

- This figure from the Kremser et al. review describes the overall sources and life cycle of the stratospheric aerosol layer.
- The role of non-sulfate aerosol has been particularly highlighted in the review paper, but the focus of this lecture is exclusively on sulfur.
- Largest single source of stratospheric sulfur are volcanic eruptions...

Volcanoes represent the largest individual source of sulfur to the stratosphere.



Eruption of Pinatubo in 1991. Photograph courtesy of the U.S. Geological Survey

In 1991, Pinatubo injected 20 Tg of sulfur directly into the stratosphere, two orders of magnitude more than the other sulfur sources discussed here contribute annually.

- ...and when a big one goes off, then the amount of sulfur injected exceeds all non volcanic sources of stratospheric sulfur by far.

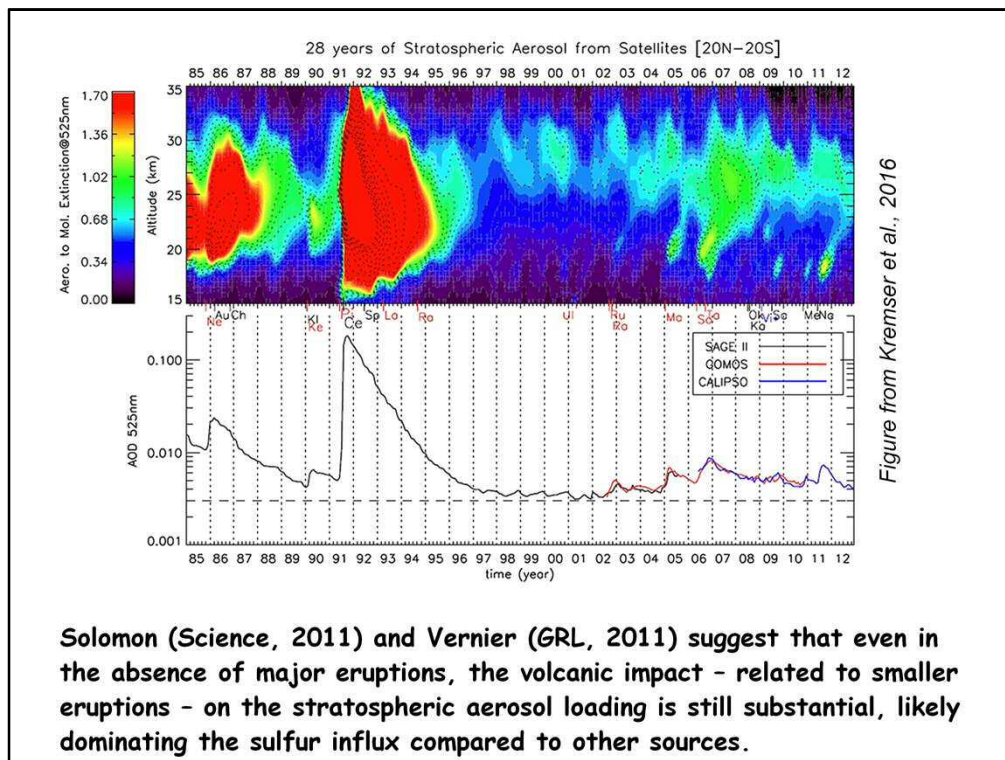


Figure from Kremser et al., 2016

- Susan Solomon, Jean-Paul Vernier and co-workers have shown that even without large Pinatubo-like eruptions, contributions from medium and small eruptions reaching the stratosphere or the TTL can still dominate the sulfur flux to the stratosphere.
- It has been shown that such small and medium size volcanic eruptions are responsible for the observed positive trend in stratospheric aerosol loading starting around the year 2000, and a number of recent studies including both the analysis of satellite observations and model studies support this

Volcanic eruptions are episodic events, and the amount of sulfur emitted by a single eruption varies strongly. Therefore, **the volcanic stratospheric sulfur source is entirely unpredictable on climatological timescales.**

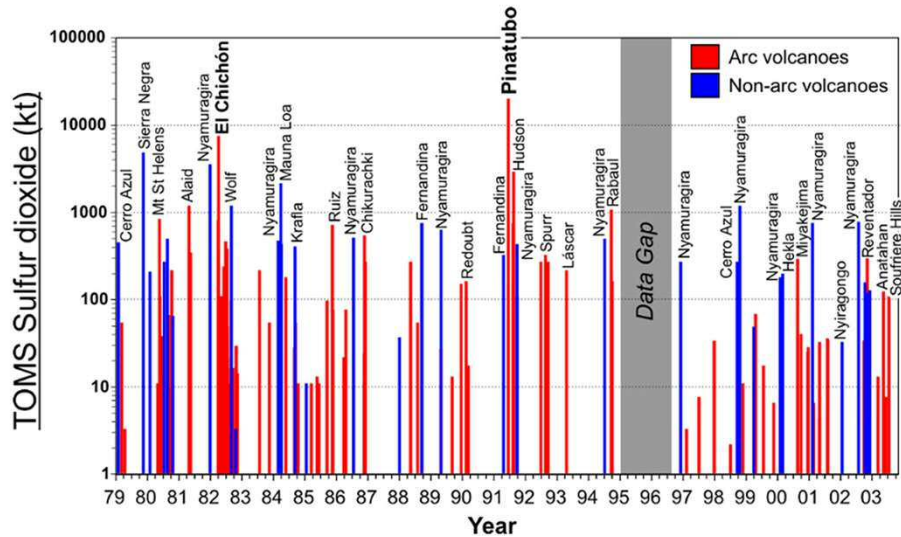


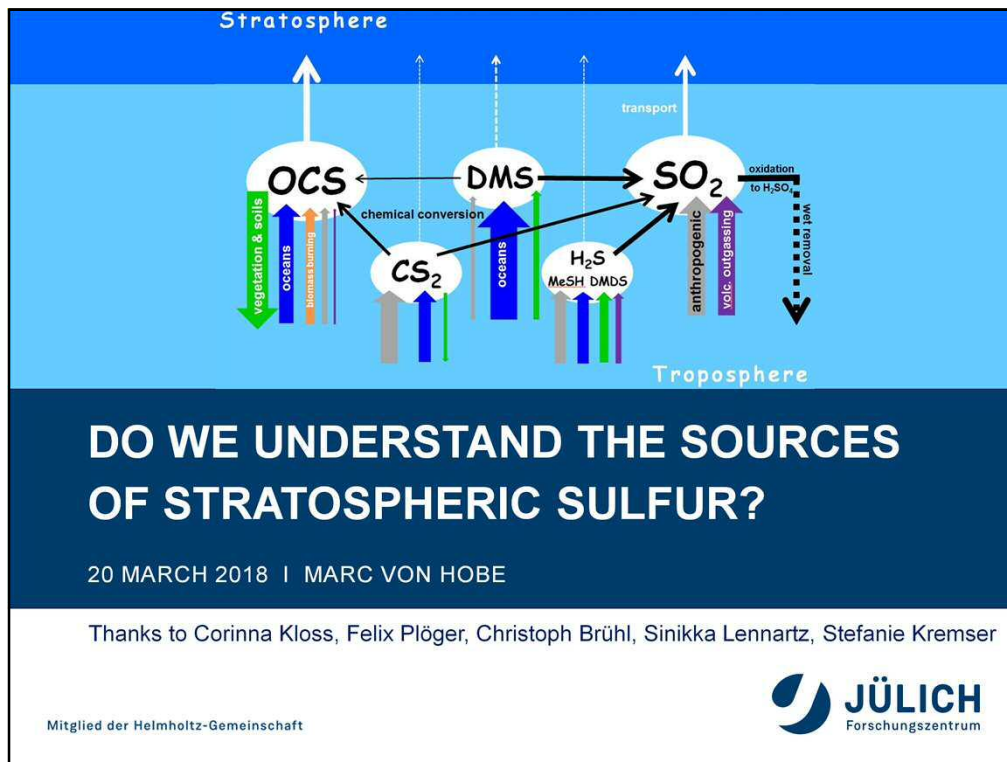
Image: TOMS Volcanic Emissions Group

- While we can reasonably well estimate the climate impact of a given or a theoretical eruption, we can't tell when and how often volcanic eruptions will occur.
- **Both frequency and magnitude are highly variable and entirely unpredictable on climatological timescales, so that it's really difficult to include volcanoes in our long term climate predictions.**

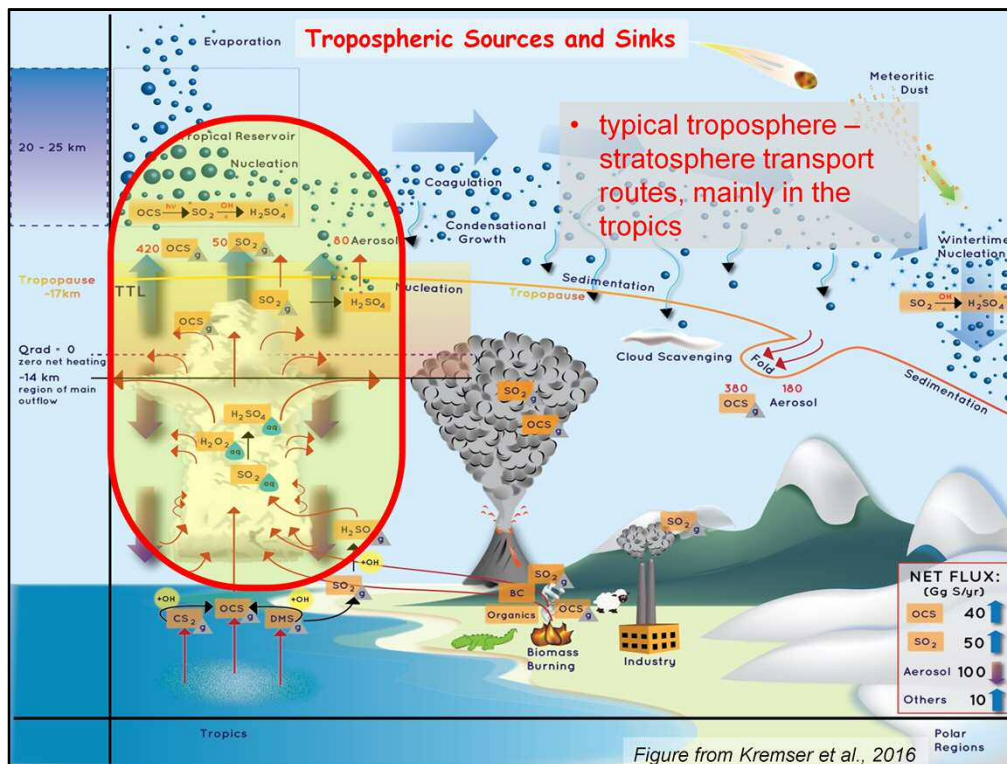
Here, focus on the non-volcanic sources of stratospheric sulfur...

- Can we quantify them?
- Can we parameterise them in models?
- Can we predict future climate interactions?

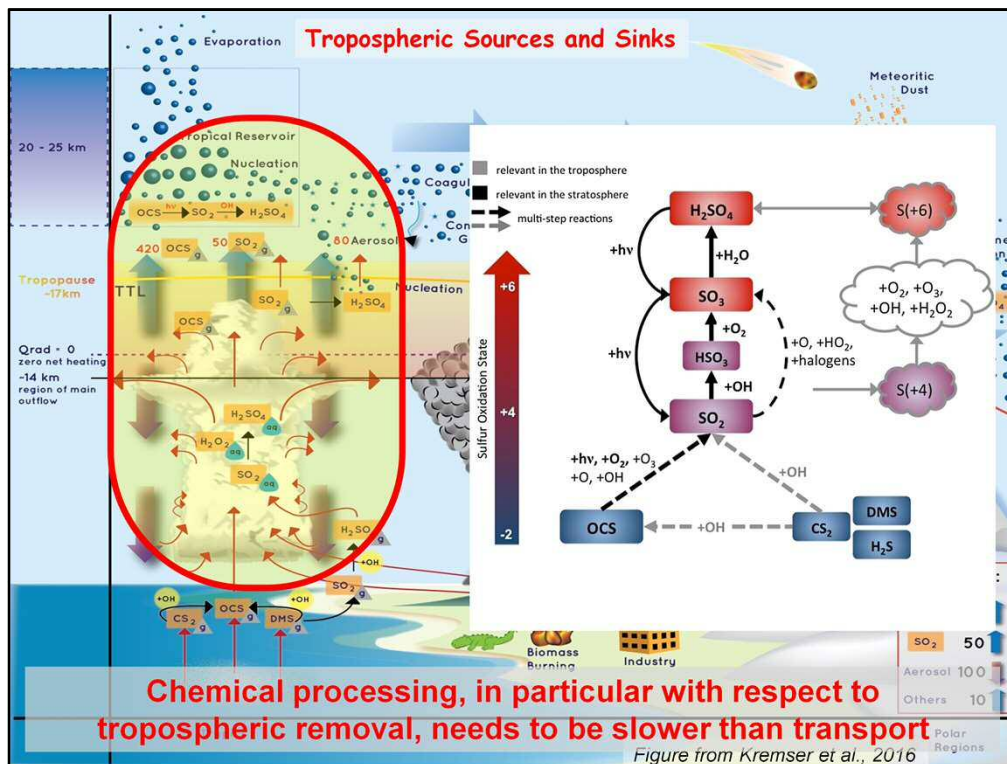
- In this keynote on stratospheric sulfur, I focus on non volcanic sources.
- They are essentially related to biogeochemical processes and anthropogenic emissions, and those can in most cases at least be estimated.
- In terms of making long term climate predictions, three questions are important:
 - Can we quantify them?
 - Can we parameterise them in models?
 - Can we predict future climate interactions?
- In this lecture, I concentrate on the first question and on our qualitative and quantitative understanding of the various sources that is prerequisite for any model parameterizations needed to help us with the last question.



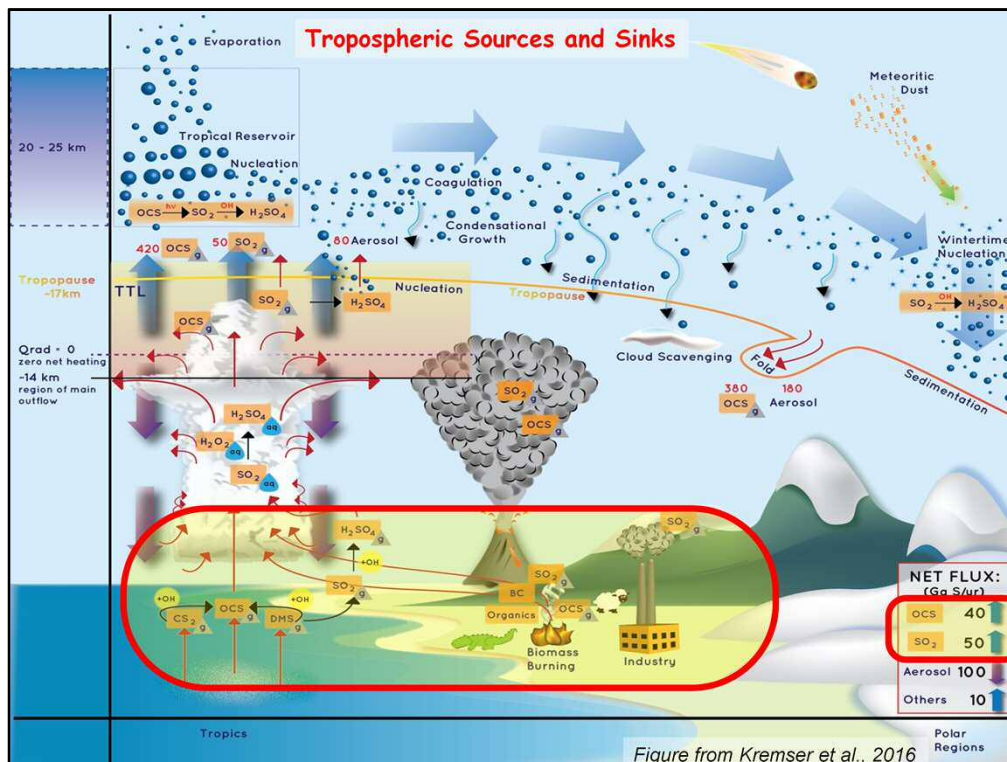
- A number of people have directly or indirectly contributed to this lecture by being involved in the acquisition of some unpublished data shown, in preparing figures, or in shaping some ideas presented through intensive collaboration and correspondence in the past.



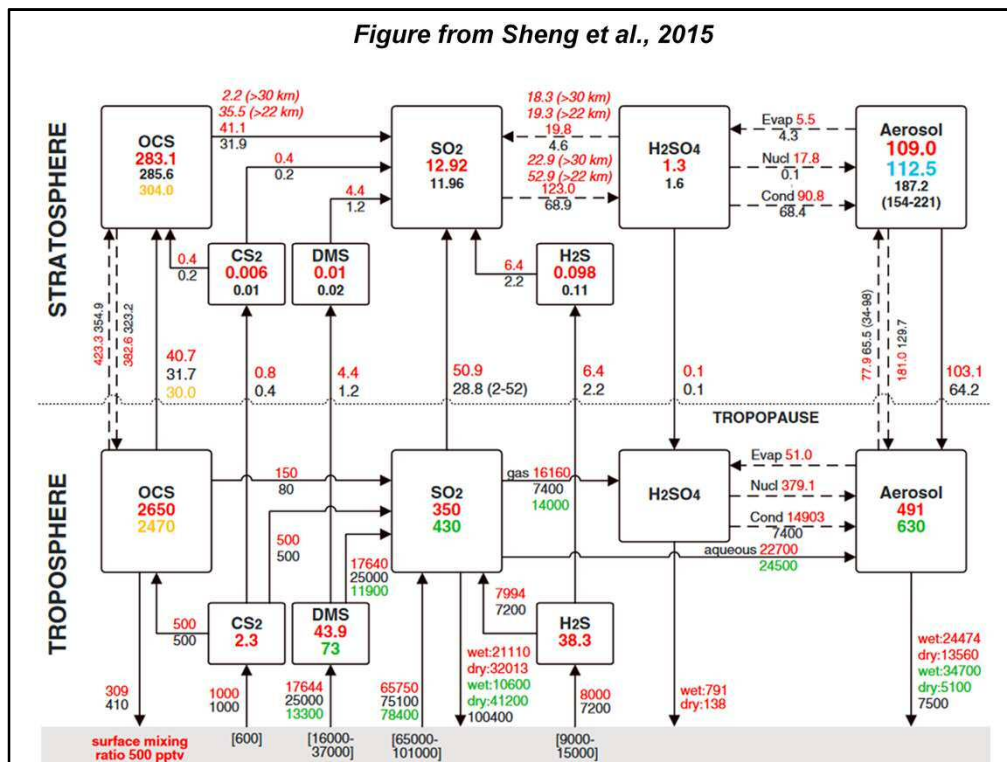
- Sulfur emitted by whatever process into the tropospheric boundary layer must follow the “standard” transport pathways to get into the stratosphere
- Troposphere-stratosphere transport occurs mainly in the tropics
- A very efficient route of fast vertical transport from the boundary layer is convection that acts as an „elevator“, lifting air to the „level of zero radiative heating“ or even higher
- A region, where the boundary layer is particularly rich in sulfur gases and other potential aerosols and precursors mainly due to anthropogenic activities, and where a particularly efficient vertical transport occurs in boreal summer, is southern Asia. I will touch on the special role of the so-called „Asian Monsoon Anticyclone“ several times in this lecture



- One „problem“ for the tropospheric sulfur in „trying“ to reach the stratosphere is the oxidizing nature of our atmosphere
- Chemical conversions always go from lower to higher oxidation state, so that all emitted sulfur compounds will eventually end up as sulfuric acid, the most oxidized form of sulfur (there are a few exceptions to this „oxidizing rule“, e.g. the photolysis of sulfuric acid forming SO_2 in the upper atmosphere shown for example by Höpfner et al., ACP, 2013, but for our considerations of transport from the troposphere to the stratosphere, that is not relevant).
- Because sulfuric acid in the troposphere is almost quantitatively removed before reaching the stratosphere, mainly by wash out and wet deposition, the sulfur compounds really should make it to the stratosphere before the oxidation chain is completed, or in other words: transport needs to be faster than the chemical processing



- Before they can be transported and chemically processed, the various sulfur compounds have to be released to the atmosphere, and **one very important aspect for quantitatively understanding the sulfur flux to the stratosphere is a good knowledge of the sources and sinks of the various sulfur compounds on the ground.**
- Essentially, when you know the surface fluxes and fully understand the chemistry and transport processes, then you can easily estimate the flux into the stratosphere.
- For the two quantitatively most important sulfur gases, carbonyl sulfide and sulfur dioxide, reasonable flux estimates at least exist.
- The numbers shown in the Kremser et al. 2016 figure are from a recent study with a global model published by Sheng et al. in 2015



- I will not explain this figure from that paper in detail
- It illustrates the complexity that the model (SOCOL-AER) can handle
- Noteworthy: the red number in the upper right corner for the stratospheric aerosol loading from the simulation corresponds extremely well to the blue number derived from the stratospheric aerosol mass derived from Sage-II using the SAGE-4λ method (note that the agreement is not quite so good anymore with the new CMIP6 dataset).
- Apparently, we are not doing too badly in terms of modelling the sulfur flux to the stratosphere and the conversion to aerosol
- Nevertheless, there are still a few question marks with respect to current or future fluxes
- One characteristic of the model is that for carbonyl sulfide it does not use tropospheric fluxes but a constant surface mixing ratio of 500 ppt
- This will be discussed later
- First look at sulfur dioxide (SO₂)...

Sulfur Dioxide, SO₂

An anthropogenic contribution to stratospheric sulfur?



- Anthropogenic SO₂ emissions far outweigh natural non-volcanic sources

- Hofmann et al., GRL, 2009:

„...it appears that a large increase in coal burning since 2002, mainly in China, is the likely source of sulfur dioxide that ultimately ends up as the sulfate aerosol responsible for the increased backscatter from the stratospheric aerosol layer.”

“The 50 TgS global total emissions in 2005 suggests that about 0.6–0.8% of the sulfur would need to enter the stratosphere to sustain the 0.3 – 0.4 TgS aerosol seasonal variation.”

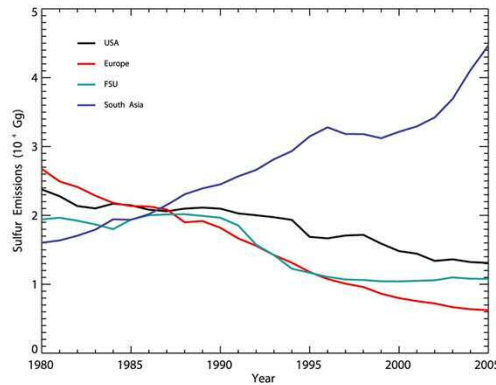


Figure from Kremser et al., 2016

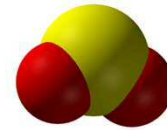
- Neely et al., GRL, 2013:

„...moderate volcanic eruptions, rather than anthropogenic influence, are the primary source of the observed increases in stratospheric aerosol.”

- Today, anthropogenic emissions of SO₂ dominate the global direct emissions by all non-volcanic sources
- Looking at the increase in global SO₂ emissions over the last decades particularly in Asia, Hofmann and co-workers suggested anthropogenic SO₂ emissions as an alternative explanation for the observed increase and variability in stratospheric aerosol loading since the year 2000, and this seems not so far fetched because really only a small fraction (< 1 %) of the anthropogenic SO₂ reaching the stratosphere could fully account for the observations.
- As mentioned earlier, more studies support the „small volcanoes“ hypothesis, and this is also the conclusion made by Neely and coworkers who directly compared the two in a modelling approach.
- However, we cannot rule out a contribution from anthropogenic sulfur emissions, and therefore it is worthwhile to look more closely at anthropogenic SO₂.

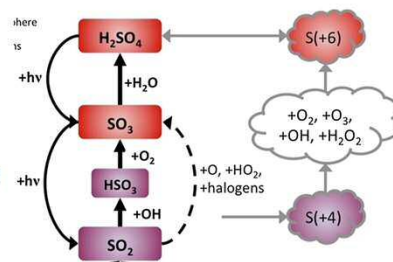
Sulfur Dioxide, SO₂

Decay vs. vertical transport – a close race:



Slow ascent

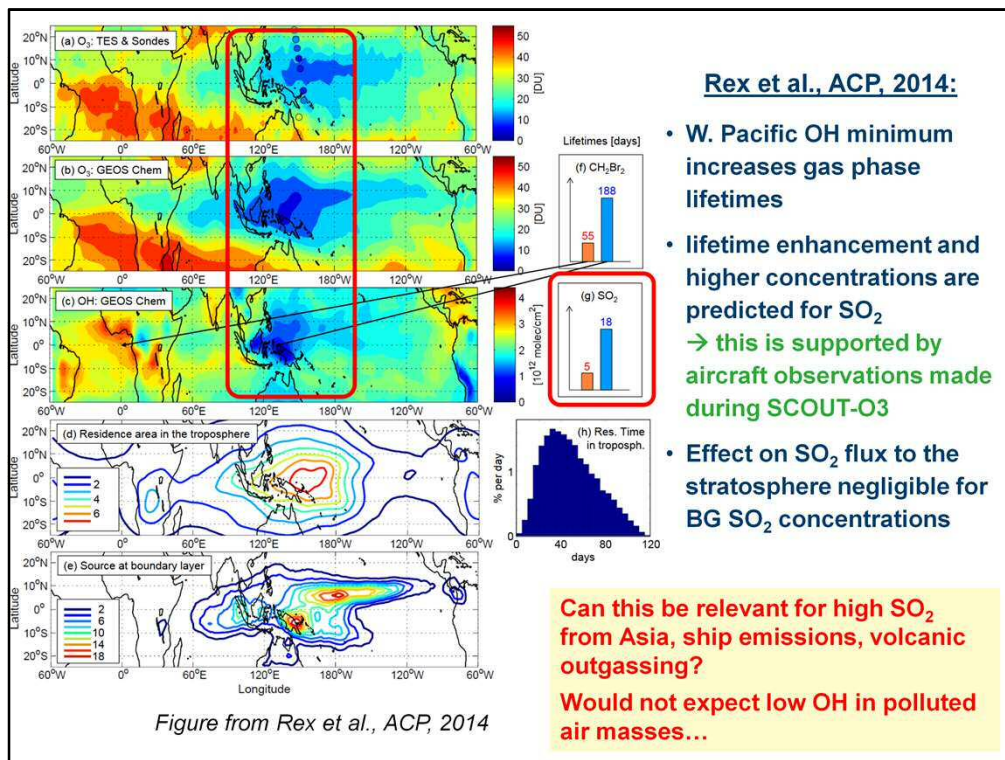
- only gas phase reactions
- SO₂ lifetime on the order of days
- H₂SO₄ wash out at cold point?



Convective transport

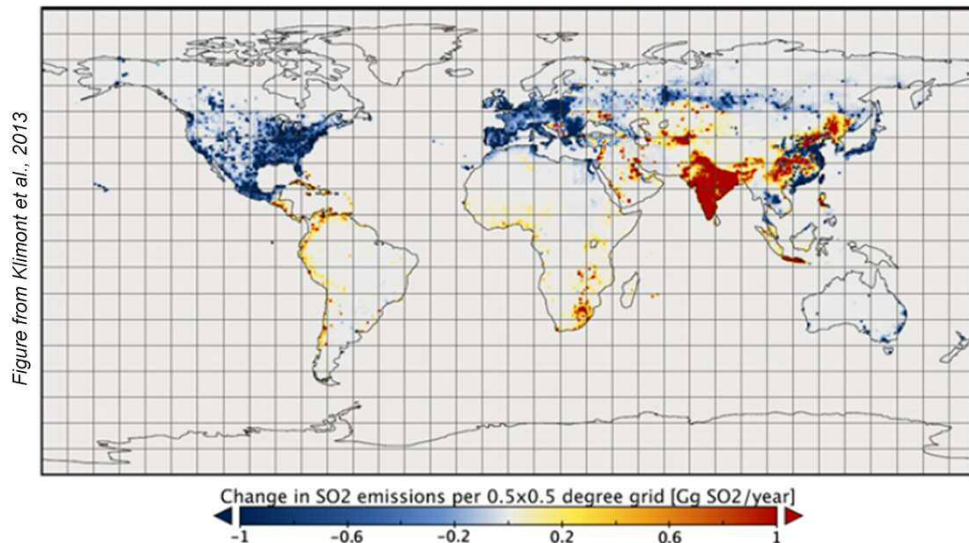
- fast heterogeneous processing
- SO₂ lifetime on the order of minutes
- immediate H₂SO₄ wash out

- For SO₂, the aforementioned „chemistry vs. transport“ is a close race.
- That is the case in two regimes:
 - Outside clouds, SO₂ has a lifetime on the order of days, but without convection, transport times are usually at least that long
 - With convection, transport is much faster, but heterogeneous processing usually leads to shorter lifetimes and rapid conversion to H₂SO₄, which is subsequently washed out



- Potential „slow“ transport of SO₂ into the stratosphere was suggested by Markus Rex and coworkers in a 2014 ACP paper.
- A minimum in OH, is the main oxidant in the troposphere, over the Western Pacific could increase lifetimes of numerous trace gases including SO₂ in that area (this is actually supported by aircraft observations made in that area during SCOUT-O₃ in 2005).
- For SO₂, Rex et al. calculate a lifetime of 18 days, and with the distribution of tropospheric residence times over trajectory ensembles peaking at about 35 days, some SO₂ will likely survive all the way to the cold point tropopause
- However, for background SO₂ mixing ratios of a few tens ppt, this will not amount to a substantial flux.
- Air masses containing enhanced SO₂ such as plumes from Asia or air affected by ship emissions or volcanic outgassing at the surface will most likely not be low in OH, because there tends to be also NO_x and other gases preventing OH from really reaching such extremely low values as often found over the Western Pacific

How about convective transport over Asia?



The boundary layer in much of Asia is loaded with SO₂ and other sulfur precursors (as well as organics and non-sulfate aerosols).

- Next, let's assume we have the "fast regime" with convective transport occurring coincident with large SO₂ emissions and thus amounts in the troposphere.
- This is the case in Asia, where SO₂ mixing ratios in the boundary layer are high, and where emissions have been constantly increasing according to several studies.
- This figure from Klimont et al. shows SO₂ emissions to go up rapidly over India and parts of China...

How about convective transport over Asia?

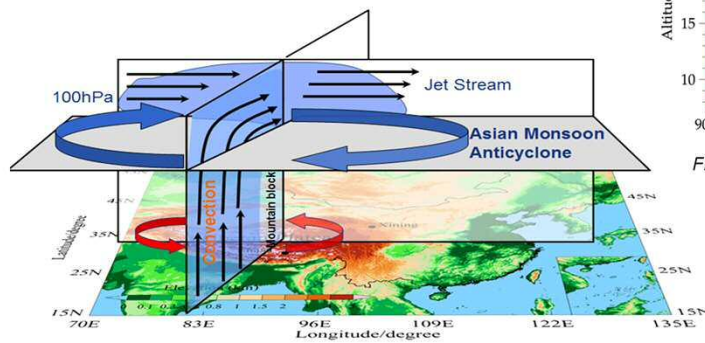


Figure courtesy of Yong Wang

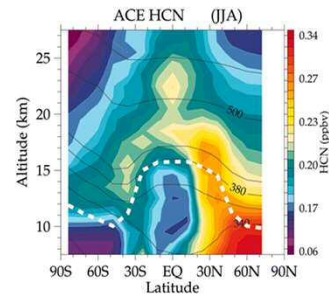


Figure from Randel et al., 2010

The Asian summer monsoon circulation provides an efficient transport pathway from the boundary layer to the stratosphere

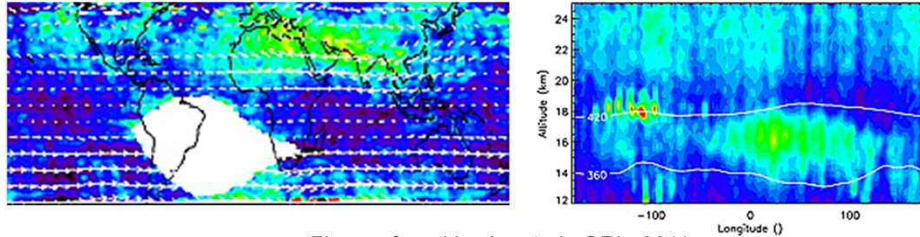
- and that same area is a hot spot of convective transport particularly in boreal summer during the Asian summer monsoon
- Convection here does rarely reach the tropopause, but typically delivers air well above the level of zero buoyancy, from where it slowly ascends further into the stratosphere.
- In 2010, Bill Randel and coworkers have published a paper in Science, suggesting that this transport pathway potentially leads to significant amounts of anthropogenic pollutants reaching the stratosphere, and their figure of the zonal and vertical distribution of HCN measured by ACE-FTS suggests that some of this air can reach the tropical pipe, a result that has been corroborated in recent years.

How about convective transport over Asia?

Vertical transport of aerosol or aerosol precursors (likely of anthropogenic origin) in the AM anticyclone regularly lead to formation of an

“Asian Tropopause Aerosol Layer (ATAL)”

detected by CALIPSO and SAGE-II. ATAL may constitute a primary source of non-volcanic aerosol for global UT and LS (Vernier *et al.*, GRL, 2011).



Figures from Vernier *et al.*, GRL, 2011

Balloon and aircraft measurements (Vernier *et al.*, GRL, 2015) show that

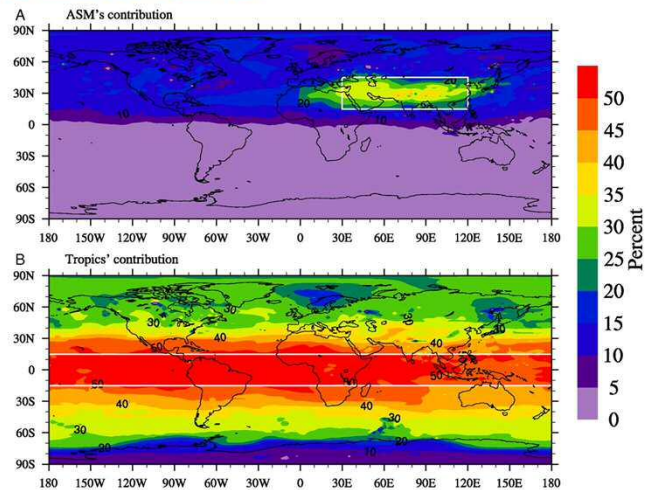
- aerosols at lower altitudes of the ATAL largely composed of carbonaceous and sulfate materials
- ATAL supplied by deep convection over the Indian subcontinent

- Evidence that this route of transport could play a role for SO₂ comes from the observation of an aerosol layer termed ATAL by Vernier and coworkers that occurs more or less coincident in space and time with the Asian Monsoon Anticyclone.
- Sulfate has been suggested early on to be at least a major component of ATAL, and there is observational evidence supporting that.
- *However, the presentations by Stephan Borrmann and Ralf Weigel show that there is more to ATAL than just sulfate aerosol, and that sulfate may not even be the major component.*

How about convective transport over Asia?

POPS observations over China and model simulations, *Yu et al., PNAS, 2017*:

- aerosol enhancement around the TP a robust feature linked to convective transport of polluted air masses from Asia
- Particles from AM anticyclone spread throughout N.H. lower stratosphere and contribute ~15% to N.H. stratospheric column aerosol surface area on an annual basis

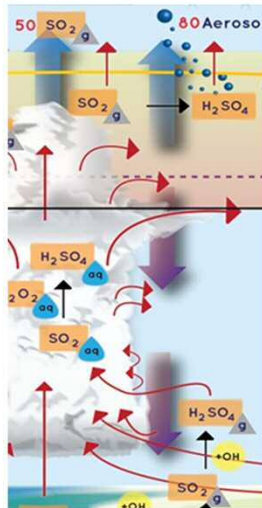


- Irrespective of the amount of sulfate it contains, the ATAL has been shown to be a rather robust and recurring feature
- Yu and coworkers have shown in a recent paper that, at least in a nudged model simulation, the aerosol exported from the ATAL makes up about 15 % of the N.H. stratospheric column aerosol surface area on an annual basis. This is not as much as the contribution from what's lifted up in the tropics, but still a significant number!
- Observations from the OHP Lidar shown by Sergey Khaykin at least qualitatively support the export of ATAL aerosol to the extratropical lowermost stratosphere (LMS)

How about convective transport over Asia?

Open Questions

How much $\text{SO}_2/\text{H}_2\text{SO}_4$ actually "survives" the convective transport?



SO_2 scavenging in convective clouds is very efficient but not well constrained and depends on microphysics (e.g. Bela et al., JGR, 2016)

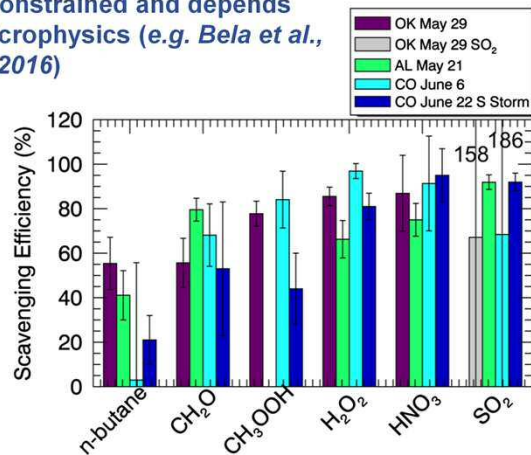


Figure from Bela et al., JGR, 2016

- **Quantitatively**, there are still open questions
- One is how much SO_2 actually survives the convective transport without being washed out as H_2SO_4 . In other words: if we have 1 or 10 or even 100 ppb SO_2 in the boundary layer in an area of strong convection, how much SO_2 will we find in the convective outflow?
- A definite quantitative answer here is lacking, although there have been some recent investigations of the scavenging efficiencies of trace gases in convective clouds by aircraft observations in over North America. For SO_2 , the scavenging efficiency is high, but less than 100 %, so that we can expect some fraction of the SO_2 entering the convection in the boundary layer or in the free troposphere to still be present in the convective outflow.

How about convective transport over Asia?

Open Questions

How much $\text{SO}_2/\text{H}_2\text{SO}_4$ actually “survives” the convective transport?

How much $\text{SO}_2/\text{H}_2\text{SO}_4$ is lost during slow ascent and at the CP TP?

- It is unlikely that all SO_2 present in the convective outflow makes it to the stratosphere; for example, the frequent occurrence of cirrus clouds in the Asian Monsoon anticyclone can lead to further removal of the SO_2 converted to H_2SO_4 .
- Overall, we are not yet in a position to quantitatively assess what fraction of SO_2 is lost during the full vertical transport time, and how much „makes it through“

How about convective transport over Asia?

Open Questions

How much $\text{SO}_2/\text{H}_2\text{SO}_4$ actually “survives” the convective transport?

How much $\text{SO}_2/\text{H}_2\text{SO}_4$ is lost during slow ascent and at the CP TP?

Is the remaining $\text{SO}_2/\text{H}_2\text{SO}_4$ exclusively exported to the N.H. LMS, or is there also a contribution into the tropical pipe?

Using a Lagrangian transport model, Ploeger et al. (ACP, 2017) show two main transport pathways from the anticyclone:

- (i) into the tropical stratosphere (tropical pipe)
- (ii) into the N.H. extratropical LS

Maximum anticyclone air mass fractions reach around 5 % in the tropical pipe and 15 % in the extratropical LMS over the course of a year.

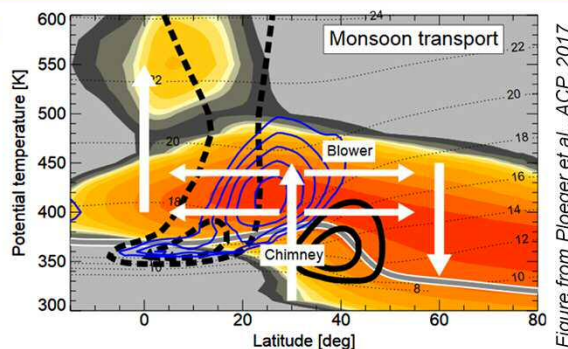


Figure from Ploeger et al., ACP, 2017

- If we assume that some amount of SO_2 does cross the cold point tropopause, there is still uncertainty where it goes:
- Is the air from the Asian monsoon only exported to the N.H. LMS with any sulfate aerosol present leading to significant aerosol loading in that layer over a time frame of approximately one year? Or does some fraction reach the tropical pipe and contributes to the main Junge layer above 20 km?
- Ploeger et al. have shown in 2017 that much of the anticyclone air is indeed exported to the N.H. LMS, but that about 5 % make it into the tropical pipe, consistent with similar studies for example by Garny and Randel, 2016. But these are all modelling studies with some support from satellite measurements with a vertical resolution of a few km.

How about convective transport over Asia?

Open Questions

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Hopefully, Geophysica observations from 2017 StratoClim campaign at KTM will provide some answers...

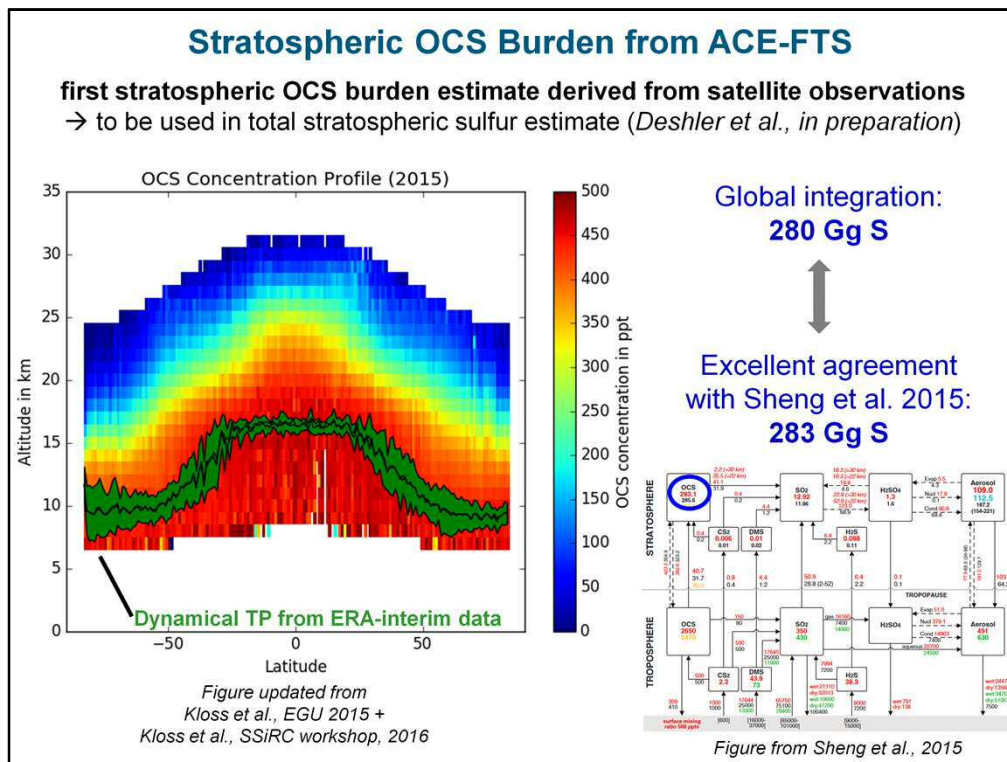
- We certainly hope that observations of transport tracers, SO_2 , aerosol amounts and properties obtained last summer with the Geophysica aircraft in Kathmandu, Nepal, will help to gain further insights on all three questions.

Carbonyl Sulfide, OCS

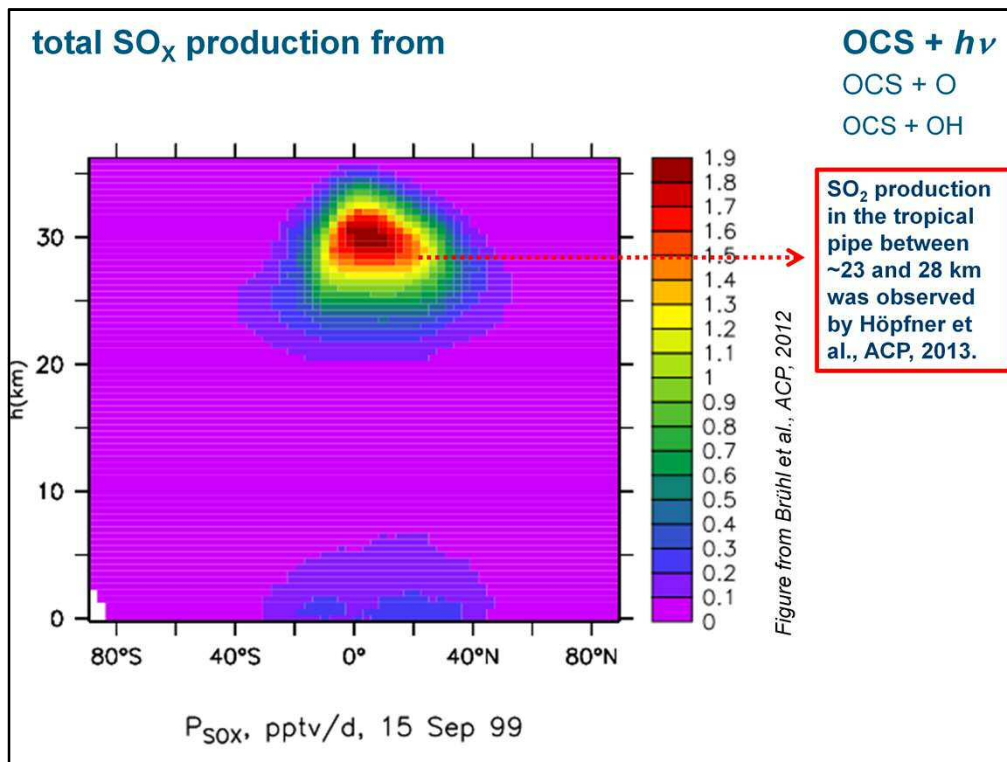


- at ~500 ppt most abundant sulfur gas in the atmosphere
- potent greenhouse gas, current forcing $\sim 0.008 \text{ W m}^{-2}$ (Brühl et al., 2012)
- chemically stable, tropospheric lifetime $\sim 2\text{--}5$ years (vegetation sink!)
→ all transport pathways open!
- contributes between 56 % (Sheng et al., 2015) and 70 % (Brühl et al., 2012) of background stratospheric aerosol

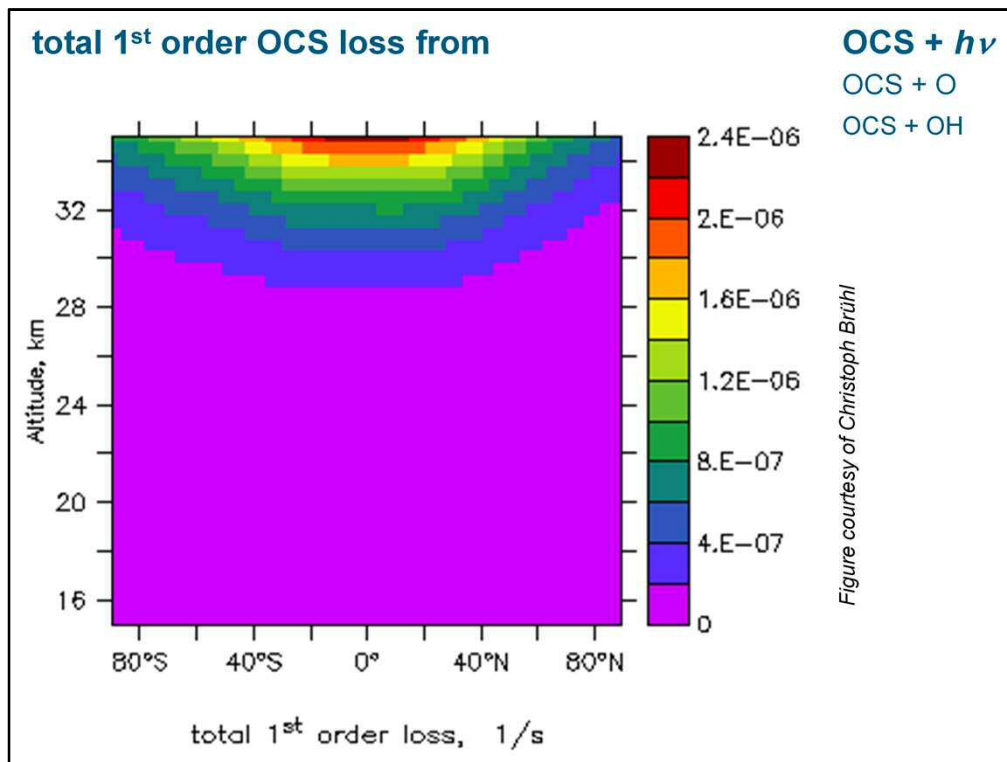
- The next gas, carbonyl sulfide (OCS), is remarkably stable and by far the most abundant sulfur gas in the atmosphere.
- Estimates of its tropospheric lifetime range from 2 to 5 years, controlled mainly by vegetation and soil sinks on the ground and not by chemical destruction in the atmosphere.
- Because of its stability, OCS is not removed in the free troposphere and can reach the stratosphere via all troposphere-stratosphere transport pathways.
- Only in the stratosphere under intense VU radiation, OCS is converted to SO_2 and then H_2SO_4 , contributing about two thirds of the background or non-volcanic stratospheric aerosol load according to the latest estimates from models.
- The climate forcing of the stratospheric aerosol originating from OCS is more or less balanced by greenhouse gas forcing exerted by tropospheric OCS, as was explicitly pointed out for the first time by Christoph Brühl and coworkers in their 2012 ACP publication.



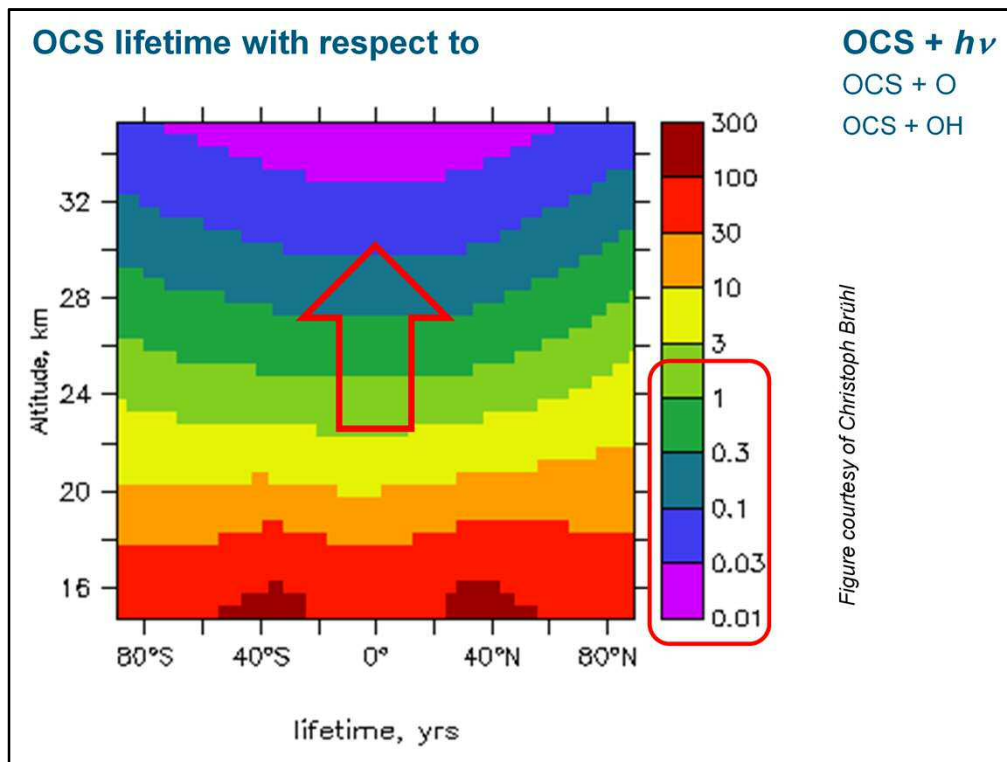
- In terms of numbers, models appear to be doing an excellent job in estimating stratospheric OCS
- Even with the somewhat simplistic assumption of a constant 500 ppt OCS at the surface, the aforementioned SOCOL-AER model used by Sheng et al. simulates almost exactly the same amount of OCS in the stratosphere that we get from vertically integrating all OCS above the tropopause over the entire globe from ACE-FTS satellite measurements (done and presented on several occasions by Corinna Kloss, intended to be published in a paper on the observed stratospheric sulfur and aerosol burden by Deshler et al.)



- Given the high chemical stability and rather moderate variability of OCS in the troposphere, and the rather straightforward chemistry in the stratosphere, coupled with the known ability of modern climate models to get the transport approximately right (especially when they are nudged), maybe the agreement of these numbers is not so surprising after all.
- In Christoph's 2012 ACP paper it was shown that the conversion of OCS to SO₂ takes place almost exclusively above 23 km in the tropical pipe, and the observation of enhanced stratospheric SO₂ in exactly this region by the Envisat MIPAS instrument shown in the Höpfner et al. 2013 paper supports this model result.

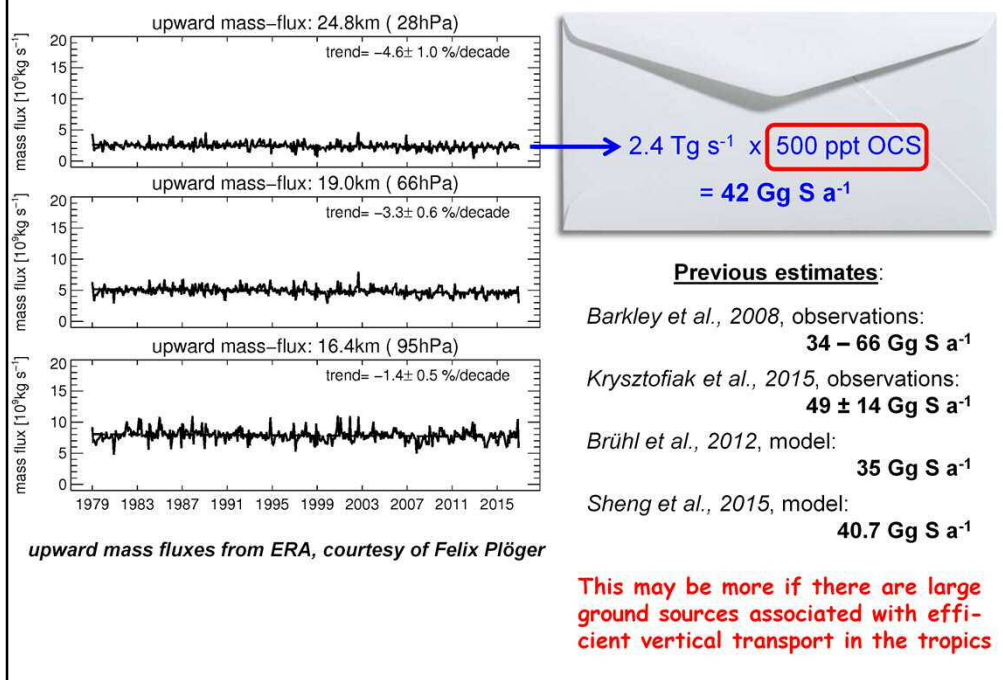


- Christoph provided further plots of the first order loss rate, i.e. the same plot as in the paper but with the OCS concentration removed...



- ...and by the zonally and vertically resolved photochemical lifetime of OCS.
- **The lifetime in the troposphere and in the lower stratosphere is much longer than typical transport times and chemical removal at these altitudes is negligible compared to the ground sinks.**
- As a consequence, any OCS transported to the stratosphere but then moving along the lower branch of the Brewer Dobson circulation (BD) will more or less quantitatively go back to the troposphere as OCS, explaining the large difference between the total and net OCS flux in the models.
- When OCS reaches about 23 to 25 km, which from below will naturally happen in the tropics, then the photochemical lifetime rapidly declines with altitude and becomes shorter than the transport time, so that any OCS entering the tropical pipe and reaching 25 km altitude will be quantitatively converted to SO₂

OCS in the stratosphere



- Multiplying the total upward mass flux at 25 km in the tropical pipe (calculated by my colleague Felix Ploeger from ERA interim) by the tropospheric and LMS average 500 ppt OCS should yield the **net annual OCS sulfur flux into the stratosphere**. Indeed, the result of this calculation nicely agrees with estimates from both models and observations.
- One implication is that in terms of climate sensitivity, **any significant future trend in the upward mass flux will have an impact on how much sulfur is contributed to the Junge layer by OCS**.
- Another implication is that if there are large OCS sources in the tropics close enough in space and time to where the most efficient vertical transport occurs, then the OCS mixing ratio in the air entering the tropical pipe may be higher and the flux may be larger. There are at least some data such as Envisat-MIPAS observations in the tropical UT (Glathor et al., 2017) suggesting that this may actually be the case.

Carbonyl Sulfide, OCS



- at ~500 ppt most abundant sulfur gas in the atmosphere
- potent greenhouse gas, current forcing $\sim 0.008 \text{ W m}^{-2}$ (Brühl et al., 2012)
- chemically stable, tropospheric lifetime $\sim 2\text{--}5$ years (vegetation sink!)
 - all transport pathways open!
- contributes between 56 % (Sheng et al., 2015) and 70 % (Brühl et al., 2012) of background stratospheric aerosol
- pre-industrial abundance ~ 70 % of today's value (ice core data, Aydin et al., 2008), negligible trends (< 1 %) in modern measurement era
- tropospheric budget is **still/again** highly uncertain
 - some question marks on the quantification of the stratospheric source
 - implications for the prediction of future trends and potential climate feedbacks

- Let's go back to the troposphere and look in detail at trends and the tropospheric budget, because it does have direct implications for the amount of OCS being transported to the stratosphere, especially with respect to future trends and potential climate feedbacks
- According to ice-core records, atmospheric OCS mixing ratios have risen from approximately 350 ppt to 500 ppt since the start of the industrialization around 1800.
- This increase appears to have stopped, and modern instrumental records do not show any significant OCS trend over the past three decades.
- For some time between 1800 and the mid-1900s, OCS sources must have exceeded sinks. One factor is obviously the addition of anthropogenic emissions as a new source, but unless we're grossly underestimating them, they can't fully explain the increase from 350 to 500 ppt, and most likely, some reduction in vegetation and/or soil uptake of OCS also happened during that time. This is discussed in some detail by Campbell et al., GRL, 2015).
- **The fact that the rising OCS trend has come to a halt means that the current budget must be nearly balanced, i.e. sources should approximately equal sinks.**
- Indeed, around the year 2000, budget estimates published by Watts (2000) and Kettle et al. (2002) were balanced, and at that time we thought that we knew the size of the various sources and sinks quite well...
- ...but when you think that you understand something sufficiently well and are about to close a "scientific chapter", someone comes along and puts everything you think you know into question...

The vegetation sink and OCS as a proxy for GPP

- Mechanistic studies on vegetation (*Sandoval-Soto et al., 2005*) and soil (*Van Diest and Kesselmeier, 2008*) suggest that they may take up more OCS than previously thought.
- *Montzka et al., 2007*: vertical gradients and N.H. seasonality suggest a larger OCS sink from the terrestrial biosphere

→ Motivated further research on vegetation (e.g. *Campbell et al., 2017*) and soil uptake (e.g. *Whelan et al., ACP, 2016*; *Wu et al., ACP, 2018*; *Kaisermann et al., currently ACPD*)

Berry et al., 2013

Comparing drawdown of CO₂ with COS could provide **additional constraints on differential responses of photosynthesis and respiration** to environmental forcing. The **separation of these two distinct processes is essential to understand the carbon cycle** components.

- Both laboratory experiments and atmospheric observations gave some indication that the largest sink, vegetation, and also the second largest sink, soils, may take up significantly more OCS than we all thought at the time. This warrants further investigation, and it is good to see quite a few groups intensely working on better quantifying the plant and soil sinks over a wide range of ecosystems
- However, new and much larger numbers for the global vegetation and soil sinks may have been produced a bit too quickly.
- Some motivation to do so was tied to the idea of using OCS as a proxy for gross primary production: it is well known that OCS is taken up by plants via the same pathway taking up CO₂ for photosynthesis; but unlike CO₂, OCS is not emitted by plants by any respiration process.
- Therefore, if the ratio of CO₂ to OCS uptake is reasonably constant, or if we least understand it and have the ability to scale it to different ecosystems, then we can **potentially use OCS to estimate the photosynthetic uptake of CO₂ by land vegetation**. There are a few convincing papers that have demonstrated this for individual ecosystems...

The vegetation sink and OCS as a proxy for GPP

Berry et al., 2013

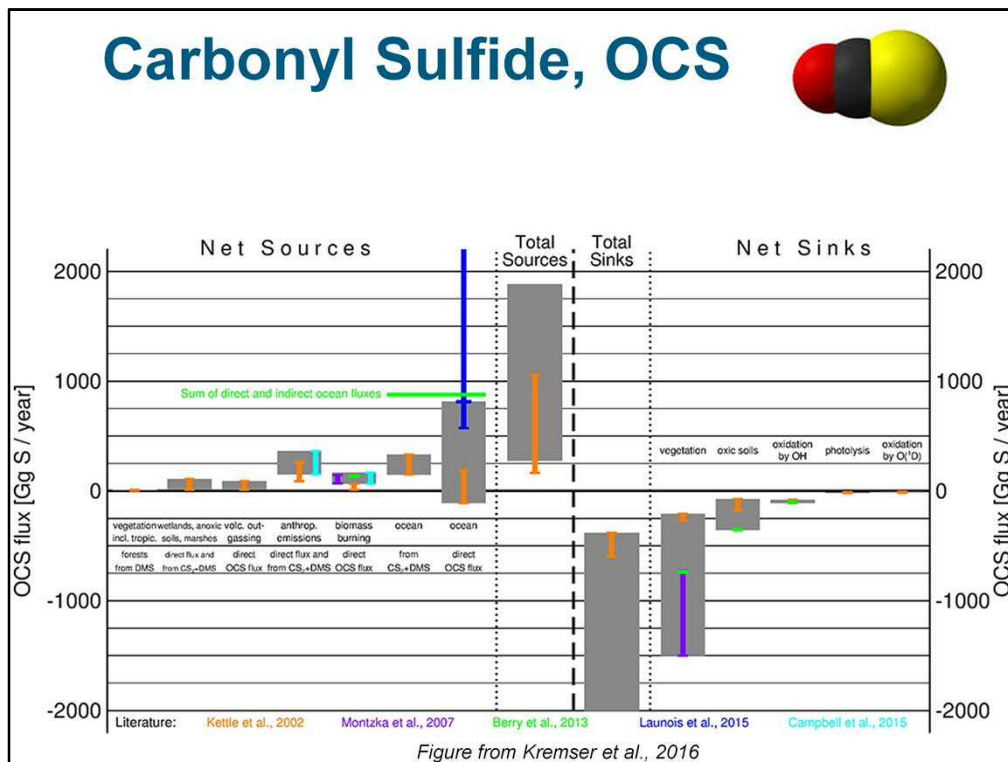
“...illustrate what COS measurements might tell us about carbon cycle processes”

Modeling framework for interpreting OCS data:

- implemented mechanistic and empirical descriptions of leaf and soil OCS uptake into a global carbon cycle model to obtain **new estimates of the OCS land flux**
- introduced these revised boundary conditions into CTM to simulate global OCS and CO₂ in the global atmosphere
- **need new source to balance 3x increase in global vegetation sink: found in the tropical oceans based on a simple inversion approach**

- ...but I am not yet convinced that this will actually work on a global scale as well as some people think or hope.
- Some colleagues came to the conclusion, that there *must* be a large additional OCS source, which *must* be much larger OCS emissions from the tropical oceans than previously thought.

Carbonyl Sulfide, OCS



- When we put together an OCS budget estimate for the Kremser et al. review paper we extended the uncertainty ranges on the vegetation and soil sinks to cover both, the old estimates (mostly from Kettle et al., shown with their original uncertainties by the orange bars) and the new numbers suggested in by Montzka et al., Berry et al. and others.
- The budget then becomes grossly unbalanced, which we know it isn't from the absence of a significant trend, so we did what most of these new studies suggested: we extended the known ocean source upwards by roughly the same amount (this is actually supported by global ocean biogeochemical modelling study published in 2015 by Launois and coworkers, see below).
- So, the key take home message from the budget figure in Kremser et al. is, that the uncertainties on the total OCS sources and sinks are still (or rather: again) ridiculously large.

Old and new hypotheses on the global budget

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

	<i>Kettle et al.</i> [2002] ^a	<i>Montzka et al.</i> [2007]	<i>Suntharalingam et al.</i> [2008] ^b	<i>Berry et al.</i> [2013] ^c	<i>Kettle et al.</i> 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

^aValues in parentheses were used for the first EMAC simulation.

^bKettle et al. modified, with excess of sink over sources.

^cFluxes used for the PCTM simulation presented here.

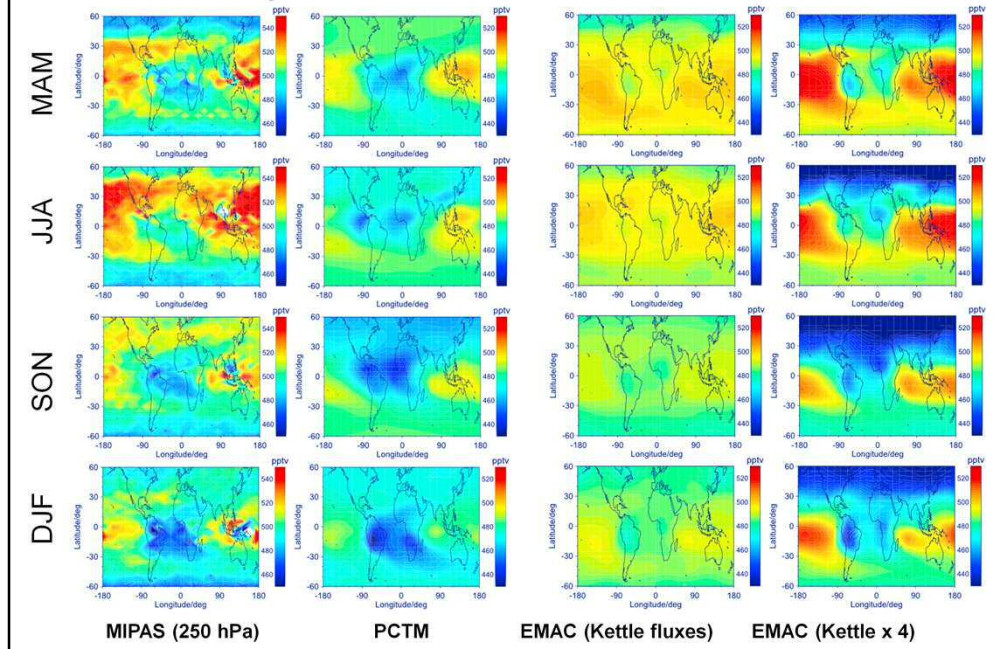
^dFluxes used for the second EMAC simulation. Plant uptake increased by a factor of 4, balanced by increased oceanic emissions in the latitude band 20°S–20°N, similar as in *Berry et al.* [2013].

Table from Glatthor et al., 2015

- The different estimates of these sources and sinks and their recent „evolution“ is summarized in this table from a paper by Norbert Glatthor and coworkers.

The „Tropical missing source“

Figures 1 and 2 from Glatthor et al., 2015



- The same paper supports a hypothetical „missing source“ in the tropics.
- The main focus is on MIPAS satellite observations of OCS in the upper troposphere, shown in the left column for the 250 hPa level for different seasons from boreal spring on top to boreal winter on the bottom.
- Without discussing the paper or the figure in detail, one important thing to note is that highest OCS mixing ratios are observed in the tropics and subtropics, and especially in the spring and summer seasons over the tropical and subtropical Pacific ocean.
- While none of the model simulation results shown in the other columns really reproduces the observations too well in all locations, only a simulation with Kettle et al. fluxes multiplied by 4 and the entire “additional” ocean flux released in the 20 °S to 20 °N latitude band reproduces the observed high mixing ratios over the Pacific reasonably well.
- So have we really underestimated OCS emissions from the tropical oceans by that much?
- Let’s look at some recent studies on the ocean source of OCS...

The (tropical) ocean source - recent studies

From Sinikka Lennartz's talk this morning, we have learned that

“As a result from measurements and a model consistent with the existing database, significantly higher direct emissions of OCS than previously estimated are very unlikely.”

consistent with her recent paper (Lennartz et al., ACP, 2017):

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

Parameter	OASIS	ASTRA-OMZ	Pacific Warm Pool
SST [°C]	27.0±1.0	19.6±2.6	28.9±0.9
SSS [g kg ⁻¹]	35.0±0.3	35.1±0.3	34.5±0.42
wind speed [m s ⁻¹]	8.2±1.7	7.5±1.8	5.3±0.4
a ₃₅₀ [m ⁻¹]	0.039±0.02	0.146±0.02	0.050±0.08
I [W m ⁻²]	226.5±303.0	196.4±283.1	206.4±286.6*
pH [-]	8.03±0.01	~**	8.07±0.01
MLD [m]	43.3±15.8	18.9±7.5	35.9±14.1

...and conditions in the Indian Ocean are similar to Pacific Warm Pool

- Sinikka's presentation has already provided convincing arguments that significantly higher OCS emissions from the ocean than estimated 15 years earlier by Kettle et al. and many others are unlikely.
- Early in 2017, she has already published a paper with the same conclusion, providing direct observational evidence for moderate or even slightly negative open ocean fluxes in the tropical Indian ocean, which in terms of the parameters governing OCS production and destruction in the water is similar to the tropical Western Pacific, where many claim the large ocean emissions needed to balance the new budget to originate from.

The (tropical) ocean source - recent studies

From Sinikka Lennartz's talk this morning, we have learned that

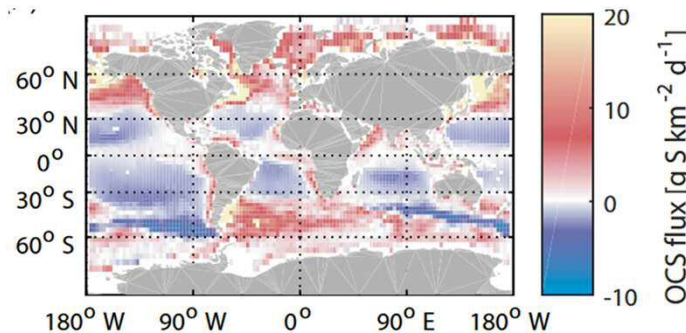
“As a result from measurements and a model consistent with the existing database, significantly higher direct emissions of OCS than previously estimated are very unlikely.”

consistent with her recent paper (Lennartz et al., ACP, 2017):

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

Global picture

- Integrated emissions ~ Kettle et al. (2002)
- Low emissions in the tropics
- Highest open ocean fluxes in S. Ocean



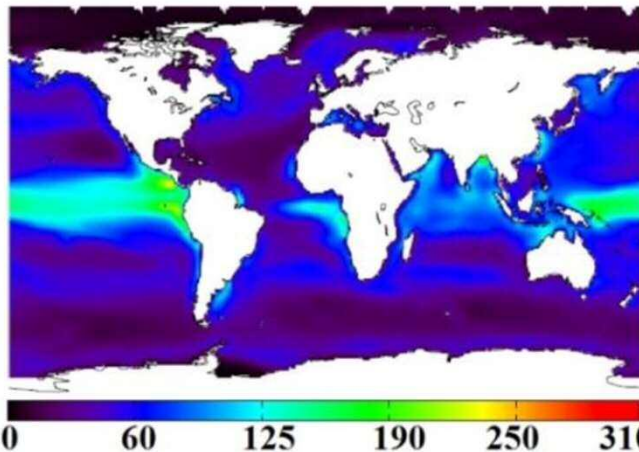
- Sinikka also used a rather detailed process model of OCS in seawater on a global scale to extrapolate observations. In the model, sea-air OCS fluxes are also lower in the tropics and subtropics than at higher latitudes, and the integrated flux is not so different from that given in Kettle et al.
- The model predicts high OCS emissions at northern high latitudes and from the Southern Ocean.

The (tropical) ocean source - recent studies

Much higher direct OCS emissions have been predicted by Launois et al., ACP, 2015:

A new model for the global biogeochemical cycle of carbonyl sulfide

– Part 1: Assessment of direct marine emissions with an oceanic general circulation and biogeochemistry model



- Depending on model setup, global flux estimates range from 573 – 3997 Gg S a⁻¹
- Low and medium estimates (813 Gg S a⁻¹) consistent with „missing source“
- Particularly high OCS concentrations and emissions in tropics

...but I don't fully understand their math...

- Quite different results were obtained by Launois et al., ACP, 2015
- It is a pure modelling study (i.e. not based on observational evidence), but the approach is actually quite sophisticated, coupling an oceanic general circulation model with a biogeochemistry model, and extensive sensitivity runs for some of the most critical parameters. The processes relevant for OCS are all there, and parameterizations are similar to the ones used by Sinikka.
- Therefore, the much higher OCS water concentrations and sea-air fluxes in Launois' simulations (in any set-up) than in Sinikka's model, particularly in the tropics, are more than surprising.
- What's very nice about the Launois et al. paper is that it provides the full suite of information (exact process equations, relevant forcing data, intermediate results, ...) so that one can reproduce their calculations and see how they evolve towards the maps of seawater concentrations and fluxes shown in the paper.
- When doing that, I came across one issue that I don't understand...

The (tropical) ocean source - recent studies

Much higher direct OCS emissions have been predicted by Launois et al., ACP, 2015:

A new model for the global biogeochemical cycle of carbonyl sulfide

– Part 1: Assessment of direct marine emissions with an oceanic general circulation and biogeochemistry model

③ Hydrolysis

$\text{H}_2\text{O} + \text{OCS} \leftrightarrow \text{H}_2\text{S} + \text{CO}_2$ and $\text{OH}^- + \text{OCS} \leftrightarrow \text{HS}^- + \text{CO}_2$
hydrolysis constants: Kamysny et al. (2003), Elliott et al. (1989)

→ 1st order in OCS:
Hydr. Rate = $k_h [\text{OCS}]$

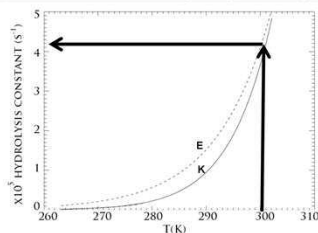


Figure 2. Temperature dependence of hydrolysis rates implemented in NEMO-PISCES. The relationships are represented for pH = 8.2, and taken from Elliott et al. (1989) (E, dashed line) and Kamysny et al. (2003) (K, solid line).

Tropics:

SST ~ 27 °C → $k_h \sim 0.15 \text{ h}^{-1}$

- ...and this is the OCS hydrolysis rate, a first order process that strongly depends on temperature.
- This temperature dependence is well established (and shown in the Launois et al paper, Figure 2), and the first order rate k_h constant at seawater temperatures typical for the tropical ocean is about 0.15 per hour.

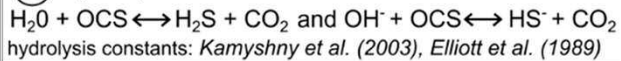
The (tropical) ocean source - recent studies

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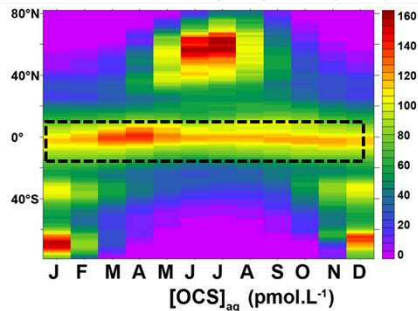
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→ 1st order in OCS:
Hydr. Rate = $k_h [\text{OCS}]$



Tropics:

SST ~ 27 °C → $k_h \sim 0.15 \text{ h}^{-1}$

$[\text{OCS}]_{\text{Launois}} \sim 130 \text{ pmol L}^{-1}$

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

- To obtain the OCS hydrolysis rate, k_h has to be multiplied by the OCS concentration. Using 130 pmol per liter from the latitude-time plot of the zonal monthly mean OCS concentration given in the paper supplement yields about 20 pmol per liter per hour OCS being lost by hydrolysis...

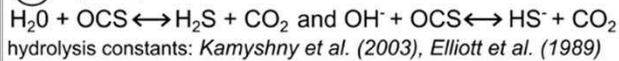
The (tropical) ocean source - recent studies

Much higher direct OCS emissions have been predicted by Launois et al., ACP, 2015:

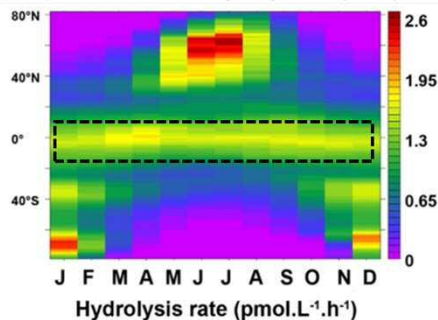
A new model for the global biogeochemical cycle of carbonyl sulfide

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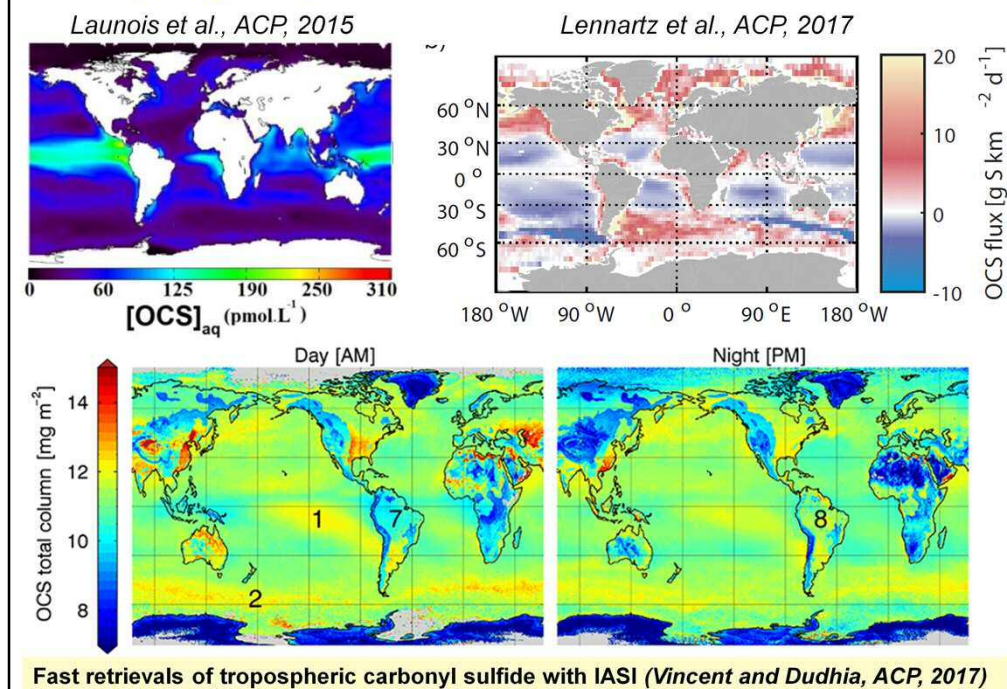
$[\text{OCS}]_{\text{Launois}} \sim 130 \text{ pmol L}^{-1}$

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

? ? ? ? ?

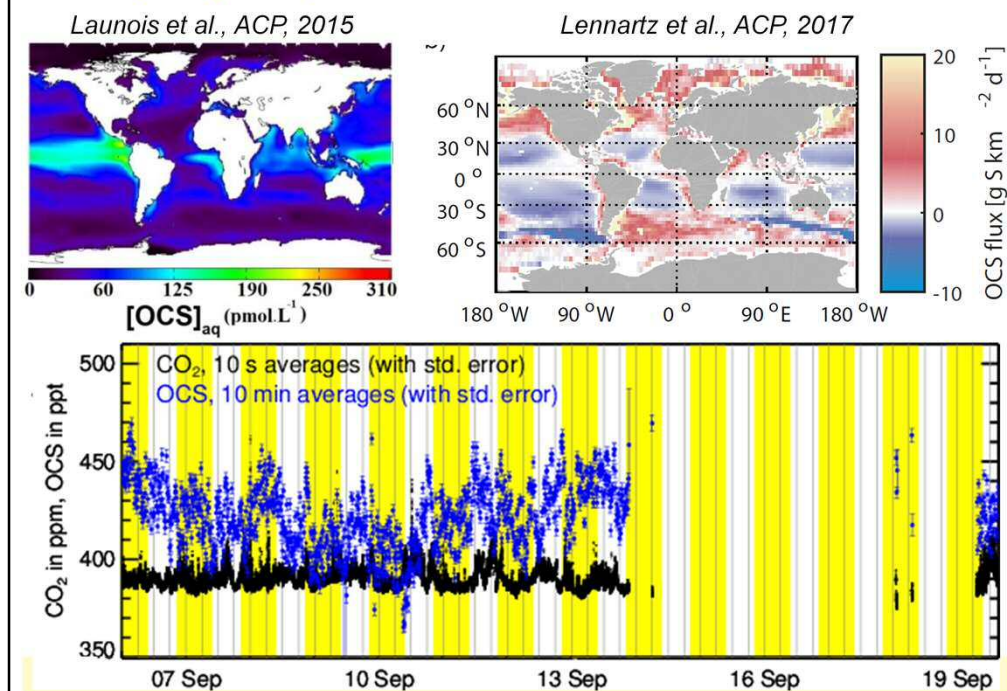
- ...which is clearly not consistent with the corresponding latitude time plot of the hydrolysis rate in the model (Launois et al., Figure 8) that suggests a hydrolysis rate in the tropics of about 2 pmol per liter per hour, i.e. smaller by about a factor of 10.
- Averaging effects (e.g. related to the strong diel OCS cycle) cannot have such a large effect: this simply does not make sense! And it would have a tremendous effect on the simulated tropical OCS concentrations!

The (tropical) ocean source - recent studies



- Further evidence supporting the smaller tropical OCS fluxes suggested by Lennartz et al. comes from observations of atmospheric OCS such as maps of column OCS from IASI recently published by Vincent and Dudhia showing similar patterns as Sinikka's model ...

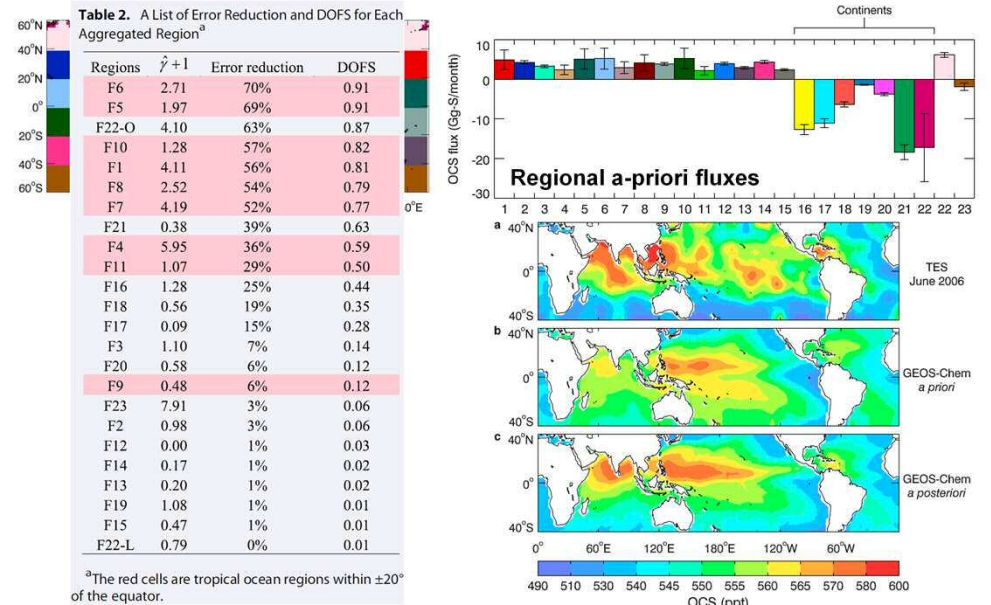
The (tropical) ocean source - recent studies



- ...as well as yet unpublished in-situ OCS measurements we obtained at the StratoClim ground station in Palau in the West Pacific (made together with AWI and the local Coral Reef Research Foundation) never exceeding 500 ppt and not showing a strong diel cycle

The (tropical) ocean source - recent studies

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



- Another study that appears to confirm large OCS fluxes from the tropical ocean is an inverse modelling study based on satellite observations of tropospheric OCS over the oceans made by Aura-TES.
- Le Kuai and coworkers divided the world into regions or „boxes“, for which we can expect more or less homogeneous OCS fluxes. For each box, they define an „a-priori flux“ based on the inventory given in the Berry et al. paper with the enhanced land vegetation sink and, in this case, an extra ocean source of the same magnitude distributed equally over all “ocean boxes” between 40°S and 40°N latitude. The a-priori flux is always negative in land boxes due to the vegetation and soil sinks, and always positive over ocean areas.

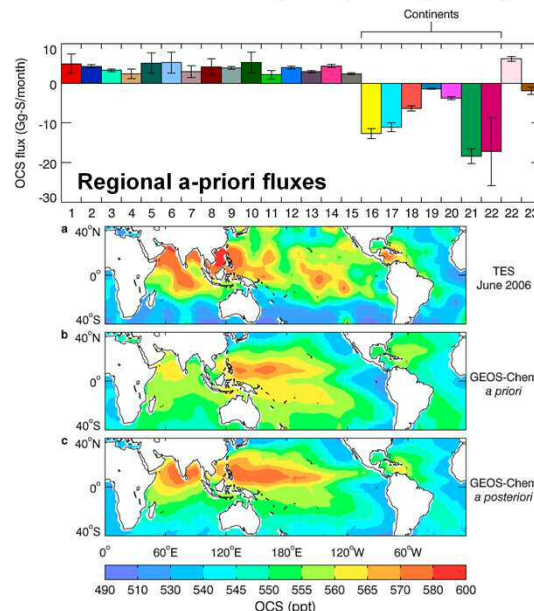
The (tropical) ocean source - recent studies

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

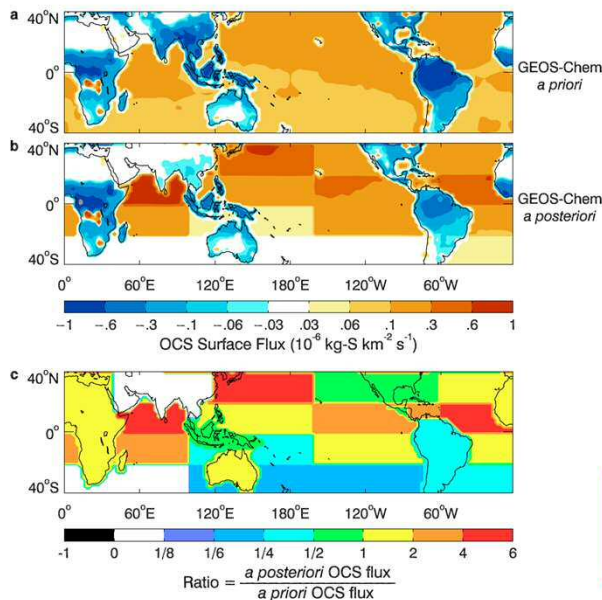
^aThe red cells are tropical ocean regions within $\pm 20^\circ$ of the equator.



- Another study that appears to confirm large OCS fluxes from the tropical ocean is an inverse modelling study based on satellite observations of tropospheric OCS over the oceans made by Aura-TES.
- Le Kuai and coworkers divided the world into regions or „boxes“, for which we can expect more or less homogeneous OCS fluxes. For each box, they define an „a-priori flux“ based on the inventory given in the Berry et al. paper with the enhanced land vegetation sink and, in this case, an extra ocean source of the same magnitude distributed equally over all “ocean boxes” between 40°S and 40°N latitude. The a-priori flux is always negative in land boxes due to the vegetation and soil sinks, and always positive over ocean areas.
- Fluxes are then optimized in an inversion of a GEOS-Chem simulation against the TES observations. For each box, an optimized scale factor is computed, and the highest scale factors are indeed found in the tropical oceans.
- One characteristic of the approach is that the scale factor cannot change sign, so a sink box will always remain a sink box and a source box will always remain a source box (as explicitly stated in the paper: *“The covariance matrix is adjusted to ensure that the a posteriori γ cannot be less than 1; i.e., a source or sink must remain as a source or sink after the inversion since the ratio defined between a posteriori flux and a priori flux is $1 + \gamma$.”* ; Another constraint: *“In this work, the net total flux will be kept constant during the inversion to maintain a global balanced budget”*)

The (tropical) ocean source - recent studies

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



Sign of the flux is fixed!!!

→ **Continents are net sinks by default**

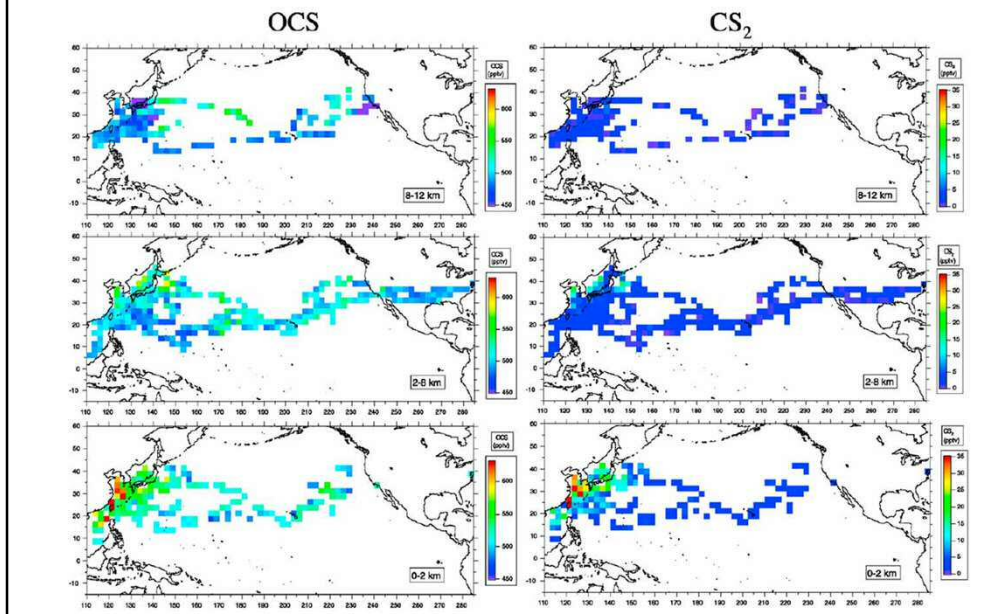
→ **inversion must find extra sources in the oceans**

“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.**”

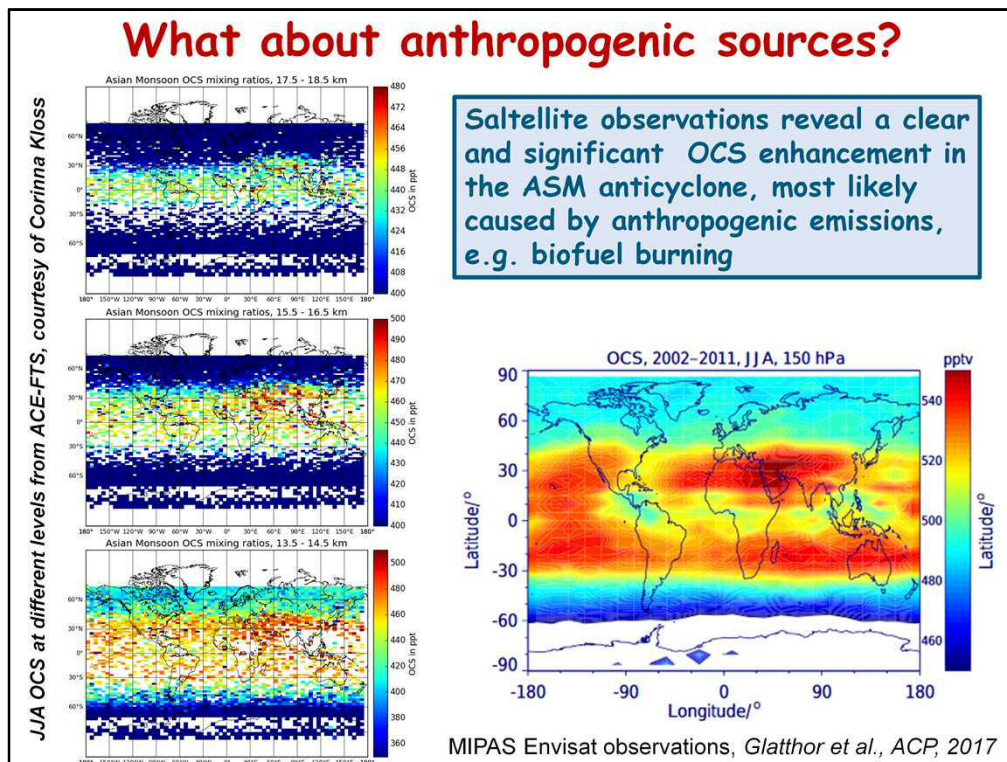
- Comparing a posteriori and a priori fluxes, the model has scaled up the ocean boxes surrounding Asia most. From this, Kuai et al. conclude that the strongest fluxes originate from the west Pacific and northern Indian Ocean near Southeast Asia...
- ...but given the constraint of the flux signs being fixed, and noting that the model has scaled down the Asian continental flux to almost zero: **how relevant is this result?**
What if anthropogenic OCS sources exceed the vegetation sink in Asia?

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**.



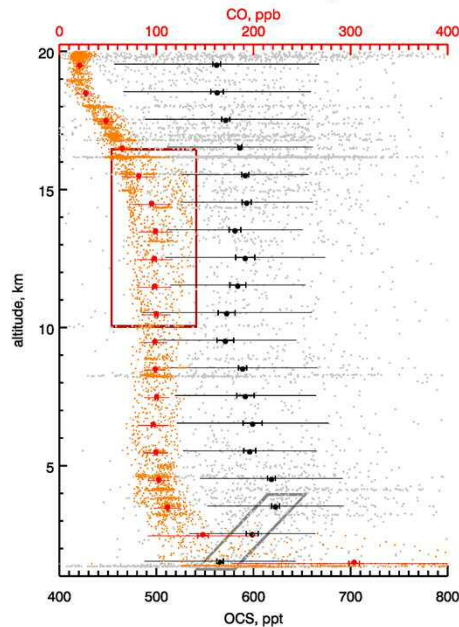
- Evidence supporting this alternative conclusion comes from a 2004 JGR paper by Nicola Blake and coworkers:
- Airborne observations of elevated OCS (> 500 ppt) over much of the Pacific ocean during TRACE-P (Feb – Apr 2001) are consistent with TES and MIPAS satellite observations and with more recent airborne observations from the HIPPO campaign (also described in Kuai et al.)
- **Blake et al. make a convincing case in tracing the observed OCS mixing ratios to sources in Asia using trajectory analyses and correlations with anthropogenic tracers.**



- We can also see a clear signature of elevated OCS from most likely anthropogenic sources in both ACE-FTS and MIPAS satellite observations over Asia in the monsoon season.
- In the ASM anticyclone that is characterized by rapid uplift of boundary layer air and isolated against surrounding air in the upper troposphere, we see the enhancement clearly at different levels in the ACE-FTS data in these plots that my former PhD student Corinna Kloss prepared, and we also see it in the MIPAS Envisat data published by Glatthor et al.

What about anthropogenic sources?

AMICA observations during StratoClim
Kathmandu, Jul/Aug 2017



Possible explanations for vertical gradient in KTM lower troposphere:

- Biofuel burning in Kathmandu not as important as in other regions in Asia
- Direct OCS emissions in Asia not significantly enhanced, but high emissions of CS_2 , which is converted to OCS and SO_2 on a time scale of hours to days
- Local sinks (vegetation, soils) near KTM cause low OCS in KTM valley

- Our own airborne data, obtained with the new AMICA instrument during the Geophysica flights from Kathmandu during StratoClim, show OCS mixing ratios closer to 600 ppt than the tropospheric average of 500 ppt over Nepal and the surrounding area.
- The enhancement being less pronounced in the lowest 3 km over Kathmandu suggests that either i) OCS sources such as biofuel burning are not as prominent in Kathmandu than in other regions in Asia, or ii) that local vegetation and soil uptake is offsetting the emissions, or iii) that the largest part of the emissions is in the form of CS_2 , which needs some hours in the atmosphere to be converted to OCS. We can't tell at this point, but our **airborne observations clearly support direct or indirect anthropogenic OCS emissions from Asia.**

What about anthropogenic sources?

Campbell et al., 2015: Larger anthropogenic OCS source than in the Kettle et al. climatology, particularly from anthropogenic CS₂

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
	<i>Anthropogenic CS₂</i>		
Approach	<i>Peyton et al. [1976]</i>	<i>Blake et al. [2004]</i>	See section 2
Source	116 ± 58	414 ± 207	190 ± 70
	<i>Aluminum</i>		
Approach	<i>Harnisch et al. [1995]</i>	<i>Harnisch et al. [1995]</i>	See section 2
Source	44 ± 22	99 ± 50	30 ± 7
	<i>Coal</i>		
Approach	<i>Khalil and Rasmussen [1984]</i>	<i>Khalil and Rasmussen [1984]</i>	See section 2
Source	20 ± 10	24 ± 12	60 ± 30
Total	180 ± 90	537 ± 269	257 ± 107

^aAll units are COS as Gg S yr⁻¹.

^bKettle et al. [2002].

^cEstimates are for most recent years for which industry data are available which are 2013, 2012, and 2011 for rayon, aluminum, and coal, respectively.

^dWe estimate the present source by applying current industry production (2011–2013) to the emission factors used in the most recent COS inventories.

- The observational evidence from satellites and aircraft supports a recent inventory published in GRL by Campbell et al., who suggest an anthropogenic OCS source approximately 50 % larger than the Kettle et al. budget, and explicitly discuss increasing emissions from Asia in recent years.
- While this is not enough to explain the gap in the budget resulting from the new vegetation sink estimates, it certainly shows us that the oceans are not the only suspect when searching for higher OCS emissions.

“Minor” reduced sulfur species: CS₂, DMS, H₂S and a few others...

- usually low mixing ratios, up to a few 10s ppt
- some large ground sources leading to significant fluxes

- Several shorter lived reduced sulfur species are found in the atmosphere in abundances typically on the order of tens ppt.
- Such relatively moderate mixing ratios don't mean that there aren't any significant emissions...

Budgets from Watts, 2000

Table 7
Global sources and sinks of CS₂ to the atmosphere

Source/sink	Annual flux (Tg a ⁻¹)
<i>Sources</i>	
Open ocean	0.11 ± 0.04
Coastal ocean (including salt-marsh and estuaries)	0.07 ± 0.04
Anoxic soils	0.07 ± 0.06
Wetlands	0.02 ± 0.02
Volcanism	0.05 ± 0.04
Anthropogenic	0.34 ± 0.17
Total source	0.66 ± 0.19
<i>Sinks</i>	
Reaction with OH	0.57 ± 0.25
Oxic soils	0.44 ± 0.38
Total sink	1.01 ± 0.45
Total imbalance	0.35 ± 0.49

Table 10
Global sources and sinks of DMS to the atmosphere

Source/sink	Annual flux (Tg a ⁻¹)
<i>Sources</i>	
Oceans	20.70 ± 5.20
Salt-marshes and estuaries	0.07 ± 0.06
Vegetation	1.58 ± 0.86
Tropical forests	1.60 ± 0.50
Soils	0.29 ± 0.17
Wetlands	0.12 ± 0.07
Anthropogenic	0.13 ± 0.04
Total source	24.49 ± 5.30

Table 8
Global sources and sinks of H₂S to the atmosphere

Source/sink	Annual flux (Tg a ⁻¹)
<i>Sources</i>	
Open ocean	1.50 ± 0.60
Coastal ocean	0.30 ± 0.10
Salt-marshes and estuaries	0.50 ± 0.35
Vegetation	0.37 ± 0.07
Tropical forests	0.42 ± 0.12
Soils	
(not tropical forest soils)	0.002 ± 0.002
Wetlands	0.20 ± 0.21
Volcanism/Geothermal	1.05 ± 0.94
OCS + OH	0.08 ± 0.07
Anthropogenic	3.30 ± 0.33*
Total source	7.72 ± 1.25
<i>Sinks</i>	
Reaction with OH	8.50 ± 2.80 ^b
Total sink	8.50 ± 2.80
Total imbalance	0.78 ± 3.1

The main sink of DMS in the atmosphere is reaction with OH by day, and NO₃ by night

- Looking at global budgets compiled in 2000 by Simon Watts:
- Large DMS sources, particularly ocean emissions (they have been corrected upward to ~ 28 Tg a⁻¹ in a recent climatology of oceanic DMS emissions by Lana et al.). The global DMS source exceeds even the upward scaled OCS emissions by more than a factor of 20, and is roughly half the global anthropogenic SO₂ emissions
- The main or in some cases the only significant sink for all of three gases listed here is the reaction with OH in the atmosphere.

“Minor” reduced sulfur species: CS₂, DMS, H₂S and a few others...

- usually low concentrations, up to a few 10s ppt
- some of them still have large ground sources leading to significant fluxes
- all readily react with OH with fairly short lifetimes (~hours), preventing them from being transported to the stratosphere

- Therefore, lifetimes are short, and rapid destruction is the reason why we don't see larger concentrations except in regions with very strong sources.
- The short lifetime also means that they are more or less quantitatively converted before making it to the stratosphere.
- Note that Marandino et al. (ACP, 2013) suggest high oceanic DMS emissions coinciding with fast vertical transport could lead to some unconverted DMS making it into the UT and even into the LS. This is qualitatively supported and quantitatively constrained by aircraft observations of up to 10 ppt made during the HIPPO and ATTREX campaigns: possibly significant for the LMS, but not for upper branch BD and Junge layer, because 10 ppt is minor compared to 500 ppt OCS.

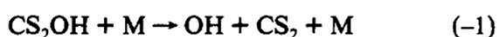
“Minor” reduced sulfur species: CS₂, DMS, H₂S and a few others...

- usually low concentrations, up to a few 10s ppt
- some of them still have large ground sources leading to significant fluxes
- all readily react with OH with fairly short lifetimes (~hours), preventing them from being transported to the stratosphere
- a major product of the OH oxidation is SO₂. H₂S and DMS make a contribution to the tropospheric SO₂ budget.
- Some CS₂ and DMS is also converted to OCS

- Main final product of DMS, H₂S and CS₂ oxidation is SO₂, and the contribution of DMS and H₂S to the tropospheric SO₂ budget is significant.
- Conversion of the two compounds containing carbon-sulfur bonds, CS₂ and DMS can partially yield OCS (this is shown in OCS budgets as „indirect“ OCS emissions).
- Now take a closer look at these conversions: prepare for some chemistry!

Reaction of CS₂ with OH

simplified from *Stickel et al., J. Phys. Chem, 1993*



When CS₂ reacts with OH in the atmosphere, ~ 83 % of its sulfur convert to OCS, the rest to SO₂

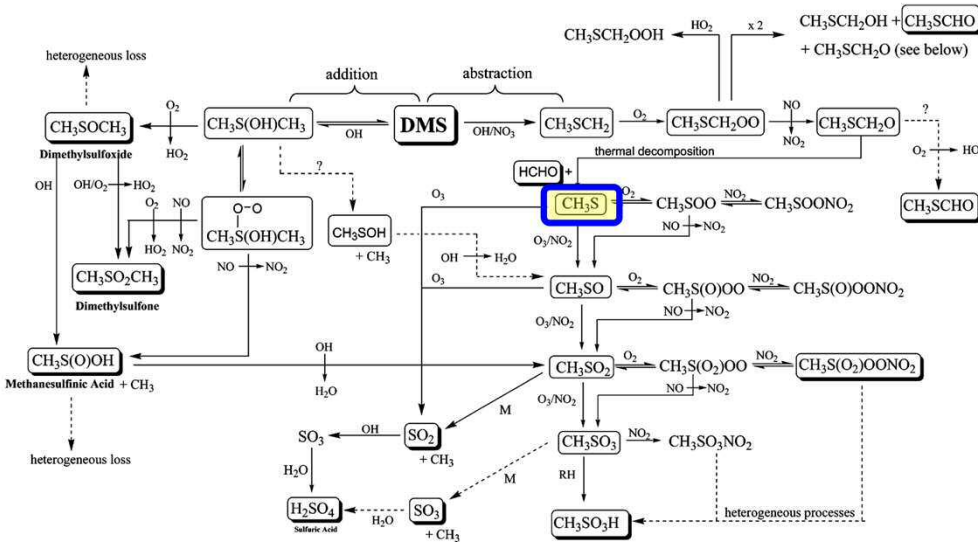
- In 1993, Stickel et al. have formulated the detailed mechanism for the reaction of CS₂ with OH, and measured rates and quantum yields in the laboratory
- It's more complex than shown here, because there are a few more minor pathways and competing reactions, but by and large, this set of reactions is what we need to look at.
- In a first step, OH attaches to CS₂ (this reaction can go back and forth, so there is an equilibrium).
- The CS₂OH intermediate reacts with molecular oxygen via two major routes. The quantitatively more important yields an OCS molecule, while all the other sulfur products of both channels will eventually end up as SO₂
- An overall yield of 83 % OCS from the reaction of CS₂ with OH is deduced, and this is expected to be fairly constant in the atmosphere.

“Minor” reduced sulfur species: CS₂, DMS, H₂S and a few others...

- usually low concentrations, up to a few 10s ppt
 - some of them still have large ground sources leading to significant fluxes
 - all readily react with OH with fairly short lifetimes (~hours), preventing them from being transported to the stratosphere
 - a major product of the OH oxidation is SO₂. H₂S and DMS make a contribution to the tropospheric SO₂ budget.
 - Some CS₂ and DMS is also converted to OCS
 - Production from CS₂ is a significant OCS source, tied closely to the CS₂ source strength
 - For DMS, an OCS product yield of ~0.7 % has been suggested by *Barnes et al. (1994 + 1996; confirmed by Albu et al., 2008)* and used ever since...
- ...let's look at this in a bit more detail (careful: chemistry!)

- So CS₂ is a significant OCS source, that we can quantify as well as we can quantify the CS₂ budget.
- Anthropogenic emissions of CS₂ are particularly large and uncertainties are significant. There is also a significant natural source from the ocean, that is also not very well constrained.
- Global sources of DMS are about 30 times larger than CS₂ sources. But unlike CS₂, where for almost every molecule reacting with OH, one OCS molecule is produced, OCS is only a very minor byproduct of the DMS oxidation: a product yield of 0.7 % has been observed in two laboratory studies, which is generally applied to the whole atmosphere in models or budget estimates.
- Look at this in more detail: more chemistry!

Simplified reaction scheme for the OH and NO₃ radical-initiated oxidation of dimethyl sulfide from *Barnes et al., 2006*

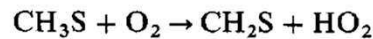


It has been suggested that the route to OCS proceeds essentially via the methylthiyl radical (*Barnes et al., 1994 + 1996; Albu et al., 2008*).

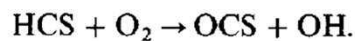
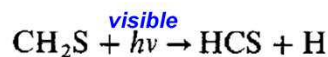
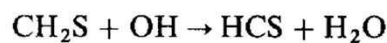
- This (simplified!!!) reaction scheme of the DMS oxidation was sketched out in a review by Barnes et al.
- From the laboratory experiments and also from mechanistic considerations, any substantial production of OCS in this scheme can only proceed via the methylthiyl radical, $\text{CH}_3\text{S}\cdot$, that can react with molecular oxygen (O_2) in two different ways: (i) an addition equilibrium shown in the big scheme...

Simplified reaction scheme for the OH and NO₃ radical-initiated oxidation of dimethyl sulfide from *Barnes et al., 2006*

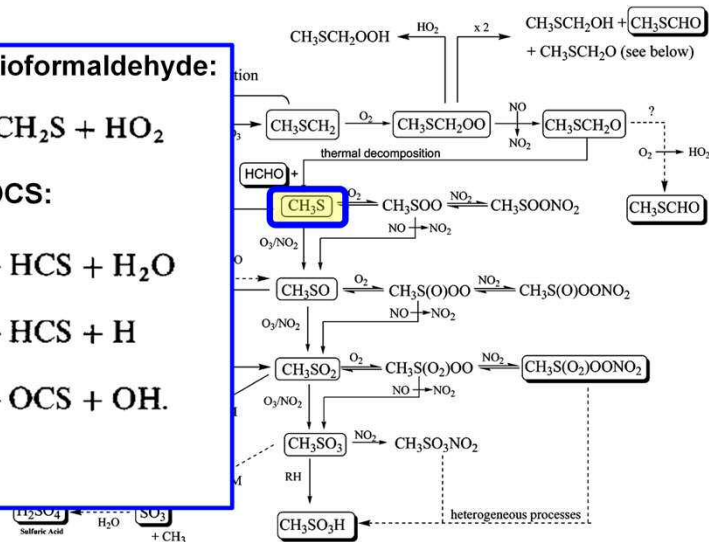
1. Formation of thioformaldehyde:



2. Conversion to OCS:



(*Barnes et al., 1996*)

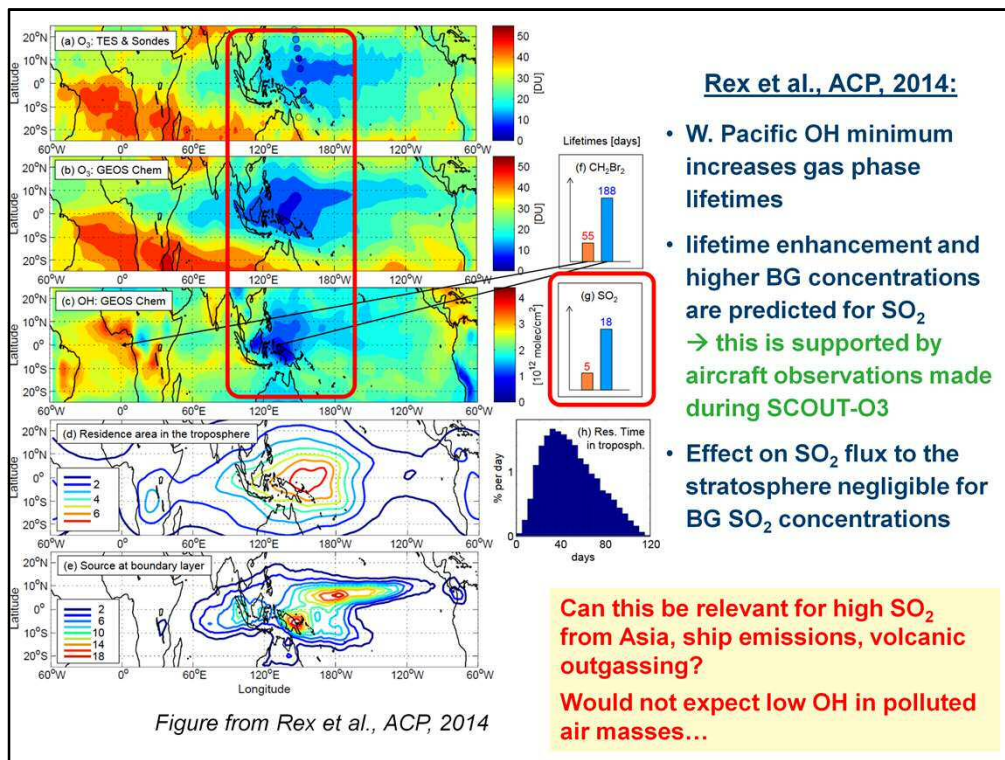


It has been suggested that the route to OCS proceeds essentially via the methylthiyl radical (*Barnes et al., 1994 + 1996; Albu et al., 2008*).

- ...and (ii) the abstraction of a hydrogen atom giving the reasonably stable thioformaldehyde that can either further react with OH or be photolyzed by visible light to give another radical, HCS, that readily converts to OCS when it collides with another O₂ molecule.
- Adding NO_x to the reaction system will quantitatively quench OCS production because NO_x efficiently scavenges the methylthiyl radical (an OCS product has never been observed in the laboratory if NO_x was added to the experiment). In the atmosphere, it is likely that the 0.7 % conversion will go down to zero in a polluted, NO_x rich atmosphere.

[illegible]

- What will happen in the remote marine boundary layer, where NO_x may actually be even lower than in the „no NO_x laboratory experiments“?
- The methylthiyl radical is not scavenged anymore, and quite a few routes in the reaction mechanism become slow or unimportant under these conditions.
- The product of the O_2 addition reaction with CH_3S tends to react with NO or NO_2 , so this equilibrium is shifted and the O_2 abstraction channel producing OCS should become relatively more important (note: there is a “bypass” of the one reaction step in the formation of CH_3S that requires NO_x)
- In an even cleaner atmosphere where ozone and OH are also reduced to extremely low concentrations, further channels will be slowed or even blocked (note: to produce the methylthiyl radical, we only need OH in the very first step, so that it depends on OH at most as much as all other channels here).
- Where would we expect to find such extremely clean conditions?



- Maybe in the OH hole over the Western Pacific warm pool that was already mentioned in the context of SO₂.

Simplified reaction scheme for the OH and NO₃ radical-initiated oxidation of dimethyl sulfide from Barnes et al., 2006

The diagram illustrates the following reaction pathways:

- Initiation:** DMS reacts with OH or NO₃ radicals.
- Addition Pathway:** Leads to CH₃S(OH)CH₃, which can further react with O₂ to form CH₃SO₂CH₃ (dimethylsulfolene) or CH₃S(OH)CH₃.
- Abstraction Pathway:** Leads to CH₃SCH₂, which reacts with O₂ to form CH₃SCH₂OO•, eventually leading to CH₃SCH₂O• and CH₃SCHO.
- Other Intermediates:** CH₃SO•, CH₃SO₂•, CH₃SO₂(O)OO•, CH₃S(O₂)OO•, CH₃SO₃H, and CH₃SO₃• are also shown.

A green box highlights the following reaction sequence:

$$\text{Cl} + \text{CH}_3\text{SCH}_3 \rightarrow \text{CH}_3\text{SCH}_2 + \text{HCl}$$
$$\rightarrow [(\text{CH}_3)_2\text{S}-\text{Cl}]^*$$
$$[(\text{CH}_3)_2\text{S}-\text{Cl}]^* + \text{M} \rightarrow \text{CH}_3\text{S} + \text{CH}_3\text{Cl} + \text{M}$$
$$\rightarrow \text{CH}_3\text{SCl} + \text{CH}_3 + \text{M}$$
$$\rightarrow (\text{CH}_3)_2\text{S}-\text{Cl} + \text{M}$$

Some equilibria will be shifted...
...and another oxidant becomes relatively more important

- Some routes will be blocked and some equilibria will be shifted, making the production of CH_3S faster and more important in relative terms compared to less clean conditions.
- Furthermore, when OH is very low, other oxidants can take over. In the remote marine boundary layer, the chlorine radical is a likely candidate for such a scenario.
- In that case, a chlorine radical takes over the role of OH in this first abstraction reaction of DMS. And, just like OH, Cl can also react with DMS by an addition reaction producing an intermediate.
- Interestingly, this can thermally decompose to the stable methyl chloride and a methylthiyl radical!
- **These thoughts are by no means quantitative, they are rather hypothetical, probably even speculative, but it seems at least possible that in certain marine environments such as the very clean atmosphere over the Werstern Pacific, a larger fraction than 0.7 % of DMS is converted to OCS.**
- Besides anthropogenic emissions over Asia, a larger DMS-to-OCS conversion ratio could be a second possible explanation for the elevated OCS observed in the UT over the Pacific, and it may contribute to balancing the OCS budget should the larger numbers for the vegetation and soil sinks be corroborated.

“Minor” reduced sulfur species: CS₂, DMS, H₂S and a few others...

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Invited review

Anthropogenic contributions to global carbonyl sulfide, carbon disulfide and organosulfides fluxes



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ABSTRACT

Previous studies of the global sulfur cycle have focused almost exclusively on oxidized species and just a few sulfides. This focus is expanded here to include a wider range of reduced sulfur compounds. Inorganic sulfides tend to be bound into sediments, and sulfates are present both in sediments and the oceans. Sulfur can adopt polymeric forms that include S–S bonds. This review examines the global anthropogenic sources of reduced sulfur, updating emission inventories and widening the consideration of industrial sources. It estimates the anthropogenic fluxes of key sulfides to the atmosphere (units Gg S a^{−1}) as: carbonyl sulfide (total 591: mainly from pulp and pigment 171, atmospheric oxidation of carbon disulfide 162, biofuel and coal combustion, 133, natural 898 Gg S a^{−1}), carbon disulfide (total 746: rayon 395, pigment 205, pulp 78, natural 330 Gg S a^{−1}), methanethiol (total 2119: pulp 1680, manure 330, rayon and wastewater 102, natural 6473 Gg S a^{−1}), dimethyl sulfide (total 2197: pulp 1462, manure 660 and rayon 36, natural 31,657 Gg S a^{−1}), dimethyl disulfide (total 1103: manure 660, pulp 273, natural 1081 Gg S a^{−1}). The study compares the magnitude of the natural sources: marine, vegetation and soils, volcanoes and rain water with the key anthropogenic sources: paper industry, rayon-cellulose manufacture, agriculture and pigment production. Industrial sources could be reduced by better pollution control, so their contribution may lessen over time. Anthropogenic emissions dominate the global budget of carbon disulfide, and some aromatic compounds such as thiophene, with emissions of methanethiol and dimethyl disulfide also relatively important. Furthermore, industries related to coal and bitumen are key sources of multi-ringed thiophenes, while food production and various wastes may account for the release of significant amounts of dimethyl disulfide and dimethyl trisulfide.

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- Some more specific details about the anthropogenic sources of OCS, CS₂ and DMS, and other sulfur gases that contribute to the tropospheric sulfur budget are compiled in a recent review by Chon-Lin Lee and Peter Brimblecombe

“Minor” reduced sulfur species: CS₂, DMS, H₂S and a few others...

Table 1

Summary table of anthropogenic and for comparison natural emissions Gg S a⁻¹. Superscripts prefixed in Greek letters give range taken from literature. Superscripts in Roman letters give other additional information.

Sources	OCS	CS ₂	MeSH	DMS	DMDS	Thioa*	BTs	DBT	Total
3.1 Biomass burning	^a 43	^a 1.8		^a 6	^a 119				170
3.2 Biofuel combustion	^b 73.1	2.9						0.035	75
3.3 Pulp and paper industry	97.2	78.5	1680 ^b	1462	273 ^c	17			3608
3.4 Rayon/cellulosics manufacture		^c 395	51.4 ^d	35.6					482
3.5 Manure	*	*	330	^b 660 ^e					1650
3.5 Paddy fields	0.38	26.9	0.76	25	0.57				53.6
3.6 Pigment industry	74	205							279
3.7 Food processing	0.63		*	3.97	28.9 ^f				33.5
3.8 Gas industry	0.7		4.8	0.84 ^g	0.1 ^h		^e 0.005 ⁱ	ⁱ 0.003 ^j	6.45
3.9 Wastewater	0.022	1.03	51	3.4	21.4				76.9
3.10 Aluminium industry	^k 30	4						*	34
3.11 Coal combustion	^l 60	0.33				0.32	0.16 ^k	0.22 ^l	61
3.11 Coke production	9	14				14	3		40
3.12 Bitumen production and use								^m 7	7
3.13 Vehicles	ⁿ 6	ⁿ 0.3				*	*	0.071 ⁿ	6.37
3.16 Shipping	30	1.5				*	*	1.5 ^o	33
3.14 Tyre wear	11.7	15.5							27.2
3.14 Tyre combustion	0.064		0.043			0.098 ^p	0.185 ^q		0.39
3.15 Landfill and waste	0.079	0.19	0.34 ^r	0.26	0.008	0.0004			0.88
3.17 Brickmaking		0.03							0.03
3.18 Oxidation#	162								162
Subtotal	598	747	2119	2197	1103	31.4	3.35	8.83	6807
Natural sources†	(4.1)	(4.2)	(4.3)	(4.4)	(4.5)	(4.6)			
Saline and ocean water	^s 887 ^s	^p 243 ^s	^r 4738	^t 28,187 ^r	213 ^t				34,268
Vegetation and soils		^u 70	1735	3470	868				6142
Volcanoes	^v 11	^v 17	*			^u 0.1			28.1
Oxidation#	158								158
Subtotal	1056	330	6473	31,657	1080	0.1	0	0	40,596
Total sources	1654	1077	8592	33,854	2184	31.5	3.35	8.83	47,403
Industry ^u	272	697	1741	1502	304	31.4	3.35	7.22	4557
Agriculture ^v	0.38	26.9	331	685	661				1704

- It provides a large amount of very detailed and sometimes surprising information, and it must have been a big effort to compile all the numbers in there.

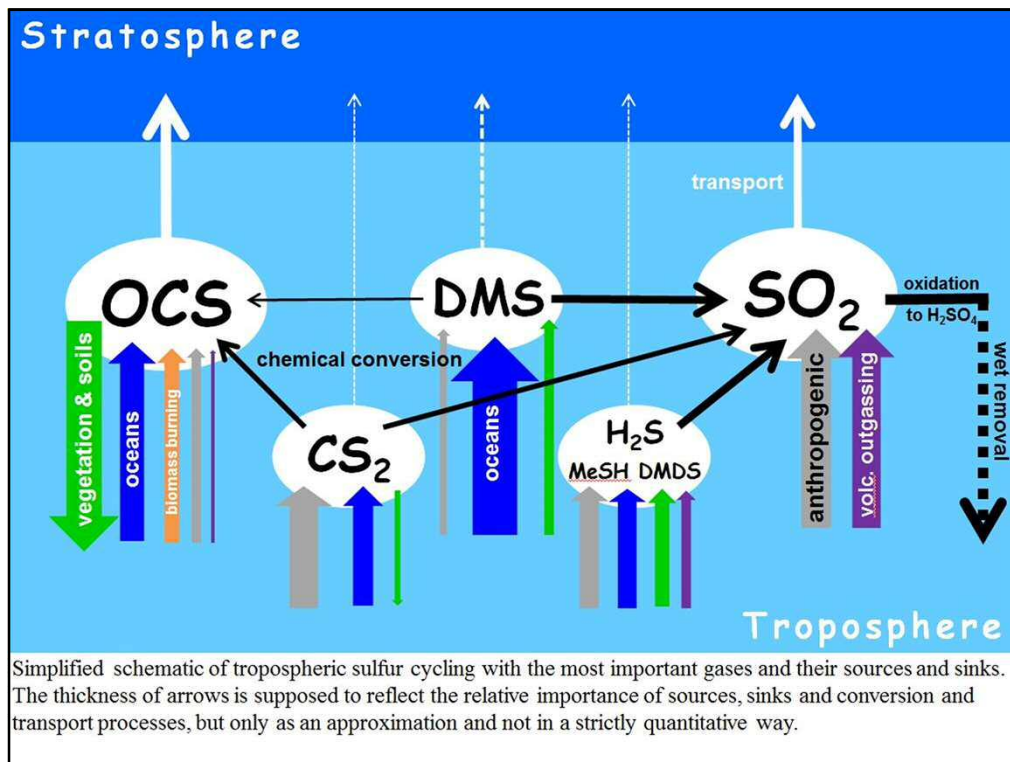
Take home messages

- Amount and variability of stratospheric aerosol is mainly governed by volcanoes, but there is a sizeable non-volcanic background.
- The largest fraction of this originates from OCS. We can quantify and model this contribution well under current conditions solely based on the tropospheric OCS mixing ratio.
- Significant gaps in our understanding of the tropospheric cycling of OCS still exist:
 - how large is the global sink due to vegetation and soils?
 - is the observed OCS enhancement in the UT over the tropical Pacific caused by emissions from Asia or by DMS from the ocean?
 - And can this explain a possible "missing sink"?

Take home messages

- Amount and variability of stratospheric aerosol is mainly governed by volcanoes, but there is a sizeable non-volcanic background.
- The largest fraction of this originates from OCS. We can quantify and model this contribution well under current conditions solely based on the tropospheric OCS mixing ratio.
- Significant gaps in our understanding of the tropospheric cycling of OCS still exist. We should close them in order to assess possible climate interactions and predict future changes.
- Anthropogenic SO₂ contributes to aerosol levels in the LMS, and it is quite possible that some fraction also makes it to the "overworld". This is difficult to quantify due to lack of full understanding of scavenging in convection and further processing in the TTL and ASM anticyclone, but new observations may help.
- **Don't forget about the non-sulfur contributions!**

Extra Slides



OCS Satellite Record

Towards a multi satellite global record?

	ACE-FTS	ENVISAT-MIPAS	AURA-TES
Time period	02.2004 – ...	06.2002 – 04.2012	08.2004 – ...
Spectral band	2036–2056 cm ⁻¹	839–876 cm ⁻¹	2034 – 2075 cm ⁻¹
Viewing Geometry	Solar Occultation	Limb Emission	Limb/Nadir
Sampling Frequency	~ 30 scans per day	~ 1400 scans per day	„global survey“
Altitude range	8 – 31 km (equator) 6 – 23 km (high lat)	6 – 40 km	< ~ 15 km
Vertical resolution	2 – 6 km	4-5 km below 15 km, up to 15 km above	sensitive in the mid-troposphere with a peak sensitivity typically between 300 and 500 hPa

AURA-TES vertical sampling

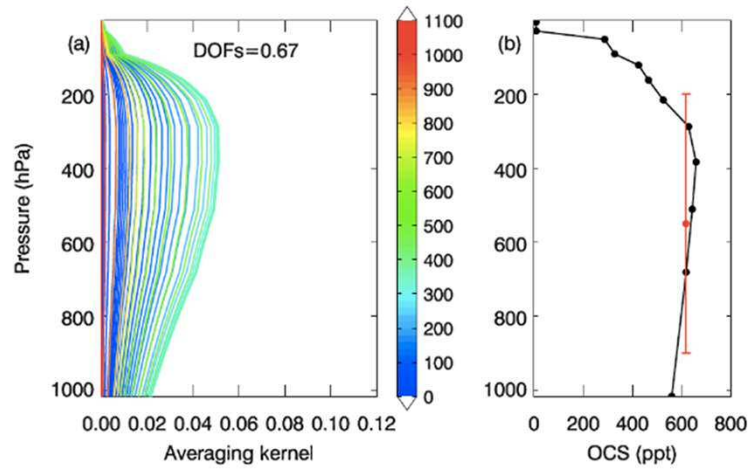


Fig. 5. (a) Averaging kernels for different vertical levels in colored lines. (b) Retrieved OCS profile (black line with dots) and its corresponding tropospheric OCS in red.

Kuai, et al., *Characterization of Aura TES carbonyl sulfide retrievals over ocean*

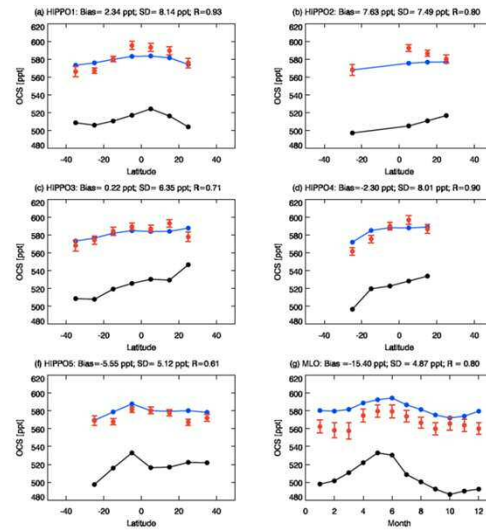
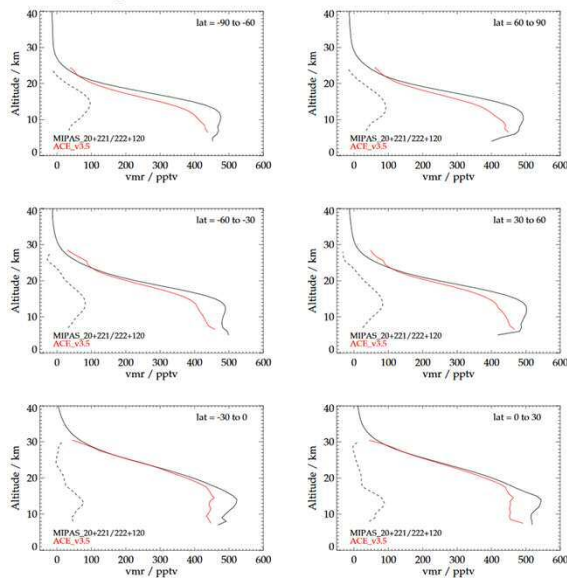


Fig. 8. Individual comparison between TES multiyear monthly means and in situ data for latitudinal patterns (a–f) and seasonal variations (g). Original in situ data averaged over latitude bins in black; in situ data applied with TES operator in blue; TES data in red. Bias, standard deviation (SD) and correlations (R) for the comparison between blue and red are given. Error bar represents the error on the mean (standard variation within the grid bin divided by the square root of the number of observations).

Towards a multi satellite global record?

Large difference (~100 ppt!) between ACE and MIPAS near TP

Figure 4 from Glatthor et al., 2016:



- **ACE-FTS:**
homogeneous throughout free troposphere, starting to decrease with altitude around TP
 - **MIPAS:**
higher OCS in the TP region than in the free troposphere
- How to explain this?**
- fast transport mechanism from OCS loaded boundary layer bypassing the 5-10 km region
 - OCS source gas transported to the UTLS and then converted to OCS

Implications for scientific understanding!

→ understanding of OCS cycling and transport and parameterization in models may be significantly different depending on which satellite data set we use to constrain the models

Towards a multi satellite global record?

Figure from Barkley et al., 2008:

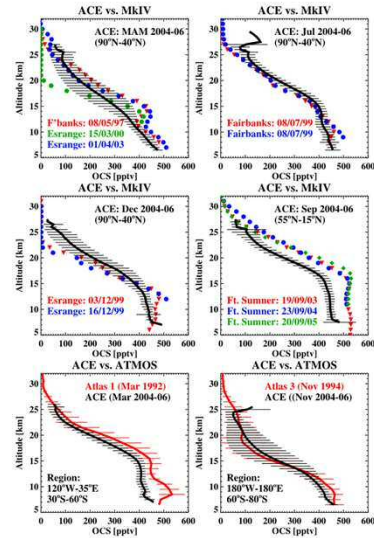
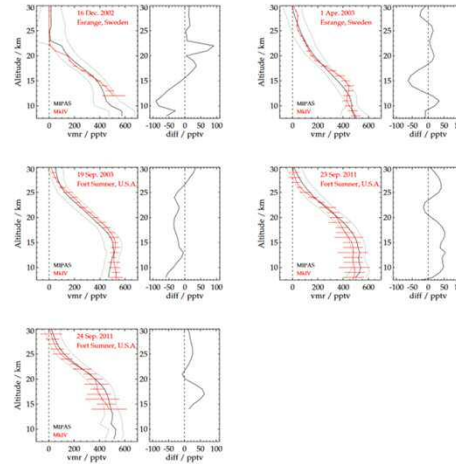


Figure 2 from Glatthor et al., 2016:



"The local maxima of the MIPAS profiles in the upper troposphere might partly be due to retrieval instabilities. However, we cannot exclude that they are realistic."

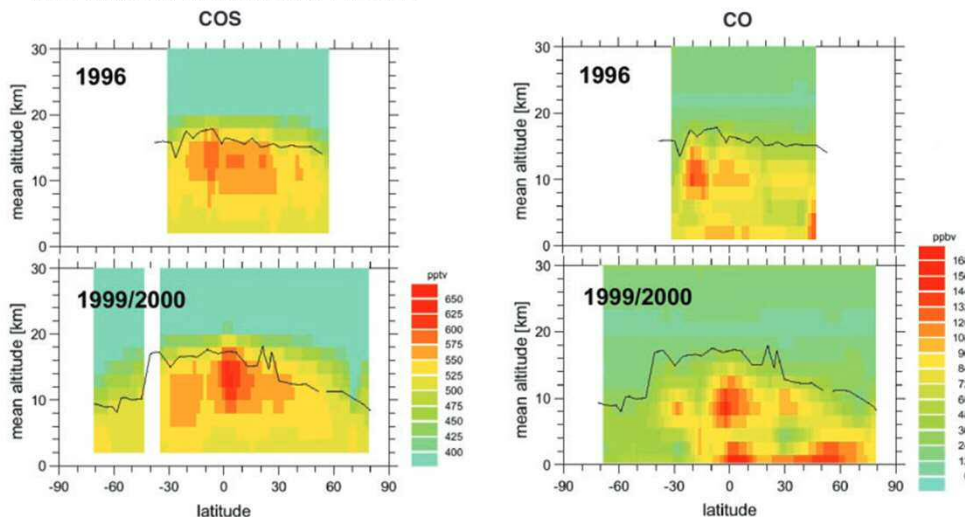
Issue is unresolved and urgent!

OCS
Biomass
Burning

Biomass burning

Notholt et al., 2003:

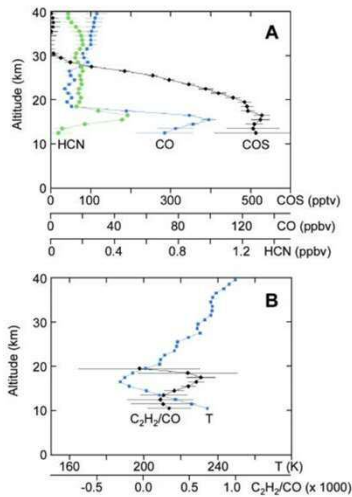
- found OCS mixing ratios at trop TP 20 to 50% larger than assumed in models (analysis of ground-based FTIR and spaceborne ATMOS spectra)
- enhanced OCS levels correlated with high CO and HCN
- backward trajectories and global maps of fire statistics suggest biomass-burning emissions as main source of the enhanced TTL OCS



Biomass burning

Notholt et al., 2003:

- found OCS mixing ratios at trop TP 20 to 50% larger than assumed in models (analysis of ground-based FTIR and spaceborne ATMOS spectra)
- enhanced OCS levels correlated with high CO and HCN
- backward trajectories and global maps of fire statistics suggest biomass-burning emissions as main source of the enhanced TTL OCS



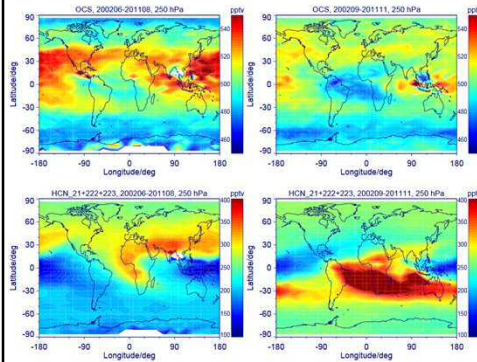
Results indicate that at the stratospheric entry point, a much larger fraction of the ambient COS comes from biomass-burning events than previously thought

Barkley et al., 2008:

- Elevated OCS at low S. latitudes, correlated with elevated CO and HCN: consistent with a significant pyrogenic source
- ACE does not observe the >600 pptv OCS mixing ratios reported by Notholt et al.

Biomass burning

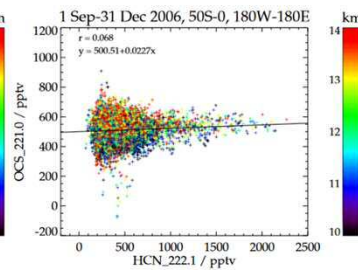
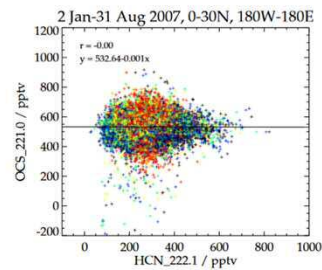
Figures 10 and 11 from Glatthor et al., 2016:



No apparent correlation between OCS and HCN in MIPAS observations

BUT

- Very different sources and sinks apart from biomass burning
- Can a weak signal be detected given the OCS precision?



**OCS and CS₂
anthropogenic
sources**

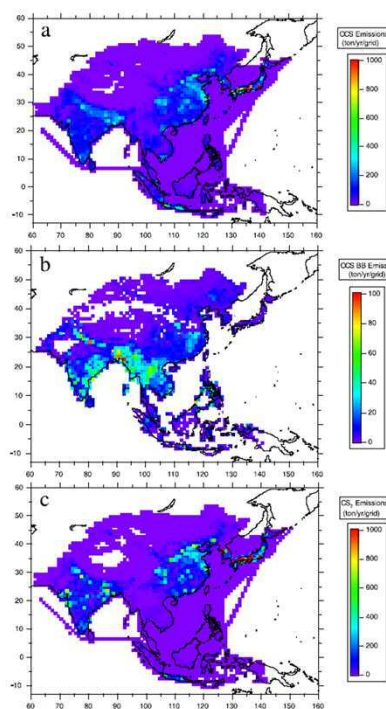


Figure 1. Maps of the gridded emission distributions of OCS from (a) anthropogenic sources, (b) biomass burning, and (c) anthropogenic CS₂ emissions. White areas represent very low emissions.

Country/Region	Combustion					Agriculture							Total (Natural Plus)
	Coal	Petrol	Heating	Transport		Biomass Burning	Industrial Production	Rice	Fertilizer	Animal	Landfills	Anthropogenic	
China	4.4	1.4	1.9	1.4	8.5	15.7	2.3	0.006	0.009	0.009	53.7		
Japan	0.62	0.61	0.16	0.25	0.14	9.8	0.14	0.002	0.002	0.11	11.7		
Rest of east Asia	0.62	0.24	0.87	0.26	0.08	2.6	0.15	0.003	0.002	0.23	3.2		
Southeast Asia	0.27	0.48	0.10	0.52	1.28	2.4	0.3	0.002	0.003	0.23	35.5		
Rest of east Asia	1.4	0.50	16.8	0.64	6.8	5.7	3.5	0.04	0.002	0.003	32.3		
Rest of south Asia	0.048	0.11	5.9	0.10	2.3	0.01	1.2	0.01	0.005	0.006	9.7		
Asia total	7.3	3.4	56.6	3.1	31.2	33.9	10.7	0.01	0.002	0.005	146		
Global estimates													
Khalil and Rasmussen [1984]	36			6	70	82					194	1310	
Khalil and Rasmussen [1984]	36			10	200	50					340	2000	
Chen and Davis [1993]	36			4	140	2					182	1140	
CS ₂													
China	0.857	0.12	0	0.11	0	40.5	1.7	0.015	0.014	0.014	42.5		
Japan	0.007	0.051	0	0.020	0	17.3	0.099	0.004	0.003	0.003	17.5		
Rest of east Asia	0.008	0.020	0	0.013	0	2.3	0.11	0.009	0.003	0.003	2.5		
Southeast Asia	0.004	0.004	0	0.043	0	2.4	0.4	0.004	0.005	0.005	4.9		
Rest of east Asia	0.021	0.041	0	0.013	0	26.8	2.5	0.019	0.004	0.004	29.4		
Rest of south Asia	0.0007	0.007	0	1.2	0.09	0.03	0.003	0.003	0.003	0.003	2.1		
Asia total	0.997	0.28	0	0.25	0	90.5	7.7	0.03	0.03	0.03	99		
Global estimates													
Khalil and Rasmussen [1984]	0										340	660	
Khalil and Rasmussen [1984]	0										370	2000	
Chen and Davis [1993]	0			0.1	0	313					313	540	

*Emissions are in Gg yr⁻¹.

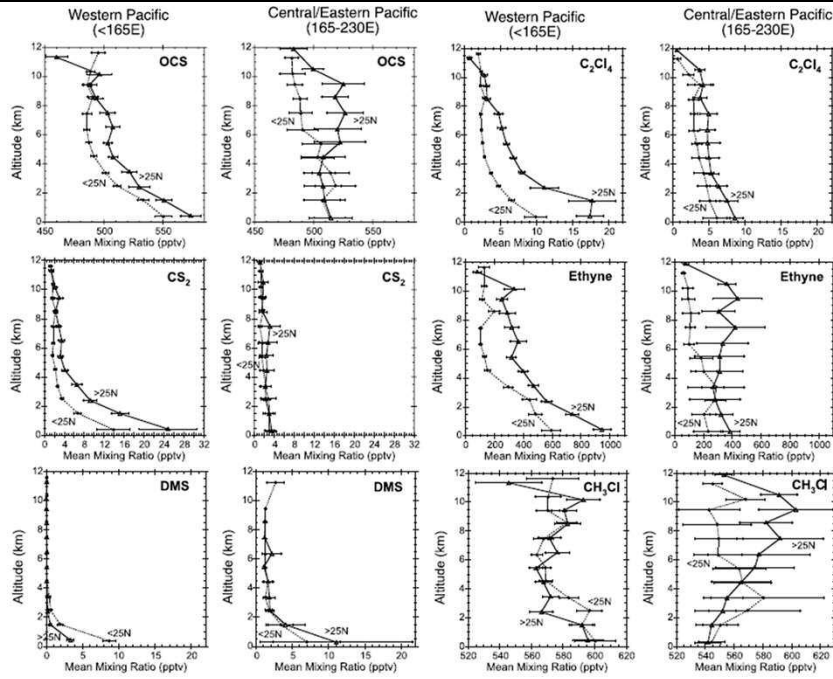


Figure 3. Mean vertical profiles for selected trace gases in 1 km altitude increments over the western Pacific (<165°E) and central/eastern Pacific (165°E–230°E) during TRACE-P. Error bars represent 95% confidence level of the mean.

From Blake et al., 2004

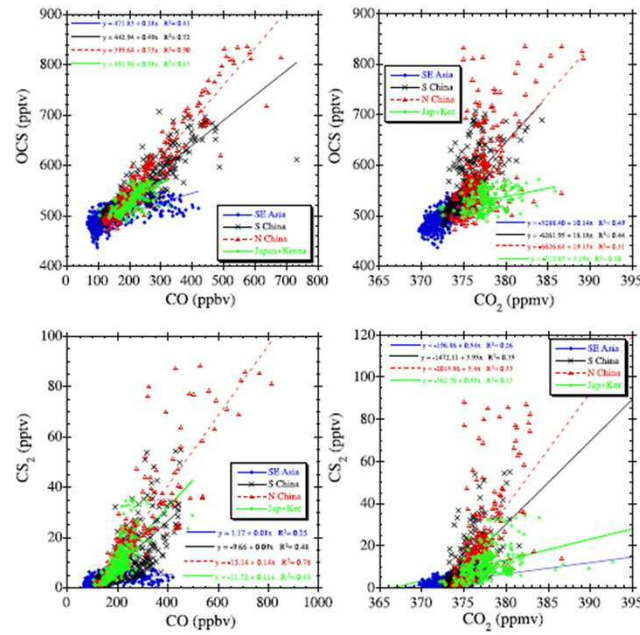
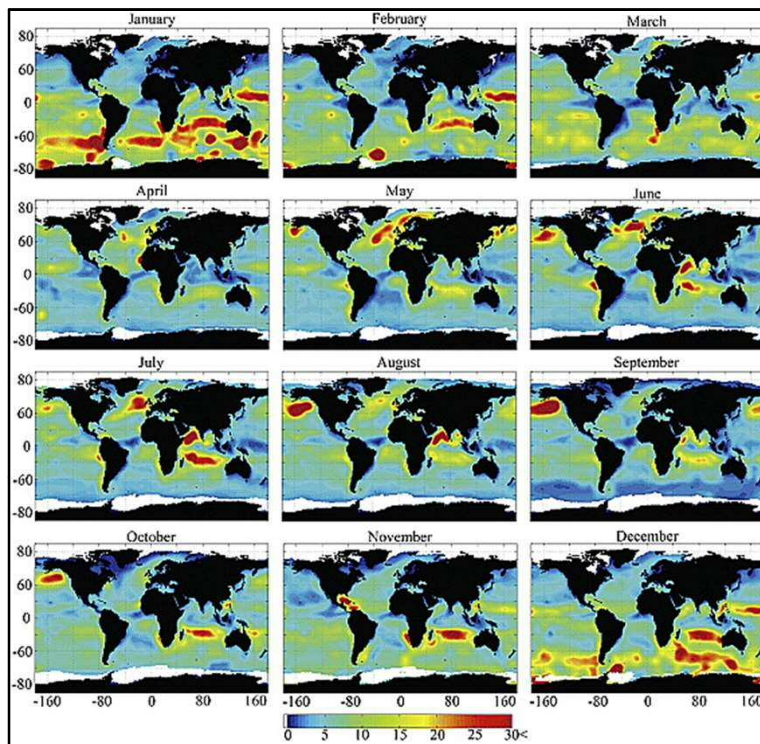


Figure 8. Plots of OCS and CS₂ versus CO and CO₂ for air masses defined in Figure 6. Continental SE Asia (blue solid circles), south China (black crosses), north China (red open triangles) and Japan plus Korea (green open circles). (Note that the highest 5% of the data have been removed to better represent regional averages.)

Oceanic DMS climatology



Monthly
climatology of
DMS fluxes (μmol
 $\text{S/m}^2\text{d}$).

Lana et al., 2011