



# Retrieval of several CFCs/HCFCs/HFCs at Rikubetsu and Tsukuba in Japan, and Syowa Station, Antarctica

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# Contents of Today's Talk

- Recent trends of CFCs, HCFCs, and HFCs
- Retrieval of CFCs, HCFCs, and HFCs from FTIR spectra
- Future perspective
- Summary

# Global Warming Potentials

	Gas	ODP	Lifetime (yr)	GWP(AR5)	Major sectors
CFC	CFC-11	1.0	45	4660	Closed foam, Open foam, Aerosols, etc
	CFC-12	1.0	100	10200	Refrigerant (automobile air-conditioning, refrigeration etc)
	CFC-113	0.8	85	5820	Solvent (Electronic component, dry-cleaning etc)
	CFC-114	0.8	190	8590	Open foam
HCFC	HCFC-22	0.055	11.9	1760	Refrigerant (room air-conditioning, commercial refrigeration etc)
	HCFC-141b	0.11	9.2	782	Closed foam, Open foam, Solvent(Electronic component), etc
	HCFC-142b	0.065	17.2	1980	Open foam
HFC	HFC-23	0	222	12400	By-product of HCFC-22 production, Feed stock
	HFC-32	0	5.2	677	Refrigerant (air-conditioning, refrigeration etc)
	HFC-125	0	28.2	3170	Refrigerant (air-conditioning, refrigeration etc)
	HFC-134a	0	13.4	1300	Refrigerant (automobile air-conditioning, refrigeration etc)
	HFC-143a	0	47.1	4800	Refrigerant (air-conditioning, refrigeration etc)
	HFC-152a	0	1.5	138	Aerosols
PFC	CF4	0	50000	7390	AL production, Semiconductor Manufacturing, etc
	C2F6	0	10000	12200	AL production, Semiconductor Manufacturing, etc
SF6	SF6	0	3200	22800	Semiconductor Manufacturing, Electric Utilities, etc

# Phase out Schedule of CFCs/HCFCs/HFCs under the Montreal Protocol

Protocol	Regulation	Target gas	Greenhouse Gas (GHG)	Ozone Depleting Substances (ODS)
KYOTO	Emissions	CO2, CH4, H2O, HFCs, PFCs, SF6	Yes	No
MONTREAL	Productions Consumptions	CFCs, HCFCs, Halons, Carbon tetrachloride, 1,1,1-trichloroethane, Methyl bromide	Yes	Yes

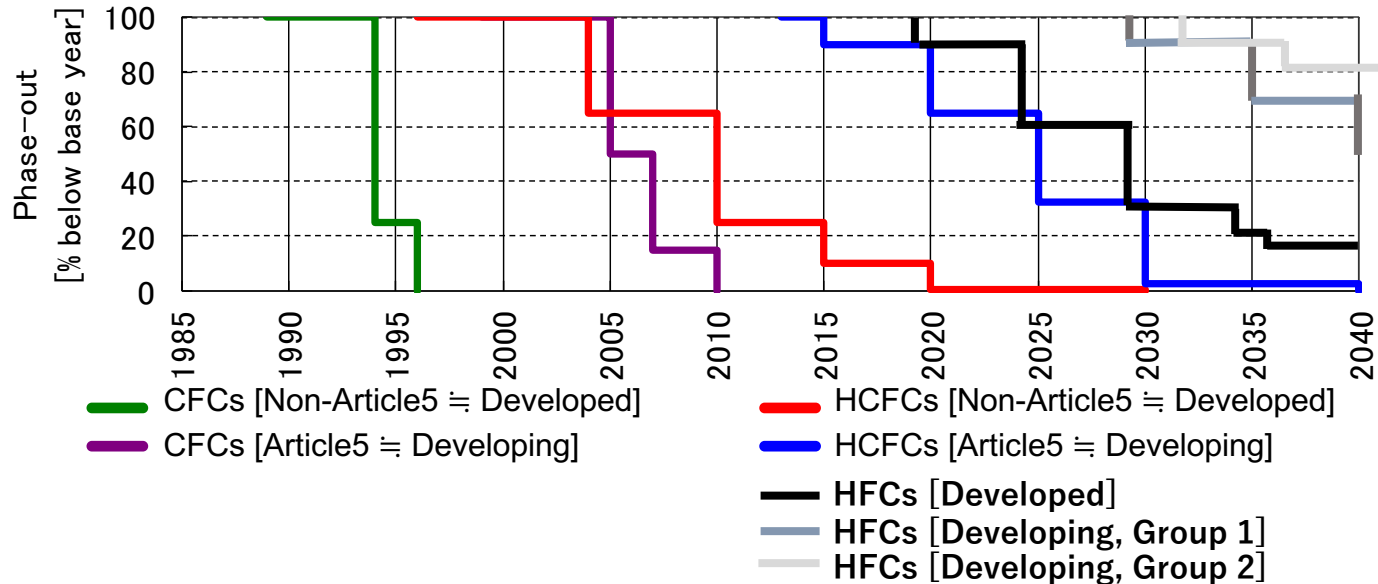
Kigali Amendment  
(2016.10)

Productions  
Consumptions

HFCs

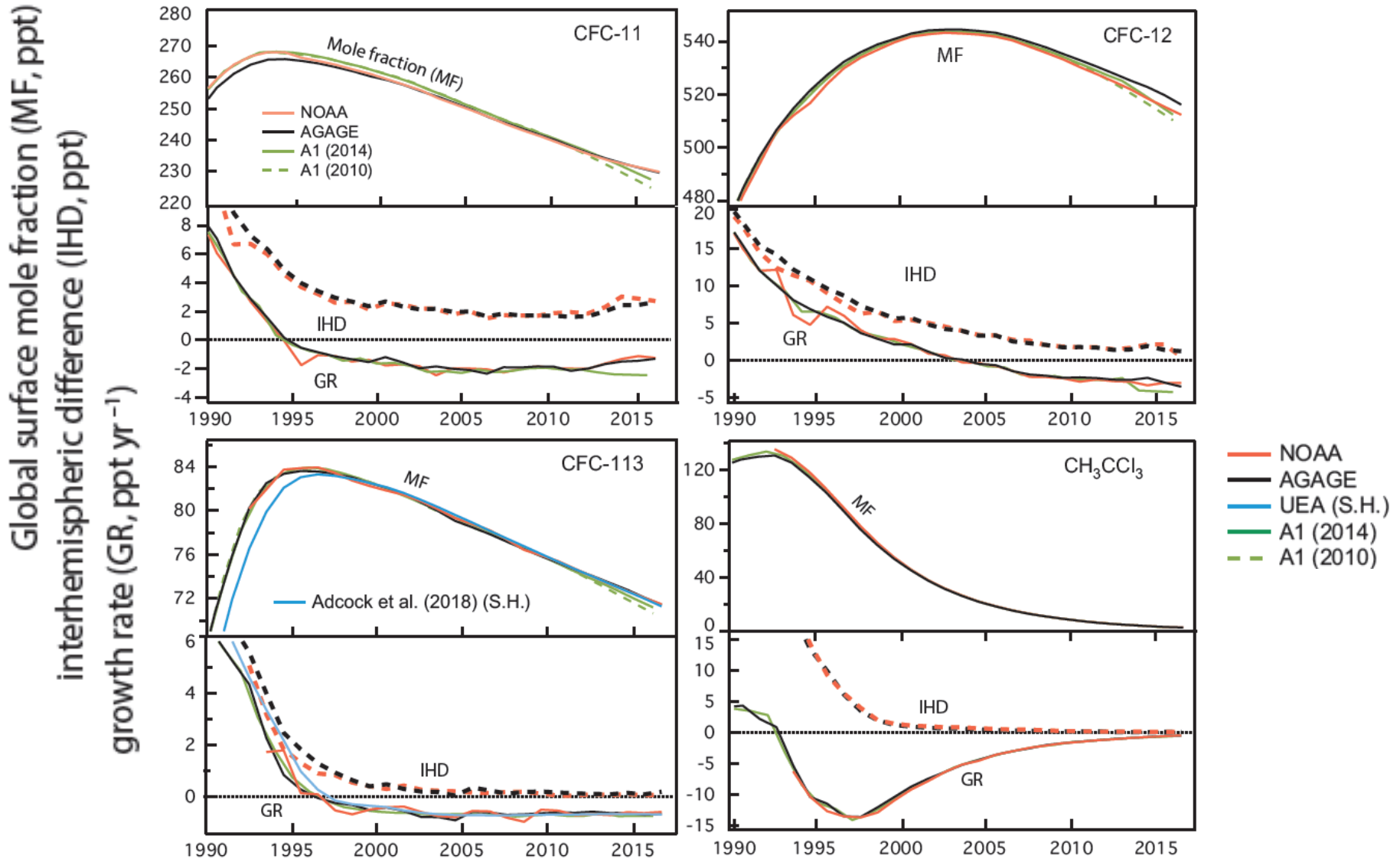
Yes

No



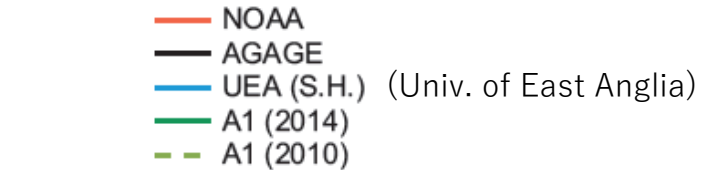
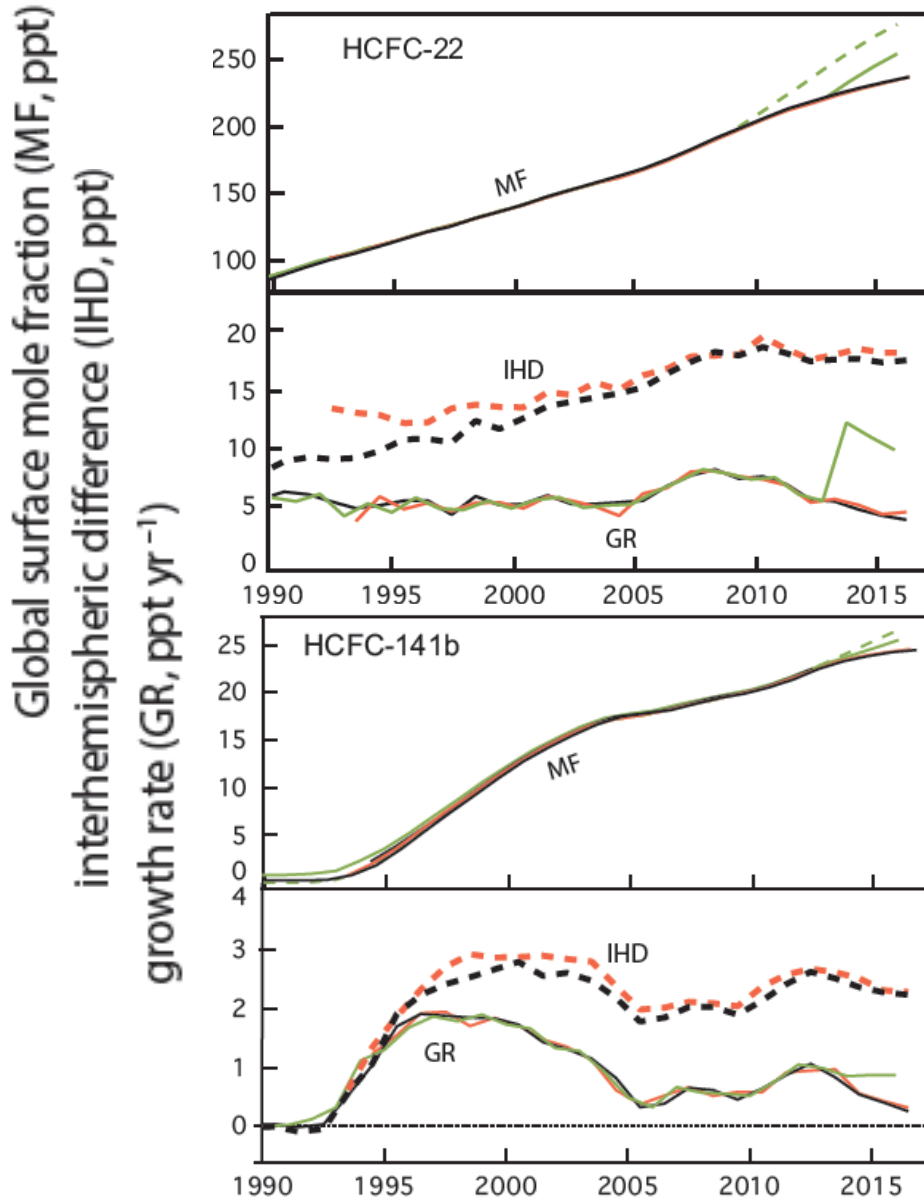


# Global Mole Fraction of CFCs

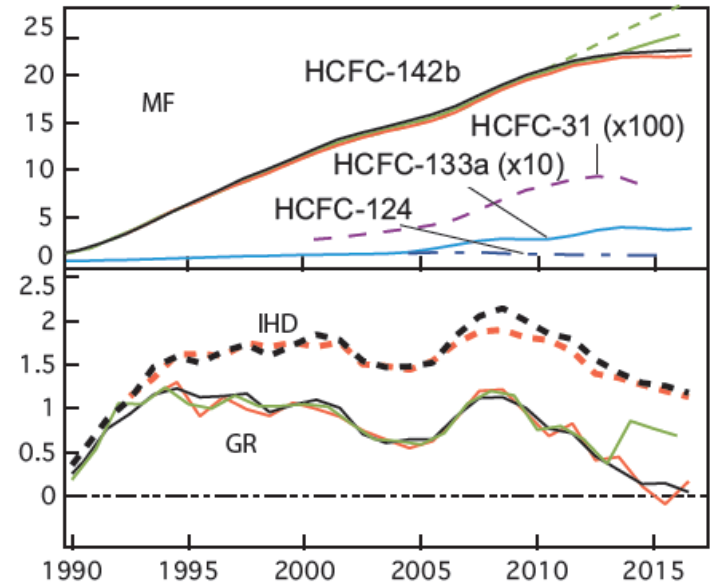




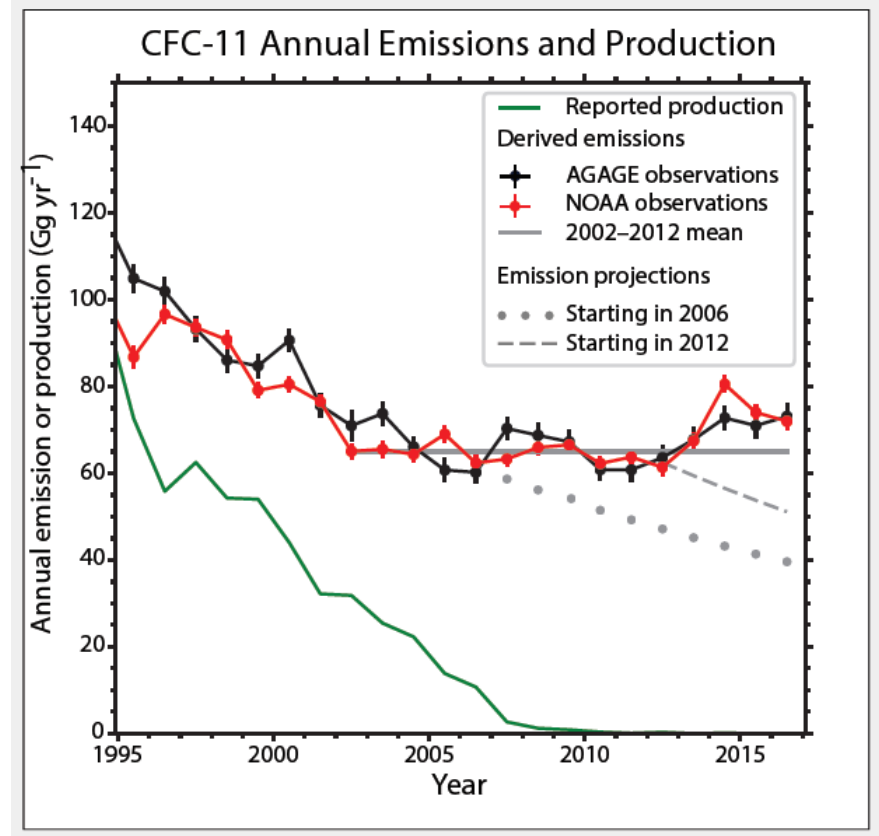
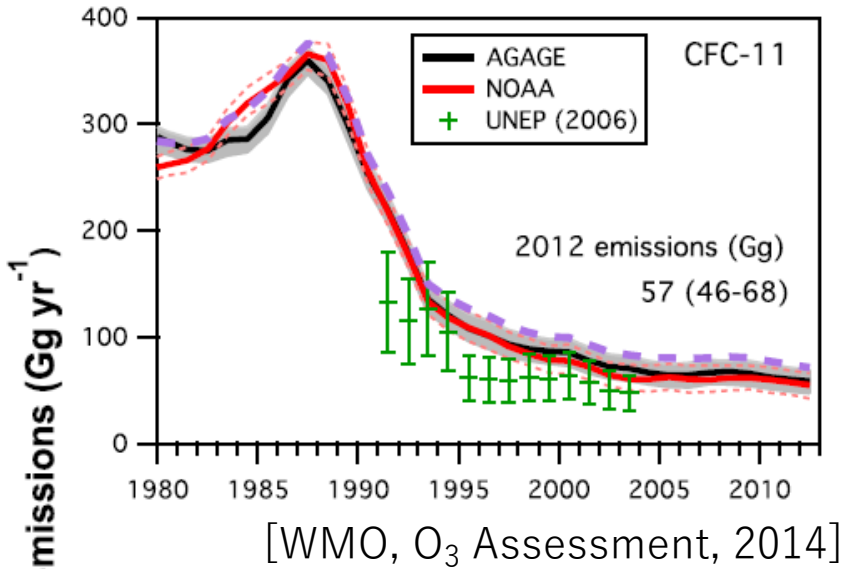
# Global Mole Fraction of HCFCs



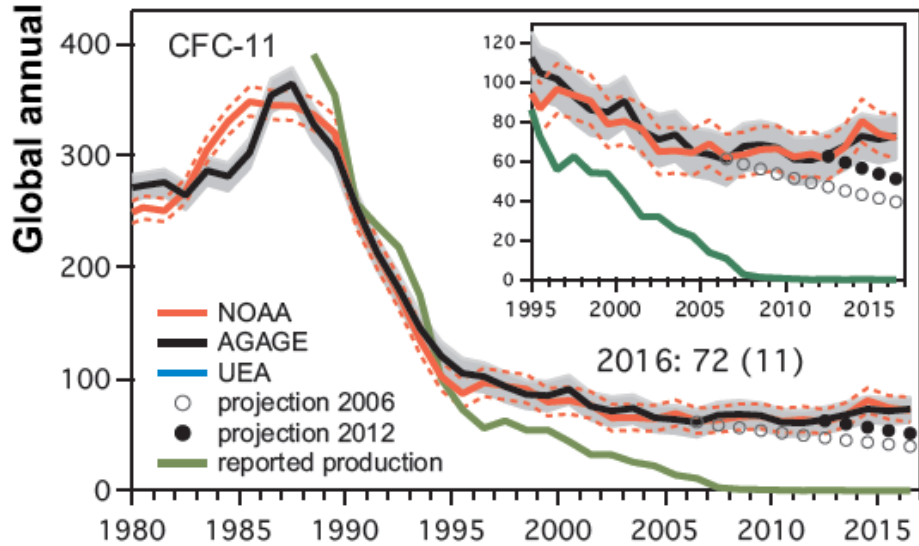
[WMO, O<sub>3</sub> Assessment, 2019]



# Global Emissions of CFC-11

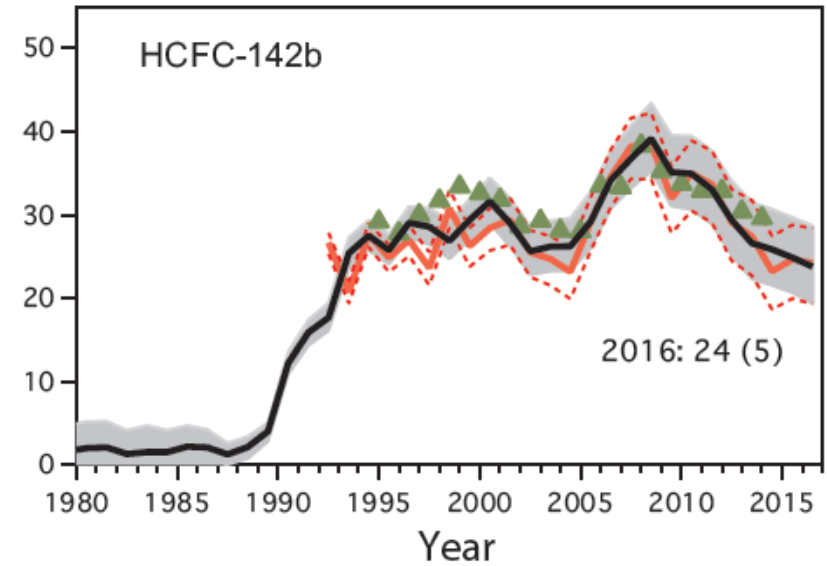
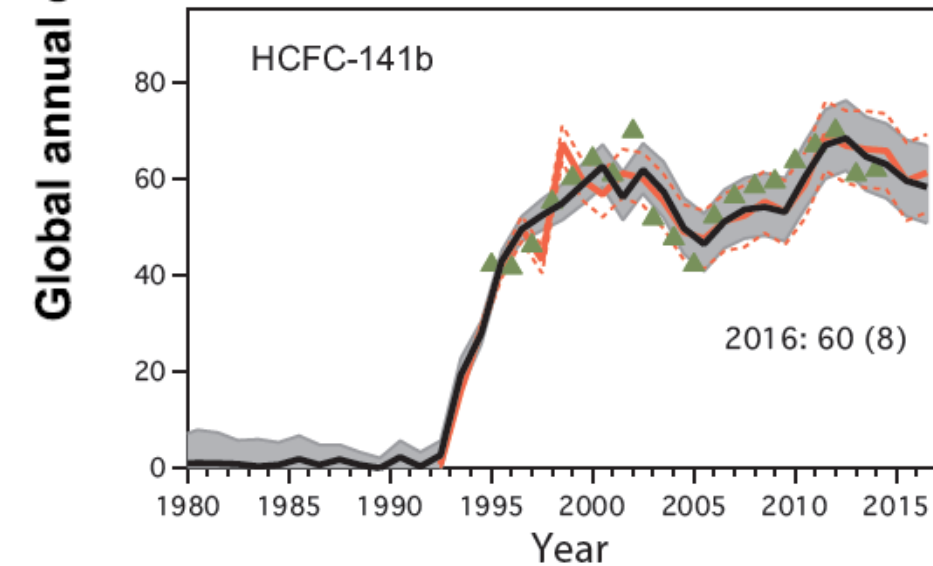
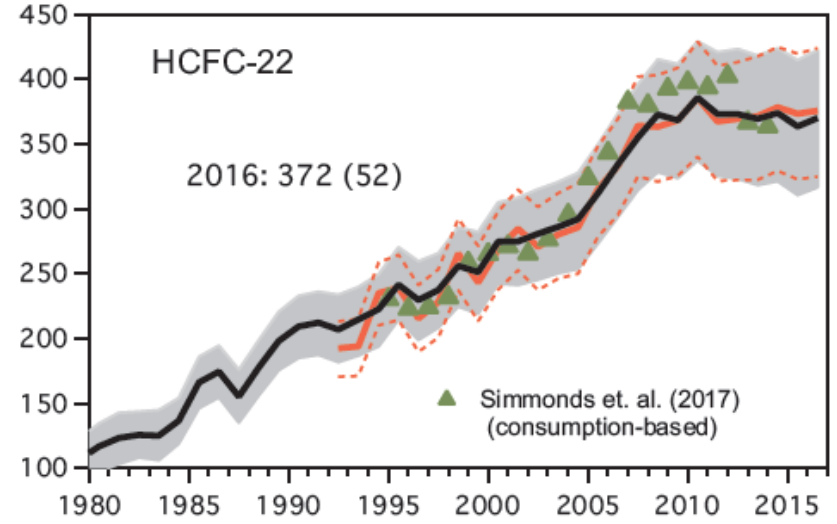
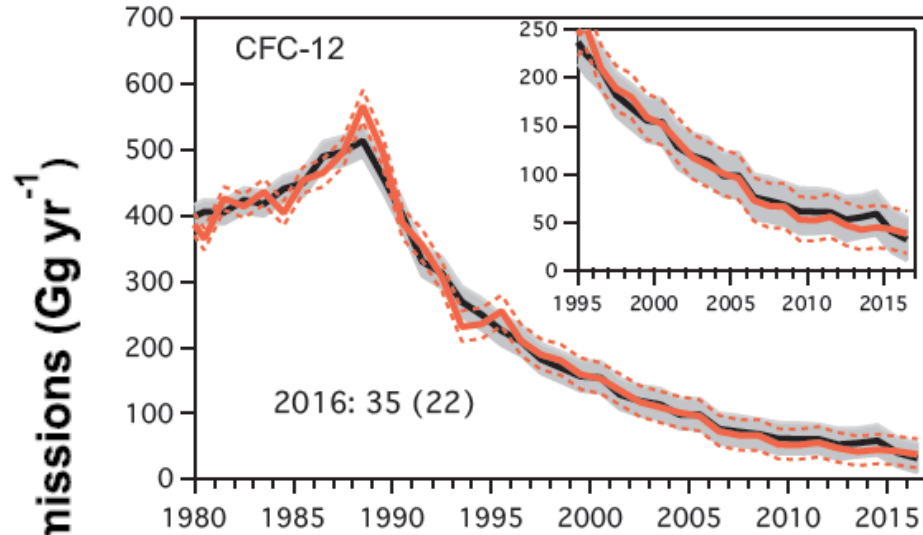


[WMO, O<sub>3</sub> Assessment, 2019]





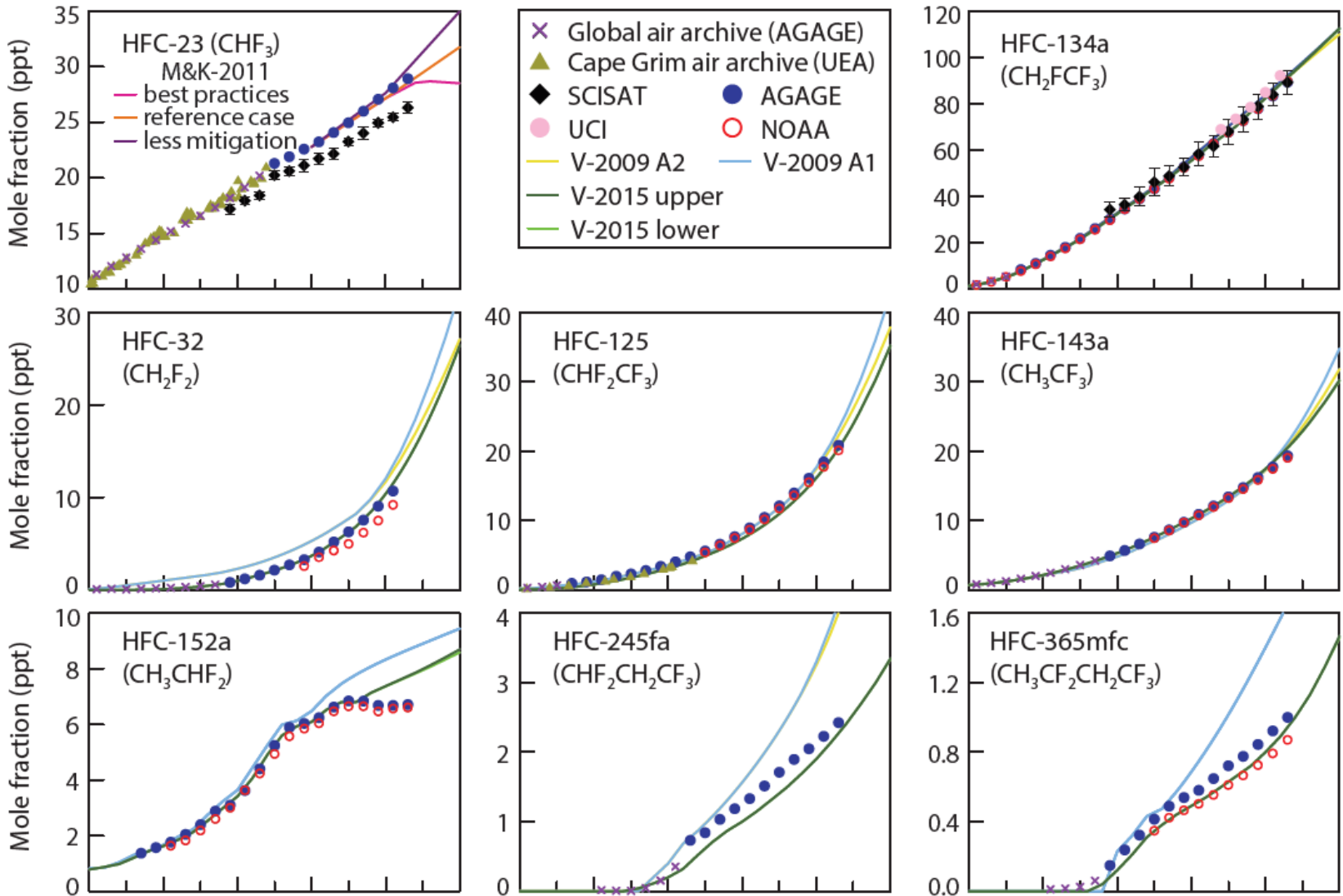
# Global Emissions of CFC-12/HCFCs





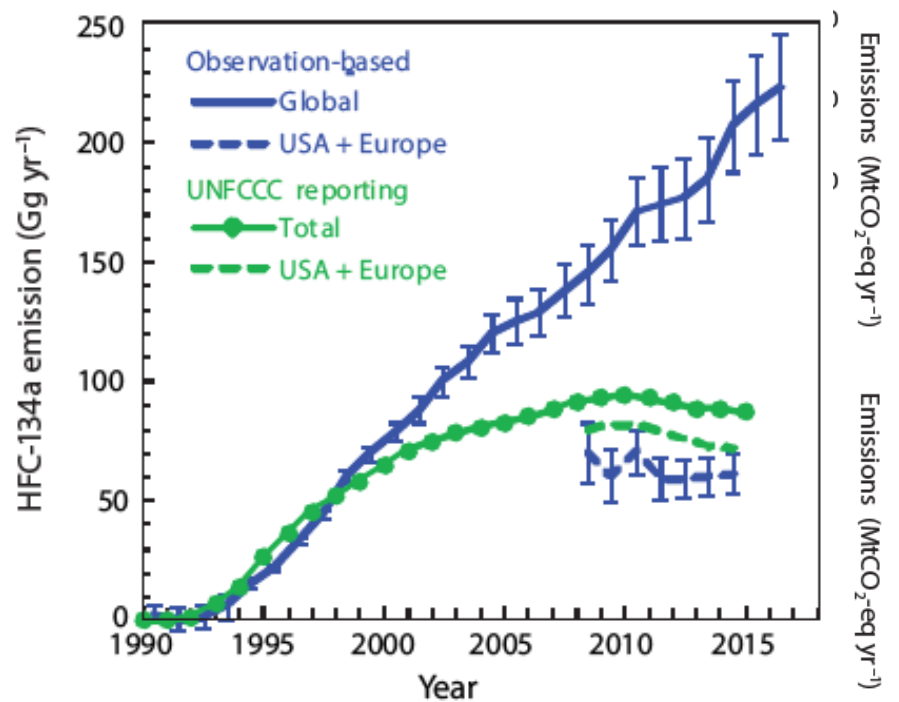
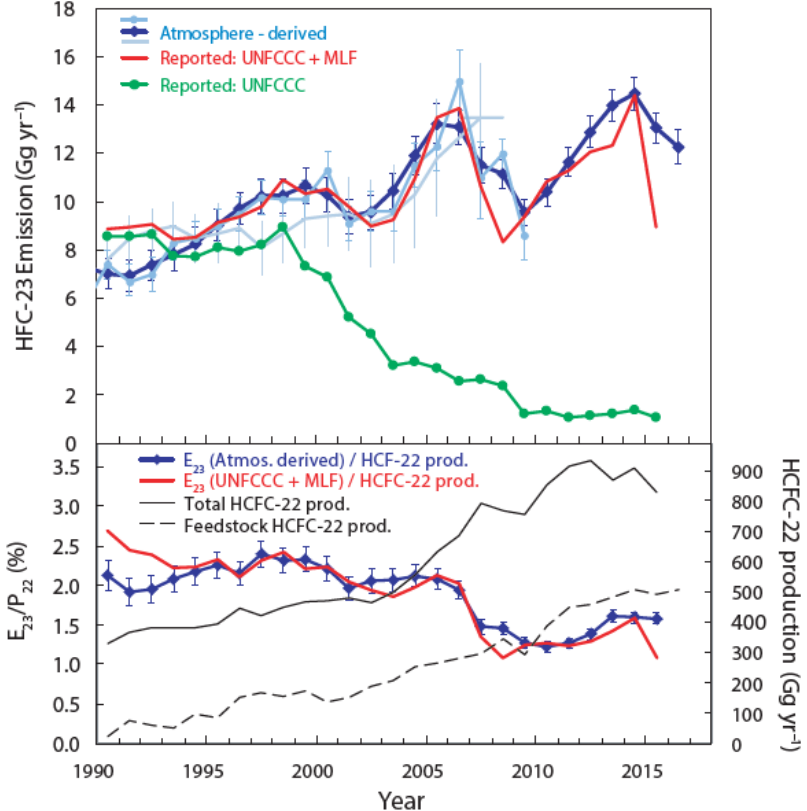
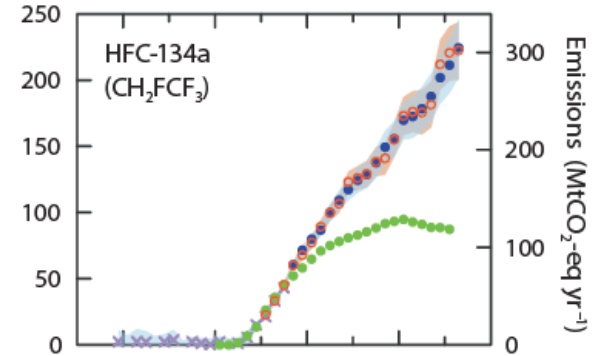
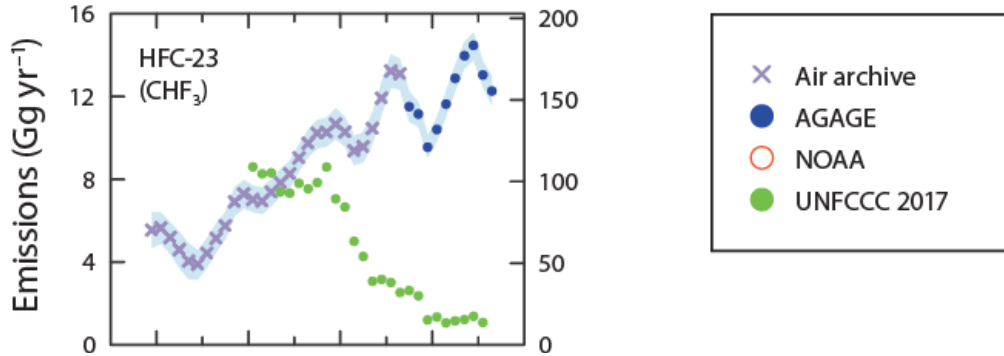


# Recent Trends of HFCs

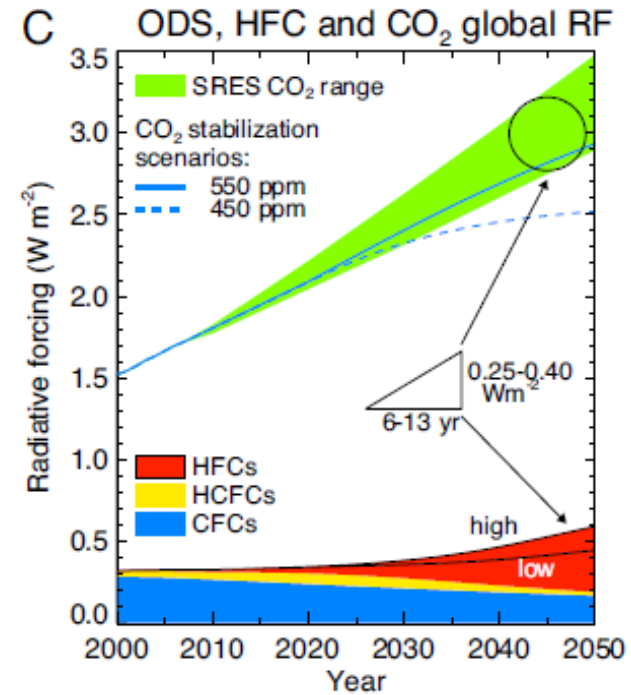
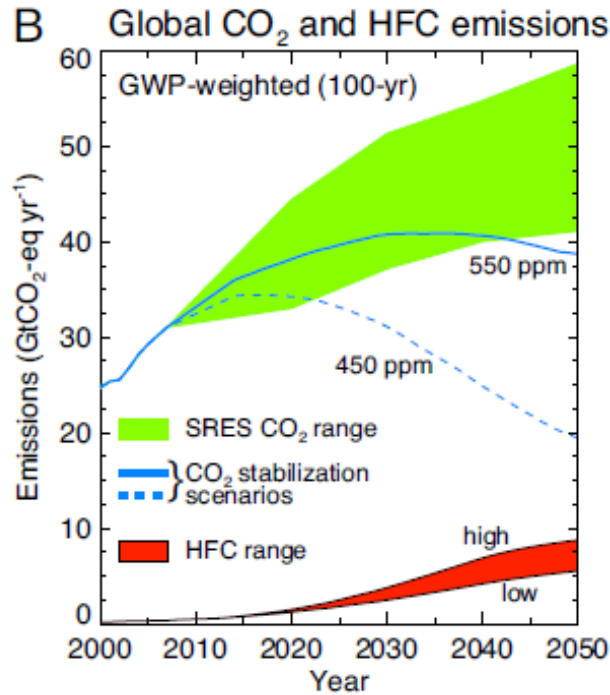
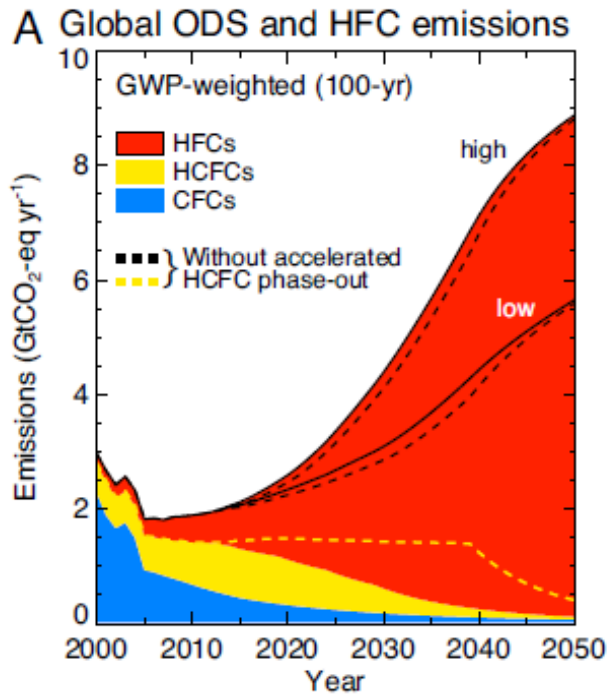




# Recent Emissions of HFCs

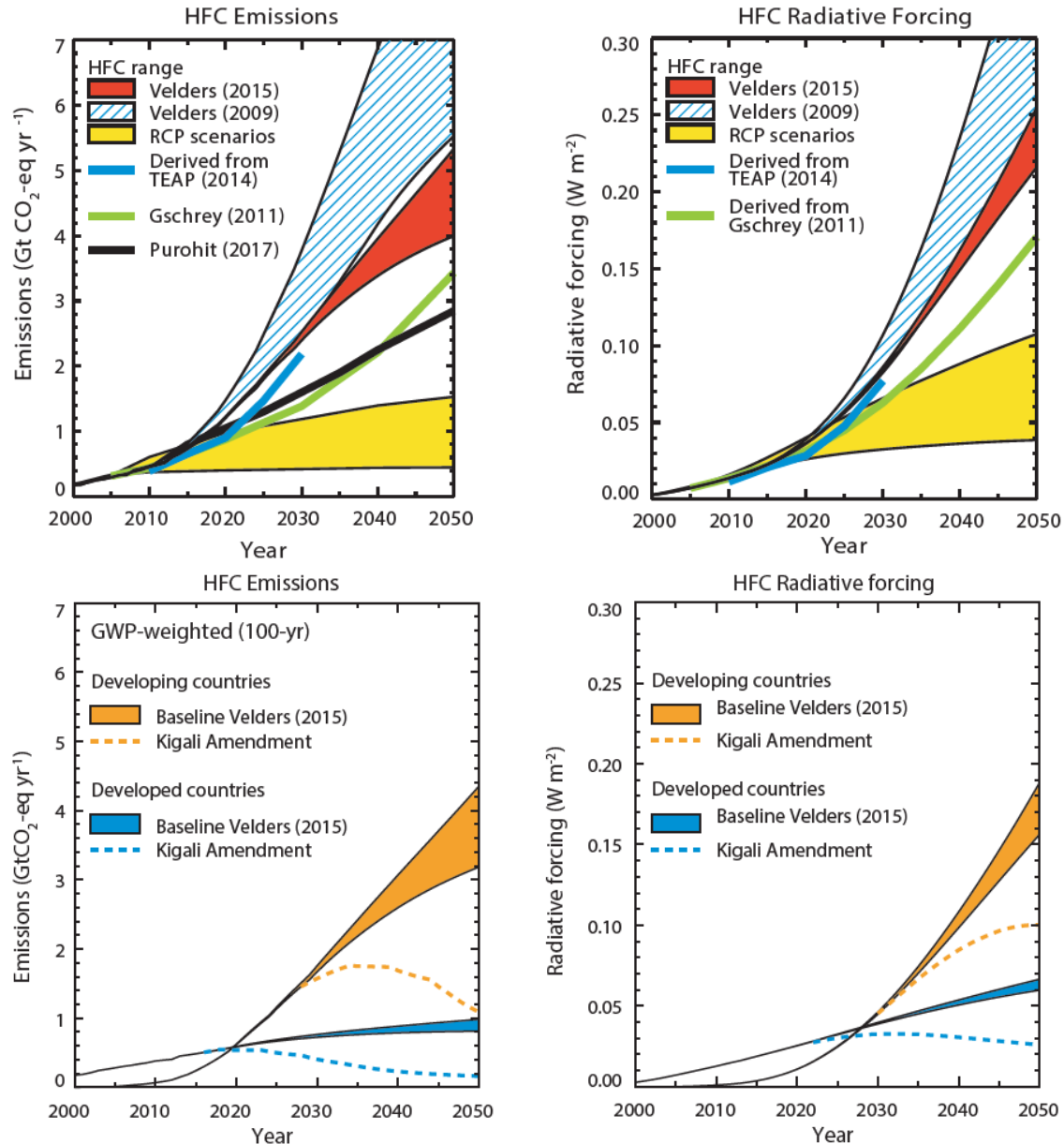


# Effect of CFC/HCFC/HFC Emissions



[Velders et al., 2009, PNAS]

# Effect of CFC/HCFC/HFC Emissions



[WMO, O<sub>3</sub> Assess., 2019]



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# HCFCs/HFCs Candidates for FTIR Retrievals

Gas Species	Mixing Ratio (pptv)@ 2012	GWP	Lifetime (y)	IR-Intensity (1)	IR-Intensity (2)	Toon's Pseudo Line List
SF <sub>6</sub> *	8	22,800	3,200	182	18	○
HCFC-22*	220	1,810	12	398	335	○
HCFC-141b*	22	725	9.4	16	17	○
HCFC-142b*	20	2,310	18	46	26	○
HFC-23*	25	14,800	228	370	37	○
HFC-134a	70	1,430	14	100	72	◎
HFC-143a	13	4,470	51	58	11	
HFC-125	11	3,500	31	39	12	
HFC-32	6	675	5.4	4	8	
HFC-245fa	1.5	1,030	8	2	2	

MR\*GWP

MR\*GWP/LT(<100)



# Analyzed Data from 3 FTIR Sites

- **Antarctic Syowa Station (69.0°S, 39.6°E, 20m a.s.l.)** - *A candidate site of the NDACC InfraRed Working Group (IRWG)*
  - Bruker IFS-120M Fourier Transform Spectrometer - *Operated in 2007, 2011 and 2016. FTIR operations have closed now.*
- **Rikubetsu (43.46°N, 143.77°E, 380m a.s.l.), Hokkaido, Japan** - *An NDACC IRWG site*
  - Bruker IFS-120M Fourier Transform Spectrometer - *Operated during the period of 1995 to 2010. Now operating the IFS-120/5HR.*
- **Tsukuba (36.05°N, 140.12°E, 31m a.s.l.), Ibaraki, Japan** - *A candidate site of the NDACC IRWG*
  - Bruker IFS-125HR Fourier Transform Spectrometer - *Operating as the NDACC mode since 2014.*



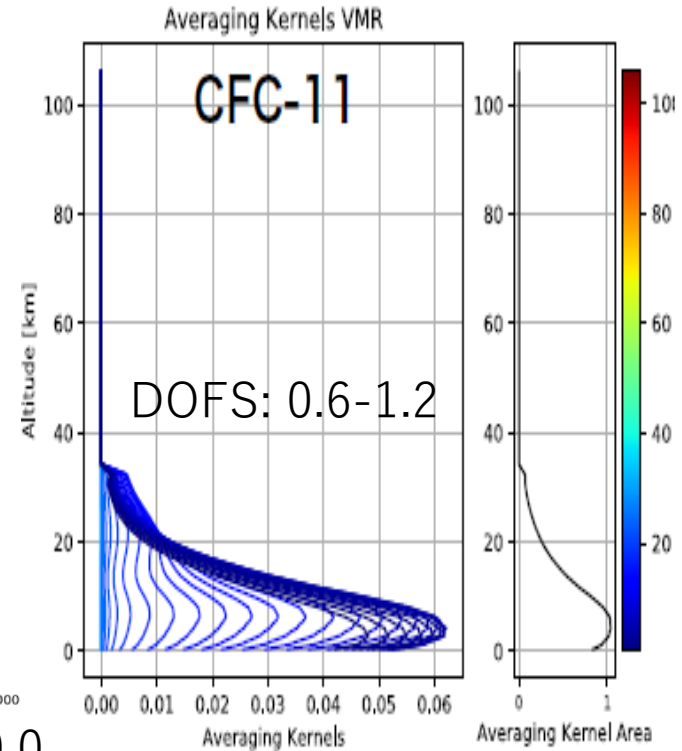
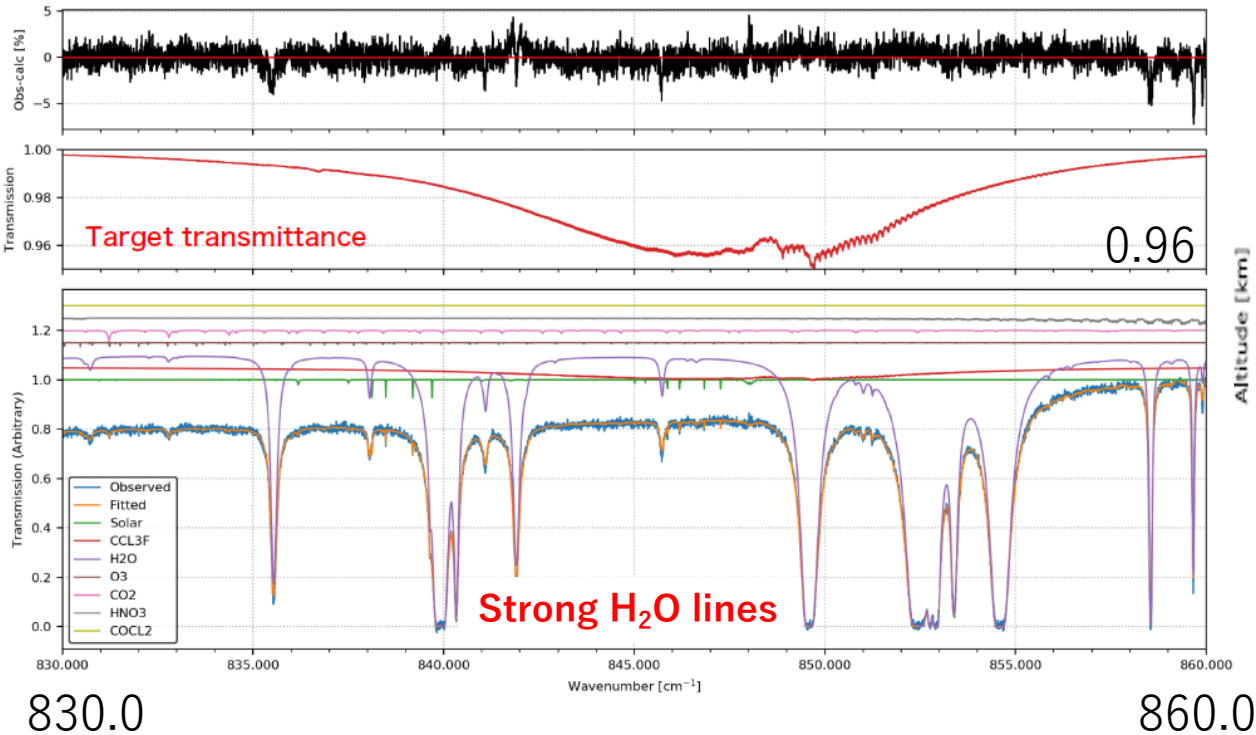
# Retrieval Parameters

Target species	CFC-11	CFC-12	HCFC-22	HCFC-142b	HFC-23
Microwindows [cm <sup>-1</sup> ]	830.0 - 860.0	1160.2 - 1161.4	828.60 - 831.0	1191.7 - 1195.2	1138.5 - 1148.0 1154.0 - 1160.0
Profile retrieval	CFC-11, H <sub>2</sub> O	CFC-12, N <sub>2</sub> O, O <sub>3</sub>	HCFC-22	HCFC-142b, H <sub>2</sub> O, HDO	HFC-23, N <sub>2</sub> O, O <sub>3</sub>
Column retrieval	O <sub>3</sub> , CO <sub>2</sub> , HNO <sub>3</sub> , COCl <sub>2</sub>	CH <sub>4</sub> , H <sub>2</sub> O	CO <sub>2</sub> , O <sub>3</sub> , H <sub>2</sub> O	N <sub>2</sub> O, O <sub>3</sub> , CH <sub>4</sub>	H <sub>2</sub> O, CH <sub>4</sub> , HDO, CFC-12, HCFC-22
Spectroscopic data	Pseudo-line list, HITRAN2008				
Background correction	slope, curvature, zshift	slope, curvature, zshift	slope, zshift	slope, curvature, zshift	slope, curvature, zshift
A priori profiles	WACCM ver.6			Naik et al. (2000)	
ILS	LINEFIT14				



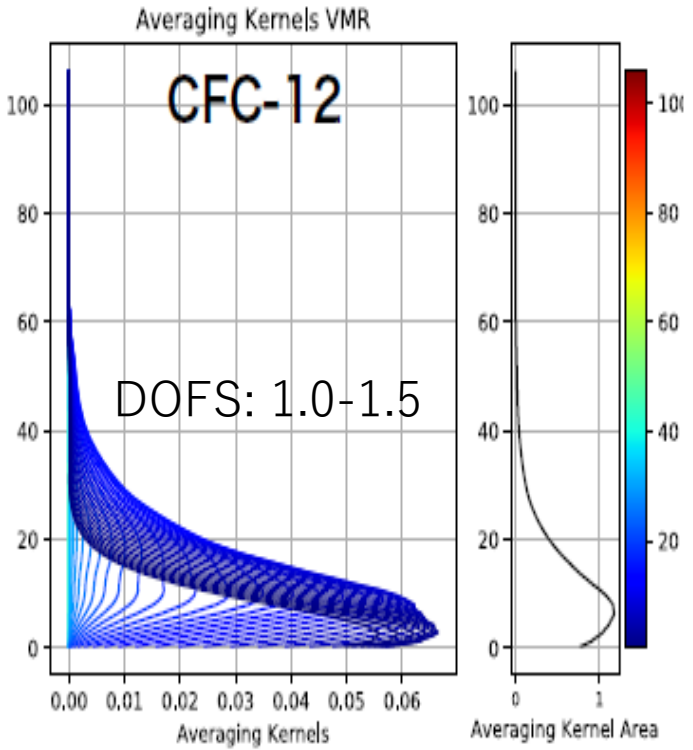
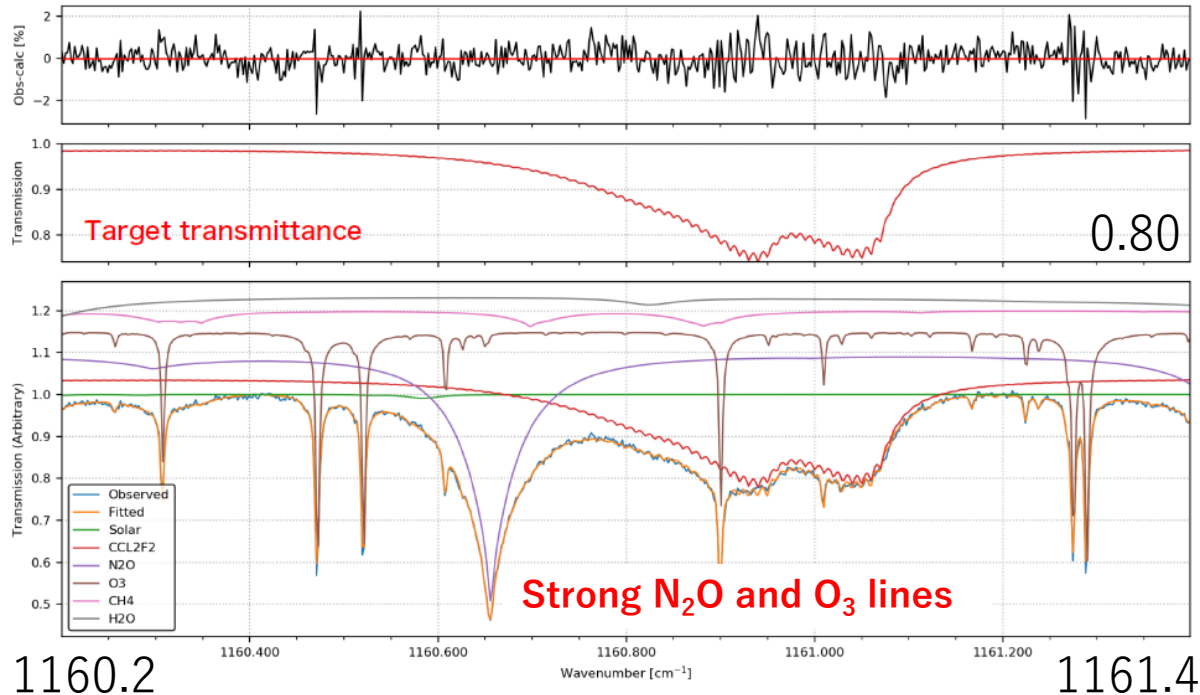
# Fitting Example (CFC-11)

## CFC-11



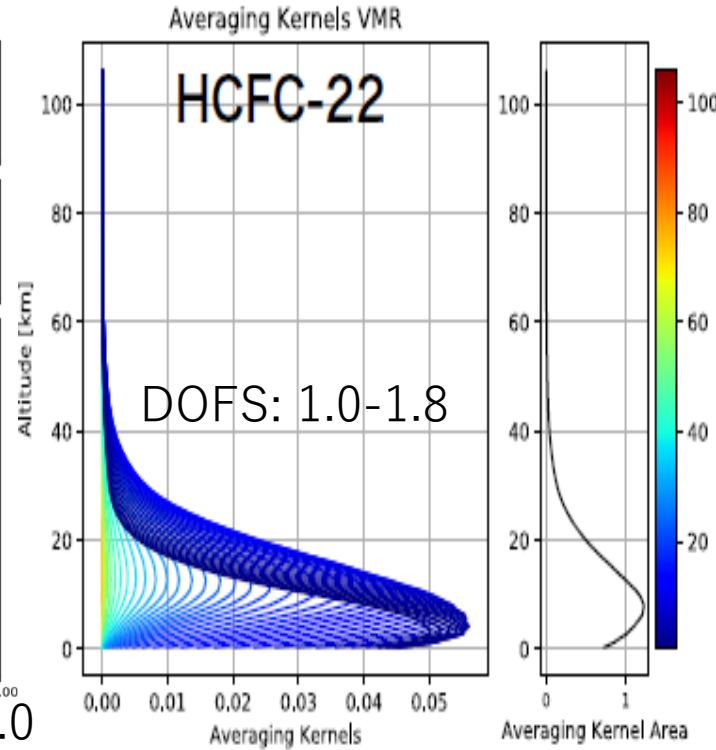
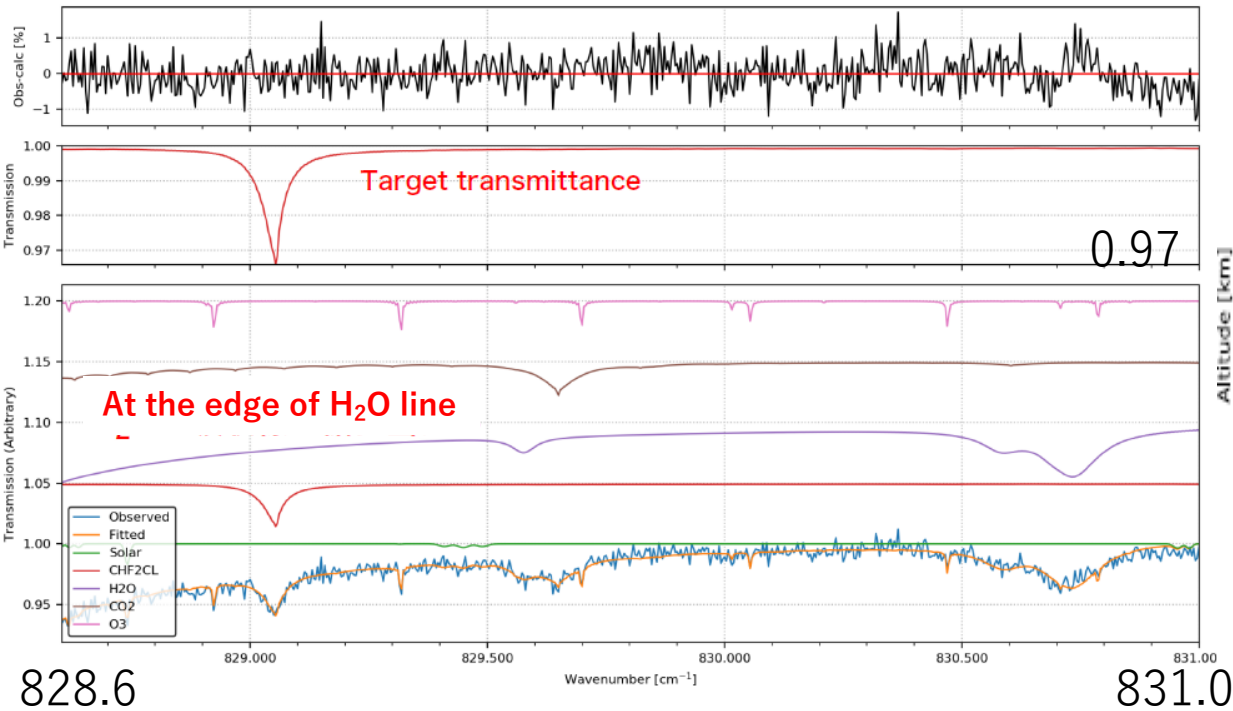
# Fitting Example (CFC-12)

## CFC-12



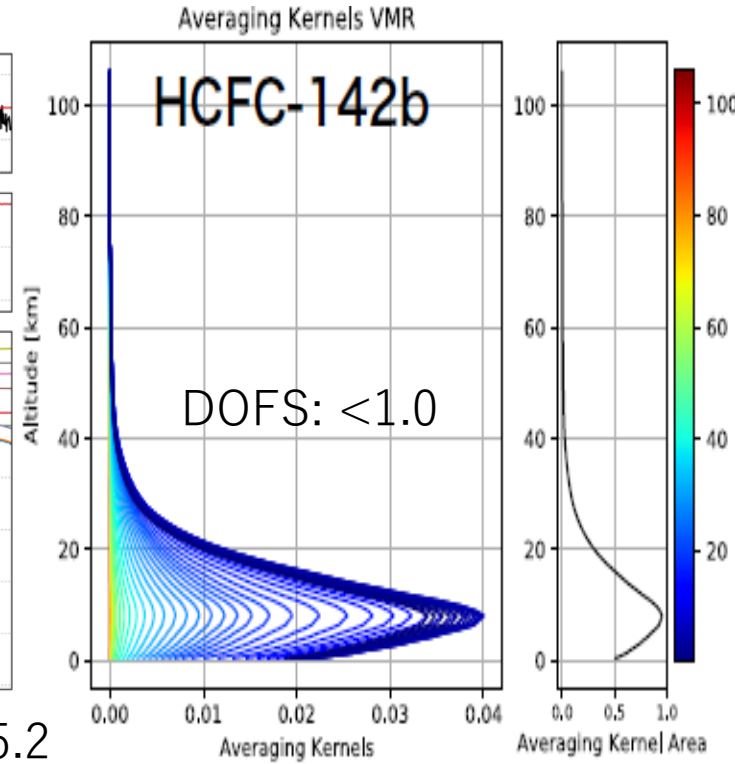
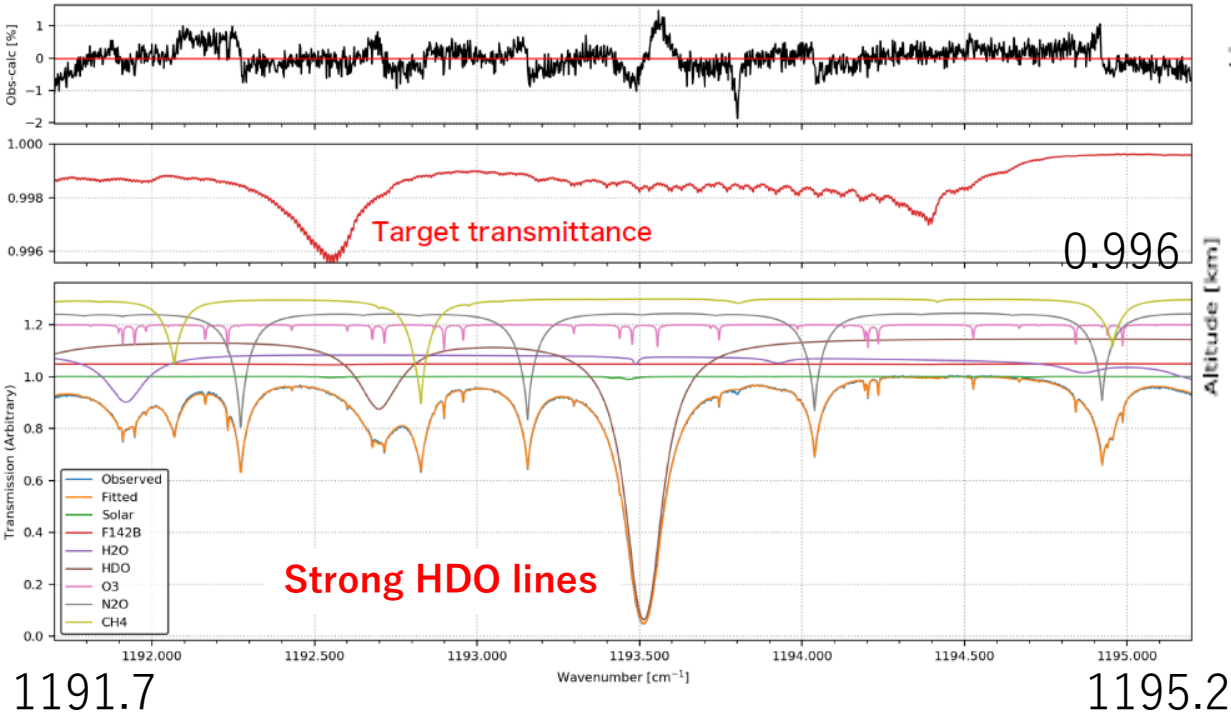
# Fitting Example (HCFC-22)

## HCFC-22



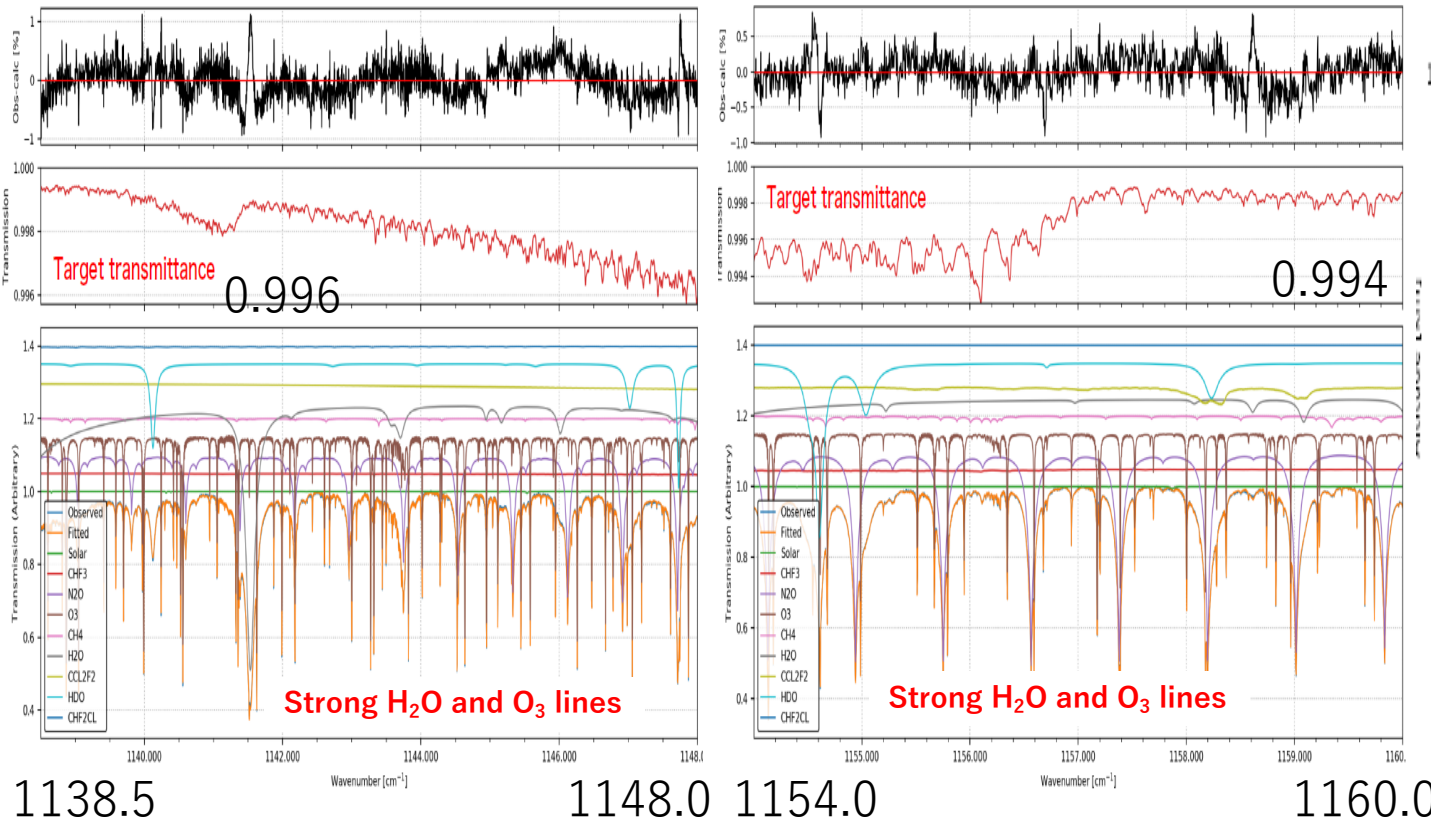
# Fitting Example (HCFC-142b)

## HCFC-142b

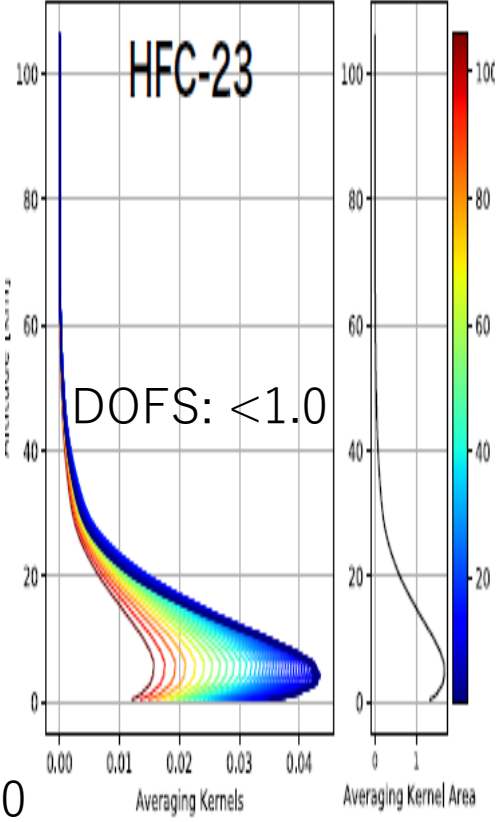


# Fitting Example (HFC-23)

## HFC-23

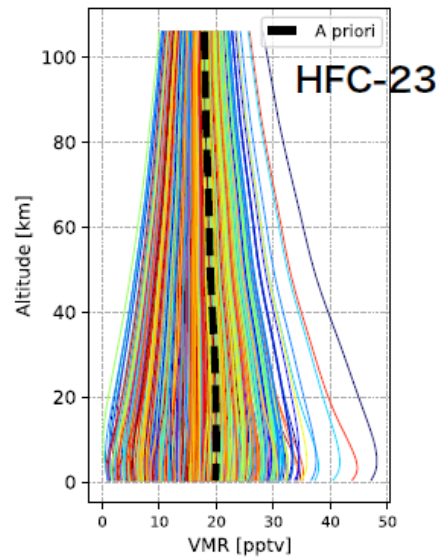
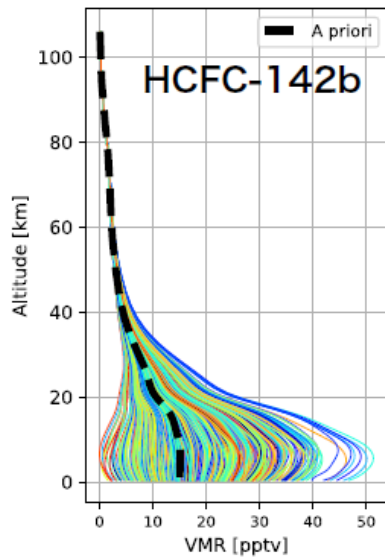
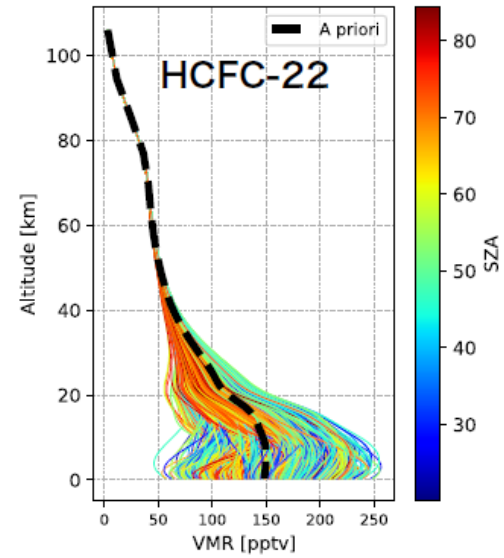
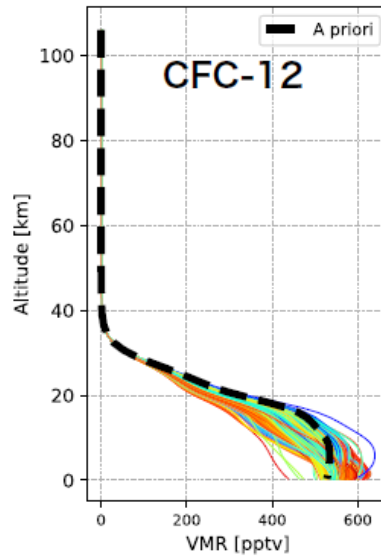
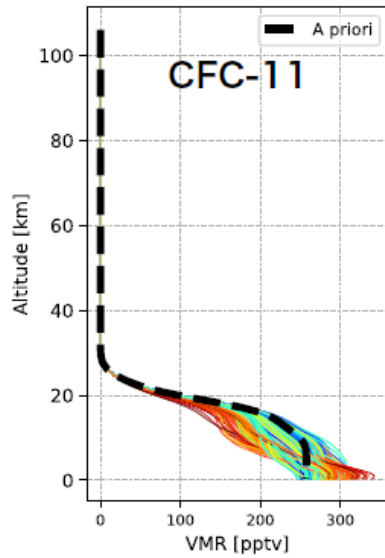


## Averaging Kernels VMR



Avoiding very strong H<sub>2</sub>O line at 1151 cm<sup>-1</sup>

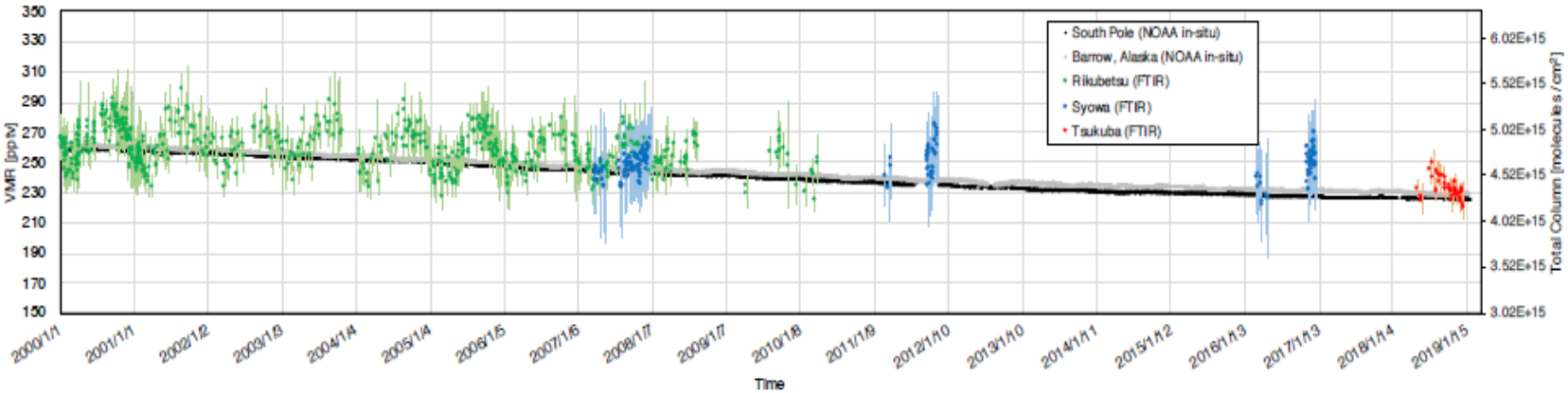
# Retrieved Profiles





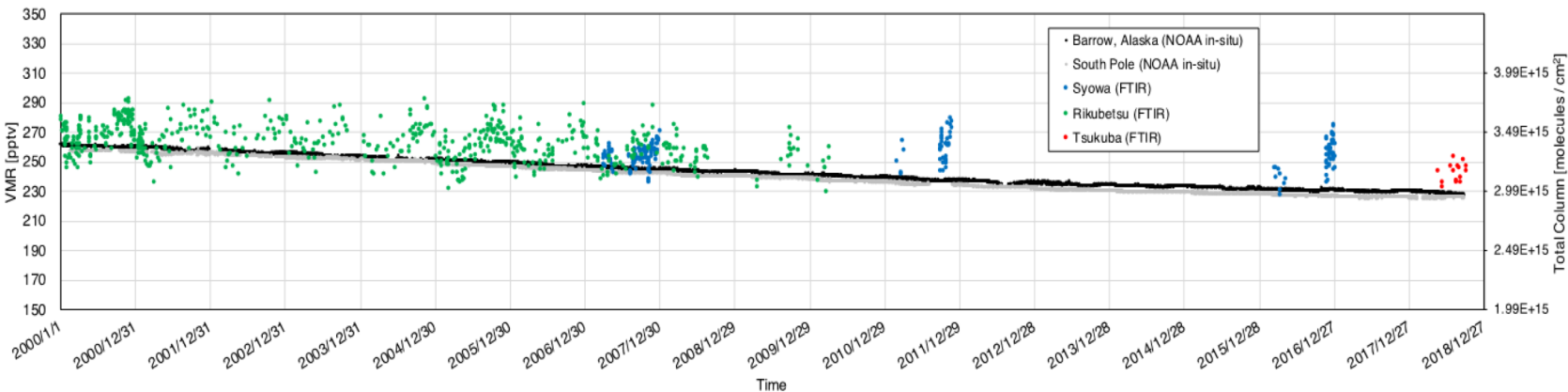
# Time Series of FTIR Observations CFC-11 (Total / Tropospheric Column)

Total Column



<FTIR>  
 Rikubetsu  
 Syowa St.  
 Tsukuba

Surface - 8 km

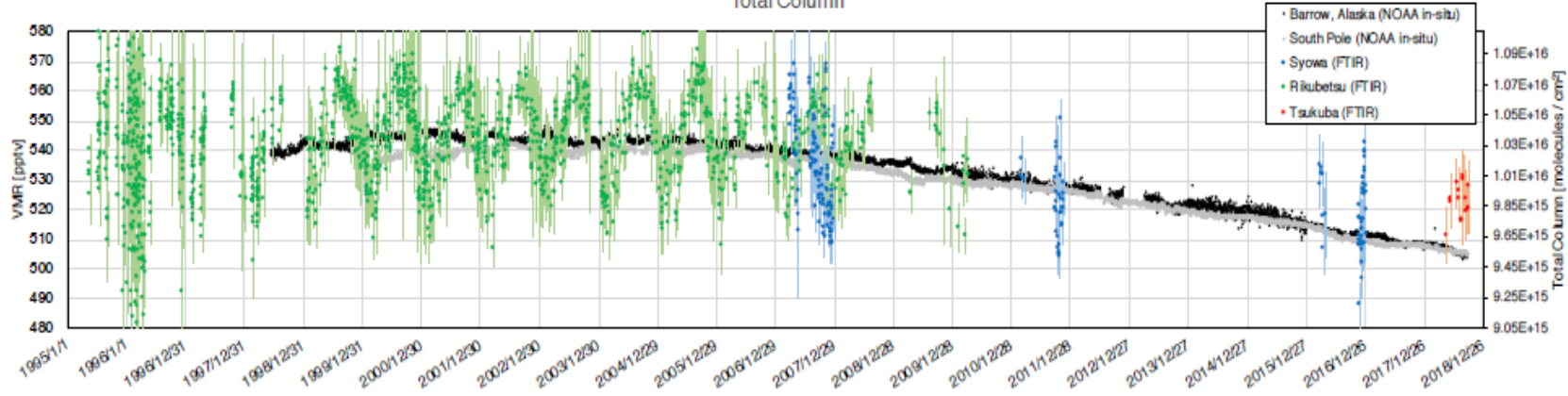


<Flask>  
 South Pole  
 (NOAA)  
 Barrow  
 (NOAA)



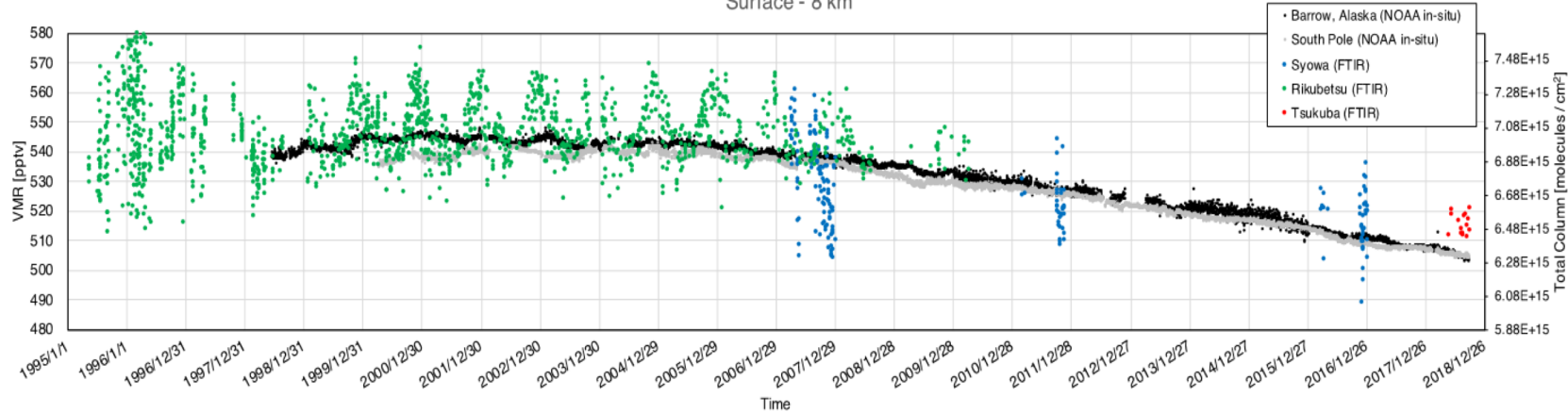
# Time Series of FTIR Observations CFC-12 (Total / Tropospheric Column)

Total Column



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Tsukuba

Surface - 8 km



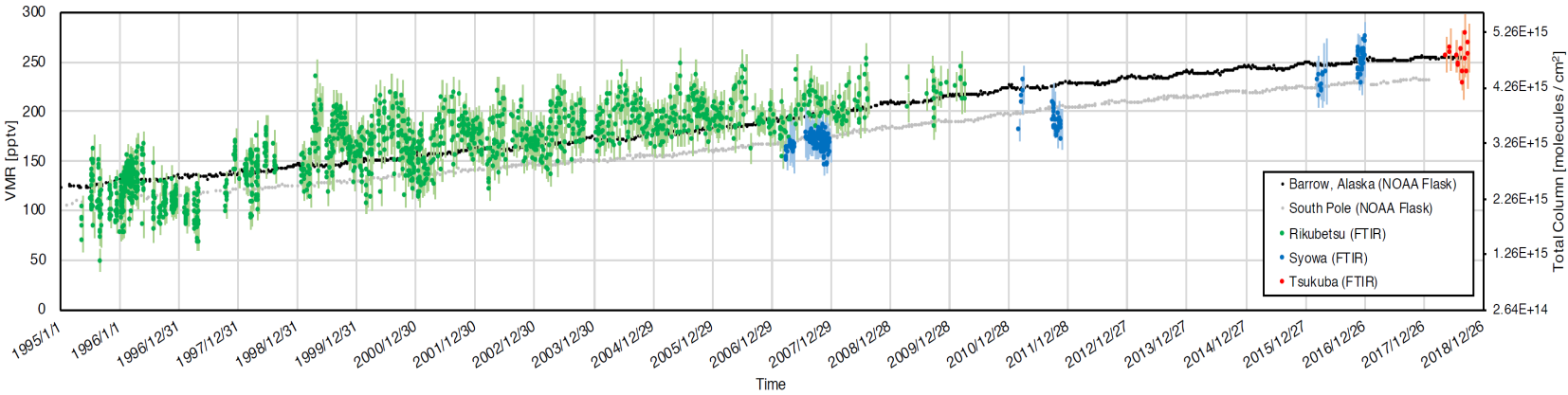
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(NOAA)  
Barrow  
(NOAA)





# Time Series of FTIR Observations HCFC-22 (Total / Tropospheric Column)

Total Column



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Syowa St.  
Tsukuba

Surface - 8 km

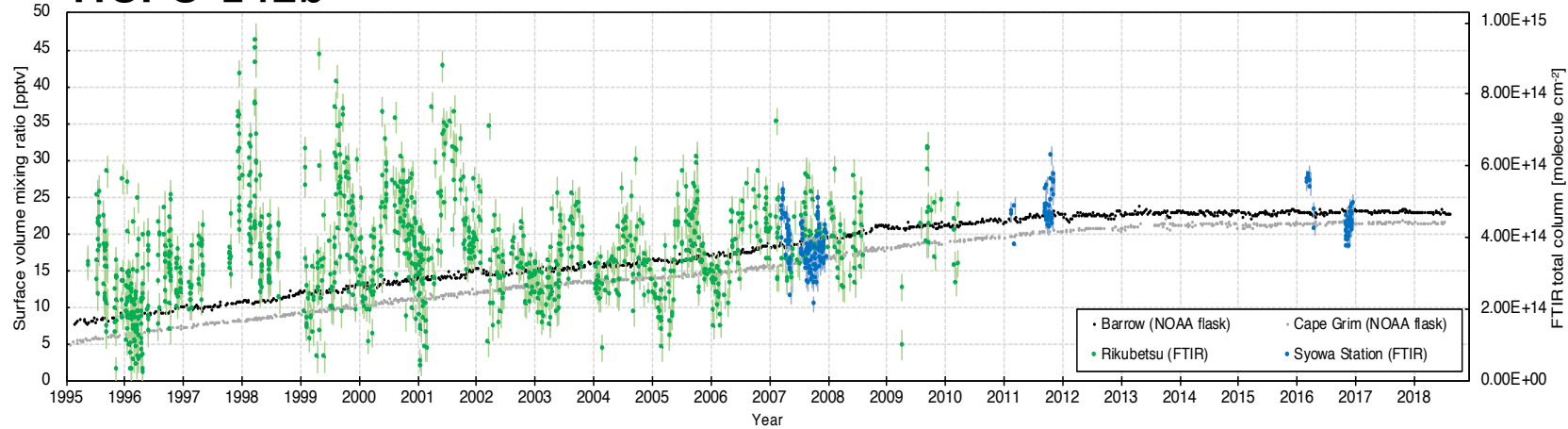


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# Time Series of FTIR Observations HCFC-142b, HFC-23 (Total Column)

## HCFC-142b

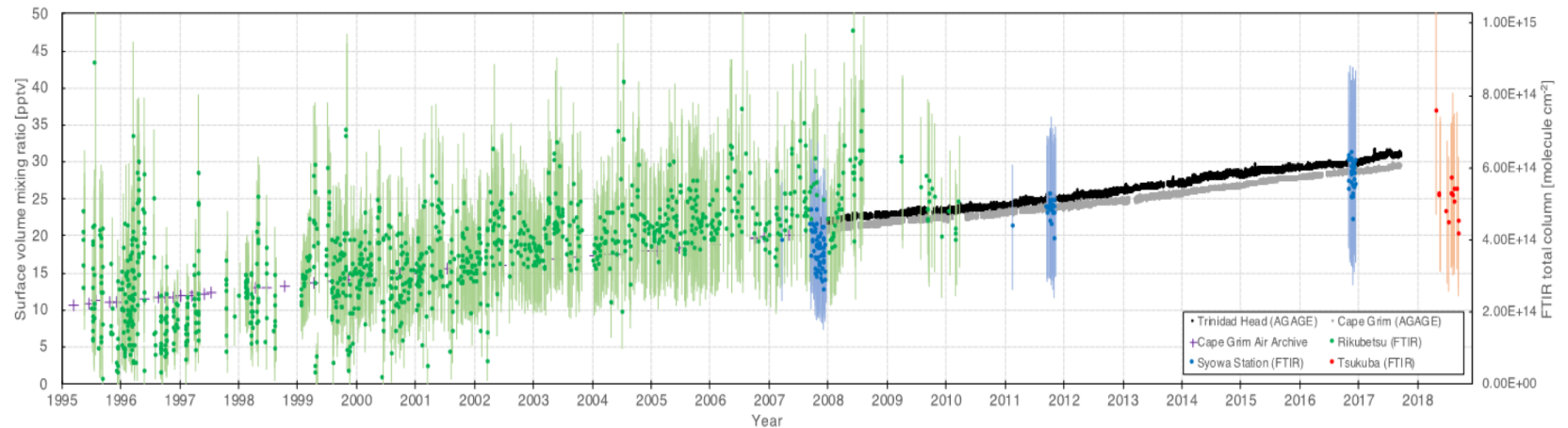


<FTIR>  
Rikubetsu

Syowa St.

Tsukuba

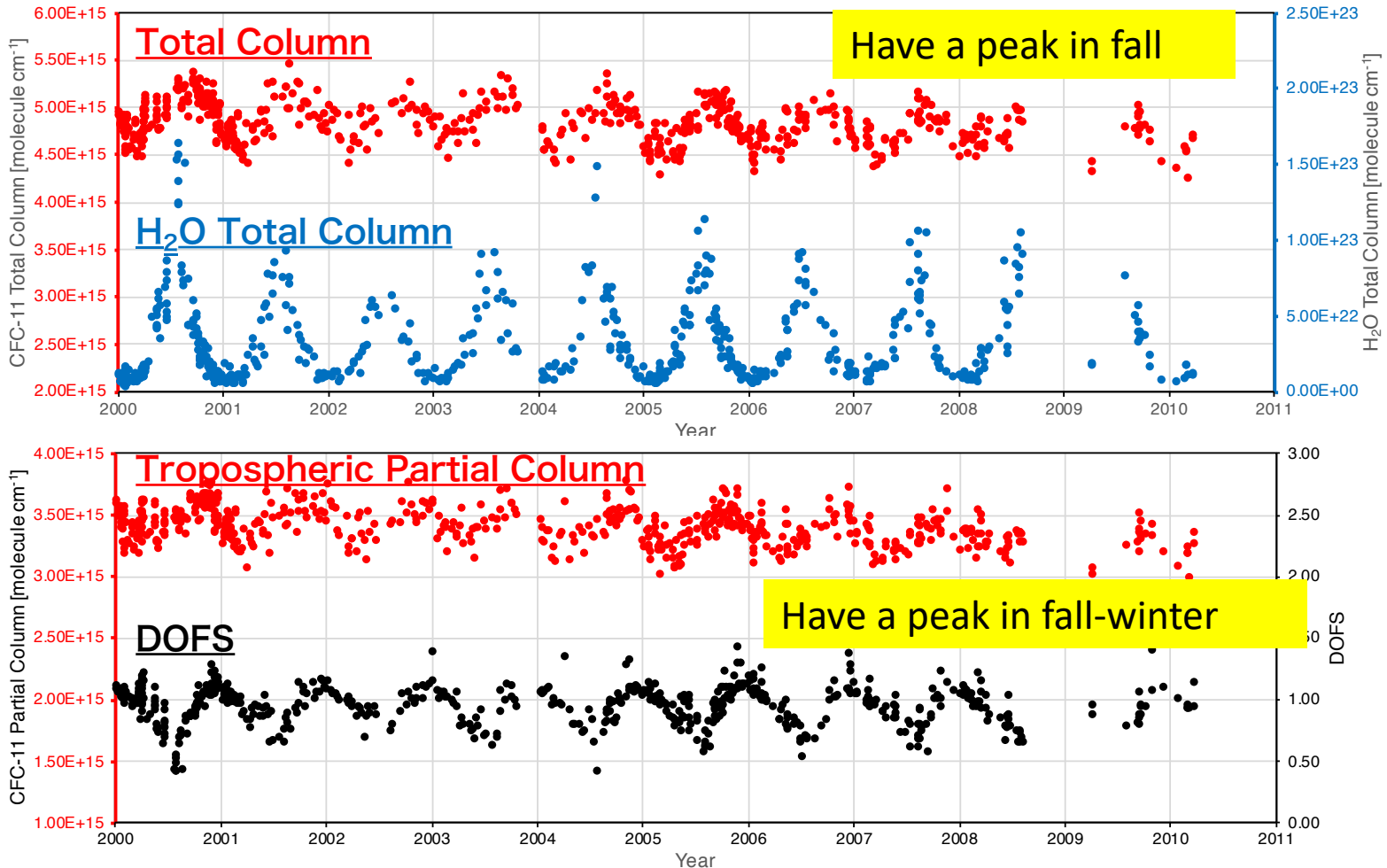
## HFC-23



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(NOAA)  
(AGAGE)

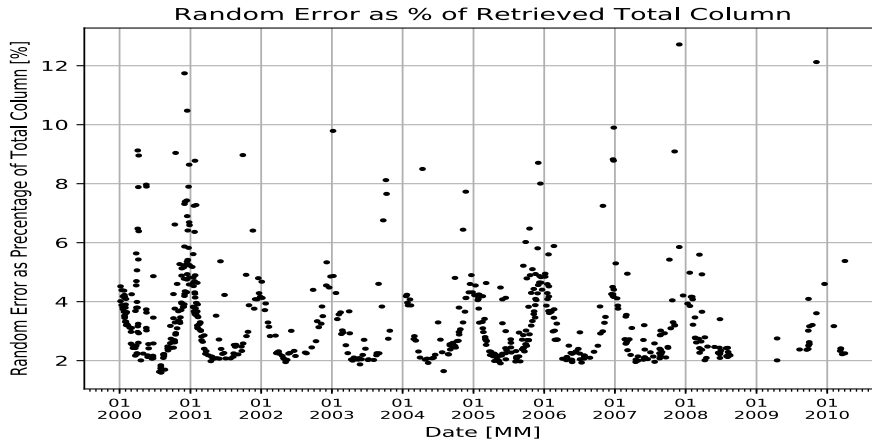
Barrow  
(NOAA)  
Trinidad  
(AGAGE)

# Why There Exists Seasonal Variations? (CFC-11)

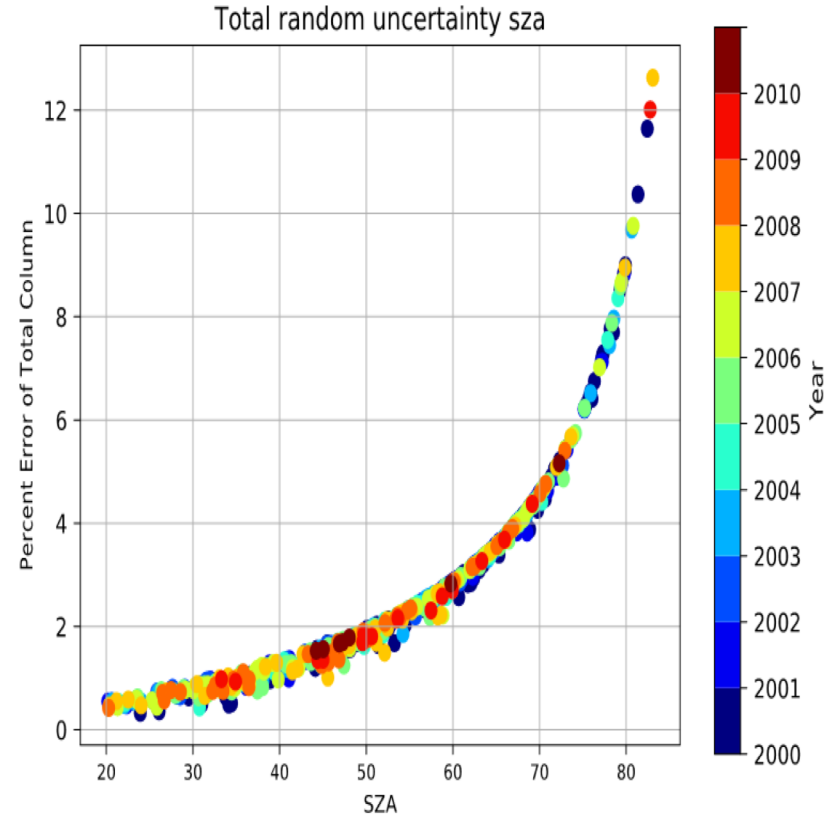
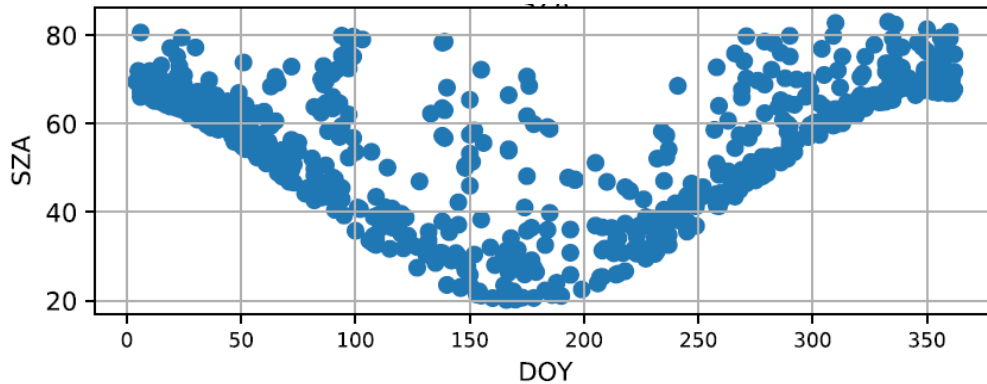


- Few months delay between total and tropospheric columns.
- Total column has similar seasonal variation with H<sub>2</sub>O total column.
- Tropospheric column has similar seasonal variation with DOFS.

# Why There Exists Seasonal Variations? (CFC-11)



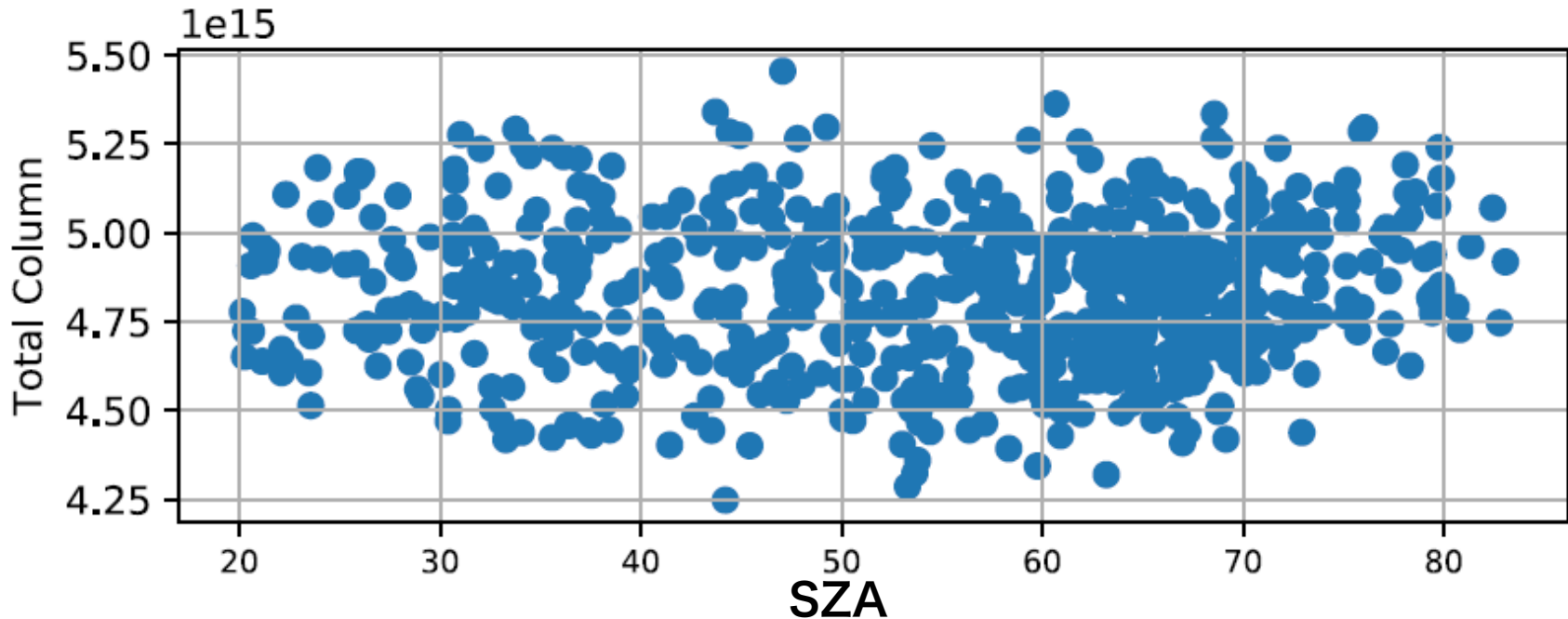
## Measurement Solar Zenith Angles



- Random error is larger in winter than summer due to larger SZA.
- Measurement SZAs are generally larger in winter than in summer.
- Larger random error in winter is due to larger SZAs in winter.

# Why There Exists Seasonal Variations? (CFC-11)

## Total Column of CFC-11 at different SZAs

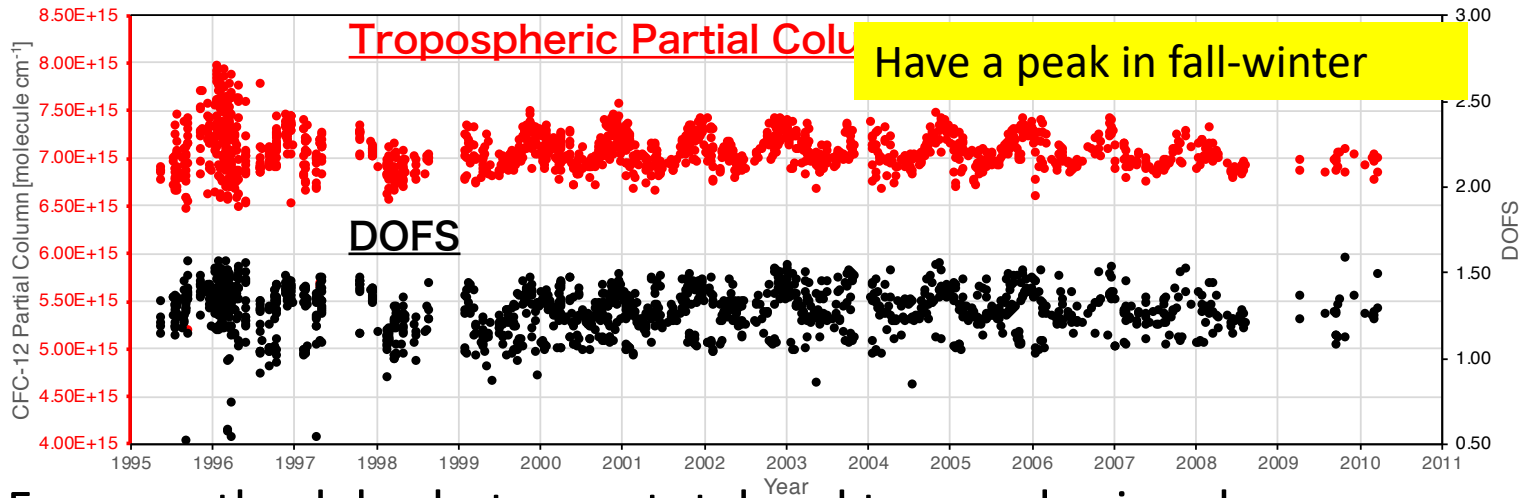
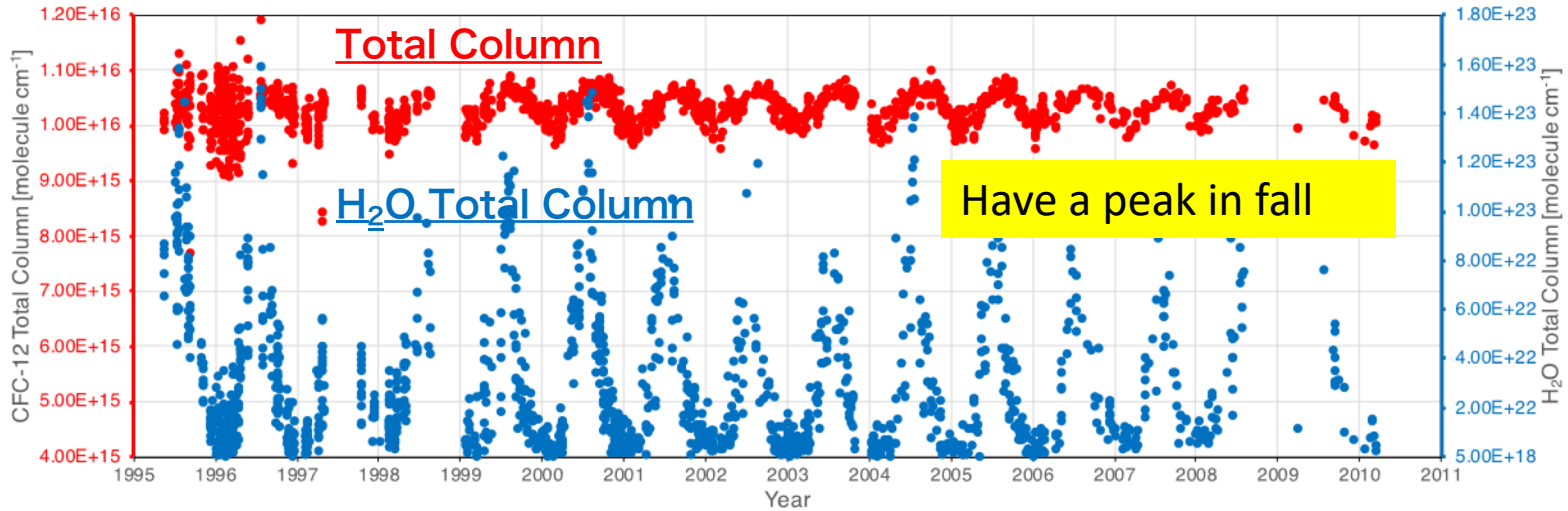


- Average measurement SZA is larger in winter than in summer.
- Total / tropospheric columns of CFC-11 is larger in fall than in spring.
- The cause of seasonal variation of CFC-11:

Effect of water vapor / Tropopause height ???

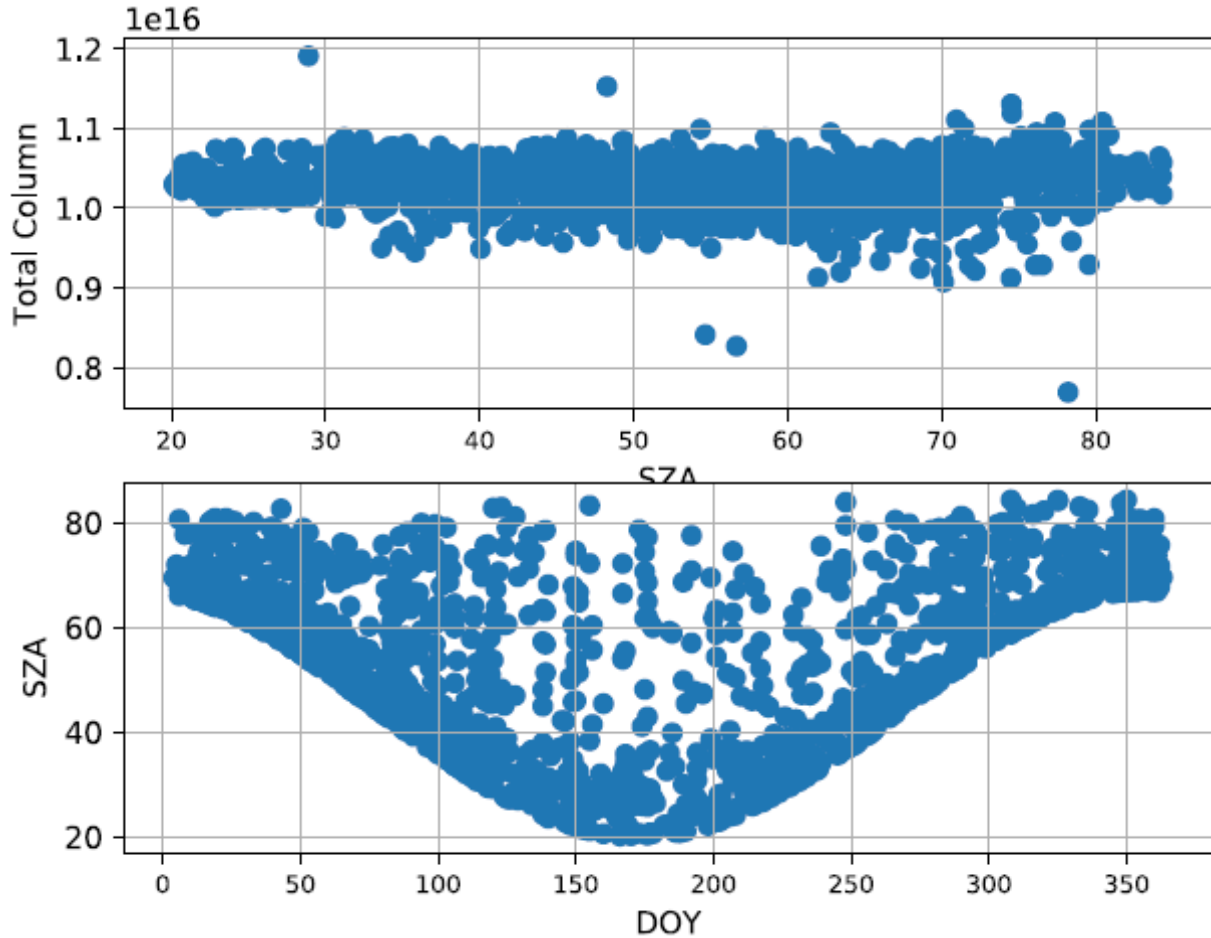


# Why There Exists Seasonal Variations? (CFC-12)



- Few months delay between total and tropospheric columns.
- Total column has similar seasonal variation with H<sub>2</sub>O total column.
- DOFS has less seasonal variation.

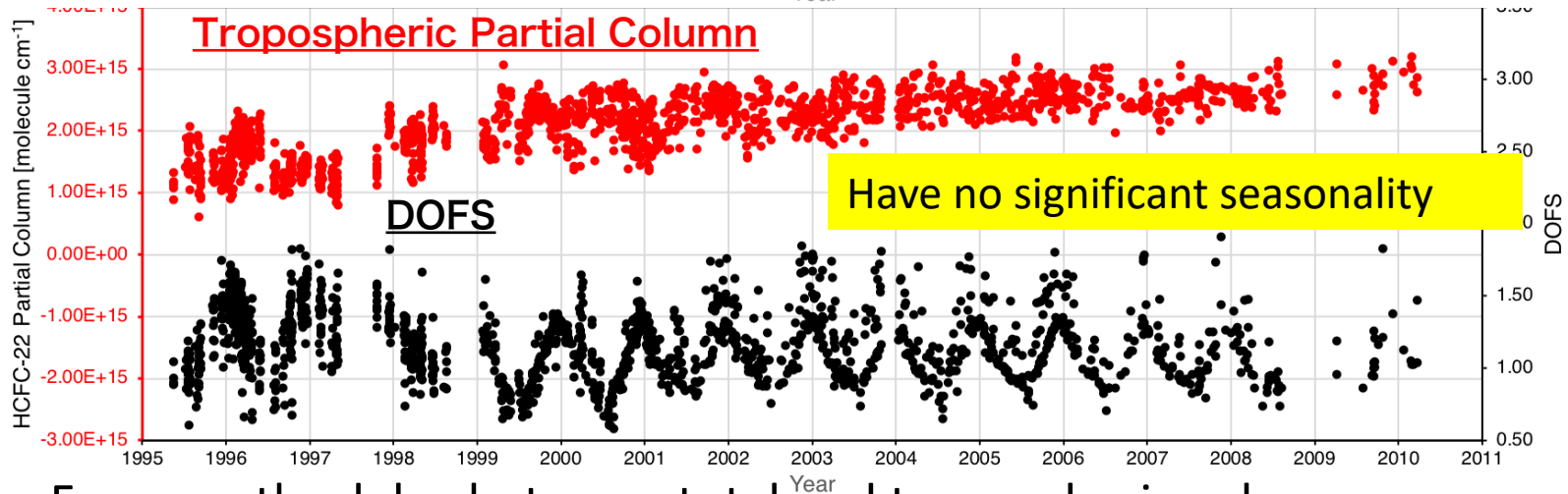
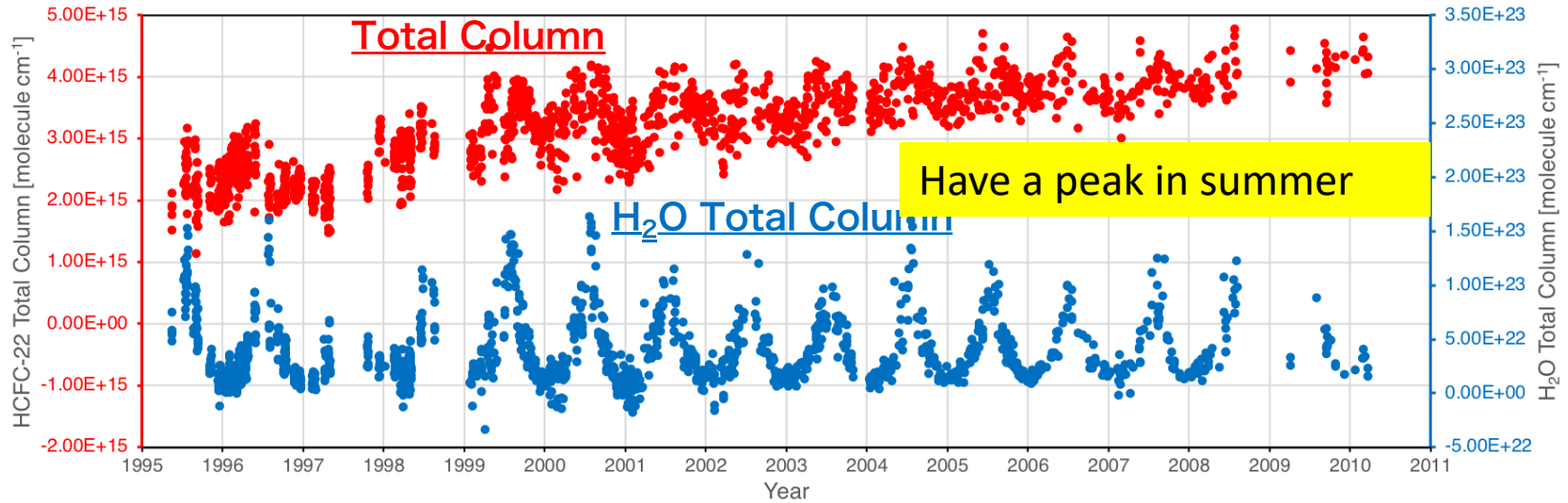
# Why There Exists Seasonal Variations? (CFC-12)



- We have high SZA data even in summer.
- There are no SZA dependence on CFC-12 columns.
- The cause of seasonal variation of CFC-12:

Effect of water vapor / Tropopause height ???

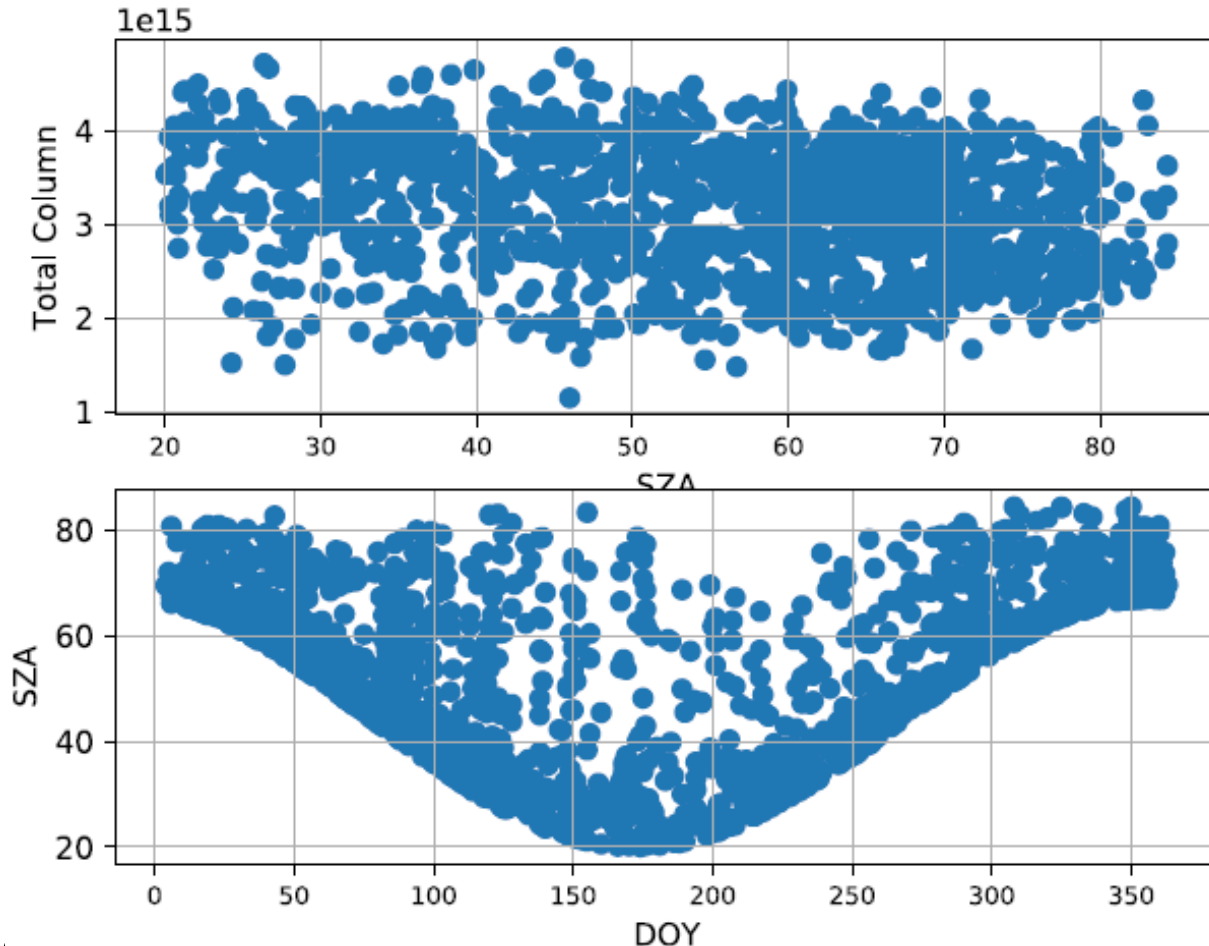
# Why There Exists Seasonal Variations? (HCFC-22)



- Few months delay between total and tropospheric columns.
- Total column has similar seasonal variation with H<sub>2</sub>O total column.
- DOFS has less seasonal variation.



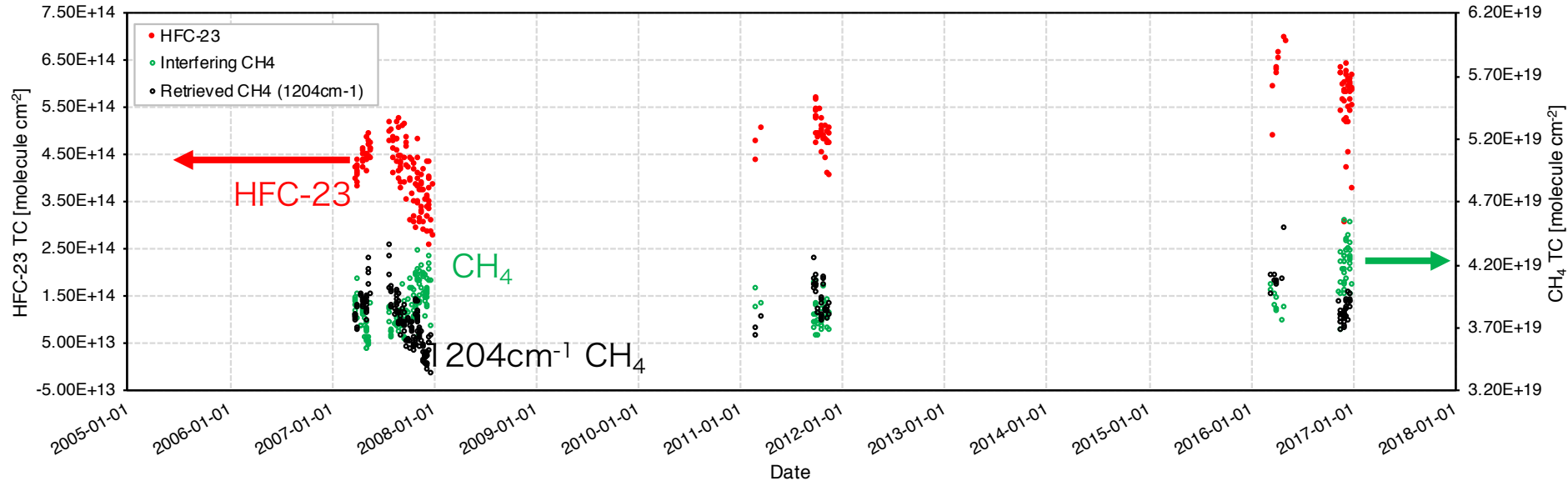
# Why There Exists Seasonal Variations? (HCFC-22)



- We have high SZA data even in summer.
- There are no SZA dependence on HCFC-22 columns.
- The cause of seasonal variation of HCFC-22 total column:

Effect of tropopause height / local emission ???

# Problem in HFC-23 fitting



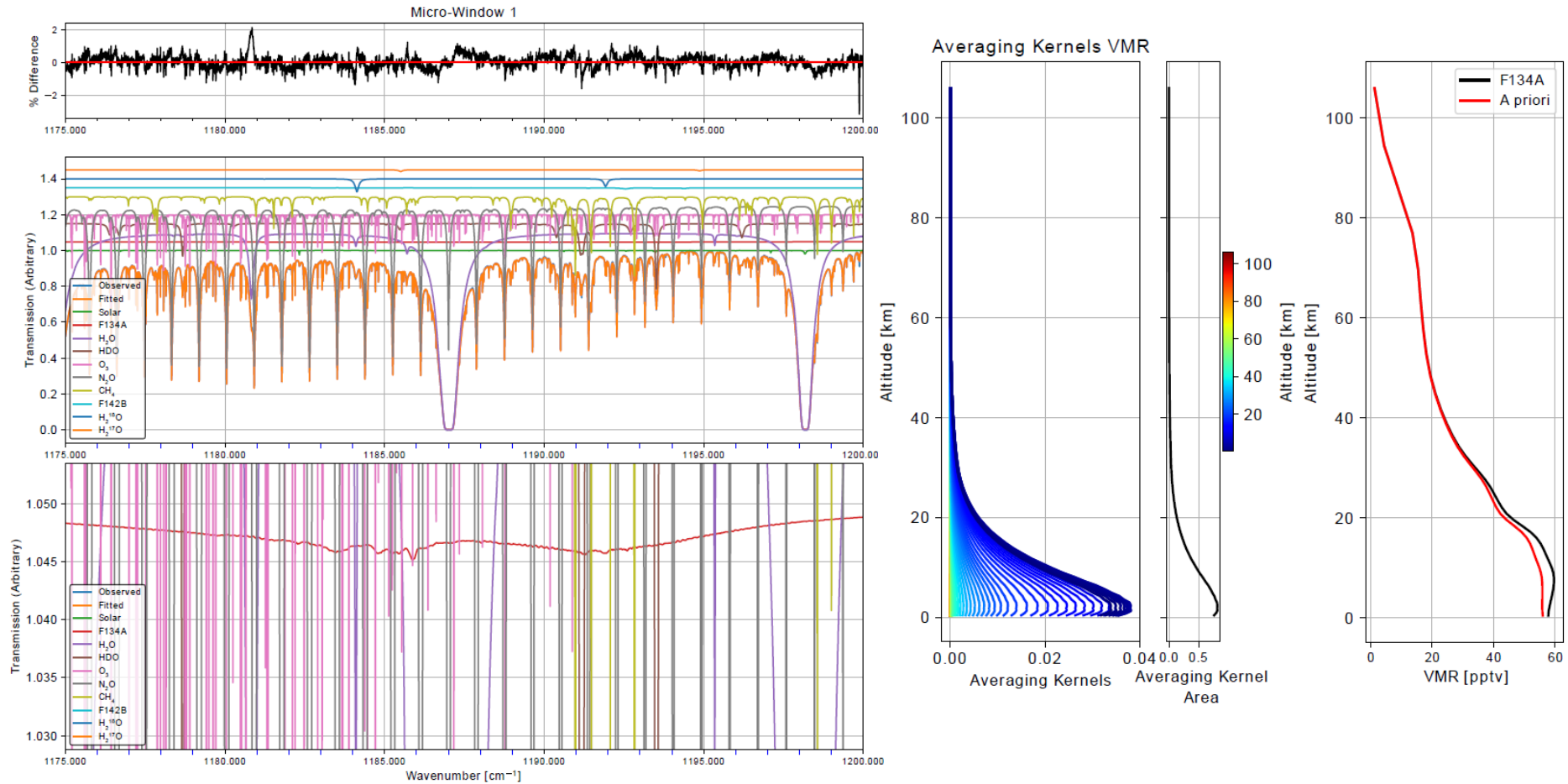
- Anti-correlation was found between retrieved HFC-23 and CH<sub>4</sub>.
- This anti-correlation might be due to the weak absorption features of HFC-23 and CH<sub>4</sub> which are overlapped.
- In order to avoid this, CH<sub>4</sub> was previously retrieved using different microwindow around 1204 cm<sup>-1</sup>, and was given as a fixed value at HFC-23 retrieval. → See Poster by Takeda et al. for detail.



# Summary

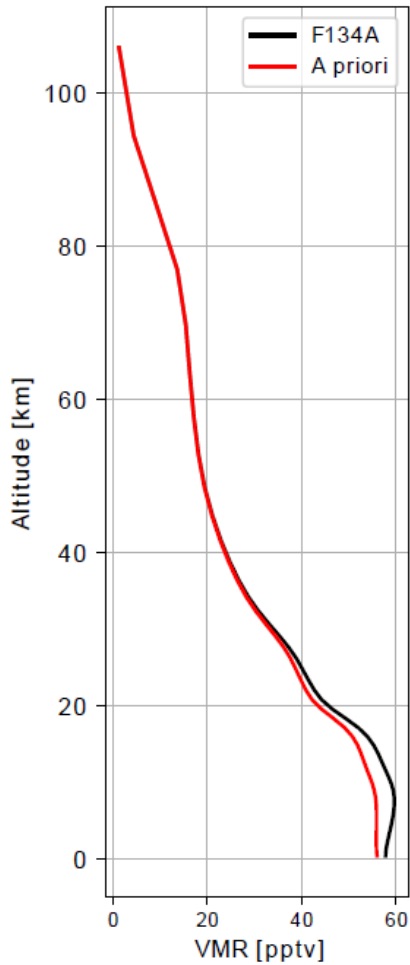
- Several CFCs, HCFCs, and HFCs were retrieved from FTIR spectra taken at Rikubetsu, Syowa Station, and Tsukuba.
- In general, measured FTIR VMR agreed with surface sampling data well.
- There exists seasonal variations in retrieved CFC-11, CFC-12, HCFC-22, and HCFC-142b total columns.
- Tropospheric column of HCFC-22 shows no seasonal variations, but those for CFC-11 and CFC-12 remains, whose causes may be either tropopause height or H<sub>2</sub>O? Need for improved strategy (ex. Pre-retrieval of H<sub>2</sub>O or use improved ATM16 H<sub>2</sub>O lines).
- We succeeded to retrieve HFC-23 total column from g/b FTIR for the first time.

# Fitting Example (HFC-134a)

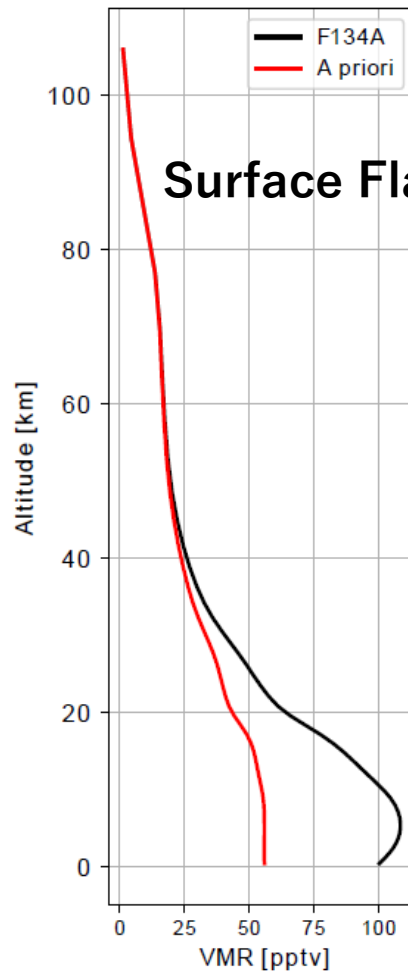


# Retrieved Profiles at Rikubetsu (HFC-134a)

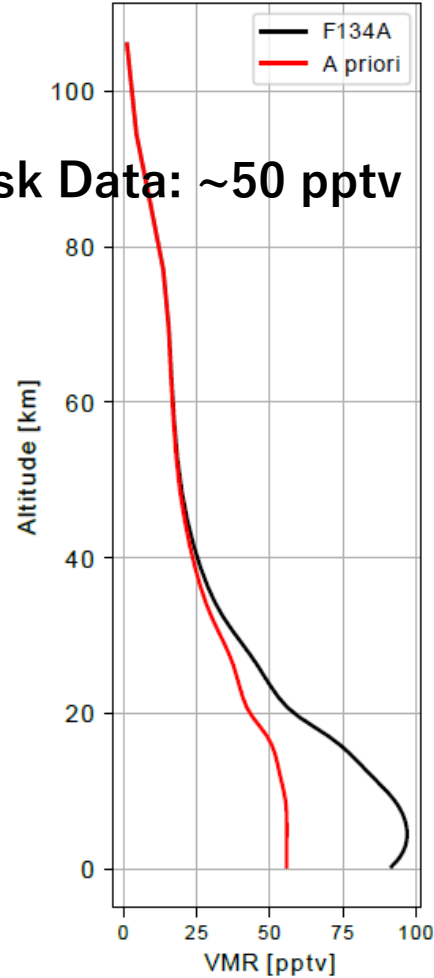
Jan. 11, 2008



Jan. 29, 2008



Apr. 9, 2008



Aug. 7, 2008

