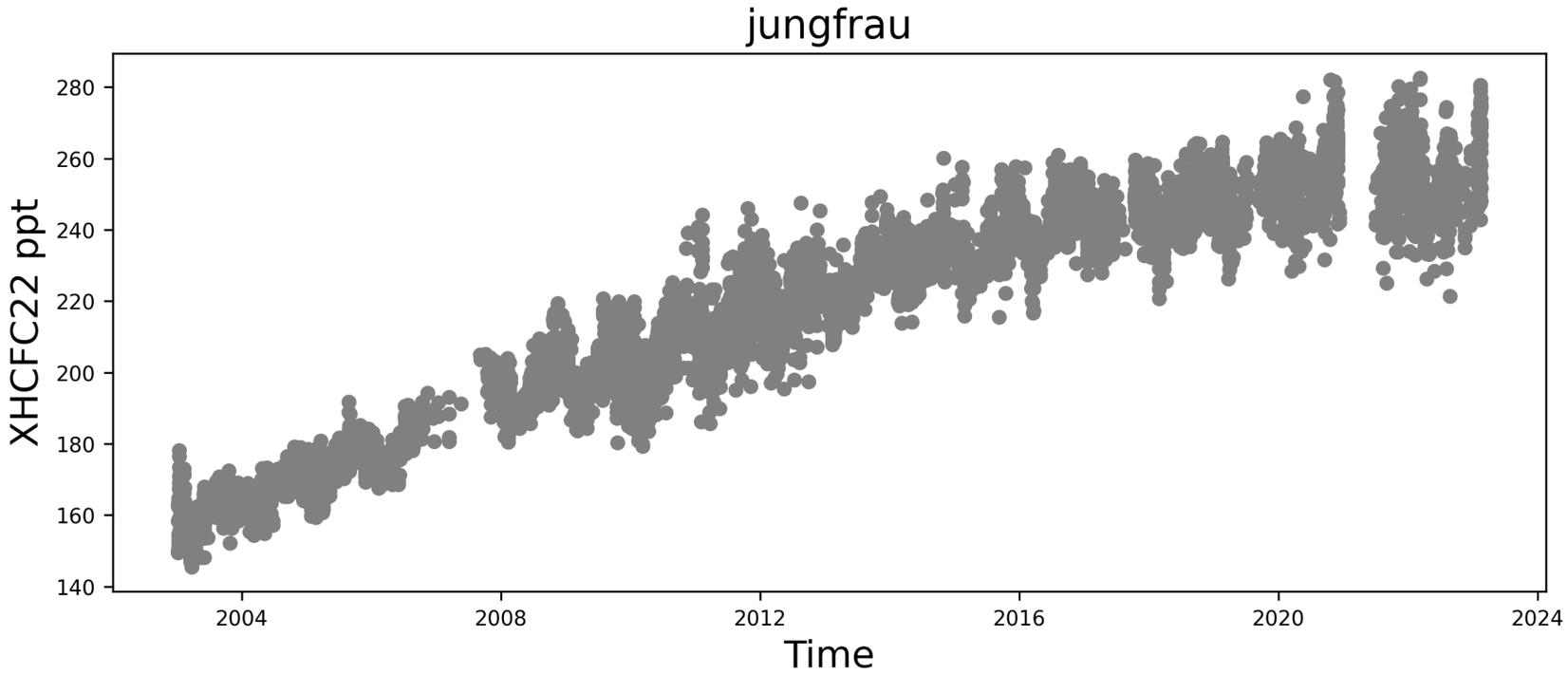

N = 1534
7.041 ± 0.117 ppt/y
XHCFC22 ppt
300
250
200
150
100
2000
2004
2008
2012
2016
2020

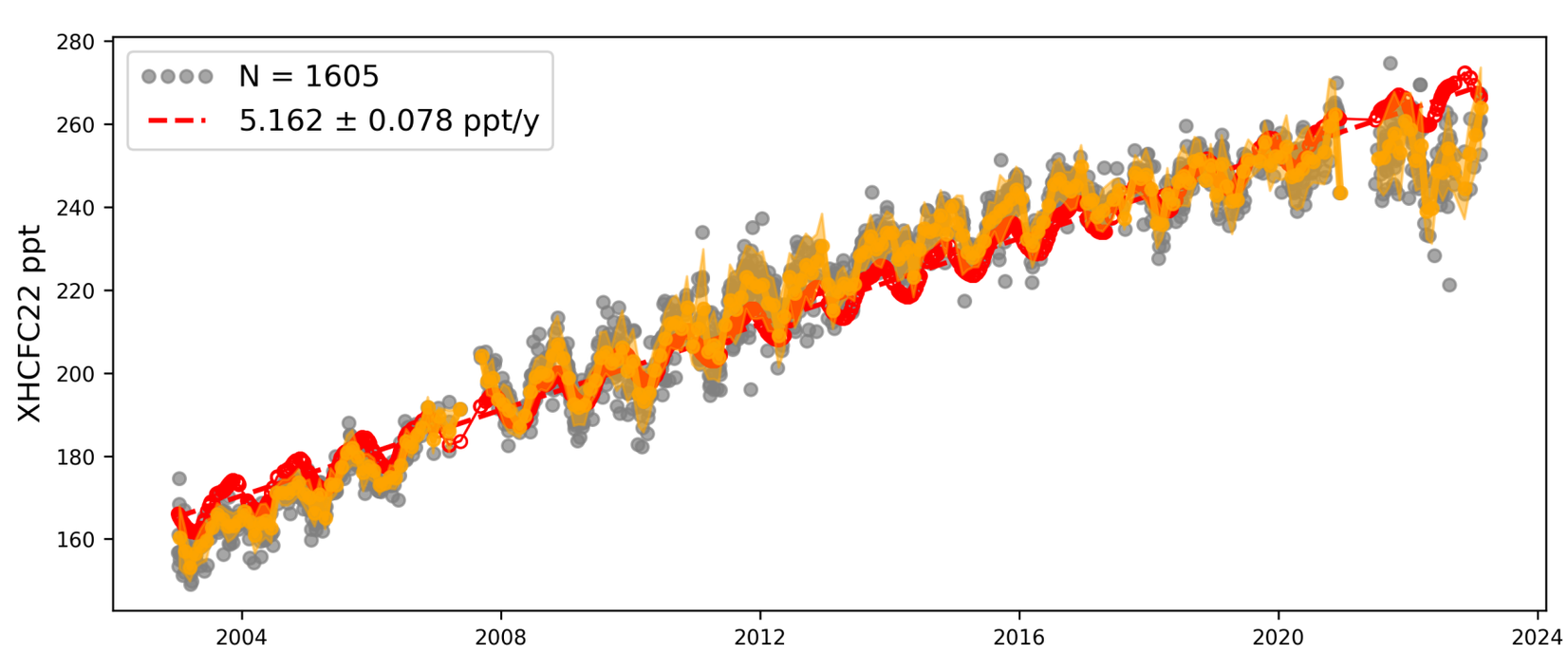
# Harestua


harestua
XHCFC22 ppt
300
250
200
150
100
1996
2000
2004
2008
2012
2016
2020
Time

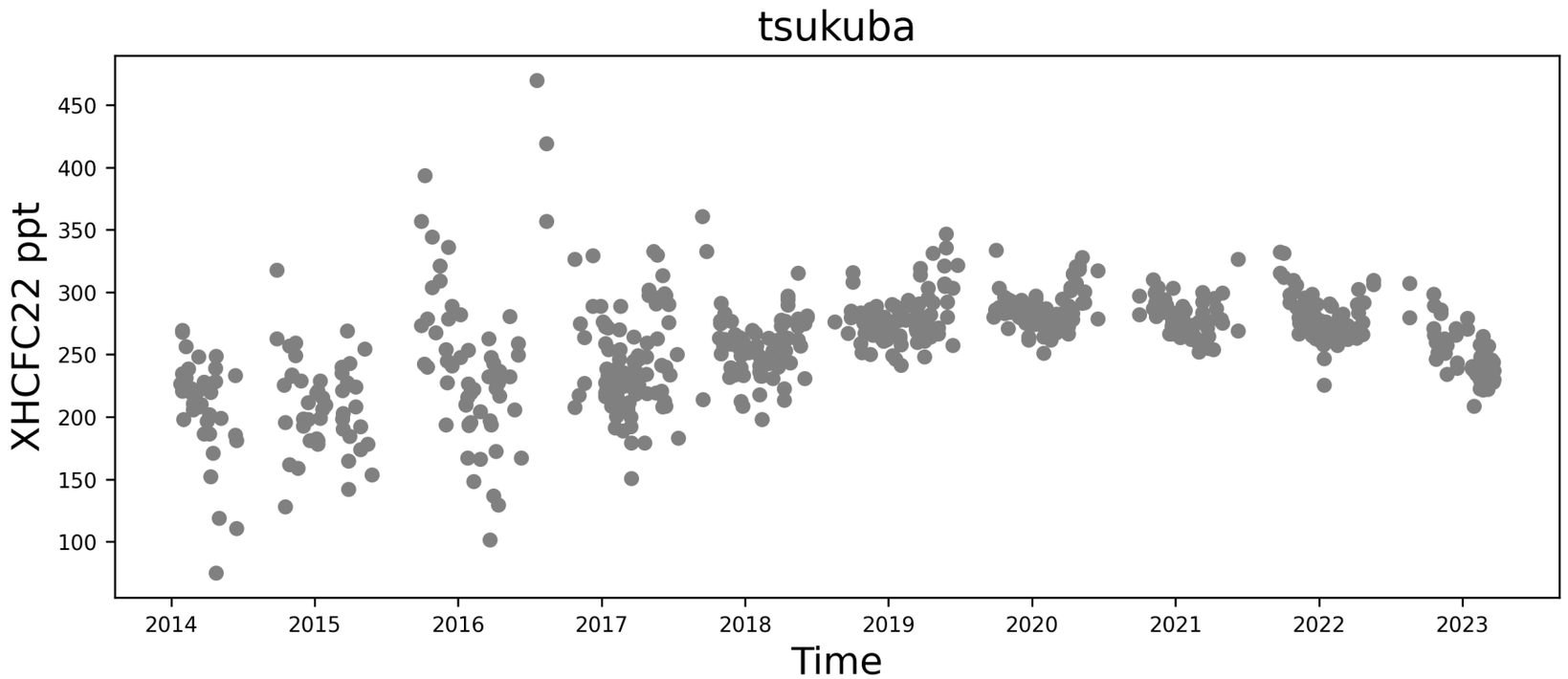

N = 1148
5.715 ± 0.044 ppt/y
XHCFC22 ppt
275
250
225
200
175
150
125
100
1996
2000
2004
2008
2012
2016
2020

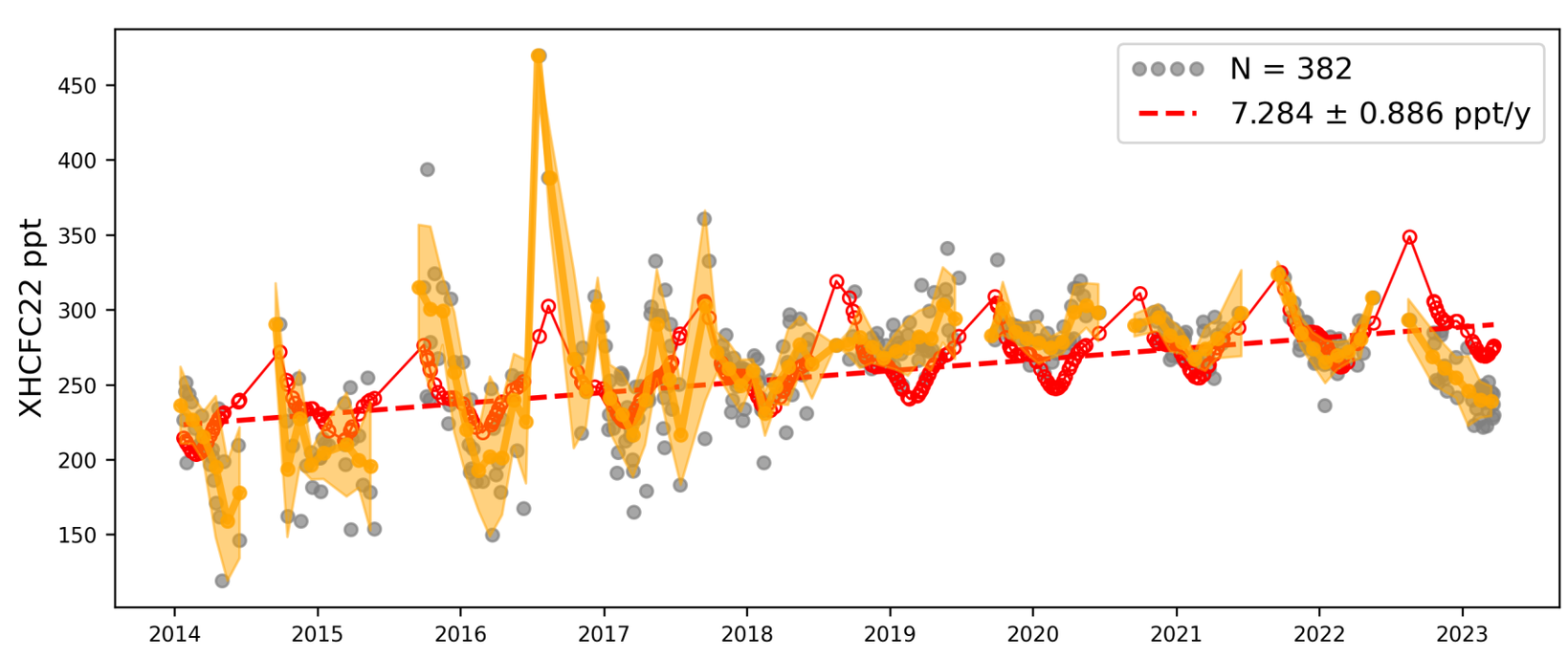
# Jungfraujoch



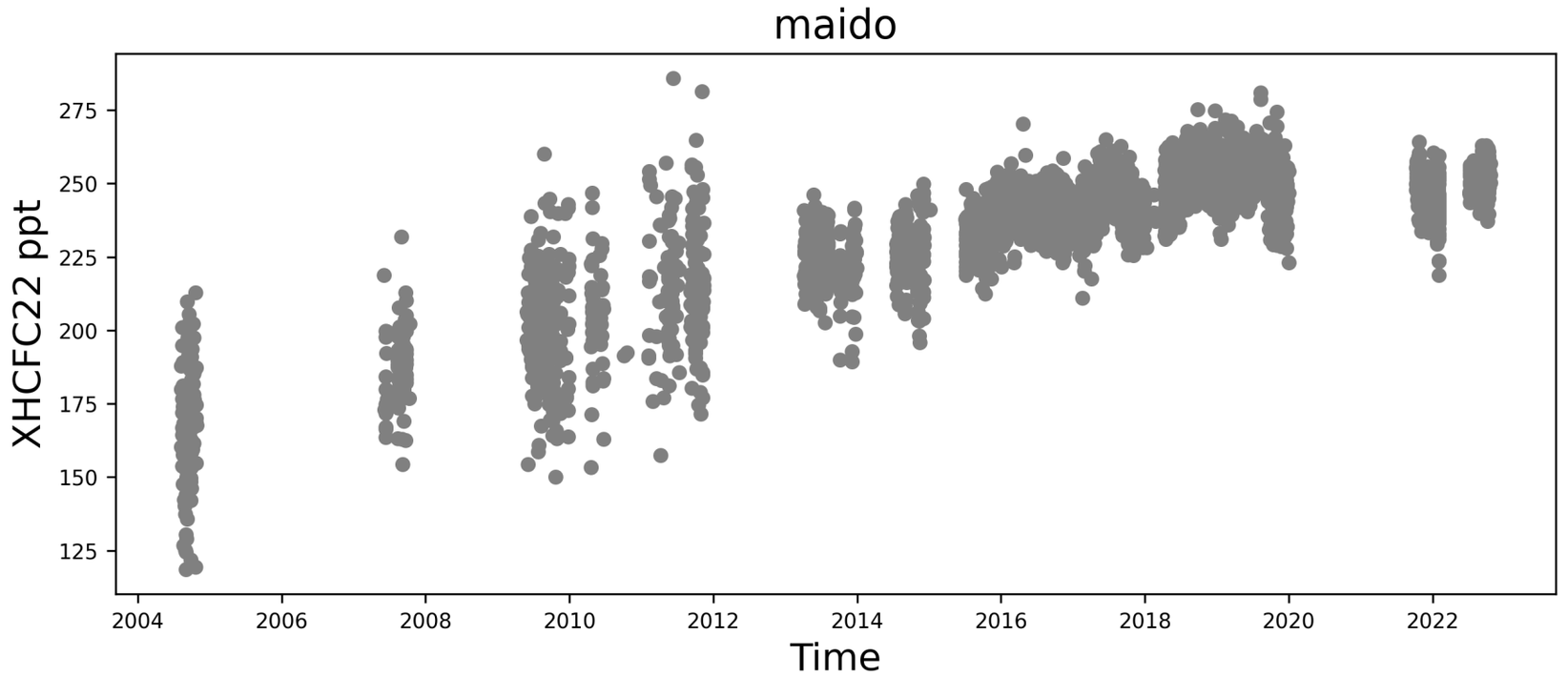



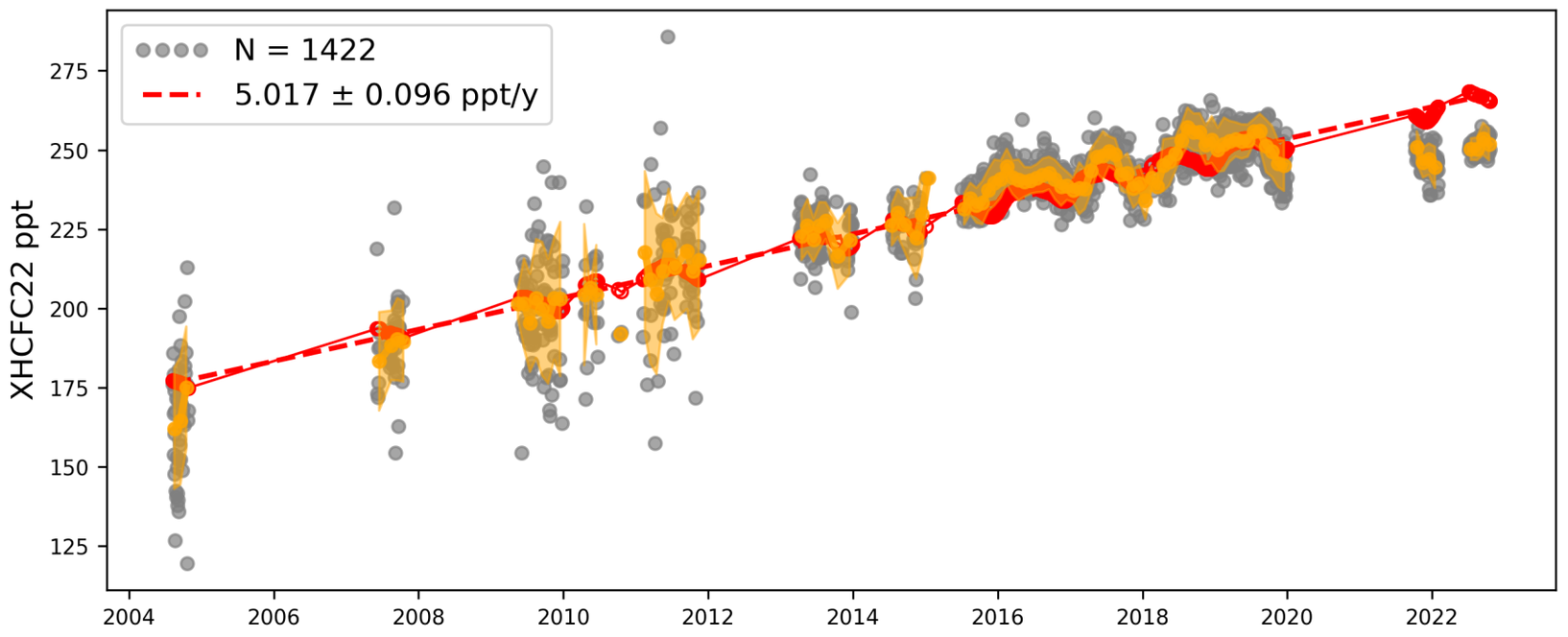
# Tsukuba


tsukuba
XHCFC22 ppt
Time
450
400
350
300
250
200
150
100
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023

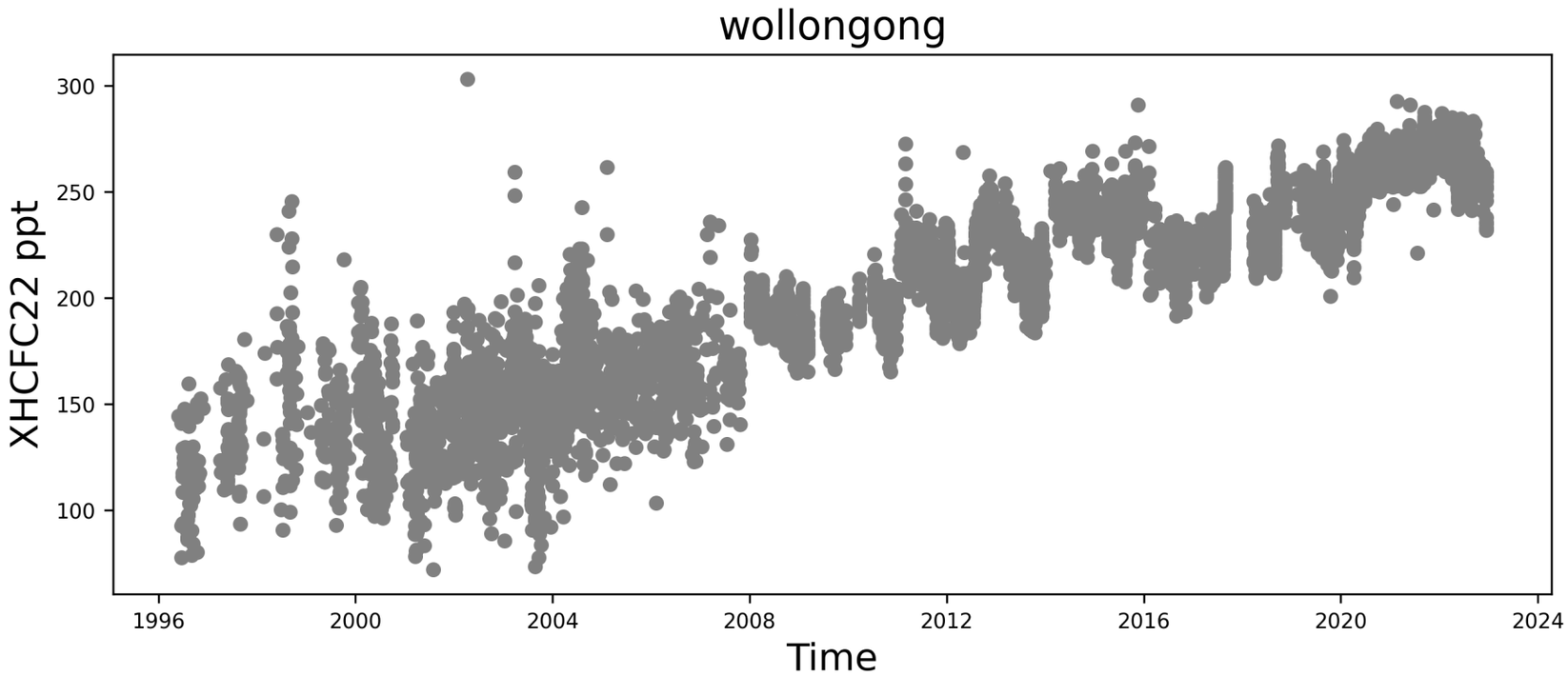

N = 382
7.284 ± 0.886 ppt/y
XHCFC22 ppt
450
400
350
300
250
200
150
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023

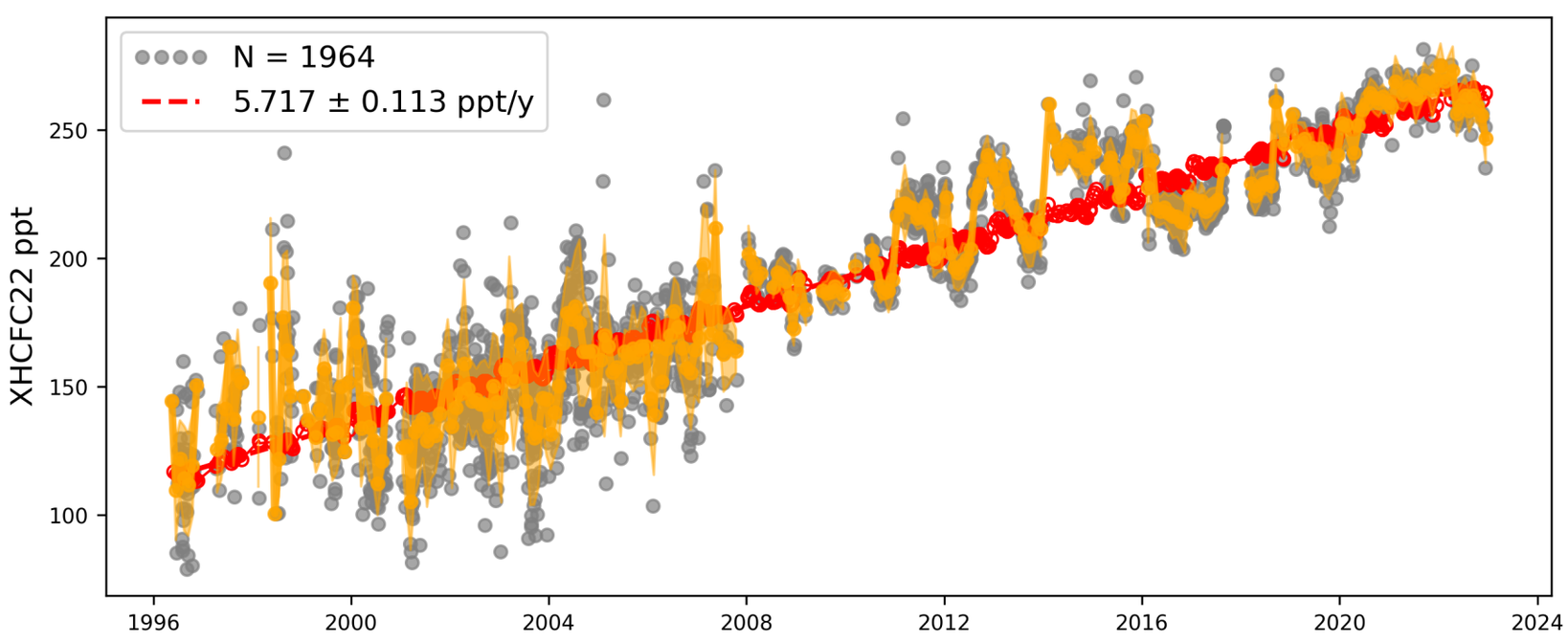
# Stdenis+Maido



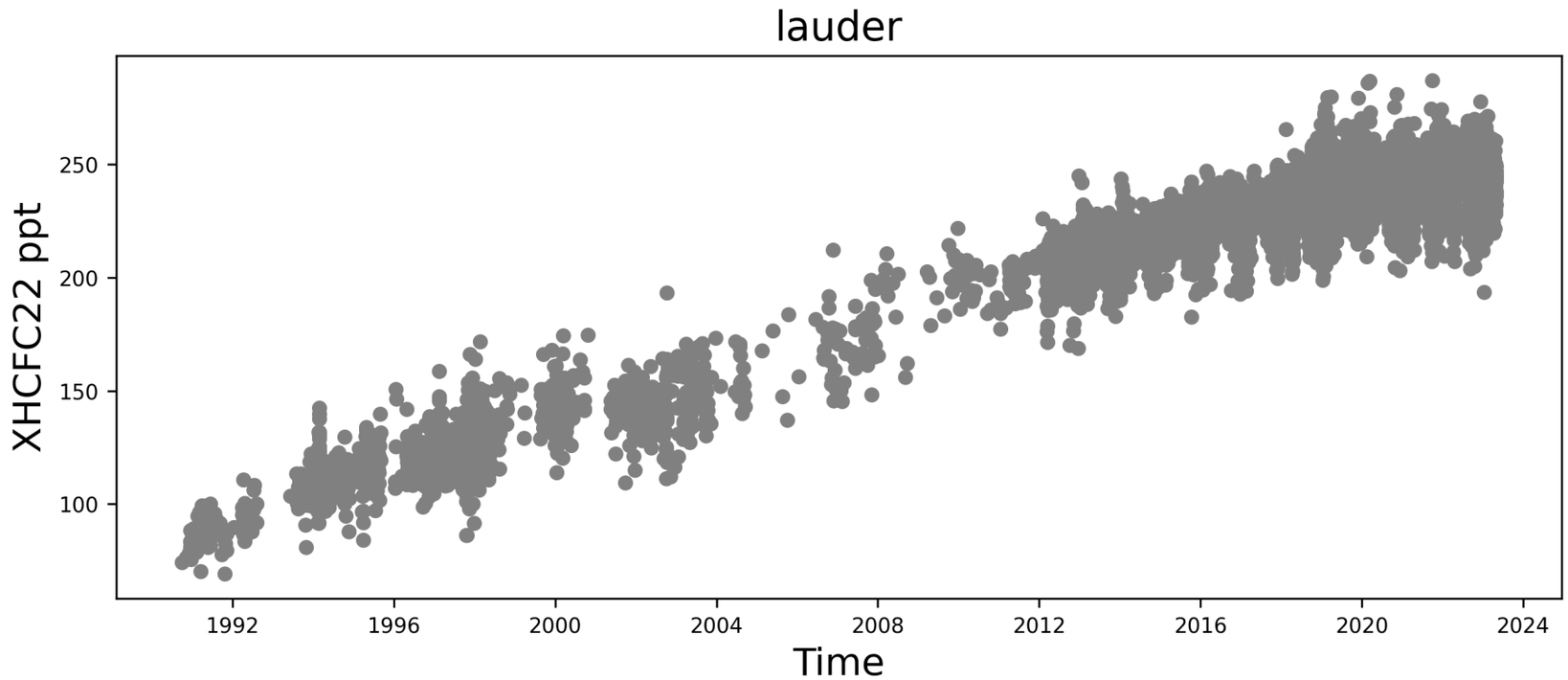



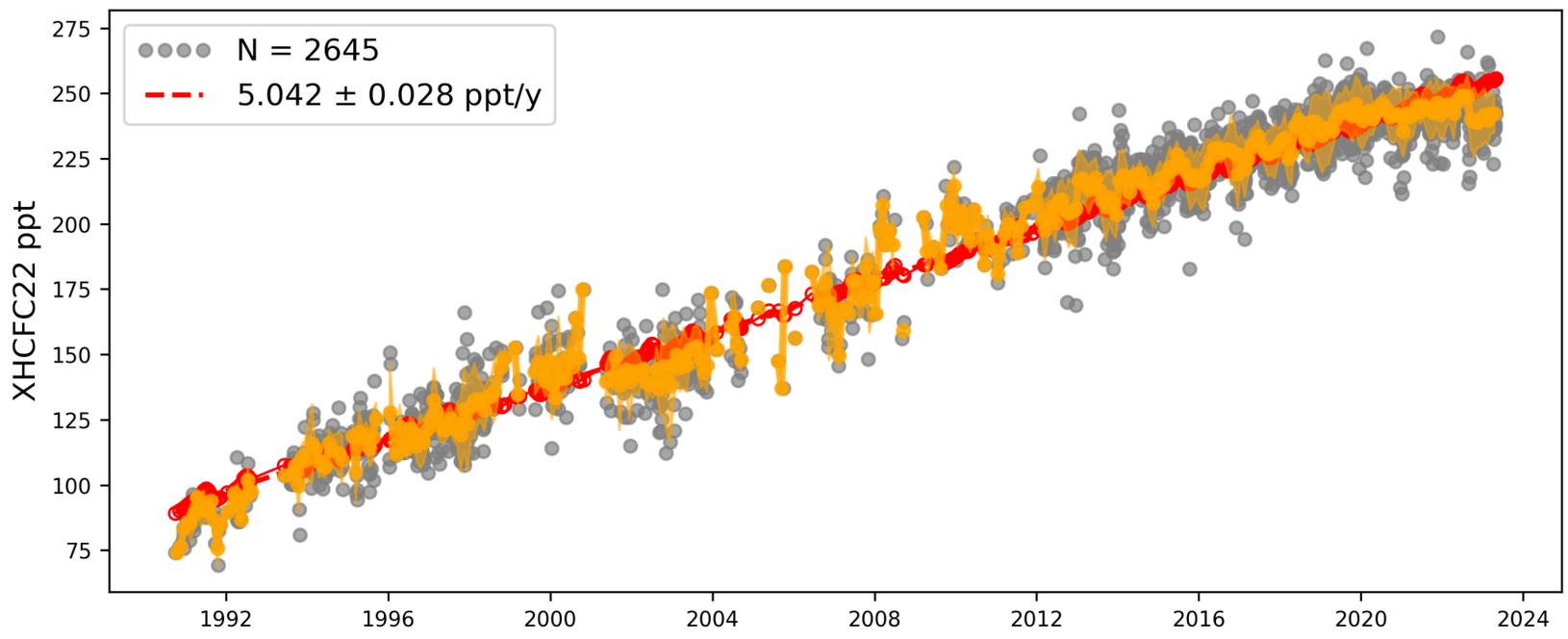
# Wollongong


wollongong
XHCFC22 ppt
300
250
200
150
100
1996
2000
2004
2008
2012
2016
2020
2024
Time

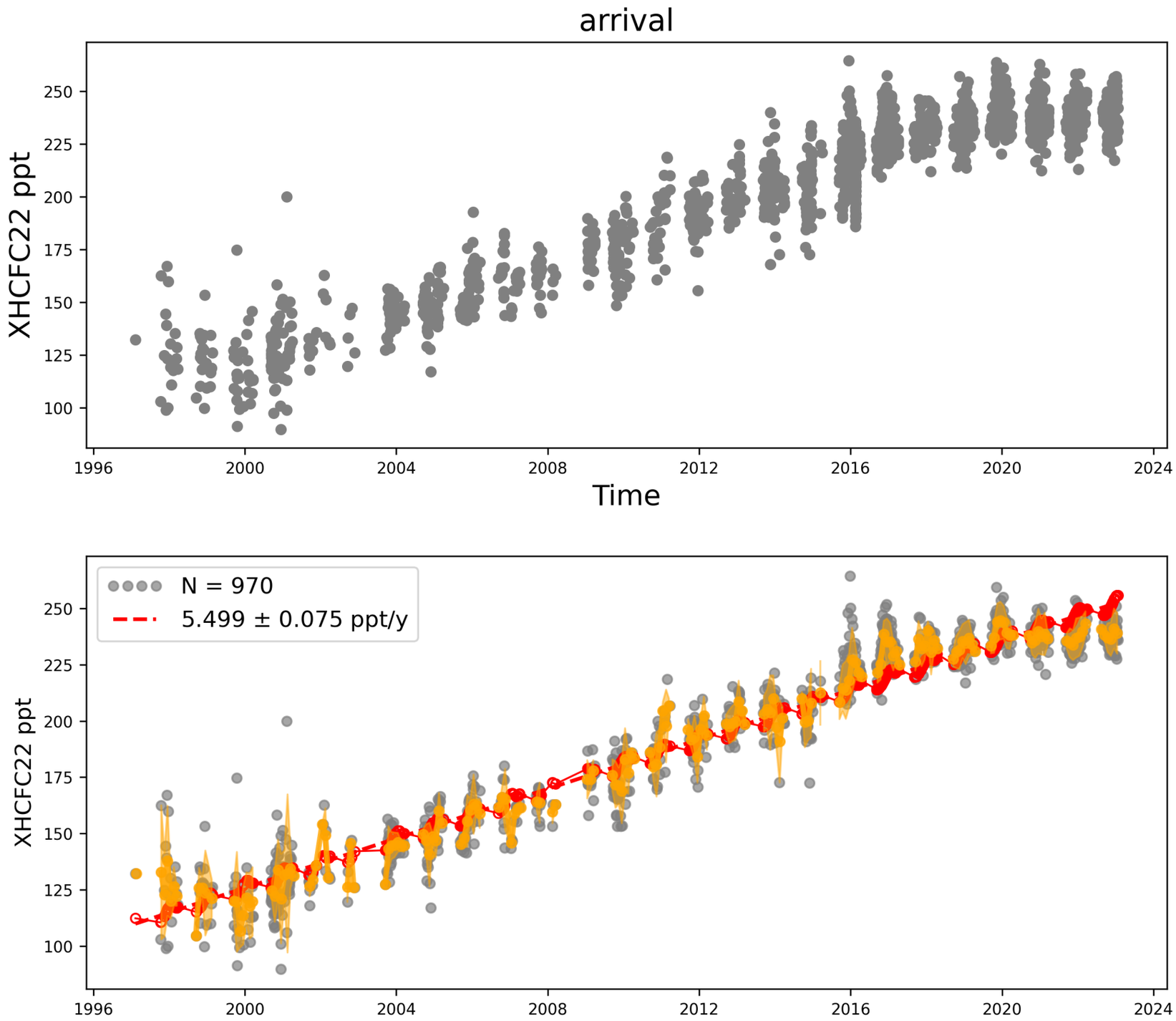

N = 1964
5.717 ± 0.113 ppt/y
XHCFC22 ppt
250
200
150
100
1996
2000
2004
2008
2012
2016
2020
2024

# Lauder

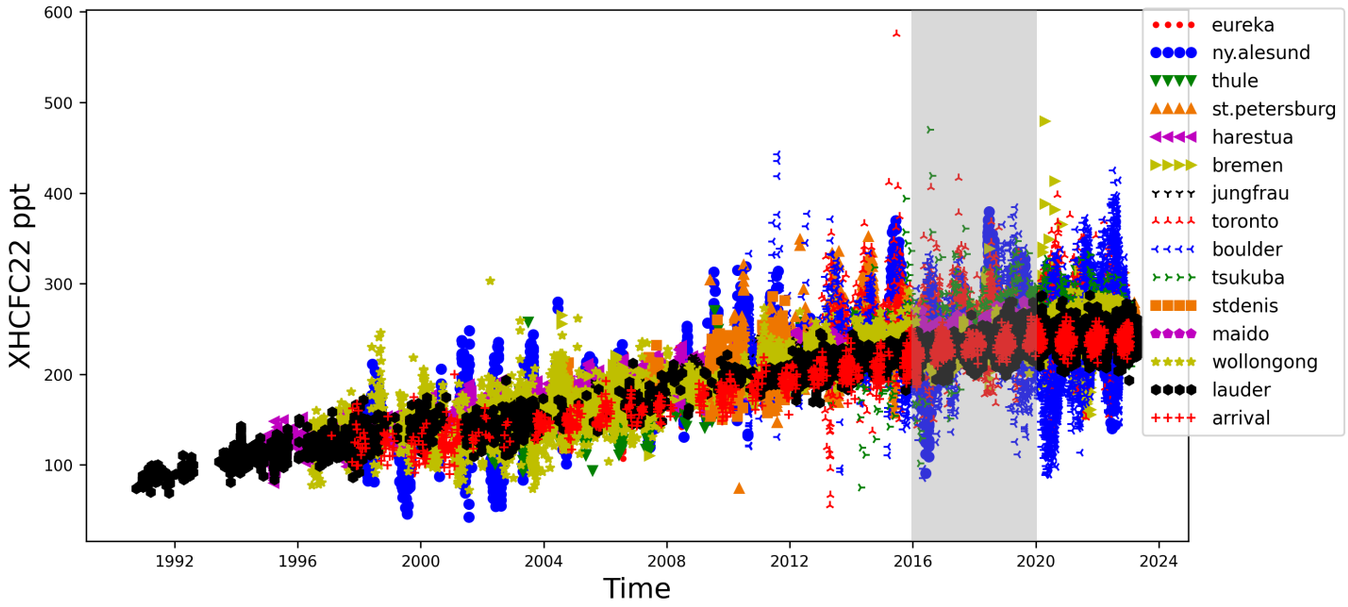

lauder
XHCFC22 ppt
250
200
150
100
1992
1996
2000
2004
2008
2012
2016
2020
2024
Time

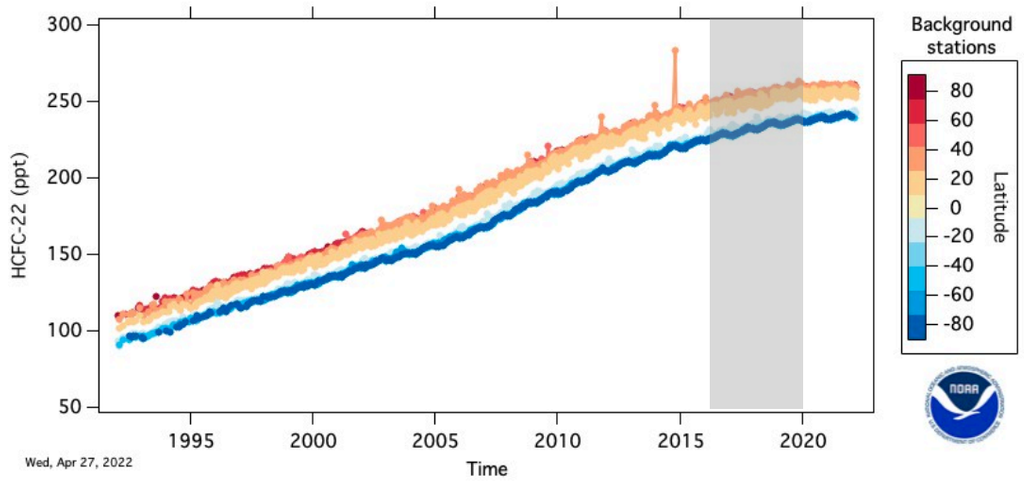

N = 2645
5.042 ± 0.028 ppt/y
XHCFC22 ppt
275
250
225
200
175
150
125
100
75
1992
1996
2000
2004
2008
2012
2016
2020
2024

# Arrival Heights



# NH - SH



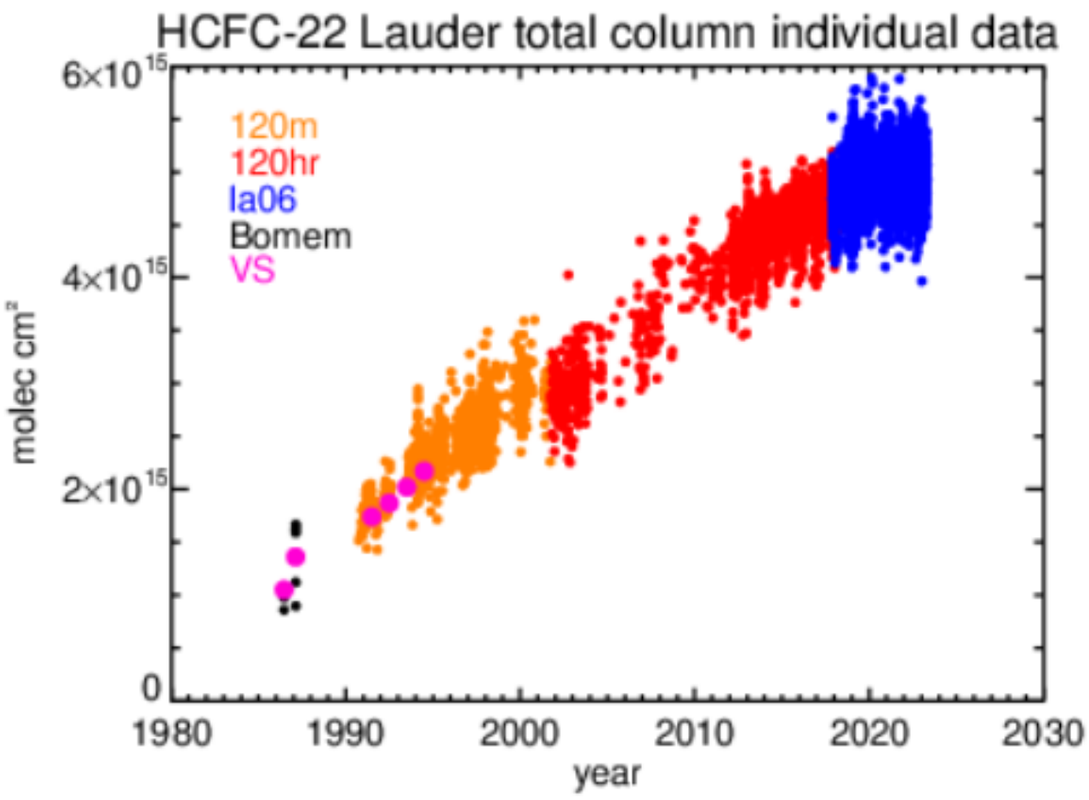



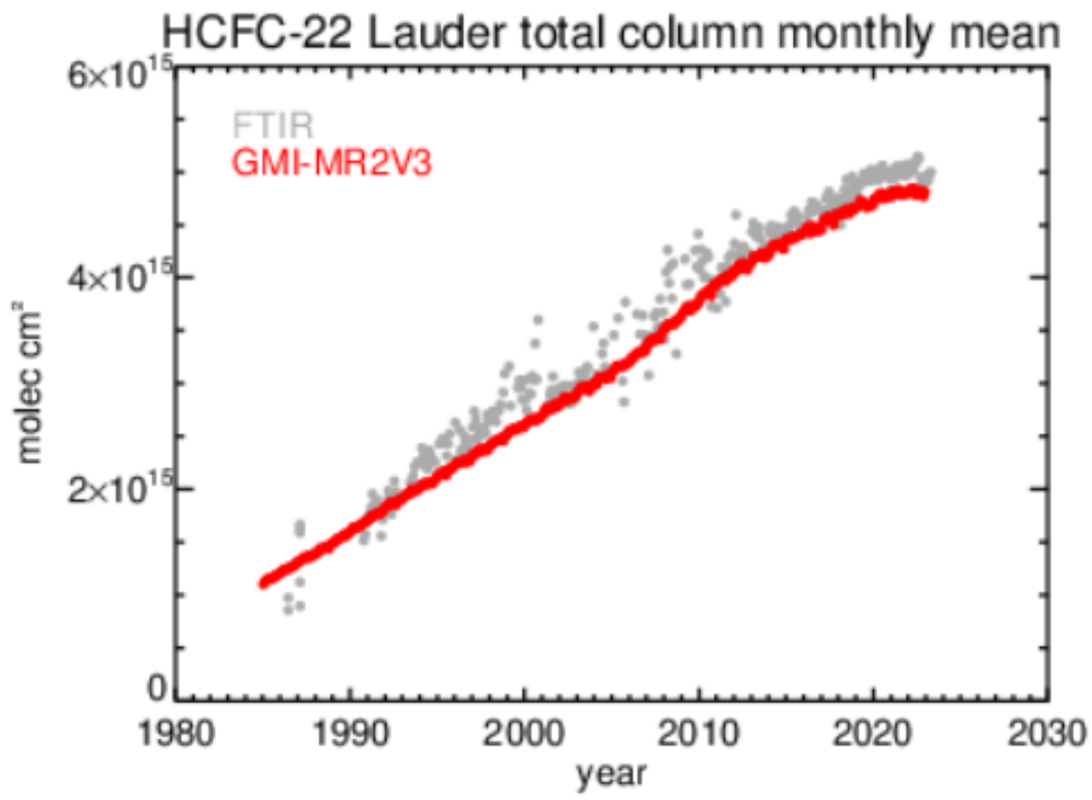

**NH-SH = ~18 ppt**

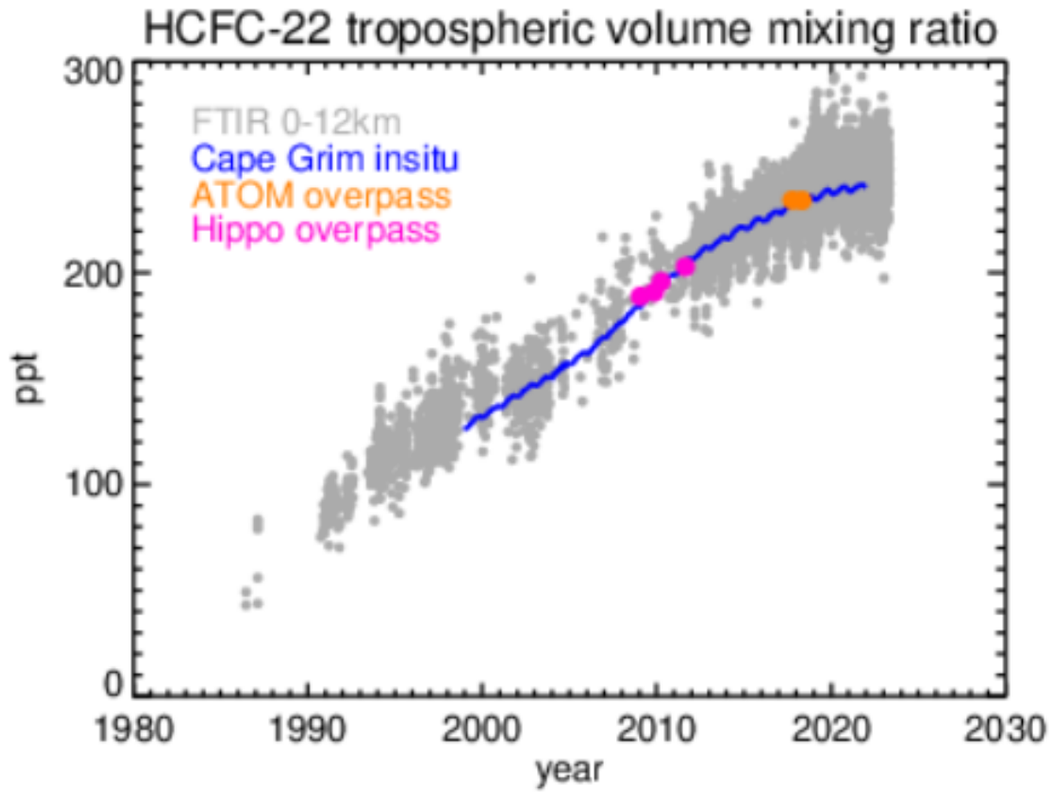
**Year: 2016-2019 (4 years)**
**NH: Thule, Eureka, Harestua, Jungfraujoch**
**SH: Maido, Wollongong, Lauder, Arrival**

| | Thule | Eureka | Harestua | Jungfraujoch | Maido | Wollongong | Lauder | Arrival |
|---|---|---|---|---|---|---|---|---|
| N | 1780 | 4471 | 672 | 1121 | 2885 | 1931 | 2211 | 550 |
| mean VMR | 260.90 | 243.78 | 247.88 | 244.59 | 244.27 | 229.63 | 234.11 | 230.46 |
| mean VMR | 249.28 | | | | 234.62 | | | |
| NH-SH | 14.67 ppt | | | | | | | |

# Lauder XHCFC-22 against model and in situ measurements



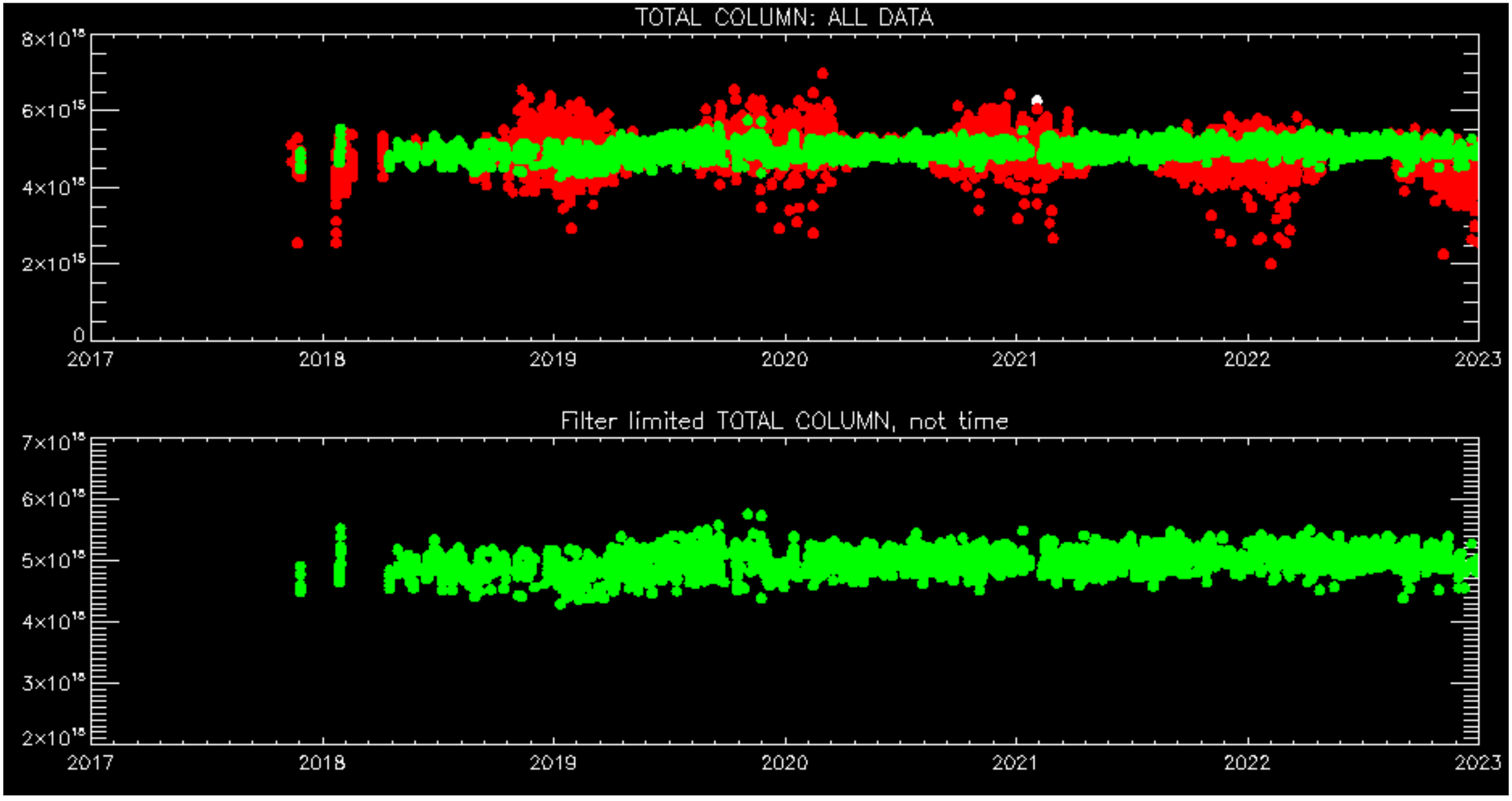




- **Good agreement with several FTIR instruments**
- **Good agreement with GMI model**
- **Good agreement with surface measurements**

**Courtesy of Dan Smale (dan.Smale@niwa.co.nz)**

# Curvature issue




**Courtesy of Dan Smale (dan.Smale@niwa.co.nz)**

# Conclusions & plans

- **The HCFC-22 NDACC-IRWG FTIR harmonized retrieval study is ongoing**
- **The retrieval strategy is ready**
- **We still miss some sites (you are still very welcome if you want to join now)**
- **Inter-comparison with surface measurements and model simulations will be carried out**
  - **GMI**
  - **TOMCAT?**

# Thanks for your attention !