



# OCS OBSERVATIONS AND WHAT WE MAY LEARN FROM THEM

20 MARCH 2018 I MARC VON HOBE

*Thanks to Chenxi Qiu, Corinna Kloss, Stefanie Scharde, Felix Plöger, Christoph Brühl, Sinikka Lennartz, Stefanie Kremser*

Mitglied der Helmholtz-Gemeinschaft

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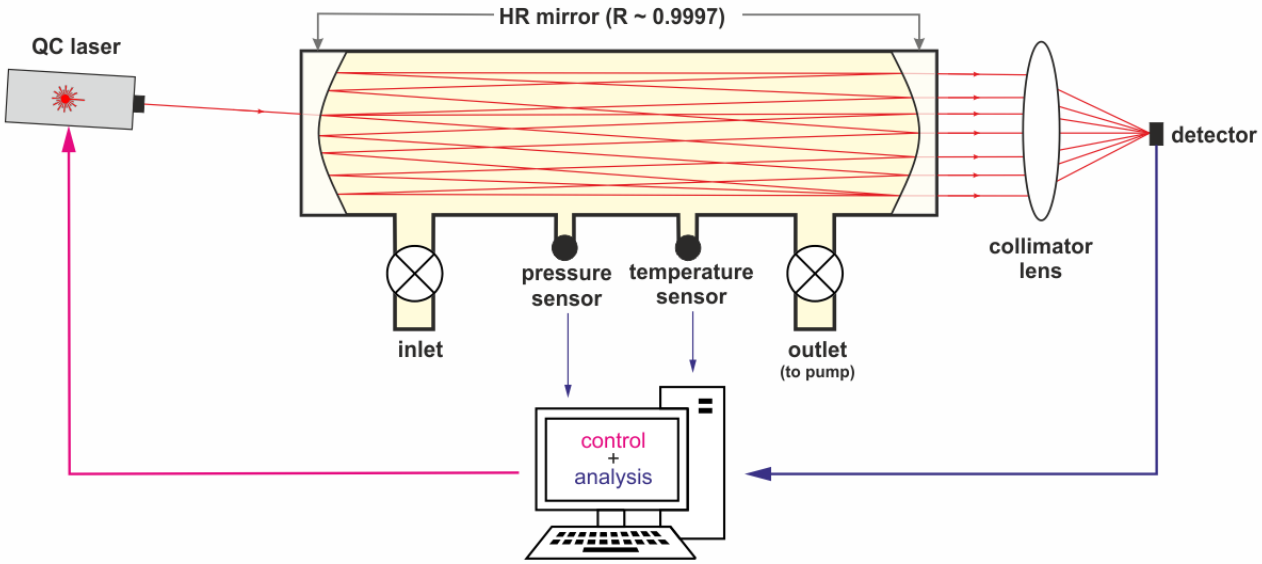
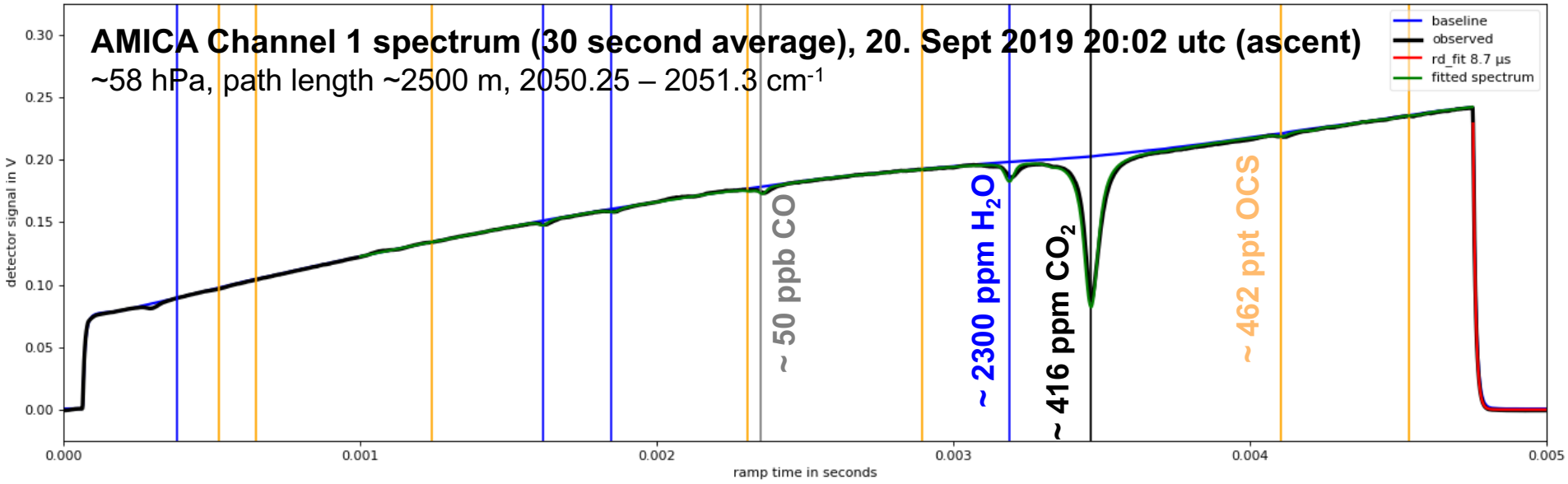
# 1. Observing OCS with ICOS

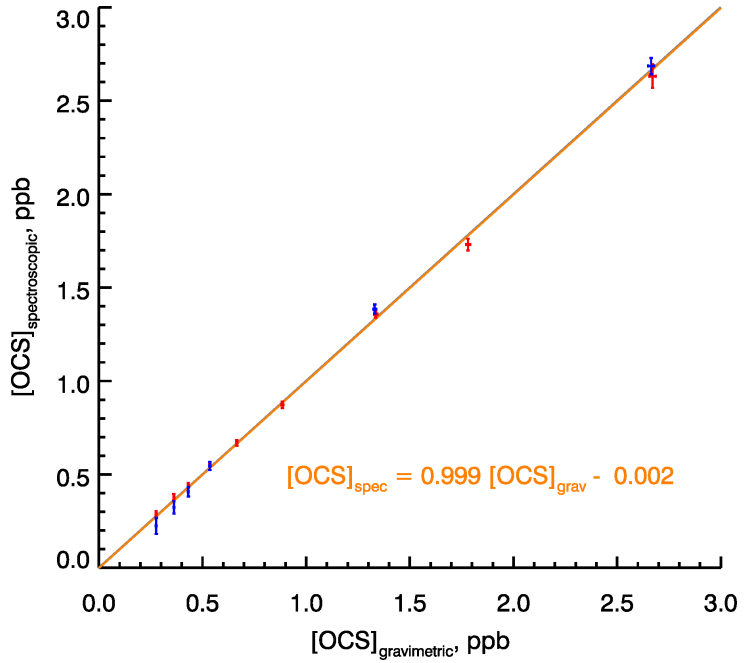
## Off-Axis Integrated Cavity Output Spectroscopy

- long path length
- robust to vibrations
- **continuous spectral scan** allows to measure multiple species and makes method “calibration free” once HITRAN line parameters have been established/validated
- extended number of simultaneously measured species
- wavelength range changeable: mirror/laser/detector combination

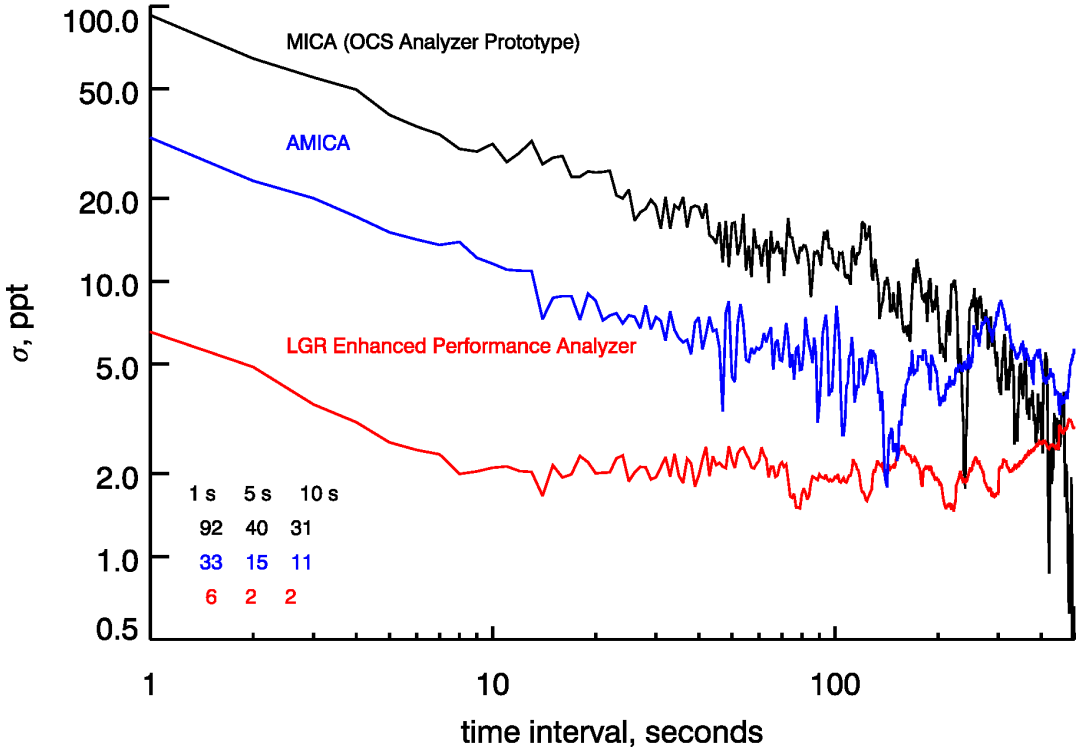


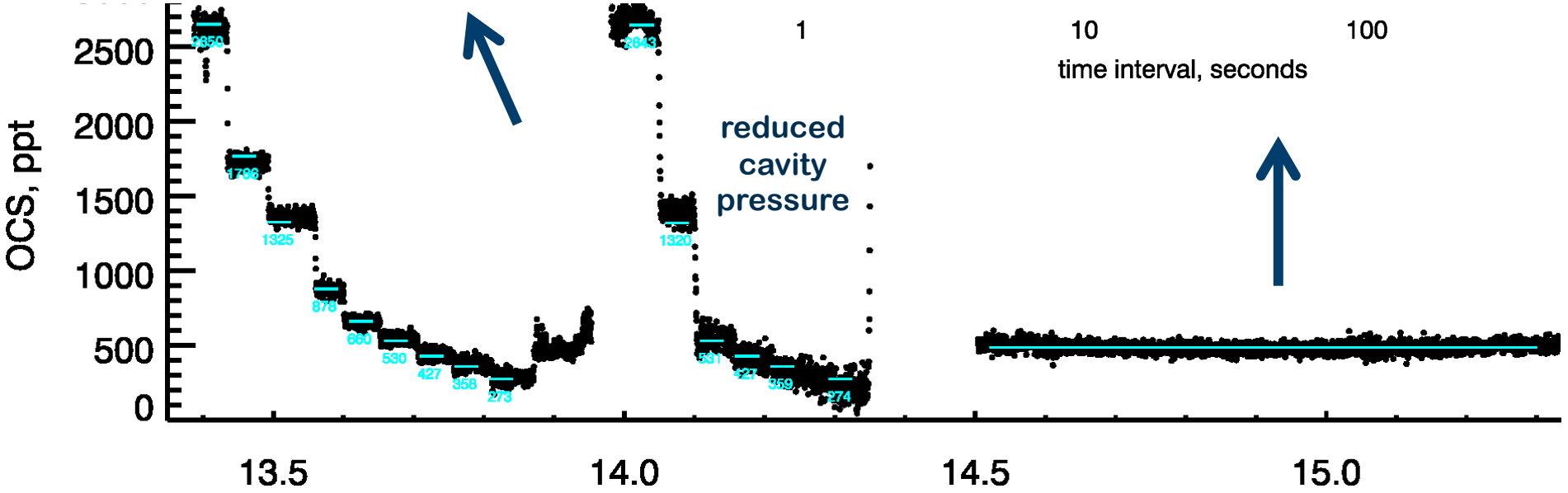



# 1. Observing OCS with ICOS




## Accuracy and Precision



# 1. Observing OCS with ICOS

## Our instruments 1: MICA

| | |
|---|---|
| 10 '12 – 04 '14 | Meteorological Tower FZ Jülich, 20 m inside canopy |
| 07/08 2014 | OASIS/RV Sonne I, Indian Ocean (*Lennartz et al., ACP, 2017*) |
| 10 2015 | ASTRA-OMZ/RV Sonne II, tropical E. Pacific (*Lennartz et al., OS, 2019*) |
| 07/08 2016 | Bhola Island, Bangladesh (Rice Paddy) |
| 09 2017 | Palau Staion, W. Pacific |
| 02 2018 | Tangaroa 1802, S. Pacific+ S. Ocean |
| 11 '18 – 03 '19 | CHINARE19, tropical/S. Pacific+ S. Ocean |
| 07/08 2019 | SCALE, S. Atlantic + S. Ocean |

# 1. Observing OCS with ICOS

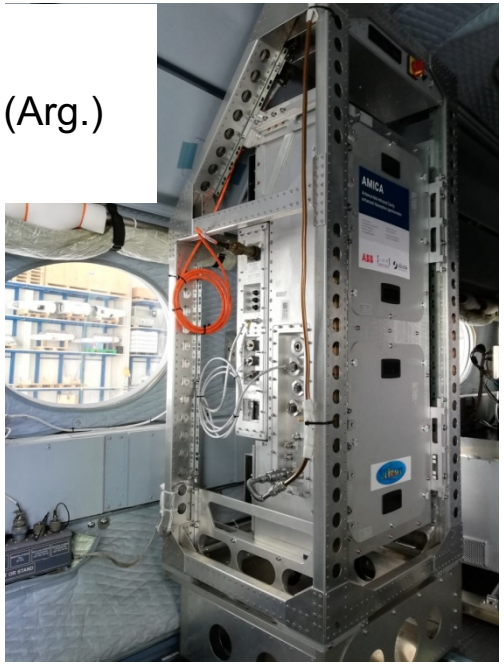
## Our instruments 2: AMICA


### Deployment on M55 Geophysica during StratoClim:

- 3 flights in Kalamata, Greece, Aug/Sep 2016
- 8 flights in Kathmandu, Nepal, Jul/Aug 2017

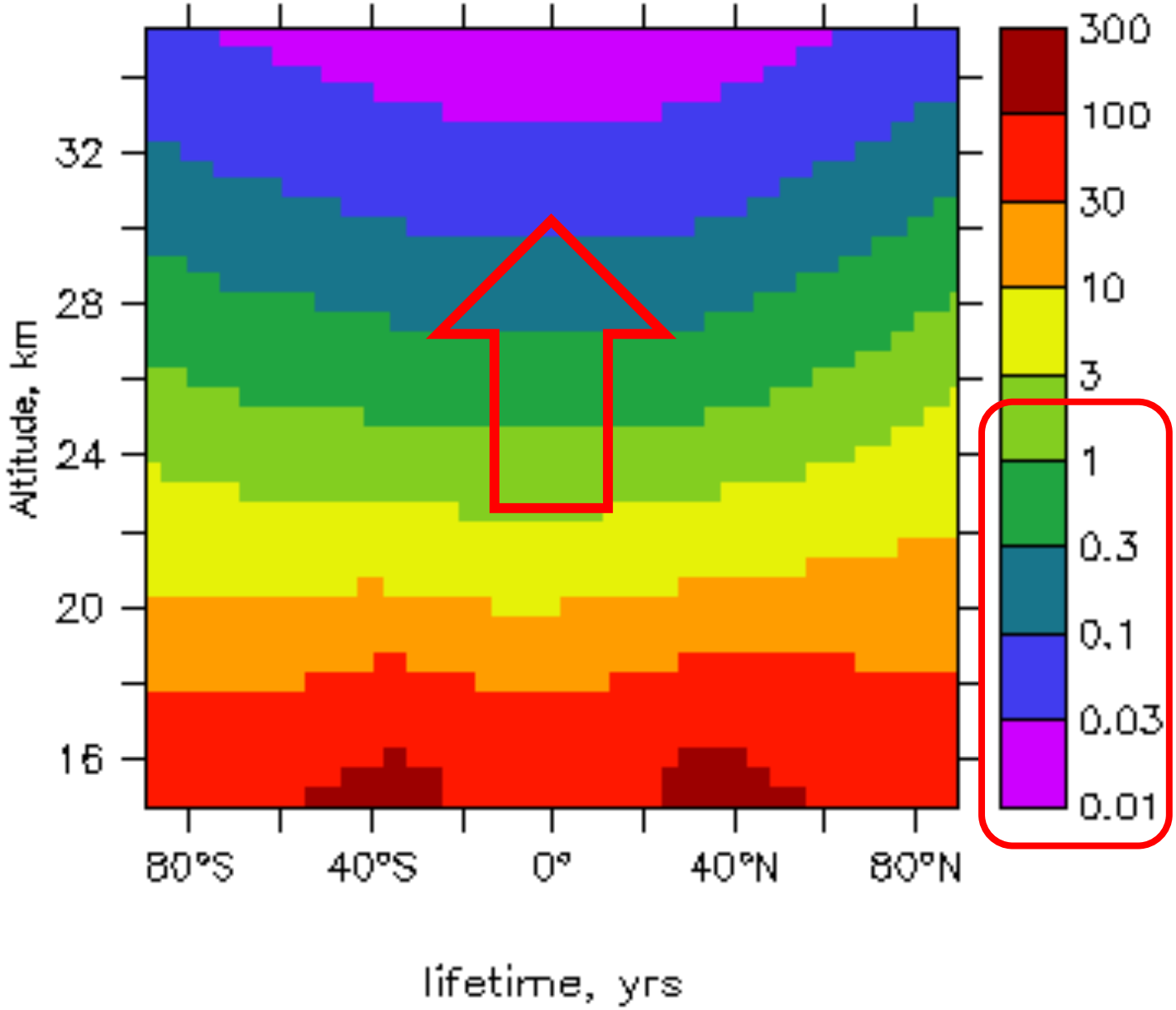
### Deployment on HALO during SOUTHTRAC Sep – Nov 2019:

- 10 transfer flights between Oberpfaffenhofen (Germany) and Rio Grande (Arg.)
- 14 local flights from Rio Grande (Argentina)



# 2. OCS in the stratosphere

## OCS lifetime with respect to



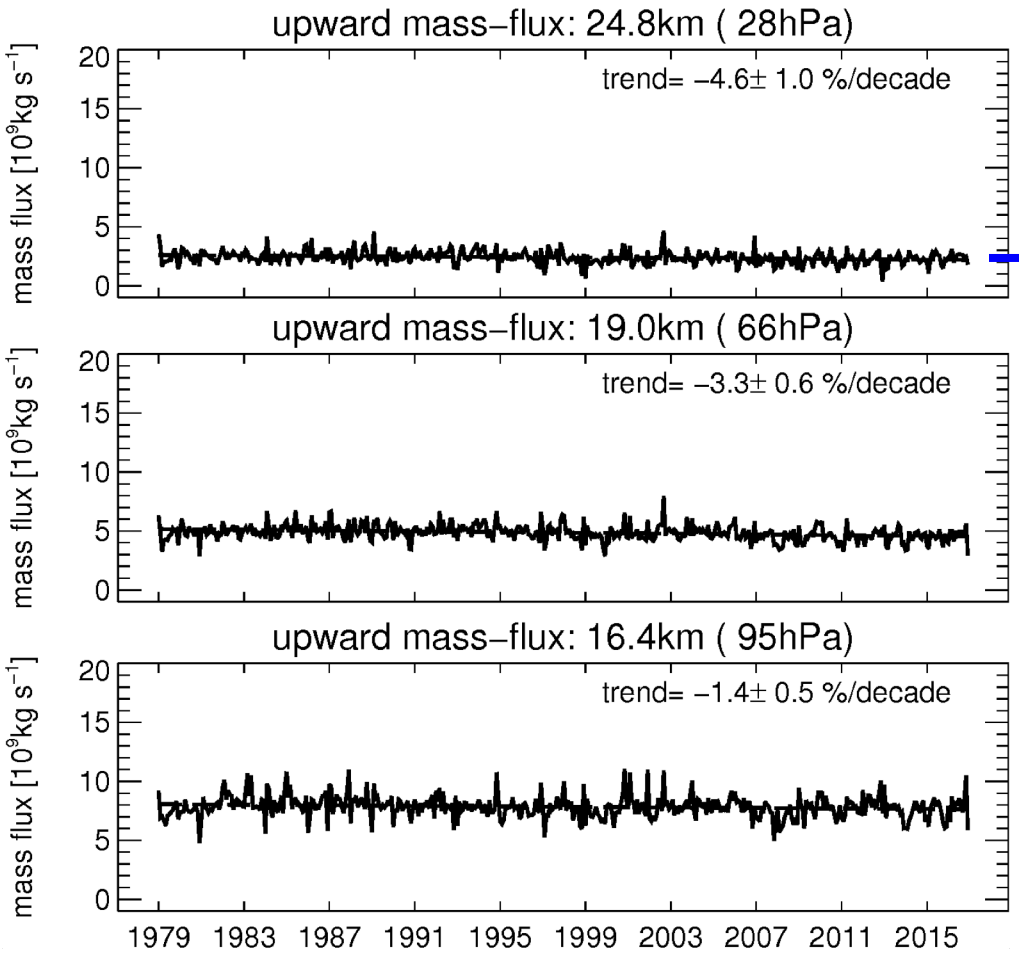

**OCS + *hν***

OCS + O

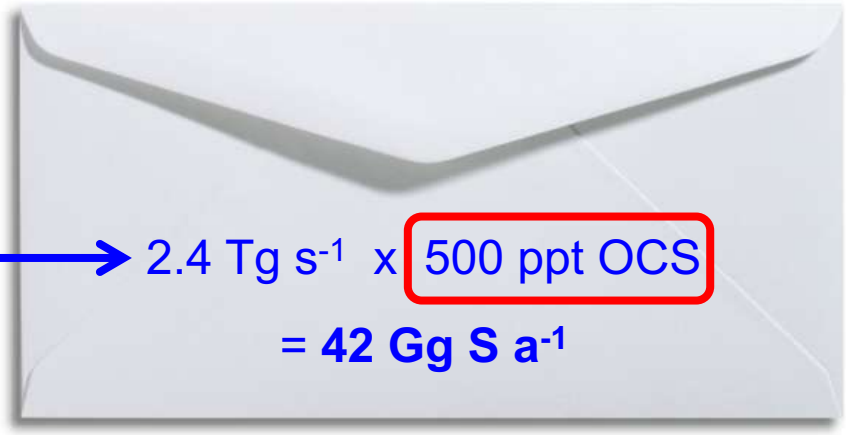
OCS + OH

*Figure courtesy of Christoph Brühl*

# 2. OCS in the stratosphere




***upward mass fluxes from ERA, courtesy of Felix Plöger***




**Previous estimates**:

*Barkley et al., 2008*, observations:
**34 – 66 Gg S $a^{-1}$**

*Krysztofiak et al., 2015*, observations:
**49 ± 14 Gg S $a^{-1}$**

*Brühl et al., 2012*, model:
**35 Gg S $a^{-1}$**

*Sheng et al., 2015*, model:
**40.7 Gg S $a^{-1}$**

**This may be more if there are large ground sources associated with efficient vertical transport in the tropics**

# 2. OCS in the stratosphere

**Well characterized by satellite data (e.g. ACE FTS and ENVISAT MIPAS) and well understood in models (e.g. Brühl et al., 2012, Sheng et al., 2015)**

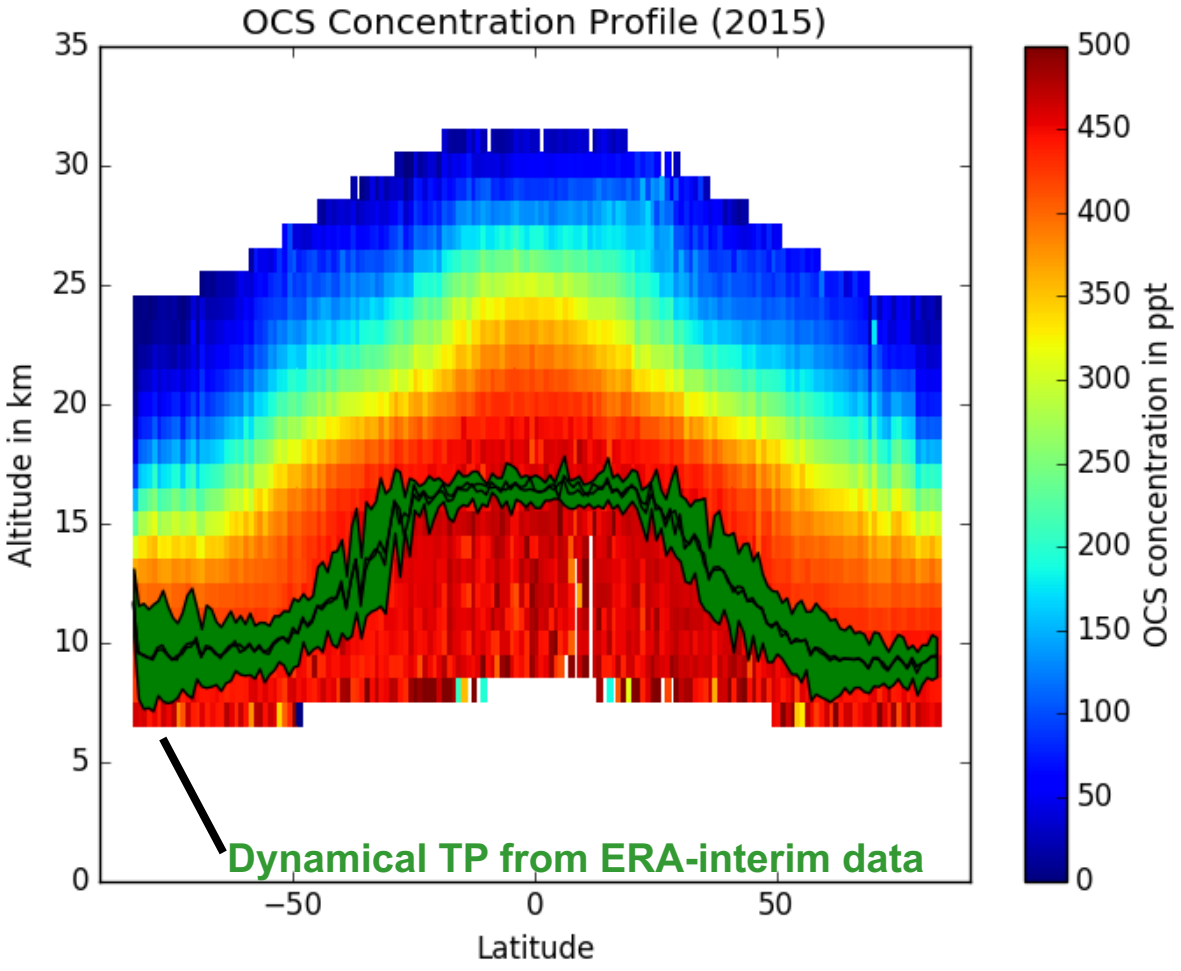



*Figure updated from*
*Kloss et al., EGU 2015 +*
*Kloss et al., SSiRC workshop, 2016*

Global integration:
**280 Gg S**

Excellent agreement
with Sheng et al. 2015:
**283 Gg S**

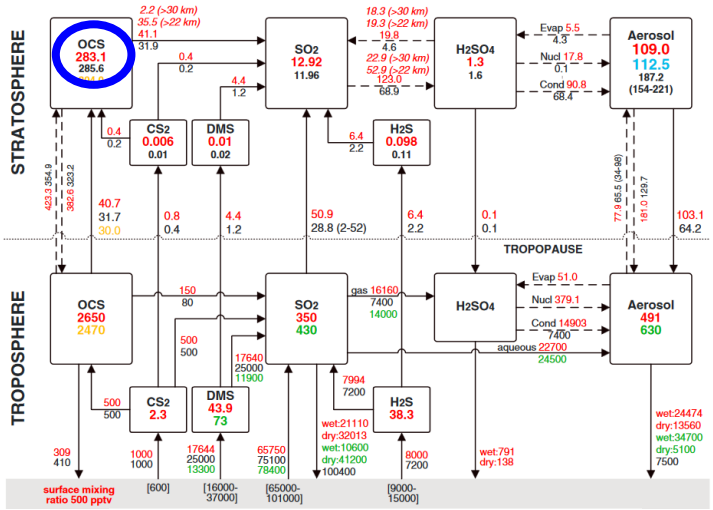


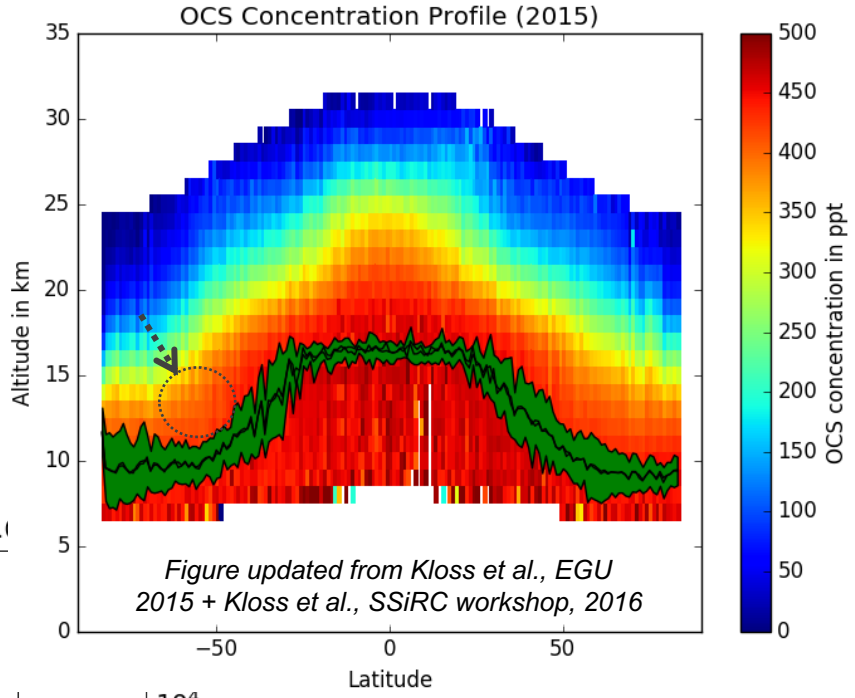

*Figure from Sheng et al., 2015*

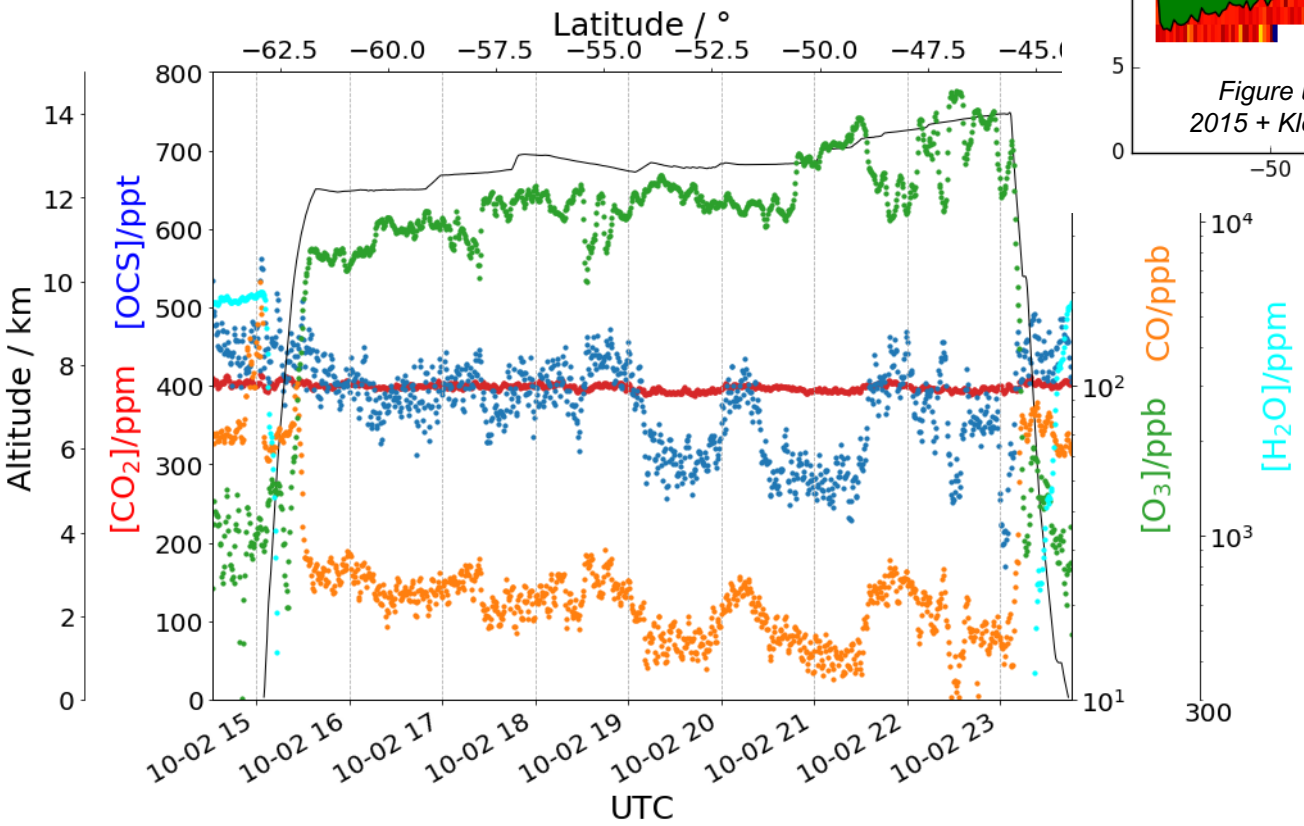
# 2. OCS in the stratosphere

**AMICA measurements during SOUTHTRAC**

**OCS depletion in aged air masses at high Southern latitudes**

**→ Correlations with age of air, age fractions and other stratospheric tracers are currently being investigated (Chenxi Qiu)**

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# 3. OCS in the troposphere

## Old and new hypotheses on the global budget

**Table 1.** Global Integrated COS Fluxes (Gg S $a^{-1}$) of Different Budget Estimations

| | *Kettle et al.* [2002][a] | *Montzka et al.* [2007] | *Suntharalingam et al.* [2008][b] | *Berry et al.* [2013][c] | Kettle et al. Modified[d] |
|---|---|---|---|---|---|
| Anthropogenic direct and indirect | 90–266 (177) | 90–266 | 180 | 180 | 177 |
| Biomass burning | 11–64 (42) | 68–144 | 42 | 136 | 42 |
| Ocean direct/indirect | 39–520 (278) | 39–520 | 230 | 876 | 992 |
| Other sources (wetland, soil) | | 13–119 | | | |
| Uptake by plants | 210–270 (238) | 730–1500 | 490 | 738 | 952 |
| Uptake by soil | 74–180 (127) | 74–180 | 127 | 355 | 127 |
| Loss by reaction with OH | 82–110 (116) | 82–110 | 82–110 | 101 | 116 |

[a]Values in parentheses were used for the first EMAC simulation.
[b]Kettle et al. modified, with excess of sink over sources.
[c]Fluxes used for the PCTM simulation presented here.
[d]Fluxes used for the second EMAC simulation. Plant uptake increased by a factor of 4, balanced by increased oceanic emissions in the latitude band 20°S–20°N, similar as in *Berry et al.* [2013].

***Table from Glatthor et al., 2015***

# 3. OCS in the troposphere

## Old and new hypotheses on the global budget

*"Taking 1%/yr as an upper limit for a statistical trend in either direction limits the source/sink imbalance to about ± 50 Gg/yr."*

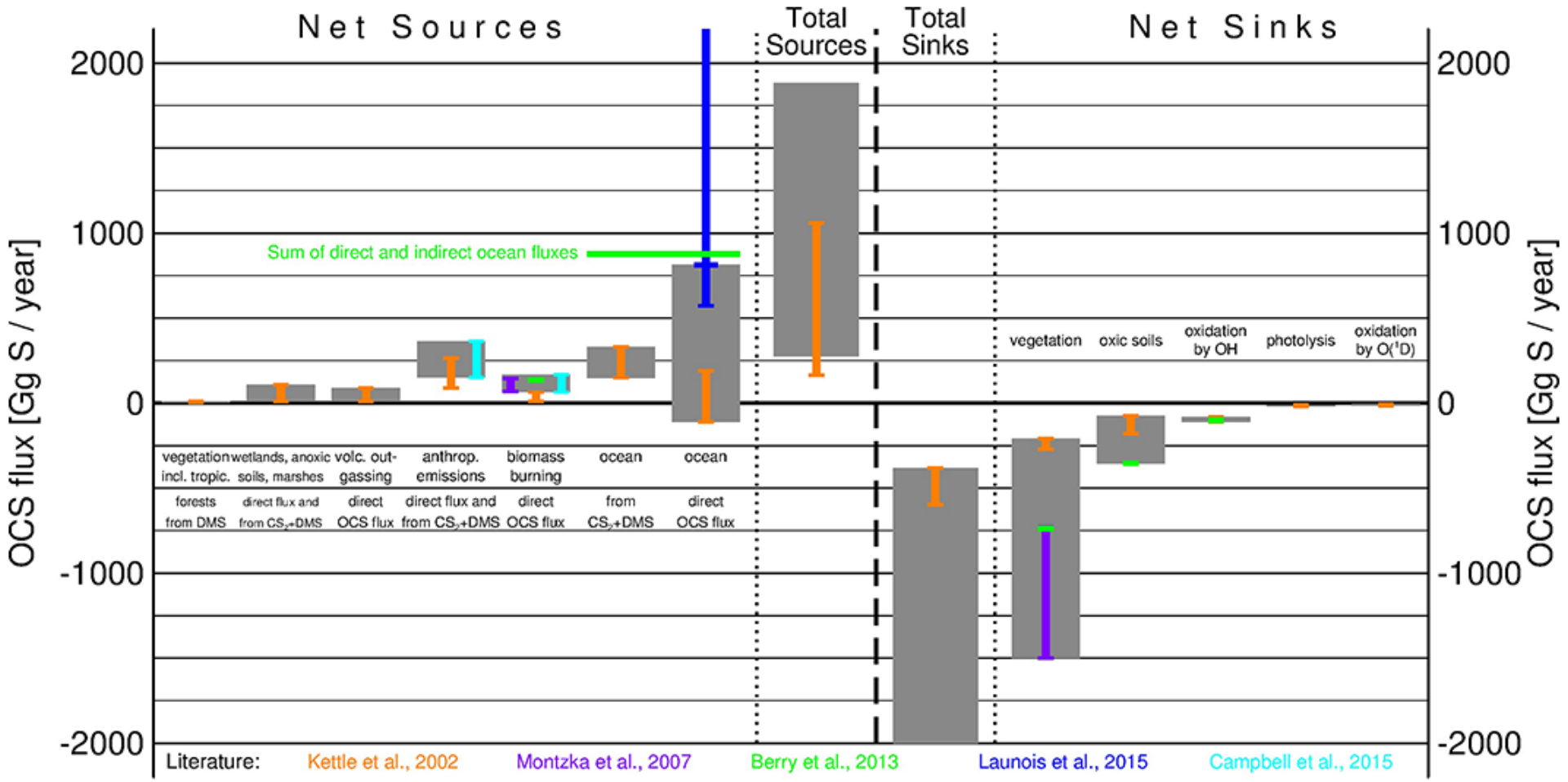
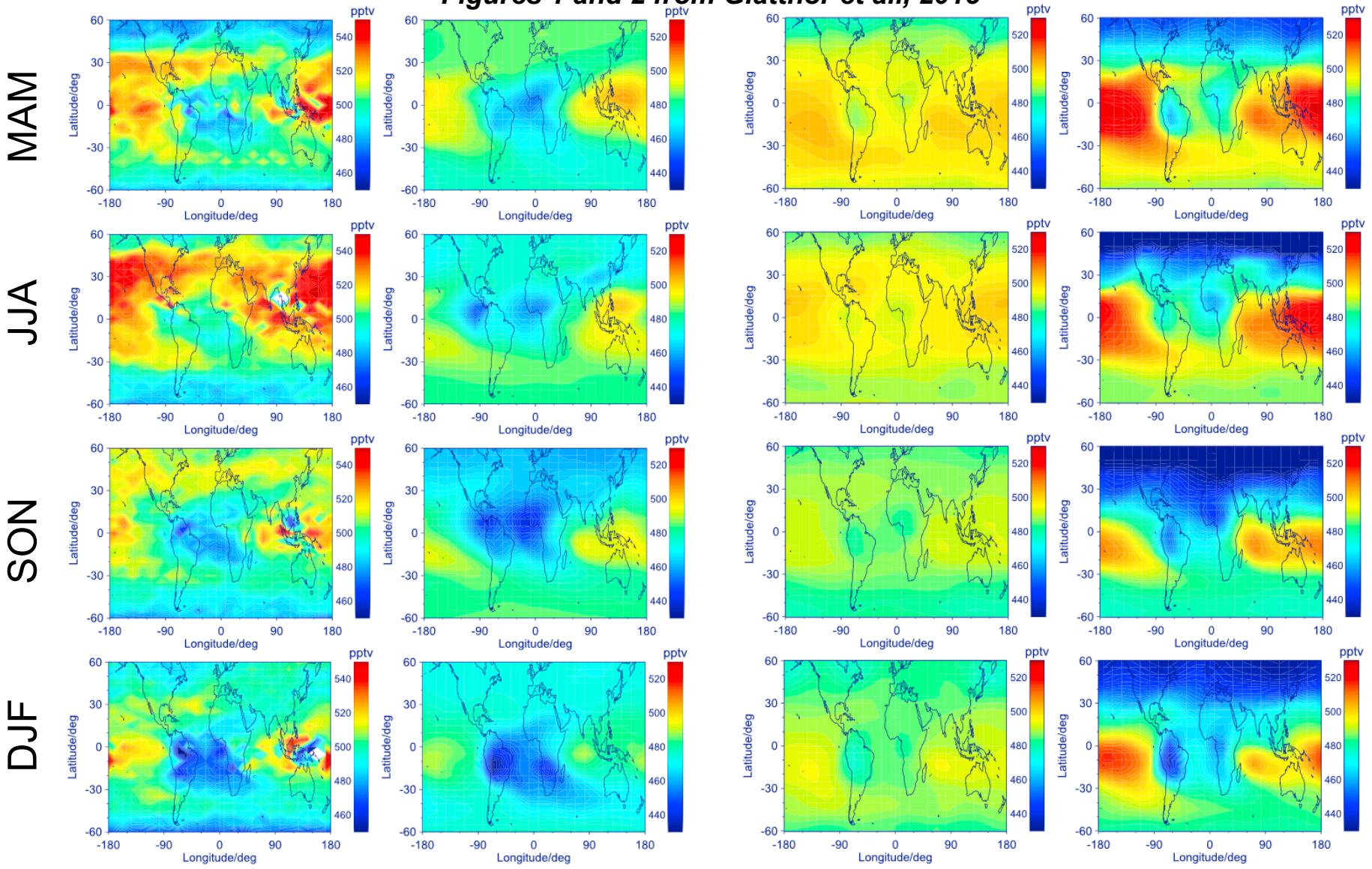



*Figure from Kremser et al., 2016*

# 3. OCS in the troposphere

## The „Tropical missing source“

***Figures 1 and 2 from Glatthor et al., 2015***



# 3. OCS in the troposphere

**OCS in the surface ocean is well understood**

**→ concentrations and fluxes can be well modelled**

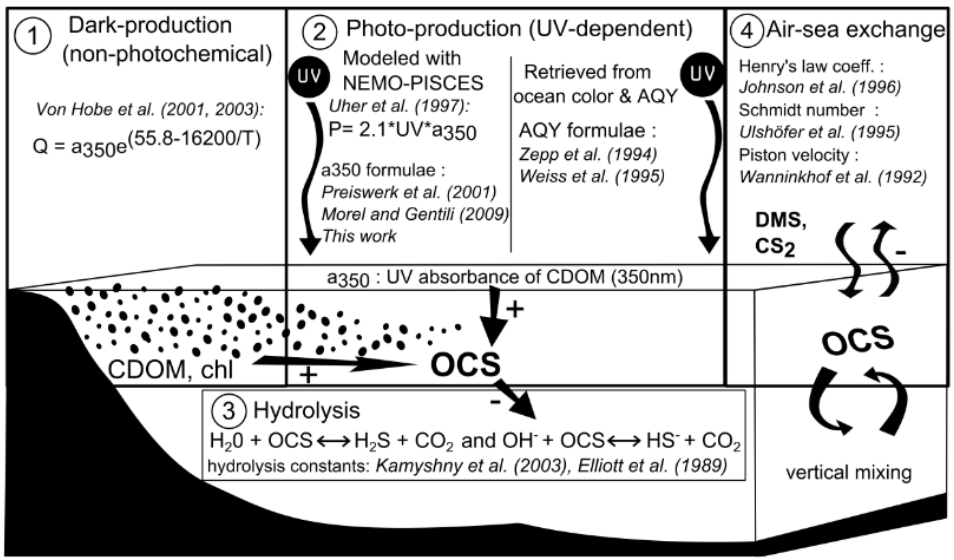
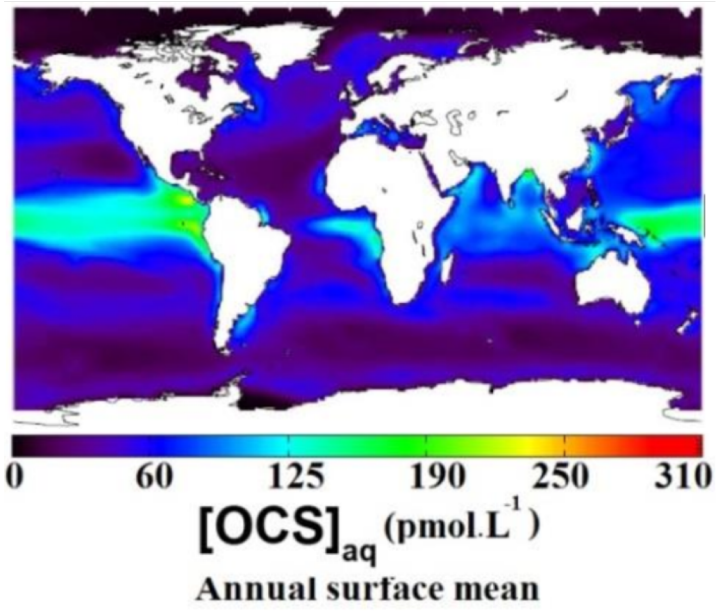


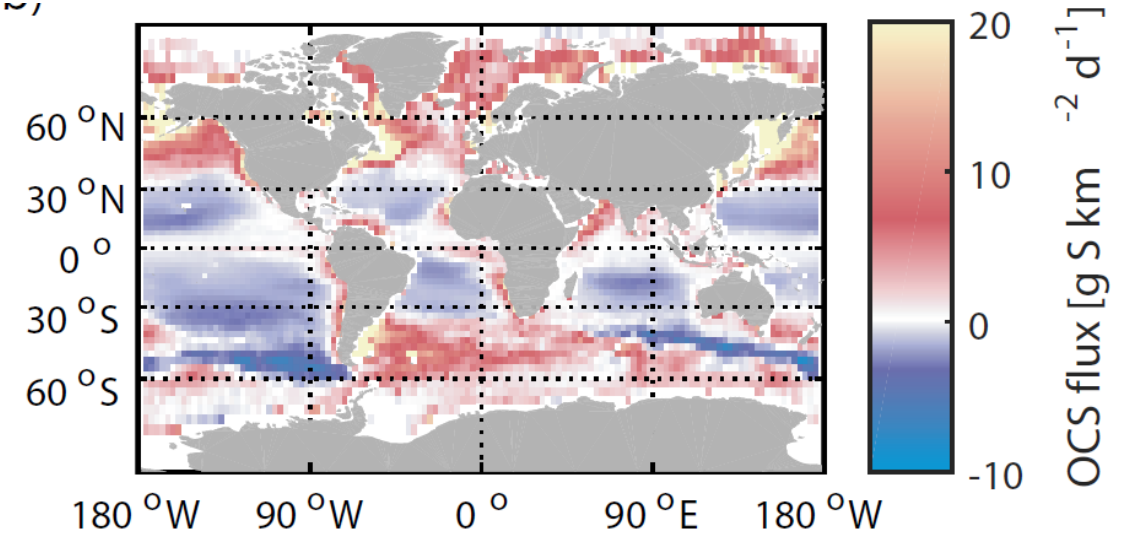

*Fig 1 from Launois et al., ACP, 2015*

*Launois et al., ACP, 2015*



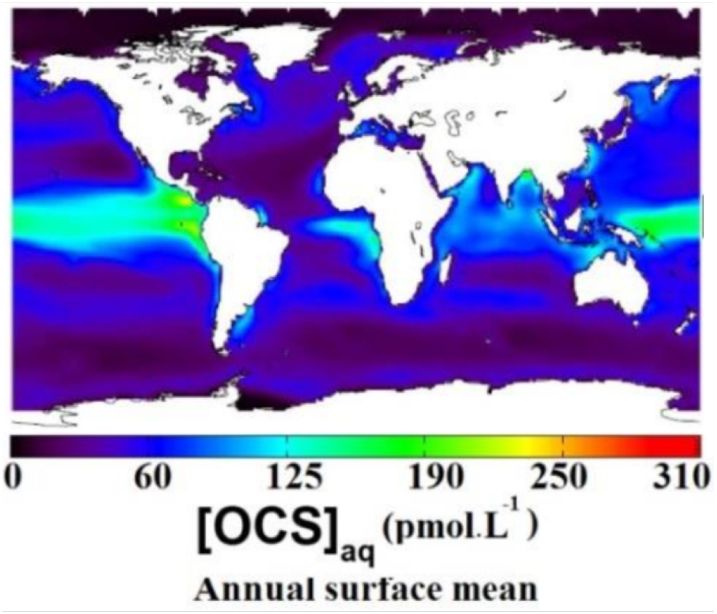

→ 813 Gg S $a^{-1}$

*Lennartz et al., ACP, 2017*




→ 130 Gg S $a^{-1}$

# 3. OCS in the troposphere

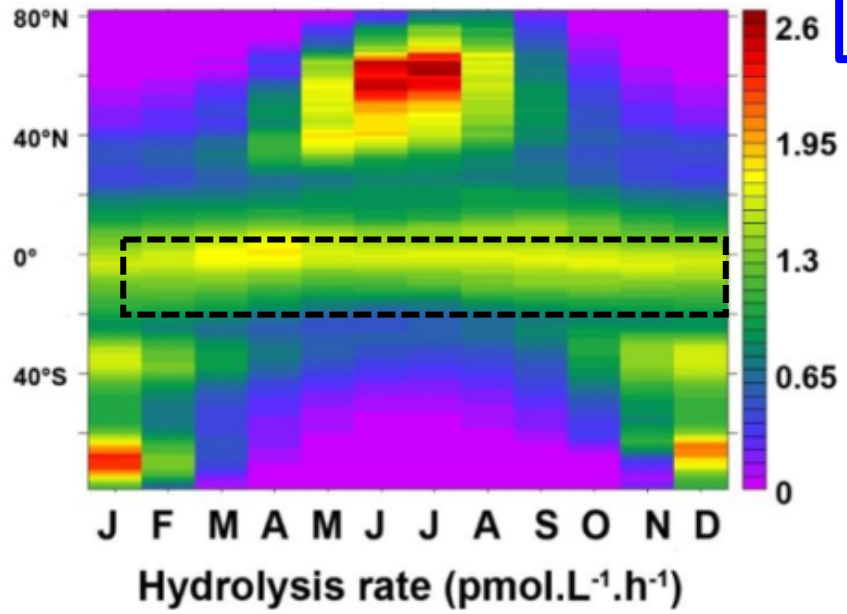



**Particularly high OCS concentrations and emissions in the tropics**

③ Hydrolysis

$H_2O + OCS \leftrightarrow H_2S + CO_2$ and $OH^- + OCS \leftrightarrow HS^- + CO_2$

hydrolysis constants: *Kamyshny et al. (2003), Elliott et al. (1989)*




→ 1st order in OCS: Hydr. Rate = $k_h$ [OCS]

**Tropics:**

**SST ~ 27 °C → $k_h$ ~ 0.15 $h^{-1}$**

**$[OCS]_{Launois}$ ~ 130 pmol $L^{-1}$**

**$k_h$ [OCS] = 20 pmol $L^{-1}$ $h^{-1}$**

# 3. OCS in the troposphere

Marine carbonyl sulfide (OCS) and carbon disulfide ($CS_2$): a compilation of measurements in seawater and the marine boundary layer

**Review status**
This discussion paper is a preprint. A revision of the manuscript is under review for the journal Earth System Science Data (ESSD).

**Sinikka T. Lennartz et al.**

## Data sets

**A database for carbonyl sulfide (OCS) and carbon disulfide (CS2) in seawater and marine boundary layer.**
S. T. Lennartz, C. A. Marandino, M. von Hobe, M. O. Andreae, K. Aranami, E. L. Atlas, M. Berkelhammer, H. Bingemer, D. Booge, G. A. Cutter, P. Cortes, S. Kremser, C. S. Law, A. Marriner, R. Simo, B. Quack, G. Uher, H. Xie, and X. Xu
https://doi.pangaea.de/10.1594/PANGAEA.905430

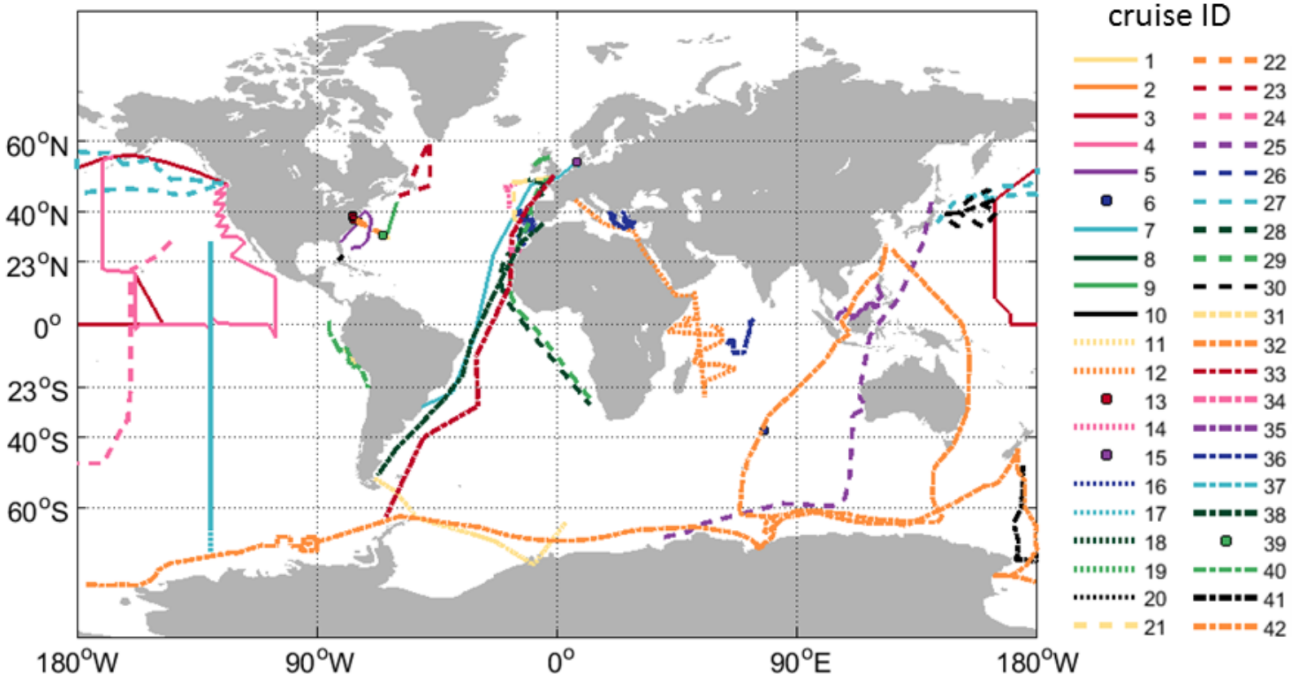
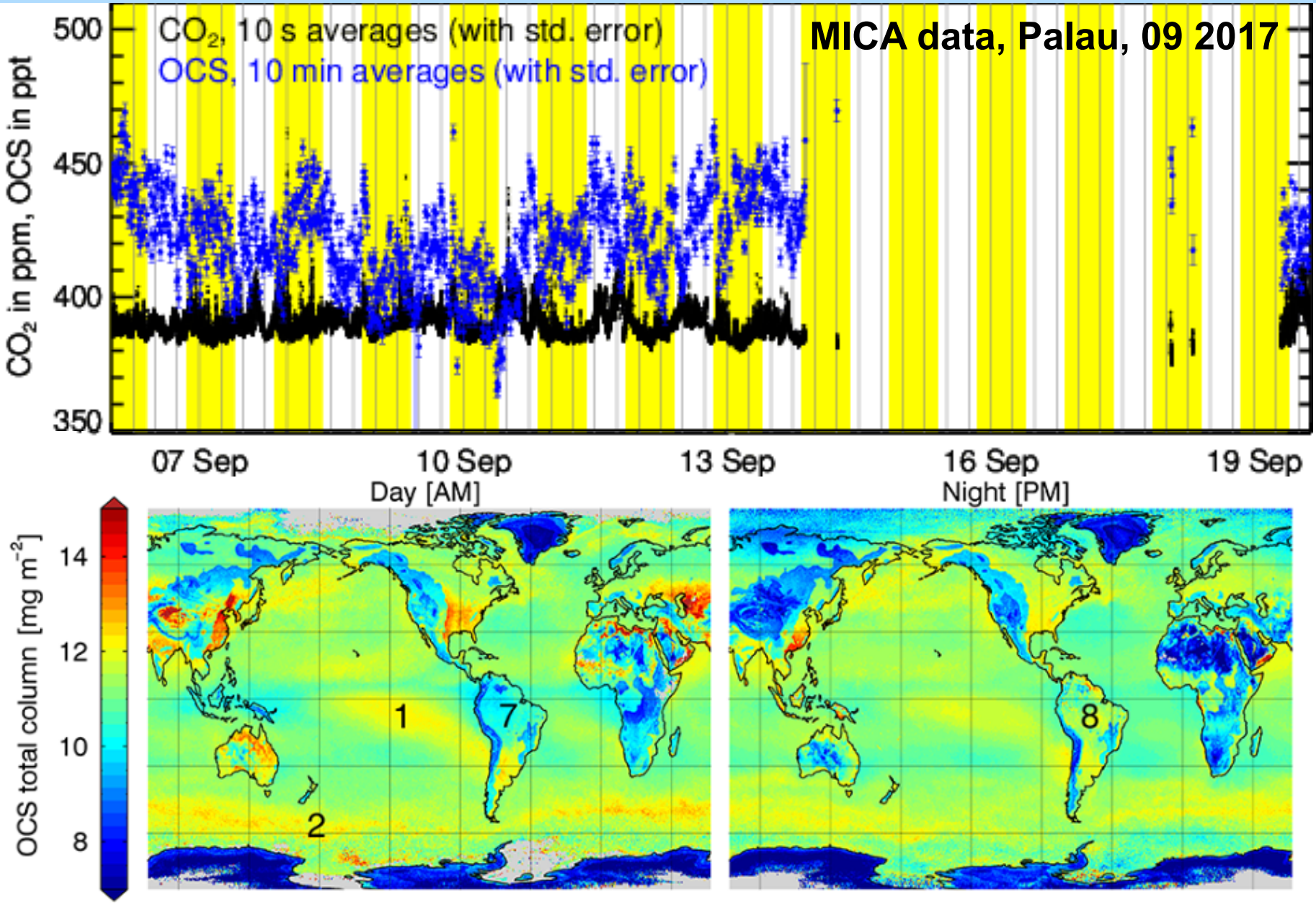



**Figure 1: Tracks of all cruises with OCS and/or $CS_2$ measurements included in the database (points depict stationary measurements). Colour coding and line styles indicate the cruise ID (compare Tab. 1).**

*So, based on the evidence available to date, I'd go with the conclusion from Lennartz et al., ACP, 2017:*

**Oceanic emissions unlikely to account for the missing source of atmospheric OCS**

# 3. OCS in the troposphere




**Fast retrievals of tropospheric carbonyl sulfide with IASI *(Vincent and Dudhia, ACP, 2017)***

# 3. OCS in the troposphere

## Estimate of carbonyl sulfide tropical oceanic surface fluxes using Aura Tropospheric Emission Spectrometer observations (*Kuai, et al., 2015*):

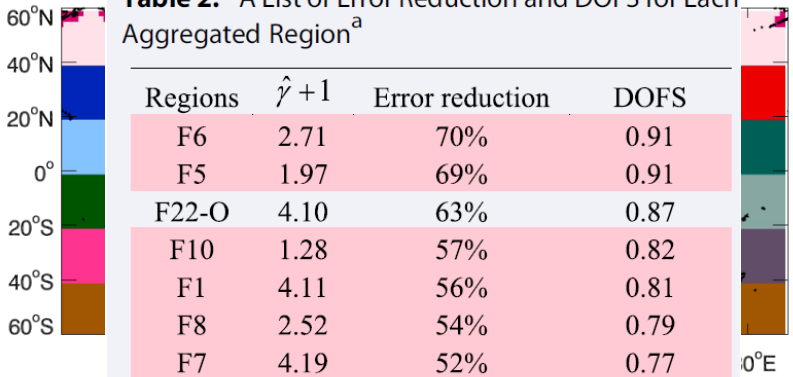
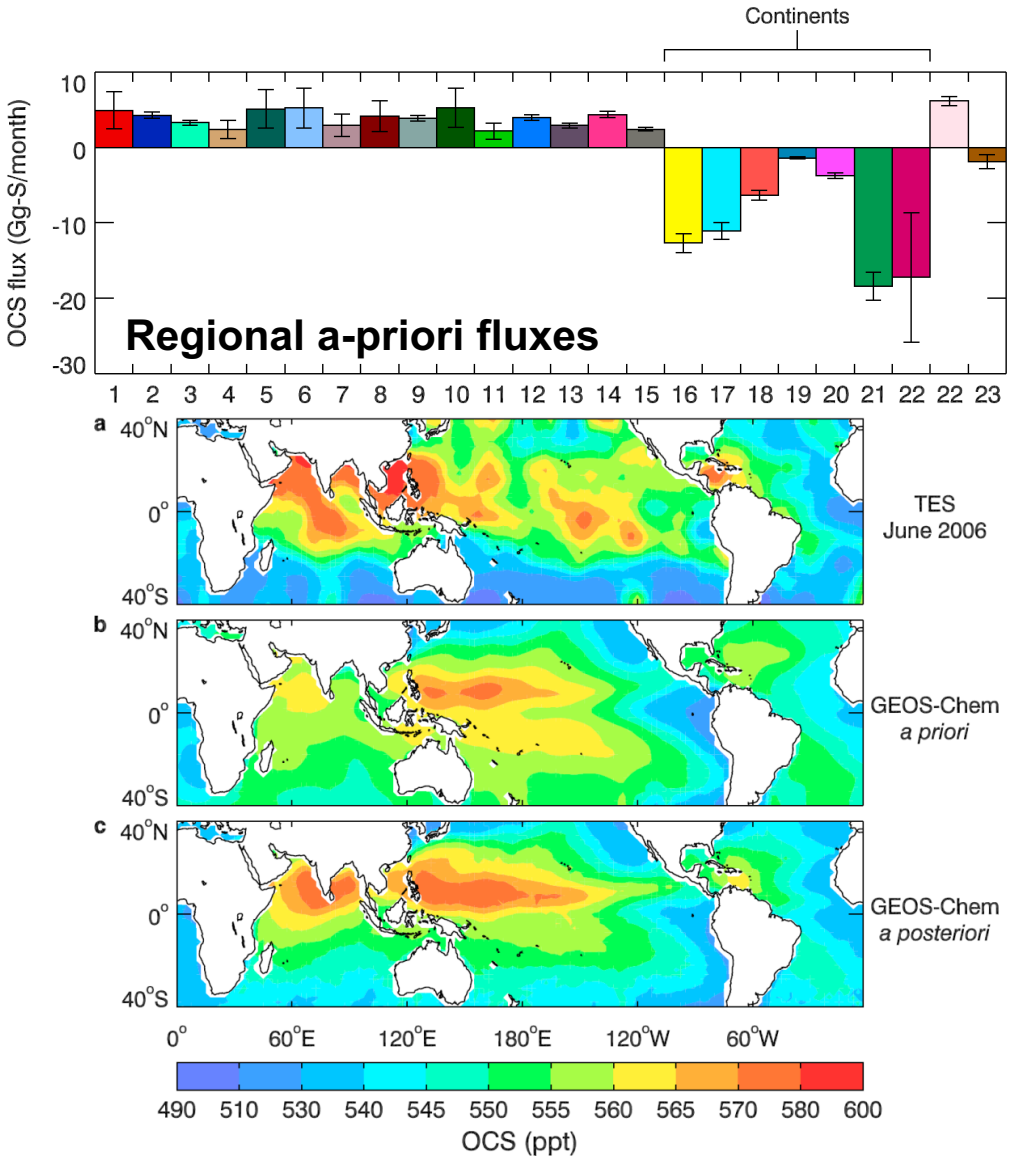



**Table 2.** A List of Error Reduction and DOFS for Each Aggregated Region[a]

| Regions | $\hat{\gamma}+1$ | Error reduction | DOFS |
|---|---|---|---|
| F6 | 2.71 | 70% | 0.91 |
| F5 | 1.97 | 69% | 0.91 |
| F22-O | 4.10 | 63% | 0.87 |
| F10 | 1.28 | 57% | 0.82 |
| F1 | 4.11 | 56% | 0.81 |
| F8 | 2.52 | 54% | 0.79 |
| F7 | 4.19 | 52% | 0.77 |
| F21 | 0.38 | 39% | 0.63 |
| F4 | 5.95 | 36% | 0.59 |
| F11 | 1.07 | 29% | 0.50 |
| F16 | 1.28 | 25% | 0.44 |
| F18 | 0.56 | 19% | 0.35 |
| F17 | 0.09 | 15% | 0.28 |
| F3 | 1.10 | 7% | 0.14 |
| F20 | 0.58 | 6% | 0.12 |
| F9 | 0.48 | 6% | 0.12 |
| F23 | 7.91 | 3% | 0.06 |
| F2 | 0.98 | 3% | 0.06 |
| F12 | 0.00 | 1% | 0.03 |
| F14 | 0.17 | 1% | 0.02 |
| F13 | 0.20 | 1% | 0.02 |
| F19 | 1.08 | 1% | 0.01 |
| F15 | 0.47 | 1% | 0.01 |
| F22-L | 0.79 | 0% | 0.01 |

[a]The red cells are tropical ocean regions within ±20° of the equator.



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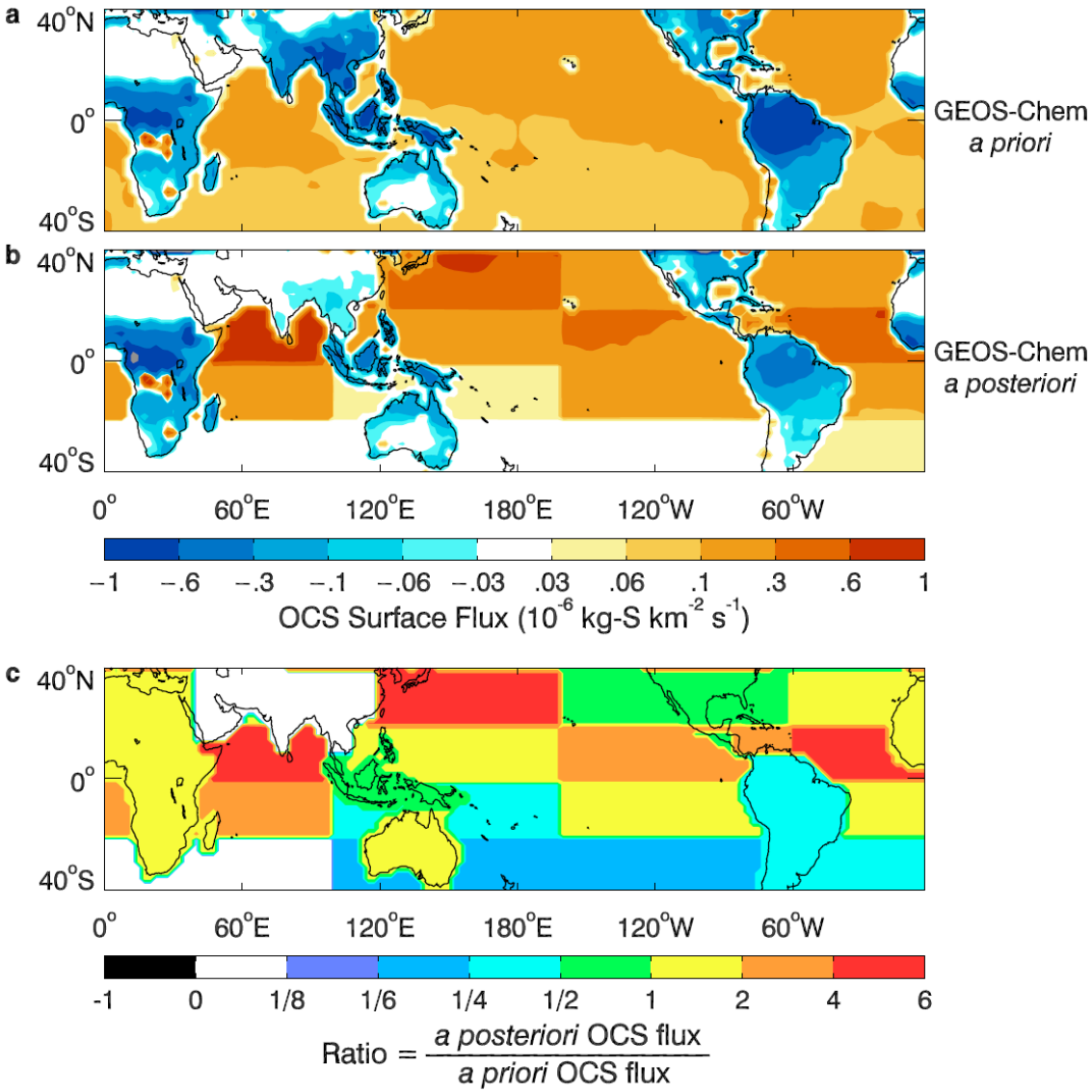



**Sign of the flux is fixed!!!**

→ **Continents are net sinks by default**

→ **inversion must find extra sources in the oceans**

"The posterior flux estimates derived by the TES data in conjunction with the GEOS-Chem atmospheric transport model support the Berry et al. [2013] hypothesis and furthermore suggest that the **strongest fluxes originate from the west Pacific and northern Indian Ocean near Southeast Asia."**

# 3. OCS in the troposphere

## What about anthropogenic sources?

***Campbell et al., 2015*: Larger anthropogenic OCS source than in the Kettle et al. climatology, particularly from anthropogenic $CS_2$**

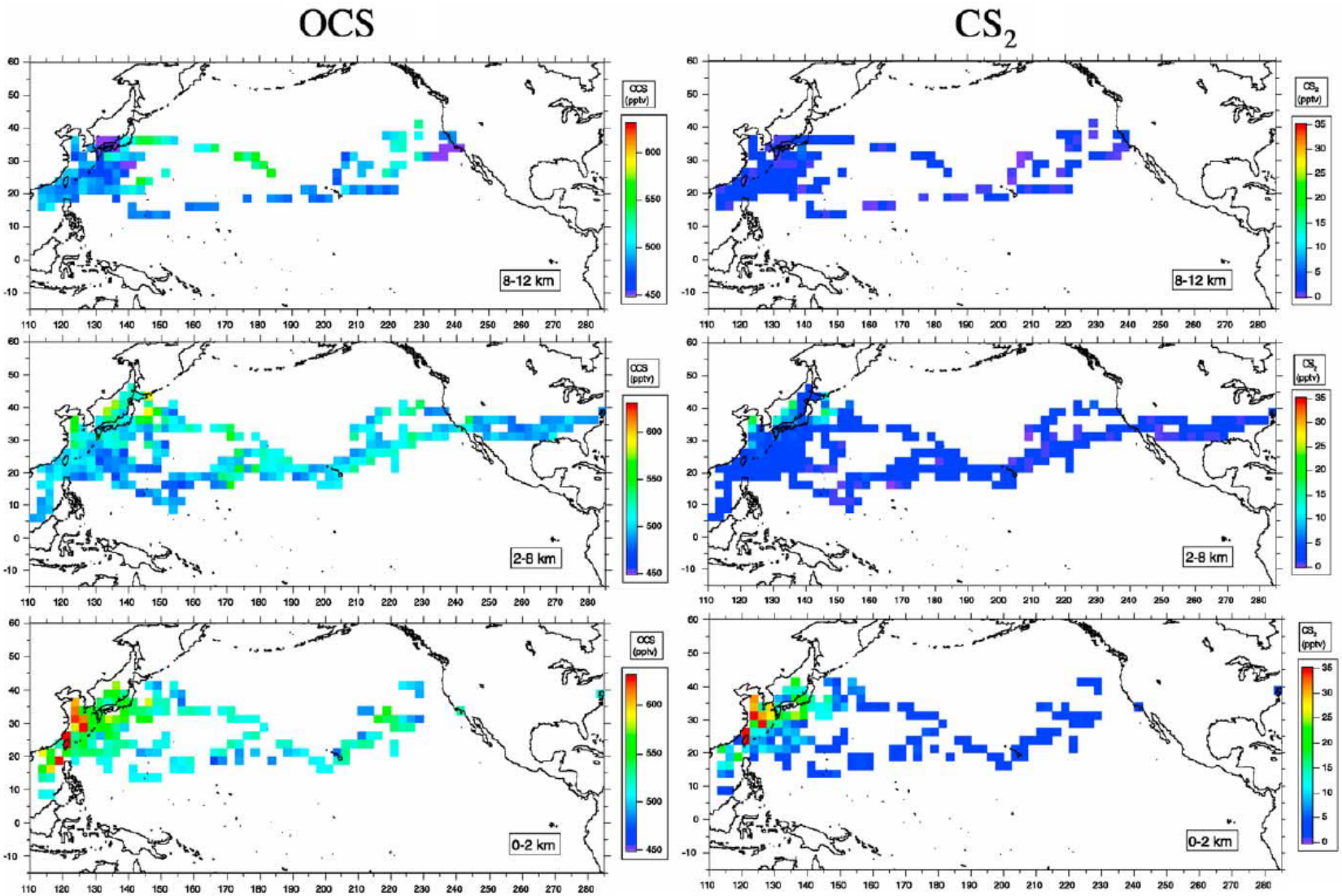
**Table 1.** Global Industrial Budgets for Direct and Indirect Sources of COS[a]

| | Climatological Inventory[b] | Year 2011–2013 Inventory[c] | |
|---|---|---|---|
| | | Previous Methods[d] | This Study |
| | *Anthropogenic $CS_2$* | | |
| Approach | *Peyton et al.* [1976] | *Blake et al.* [2004] | See section 2 |
| Source | 116 ± 58 | 414 ± 207 | 190 ± 70 |
| | *Aluminum* | | |
| Approach | *Harnisch et al.* [1995] | *Harnisch et al.* [1995] | See section 2 |
| Source | 44 ± 22 | 99 ± 50 | 30 ± 7 |
| | *Coal* | | |
| Approach | *Khalil and Rasmussen* [1984] | *Khalil and Rasmussen* [1984] | See section 2 |
| Source | 20 ± 10 | 24 ± 12 | 60 ± 30 |
| Total | 180 ± 90 | 537 ± 269 | 257 ± 107 |

[a] All units are COS as Gg S $yr^{-1}$.
[b] *Kettle et al.* [2002].
[c] Estimates are for most recent years for which industry data are available which are 2013, 2012, and 2011 for rayon, aluminum, and coal, respectively.
[d] We estimate the present source by applying current industry production (2011–2013) to the emission factors used in the most recent COS inventories.

# 3. OCS in the troposphere

## What about anthropogenic sources?

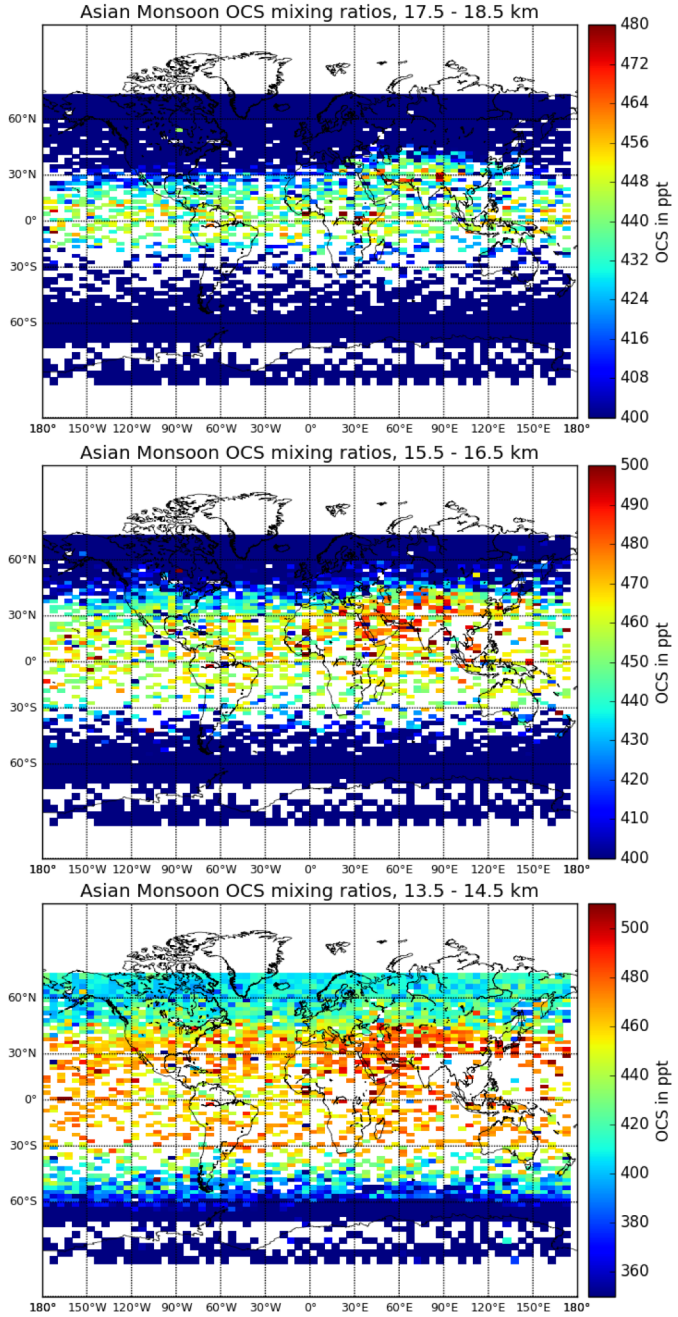



***Blake et al., 2004*: enhanced OCS in the free troposphere over much of the Pacific, traced almost exclusively to **continental and most likely anthropogenic sources.**

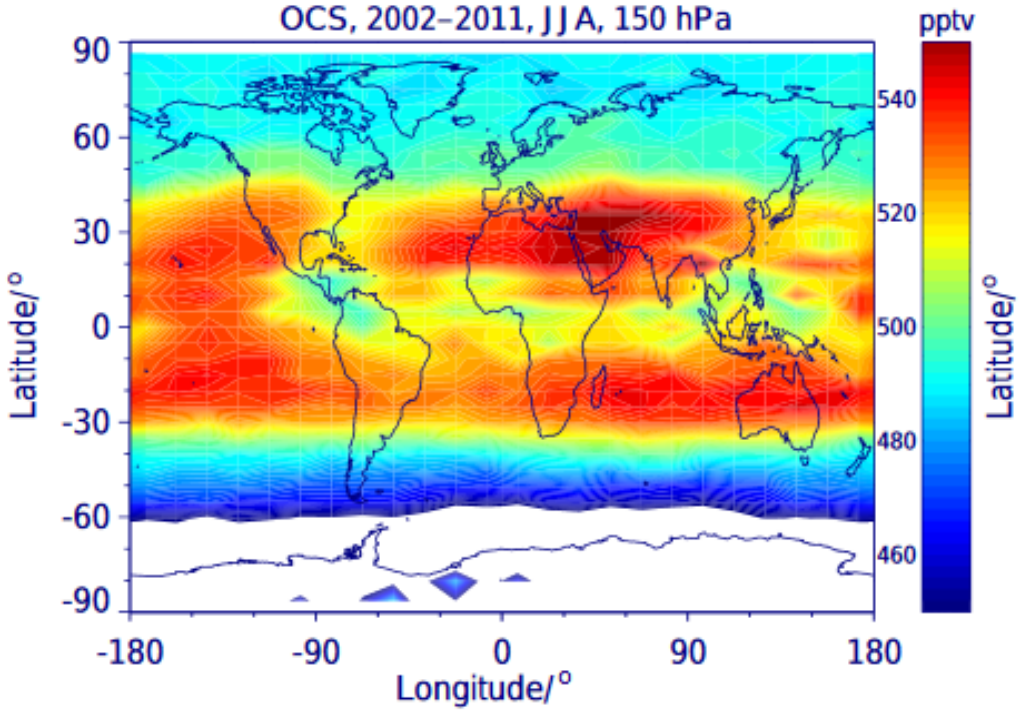
# 3. OCS in the troposphere

## What about anthropogenic sources?

Saltellite observations reveal a clear and significant OCS enhancement in the ASM anticyclone, most likely caused by anthropogenic emissions.

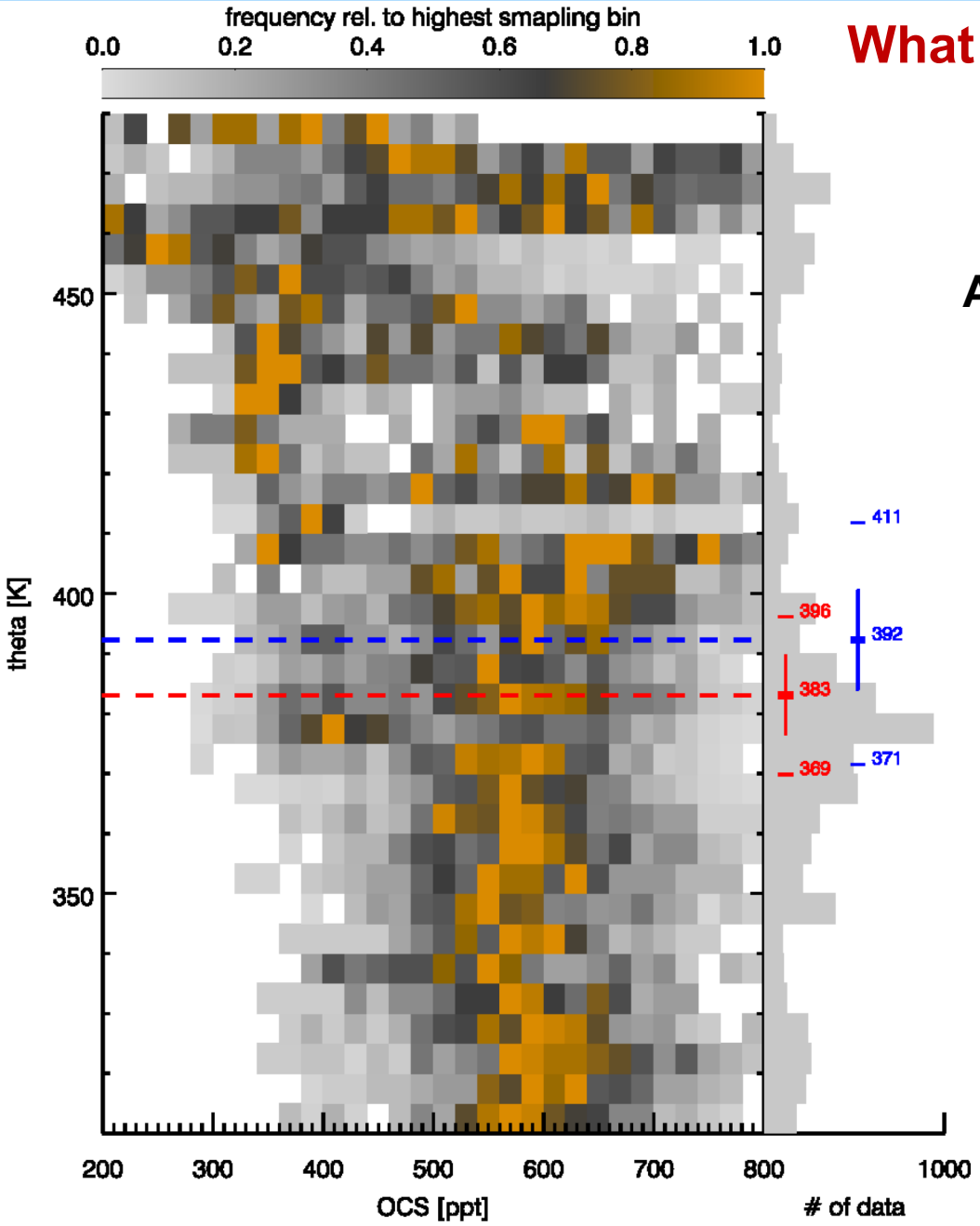



*JJA OCS at different levels from ACE-FTS, courtesy of Corinna Kloss*




MIPAS Envisat observations, *Glatthor et al., ACP, 2017*

# 3. OCS in the troposphere



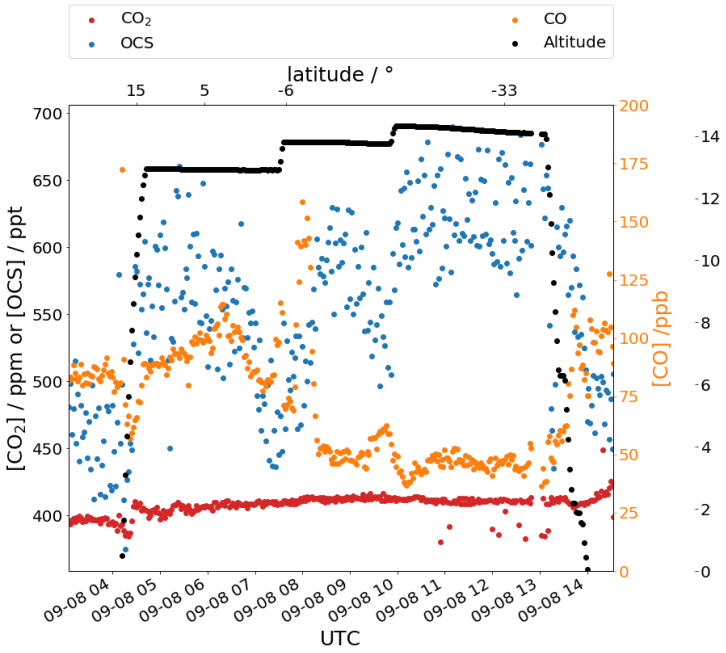

**What about anthropogenic sources?**

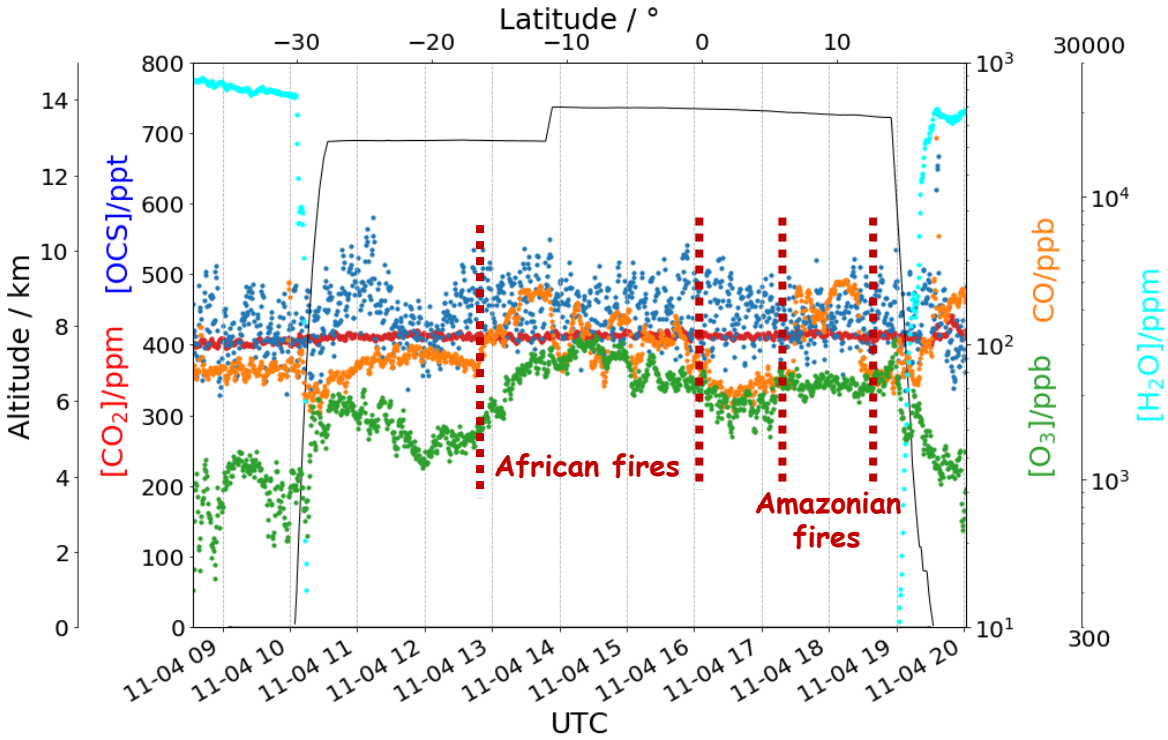
**AMICA observations StratoClim**
**Kathmandu, Jul/Aug 2017**

# 3. OCS in the troposphere

## What about anthropogenic sources?

AMICA measurements in the TTL during the SOUTHTRAC transfer flights




- **elevated CO in BB air over the Atlantic with no obvious OCS enhancement (based on emission ratios in *Andreae, 2019*, we wouldn‘t expect any)**
- **generally higher OCS in early September compared to November: could the Asian Monsoon be a source?**

**→ *Work in progress (Chenxi)***

# 3. OCS in the troposphere

## Conversion of marine DMS?

- Oceans emit ~21 Tg S $a^{-1}$ in the form of DMS (*Watts, 2000*)
- OCS has been identified as a minor product of atmospheric DMS oxidation with an OCS product yield of ~0.7 % (*Barnes et al., 1994 + 1996; confirmed by Albu et al., 2008)*
- This yield has been used ever since to derive an „indirect OCS source“ of ~150 Gg S $a^{-1}$

**…let‘s look at this in a bit more detail (careful: chemistry!)**

# Simplified reaction scheme for the OH and $NO_3$ radical-initiated oxidation of dimethyl sulfide from *Barnes et al., 2006*

1. **Formation of thioformaldehyde:**

$$CH_3S + O_2 \rightarrow CH_2S + HO_2$$

2. **Converson to OCS:**

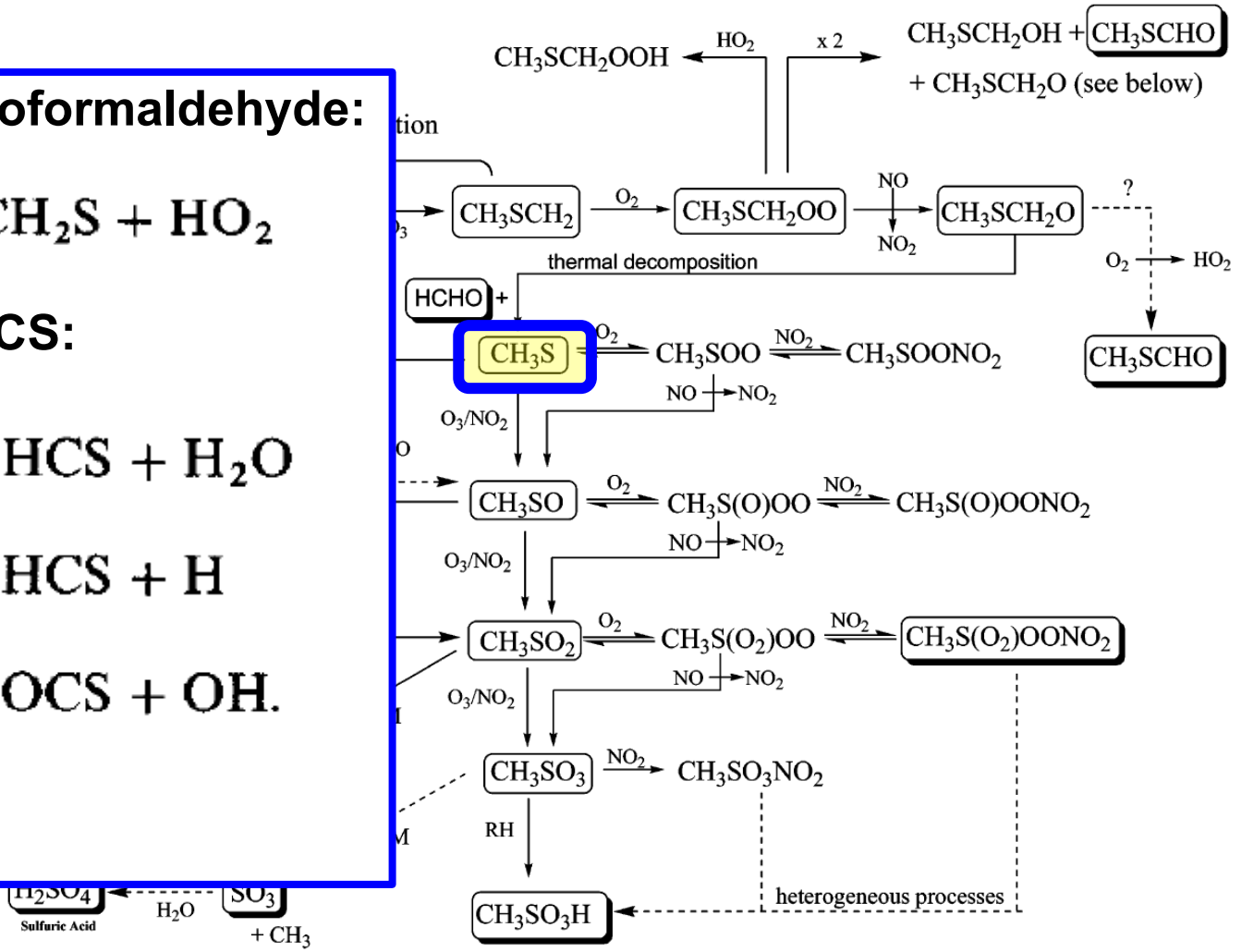
$$CH_2S + OH \rightarrow HCS + H_2O$$

*visible*

$$CH_2S + h\nu \rightarrow HCS + H$$

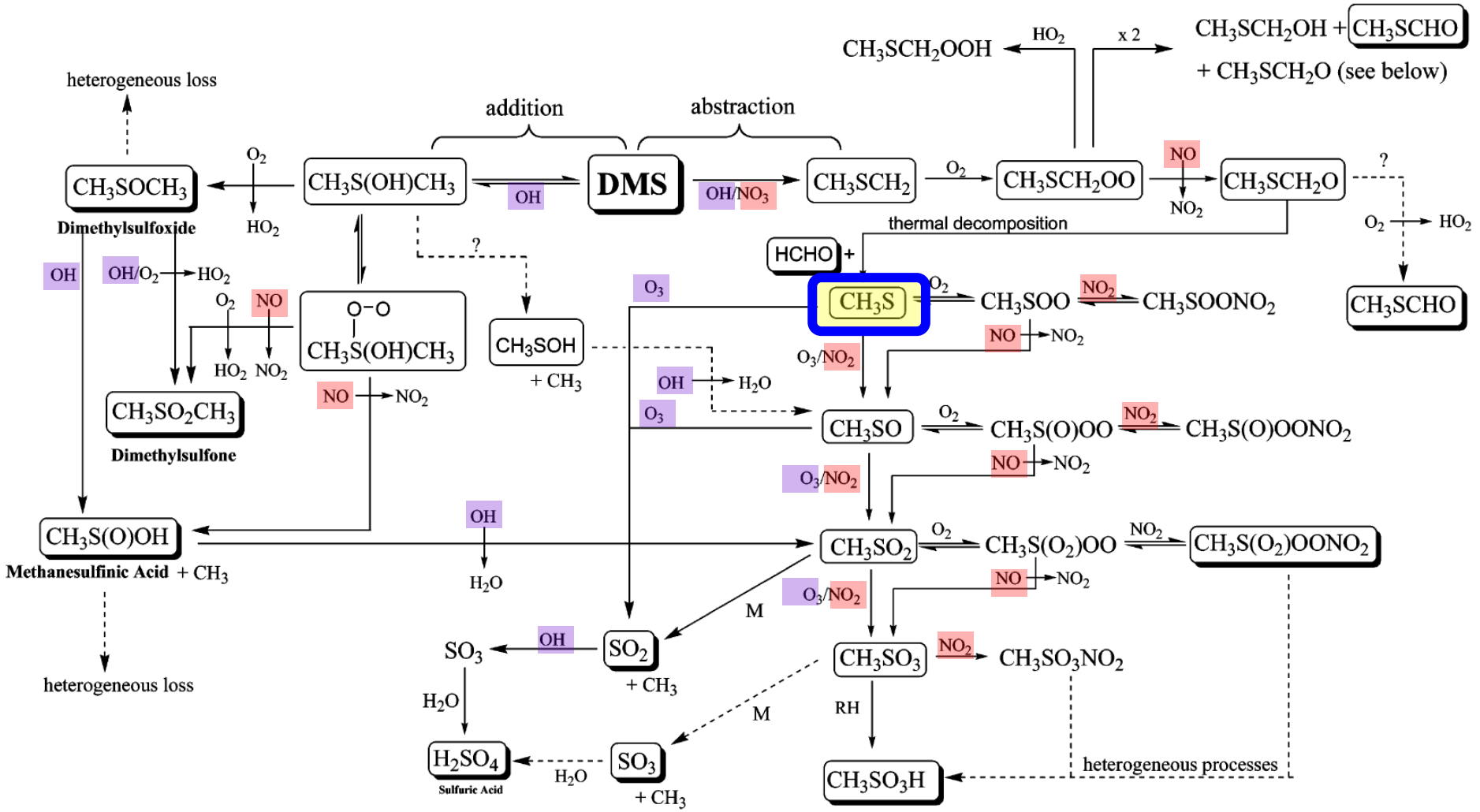
$$HCS + O_2 \rightarrow OCS + OH.$$

*(Barnes et al., 1996)*




**It has been suggested that the route to OCS proceeds essentially via the methylthiyl radical (*Barnes et al., 1994 + 1996; Albu et al., 2008*).**

# Simplified reaction scheme for the OH and $NO_3$ radical-initiated oxidation of dimethyl sulfide from *Barnes et al., 2006*




**Let‘s consider low $NO_x$ conditions (remote MBL < 10 ppt)…**

**…and now also low OH and $O_3$**

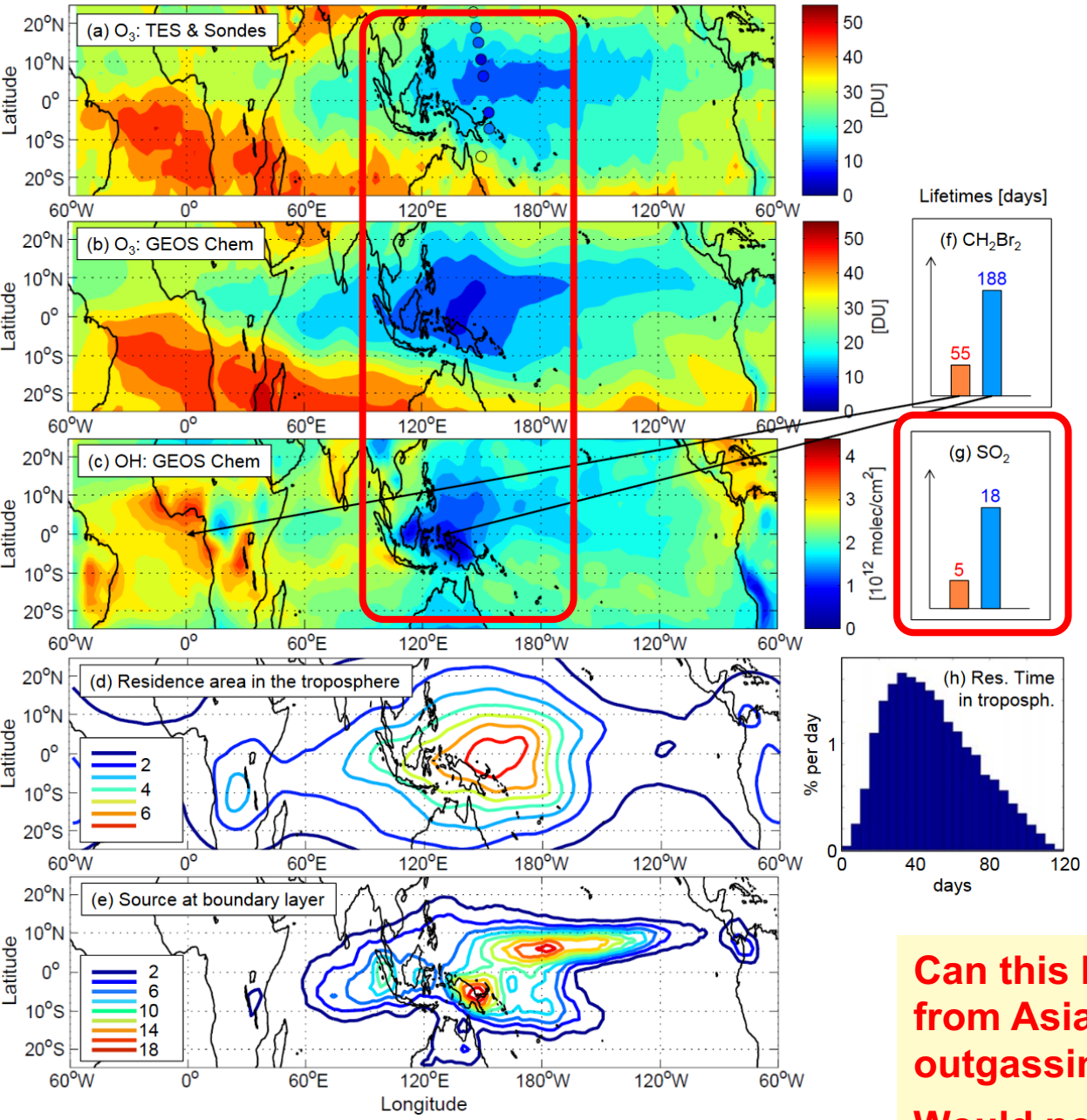



*Figure from Rex et al., ACP, 2014*

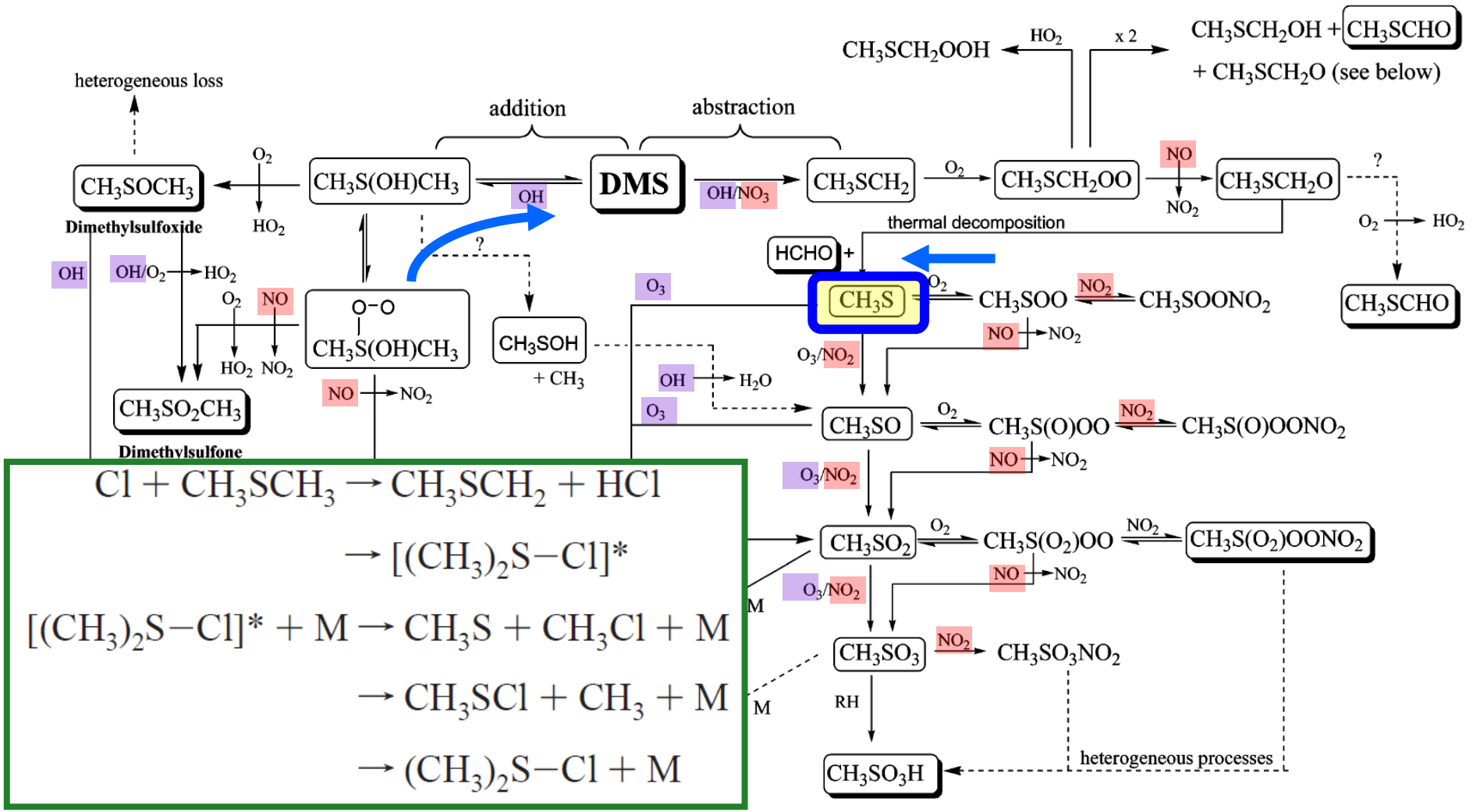
## Rex et al., ACP, 2014:

- **W. Pacific OH minimum increases gas phase lifetimes**
- **lifetime enhancement and higher BG concentrations are predicted for $SO_2$**
  **→ this is supported by aircraft observations made during SCOUT-O3**
- **Effect on $SO_2$ flux to the stratosphere negligible for BG $SO_2$ concentrations**

**Can this be relevant for high $SO_2$ from Asia, ship emissions, volcanic outgassing?**

**Would not expect low OH in polluted air masses…**

# Simplified reaction scheme for the OH and $NO_3$ radical-initiated oxidation of dimethyl sulfide from *Barnes et al., 2006*




$$Cl + CH_3SCH_3 \rightarrow CH_3SCH_2 + HCl$$

$$\rightarrow [(CH_3)_2S{-}Cl]^*$$

$$[(CH_3)_2S{-}Cl]^* + M \rightarrow CH_3S + CH_3Cl + M$$

$$\rightarrow CH_3SCl + CH_3 + M$$

$$\rightarrow (CH_3)_2S{-}Cl + M$$

**Some equilibria will be shifted…**

**…and another oxidant becomes relatively more important**

# 3. OCS in the troposphere

## Conversion of marine DMS?

- Oceans emit ~21 Tg S $a^{-1}$ in the form of DMS (*Watts, 2000*)
- OCS has been identified as a minor product of atmospheric DMS oxidation with an OCS product yield of ~0.7 % (*Barnes et al., 1994 + 1996; confirmed by Albu et al., 2008)*
- This yield has been used ever since to derive an „indirect OCS source“ of ~150 Gg S $a^{-1}$

- For now, consider this a potential *candidate* for extra OCS from the tropical Pacific…
- …experiments at the FZJ SAPHIR atmospheric simulation chamber planned for summer 2020!