COS workshop session Atmospheric measurements notes

**Mary Whelan – Questions on COS we are poised to answer**

Notes:

* Leaf-level: more COS 🡪 stomata open. There are interactions between CO2 and COS that are not completely understood 🡪 **We need more leaf experiments**
* Some plants also **produce COS** 🡪 naturally antimicrobial, garlic and cabbages
* Stomatal conductance **models** are being built into land surface models (and are already in some models)
* Non-stomatal fluxes: **soils**
* Mary made a model for **non-stomatal fluxes** using soil chamber data but it doesn’t predict the fluxes very well because there are more things that can create COS fluxes: litter and moss. It only works for agricultural fields
* Drying out soil from agriculture will emit a lot of COS
* Should we close the budget soon? Should we make it a priority?
  + COS/CO2 feedbacks
  + Plants that emit COS
  + Bryophytes
  + Litter
  + Missing regions, no observations: tundra, tropics
  + Missing source? Ocean/anthropogenic/biomass burning/unknowns
  + DMS/HPMTF
  + Atmospheric chemistry
  + Seasonal cycle
  + CS2 measurements
  + Phytoplankton?
  + Geothermal?

**Sauveur Belviso – Ongoing decline of atmospheric COS seasonal cycle amplitude over western Europe – implications for surface fluxes**

Notes:

* **Seasonal cycle amplitude decreased** about 4ppt per year
* Plants respond to decrease in COS
* Seasonality seems to be driven by anthropogenic emissions 🡪 **we have to check the Zumkehr 2018 inventory**
* Large French cities are all large COS emitters?? 🡪 rayon industries, but there are no rayon factories in France anymore
* Sauveur looked at the CS2 inventory for France
* **Zumkehr largely underestimates CS2 emissions from France** except for the Paris area. There the Zumkehr inventory largely overestimates emissons
* Sauveur also looked at the PRTR database of the US. Does not match so well with the Zumkehr inventory either
* Sauveur also looked at SO4 aerosols and COS in Europe
* Europe: Zumkehr inventory pretty good, except Paris
* FLEXPART lagrangian particle dispersion model
* **Conclusion: Zumkehr not good for regional studies**, for north America: use PRTR. For Europe: see slide for inventory databases for different countries
* Run FLEXPART

**Peter Sperlich – New system to measure carbonyl sulfide in air sample flasks from Baring Head and Fiordland National Park, New Zealand**

Notes:

* **CarbonWatch project:** initially meant for CO2 in-situ stations
* Additional flask samples for COS, CO, D14CO2, d13CO2
* Improved the model
* New Zealand version of the ICOS flask
* Nickel = not good for COS
* Developed a flask inlet system coupled to LGR
* Tested the measurement system and calibration thoroughly
* **1.2 ppt precision for COS**
* Using CO2 isotopes for seeing what the source of the air is.

**Alessandro Zanchetta – Vertical profiles of carbonyl sulfide in northern Sweden (HEMERA campaign, August 2021)**

Notes:

* Vertical profiles to validate satellite observations
* Understanding **COS stratospheric chemistry**
* Balloon-borne measurements
* AirCore samples
* Big LISA
* Analysis done with QCLS
* O2/N2 also measured
* Cotton O3 scrubbers contaminated the samples?
* **Kiruna (Sweden) VS Trainou (France): good comparison with satellite data**
* AirCores give good dataset but the discrete samples need some further analysis

LUNCH BREAK

**(online) Chinmay Mallik – COS measurements in western India**

Notes:

* Measurements in **Ahmedabad in 2013**
* Trajectories: in winter winds from north, summer, winds from south
* Uses GC for measurements
* Post-monsoon: higher [COS]
* Also had measurements of **CS2** at the same time
* **First data of COS over India**

**Chen Davidson – Isotopic evidence for sedimentary sources of COS**

Notes:

* Photoproduction and sedimentary sources of COS and CS2
* DOS = dissolved organic sulfur
* The source isotopic value controls the isotopic value of the products
* Isotopic mass balance
* This talk focusses on the **marine environment**
* There is **photoproduction and dark production.** Also hydrolysis consuming COS 🡪 also affects the isotopic fingerprint
* We expect a large difference between oxidized and unoxidized areas
* Water samples from Mediterranean Sea and Atlantic Ocean **(open water)**
* **Sediment influenced water:** Wadden Sea, tidal sand flats, a lot of organic matter
* Wadden sea has much lower isotopic values than open water
* Sedimentary source of –4‰
* **Intermediate samples:** open water but some influence from sediments and the data fall nicely between the open water and the sedimentary water samples
* Also samples in **the Red Sea during a Southerly storm** 🡪 influences the isotopic composition of the COS in the ocean water. There was an abrupt change in water temperature 🡪 mixing of deeper and shallower water
* Photoproduction: 14‰ COS, 5‰ CS2, dark production 9 to 18‰ COS, CS2 20‰. Sediment -4‰ COS, -10‰ CS2
* Unknown how the COS is formed in the sediment

**Alon Angert – Carbonyl sulfide sulfur isotope fractionation during uptake by C3 and C4 plants**

Notes:

* Normally plants take up the lighter isotopes faster, leaving the enriched COS behind
* Two main steps during plant uptake: diffusion and the activity of CA
* **Diffusion experiment** of COS in N2: -5.2‰
* **C3:** -1.6
* **C4:** much lower CA activity 🡪 Ci is higher 🡪 back diffusion
* C4: -5.4‰
* Higher CO2 🡪 CA gets saturated 🡪 higher Ci 🡪 more back diffusion 🡪 higher fractionation 🡪 that is also what they found in the measurements
* Different leaves 🡪 different results because they have different amounts of CA
* Estimate **a and b of the Fahrquhar equation**
* **Estimate Ci from the equation**
* Global estimate: epsilon for all plants **–2.3‰**
* We need more species, more conditions

**Sophie Baartman – Measurements of COS isotopologues – from biosphere to stratosphere**

COFFEE & TEA BREAK

**Anna de Vries – Carbonyl sulfide; fluxes and isotopic measurements on a forest and wetland in Finland**

Notes:

* Isotope ratios measured in wetland and forest in Finland, not the focus of the tal
* **EC data above the Siikaneva wetland. First dataset of a NH wetland COS fluxes**
* **Stable sink** of –9.15 pmol m-2 s-1
* Sink is not affected by the water table depth
* Probably because of the vegetation on the wetland: **lots of mosses**
* Small diurnal cycle, mostly driven by PAR
* Calculated GPP from CO2 and from COS at the same locations

**Eileen Gallacherr – COS isotopologue ratios and fractionations**

Notes:

* Aim of the project: **measure COS isotope ratios and clumped isotopes 13C16O34S, 13C18O32S**
* Measuring the parent **ion COS+ m/z 61, 62 and 63**
* Did a linearity characterization
* Characterized precision
* Fractionation of **COS + 2OH (COS hydroxylation)** with ascarite in the pre-concentration line
* Also measured air samples using a Tenax trap
* Started some **photolysis experiments** to see what the stratospheric photolysis would be
* Also wants to do some modelling

Questions:

* Sample size needed now to be in the linear regime?
* Why not do a nonlinearity correction?

**Marc von Hobe – Measurements of OCS from DMS, biomass burning and anthropogenic emissions in Asia**

Notes:

* **Airborne measurements with the AMICA instrument on Geophysica (Greece and Nepal) and HALO (Argentina)**
* **Experiments with DMS in the SAPHIR chamber in Jülich**
* AMA transports tropospheric air to the NH
* **Asian continent is a COS source and not a sink** 🡪 anthropogenic sources being transported over the Pacific Ocean so it could be anthropogenic and not oceanic
* Biomass burning: a lot of biomass burning tracers (CO) found during flights but no COS. Up to 600ppb of CO, no significant rise in COS 🡪 **no giant COS source from biomass burning**
* **COS from DMS from ocean, DMS 🡪 HPMTF 🡪 COS**
* SAPHIR chamber: significant COS production in yield range of 6 to 10%
* Conducting new experiments now with SAPHIR chamber and look at HPMTF photolysis
* **Conclusion:** 
  + anthropogenic Asian emissions may be underestimated
  + Biomass burning not big source
  + HPMTF might be significant pathway but large uncertainties at the moment 🡪 more measurements needed

Questions:

* Figure of StratoClim: is that data of all the flights combined? Was AMICA on all the flights with Geophysica?

**(online) Christopher Jernigan – Indirect production of OCS from aqueous and gas-phase oxidation of CMS**

Notes:

* DMS oxidation mechanism varies with the environment
* 45% of DMS is oxidized to HPMTF
* **Formation of OCS is not a fixed pathway** 🡪 multiple potential routes to COS within in DMS oxidation
* **Environmental chamber experiment:** dark and dry experiments, only OH oxidation
* **Higher yield of COS than previously found,** because of HPMTF: 13%
* **HPMTF can be lost to cloud droplets** as well
* To form a lot of COS from HPMTF it needs to be dry
* Dry lifetime HPMTF: 50 hours
* Cloudy lifetime HPMTF: 3 min
* **Can aqueous HMPTF also form COS?** HPMTF is always lost to water irreversibly and COS is not produced anymore. Everything is converted to sulfate
* When you take clouds into account, the COS production from DMS is actually reduced

SNACK BREAK

**(online) Murat Aydin – Increase in atmospheric carbonyl sulfide during the last deglaciation**

Notes:

* **Ice core data**
* Two extraction methods of air from ice cores for COS analysis: dry and wet extraction
* For wet extraction they need a solubility correction
* Analysis done with GC/MS after preconcentration
* All data are much lower than current day [COS]. It is around 250 ppt
* **Interesting trend after the Last Glacial Maximum (LGM)**
* Impurities in the ice sheet can also alter the atmospheric signal
* But they did not see correlations between COS and impurities, but they did see correlation with sodium (sea salt)
* **Production of COS in the ice sheet with the sea salt aerosols,** it does not continue for too long. Suggestive of a firn process rather than production after bubble close-off
* **During the LGM COS was 3-4x lower than after the LGM.** Large increase after the LGM
* The relative change in COS is larger than the change in CO2
* GPP increases 50-60%
* LRU increases
* But these changes cannot explain the COS changes
* **COS has to be source-driven** 🡪 oceans, all three emission pathways from oceans have probably increased during the last deglaciation

**Lei Hu – Seasonal cycle amplitude of CO2 and COS in the arctic**

Notes:

* **Seasonal cycle amplitude of CO2 at high latitudes has increased a lot in recent years**
* Increased temperature 🡪 more GPP
* CO2 fertilization 🡪 more GPP
* Increased temperature alone cannot explain the increase the amplitude
* When **normalizing with [CO2],** the trend disappears
* COS information: **ecosystem conductance has stayed constant**
* **13CO2 seasonal cycle has also stayed constant**
* **The CO2 fertilization is the most important driver,** confirmed with COS observations and modelling using SiB4
* Used carbontracker increased summer drawdown rather than an increase in respiration signal

**Discussion**

* Anyone wants to discuss a certain topic in the entire group?
* Planning of tomorrow: lab tour and kayak/boat trip, what time? Session starts at 14:00

Notes:

* Peter Sperlich: we could set up an intercomparison for the COS measurements (especially flasks)