

# THE ATMOSPHERIC CHEMISTRY EXPERIMENT (ACE): Greenhouse Gas Measurements of CO<sub>2</sub>, CFCs and HFCs

Peter Bernath

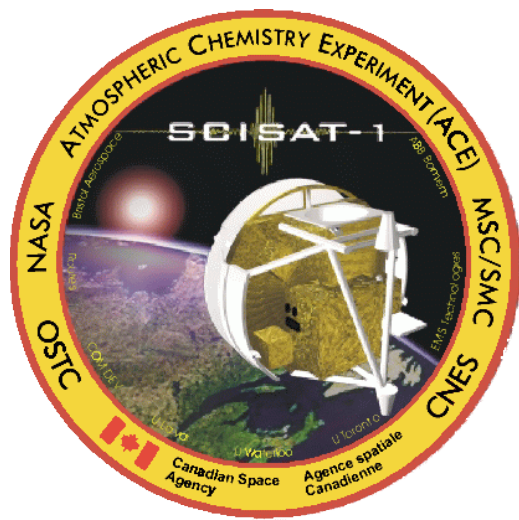


Old Dominion University, Norfolk, VA

and

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**OLD DOMINION**  
UNIVERSITY



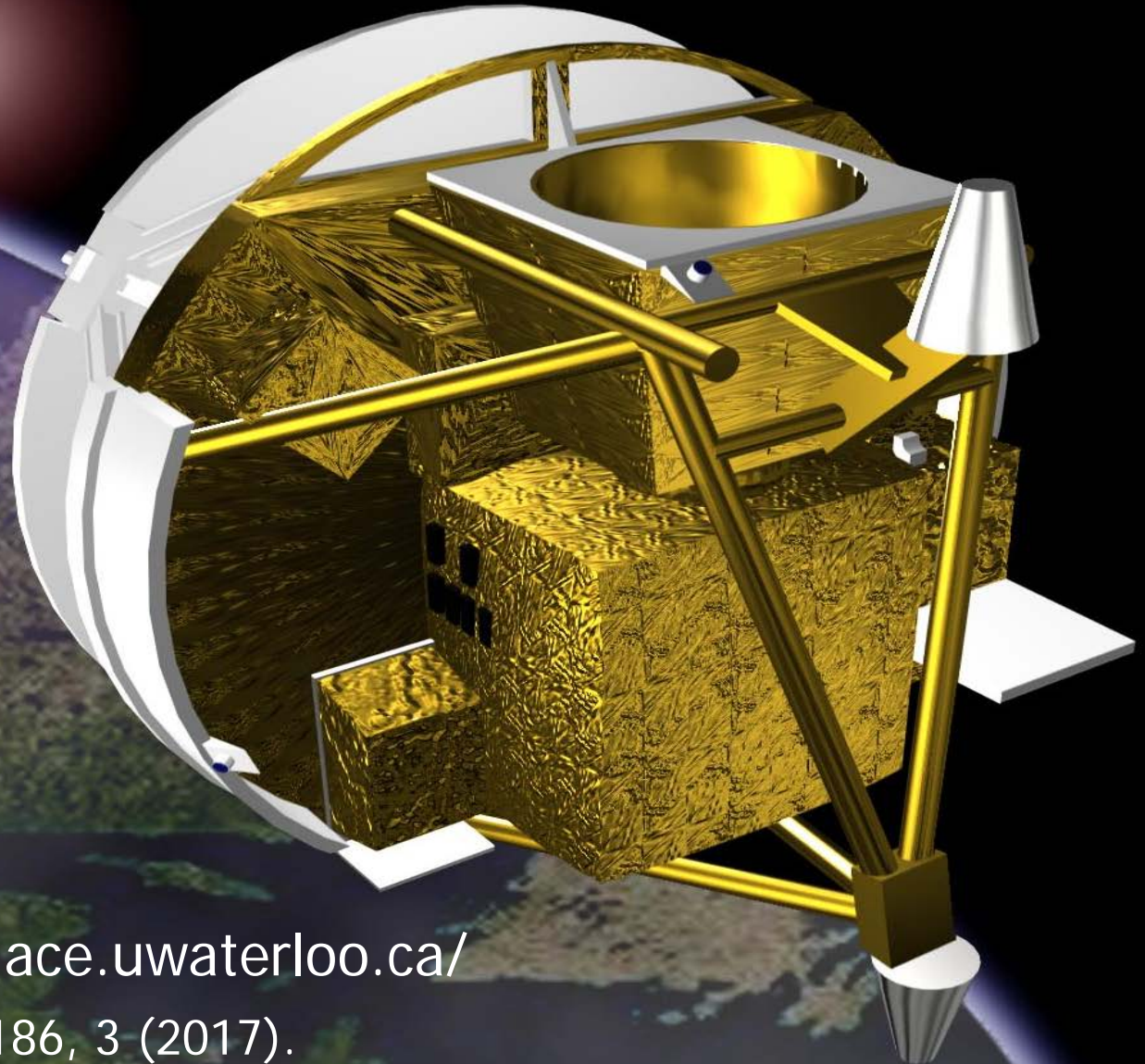
University of  
**Waterloo**



Journal of  
Quantitative  
Spectroscopy &  
Radiative  
Transfer

# ACE Satellite (Limb View)

Fourier  
transform  
spectrometer,  
 $750\text{-}4400\text{ cm}^{-1}$ ,  
 $0.02\text{ cm}^{-1}$   
resolution,  
solar  
occultation



<http://www.ace.uwaterloo.ca/>

Bernath, JQSRT 186, 3 (2017).

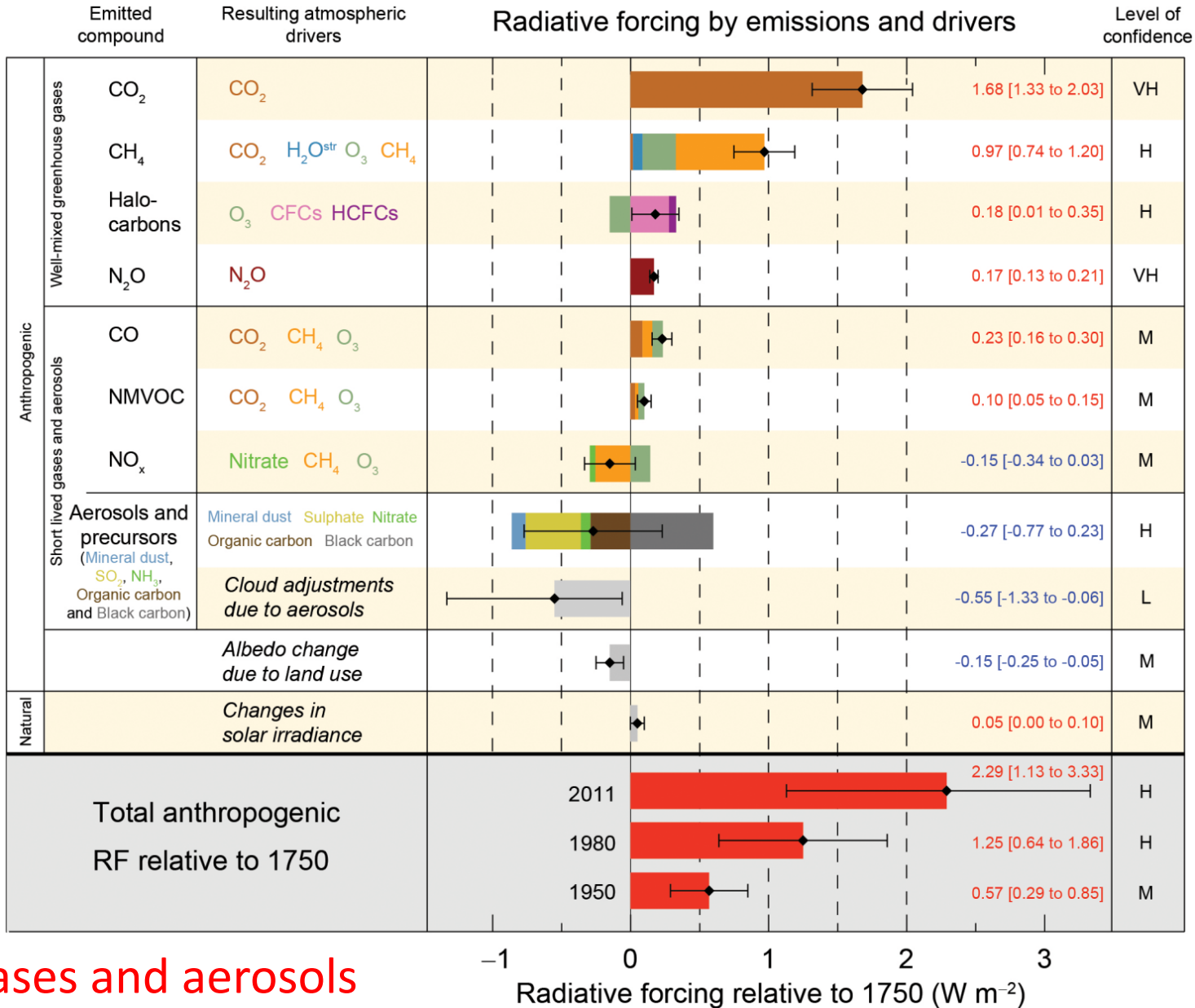
# Greenhouse Gases (IPCC 2013)

1. CO<sub>2</sub>
2. CH<sub>4</sub>
3. CFCs/HCFs/  
HFCs
4. N<sub>2</sub>O

## Indirect GHGs

1. CO
2. VOCs
3. NO<sub>x</sub>

## Aerosols



All significant gases and aerosols associated with climate change are measured by ACE mission.

# ACE-FTS Version 4.0 Species

Tracers:  $\text{H}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HO}_2\text{NO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{SO}_2$

Halogen-containing gases:  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{ClO}$ ,  $\text{ClONO}_2$ ,  $\text{CFC-11}$ ,  $\text{CFC-12}$ ,  $\text{CFC-113}$ ,  $\text{COF}_2$ ,  $\text{COCl}_2$ ,  $\text{COFCl}$ ,  $\text{CF}_4$ ,  $\text{SF}_6$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CCl}_4$ ,  $\text{HCFC-22}$ ,  $\text{HCFC-141b}$ ,  $\text{HCFC-142b}$ ,  $\text{HFC-134a}$ ,  $\text{HFC-23}$

Carbon-containing gases:  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{CO}$ ,  $\text{HCOOH}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{OCS}$ ,  $\text{HCN}$ ,  $\text{CH}_3\text{C(O)CH}_3$ ,  $\text{CH}_3\text{CN}$ ,  $\text{PAN}$ , high and low altitude  $\text{CO}_2$  as well as pressure and temperature from  $\text{CO}_2$  lines

Isotopologues:  $\text{H}_2^{18}\text{O}$ ,  $\text{H}_2^{17}\text{O}$ ,  $\text{HDO}$ ,  $\text{O}^{13}\text{CO}$ ,  $\text{OC}^{18}\text{O}$ ,  $\text{OC}^{17}\text{O}$ ,  $\text{O}^{13}\text{C}^{18}\text{O}$ ,  $^{18}\text{OO}_2$ ,  $\text{O}^{18}\text{OO}$ ,  $\text{O}^{17}\text{OO}$ ,  $\text{OO}^{17}\text{O}$ ,  $\text{N}^{15}\text{NO}$ ,  $^{15}\text{NNO}$ ,  $\text{N}_2^{18}\text{O}$ ,  $\text{N}_2^{17}\text{O}$ ,  $^{13}\text{CO}$ ,  $\text{C}^{18}\text{O}$ ,  $\text{C}^{17}\text{O}$ ,  $^{13}\text{CH}_4$ ,  $\text{CH}_3\text{D}$ ,  $\text{OC}^{34}\text{S}$ ,  $\text{O}^{13}\text{CS}$ ,  $^{15}\text{NO}_2$ ,  $\text{H}^{15}\text{NO}_3$

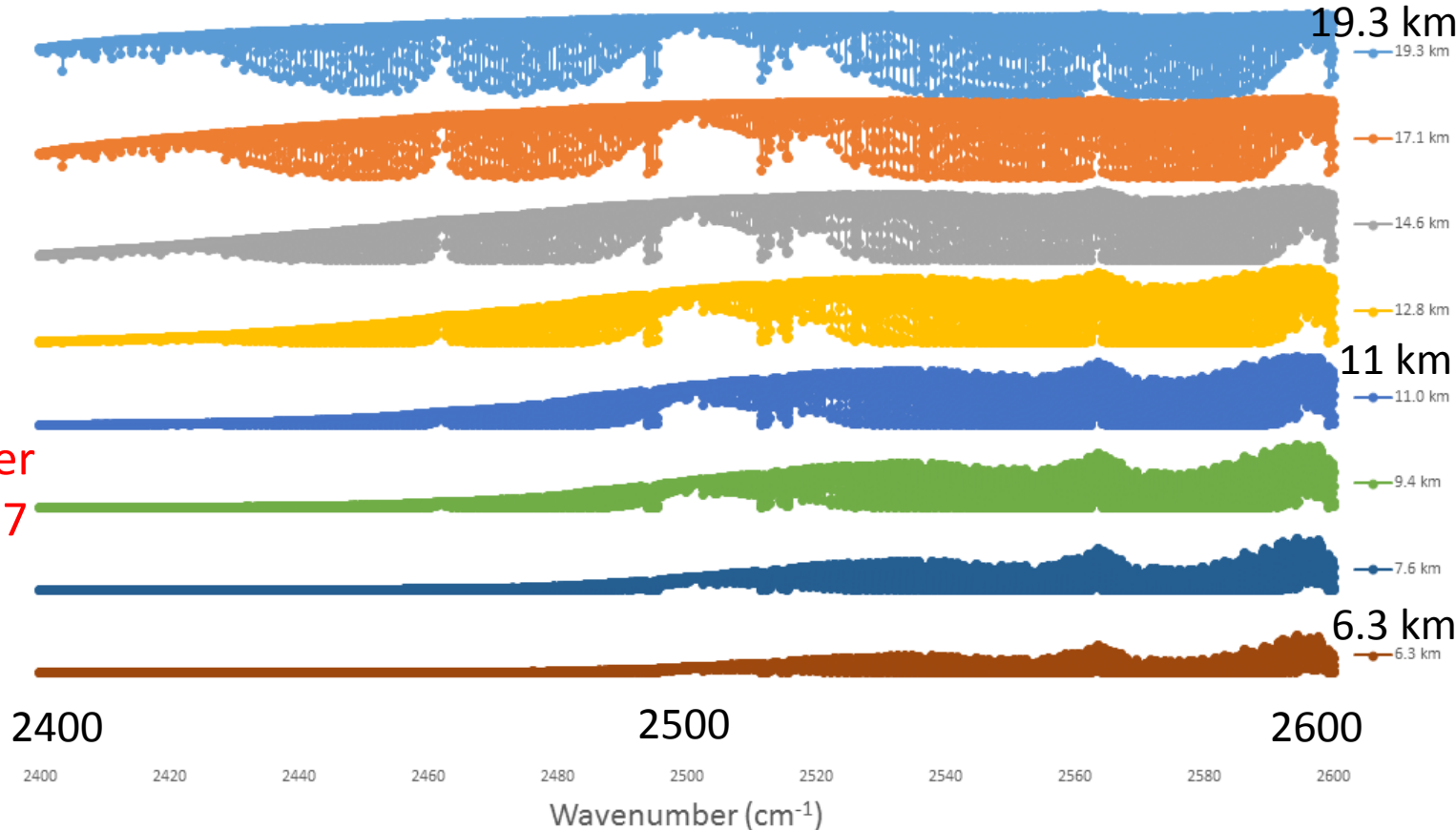
New routine species are in red.

ACE is now in its **15<sup>th</sup> year on orbit**. This **longevity** makes **trend analysis** feasible (with care). The change in atmospheric composition is the **primary driver of climate change**.

# Low Altitude CO<sub>2</sub> (Chris Boone)

- CO<sub>2</sub> is used to retrieve temperature, pressure and pointing (tangent height).
- However, at high altitude (above about 65 km) pointing is known so the CO<sub>2</sub> VMR can be determined.
- For v.4, below 17 km, temperature and pressure come from Canadian weather forecast model (GEM) and tangent height is determined from the N<sub>2</sub> continuum (collision-induced absorption). CO<sub>2</sub> can therefore be retrieved from 5-17 km.

New ACE data product is CO<sub>2</sub> VMR at low altitude: upper troposphere and extratropical lower stratosphere (5-17 km)



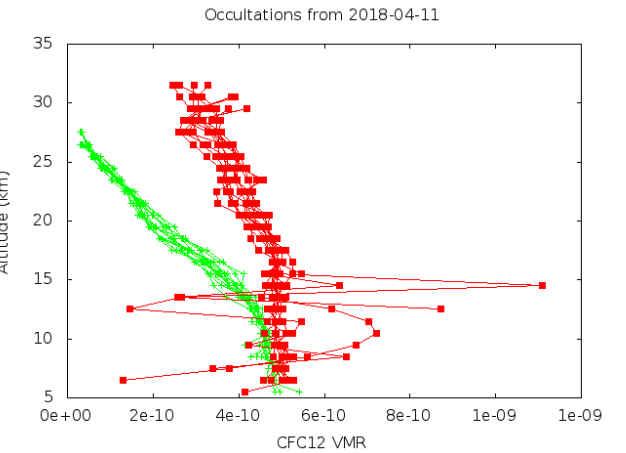
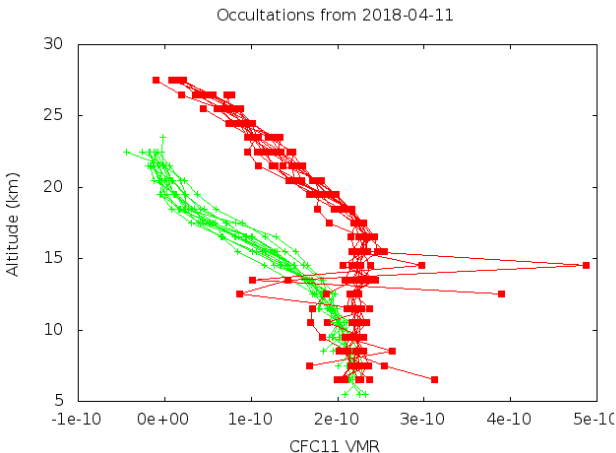
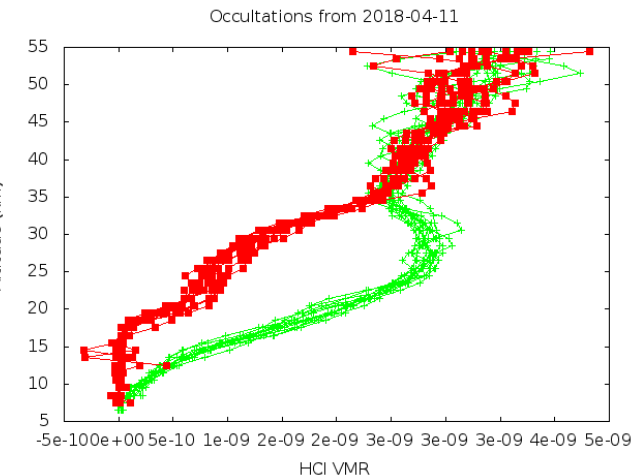
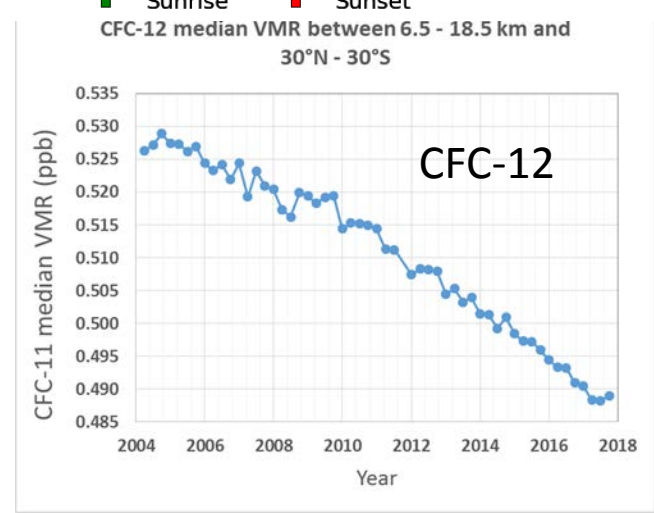
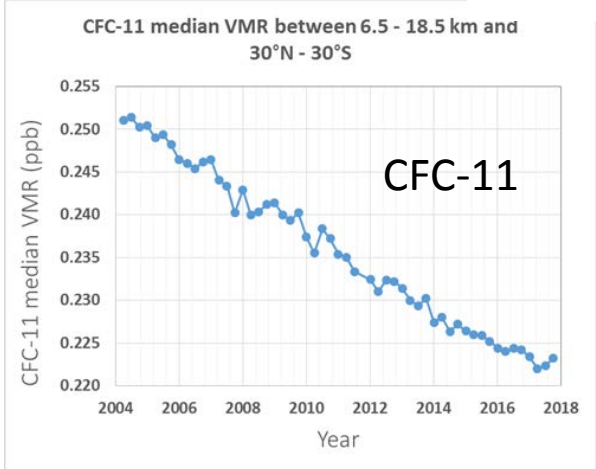
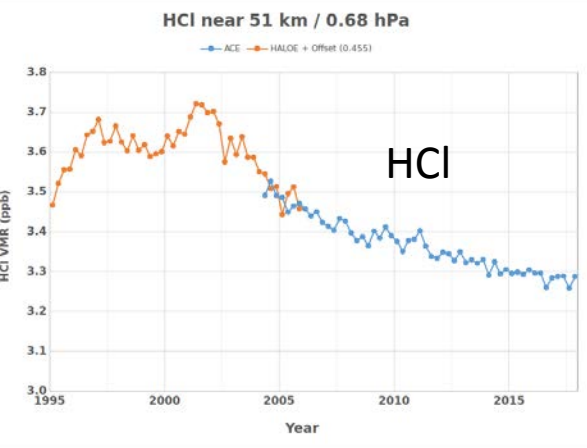
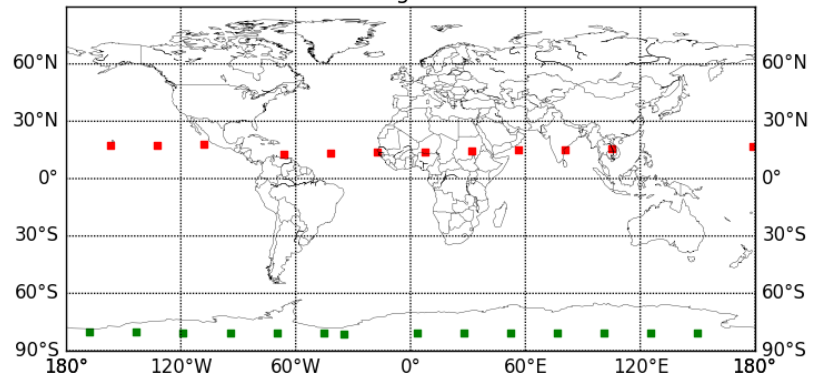
# Montreal Protocol (1987) with Amendments and Adjustments

- ❑ Montreal Protocol bans Cl- and Br-containing source gases that deplete the ozone layer and are also potent greenhouse gases.
  - ❑ Montreal Protocol is considered to be the most successful international treaty: universal acceptance.
  - ❑ CFC and Halon production is phased out now; HCFCs, which are transitional compounds with lower ozone depleting potential, are being phased out; HFCs were the final replacement compounds (no chlorine so no potential to deplete ozone), but are very powerful greenhouse gases.
  - ❑ Kigali amendment will phase out HFCs by replacing them with molecules with no chlorine and a much smaller global warming potential (HFOs).
  - ❑ ACE-FTS measures nearly 20 halogen-containing gases including all the main CFC, HCFC and HFC source gases, the  $\text{Cl}_2\text{CO}$ ,  $\text{FClCO}$ ,  $\text{F}_2\text{CO}$  intermediates as well as the final HCl and HF product gases.
- ACE monitors compliance with the Montreal Protocol.

# Montreal Protocol Metrics

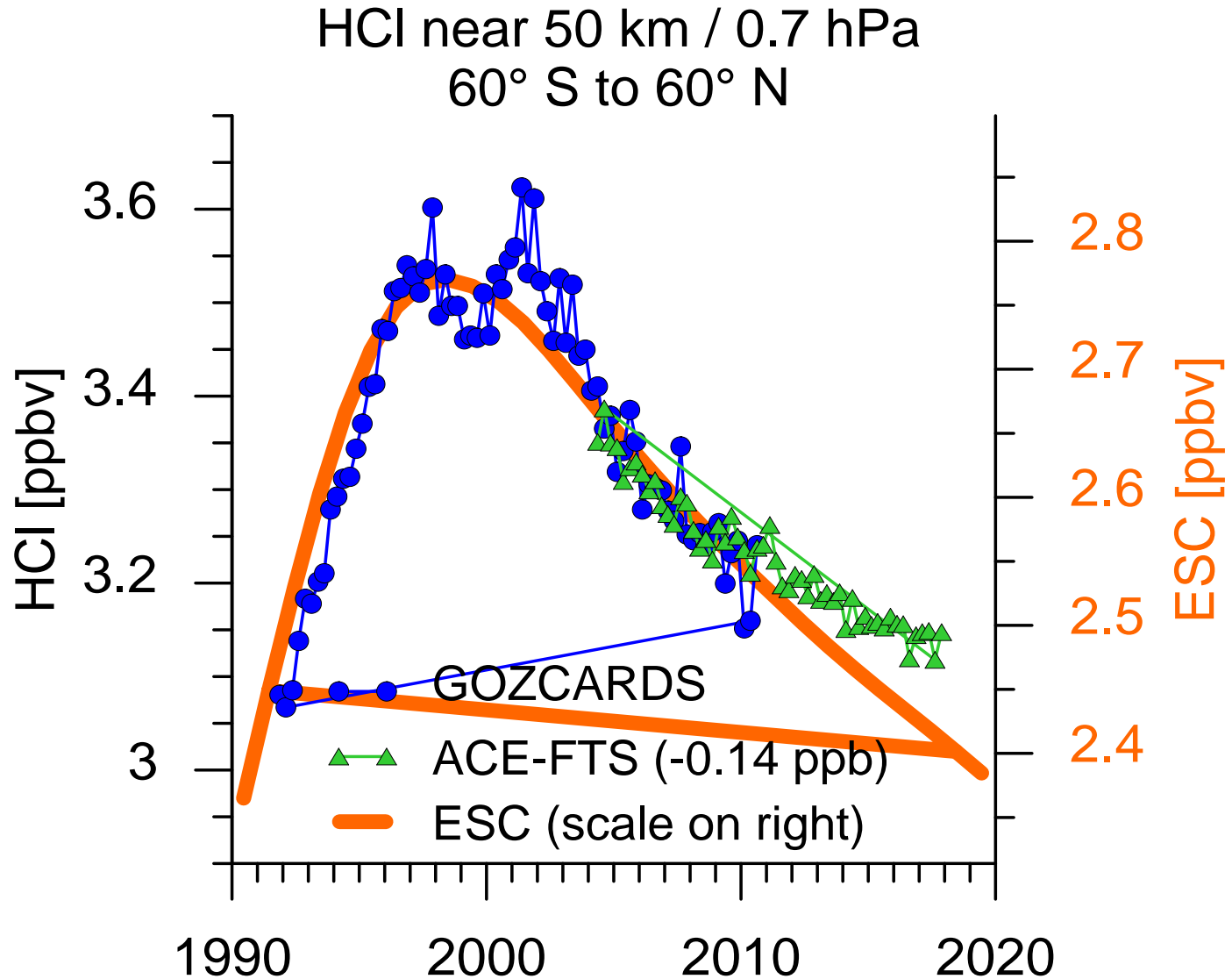
Daily profiles for HCl, CFC-11 and CFC-12, plus long term trends now on the web

Occultations from 2018-04-11  
Beta Angle = -51.5



# HCl Trends

Is global ozone recovering? By W. Steinbrecht, *et al.* *Comptes Rendus Geoscience*, Special Issue for the 30<sup>th</sup> anniversary of the Montreal Protocol





# Hydrofluorocarbons, HFCs

Science 359 (6380), 1084.  
DOI: 10.1126/science.359.6380.1084

## Slow coolant phaseout could worsen warming

As countries crank up the AC, emissions of potent greenhouse gases are likely to skyrocket

By April Reese

In the summer of 2016, temperatures in Phalodi, an old caravan town on a dry plain in northwestern India, reached a blistering 51°C—a record high during a heat wave that claimed more than 1600 lives across the country. Wider access to air conditioning (AC) could have prevented many deaths—but only 8% of India's 249 million households have AC, Saurabh Diddi, director of India's Bureau of Energy Efficiency in New Delhi, noted at the World Sustainable Development Summit there last month. As the nation's economy booms, that figure could rise to 50% by 2050, he said. And that presents a dilemma: As India expands access to a life-saving technology, it must comply with international mandates—the most recent imposed just last fall—to eliminate coolants that harm stratospheric ozone or warm the atmosphere.

"Growing populations and economic development are exponentially increasing the demand for refrigeration and air conditioning," says Helena Molin Valdés, head of the United Nations's (UN's) Climate & Clean Air Coalition Secretariat in Paris. "If we continue down this path," she says, "we will put great pressure on the climate system." But a slow start to ridding appliances of the most damaging compounds, hydrofluorocarbons (HFCs), suggests that the pressure will continue to build. HFCs are now "the fastest-growing [source of greenhouse gas] emissions in every country on Earth," Molin Valdés says.

ditch them by 2020; developing countries have until 2030.

To meet those deadlines, manufacturers have turned to HFCs, which do not destroy ozone. But they are a serious climate threat. The global warming potency of HFC-134a, commonly used in vehicle AC units, is 1300 times that of carbon dioxide. Clamping down on HFCs, a 2014 analysis found, could avoid a full 0.5°C of future warming.

As with the HCFC phaseout, developed countries agreed to make the first move: They must begin abandoning the production and consumption of HFCs next year and achieve an 85% reduction by 2036. In the United States, the transition is off to

ant emissions. An analysis done before the HFC phase-down agreement predicted that if no action were taken, HFC use in AC units would rise 2% a year in developed countries and 5.6% annually in the developing world through 2050. The agreement is unlikely to thwart that rise anytime soon: A recent UN report, which summarized studies of HFC use in Bangladesh, Chile, Colombia, Ghana, Indonesia, and Nigeria, found that use of HFCs will spike in all six countries in the coming years.

Some climate experts are more hopeful, pointing out that developing countries have an opportunity to bypass HFCs altogether. "The alternative when developed countries phased out HCFCs was HFCs. But developing countries are in a different position: They're at the beginning of phasing out HCFCs and can leap directly past HFCs" to benign alternatives, says Nathan Borgford-Parnell, regional assessment initiative coordinator for the UN's Climate & Clean Air Coalition.

India is crafting a National Cooling Action Plan that aims to do just that. It will include better city planning and building design, and it will embrace novel coolants, says Stephen Andersen of the Institute for Governance & Sustainable Development in Washington, D.C., who helped develop the plan.

Meanwhile, six AC manufacturers in India have already begun "leapfrogging" to hydrocarbon-based coolants such as R-290—refrigerant-grade propane—that have lower warming potential, says Anjali Jaiswal, the San Francisco, California-based director of the India Ini-



Novel hydrocarbon-based coolants could enable India and other developing nations to embrace air conditioning while minimizing a climate threat.

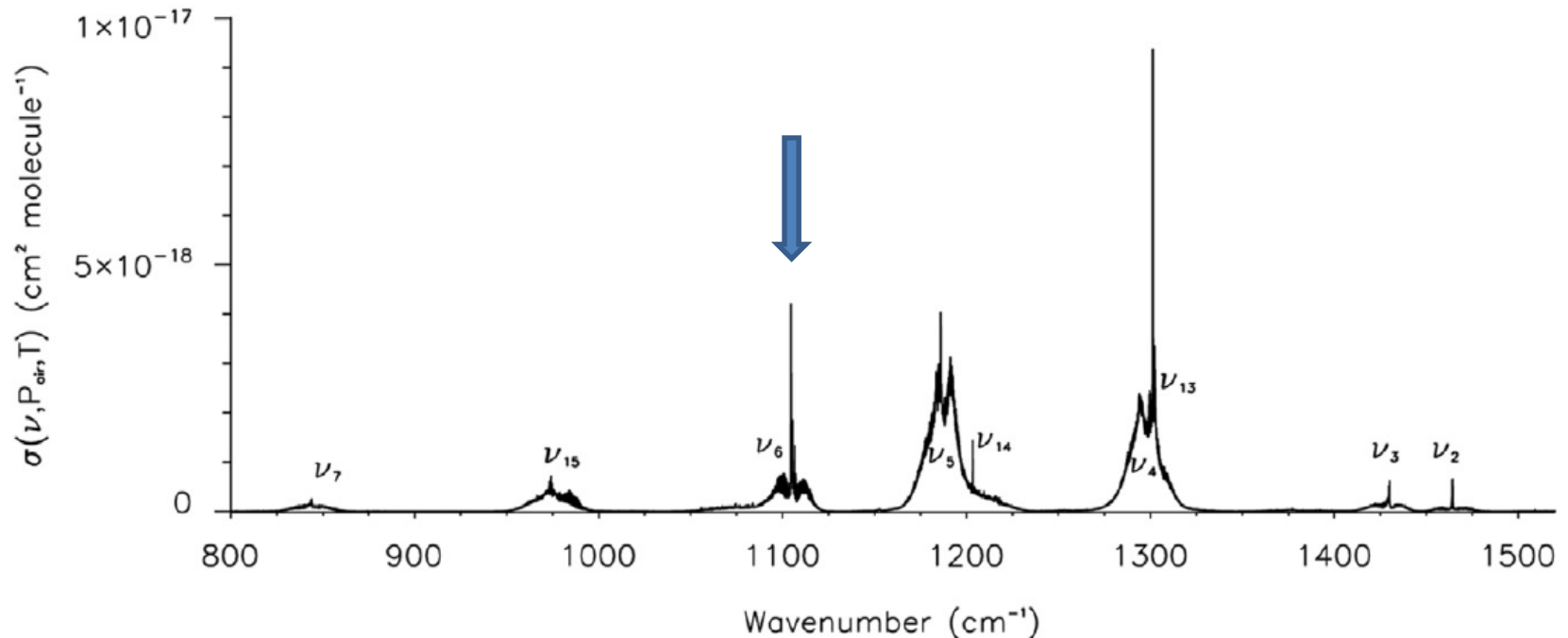
a rough start. Last August, a U.S. federal appeals court rejected an Environmental

HFC-134a ( $\text{CF}_3\text{CFH}_2$ ) is used primarily for car air conditioners and is the most abundant HFC in the atmosphere. HFC-23 ( $\text{CHF}_3$ ) is the second most abundant HFC, produced as a by-product of HCFC-22 ( $\text{CHClF}_2$ ) production.

# HFC-134a (CF<sub>3</sub>CFH<sub>2</sub>)

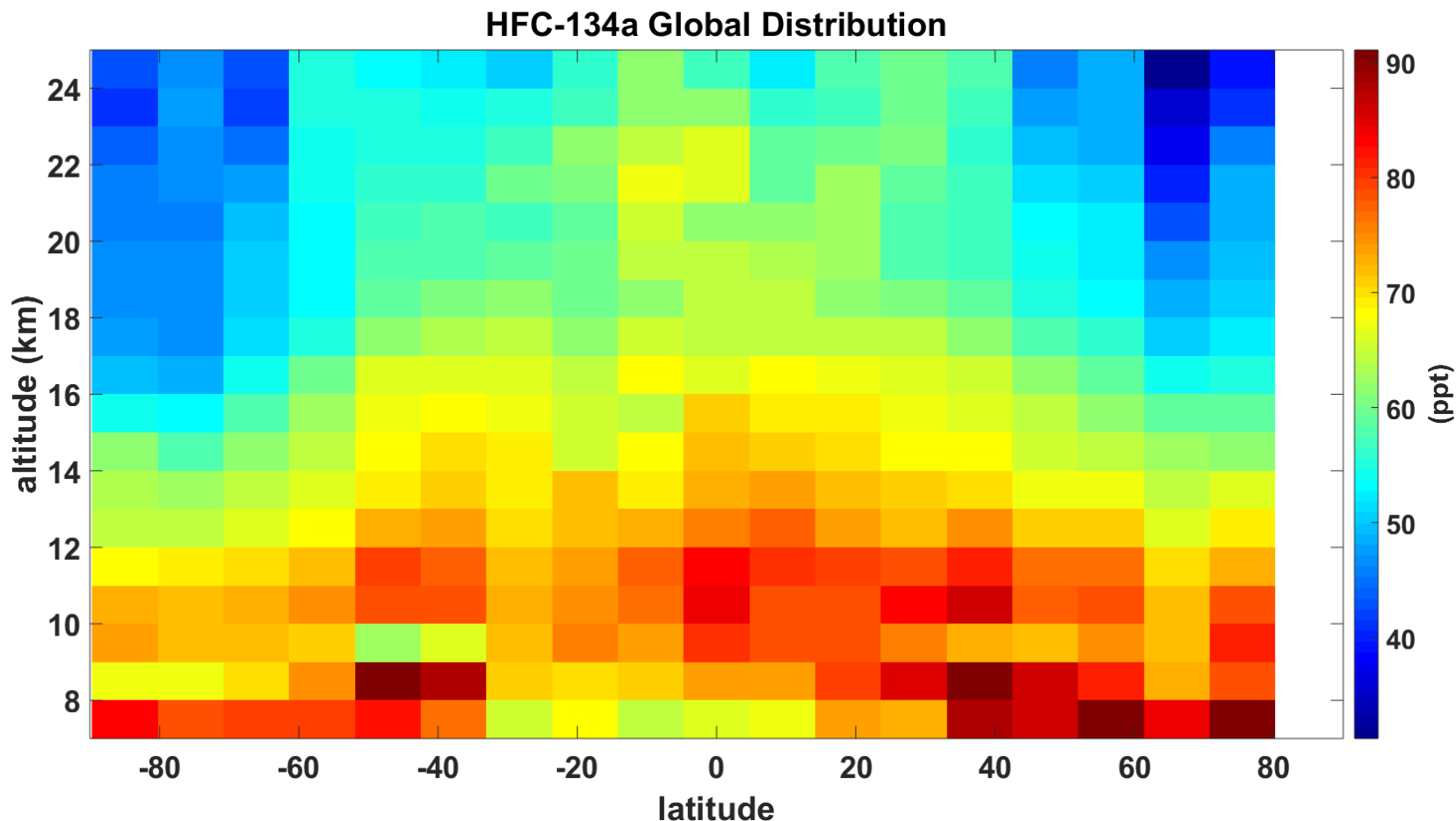
Infrared absorption cross sections for 1,1,1,2-tetrafluoroethane

Jeremy J. Harrison <sup>\*,1</sup> JQSRT 151, 210 (2015)



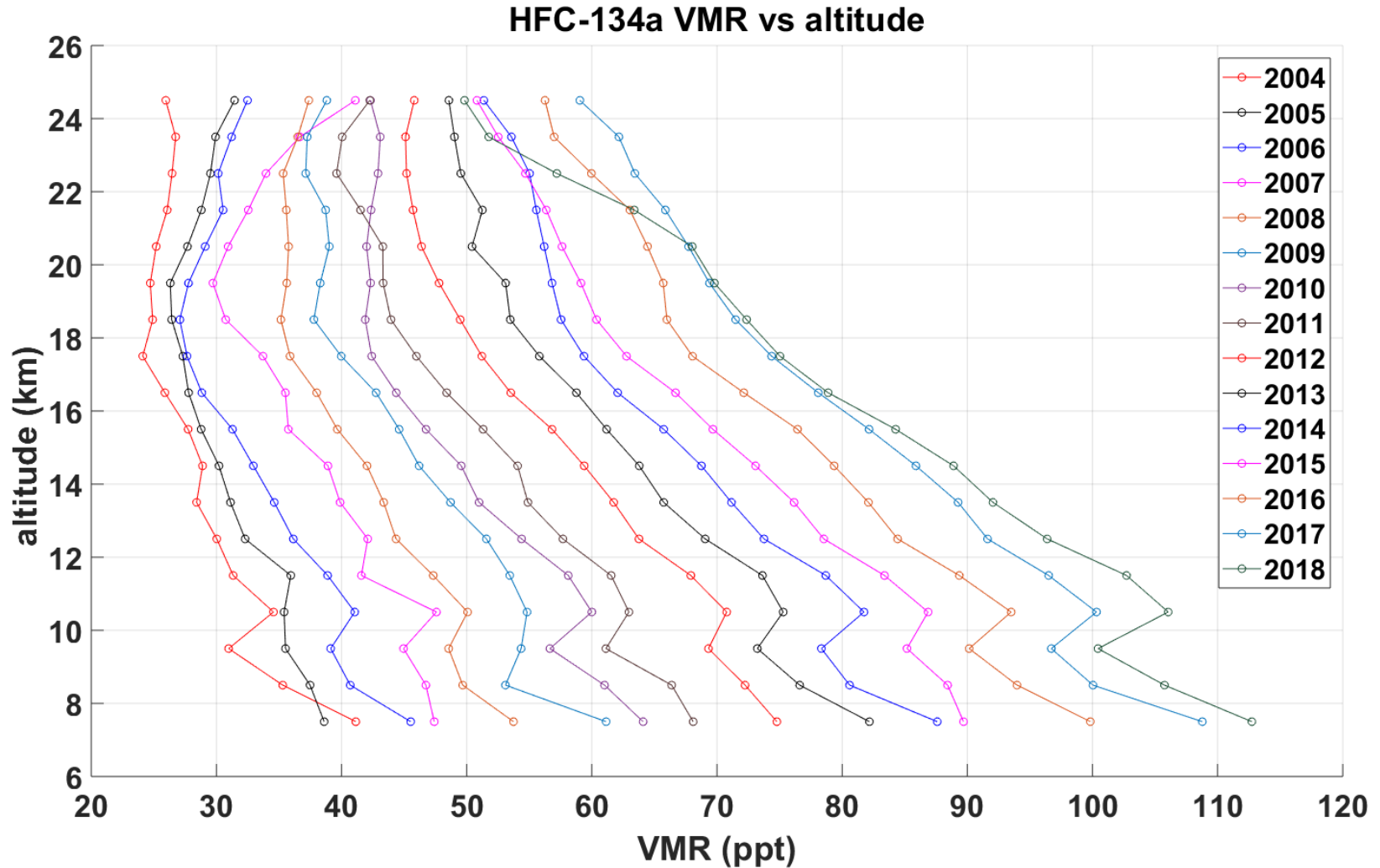
New ACE-FTS retrieval by Chris Boone uses Q-branch of  $\nu_6$  mode at  $1105 \text{ cm}^{-1}$  (not  $\nu_5$  band at  $1186 \text{ cm}^{-1}$  used previously by Nassar et al. 2006); strong interference from ozone.

# Global Distribution of HFC-134a



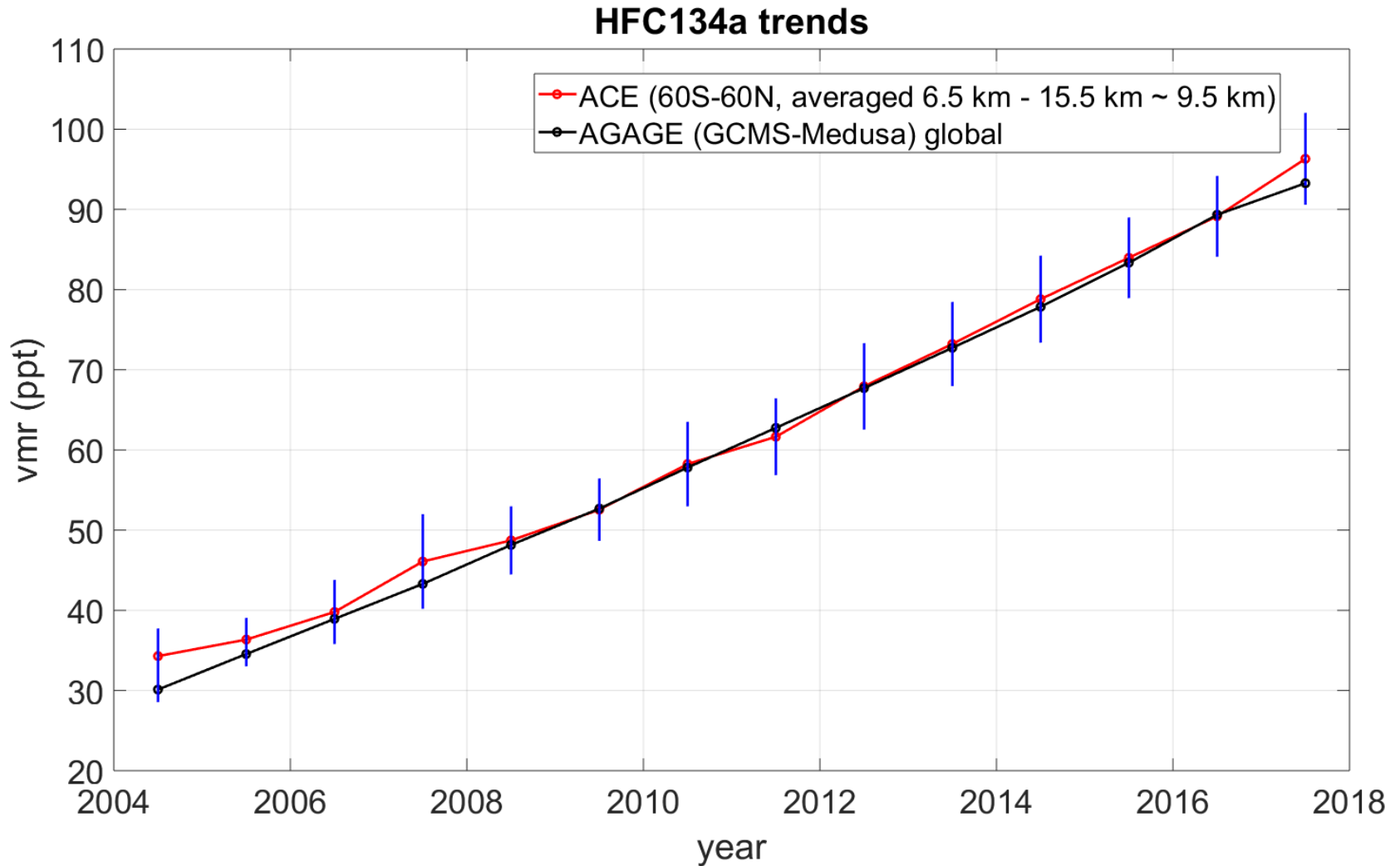
Lifetime= 13.4 yr; GWP = 1370 (100 yr); note anomalies in near extratropical tropopause at 9.5 km

# Global HFC-134a Trends



Note the anomalies near 9.5 km altitude.

# HCFC-134a Trends

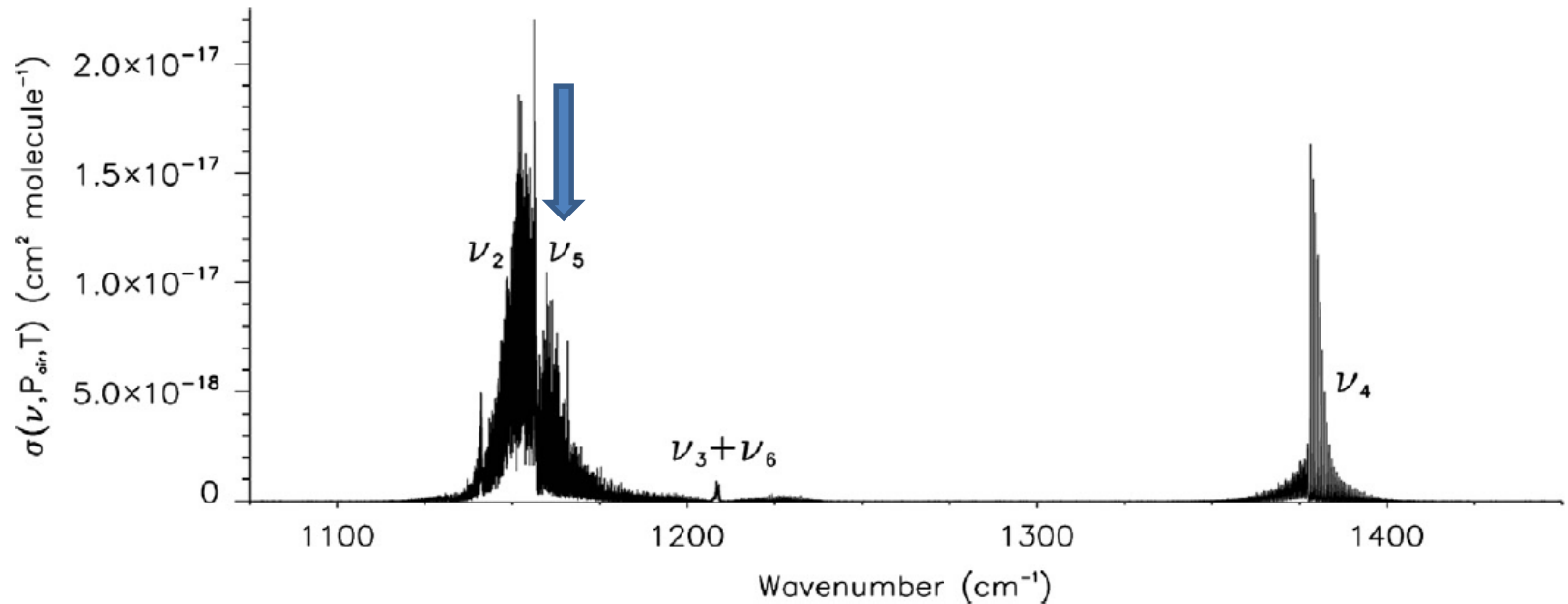


ACE trend is **+7%/year**.

# HFC-23 (CHF<sub>3</sub>)

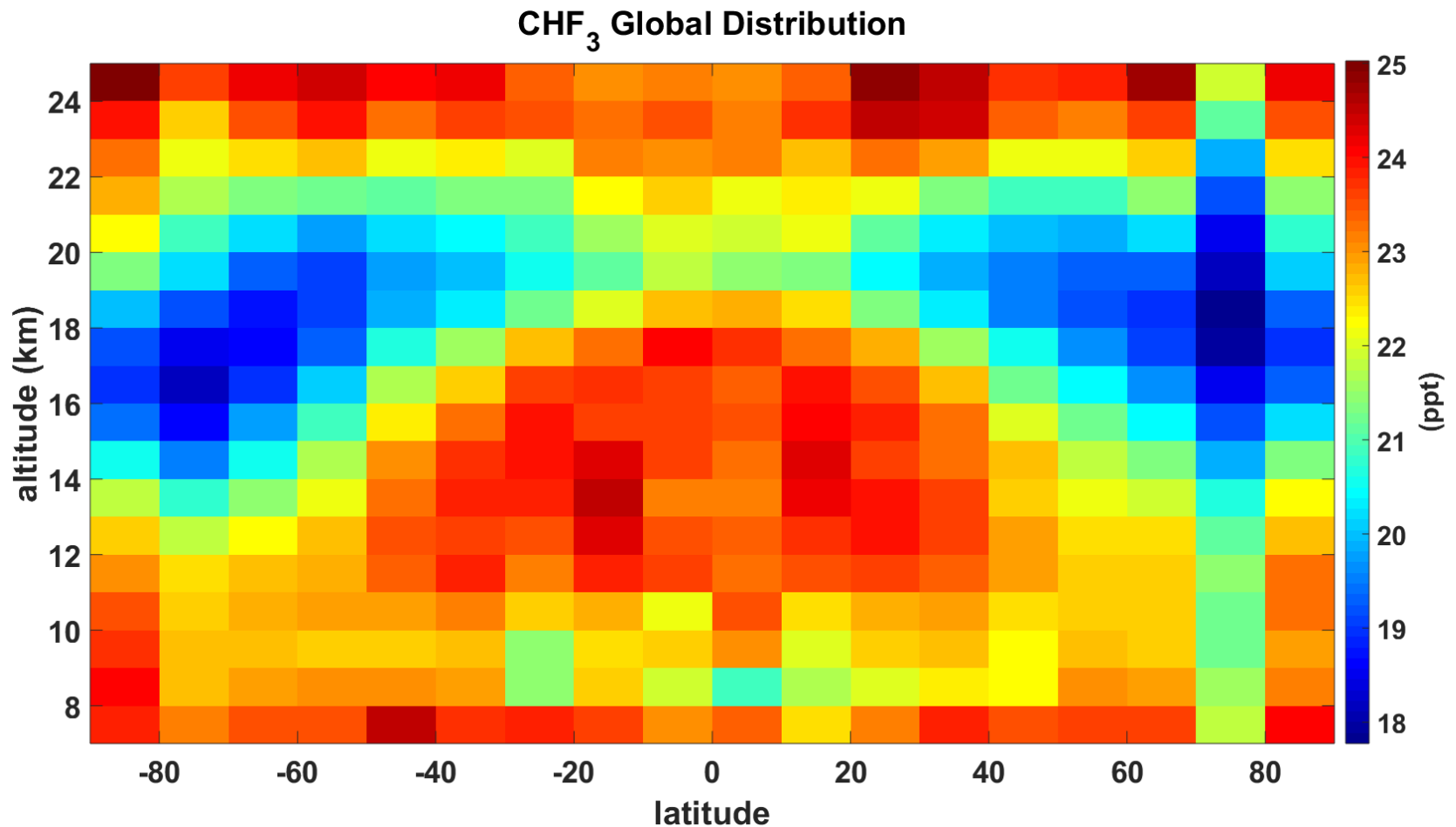
Infrared absorption cross sections for trifluoromethane

Jeremy J. Harrison\* JQSRT 130, 359 (2013)



New ACE-FTS retrieval by Chris Boone uses Q-branch of  $\nu_5$  mode at  $1157 \text{ cm}^{-1}$  (same band as used previously by Harrison et al. 2012).

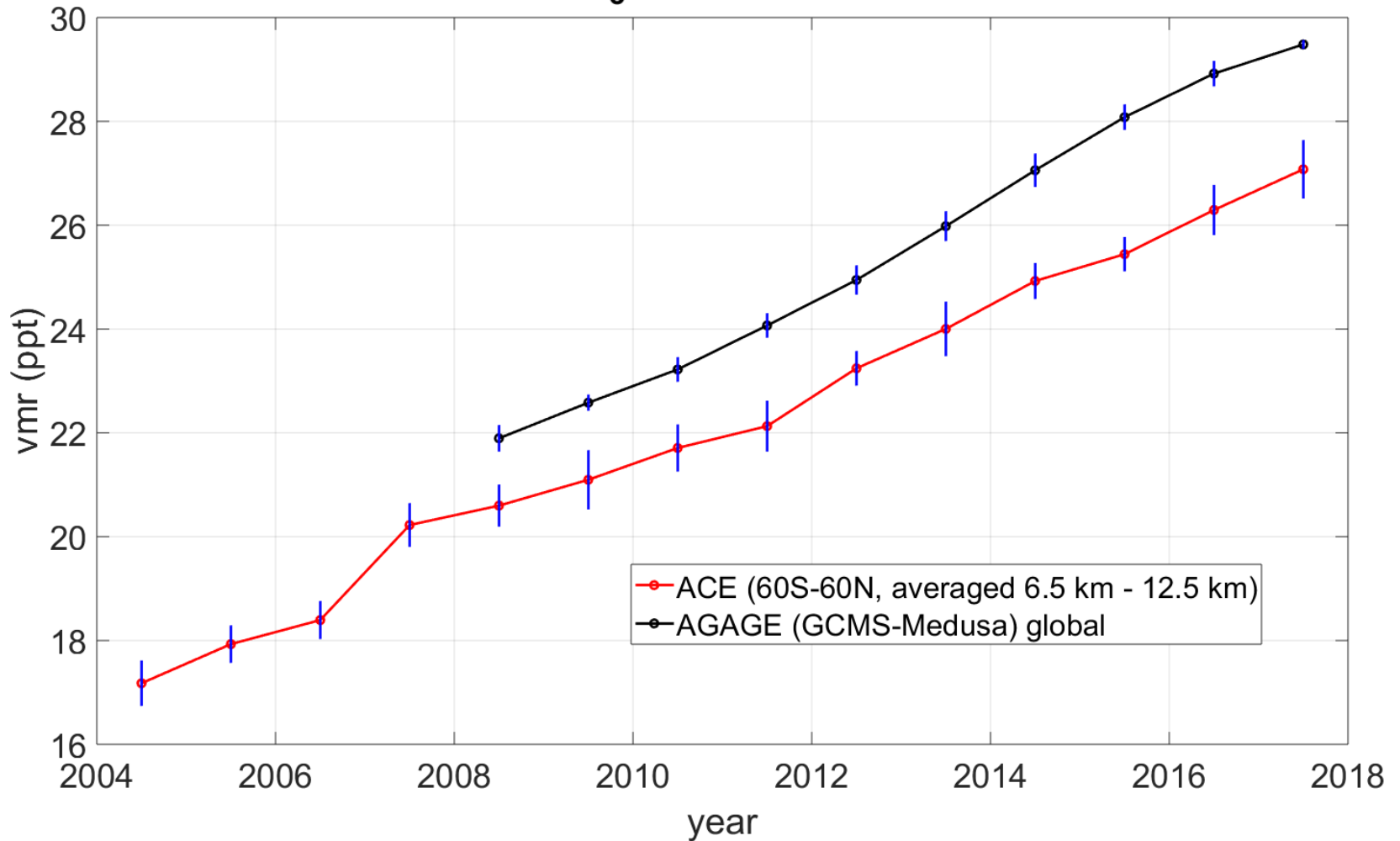
# HFC-23 Global Distribution



Lifetime = 228 yr; GWP = 12,400 (100 yr)  
cross-sections? spectral interferers?

# HFC-23 Trends

CHF<sub>3</sub> (HFC-23) trends



ACE trend is **+3%/year**.



# Acknowledgements

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Anton Fernando

# THE ATMOSPHERIC CHEMISTRY EXPERIMENT

## ACE AT 10: 15

*A Solar Occultation Anthology*

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EXPERIMENT ACE AT 10:

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PETER F. BERNATH, EDITOR

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