Atmospheric History of Carbonyl Sulfide (COS) During the 20th Century from Antarctic and Greenland Firn Air Measurements

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**COS in the atmosphere – Budget today**

- **Largest sink**: 80%
- **Largest source**: 70%
- **Current best estimates**:
  - Emissions are \( \sim 1.2 \text{TgS y}^{-1} \)
  - Lifetime is \( \sim 2 \text{ y} \)
  - Mean trop. mixing ratio just under 500 ppt
  - 1-2% more in the SH

**Canopy Uptake**

**Anthropogenic Emissions**

**Biomass Burning**

**Soils**

**Oceans emit COS, CS\(_2\), DMS**

**OH + photolysis**

- COS is used as a proxy for gross primary productivity
- It contributes to background sulfate aerosol in the stratosphere
Firn air COS records – background

- Firn air ages non-linearly with depth
- Measurements from a given depth represent average levels over many years
- The deeper in the firn, the longer the time scale of averaging
- Recovery of atmospheric records requires a formal inversion using firn model outputs (figure on the left)
- Inversions benefit from knowing past atmospheric composition (ice core data helps!)

- Firn data from

  3 Greenland campaigns: Summit (SUM) in 2006 and 2013, Renland in 2015


- Inversions conducted separately for NH and SH sites
Firm air COS measurements and MC sampling – Greenland

- **RED:** Measurement means show an increase at depth and turn around
- A statistical model with MCMC sampling to get full Bayesian inference (mc-stan.org)
- **GRAY:** Range covered in MC sims (20k runs) is proportional to estimated uncertainty at each sampling depth
- All sites display a COS increase at depth
Firn inversions – Greenland (20k MC sims)

More than 95% of sims show peak before 1980

COS at $t_0$ is forced

COS at $t_{\text{final}}$ is forced

Peak in the atmosphere in the 1970s
Firm air COS measurements – Antarctica (20k MC sims)

- Three sites show large decreases at depth
- SPO15 does not because the sampling did not reach the bottom
Firn inversion results – Antarctica (20k MC sims)

- Antarctic firn data provide a much longer atmospheric record than Greenland
- Antarctic record also displays coherent information at higher frequencies
- Record with larger variability explains the firn data better!!!
- Peak in the 1980s
Firn inversion results – Antarctica (based on 15k MC sims)

ANTARCTICA

COS (ppt)

Calendar years C.E.

Peak after 1980
Firn inversions – Greenland vs. Antarctica

- Large increase in COS evident in both atmospheres
- Peak in both hemispheres in late 20\textsuperscript{th} century
- NH peaks before SH
- Peak followed by decline to present day when the levels in two hemispheres are close to equal
- Is this variability driven by anthropogenic emission?

Ice core data prior to 1850 from both Greenland and Antarctica on a collapsed time scale
Bottom-up anthropogenic COS emissions estimates

- Bottom-up estimate of anthropogenic emissions display strong ramp-up in qualitative agreement with firn records.
- At the peak, anthropogenic emissions account for only 25% of the COS budget.
- Present-day level is not significantly lower than the peak.
6-box ocean-atmosphere model – base case (current budget)

From preindustrial to present

- Anthropogenic emissions change similar to bottom-up inventory
- Small biomass burning increase following Campbell et al. (2017)
- Oceans set at present day productivity and respond passively
- Constant uptake rate (lifetime = 2 y)

At the the Poles (60 – 90 deg)

- We get present-day levels right but no peak(s) in late 20th century
- Antarctic levels are too high in the preindustrial atmosphere
- Antarctic always higher than Greenland
6-box ocean-atmosphere model – High Anthropogenic

- Doubled anthropogenic emission in late 20th century to get a peak comparable to seen in firn air records
- GRLND exceeds ANT at the peak
- GRLND and ANT peaks are simultaneous
- No impact on preindustrial SH levels
6-box ocean-atmosphere model – High Anthropogenic, Var. Ocean

- Lower emissions from mid-high latitude SH oceans during preindustrial era
- SH ocean emissions get back to present day levels late in the 20th century
- GRLND higher than ANT most of the time
- GRLND and ANT peaks separated in time
Conclusions

• Inversions based on firn data from multiple sites display previously undocumented variability in NH and SH atmospheres

• Anthropogenic COS emissions were easily double the present day during the second half of the 20th century

• Results suggest ocean production of COS (or may be DMS) possibly changed during the 20th century

• Changes in removal rate cannot be ruled out, but difficult to constrain without understanding the behavior of ocean sources

Ongoing work

• We are funded to measure COS in a shallow ice core from Greenland, which should provide tighter constraints on Greenland firn inversions