

# Carbonyl sulfide (OCS): sources and sinks



**Roisin Commane,**  
Steve Wofsy,  
*Harvard University*

Mark Zahniser,  
*Aerodyne Research Inc.*

Laura Meredith, *MIT*

**TEAM HIPPO, ESPECIALLY**

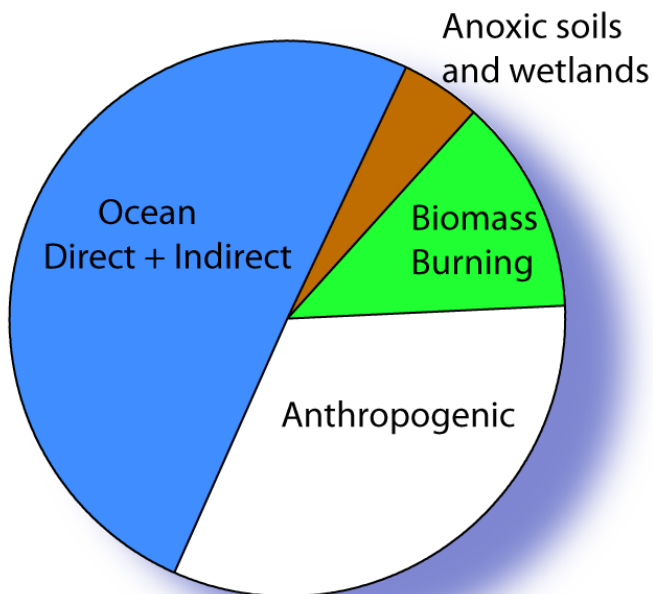
**STEVE MONTZKA, FRED  
MOORE, ETC.  
NOAA**

**PIETER TANS, ETC. *CIRES***

HIPPO Workshop, NCAR, March 17<sup>th</sup> 2011

# Sources of OCS

- Most abundant reduced sulfur compound in the troposphere
- Global mixing ratio 300~500 pptv
- Lifetime 1-5 Years?



Indirect Ocean:  $\text{DMS} + \text{OH}/\text{BrO} \rightarrow \rightarrow \text{OCS}$

Indirect Anthro:  $\text{CS}_2 + \text{OH}/\text{BrO} \rightarrow \rightarrow \text{OCS}$

Anoxic Soils:

OCS from paddy fields, marshes & wetlands

=> Large source over Pacific?

Kettle et al. 2002; Montzka et al. 2007;  
Suntharalingam et al. 2008

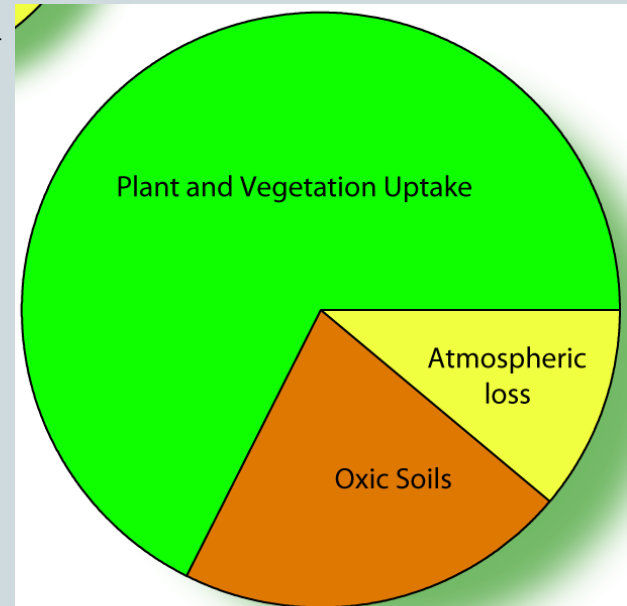
# Sinks of OCS

## Surrogate for CO<sub>2</sub> uptake by plants during photosynthesis?

- ◆ OCS hydrolysed by Carbonic Anhydrase (CA) in plants
- ◆ OCS not emitted by plants during respiration, unlike CO<sub>2</sub>
- ◆ Diurnal cycle? Min. in afternoon (max photosynthesis)
- ◆ Seasonal cycle? Min. at end of growing season
- ◆ Used to determine Net Ecosystem Exchange?
- ◆  $\text{OCS} + \text{H}_2\text{O} \rightarrow [\text{CA}] \text{H}_2\text{S} + \text{CO}_2$

## Uptake of OCS by Oxidic Soils?

- ◆ Associated with soil uptake of H<sub>2</sub>?
  - ◆ 75% loss of H<sub>2</sub> to Soil uptake
  - ◆ Uptake by micro-organisms?



Montzka et al. 2009; Suntharalingam et al. 2008

# OCS in New England



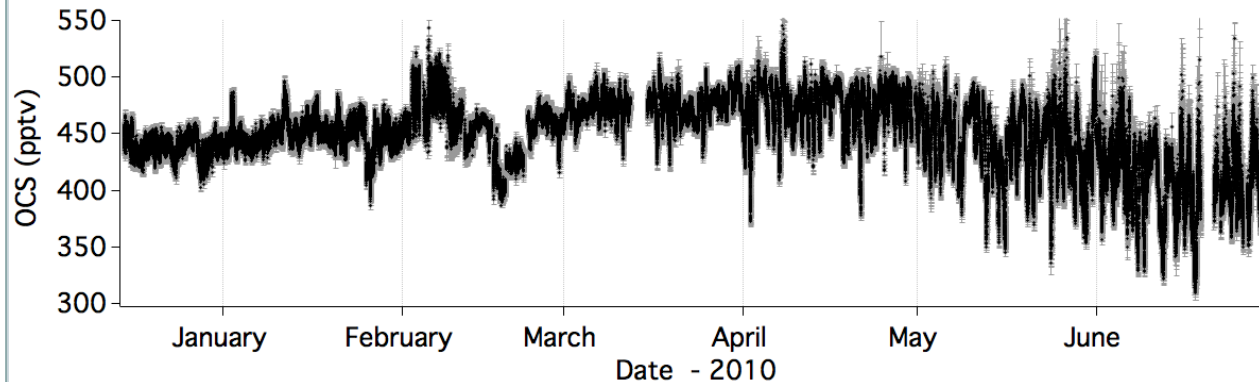
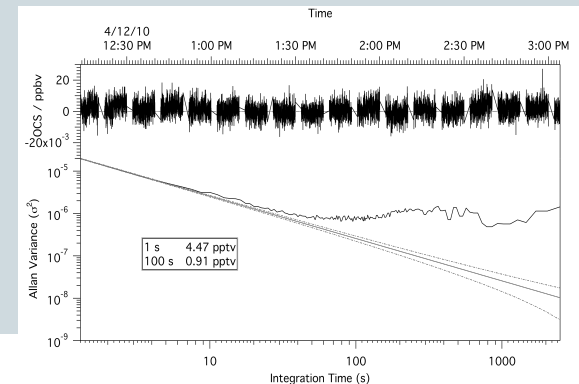
## Quantum Cascade Laser Spectroscopy: QCLS

- ◆ Tunable Infra-red Laser Differential Absorption Spectroscopy
- ◆ Continuous Wave (cw) quantum cascade laser:  $2048.495 \text{ cm}^{-1}$
- ◆ Laser and detector TE cooled: No liquid  $\text{N}_2$  required
- ◆ Astigmatic cell: 210 m path length, 5 L Volume

Baseline Standard Deviation:

1s = 4.5 pptv;

100s = 0.9 pptv



April Max

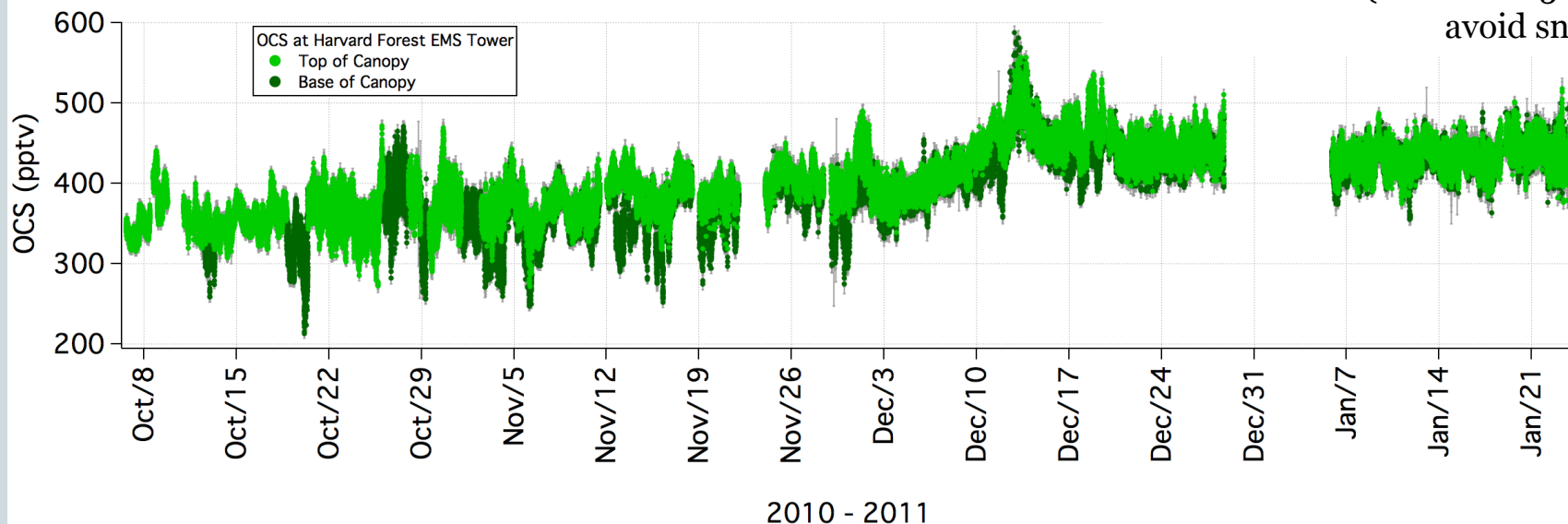
Night-time reductions  
observed from snow  
melt in March

# OCS at Harvard Forest



- Forest site in Western Massachusetts, New England
  - Long-term measurements of many chemical species: CO<sub>2</sub>, CO<sub>2</sub> fluxes, etc. to understand ecosystem exchange
  - Shorter term measurements of H<sub>2</sub> (Laura Meredith, MIT) & OCS (this study) for 2010-2011

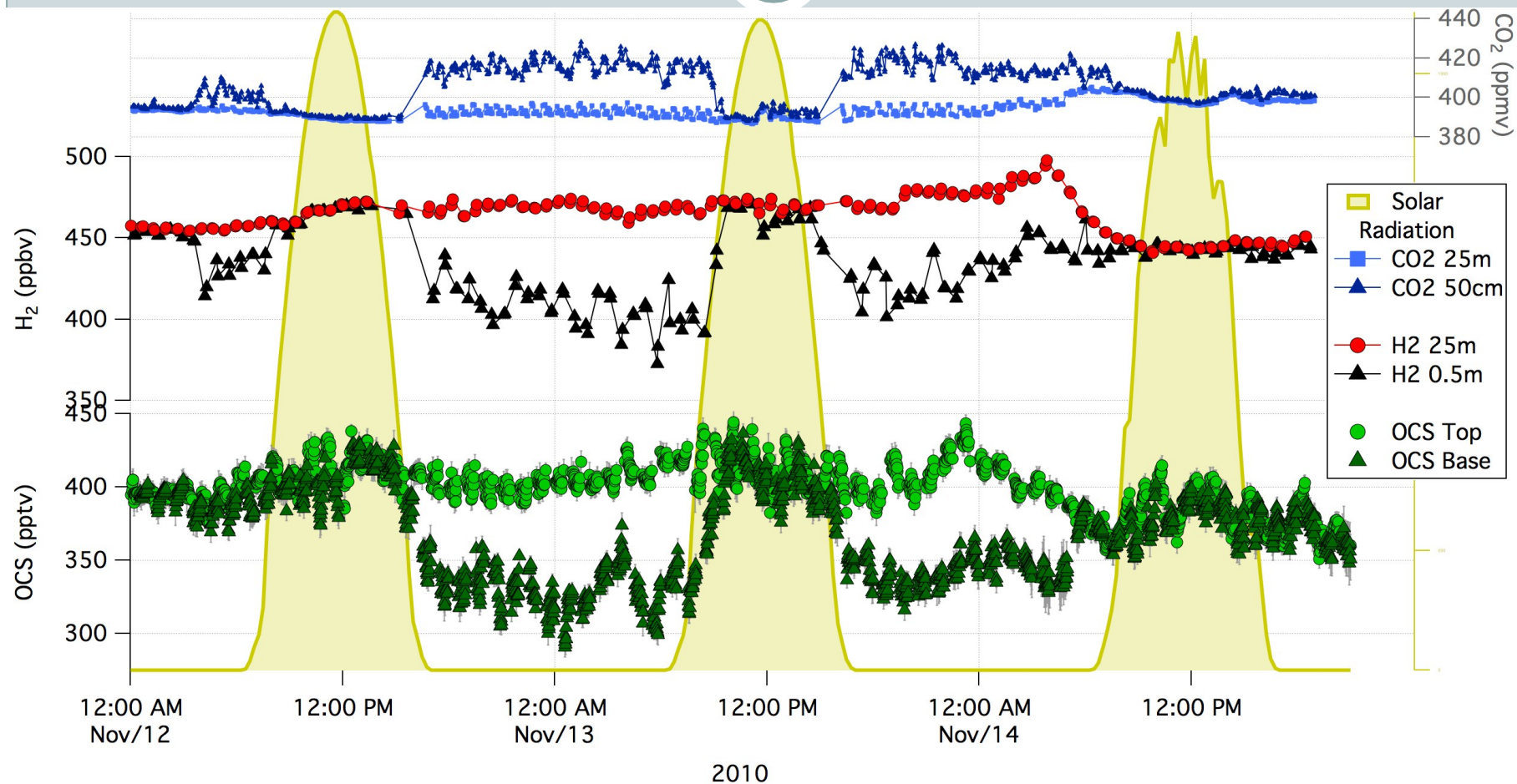
OCS sampled from 25m tower above forest canopy & 1m above forest floor (raised to 1.5m to avoid snow)



# OCS, H<sub>2</sub>, CO<sub>2</sub> in November at HF

Temperature: 3-18°C diurnally;

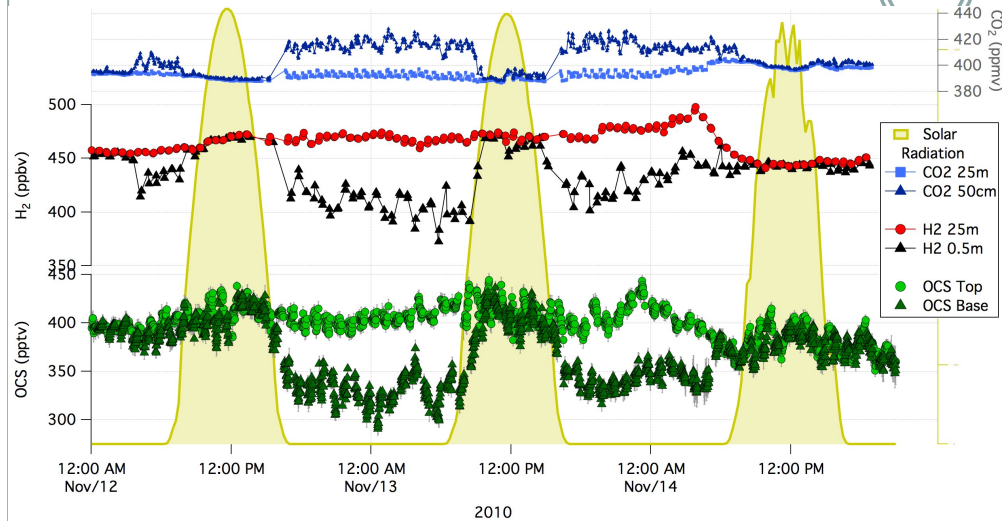
Wind Speed = 0-4 ms<sup>-1</sup>



# OCS, H<sub>2</sub>, CO<sub>2</sub> in November at HF

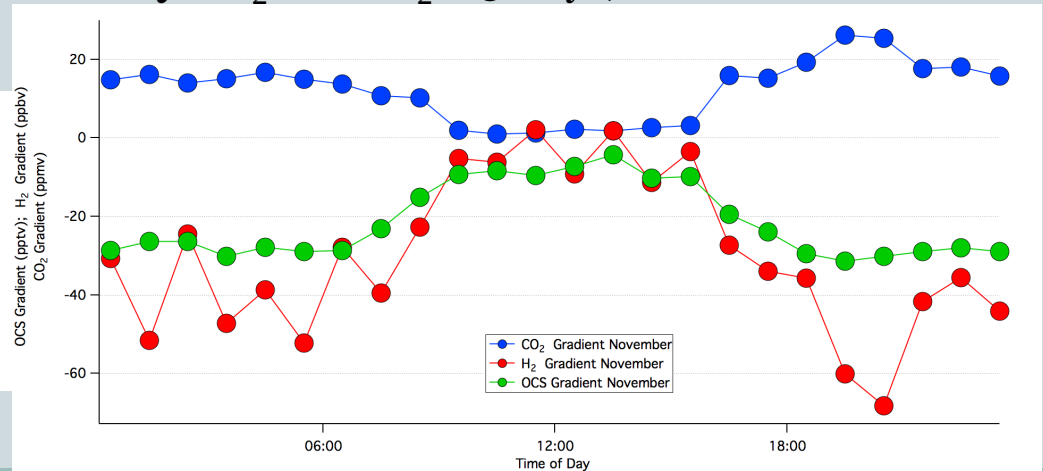
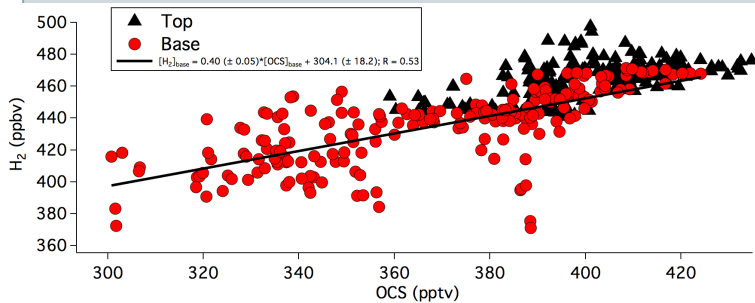
Temperature: 3-18°C diurnally;

Wind Speed = 0-4 ms<sup>-1</sup>

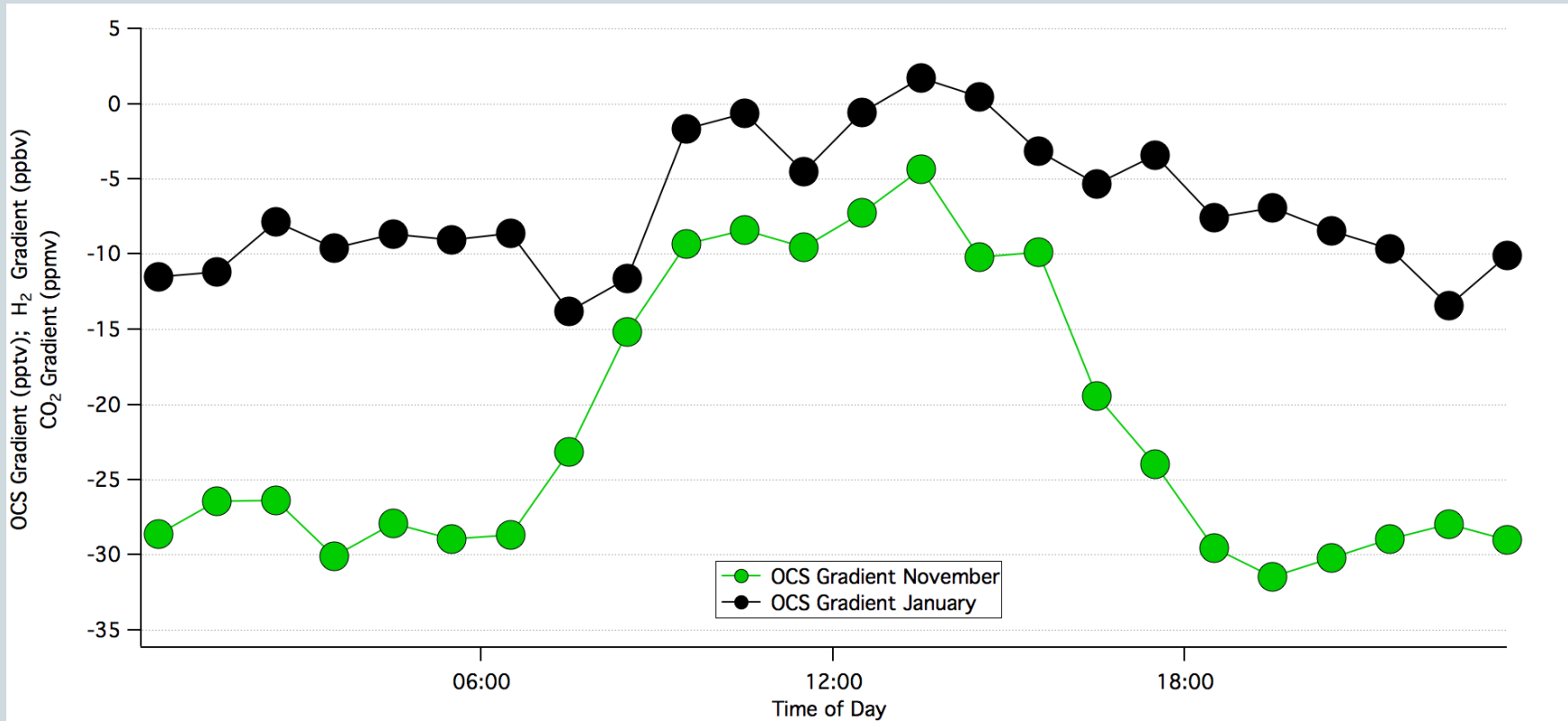


Time of Day: H<sub>2</sub> and CO<sub>2</sub> – 3 Days; OCS – all of November

H<sub>2</sub> vs OCS; R = 0.53



# OCS Gradient: November vs January



## OCS Gradient:

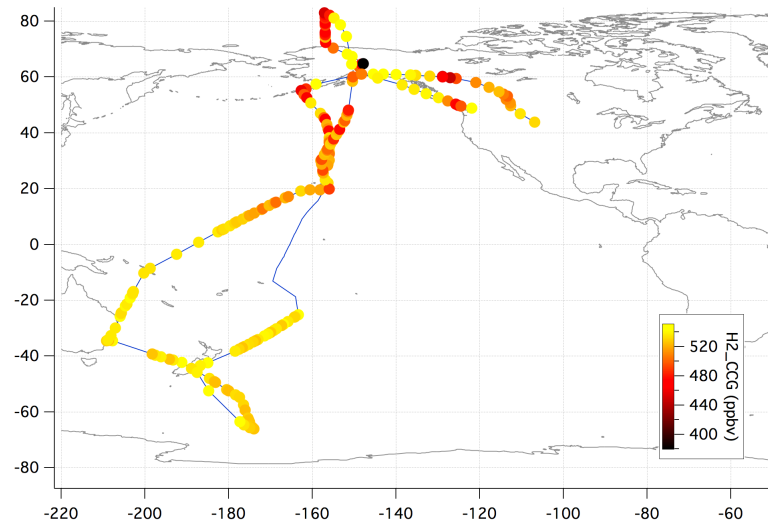
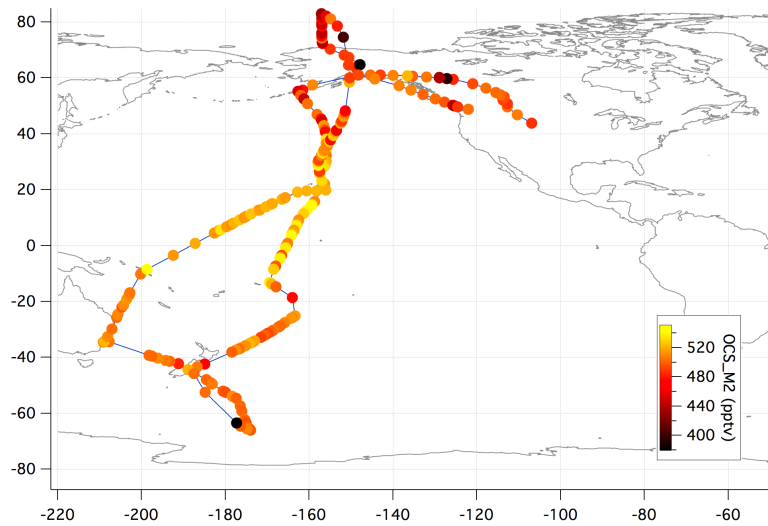
November: Night-time negative flux  
January: much less TOD shape

## H<sub>2</sub> Gradient:

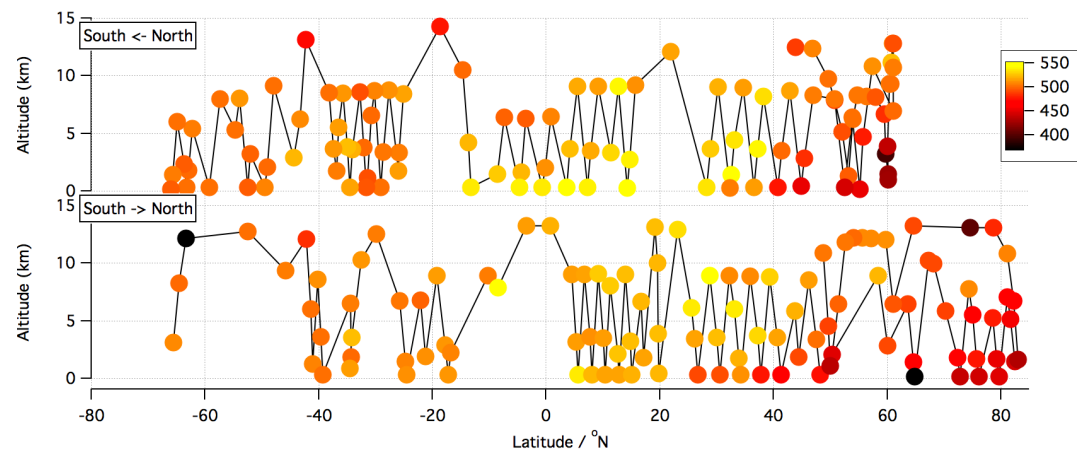
November: Night-time negative flux  
January: No gradient obvious – first look



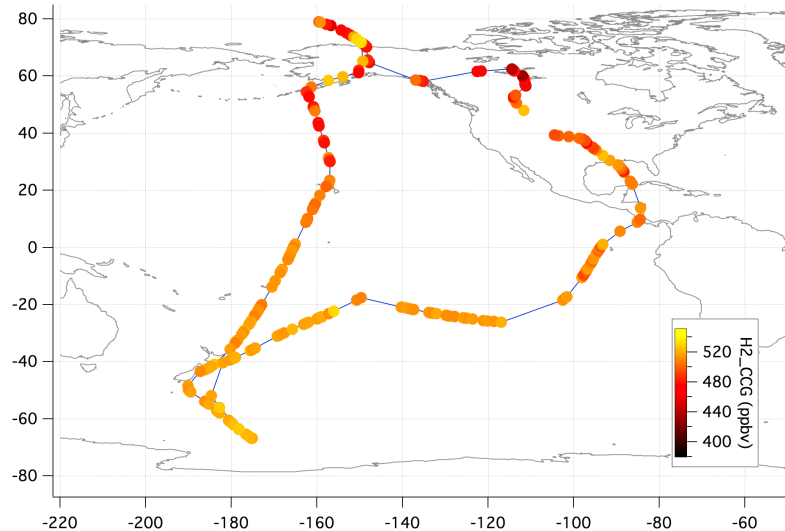
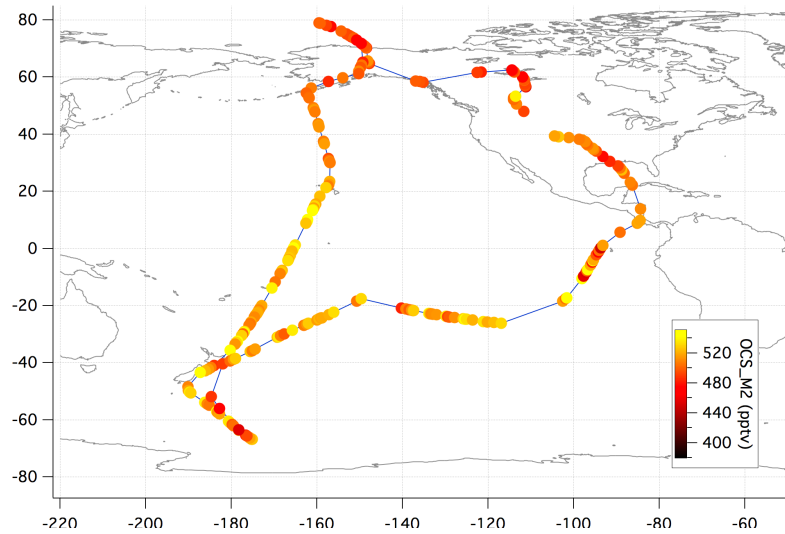
# HIPPO II: November 2009



- **OCS – M2**
  - Tropical Max
  - Min at Poles (Stratospheric?)
  - Range: 380 – 550 pptv
- **H<sub>2</sub> - CCG**
  - Southern Hemisphere (SH) Max
  - Most variability in NH
  - Range: 360 – 560 ppbv



# HIPPO I: January 2009



## ● OCS – M2

○ Tropical Max

○ Less at Poles but not as low as H1

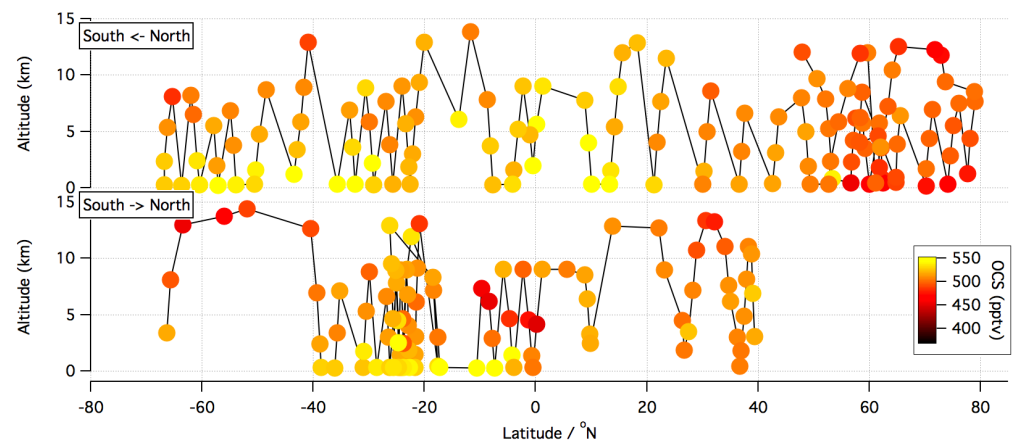
○ Range: 450 – 600 pptv

## ● H<sub>2</sub> - CCG

○ Southern Hemisphere (SH) Max

○ Most variability in NH

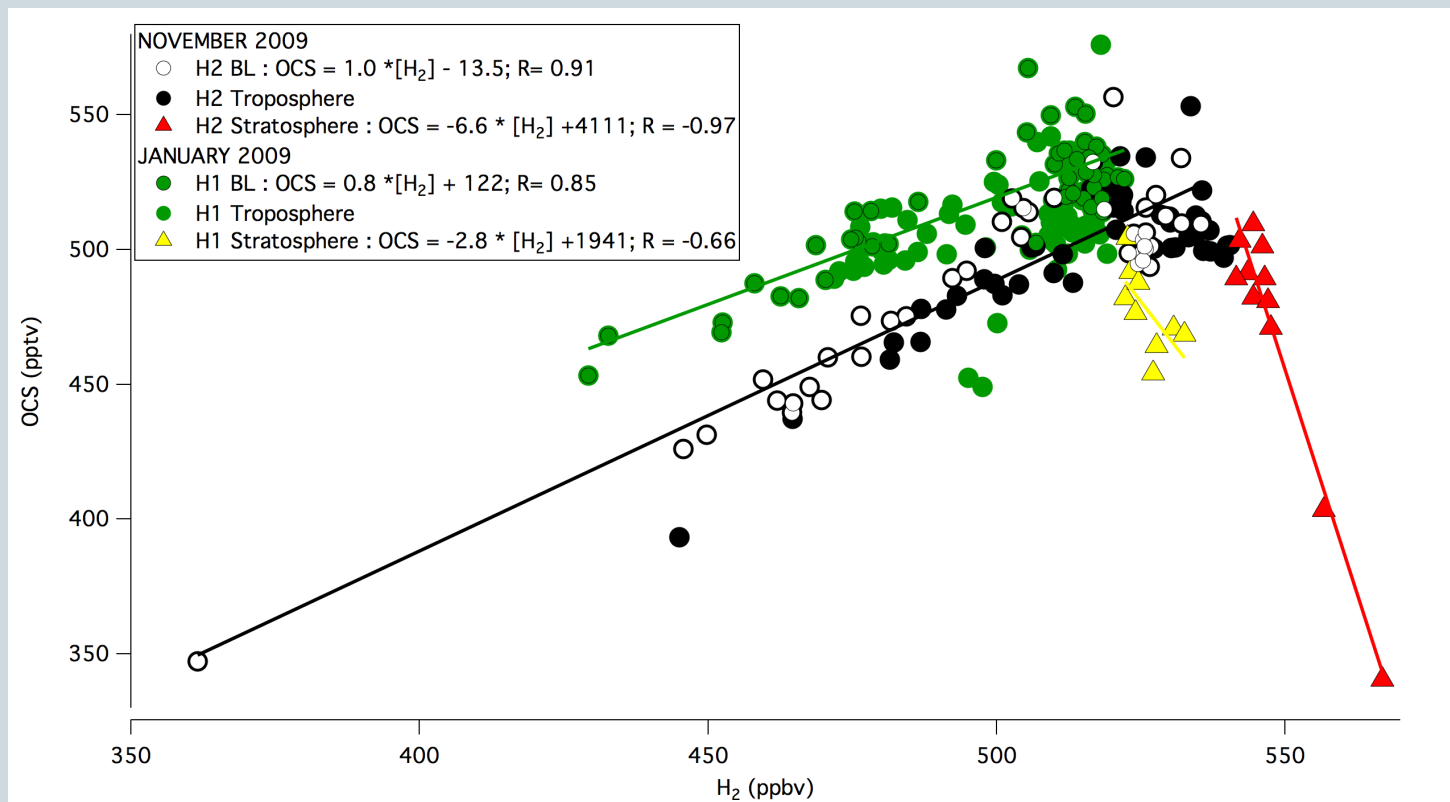
○ Range: 430 – 530 ppbv



# H<sub>2</sub> vs OCS



- November H<sub>2</sub> vs OCS: Correlation in Trop, Anti in Strat
  - Stratosphere: OCS photolysis; little H<sub>2</sub> loss (Red – Nov; Yellow – Jan)
  - BL OCS correlated with H<sub>2</sub>: OCS = 1 \* H<sub>2</sub> (NOV); OCS = 0.8 \* H<sub>2</sub> (Jan)



# Future Thoughts



- **Harvard Forest:**
  - OCS, CO<sub>2</sub> & H<sub>2</sub> measurements continuing until next year
  - Maybe find other details to look for in HIPPO data
- **HIPPO:**
  - Look at Seasonal change of OCS and H<sub>2</sub>
  - How important is OCS soil uptake?
  - Sources of OCS: DMS, CS<sub>2</sub>: Seasonal behaviour?
- **Thanks to everyone for providing data**
  - Contact: [rcommane@seas.harvard.edu](mailto:rcommane@seas.harvard.edu)
- **Happy St. Patrick's Day!**

