In situ measurements & processes driving carbonyl sulfide fluxes (OCS/COS)

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with input from lots of people credited as we go

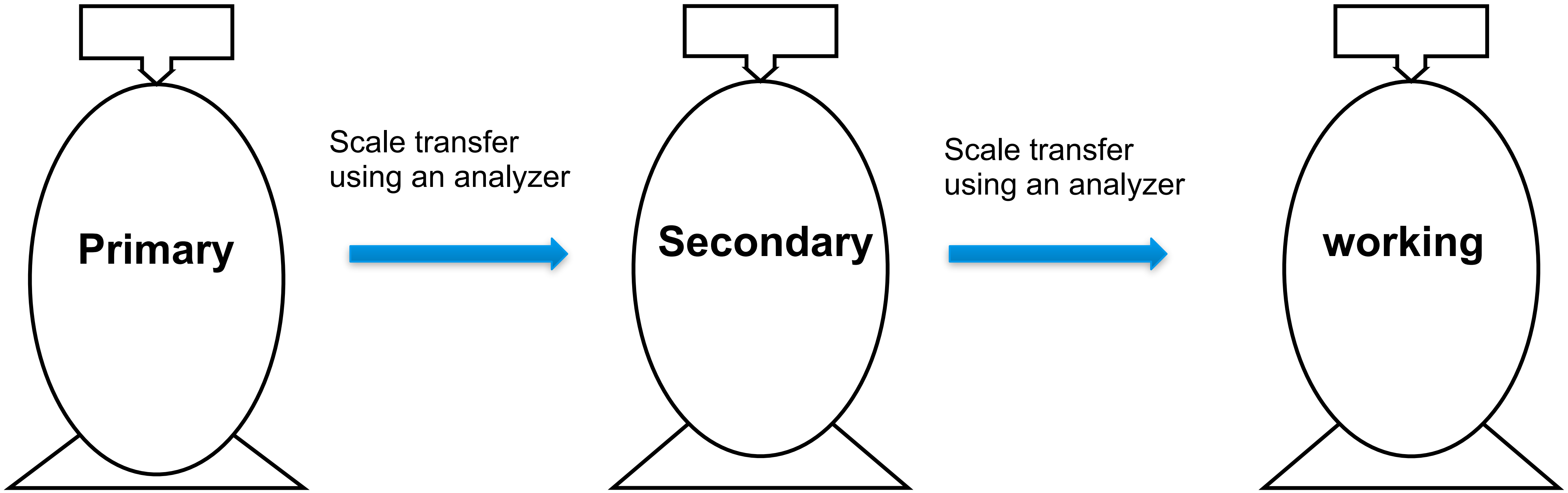
In situ Atmospheric Measurement Techniques of OCS

GC-MS analysis of **flasks** (Towers and airborne)
Steve Montzka (NOAA GMD)
Elliot Atlas (Miami)
Don Blake (Irvine)

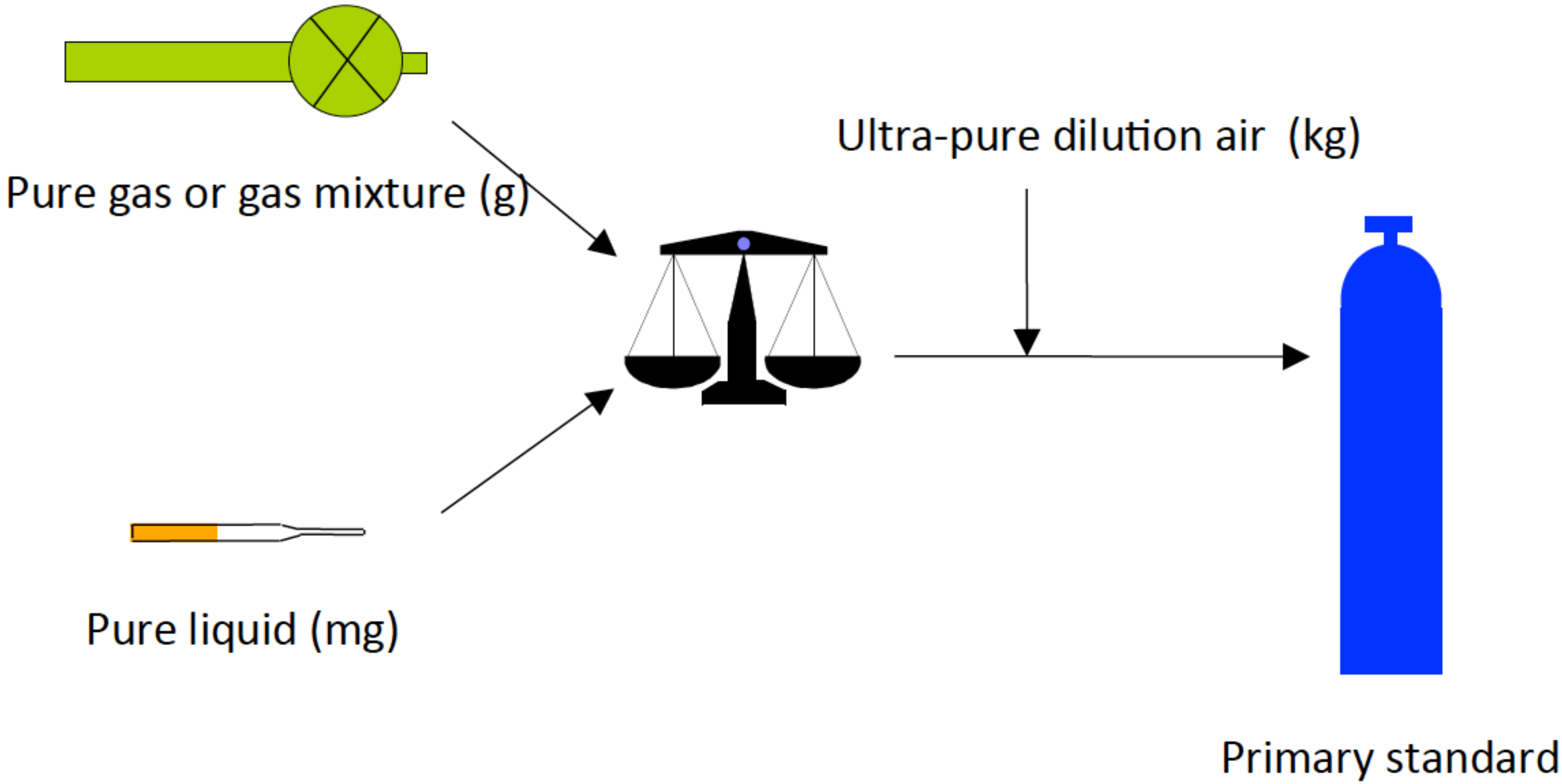
CIMS analysis of **ice cores**:
Eric Saltzman & Murat Aydin (Irvine)

Laser Absorption Spectrometers (Towers, eddy flux)
Aerodyne QCL - Mark Zahniser, Dave Nelson
Los Gatos Off-Axis ICOS

COS Scale transfer



NOAA Primary COS standard: gravimetric method



- COS pure gas: 99.9% purity
- Uncertainty ~ 0.1-0.5%

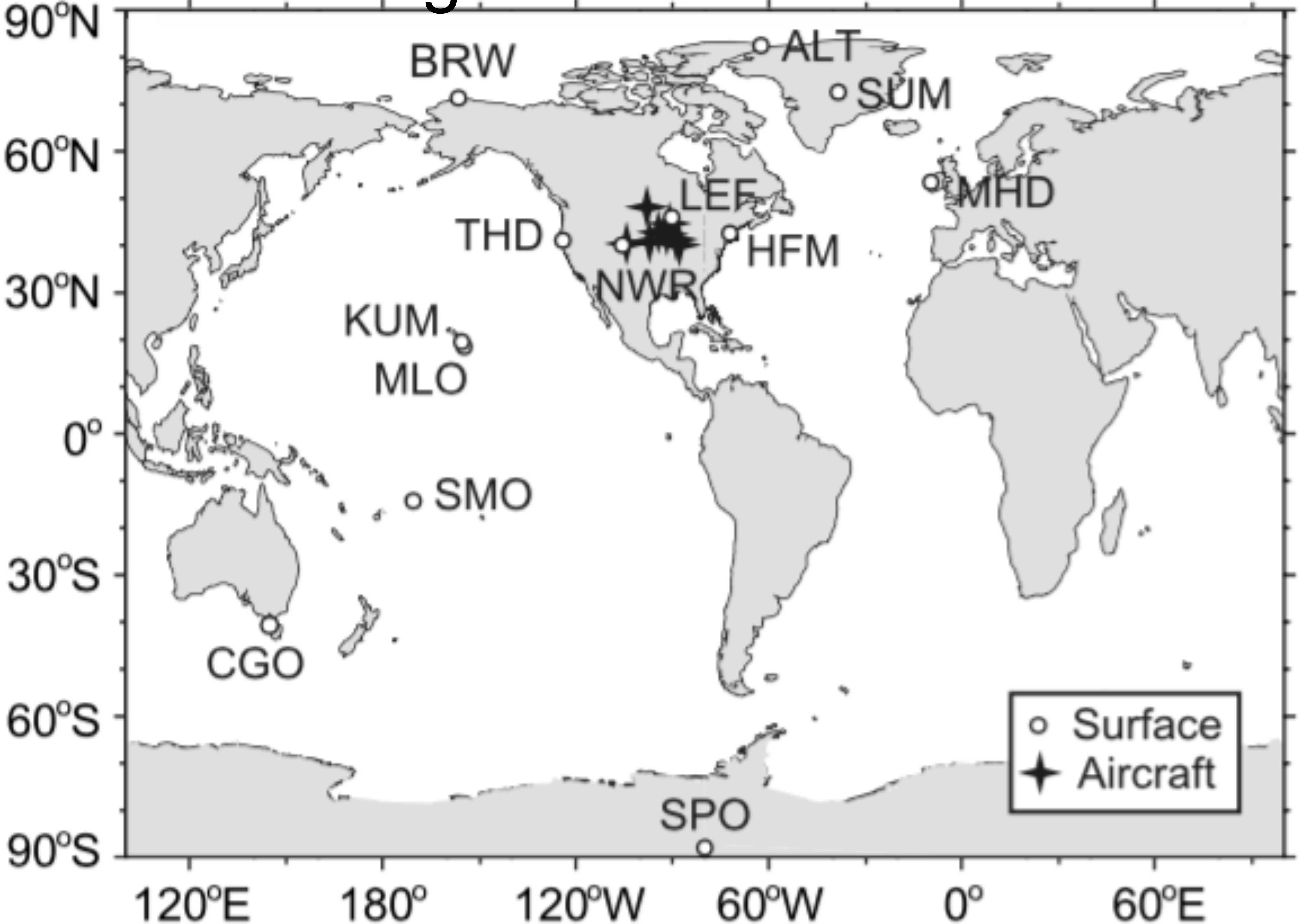
Uncertainty of QCLS COS, CO_2, CO measurements

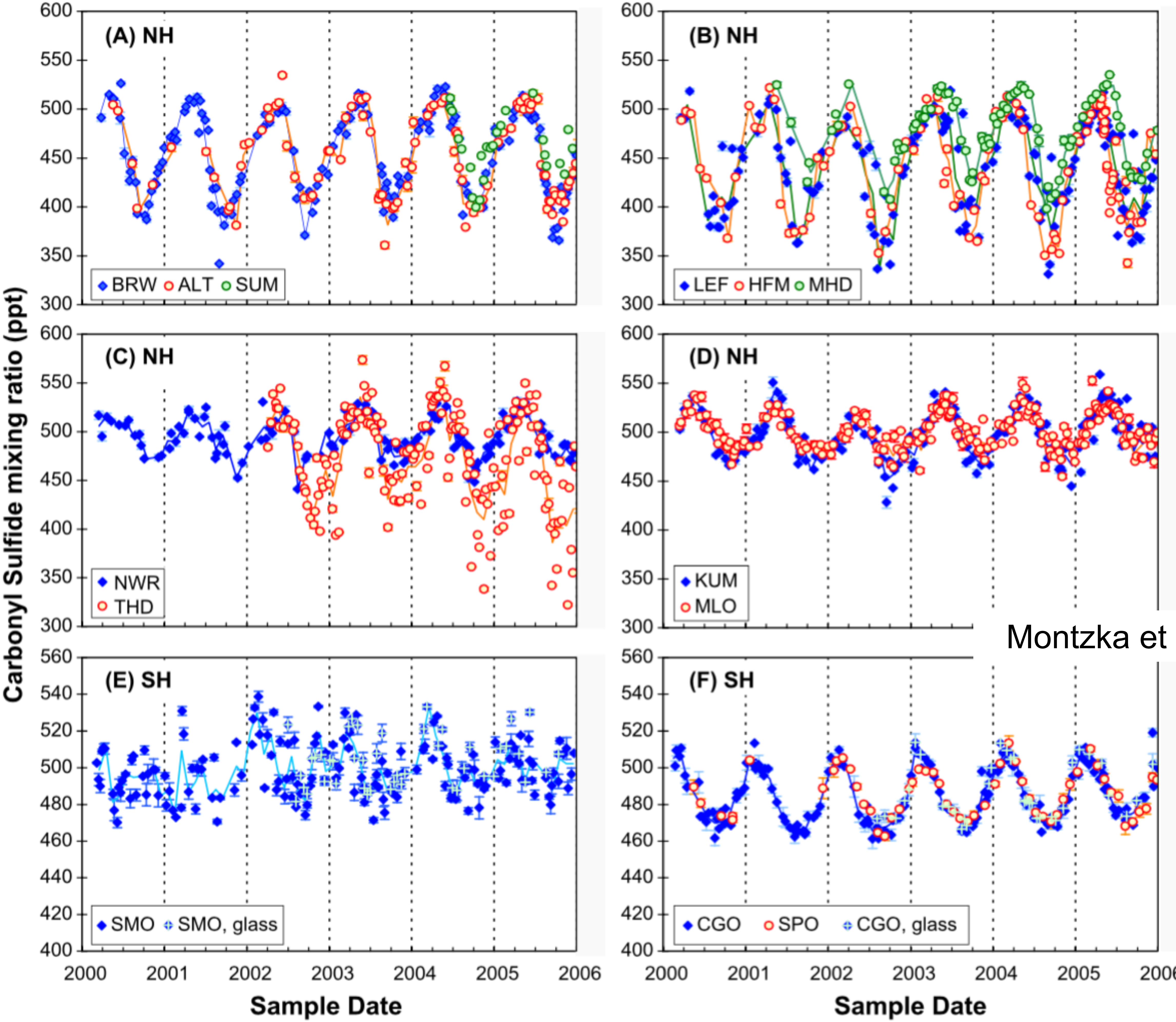
Uncertainty contributions	COS [ppt]	CO_2 [ppm]	CO [ppb]
Repeatability of the NOAA or WMO scale[a]	2.1	0.07	2.0
Transfer scale to working standards (1σ)[b]	2.8	0.12	1.7
Measurement calibration[c]	2.8	0.12	1.7
Water vapor correction (1σ)	2.9	0.10	1.1
Measurement precision (1 min)[d]	5.3	0.09	0.3
Overall uncertainty	7.5	0.23	3.3

[a] For COS: defined as the standard deviation of the measurements associated with the cylinder calibration. For CO_2 and CO: certified by the WMO central calibration laboratory (NOAA/ESRL).
[b] Average uncertainty over four cylinders in Table 2 (method 3).
[c] Using the single bias correction (see Sect. 2.2.2) it is the same as transferring the scale to the working standards.
[d] The standard deviation over minute-averaged cylinder measurements after drift correction with reference measurements every 30 min (Table 3).

Kooijmans et al., 2016

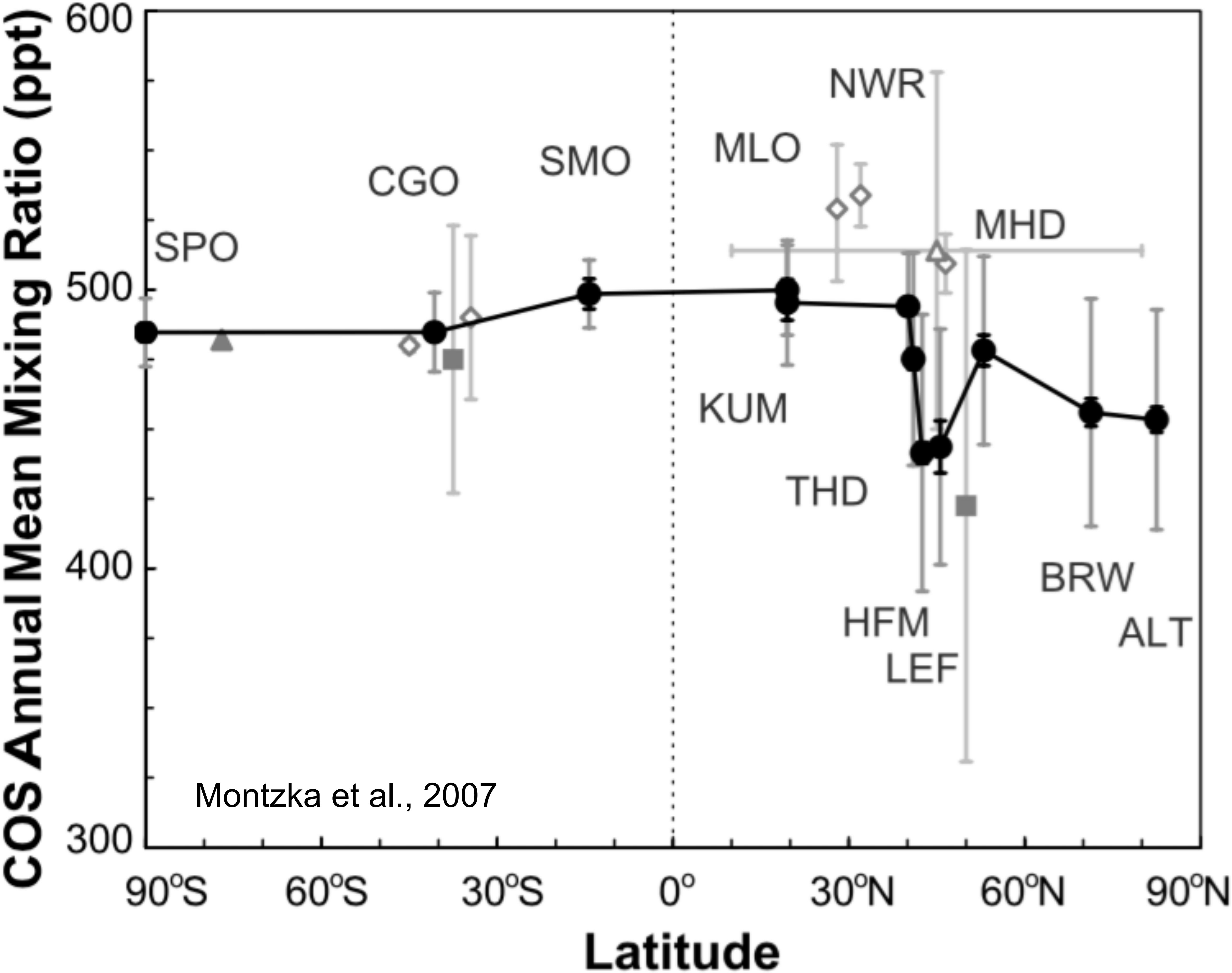
Long-term NOAA GMD



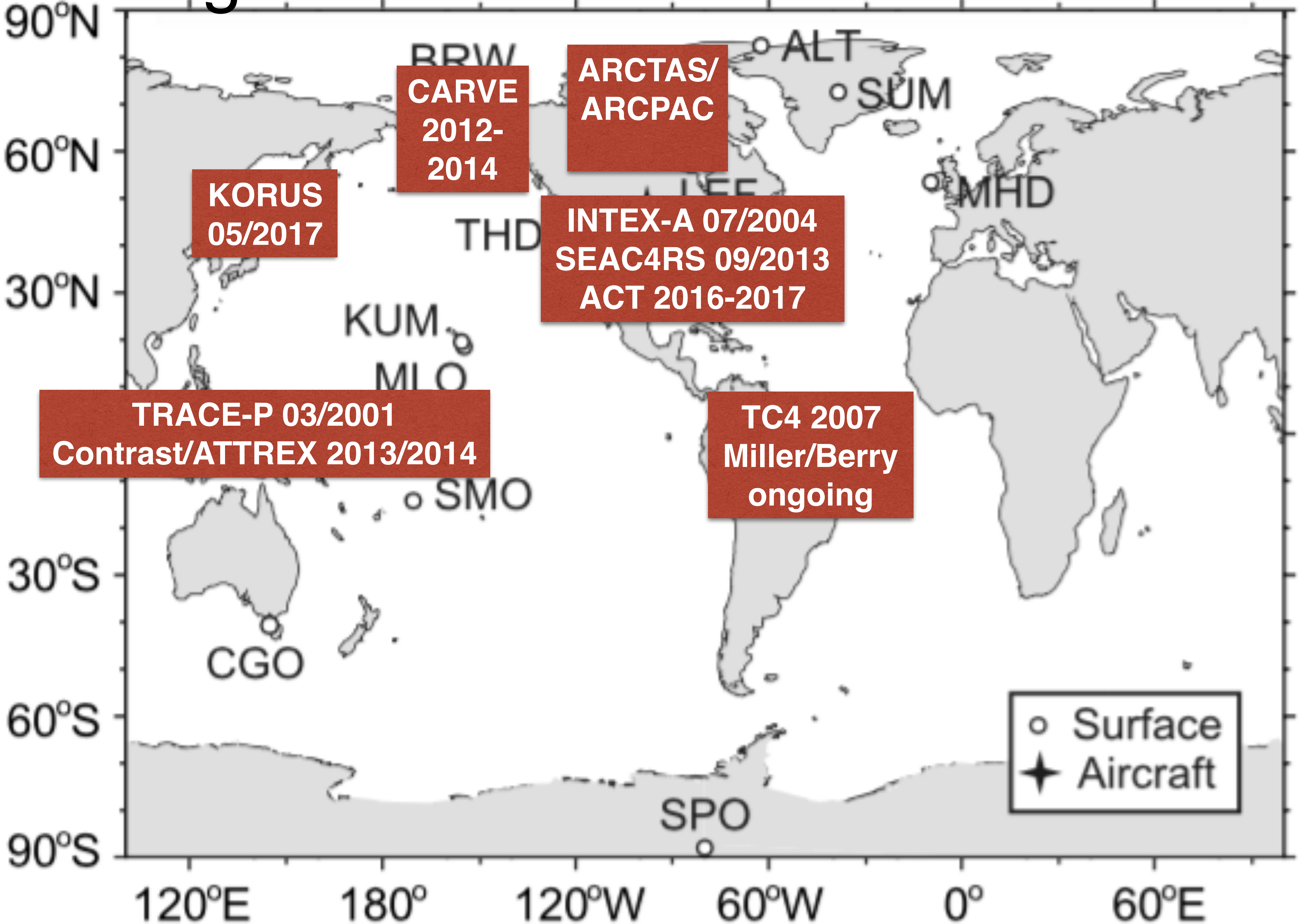


Montzka et al., 2007

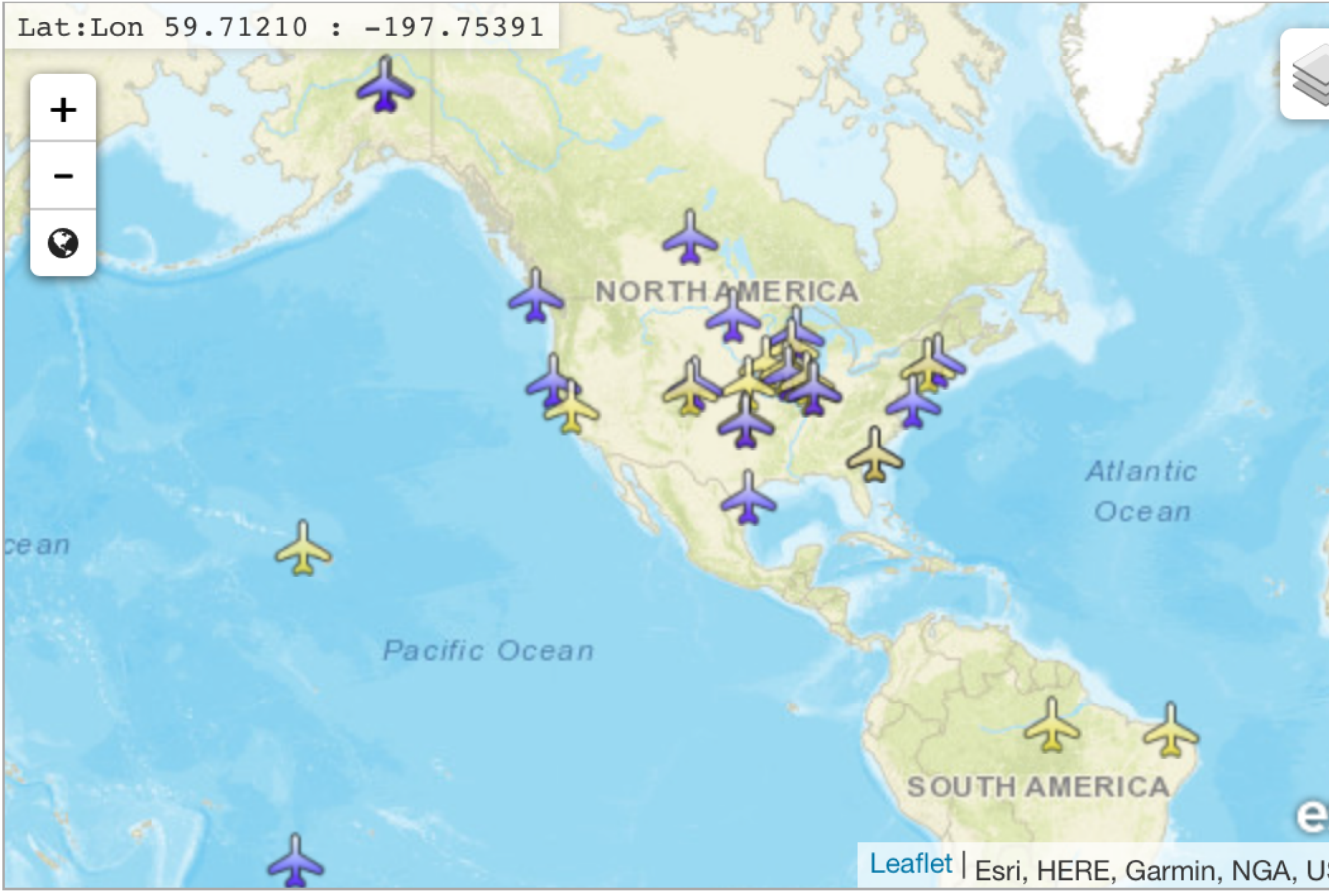
Annual mean OCS with Latitude



Targeted Airborne PFP/WAS/AWAS



Survey Flights: Long-term NOAA GMD



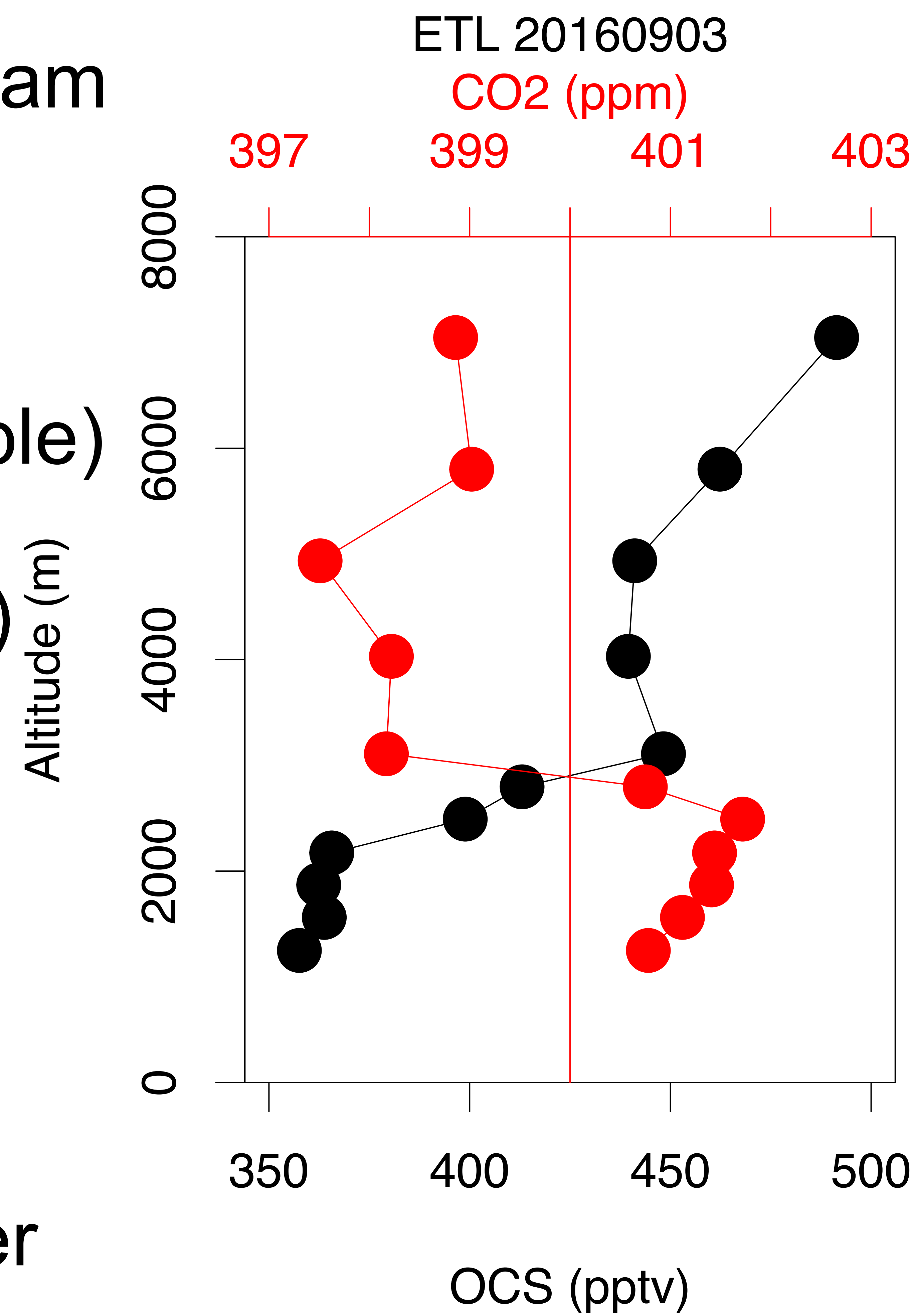
NOAA GMD Flight Program
Steve Montzka OCS

Monthly sampling
Year round (when possible)

East Trout Lake (ETL)
Northern Canada

September 2016

OCS depletion and
CO_2 enhancement in
boundary/residual layer



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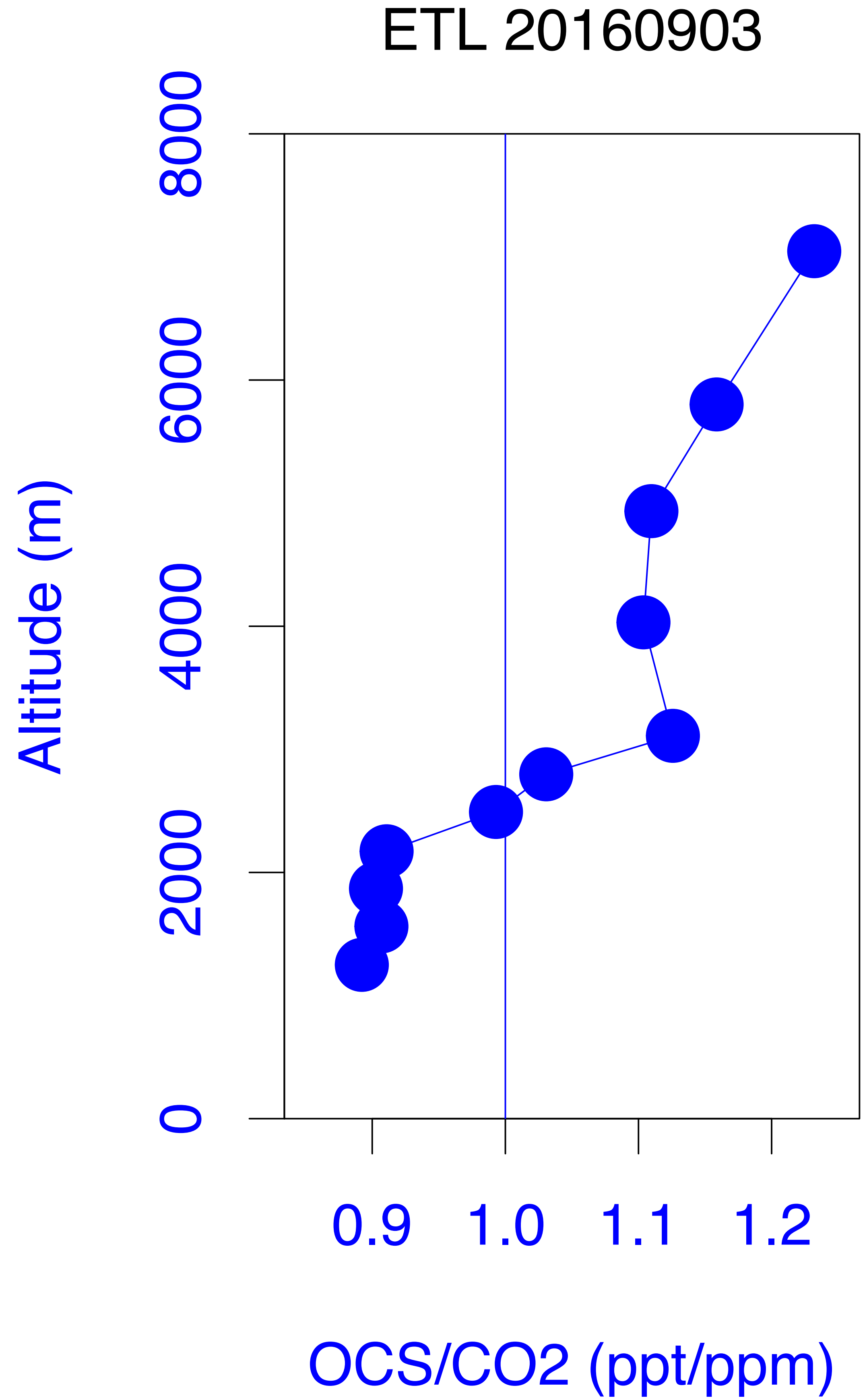
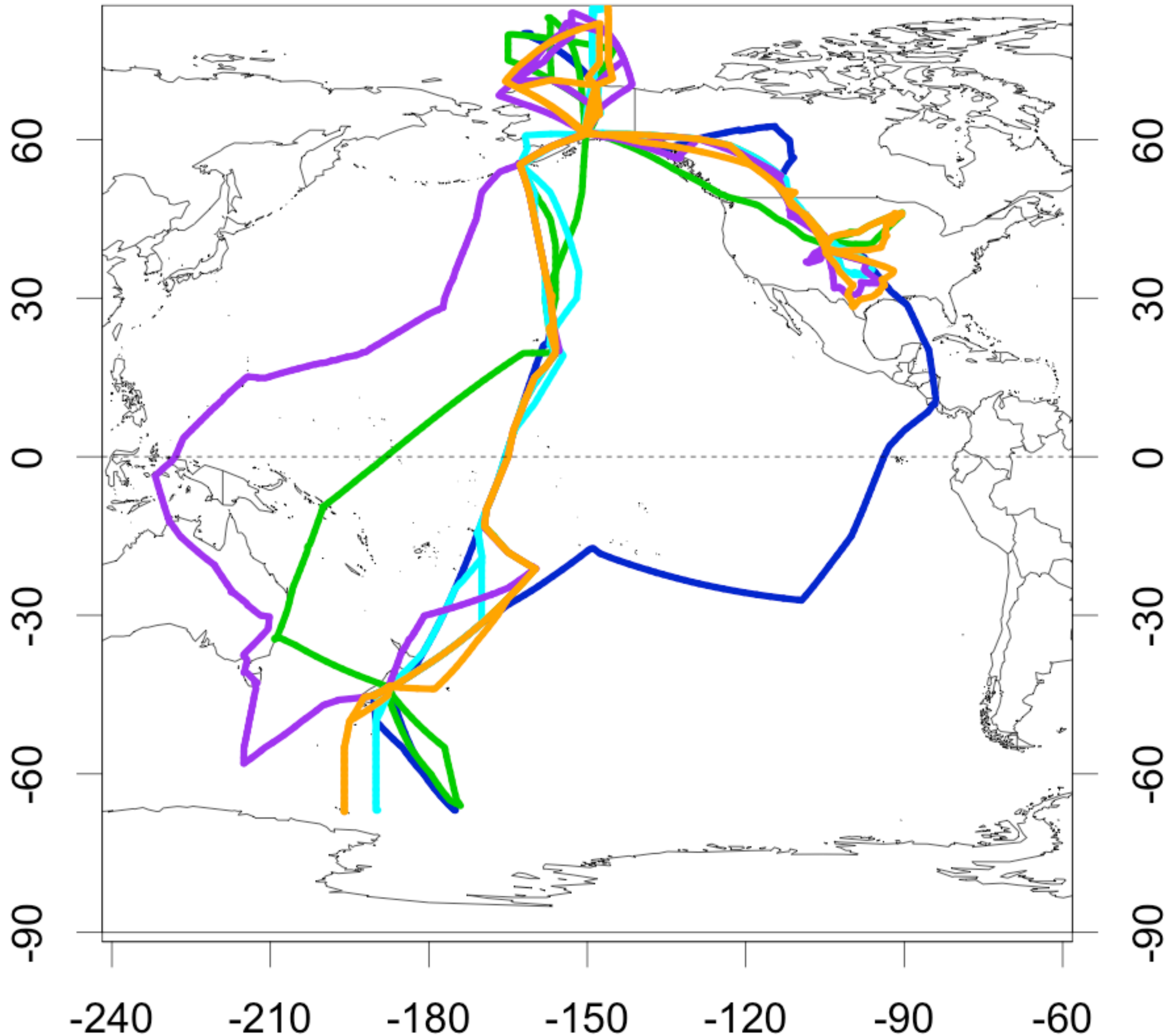
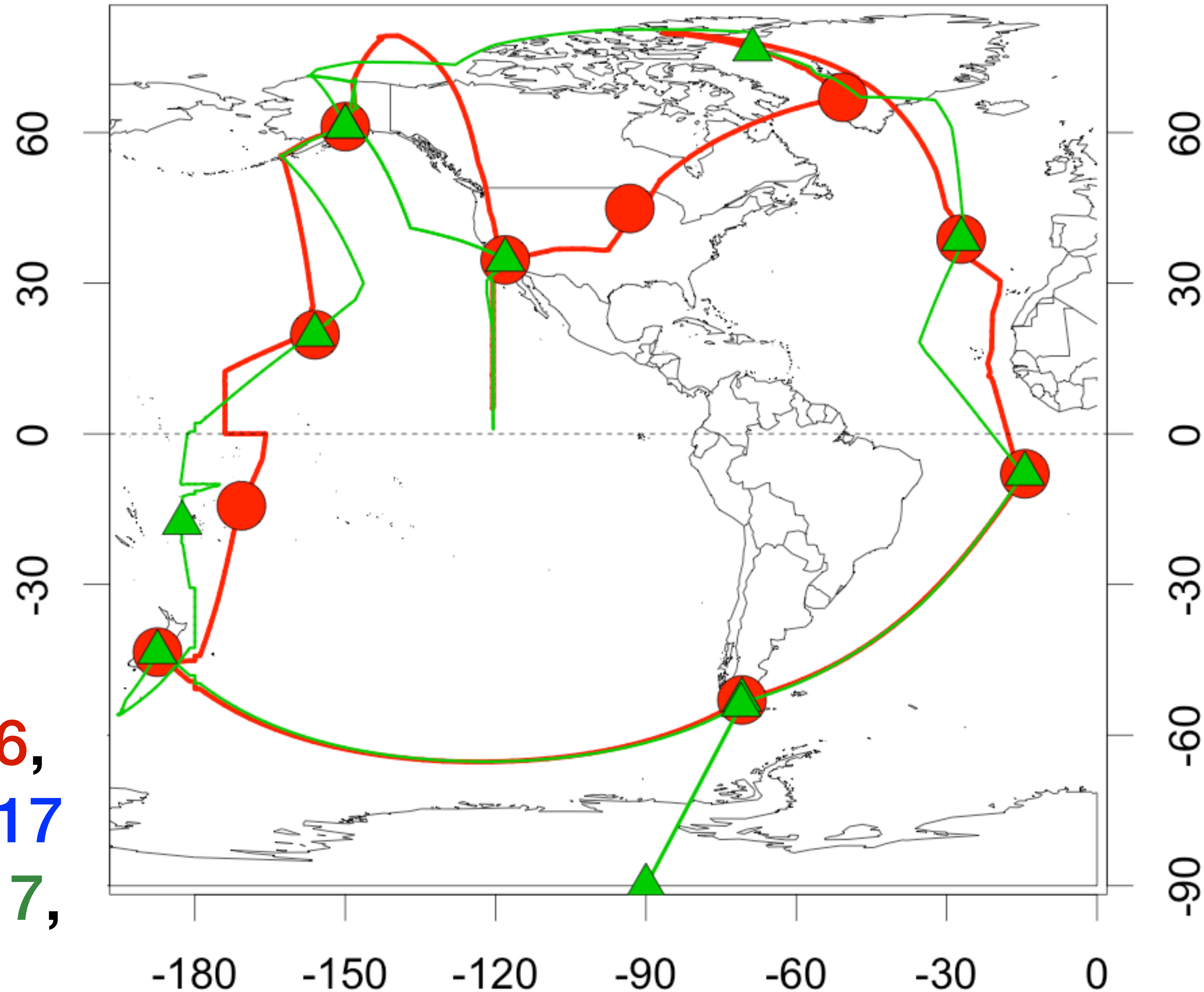


Survey Flights: HIPPO 1-5 in Pacific 2009-2011: Measured OCS in Flasks: Montzka, Atlas



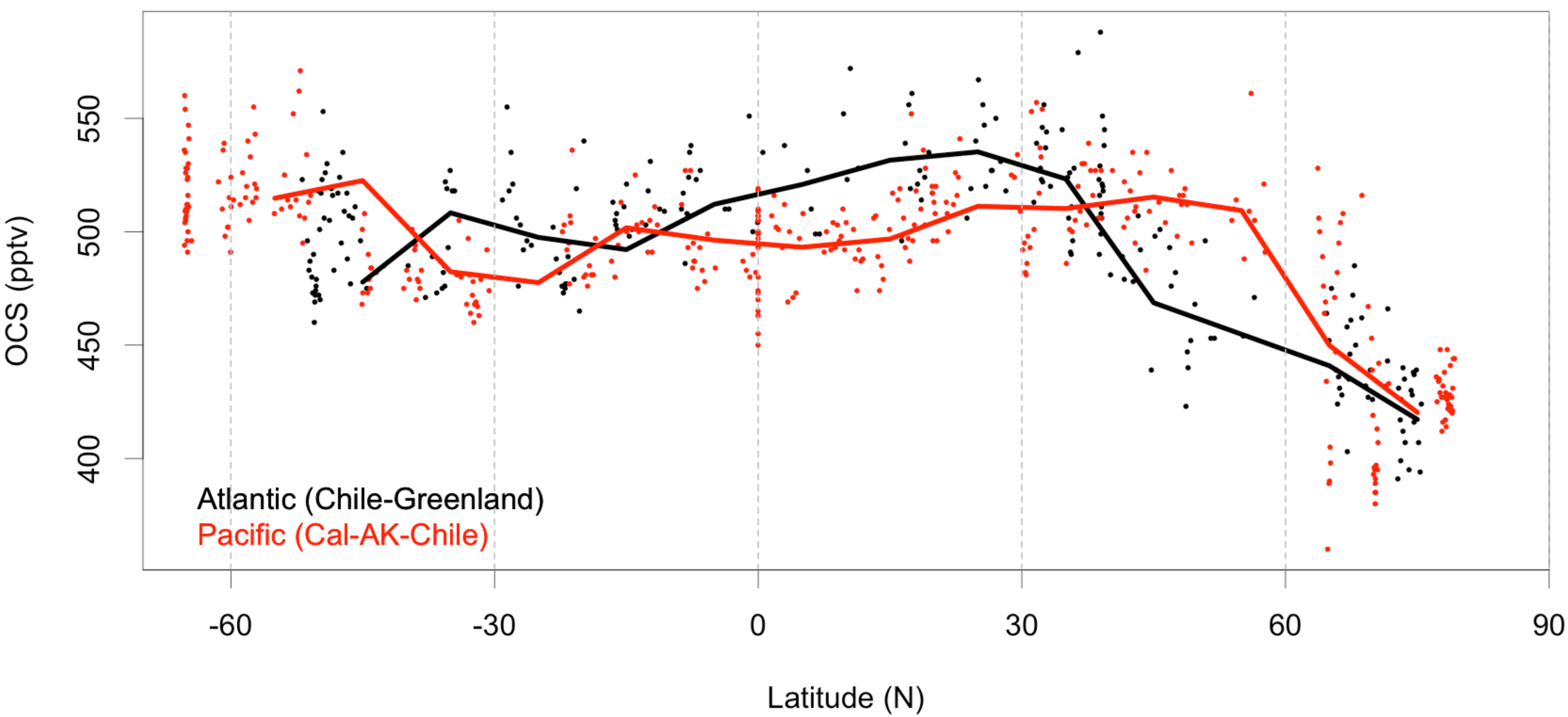
Survey Flights: ATom 1-4 Pacific & Atlantic 2016-2018
Measured OCS in Flasks: Montzka, Blake, UCATS



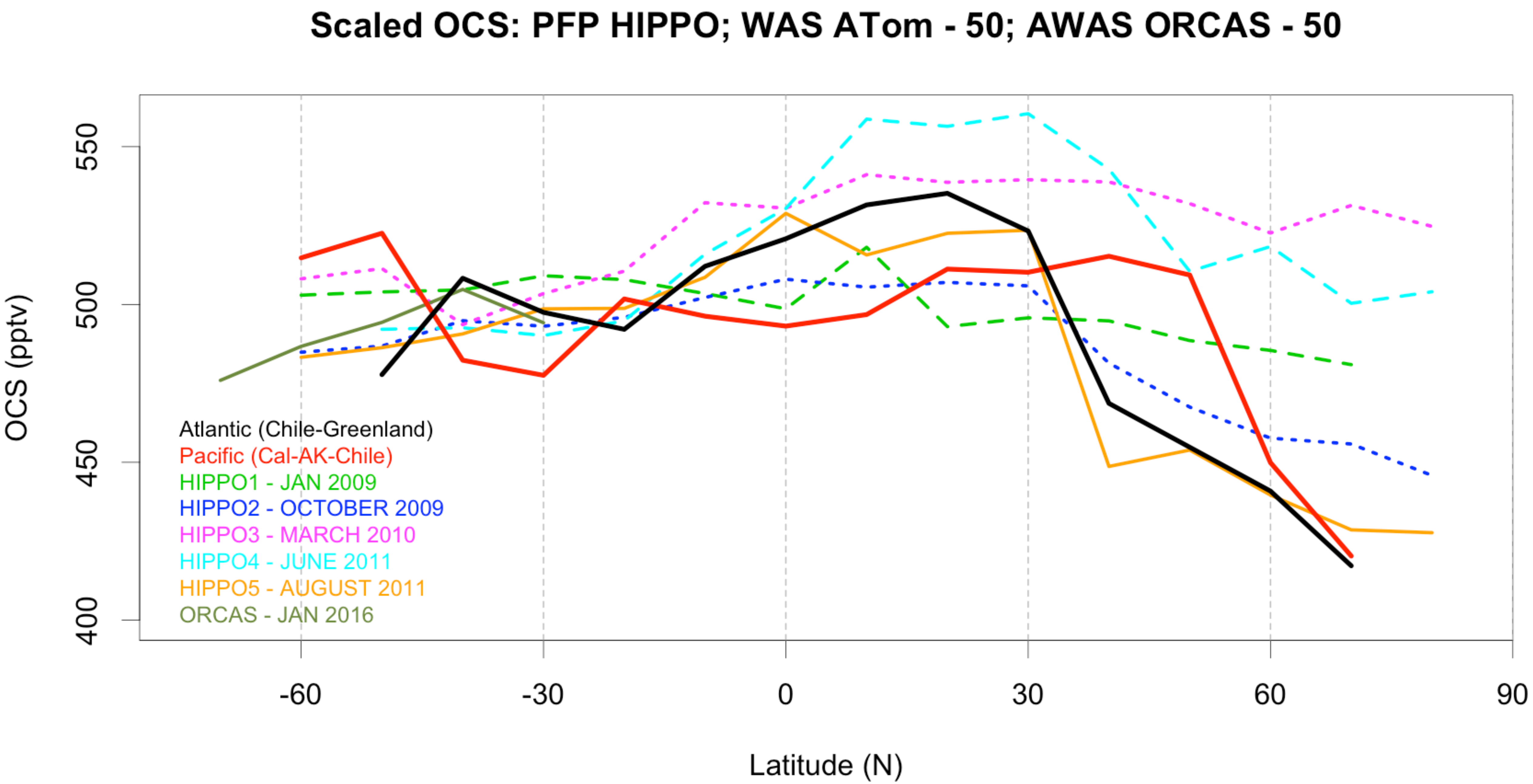
August 2016,
February 2017
October 2017,
May 2018

ATom 1 Pacific & Atlantic Aug 2016
Measured OCS in Flasks: Blake
Fresh biomass burning removed

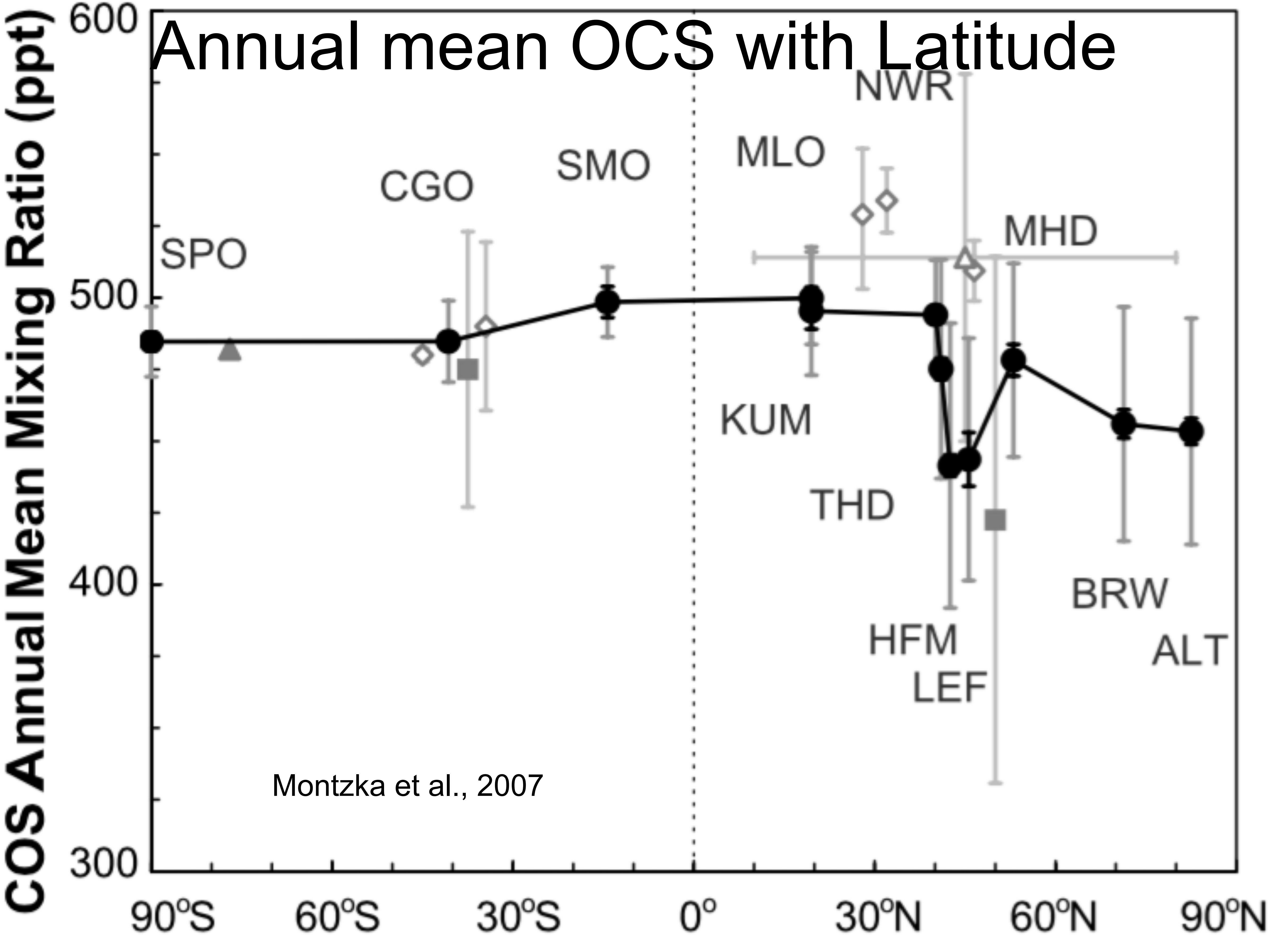
WAS - 50 pptv to scale to PFP;
Cal scale matters!



ATom 1 Pacific & Atlantic Aug 2016:
WAS ~50 pptv > PFP
ATom1 Pacific and Atlantic vs HIPPO Pacific



Annual mean OCS with Latitude



Montzka et al., 2007

What drives the OCS budget? Can we directly measure these processes/fluxes?

Direct Ocean

Vegetation / Trees

Crops

CS_2 oxidation

Lichens/ Mosses

Soils

Soils

Sources

Sinks

Wetlands

Oxidation

Anthropogenic

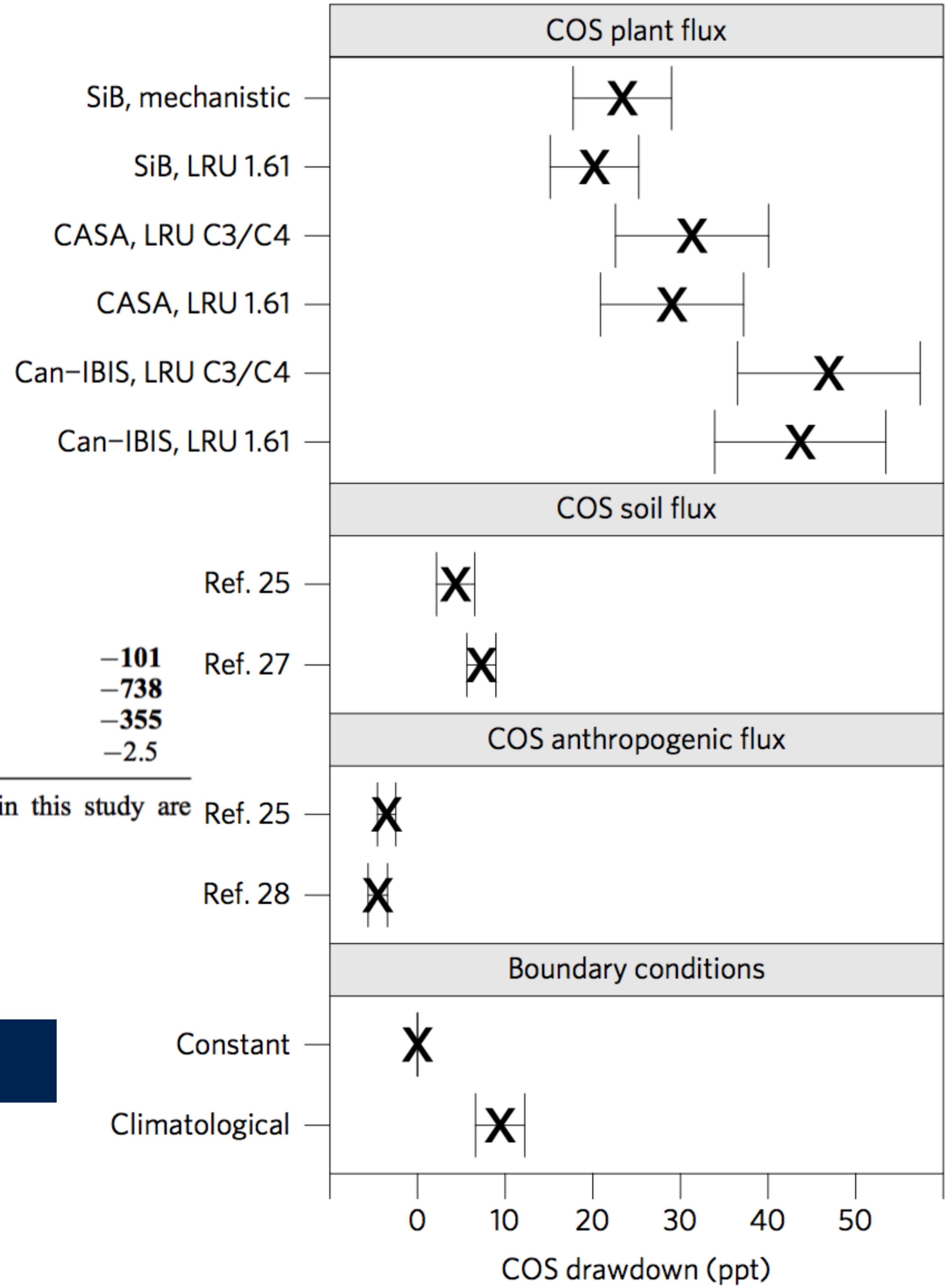
Stratospheric photolysis

Biomass Burning

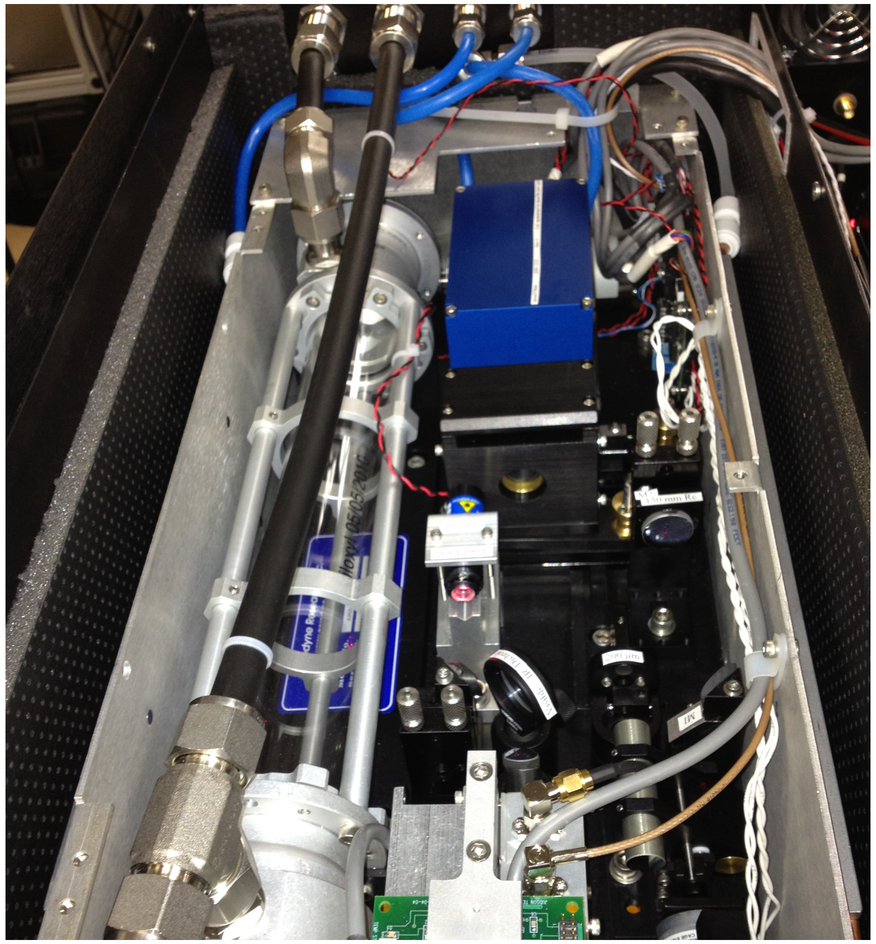
Berry et al., 2013

Sinks		
Destruction by OH Radical	−94	**−101**
Uptake by Canopy	−238	**−738**
Uptake by Soil	−130	**−355**
Net Total	−5	−2.5

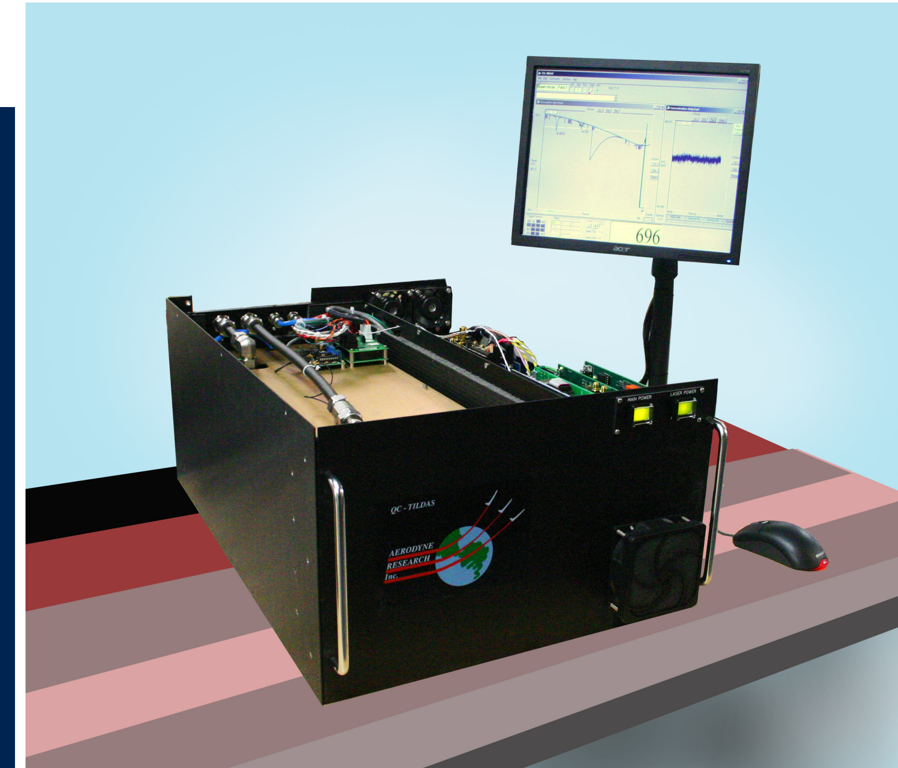
[a]Units are 1.0 × 10^9 g of sulfur. Fluxes changed in this study are highlighted with bold type.

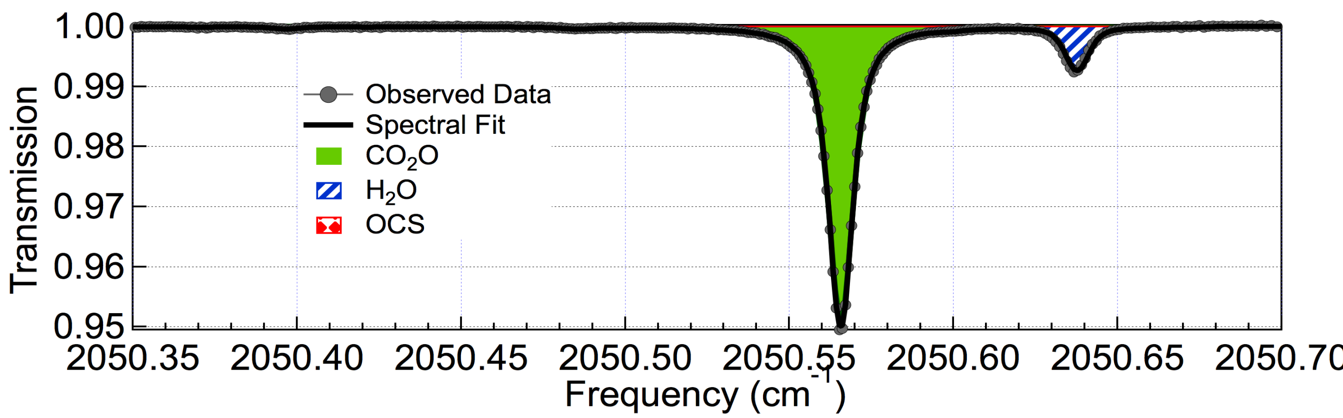


Tim Hilton



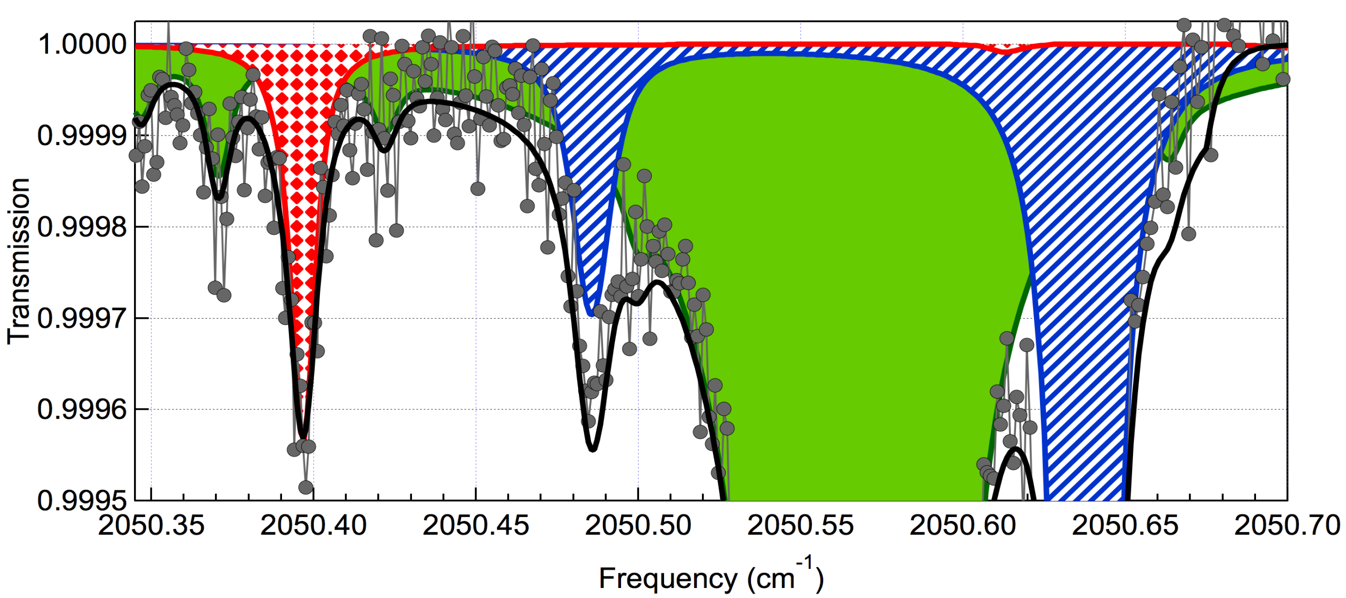
Quantum Cascade Laser Spectrometer (QCLS) mid-IR Absorption





Stimler et al., 2011; Commane et al., 2013, Commane et al., 2015,

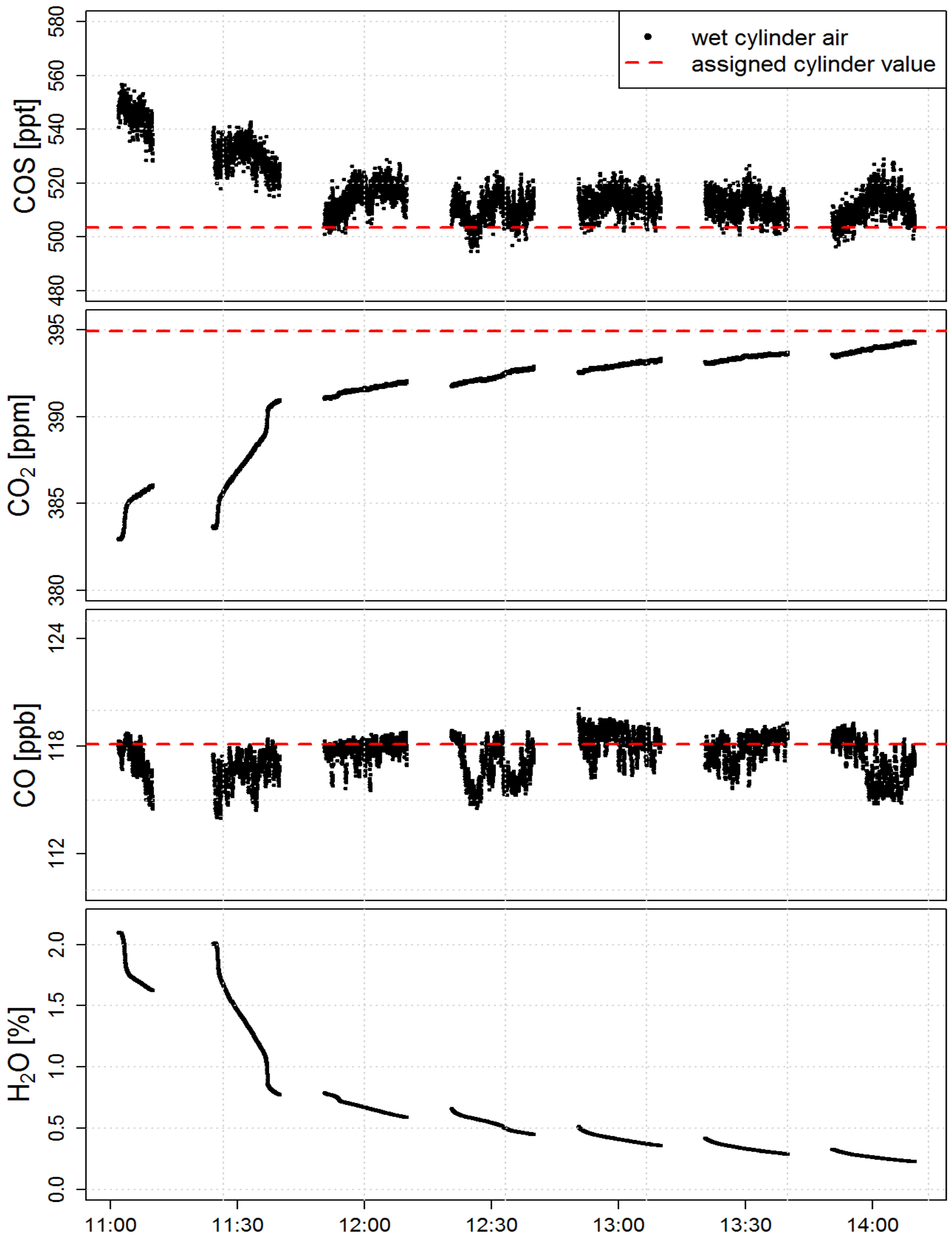
Billesbach et al., 2014, Maseyk et al., 2014, Kooijmans et al., 2016, 2017, Wehr et al., 2017

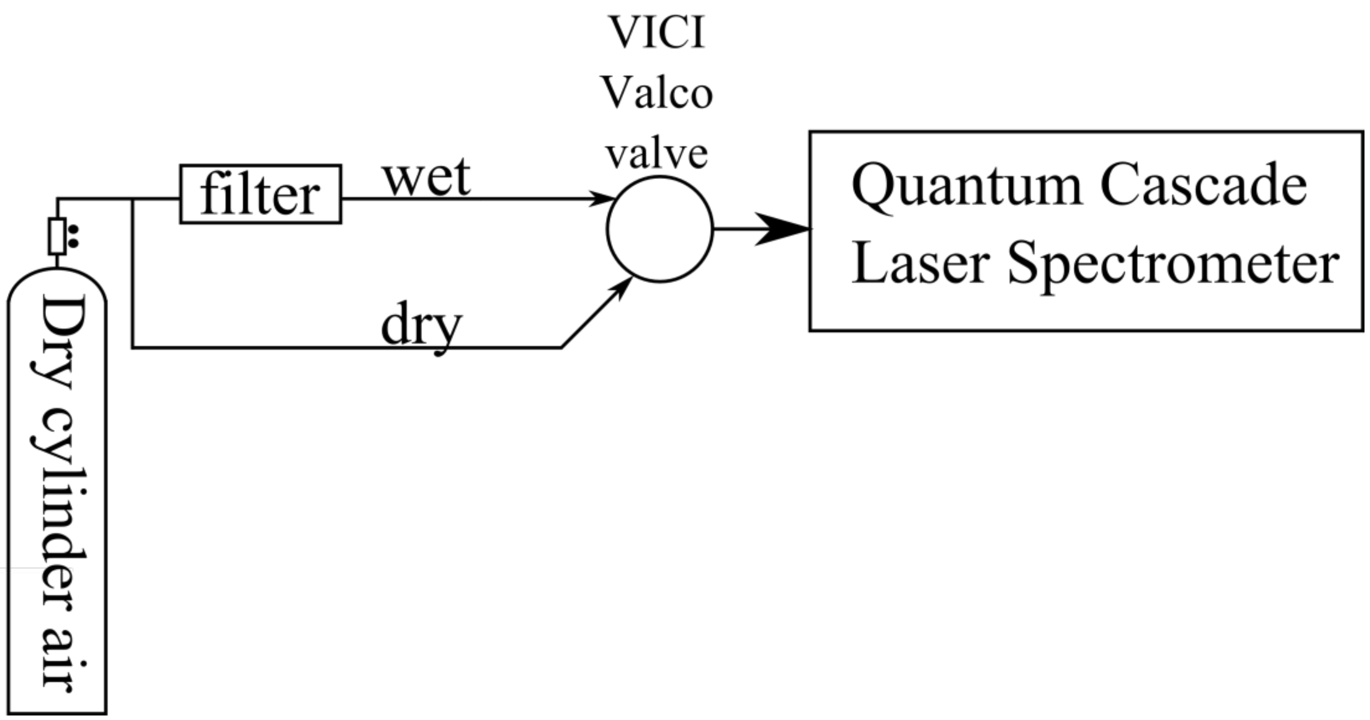


Single detector system
500mL Multipass cell volume
76 cm pathlength ; Reference Cell

Absorption Peaks @ -17° C
OCS: 2050.397 cm^{-1}
H_2O: 2050.566 cm^{-1}
CO_2: 2050.638 cm^{-1}

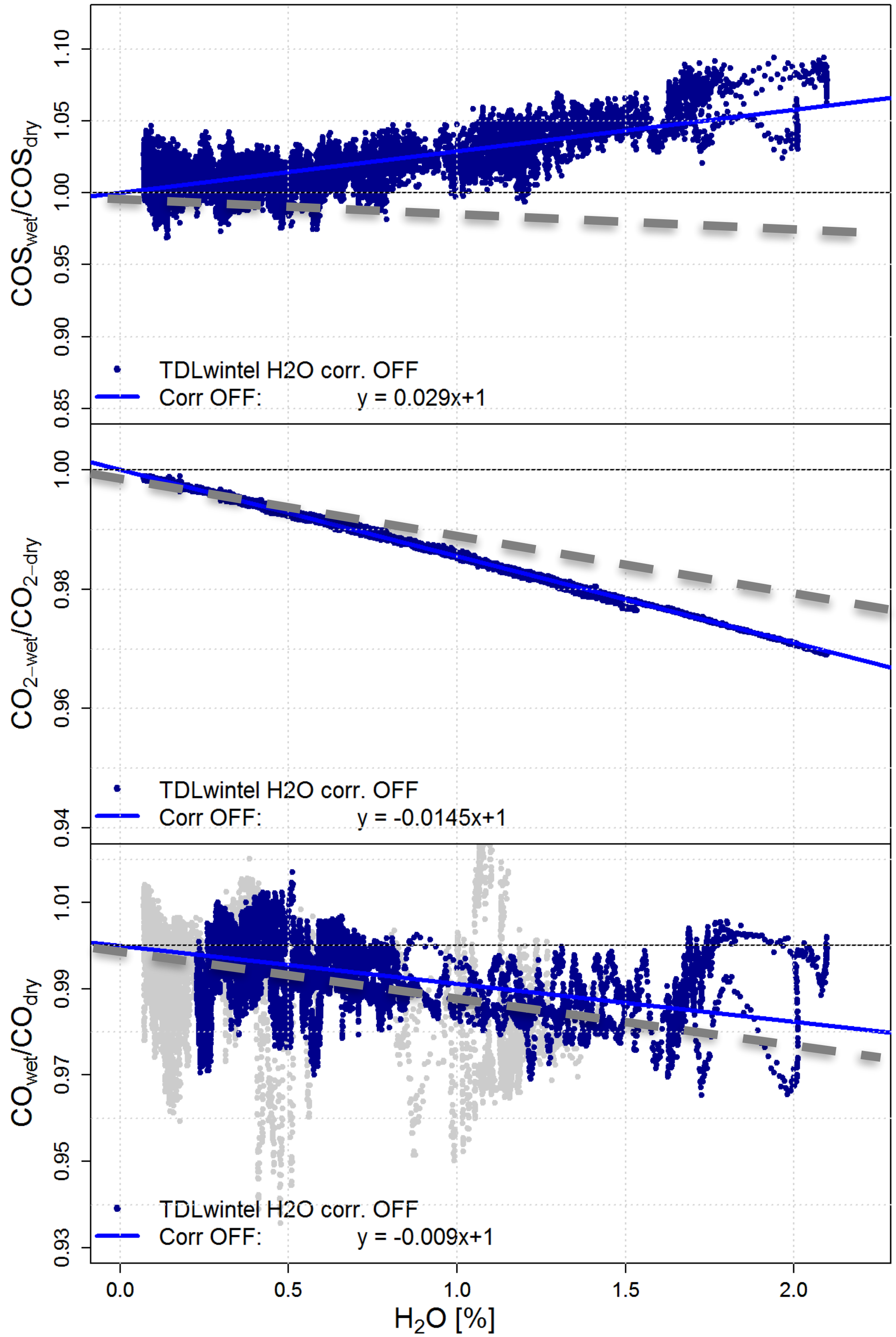
COS dry mole fractions: Water vapor corrections



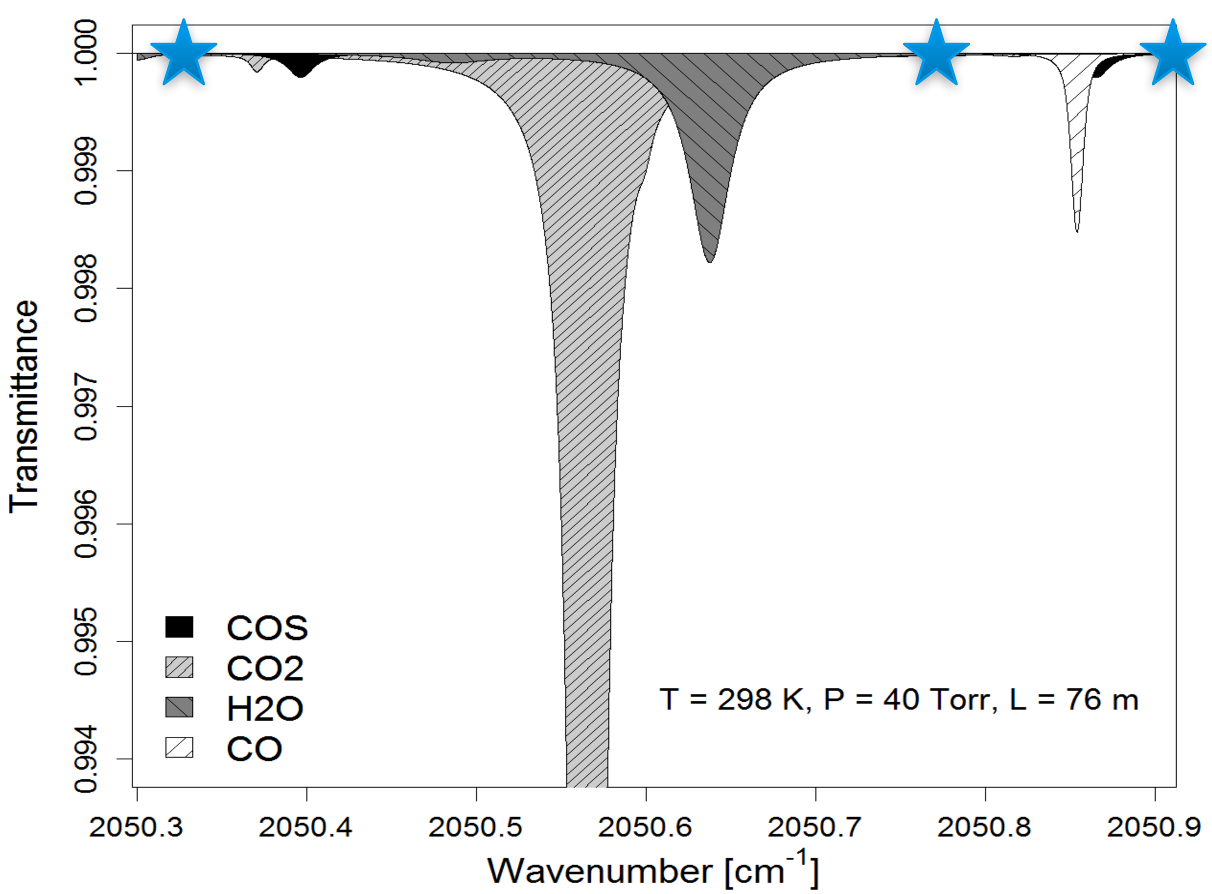


Water vapor experiment with humidified cylinder air to characterize the H_2O dependence.

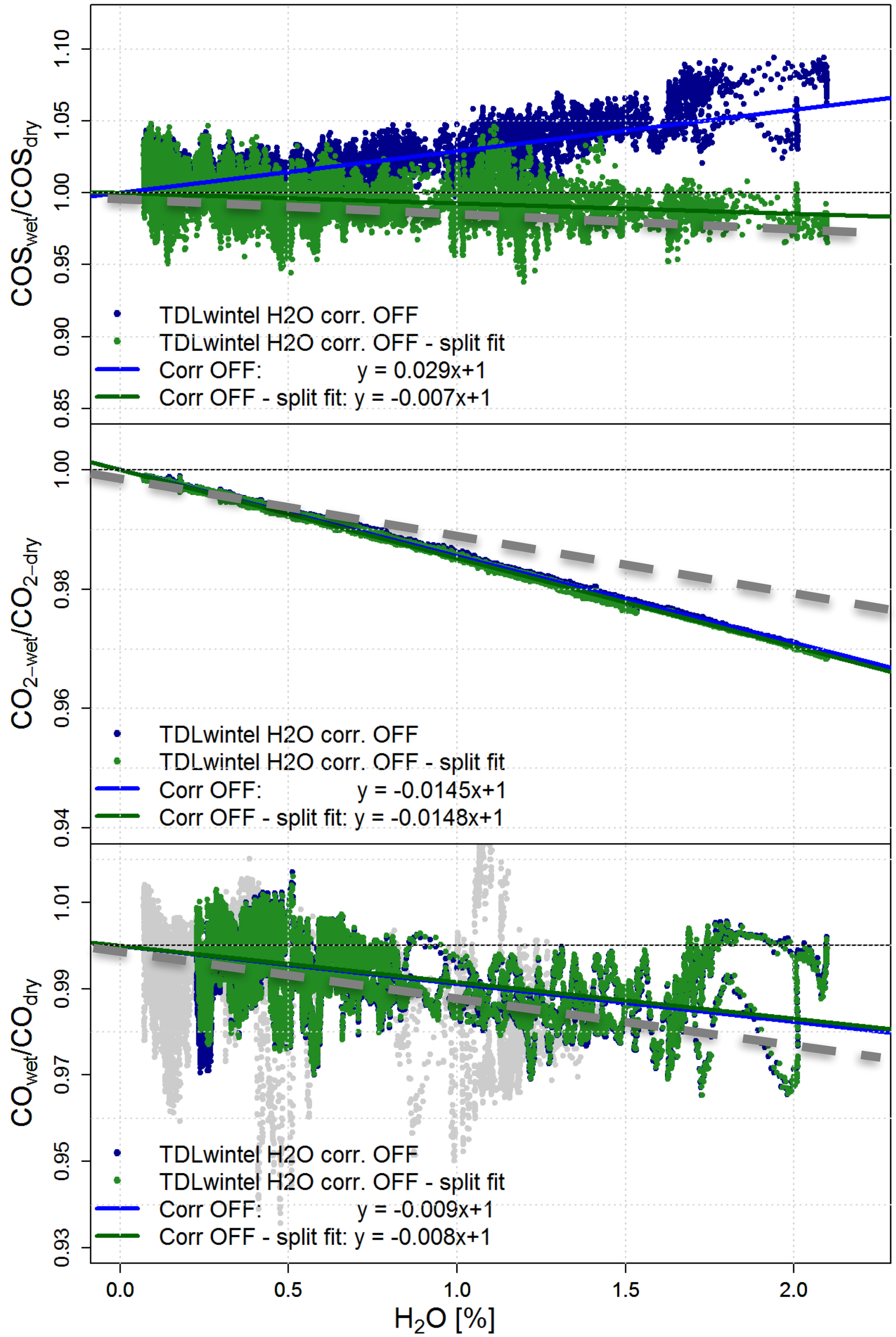
Water vapor corrections



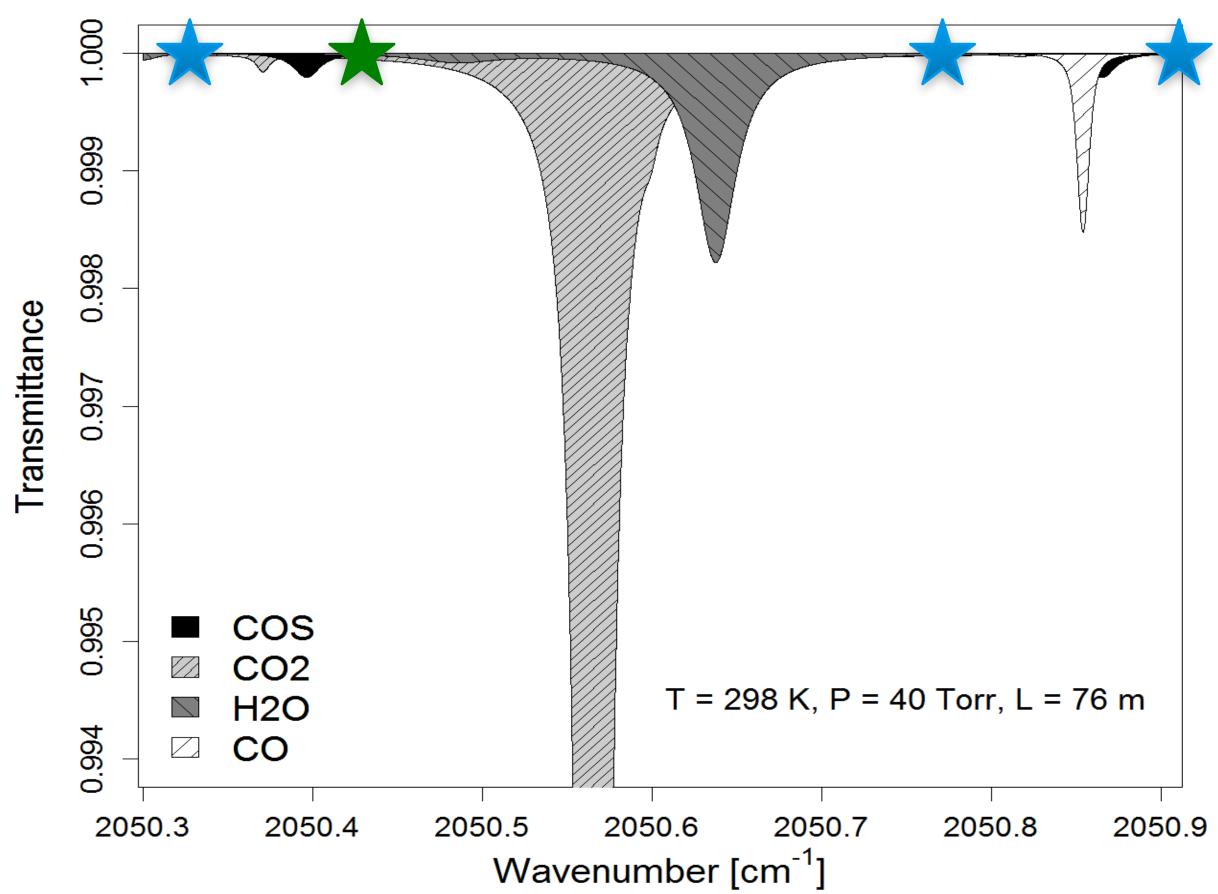
Water correction can be applied based on linear H_2O dependence.



Water vapor corrections



Updated water corrections

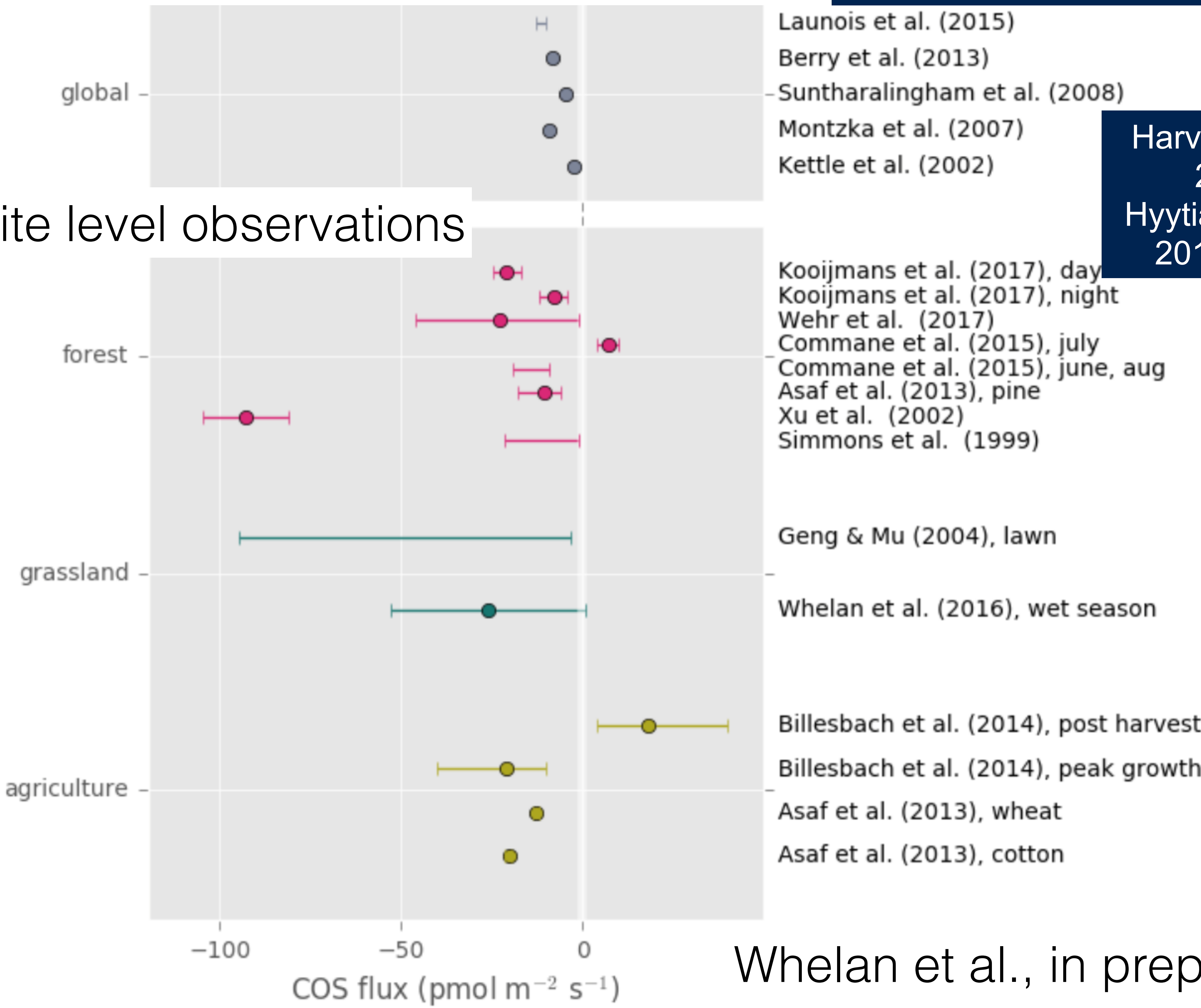


Global average land OCS uptake from modeling studies

Ecosystem Scale OCS

Harvard Forest, 2011-2013
Hyytiälä, Finland 2014? - now

site level observations



Whelan et al., in preparation

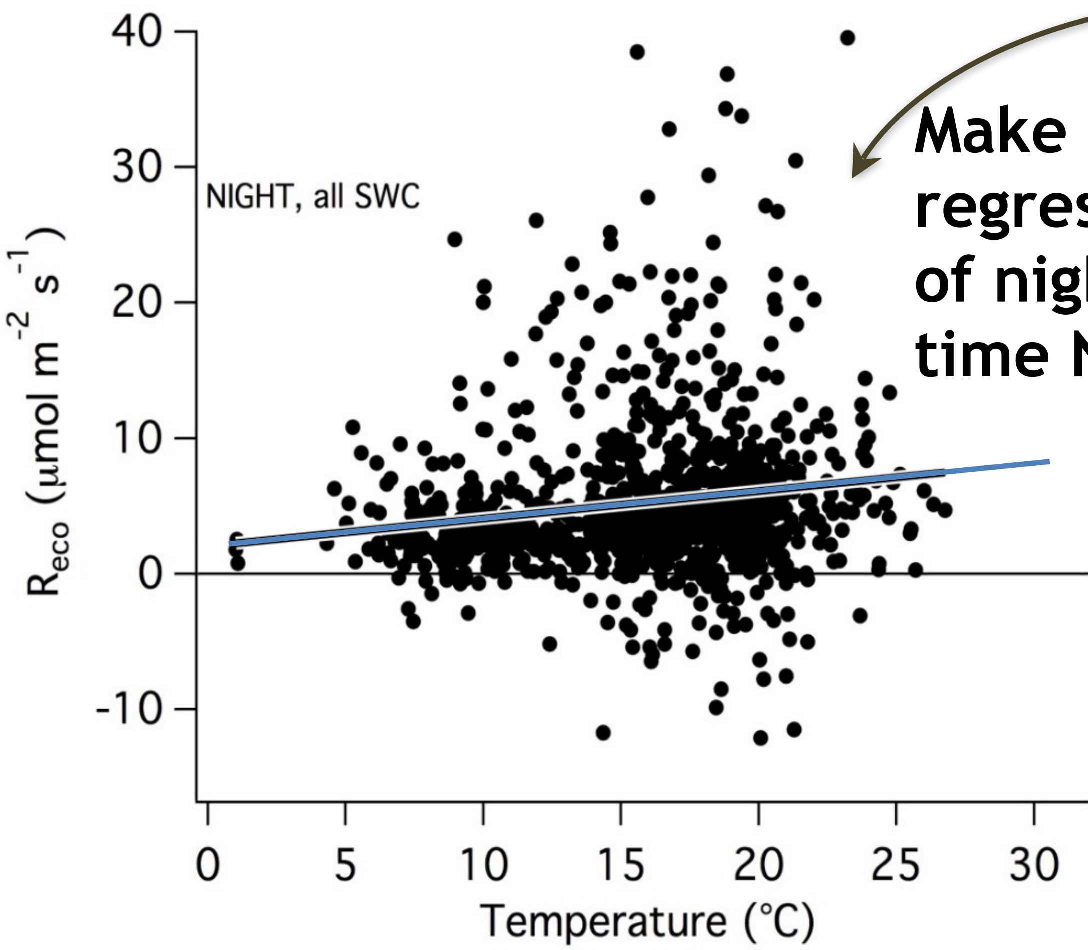
Ecosystem-scale OCS: ***What is GPP?***

Eddy Flux CO2 measures NET exchange: GPP + R_{eco}

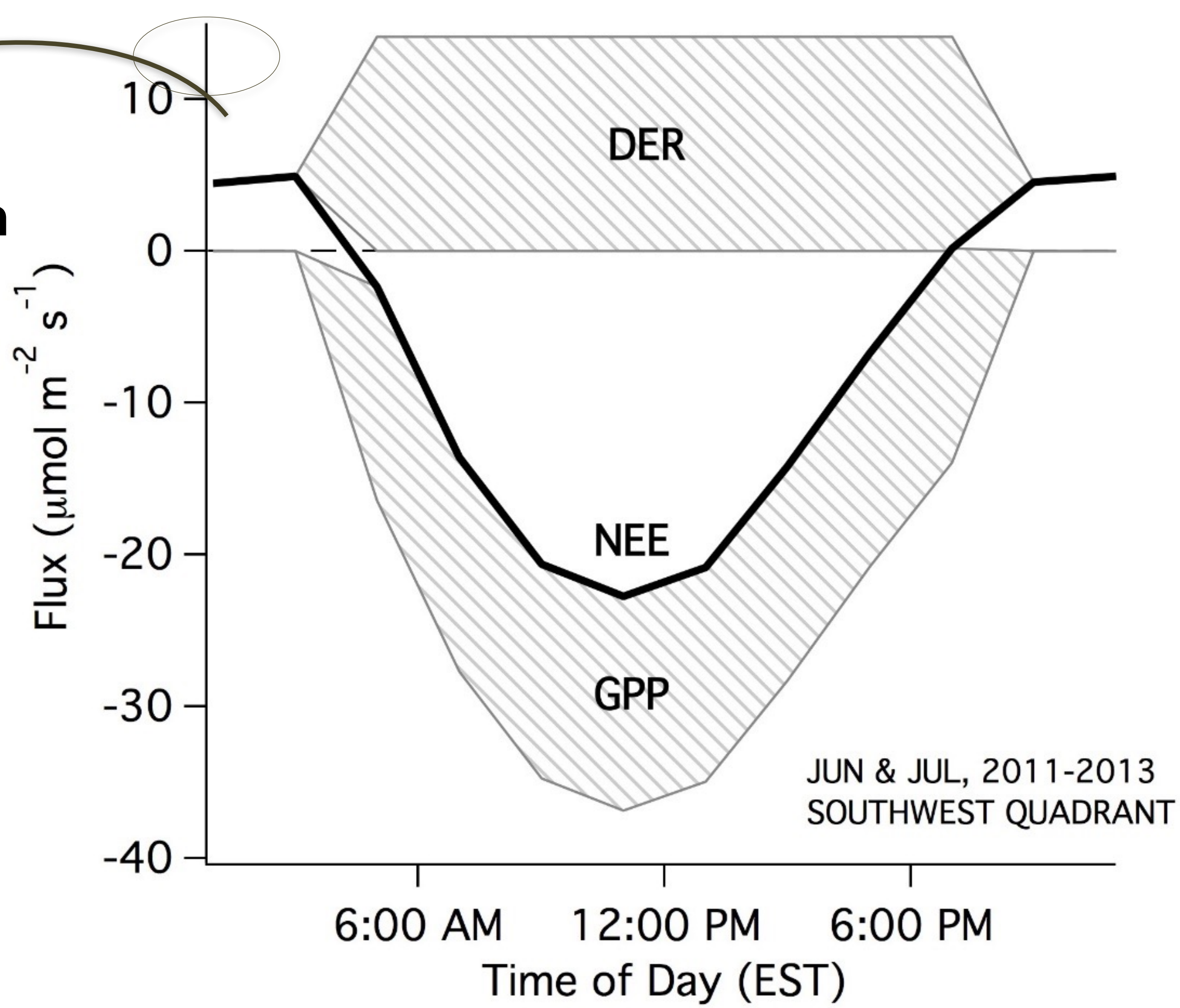
Standard Partitioning: Reichstein 2005

Daytime R_{eco} = night NEE vs soil Temp (1-2 week avg)

$GPP_{standard}$ = NEE - Daytime R_{eco}



Make regression of night-time NEE



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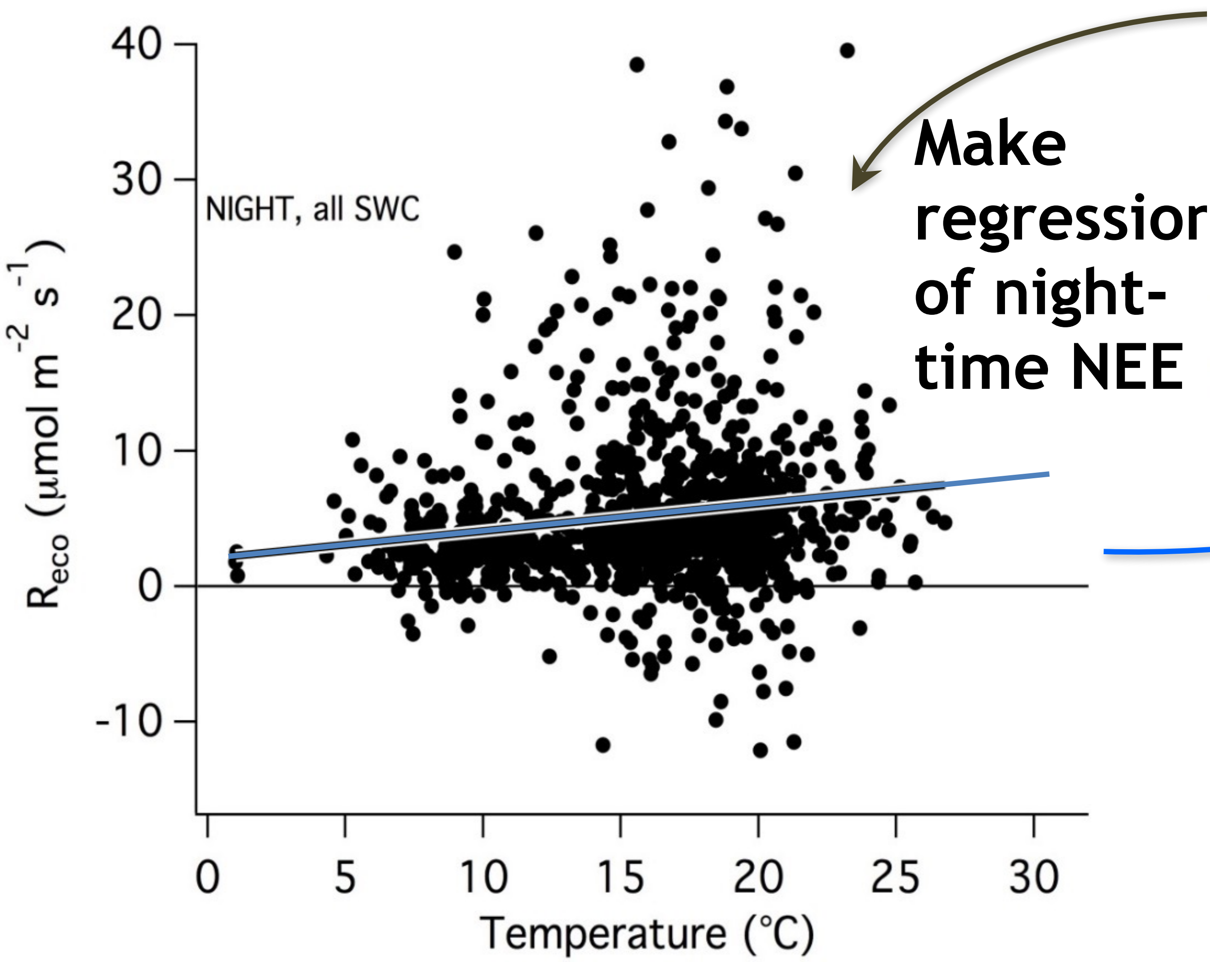

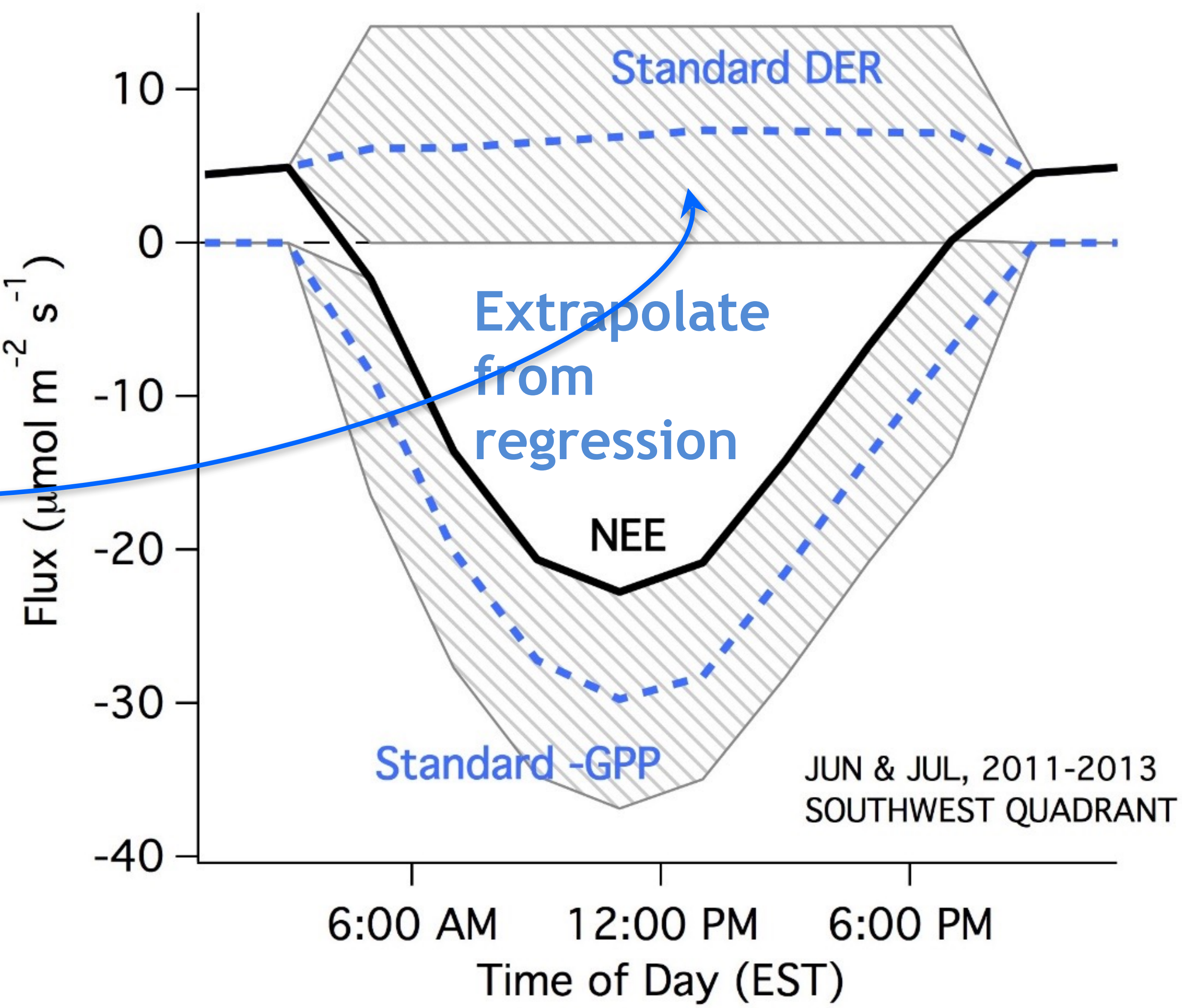

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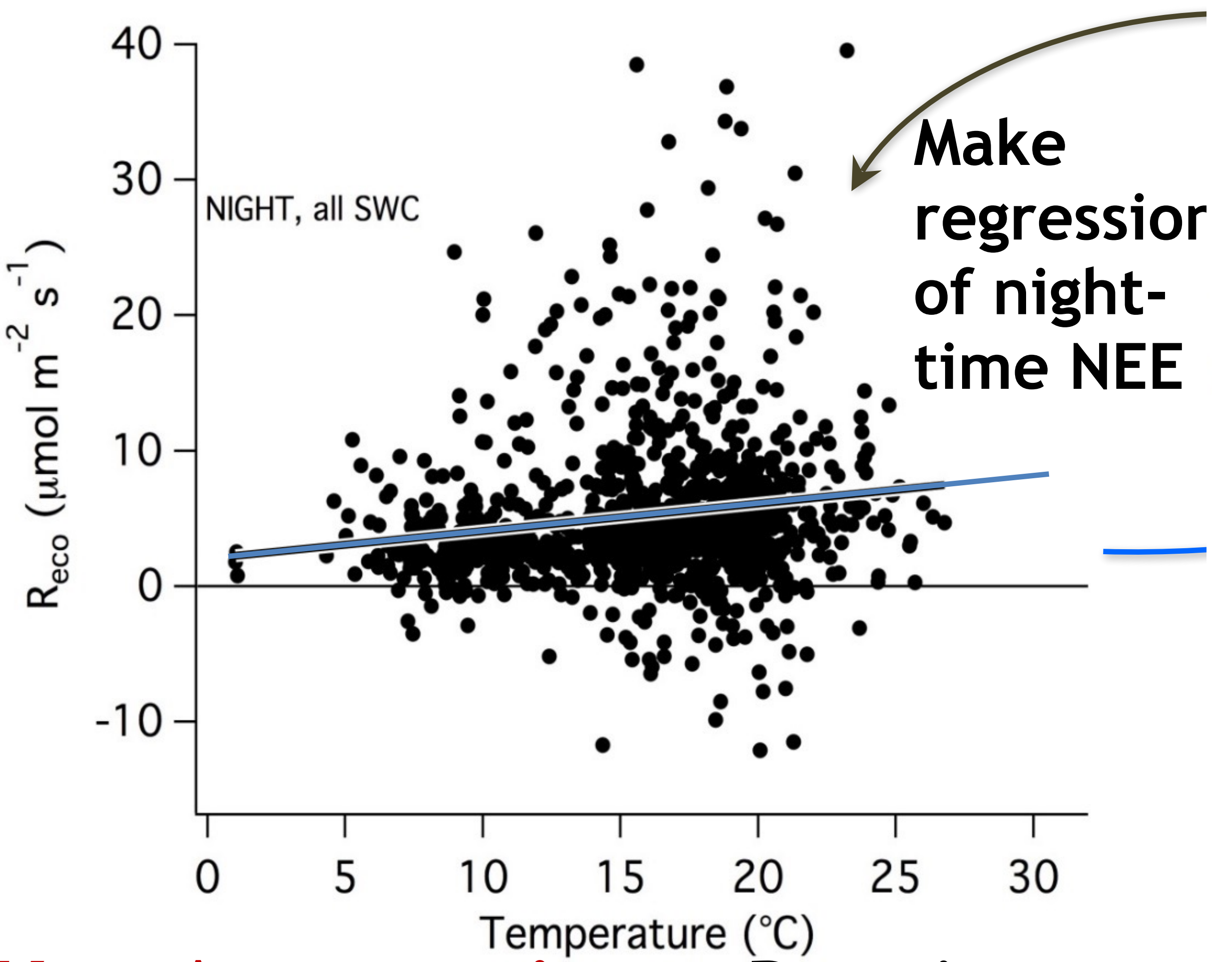

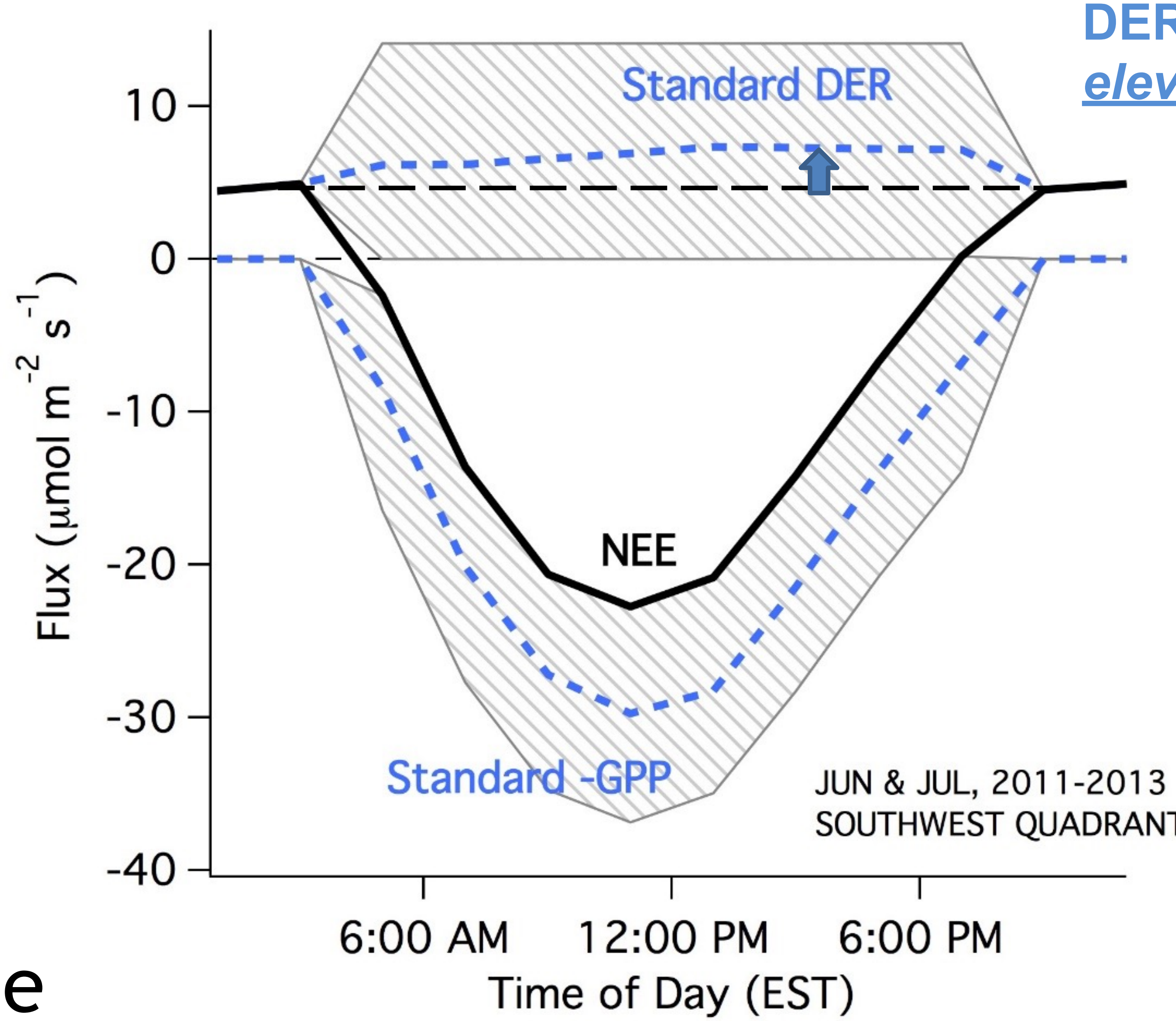

NOTE: DER is *elevated*

Key Assumption: Daytime physiology is like the nighttime