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# Atmospheric trends of long-lived halocarbons derived from 15 years of IASI/Metop measurements

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1.  
2.

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**Long-lived halogenated gases**

CFCs  
HCFCs  
HFCs  
CCl<sub>4</sub>  
SF<sub>6</sub>  
CF<sub>4</sub>

remote sensing

**IASI Instrument**

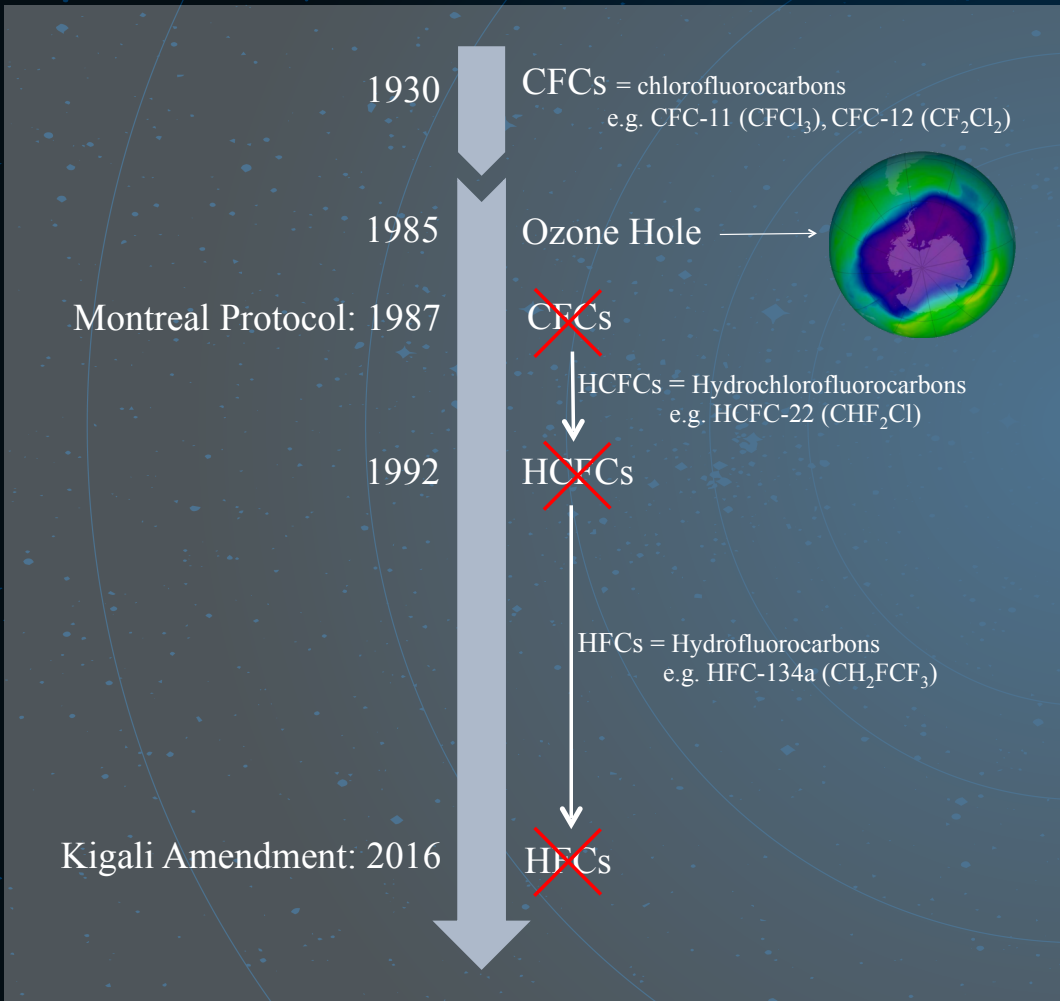
**Spectral detection**

**Retrieval methodology**  
generalized least squares estimation  
$$\hat{x} = x_0 + (K^T S^{-1} K)^{-1} K^T S^{-1} (y - \bar{y})$$

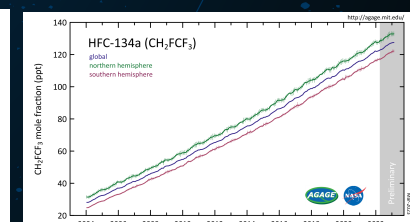
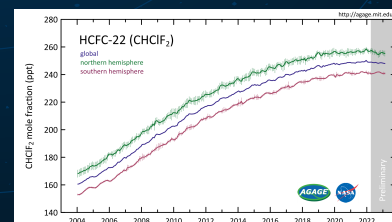
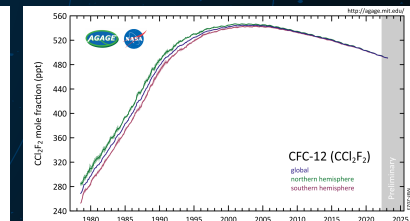
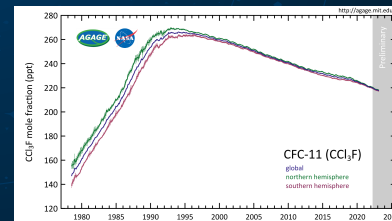
*Can nadir-pointing IR satellite sounders contribute to monitoring atmospheric concentrations of halocarbons?*

**Time series Northern midlatitudes**

**Time series Southern midlatitudes**

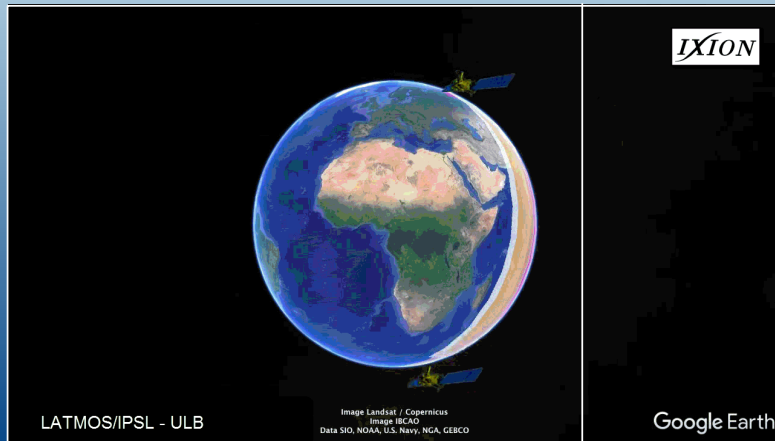


The emissions of chlorofluorocarbons (CFCs) and its substitutes have profoundly affected the chemical and radiative equilibrium of the atmosphere. The CFCs play a key role in the **depletion of stratospheric ozone** and are, just as their hydrogenated substitutes, **powerful greenhouse gases**. The emissions of most of these species are presently controlled by **international regulations**. Following the Montreal protocol and its amendments, the concentrations of the CFCs have started to decline in the early-2000. In parallel, the concentrations of the hydrogenated substitutes have increased. The exploitation of the measurements from the IASI sounder could play a key role in the monitoring of these species and thereby complement existing surface measurement networks.

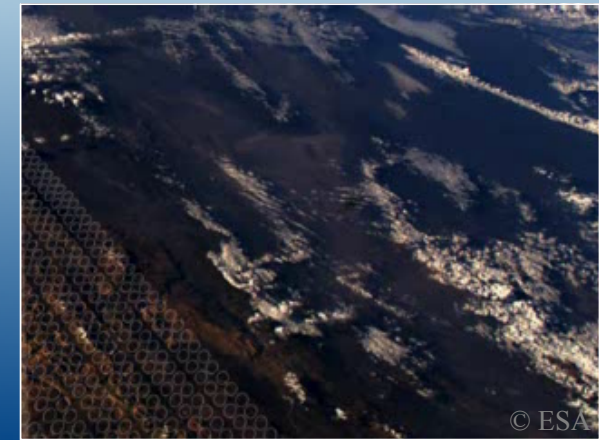
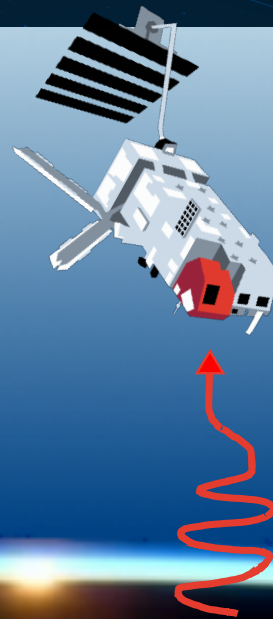




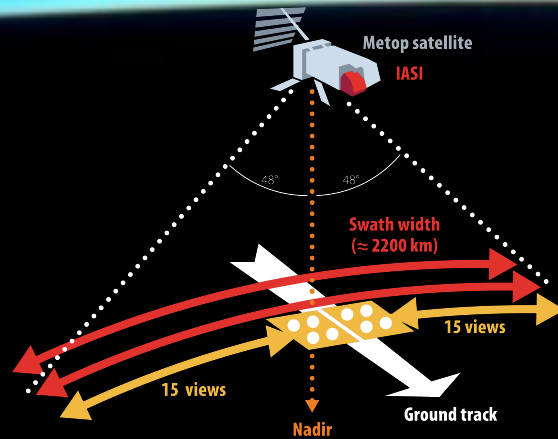
# Infrared Atmospheric Sounding Interferometer



Metop: Polar orbiting satellite



IASI: Thermal IR nadir sounder



The spatial instrument IASI is an operational hyperspectral sounder flying on-board Metop, the European meteorological satellites on **polar orbit**. It offers **quasi-global coverage bi-daily** with high horizontal resolution ( $\sim 12$  km at nadir). IASI measures a large continuous part of the **thermal infrared** ( $645\text{-}2760\text{ cm}^{-1}$ ) with **high radiometric performances**.

Long-lived halogenated species have a **weak spectral signature** in the Earth's outgoing longwave radiation, which makes their detection in individual spectra challenging. Using a particular type of spectral transformation, called **whitening**, allows for the identification of eight halogen-containing species in IASI mean spectra, i.e., **CFC-11**, **CFC-12**, **HCFC-22**, **HCFC-142b**, **HFC-134a**, **CF<sub>4</sub>**, **SF<sub>6</sub>** and **CCl<sub>4</sub>**, by remove the largest and most variable spectral features due to e.g., O<sub>3</sub>, N<sub>2</sub>O, CH<sub>4</sub> and H<sub>2</sub>O that are seen in each spectrum.

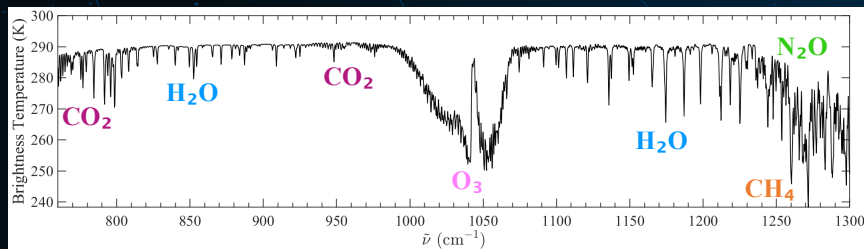
Whitening a spectrum  $y$  produces another spectrum  $\tilde{y}$  in which most of the background signal is removed and all spectral aberrations are exposed. It relies on a dataset of reference spectra from 2008, characterized by a mean spectrum  $\bar{y}$  and a covariance matrix  $S$ .

$$\tilde{y} = S^{-\frac{1}{2}} (y - \bar{y})$$

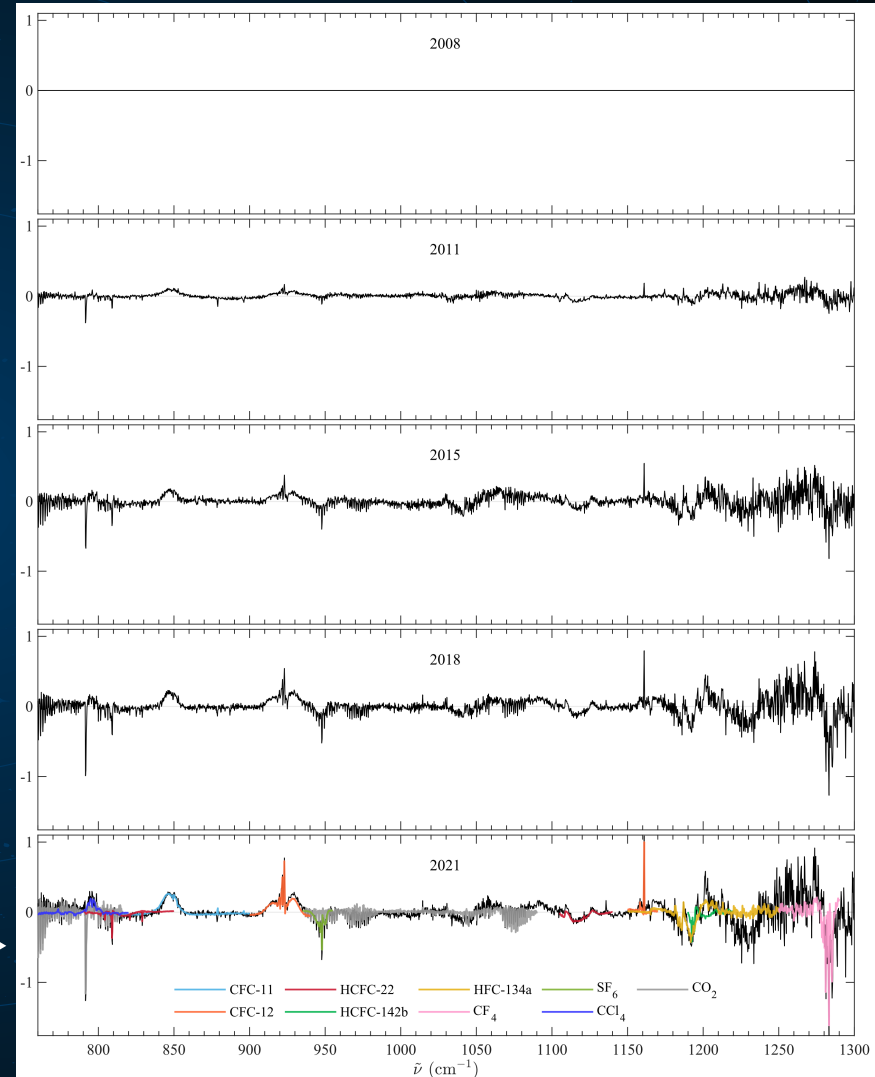
→ A positive (negative) whitened signal indicates a decrease (increase) over times.

- CFC-11, CFC-12, and CCl<sub>4</sub> are detected with a positive signal, indicating that their atmospheric abundance was smaller in 2021 than in 2008.
- HCFC-22, HCFC-142b, HFC-134a, CF<sub>4</sub> and SF<sub>6</sub> are detected with a negative signal, indicating an increase in their atmospheric abundance between 2008 and 2021.

*De Longueville et al., 2021. Identification of Short and Long-Lived Atmospheric Trace Gases From IASI Space Observations. GRL 48. doi:10.1029/2020gl091742*



whitening →



To retrieve **monthly atmospheric concentrations**, the **generalized least squares estimation** is applied on IASI monthly averaged spectra:

$$\hat{x} = x_0 + (K^T S^{-1} K)^{-1} K^T S^{-1} (y - \bar{y})$$

with  $\hat{x}$  and  $x_0$  the retrieved and reference concentrations of the target species, and  $K$  the Jacobians. This operation separates the contribution of the target, in a specific spectral range, from the atmospheric background which has a bigger impact on the signal.

**Annual trends** were derived from the retrieved time series using ordinary least squares, for the period 2008—2021.

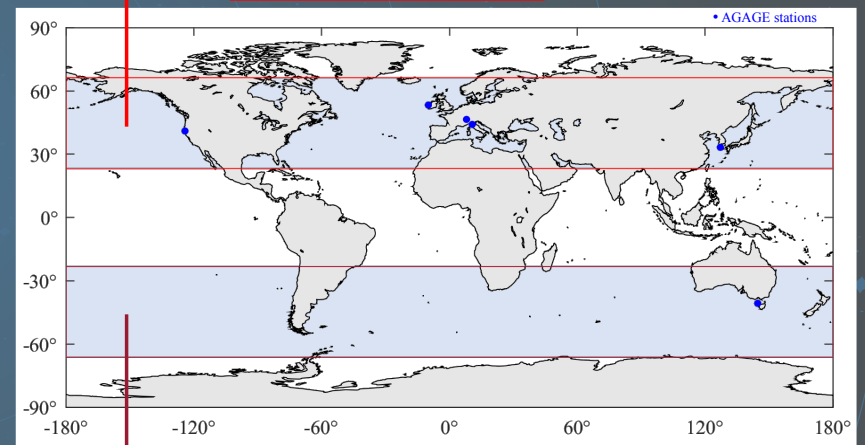
The retrieved concentrations and trends are intercompared with observations from the in situ measurements network **AGAGE** and the solar occultation sounder **ACE-FTS**.

This work focuses on **clear-sky IASI spectra** observed over **ocean** at **northern and southern mid-latitudes** for the period **2008—2022**.

S: 2008  
(~430,000 spectra)  
 $\bar{y}$ : 2008 monthly  
(~35,500 spectra)

y: 2008 → 2022 monthly  
(~35,500 spectra)

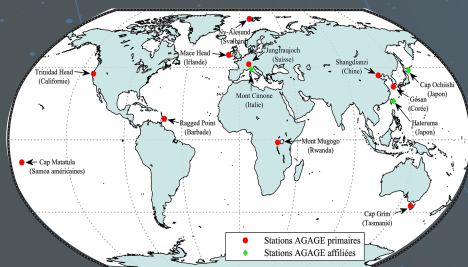
Background conditions:  
- T  
-  $\epsilon$   
- H<sub>2</sub>O, CO<sub>2</sub>, O<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>O



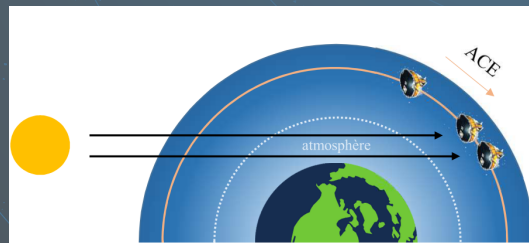
S: 2008 (~360,000 spectra)  
 $\bar{y}$ : 2008 monthly (~30,000 spectra)

y: 2008 → 2022 monthly (~31,000 spectra)

Ground-based observations (AGAGE)

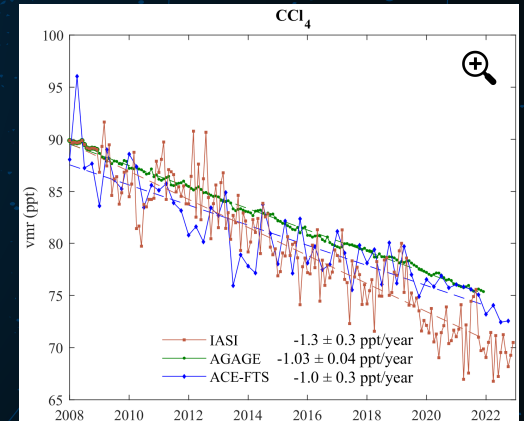
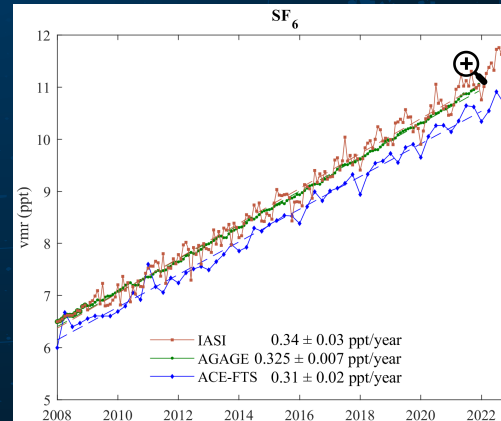
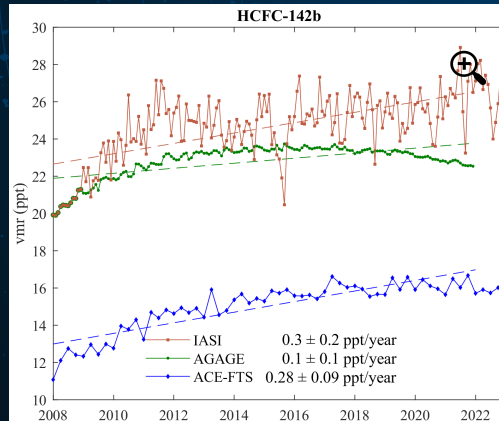
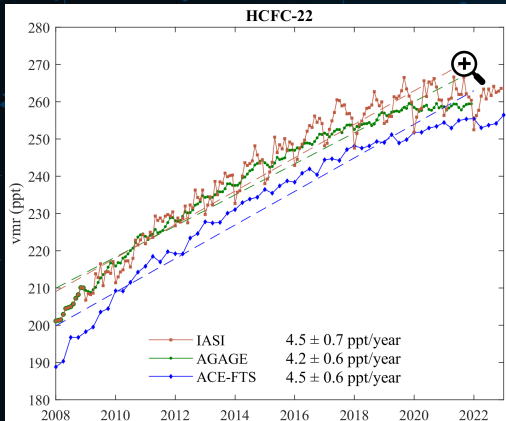
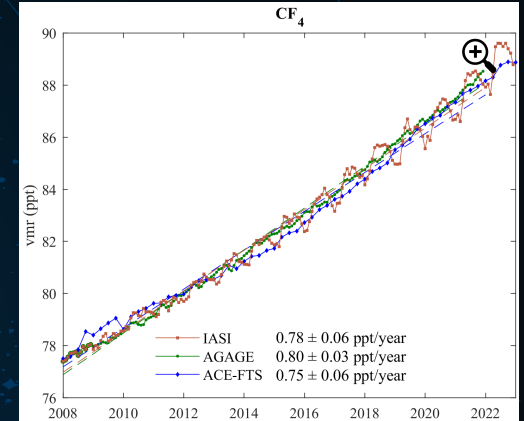
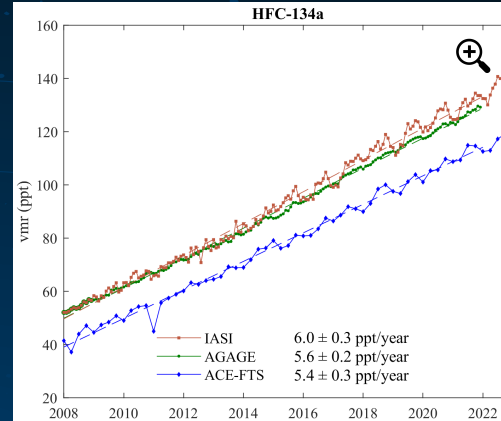
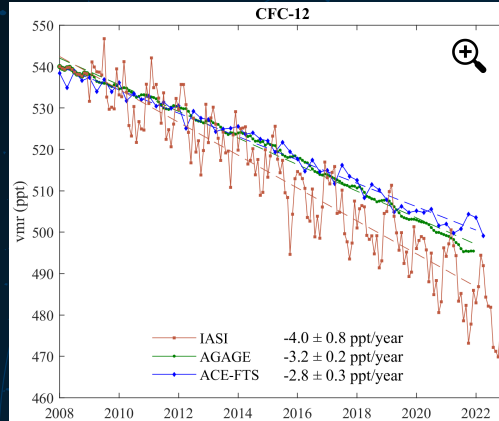
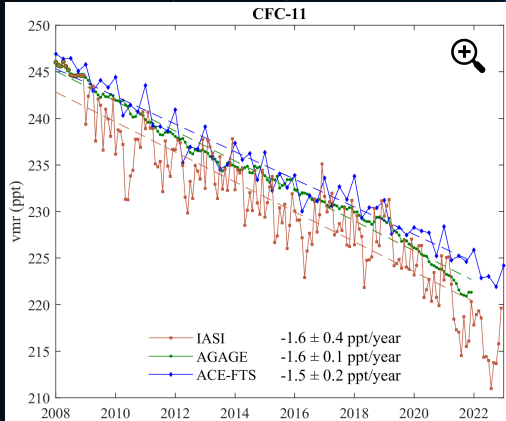


Limb satellite observations (ACE-FTS)



# Time series – Northern mid-latitudes

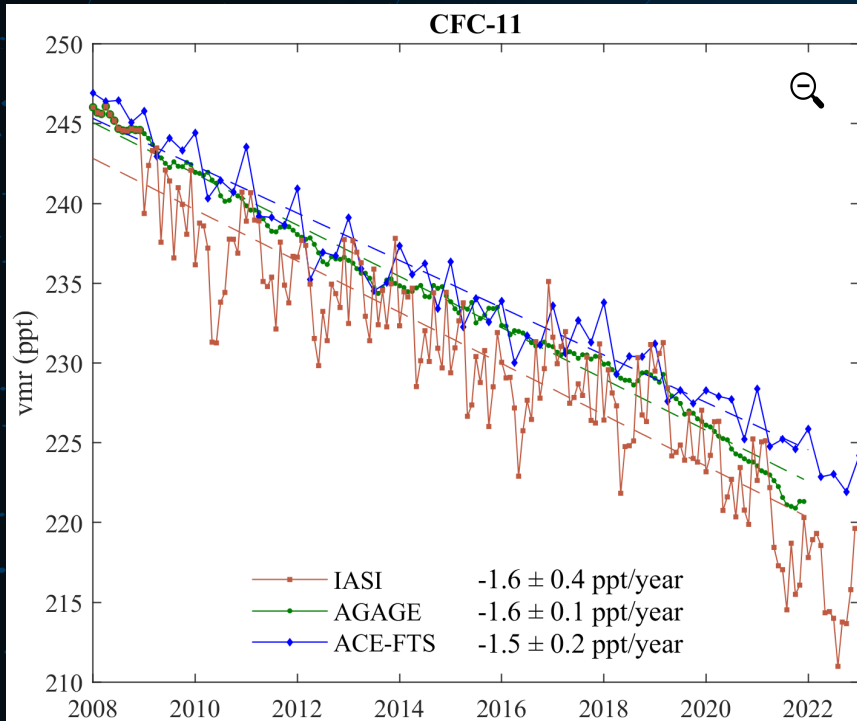
Click to zoom +





# Time series – CFC-11

Click to zoom -



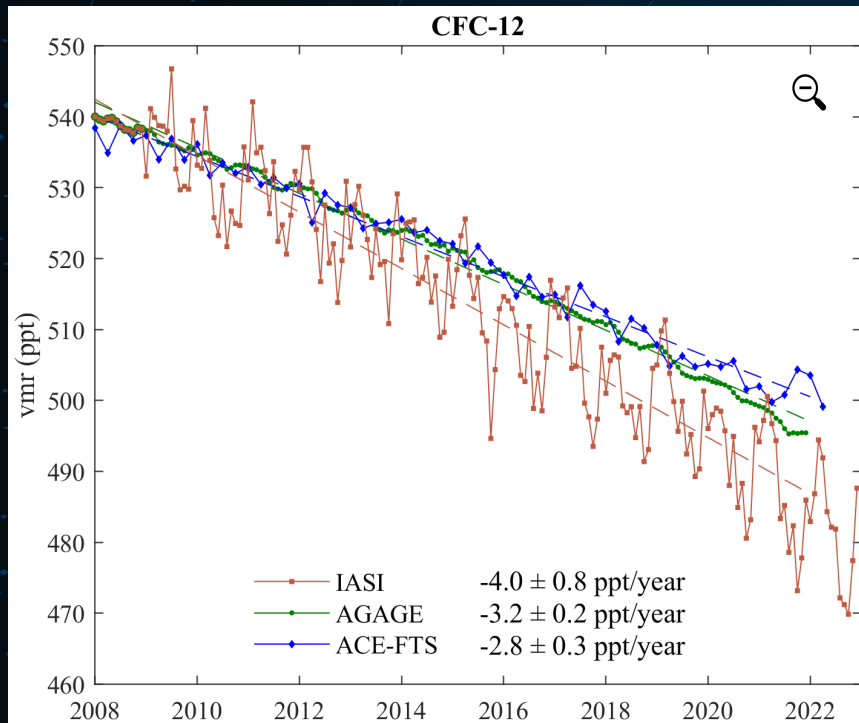
CFC-11 is the second most abundant CFC in the atmosphere after CFC-12. In response to the Montreal Protocol, its atmospheric abundance is decreasing since 2000. The trend derived from IASI shows a rate of decrease amounting  $-1.6 \pm 0.4$  ppt/year during 2008—2021, which is in excellent agreement with the one from AGAGE ( $-1.6 \pm 0.1$  ppt/year) for the same period. It is also matching within the uncertainty the  $-1.5 \pm 0.2$  ppt/year trend from the ACE-FTS. The case of CFC-11 is of particular interest in view of the reported slowdown of the decrease between 2012 and 2019, possibly due to illegal emissions. To see if these two breakpoints in the time evolution could be seen with IASI we have compared the trends for three separate periods: 2008—2011, 2012—2018 and 2019—2022 and found values of respectively  $-3 \pm 1$  ppt/year,  $-1.3 \pm 0.6$  ppt/year and  $-4 \pm 1$  ppt/year. We observe clearly a slowdown in the decline after 2012 followed by a return to normal in 2019 with an even higher rate of decrease than before 2012. While this acceleration compared to pre-2012 will have to be confirmed in the future by extending the time series, the fact that the breakpoints are well identified demonstrates the ability of IASI to capture the changes in the rate of decrease.

Retrieval parameters

Target	Spectral range (cm <sup>-1</sup> )	Interfering species
CFC-11	800—900	CO <sub>2</sub> , HNO <sub>3</sub> , HCFC-22, CCl <sub>4</sub>







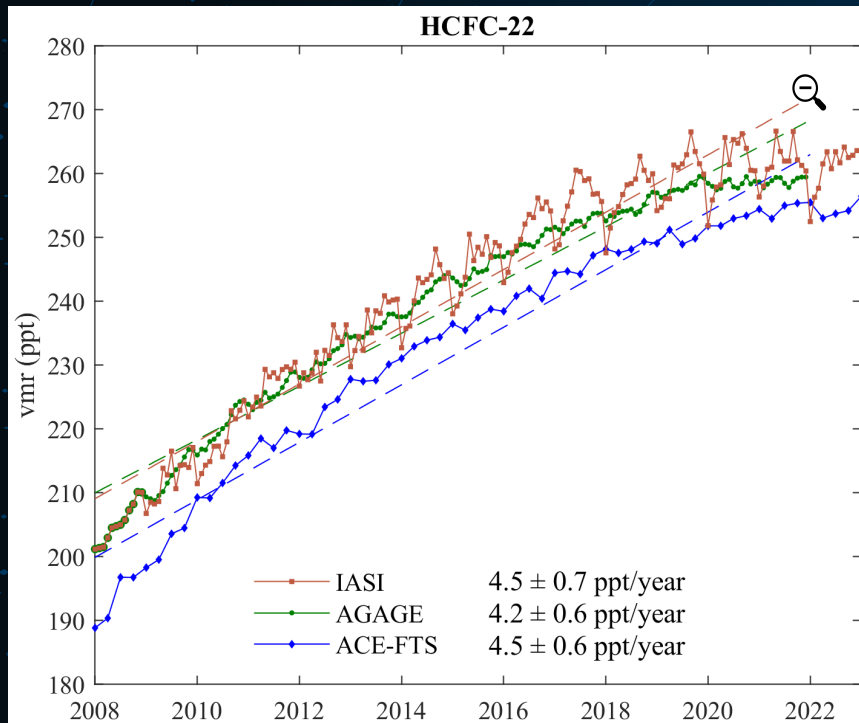
CFC-12 is the most abundant CFC in the atmosphere. In response to the Montreal Protocol, its atmospheric abundance is decreasing since 2000, like CFC-11. For CFC-12, we calculate from the IASI time series a rate of  $-4.0 \pm 0.8$  ppt/year between 2008 and 2021, which is larger than that inferred from AGAGE ( $-3.2 \pm 0.2$  ppt/year) and even more from the ACE-FTS ( $-2.8 \pm 0.3$  ppt/year). The reason for this discrepancy is not known at present but we suspect that it could be due to spectral interferences with another long-lived tracer absorbing in the same spectral region ( $900\text{--}940\text{ cm}^{-1}$ ). It is clear that more work will be needed to identify the cause of outliers in the CFC-12 time series from IASI and to improve its trend determination.

To conclude for CFC-12, we find with IASI, consistent with AGAGE and ACE-FTS, an acceleration of the rate of decrease with time with trend of  $-3 \pm 2$  ppt/year and  $-4 \pm 1$  ppt/year for the two sub-periods 2008—2011 and 2012—2021 considered.

Retrieval parameters

Target	Spectral range (cm <sup>-1</sup> )	Interfering species
CFC-12	900—940	CO <sub>2</sub> , HNO <sub>3</sub> , CFC-11, HCFC-142b, SF <sub>6</sub>



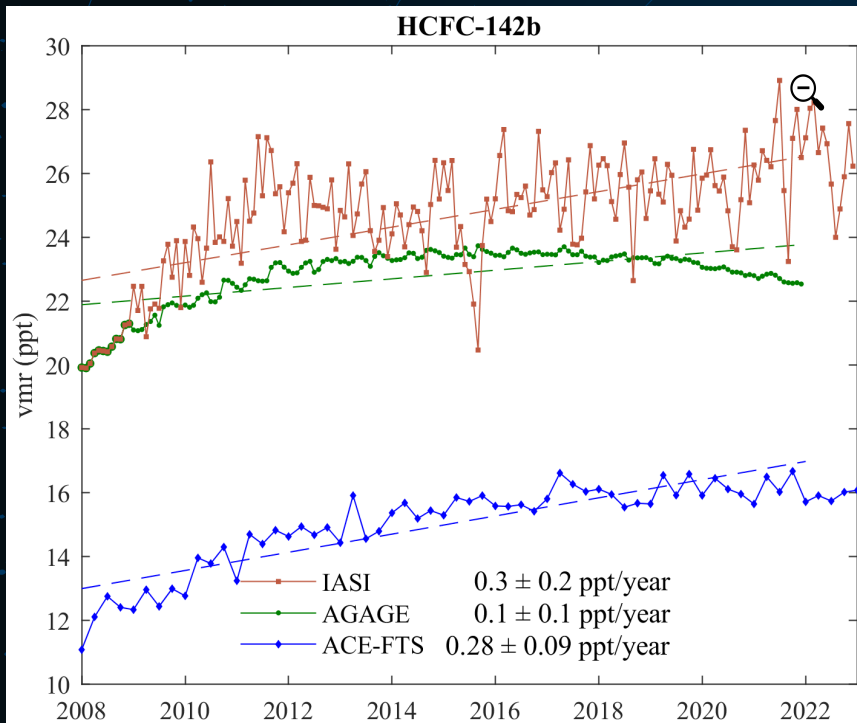


As a consequence of the regulations put on the production of CFCs, transitional HCFCs, such as HCFC-22 and HCFC-142b, have been widely used, leading to an increase of their atmospheric abundance. Starting from values of about 205 ppt in 2008 we find from IASI vmrs reaching maxima at the end of the time period, of around 262 ppt after 2021. Having been regulated themselves by the Montreal Protocol, the rate of increase is progressively slowing down. The linear regression applied over the entire 2008—2021 time period gives for HCFC-22 a growth rate of  $4.5 \pm 0.7$  ppt/year, broadly consistent with AGAGE ( $4.2 \pm 0.6$  ppt/year) and ACE-FTS ( $4.5 \pm 0.6$  ppt/year). The rate of decrease has halved between 2008—2011 ( $7 \pm 1$  ppt/year) and 2012—2021 ( $3.5 \pm 0.8$  ppt/year).

Retrieval parameters

Target	Spectral range (cm <sup>-1</sup> )	Interfering species
HCFC-22	790—850	CO <sub>2</sub> , CFC-11, CCl <sub>4</sub>

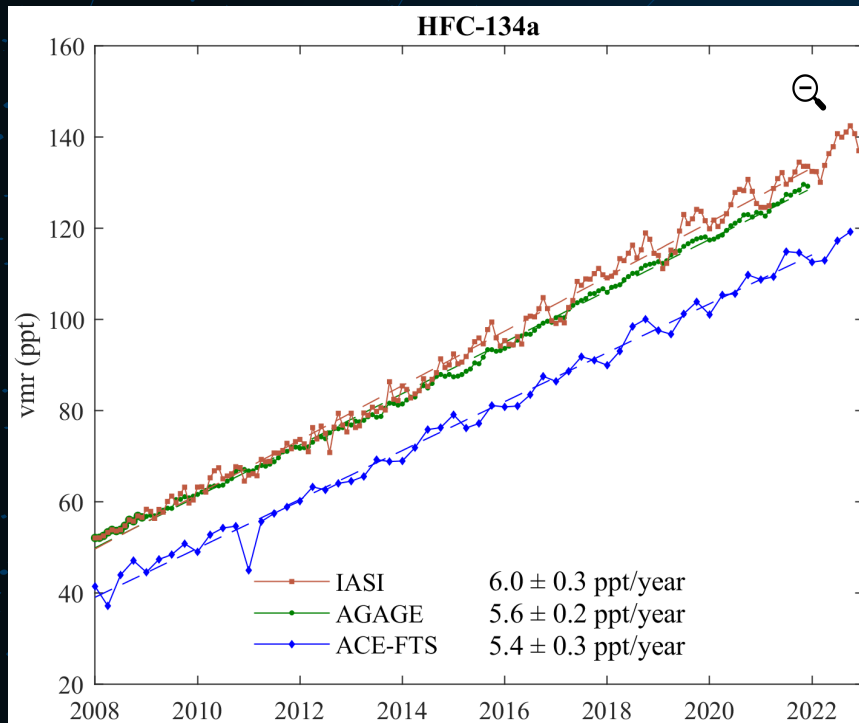




HCFC-142b shows a much smaller positive trend of  $0.3 \pm 0.2$  ppt/year than HCFC-22, which is furthermore not representative in view of the plateau appearing just after 2011 (the trend is close to zero after 2012). In that respect, the comparison with the trends obtained from the AGAGE ( $0.1 \pm 0.1$  ppt/year) and ACE-FTS ( $0.28 \pm 0.09$ ) datasets is also not relevant. Among the eight investigated species, HCFC-142b is the least well represented by linear regression.

Retrieval parameters

Target	Spectral range (cm <sup>-1</sup> )	Interfering species
HCFC-142b	1190—1220	HFC-134a



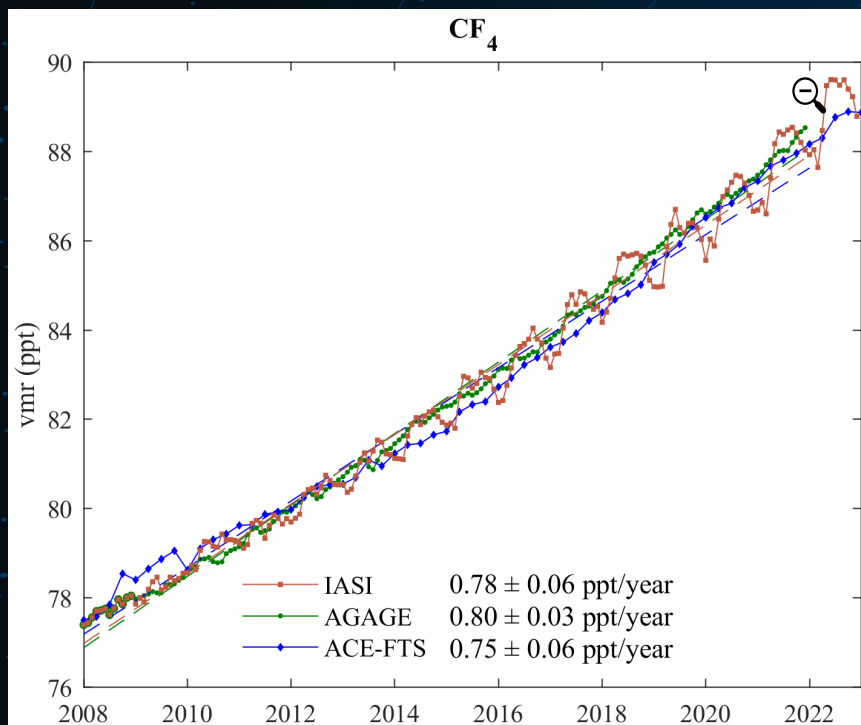
The abundance of HFC-134a is increasing rapidly as a result of its intensive use in refrigeration and air conditioning systems, as a blowing agent for polyurethane foams, and as a propellant for medical aerosols. We find from IASI a vmr of 130 ppt in 2021, more than 2.4 times its 2008 value (54 ppt). The linear trend value for the 2008—2021 IASI period is  $6.0 \pm 0.3$  ppt/year, surpassing that of HCFC-22. This trend is, taking into account the respective uncertainties, in good agreement with those from AGAGE ( $5.6 \pm 0.2$  ppt/year) and ACE-FTS ( $5.4 \pm 0.3$  ppt/year).

Retrieval parameters

Target	Spectral range (cm <sup>-1</sup> )	Interfering species
HFC-134a	1150—1250	CFC-12, HCFC-142b



## Time series – CF<sub>4</sub>



CF<sub>4</sub>, also named PFC-14, is one of the major PFCs and is emitted mostly from the industrial sector, following its use in aluminium and semiconductor production. Because of its extremely long lifetime (50,000 years), this gas reaches the mesosphere where it is photolyzed by UV radiation. Its abundance is also increasing steadily, although at a slower pace than HFC-134a. We find from IASI maximum vmrs around 88 ppt, resulting from a linear growth rate of  $0.78 \pm 0.06$  ppt/year. We find a remarkable agreement with the trends determined from AGAGE ( $0.80 \pm 0.03$  ppt/year) and ACE-FTS ( $0.75 \pm 0.06$  ppt/year).

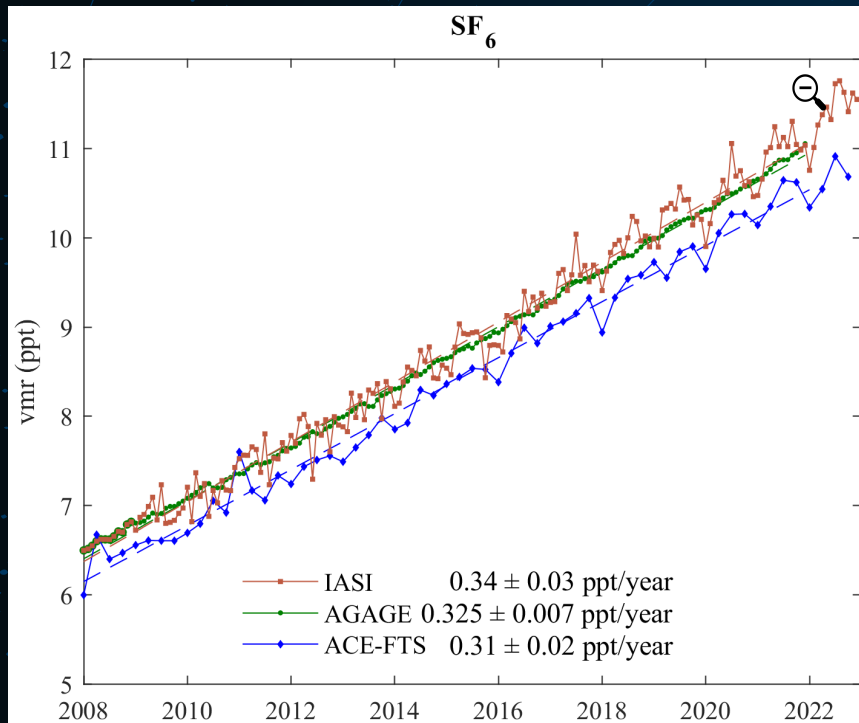
### Retrieval parameters

Target	Spectral range (cm <sup>-1</sup> )	Interfering species
CF <sub>4</sub>	1250—1290	HCFC-142b, HFC-134a





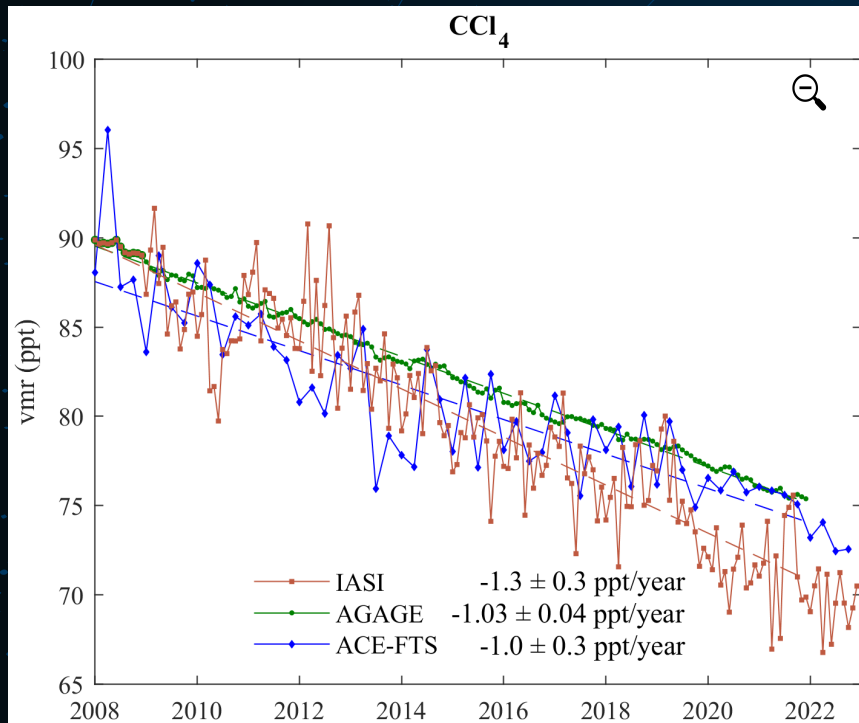
## Time series – SF<sub>6</sub>



SF<sub>6</sub> is primarily used for electrical insulation and semiconductors. Like CF<sub>4</sub>, because of its extremely long lifetime (3,200 years), it reaches the mesosphere where it is photolyzed by UV radiation or, degraded after electron attachment. Its atmospheric abundance is also increasing over time, with a linear growth rate of  $0.34 \pm 0.03$  ppt/year between 2008 and 2021. This trend value is in good agreement with AGAGE ( $0.325 \pm 0.007$  ppt/year) and ACE-FTS ( $0.31 \pm 0.02$  ppt/year).

### Retrieval parameters

Target	Spectral range (cm <sup>-1</sup> )	Interfering species
SF <sub>6</sub>	935—955	CO <sub>2</sub> , CFC-12

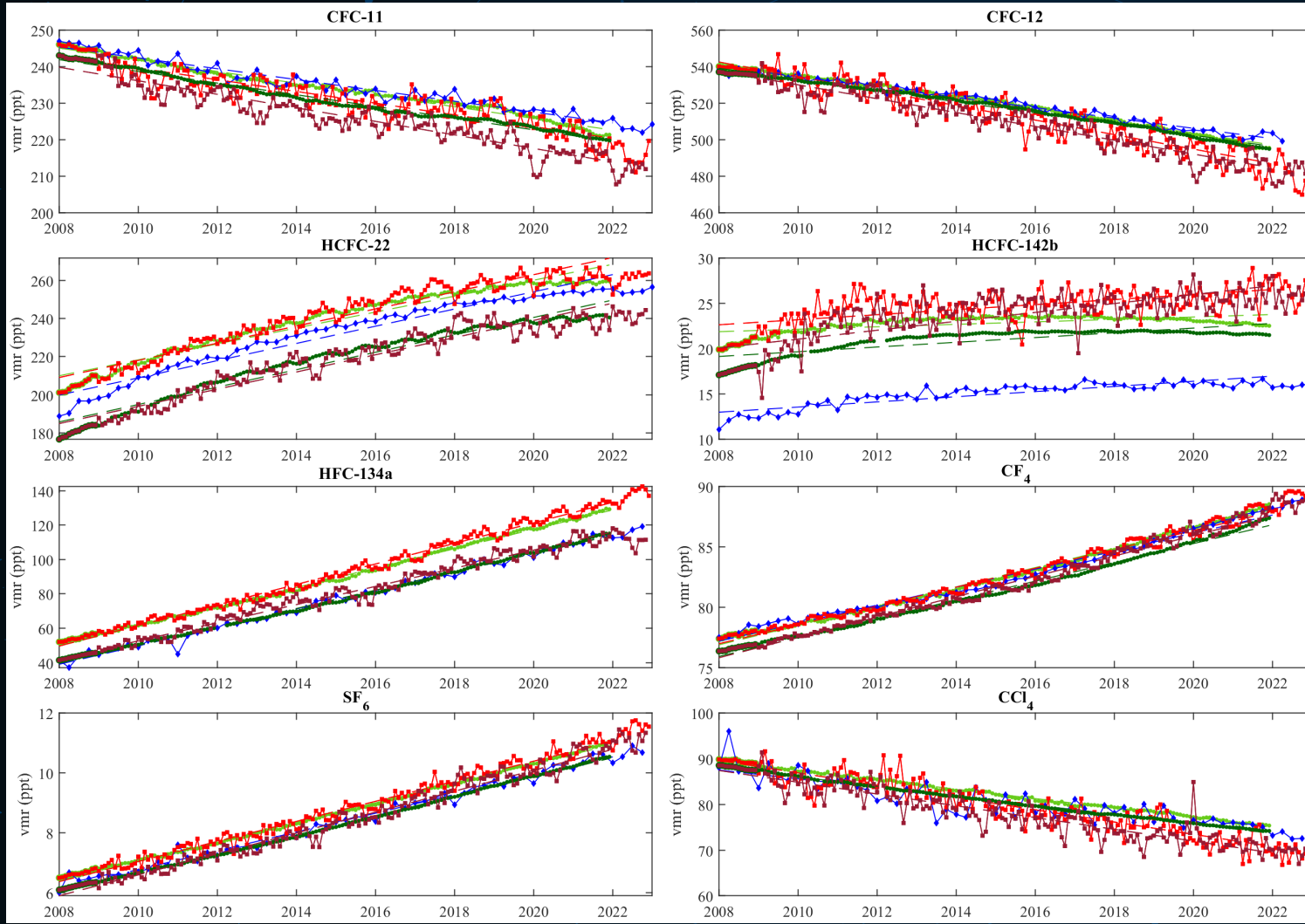


CCl<sub>4</sub> has been regulated by the Montreal Protocol for as long as CFCs, leading to a decrease in its atmospheric vmrs after a peak at around 105 ppt in the early 1990s. Starting from a vmr value of around 89 ppt in 2008, we find a minimum vmr in 2021 of about 72 ppt, corresponding to a linear rate of decline of  $-1.3 \pm 0.3$  ppt/year over the 2008—2021 time period. While it comes with a small error, this negative trend is significantly larger than that inferred from the in situ measurements ( $-1.03 \pm 0.04$  ppt/year) and even more so from ACE-FTS ( $-1.0 \pm 0.3$  ppt/year). This might be due to the overlap with CO<sub>2</sub> in the region where CCl<sub>4</sub> is retrieved (760—820 cm<sup>-1</sup>).

Retrieval parameters

Target	Spectral range (cm <sup>-1</sup> )	Interfering species
CCl <sub>4</sub>	760—820	CO <sub>2</sub> , HNO <sub>3</sub> , HCFC-22





	Annual trend (ppt/year)			
	IASI	AGAGE	ACE-FTS	
<b>CFC-11</b>	...	...	...	...
<b>CFC-12</b>	...	...	...	...
<b>HCFC-22</b>	...	...	...	...
<b>HCFC-142b</b>	...	...	...	...
<b>HFC-134a</b>	...	...	...	...
<b>CF<sub>4</sub></b>	...	...	...	...
<b>CCl<sub>4</sub></b>	...	...	...	...

<i>IASI</i>	<i>Northern mid-latitudes</i>
<i>IASI</i>	<i>Southern mid-latitudes</i>
<i>AGAGE</i>	<i>Northern mid-latitudes</i>
<i>AGAGE</i>	<i>Southern mid-latitudes</i>
<i>ACE-FTS</i>	<i>Global</i>

The temporal evolution of the atmospheric abundance of eight long-lived halogenated gases has been determined for the period 2008—2022 currently covered by IASI; a reasonable agreement was obtained with the in situ measurements from AGAGE stations and with the measurements from the ACE-FTS solar occultation sounder. However, too large discrepancies were found in the trends of CFC-12 and CCl<sub>4</sub>, for reasons which are not entirely clear at the moment.

These results are very promising in that they suggest an important role of IASI for monitoring long-lived halogenated species over time.

Future research will include the investigation of spatial variability in their trends over the globe, with a particular interest in regions suspected of fugitive emissions or regions lacking in situ measurements (e.g., India, Arabian peninsula, South America).



**Global and long-term** monitoring of halocarbons atmospheric abundances



→ Monitoring of the global evolution of the atmosphere system

→ Verification of the effectiveness of international protocols

