

# On the Emissions of HCFCs and CFCs Potentially Related to HFC Production

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***3 CSIRO Oceans and Atmosphere***

***4 Scripps Institution of Oceanography***

***5 Kyungpook Nat Univ, South Korea***

***6 Advanced Global Atmospheric Gases Experiment and contributions from Firn Air Community, NOAA, ...***

***NOAA ESRL, Boulder, 23  
– 24 May. 2017***

# Halocarbons

1<sup>st</sup> Generation

2<sup>nd</sup> Generation

3<sup>rd</sup> Generation

4<sup>th</sup> Generation

*Montreal Protocol*

CFCs  
Halon  
CCl<sub>4</sub> / CH<sub>3</sub>CCl<sub>3</sub>  
/ CH<sub>3</sub>Br

HCFCs

PFCs

HFCs

HFOs

*Kyoto Protocol*

Chlorofluorocarbons

Hydrochloro-  
fluorocarbons

Perfluorocarbons  
Hydrofluorocarbons

Hydrofluoroolefines

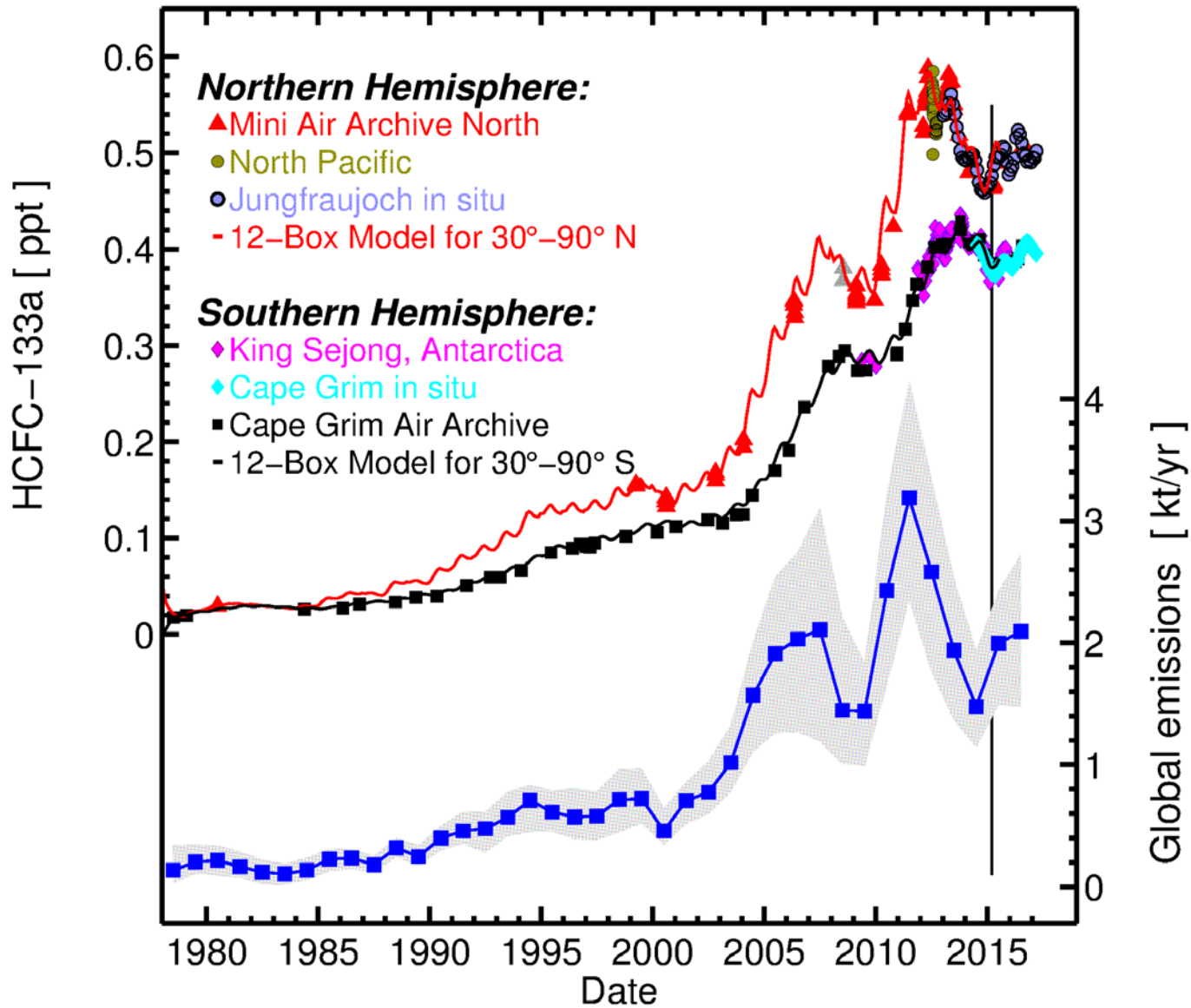
CFC-11, CFC-12,  
CFC-13, CFC-113,  
CFC-114, **CFC-115**,  
H-1211, H-1301, ....

HCFC-22, HCFC-141b,  
HCFC-142b, **HCFC-31**,  
**HCFC-133a**, HCFC-  
131, HCFC-132b....

HFC-32, HFC-125,  
HFC-134a, HFC-245fa,  
PFC-116, PFC-218 ...

HFO-1234yf, HFO-  
1234ze(E), HCFO-  
1233zd(E), ....

# HCFC-133a ( $\text{CF}_3\text{CH}_2\text{Cl}$ , lifetime 4.5 yr)



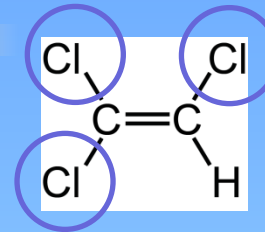
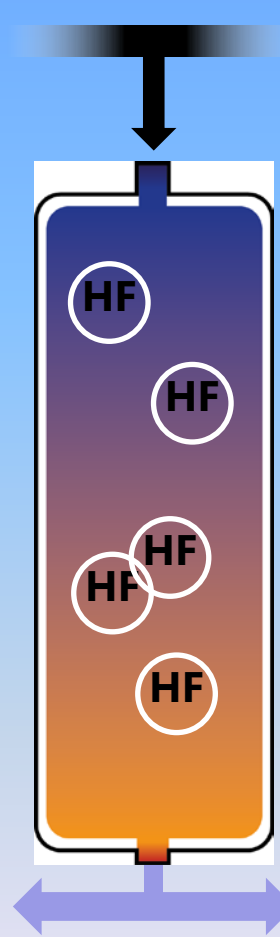
Medusa-  
GCMS

Empa-2013  
calibration  
scale

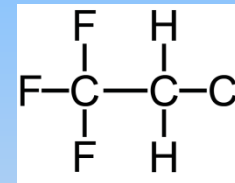
AGAGE  
12-box  
model

# HCFCs as intermediates in the HFC production

HCFC-133a

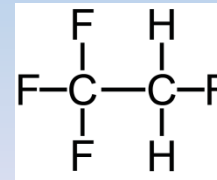


Trichloroethylene



**HCFC-133a**  
**(Chlorotrifluoroethane)**

Global Emissions:  
2 kt/yr



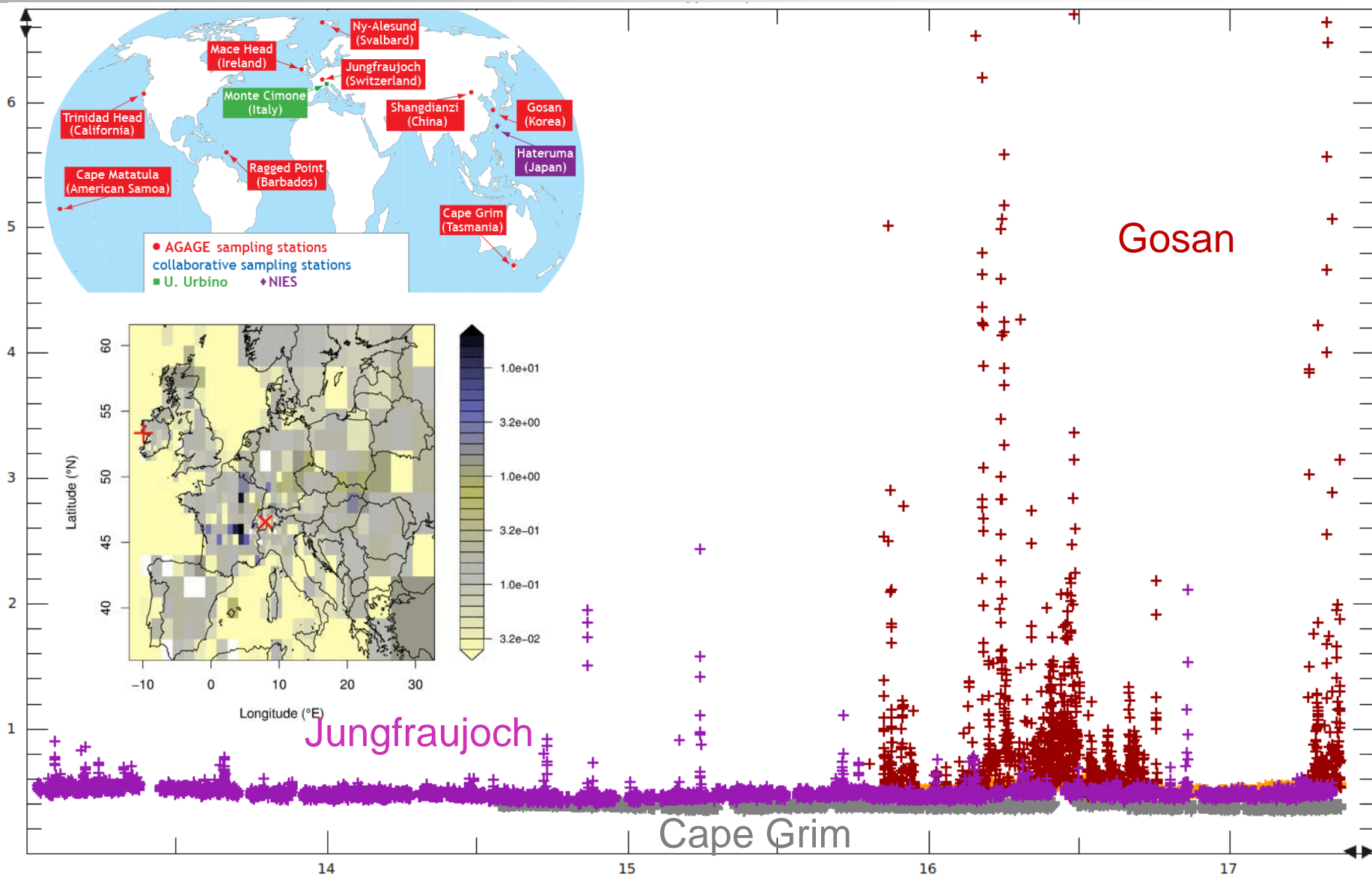
**HFC-134a**  
**(Tetrafluoroethane)**

Global Emissions:  
180 kt/yr



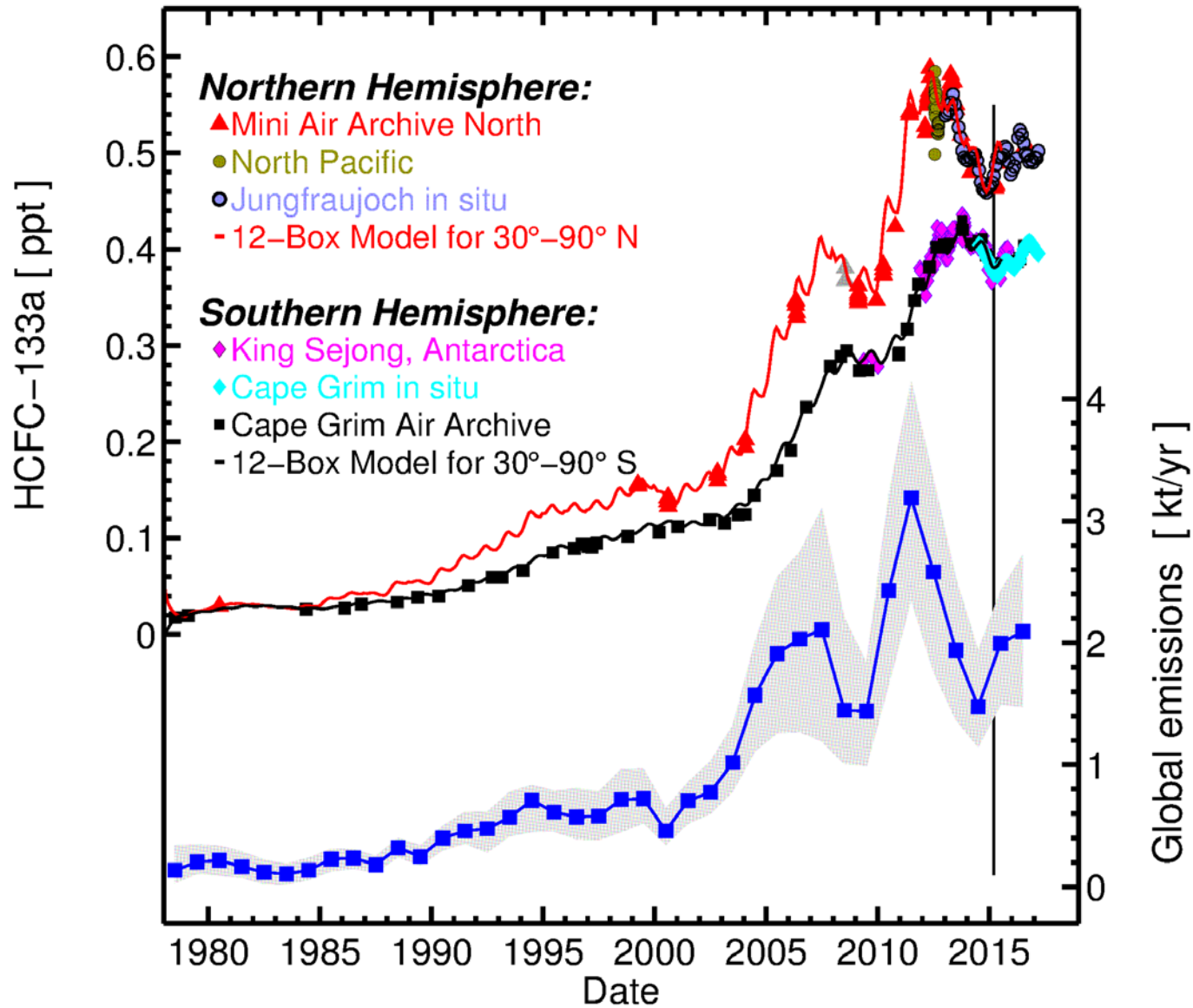
# HCFC-133a at selected AGAGE sites

Mol Fraction [ppt]

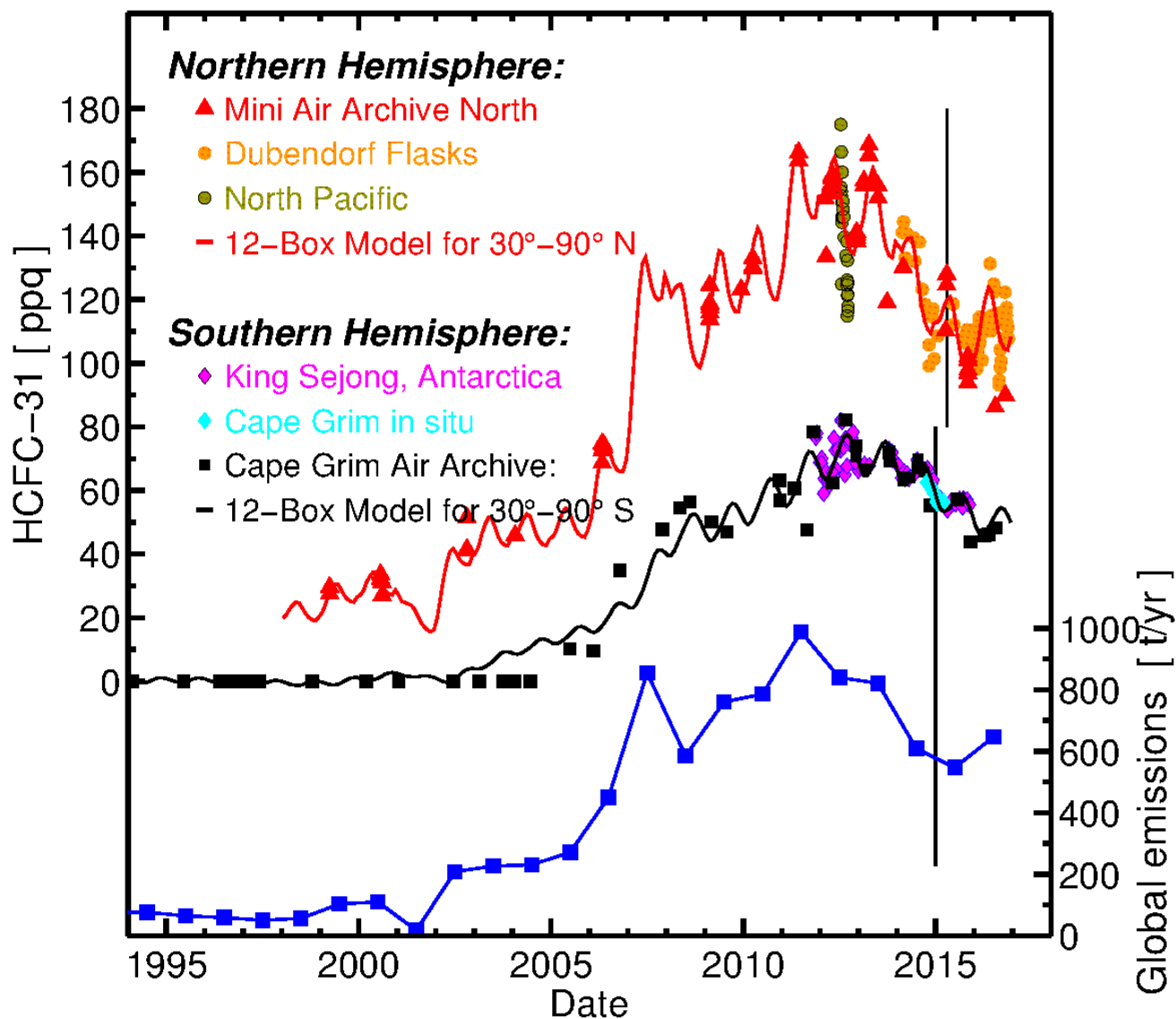


Time (years)

# HCFC-133a ( $\text{CF}_3\text{CH}_2\text{Cl}$ , lifetime 4.5 yr)



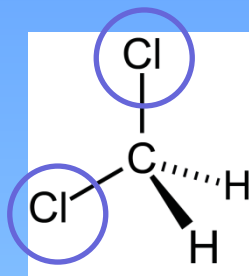
# HCFC-31 ( $\text{CH}_2\text{ClF}$ , lifetime 1.2 yr)



# HCFCs as intermediates in the HFC production

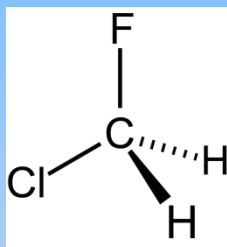
HCFC-31

Methylene Chloride



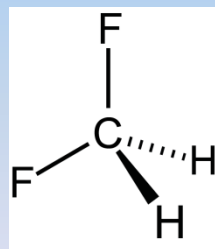
**HCFC-31**  
(Chlorofluoromethane)

Global Emissions:  
0.6 kt/yr



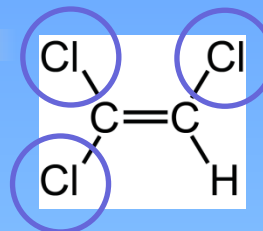
**HFC-32**  
(Difluoromethane)

Global Emissions:  
20 kt/yr



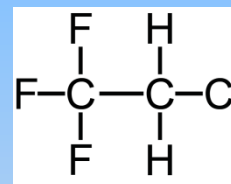
HCFC-133a

Trichloroethylene



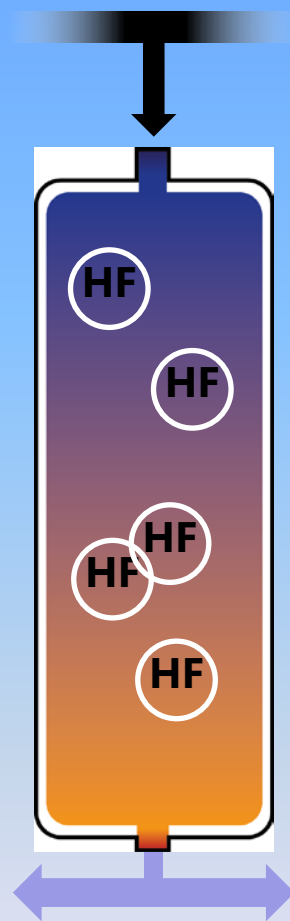
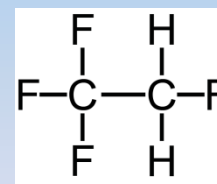
**HCFC-133a**  
(Chlorotrifluoroethane)

Global Emissions:  
2 kt/yr



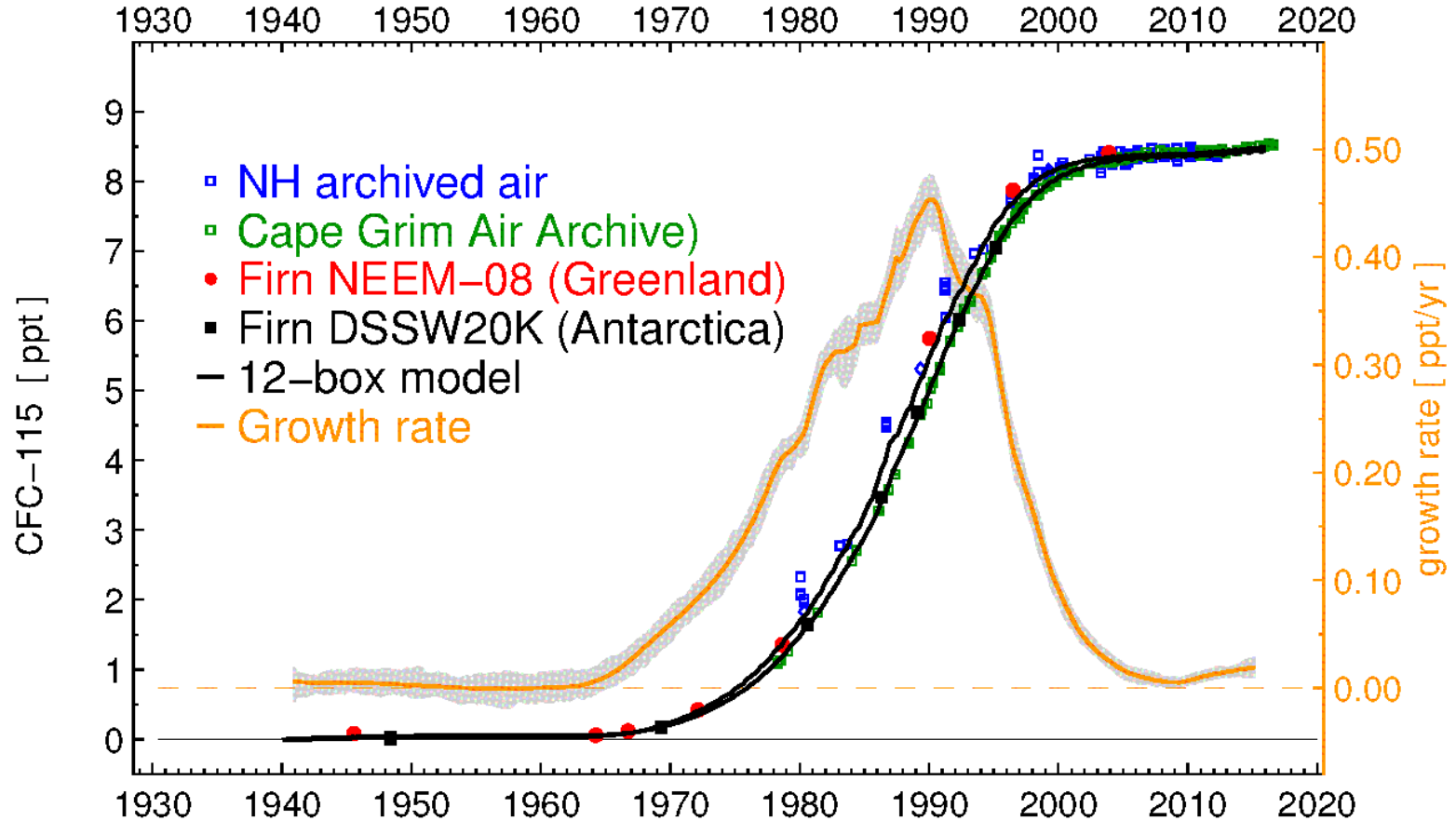
**HFC-134a**  
(Tetrafluoroethane)

Global Emissions:  
180 kt/yr

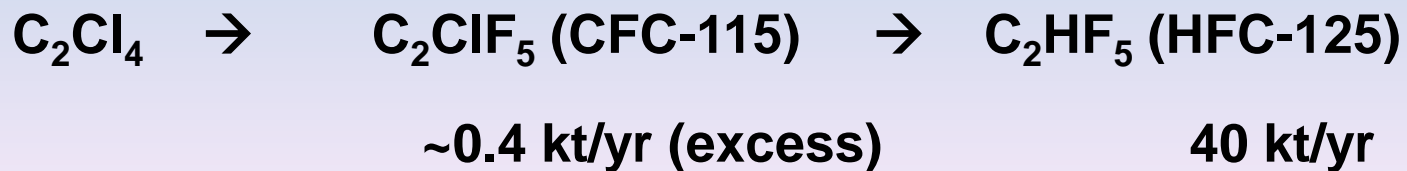
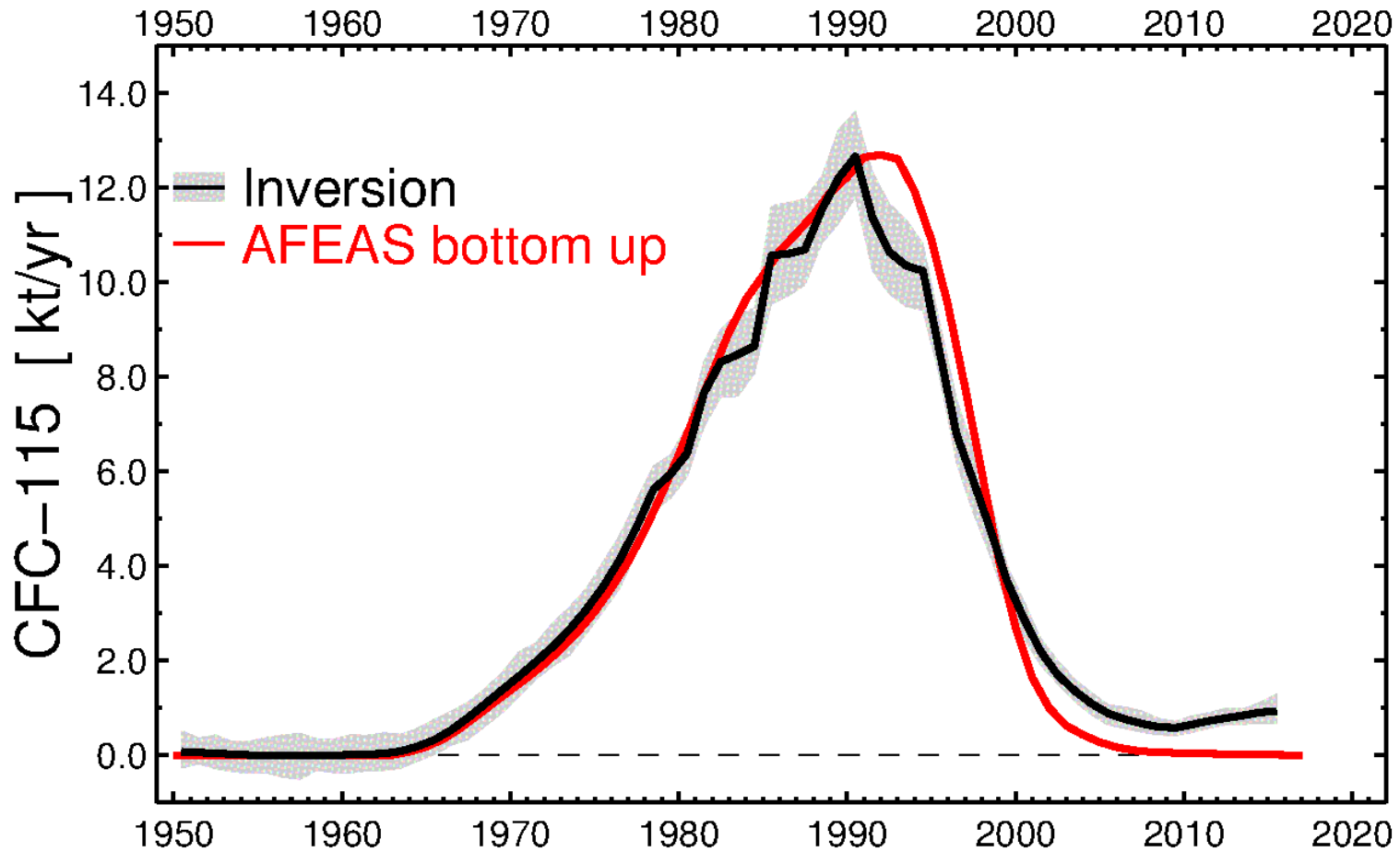




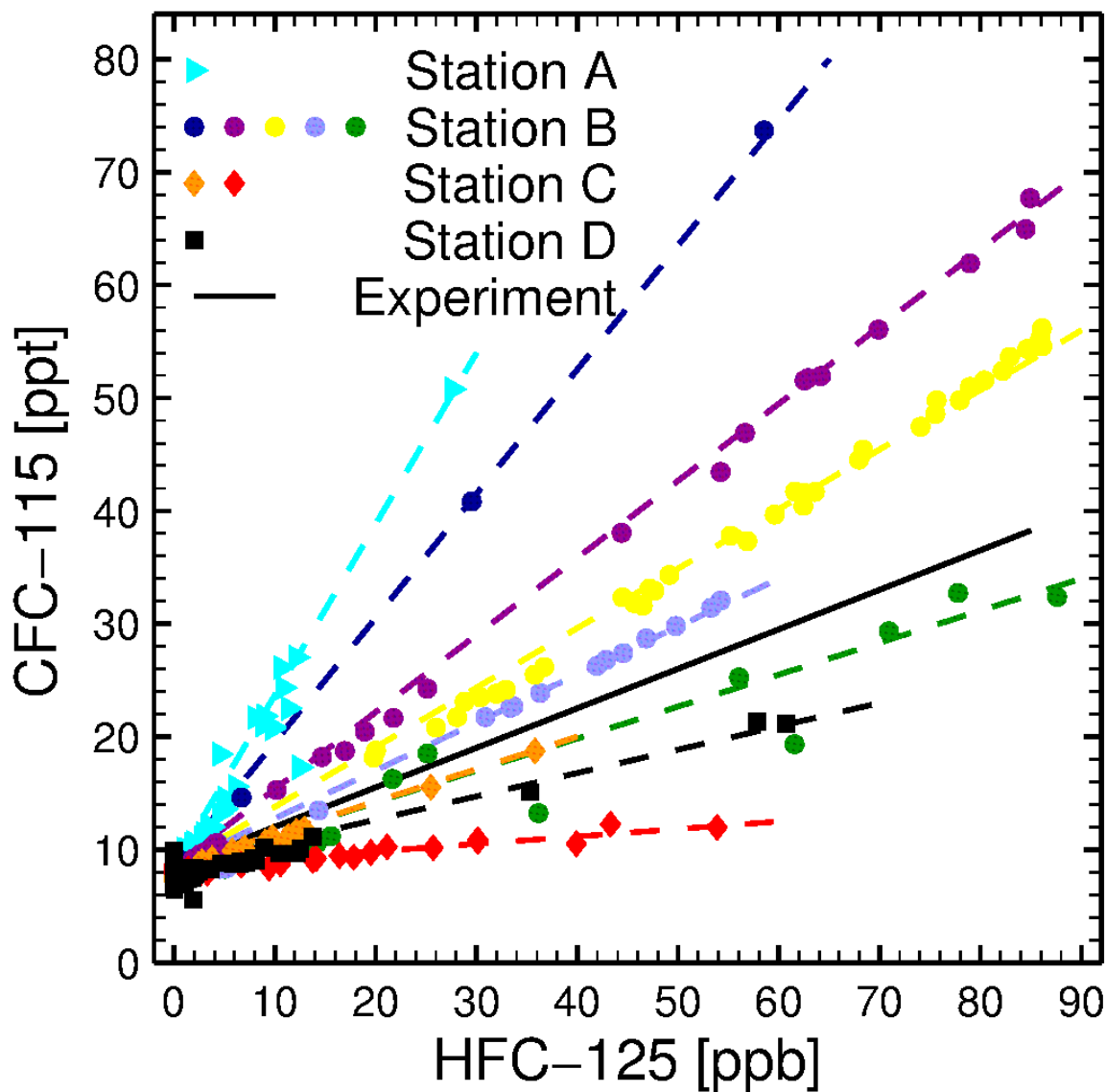
# Global CFC-115 Observations ( $\text{CClF}_2\text{CF}_3$ , lifetime 540 yr)



# Global CFC-115 emissions



# CFC-115 Impurities in the refrigerant HFC-125 (leaking ACs)

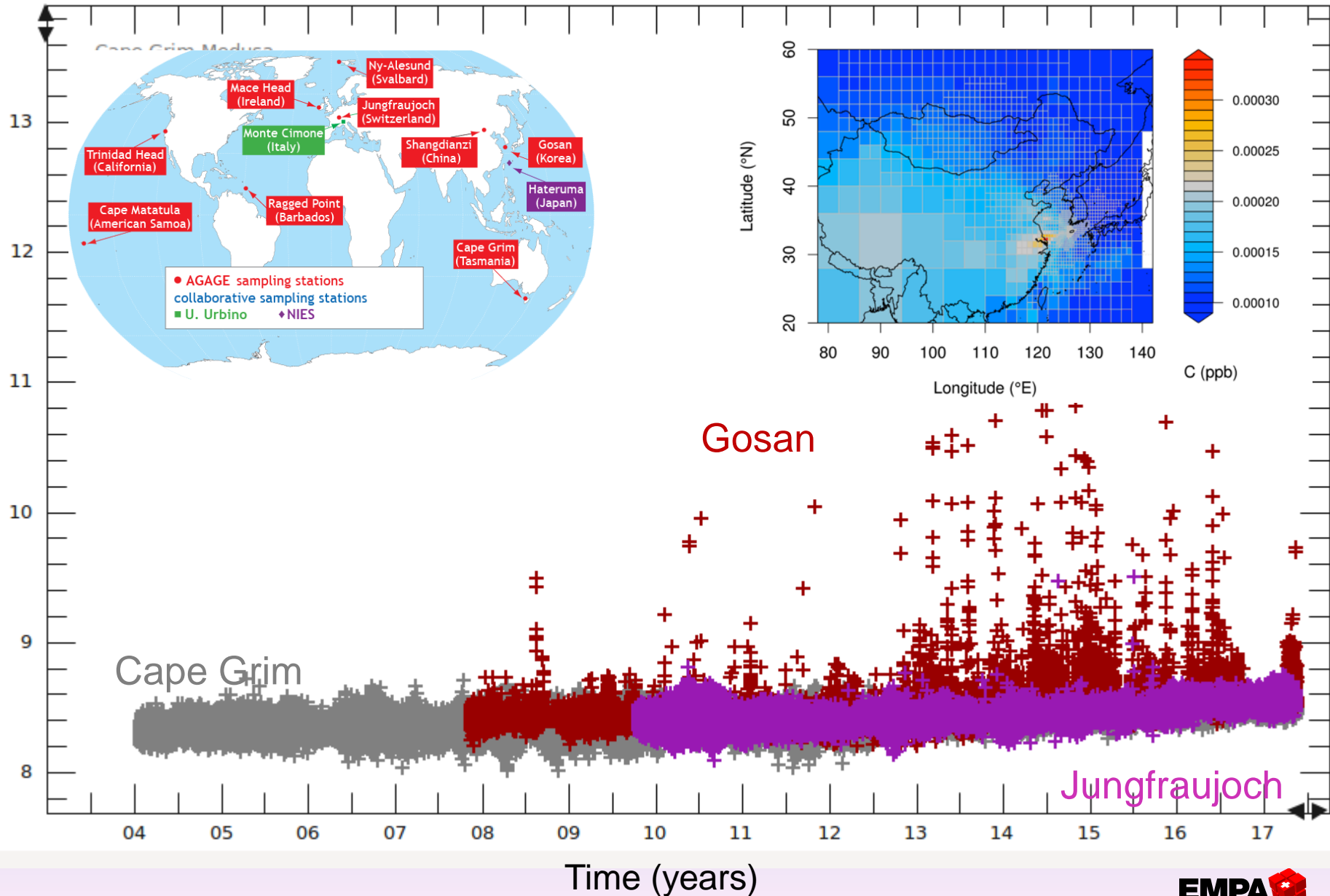


**Relationship  
dependent on AC  
Refill Batch**

$$\text{CFC-115 / HFC-125} = 1 - 7 \times 10^{-4} \text{ mol/mol}$$

40 kt/yr HFC-125  
→  
4 – 28 t/yr CFC-115

# CFC-115 at selected AGAGE sites



# Conclusions

- **Find Halocarbons with no known purposeful end use**
  - **Speculate to leak out as intermediates/byproducts from HFC synthesis**
  - **Observe and determine emission / use as tracers**

## **Acknowledgments**

- **Halclim (Swiss Federal Office for the Environment, FOEN)**
- **International Foundation High Altitude Research Station Jungfrauoch and Gornergrat (HFSJG)**
- **AGAGE (Advanced Global Atmospheric Gases Experiment)**
- **Station personnel at sites**
- **Provider of archived air samples**

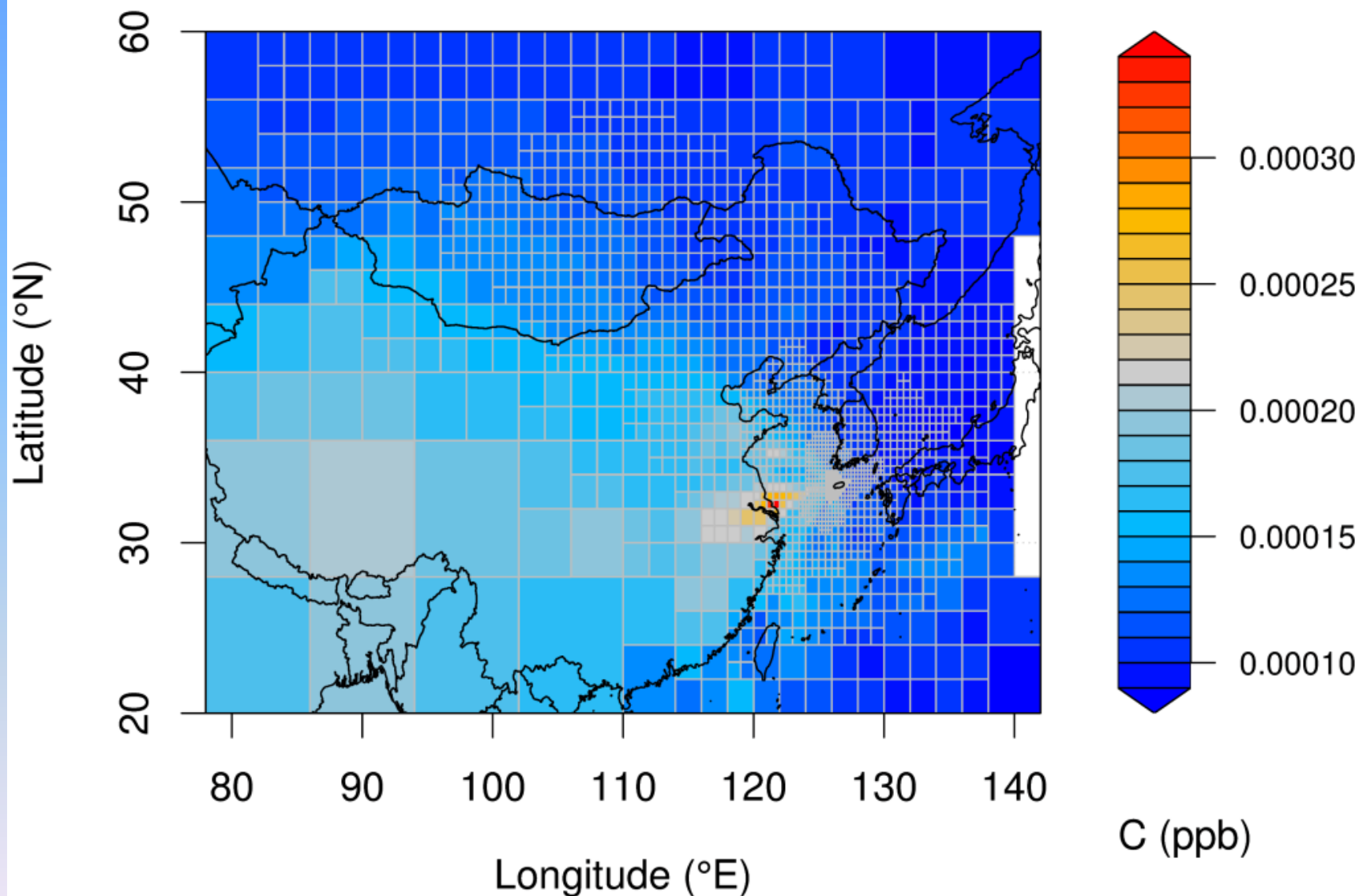


# *Title*

# *Title*

# *Title*

# CFC-115 emission hotspots (based on Gosan Measurements)

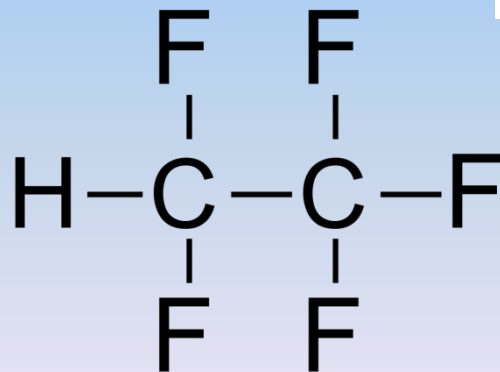
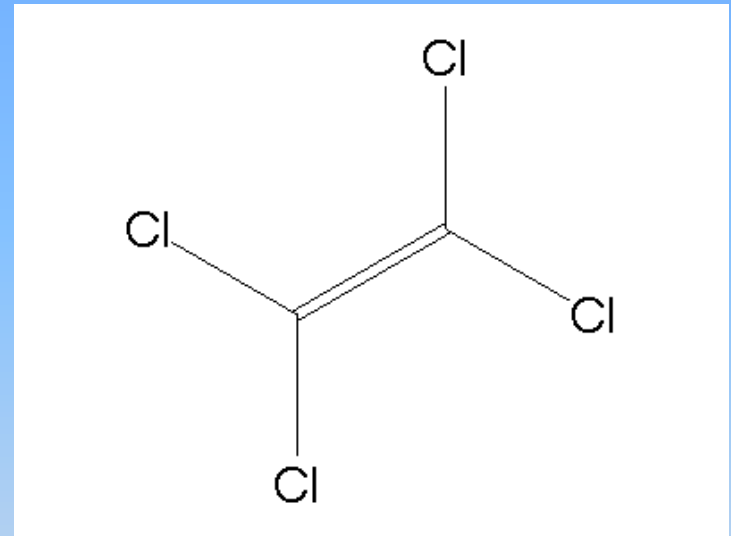
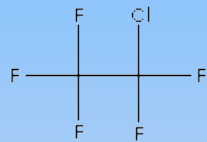
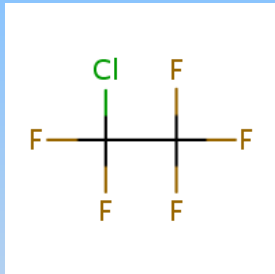
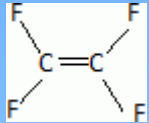


# End

- **Halclim (Swiss Federal Office for the Environment, FOEN)**
- **International Foundation High Altitude Research Station Jungfrauoch and Gornergrat (HFSJG)**
- **AGAGE (Advanced Global Atmospheric Gases Experiment)**
- **Station personnel at sites**
- **Provider of archived air samples**



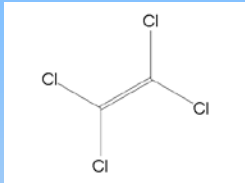
# Title



# HCFCs/CFCs as intermediates in the HFC production

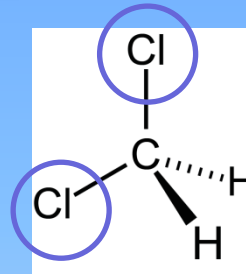
CFC-115

Tetrachloroethylene

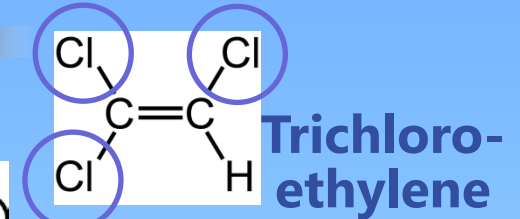


HCFC-31

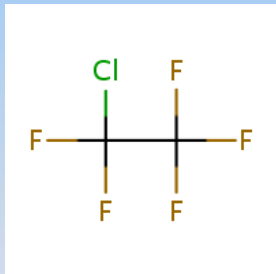
Methylene Chloride



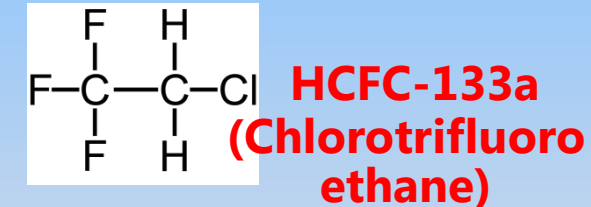
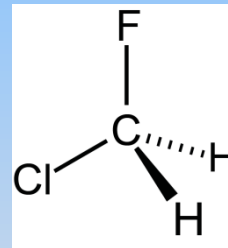
HCFC-133a



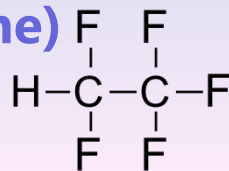
CFC-115



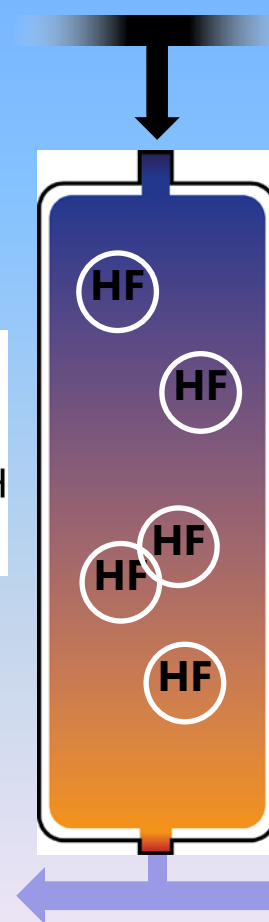
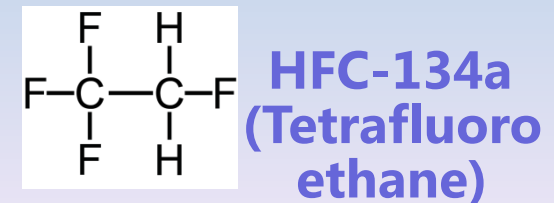
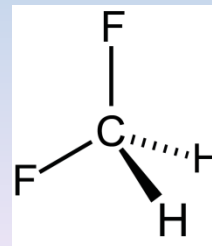
HCFC-31  
(Chlorofluoromethane)



HFC-125  
(Pentafluoroethane)



HFC-32  
(Difluoromethane)

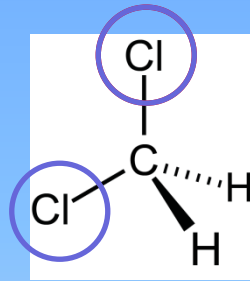


# HCFCs as intermediates in the HFC production

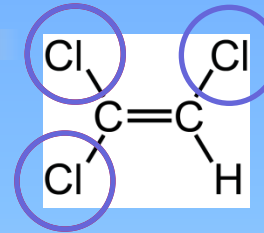
HCFC-31

HCFC-133a

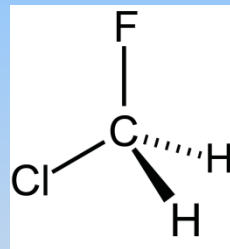
Methylene Chloride



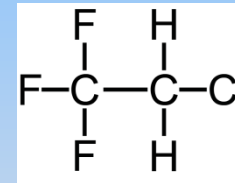
Trichloroethylene



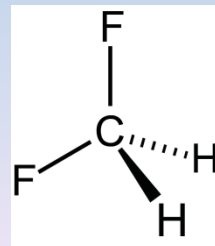
HCFC-31  
(Chlorofluoromethane)



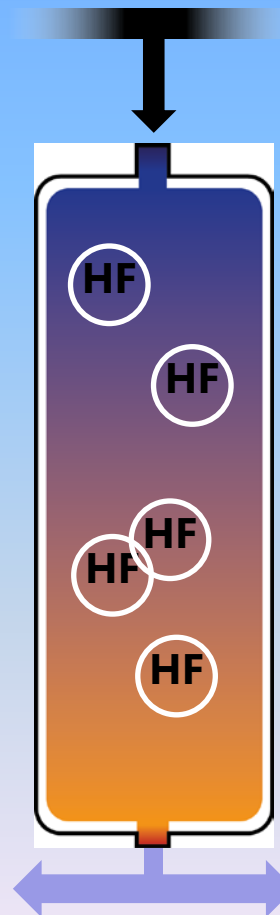
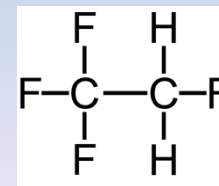
HCFC-133a  
(Chlorotrifluoroethane)



HFC-32  
(Difluoromethane)



HFC-134a  
(Tetrafluoroethane)

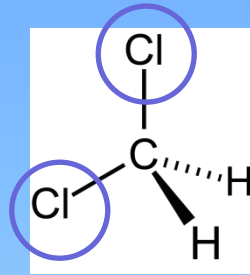


# HCFCs as intermediates in the HFC production

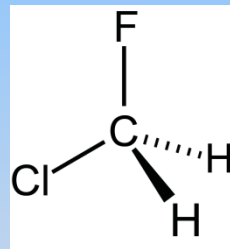
HCFC-31

HCFC-133a

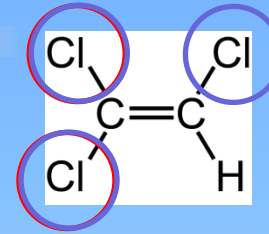
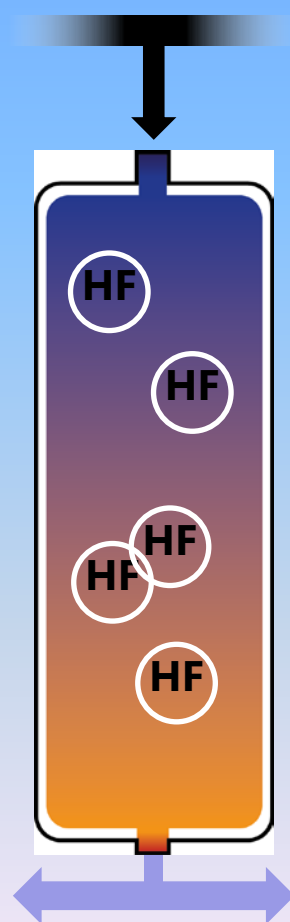
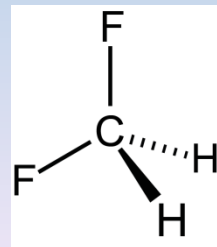
Methylene Chloride



HCFC-31  
(Chlorofluoromethane)

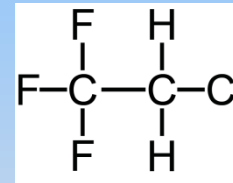


HFC-32  
(Difluoromethane)

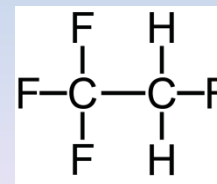


Trichloroethylene

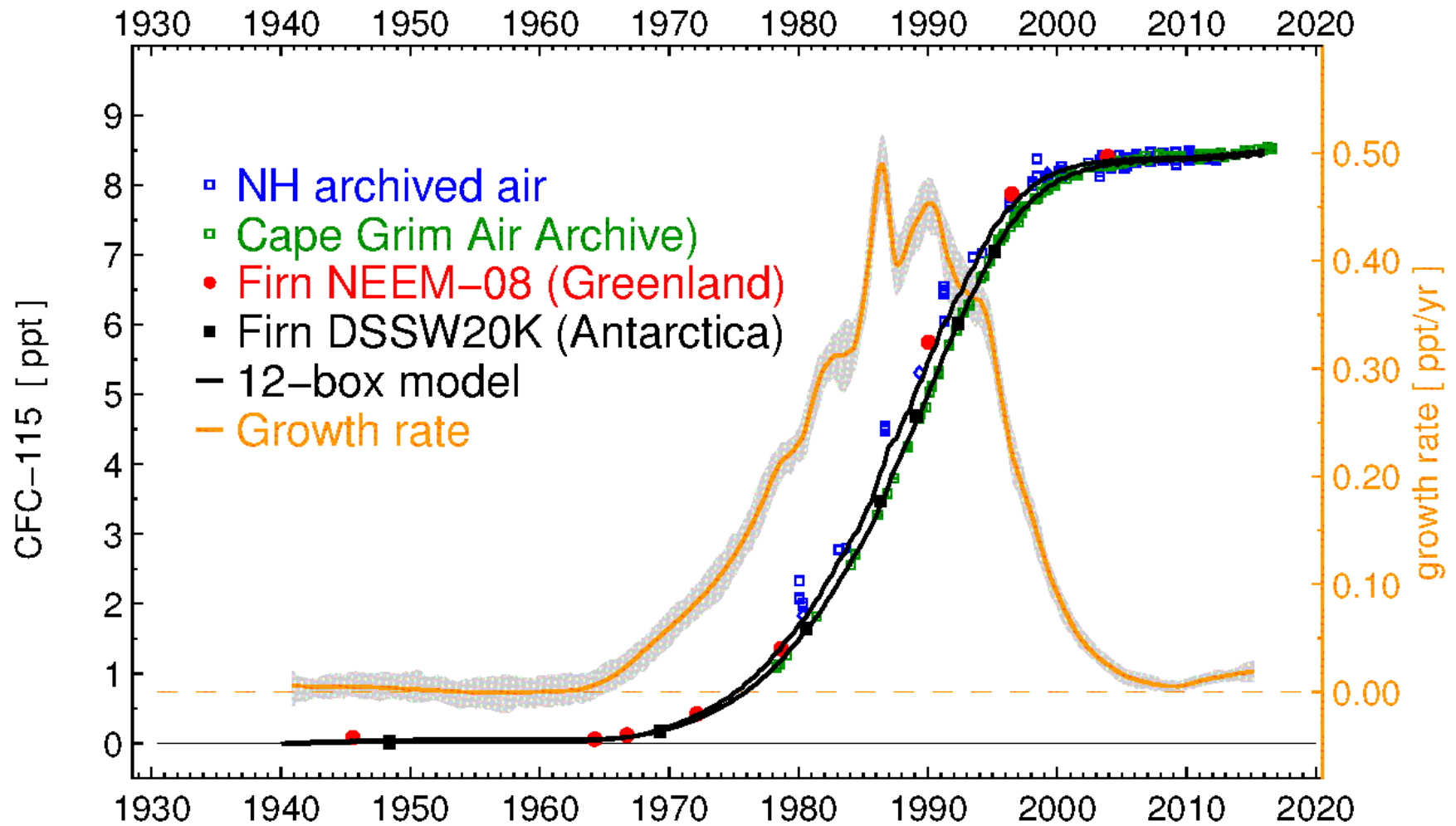
HCFC-133a  
(Chlorotrifluoroethane)



HFC-134a  
(Tetrafluoroethane)

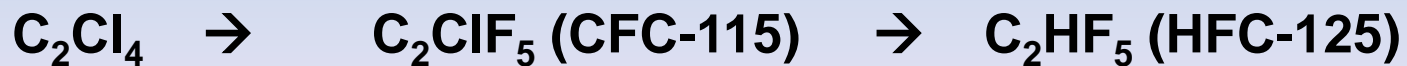
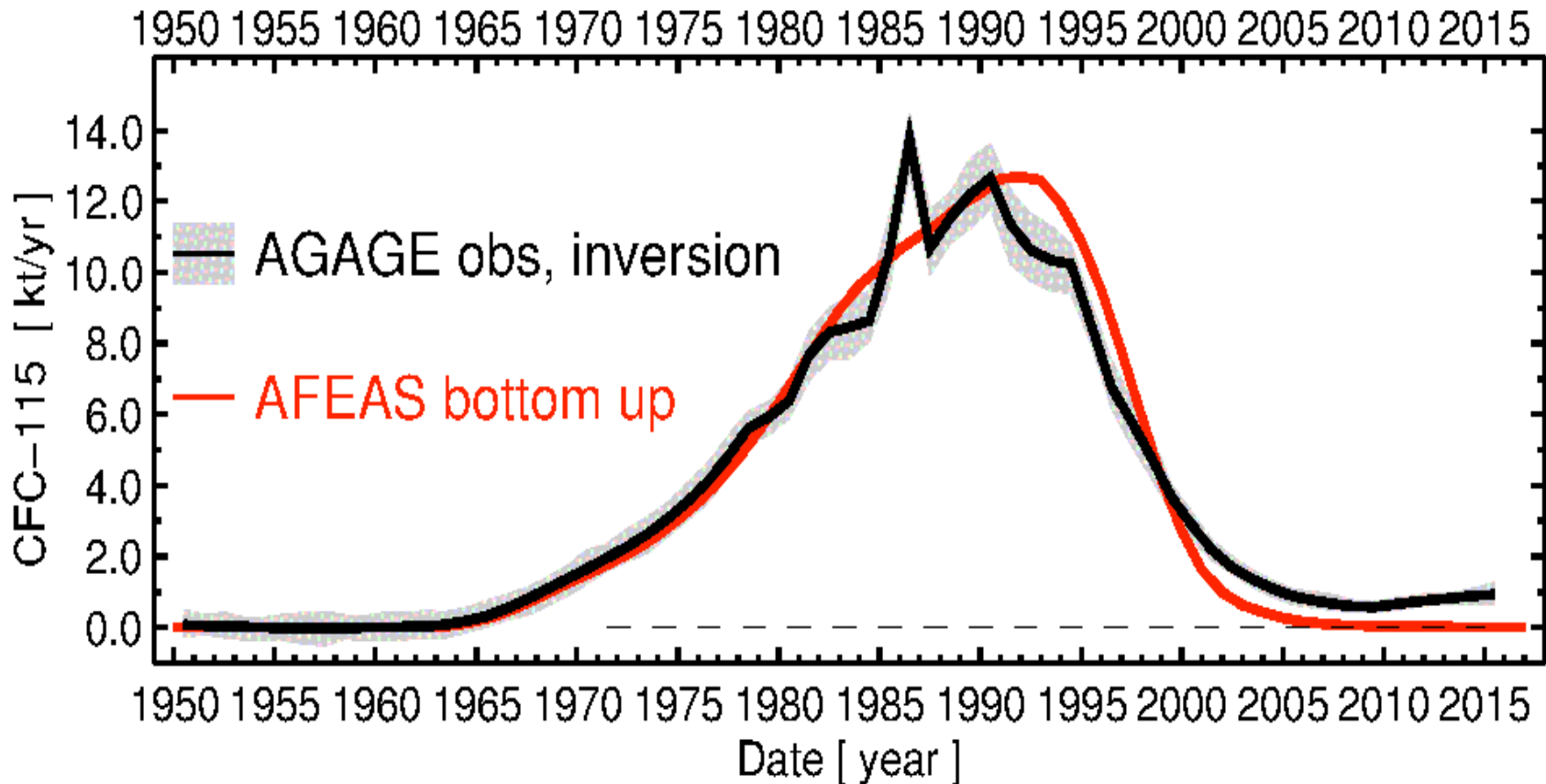


# Global CFC-115 Observations ( $\text{CClF}_2\text{CF}_3$ , lifetime 540 yr)





# Global CFC-115 emissions



# Halocarbons

1<sup>st</sup> Generation

2<sup>nd</sup> Generation

3<sup>rd</sup> Generation

4<sup>th</sup> Generation

*Montreal Protocol*

*Greenhouse Gases*

CFCs  
Halons  
CCl<sub>4</sub> / CH<sub>3</sub>CCl<sub>3</sub>  
/ CH<sub>3</sub>Br

HCFCs

PFCs  
HFCs

HFOs

*Ozone Depletion Substances*

*Kyoto Protocol*

Chlorofluorocarbons

Hydrochloro-  
fluorocarbons

Perfluorocarbons  
Hydrofluorocarbons

Hydrofluoroolefines

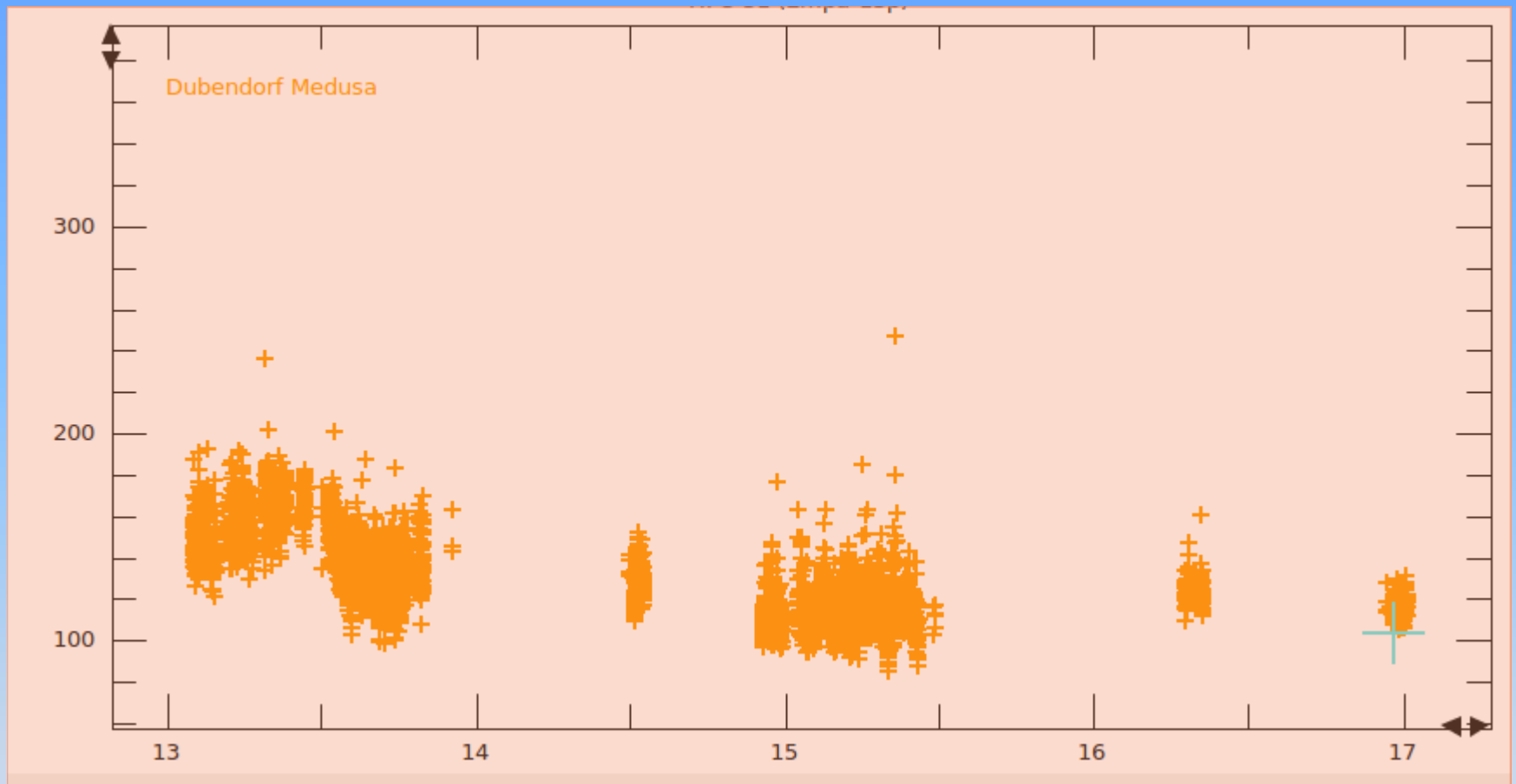
CFC-11, CFC-12,  
CFC-13, CFC-113,  
CFC-114, **CFC-115**  
H-1211, H-1301, ....

HCFC-22, HCFC-141b,  
HCFC-142b, **HCFC-31**,  
**HCFC-133a**, HCFC-  
131, HCFC-132b....

HFC-32, HFC-125,  
HFC-134a, HFC-245fa,  
PFC-116, PFC-218 ...

HFO-1234yf, HFO-  
1234ze(E), HCFO-  
1233zd(E), ....

# HCFC-31 at an urban site (Zurich-Dubendorf)



Time (years)