

# How does the S get in stratosphere?

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## Motivation

- 4-7%/year increase in strat. sulfate aerosols (1990-2009)<sup>1</sup>
- no volcanoes → transport of carbonyl sulfide (COS) and sulfur dioxide (SO<sub>2</sub>) via tropical tropopause layer (TTL) maintains aerosol layer, however, relative contributions remain uncertain
- study by Marandino et al. 2013 suggests that dimethylsulfide (DMS) entry into strat. more important than previously thought
- processes governing transport of S to strat. are poorly quantified
- high uncertainty in the dominant global sources and sinks of COS → uncertainties in global COS budgets & the drivers of long-term trends

## Main objectives

- establish climate data record of COS & estimate SH COS budget
- improve understanding of processes governing background stratospheric sulfate aerosol
  - determine relative contributions of SO<sub>2</sub>/DMS/COS in delivering S to base of TTL under (a) low OH & (b) high OH conditions (Fig. 1)

## COS retrievals from FTIR measurements

- known uncertainties in global COS budget, COS sources & sinks
- measurement sites: Lauder, New Zealand (1997-present), Wollongong, Australia (1996-present), Arrival Heights, Antarctica (1997-present)
- one micro-window: 2047.81 - 2048.21 cm<sup>-1</sup>
- SFIT4 retrieval algorithm to derive total & partial COS columns
- determine long-term trend & seasonal variation in COS columns
- work in progress...

## Sulfur transport trajectory study

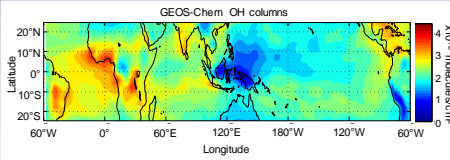
- ATLAS<sup>2</sup> model → impact of trop. OH on stratospheric SO<sub>2</sub> flux
- back trajectories → start at 400K, 2°x 2° long/lat grid, 30°N to 30°S, 120 days starting on 31 January 2010, must go to 800 hPa
- troposphere → vertical winds used for vertical motion
- upper TTL & strat. → radiative heating rates for vertical motion
- winds & heating rates → ECMWF reanalysis data; ERA-interim
- box model → run from 800 hPa to LCP; **gas-phase** & **aqueous-phase** reactions considered:
  - $SO_2 + OH + M \rightarrow HSO_3 + M$  (dominant gas phase reaction) (R1)
  - $SO_2 \cdot H_2O \leftrightarrow H^+ + HSO_3^-$  (R2)
  - $HSO_3^- + H_2O_2 \leftrightarrow H^+ + SO_4^{2-} + H_2O$  (R3)
  - $HSO_3^- + O_3 \leftrightarrow H^+ + SO_4^{2-} + O_2$  (R4)

## Outlook

- include gas-phase chemistry of other sulfur containing compounds such as DMS, COS & CS<sub>2</sub>
- derive H<sub>2</sub>O<sub>2</sub>/OH/O<sub>3</sub> fields from the same model (e.g. GEOS-Chem)
- consider an estimate of the atmospheric lifetime of SO<sub>2</sub><sup>-</sup>/H<sub>2</sub>SO<sub>4</sub> in trajectory study
- expand sensitivity study: besides varying the OH concentrations, also consider varying the SO<sub>2</sub> initial concentrations for e.g. (a) high emissions scenario (representative for typical SO<sub>2</sub> values above land & population centres) & (b) low emissions scenario (representative for tropical (30°S to 30°N) average)
- question to be answered: What are the relative contributions of SO<sub>2</sub>, DMS, and COS to the overall amount of sulfur entering the stratosphere & how do those vary with changes in OH concentrations?
- how does the result change if we interpolate SO<sub>2</sub> concentrations along trajectories over time & include volcanoes in SO<sub>2</sub> simulations?

## Chemistry & initialization

- gas to aqueous** conversion → Henry's law
- kinetic reaction rates & equilibrium const. Feichter et al.<sup>6</sup>
- HSO<sub>3</sub>** → reacts with oxygen to produce **SO<sub>3</sub>**
- SO<sub>3</sub>** → with water vapour, converted rapidly to sulfuric acid (**H<sub>2</sub>SO<sub>4</sub>**)
- H<sub>2</sub>SO<sub>4</sub>** → forming new aerosol or adding to existing ones
- initial long/lat SO<sub>2</sub> field at 800 hPa from CEM1.1 CAM-Chem<sup>7</sup>
- lat/altitude OH and O<sub>3</sub> fields from GEOS-Chem tropospheric Chemistry Transport Model<sup>3</sup>; for purely technical reasons H<sub>2</sub>O<sub>2</sub> from TOMCAT, scaled to match OH/O<sub>3</sub> from GEOS-Chem

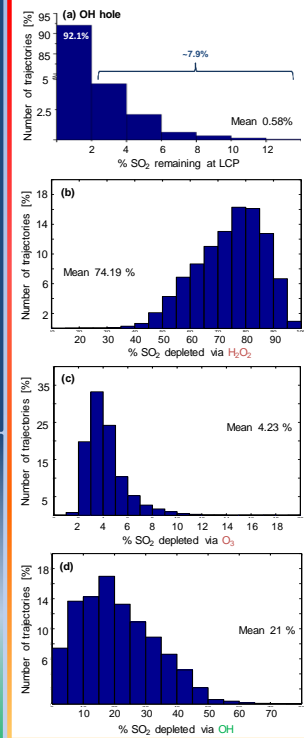


**Figure 1:** Trop. OH columns from GEOS-Chem (1-15 October 2009). Two scenarios considered:  
(i) OH zonal mean → OH 'global' scenario  
(ii) OH mean from 125°E-140°E → OH 'hole' scenario

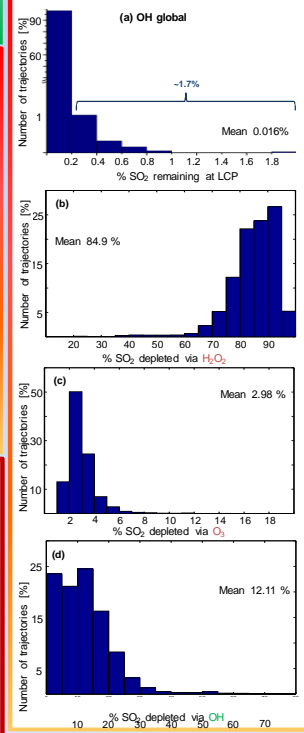
- studies of the flux of species often based on **zonal mean OH concentrations** (e.g. case (i))<sup>4</sup>
- recent study by Rex et al.<sup>5</sup> showed existence of pronounced **minimum in OH-concentrations** above the West Pacific → impact of such variability in trop. OH concentrations on stratospheric SO<sub>2</sub> flux analysed here

## Preliminary findings

- high OH scenarios** → majority of air masses transport less than 0.2 % of initial SO<sub>2</sub> to stratosphere
- OH hole** → ~8% of air masses deliver >2% of initial SO<sub>2</sub>; 36 times more SO<sub>2</sub> reaches stratosphere → if there is a role for SO<sub>2</sub> emissions for stratospheric sulfur balance, then this role is likely very sensitive to OH field (& related H<sub>2</sub>O<sub>2</sub>) & to the existence of OH minimum above West Pacific
- reaction with H<sub>2</sub>O<sub>2</sub> is dominant in converting SO<sub>2</sub> to sulfate; O<sub>3</sub> plays a less important role → important to get modelled H<sub>2</sub>O<sub>2</sub> correct (prerequisite for that are correct OH & O<sub>3</sub>)



**Figure 2:** (a) SO<sub>2</sub> in % remaining at LCP for **Low OH** → ~7.9% of all trajectories deliver more than 2% of the initial SO<sub>2</sub> to the stratosphere. The majority (92.1%) of the trajectories deliver less. Even though the amount of SO<sub>2</sub> reaching the LCP is small, it is about 36 times larger than for **High OH** (see Fig. 3) (b-d) Percentage of SO<sub>2</sub> loss due to aqueous reaction with H<sub>2</sub>O<sub>2</sub> (b), O<sub>3</sub> (c), and gas-phase reaction with OH (d). Most SO<sub>2</sub> (on average 74%) is destroyed via the reaction with H<sub>2</sub>O<sub>2</sub>. Reaction with O<sub>3</sub> seems to be less important in destroying SO<sub>2</sub> (as expected).



**Figure 3:** As for Figure 2 but for **High OH** (OH hole scenario) → Overall less SO<sub>2</sub> reaches the LCP than for **low OH**; all trajectories deliver less than 2% of initial SO<sub>2</sub>. The reaction with H<sub>2</sub>O<sub>2</sub> is the dominant reaction in depleting SO<sub>2</sub> along the trajectories; the dominance is more pronounced than in the **low OH** case. The histograms are narrower than for the **low OH** scenario; gas-phase reaction of SO<sub>2</sub> and OH deplete less SO<sub>2</sub> than in the **low OH** scenario.

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