# TROPOSPHERIC FLUXES OF OCS: MEASUREMENTS FROM THE OCEANS TO THE TERRESTRIAL BIOSPHERE



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### Atmospheric OCS

300 – 550 pptv OCS in troposphere <100 – 200 pptv OCS in stratosphere: 150 – 200 ppt at 12-20 km; 20-50 ppt at 30 km

Most abundant S compound

Stable trop conc. = balanced sources and sinks?

Lifetime 5 – 35 years

Major source of S to strat in volcanically quiescent periods [Bruhl et al, 2012]

Stratospheric mixing ratio decreases with altitude

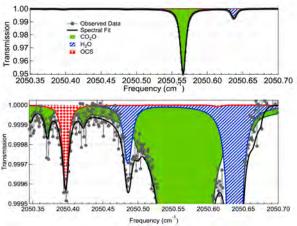
OCS  $\rightarrow$  [hv] CO + S S  $\rightarrow$  [O<sub>2</sub>] SO<sub>2</sub>

GC-MS analysis of flasks (HIPPO, SEAC4RS, ATTREX, etc.) Montzka (NOAA), Atlas (Miami), Blake (Irvine) CIMS (ice cores) Saltzman (Irvine) Balloon spectrometers

Laser Absorption Spectrometers: Aerodyne Research Inc.

# Quantum Cascade Laser Spectrometer mid-IR Absorption







Nelson et al., 2010; Stimler et al., 2011; Commane et al., 2013

Single detector system 500mL Multipass cell volume 76 cm pathlength; Reference Cell

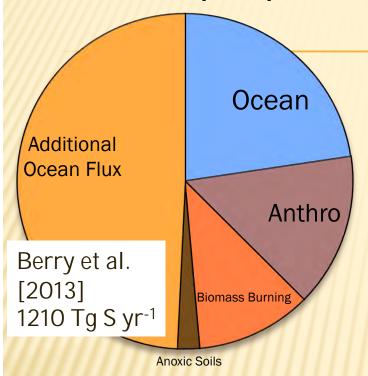
Absorption Peaks @ -17° C

OCS: 2050.397 cm<sup>-1</sup>

 $H_2O$ : 2050.566 cm<sup>-1</sup>

 $CO_2$ : 2050.638 cm<sup>-1</sup>

## Tropospheric OCS Sources and Sinks



#### Sources:

Ocean: Direct / Indirect (High latitude max in summer) Anthropogenic Biomass Burning

Oxic Soils

Berry et al.

1194 Tg S yr<sup>-1</sup>

Vegetative Uptake

[2013]

**Atmospheric** 

Loss

**Anoxic Soils** 

Balanced Budget: For right reasons?

Sinks: Vegetative Uptake Oxic Soils Atmospheric Loss

#### HIPPO 2011

GV aircraft

Flask sample followed by GC-MS

Analysis by Steve Montzka, NOAA Elliot Atlas, RSMAS Miami

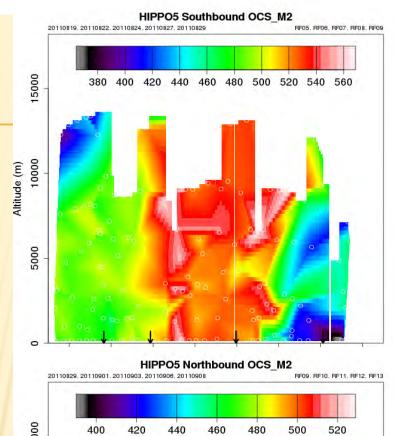
Transect of Pacific Wofsy et al 2011

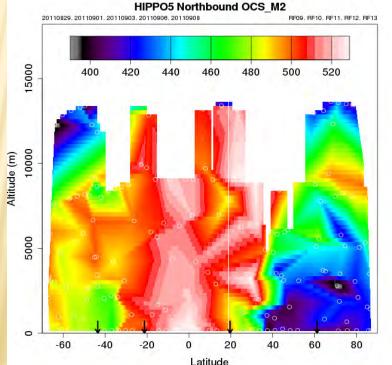
# September

Northern mid-latitude depletion recovery

Tropical mid-troposphere enhancement

\*Note change of scale





### August

Northern midlatitude depletion

Tropical midtroposphere enhancement

Large uncertainty from flask samples

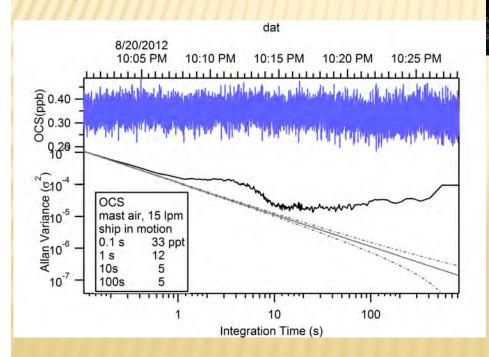
Fast response instrument – better resolution

# Eddy Covariance fluxes of OCS, CO<sub>2</sub> and H<sub>2</sub>O on Ron Brown

- Bermuda to Boston

Motion corrected sonic winds coupled with fast (10Hz) measurements

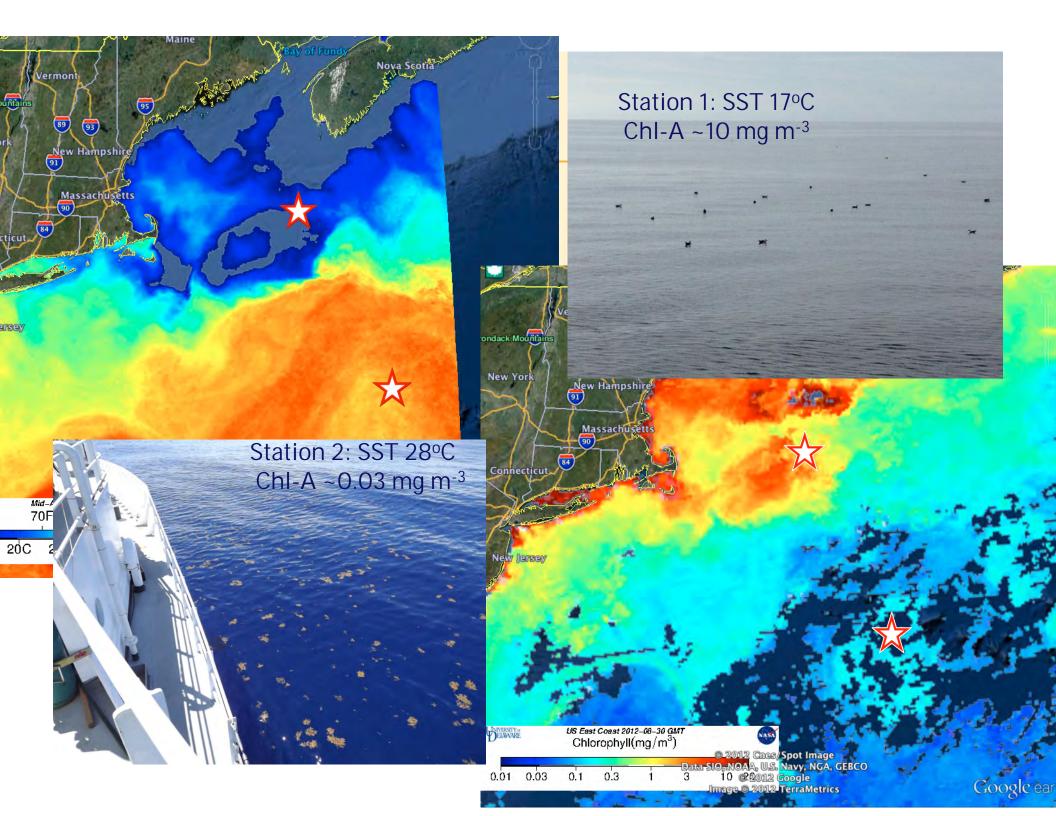
Response Time 0.6s Lag time 4s

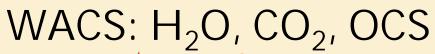


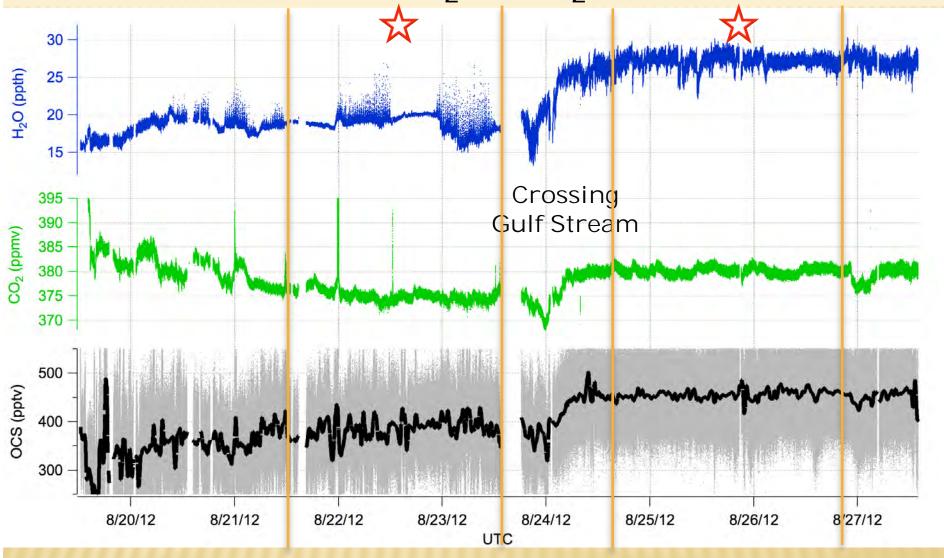
Improved to <2pptv @ 1Hz with reduced flow

Ludovic Bariteau, Chris Fairall, Sergio Pezoa – NOAA ESRL

Mike Agnese, Scott Herndon, Ryan McGovern, Barry McManus, David Nelson, Mark Zahniser – Aerodyne Research Inc.



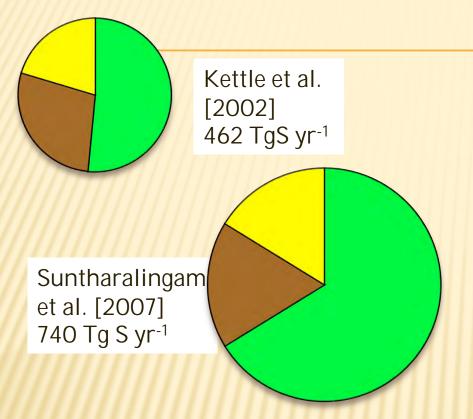




100 pptv more OCS over open ocean vs coast

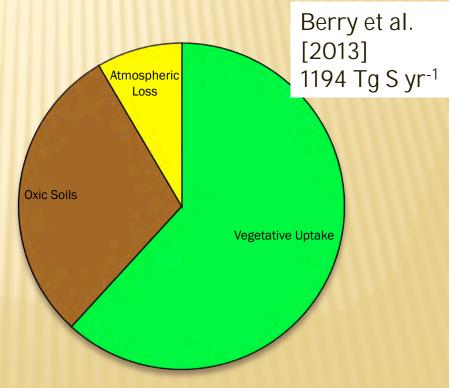
10 Hz data.

## Tropospheric OCS Sinks

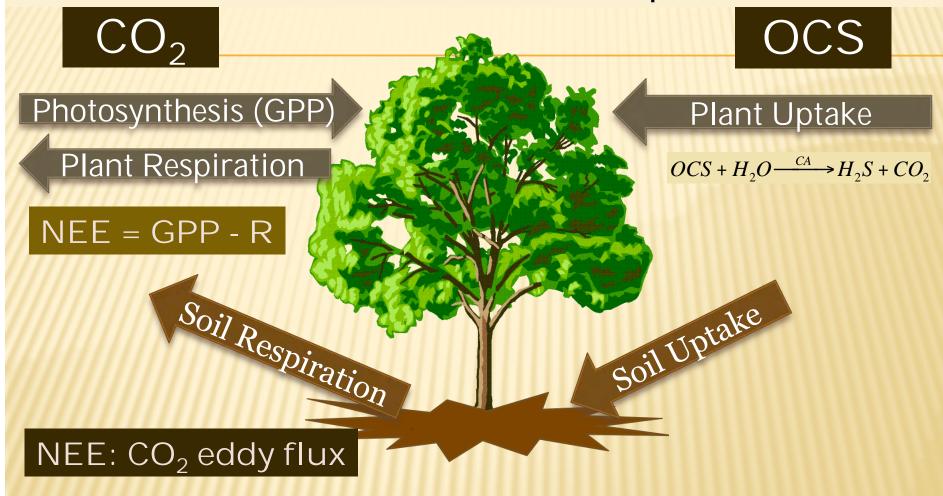


Vegetative Uptake:

Few ecosystem scale flux Estimated from leaf scale studies and lab expts.



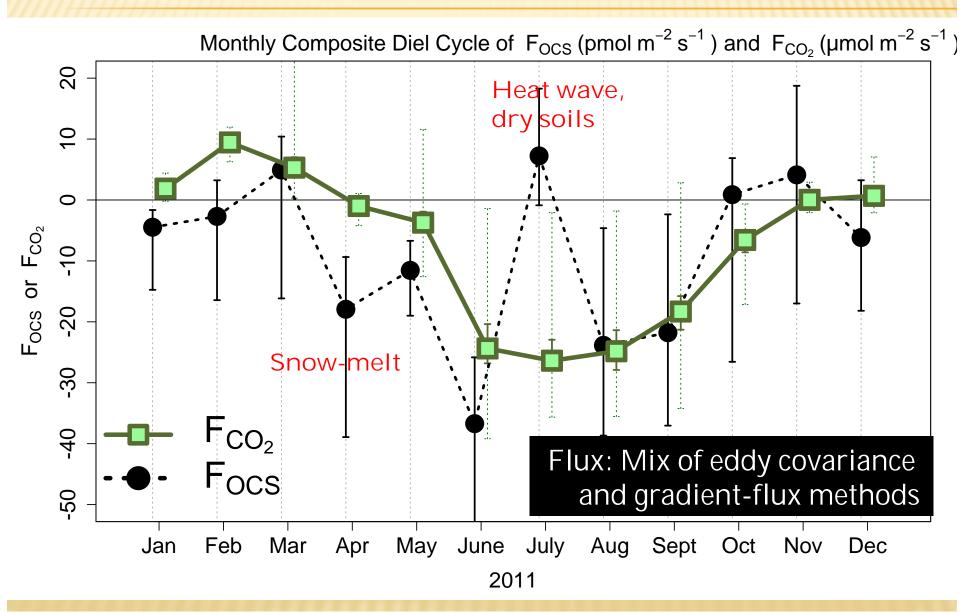
### OCS Sink: Terrestrial Uptake



Daytime R ≈ night R(T)
GPP: NOT measured
GPP ≈ NEE - R

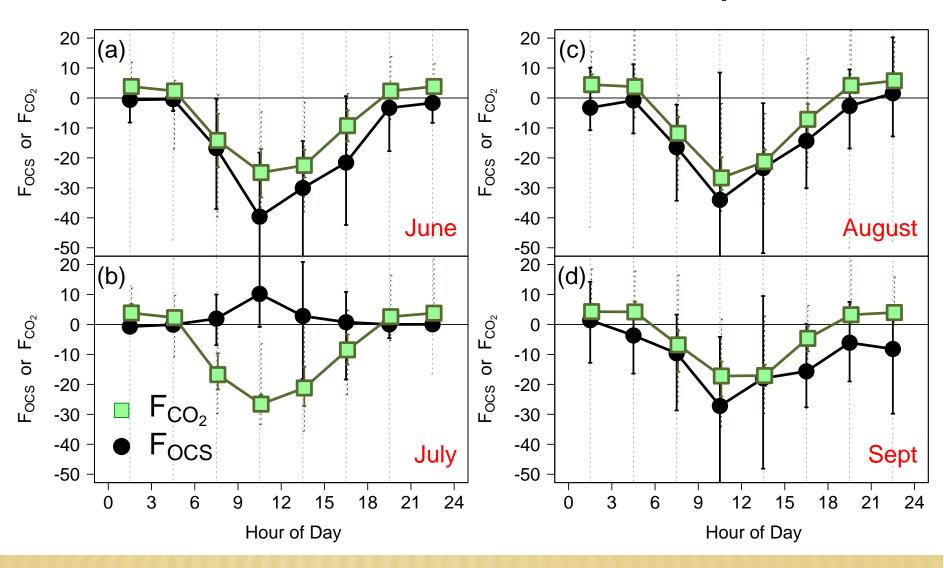
No dependence of OCS uptake on [CO<sub>2</sub>]

# Seasonal OCS Flux: Harvard Forest, MA Mid-Latitude Mixed Forest



#### Summer Diel OCS Flux

Monthly Composite Diel Cycle of  $F_{OCS}$  (pmol m<sup>-2</sup> s<sup>-1</sup>) and  $F_{CO_2}$  (µmol m<sup>-2</sup> s<sup>-1</sup>)



#### Results of Fast OCS measurements

#### Terrestrial Sink:

Bidirectional OCS flux from canopy – hot and dry Diurnal profile: Stomatal opening?

Species dependent uptake rate – conifers less

Warm soils in Sept

- Soil/incompletely closed stomata uptake

#### Oceanic OCS Source:

OCS higher over open ocean

Opposite to Kettle 2002 Budget

Agrees with HIPPO observations and Berry et al 2013

#### Thanks!

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SEAC4RS, Sept 2013 CO2, CH4, CO Cavity ring down Picarro

Daube, Pittman, Commane, McKain, Samra, Santoni, Wofsy

ATTREX, Spring 2014 Global Hawk