Constraining the Terrestrial Carbon Cycle with Atmospheric Measurements of Carbonyl Sulfide

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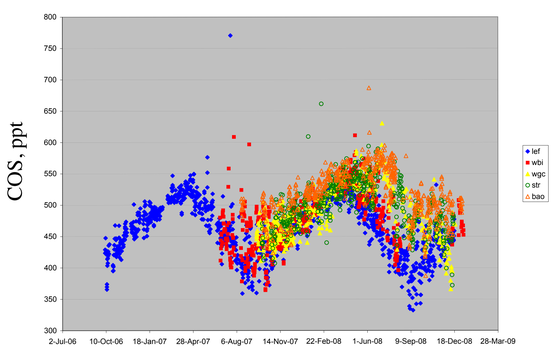
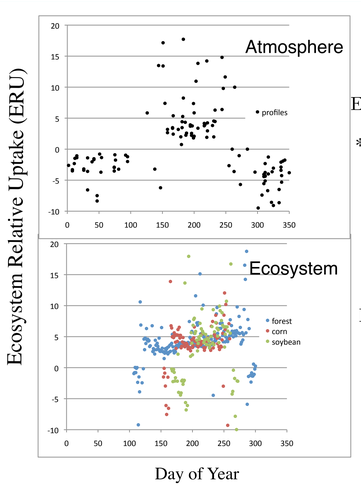
Introduction

- Carbonyl sulfide is an analog of CO_2. It participates in some key reactions of the carbon cycle, and monitoring its concentration, like that of the ^{13}C and ^{18}O isotopologs of CO_2, can provide additional information on carbon cycle processes.
- Its principle source is the ocean and uptake by leaves and soil are its principle sink. There is apparently no significant source from terrestrial ecosystems.
- Atmospheric chemistry and anthropogenic sources play a minor role in driving changes in COS concentration.
- The NOAA global monitoring network conducts flask measurements at background atmospheric sampling stations, and over N. America, regular sampling occurs at tall towers and from light aircraft in the boundary layer and free troposphere.
- Campbell et al., (2008) showed that vertical gradients in the atmosphere over N. America are primarily driven by vegetation.
- Atmospheric measurements of CO_2 alone are not sufficient to constrain the parameterizations of respiration and photo-synthesis in carbon cycle models.
- We argue that simultaneous measurements of COS and CO_2 could provide this important constraint.

Flask Measurements



Ecosytem Relative Uptake



$$\mathrm{ERU} = \epsilon \frac{[\mathrm{COS}]_{ft} - [\mathrm{COS}]_{bl}}{[\mathrm{CO_2}]_{ft} - [\mathrm{CO_2}]_{bl}}$$

* where

$$\epsilon = \frac{[\mathrm{CO_2}]_{bl}}{[\mathrm{COS}]_{bl}} \approx 1 \cdot 10^6$$

$$\mathrm{ERU} = \frac{-2.2 \cdot \mathrm{GPP}}{\mathrm{NEE}}$$

* where 2.2 is the ratio of COS uptake to GPP (Campbell et al., 2008)

For inversion:

$$\frac{\mathrm{RECO}}{\mathrm{GPP}} = \frac{2.2 - \mathrm{ERU}}{\mathrm{ERU}}$$

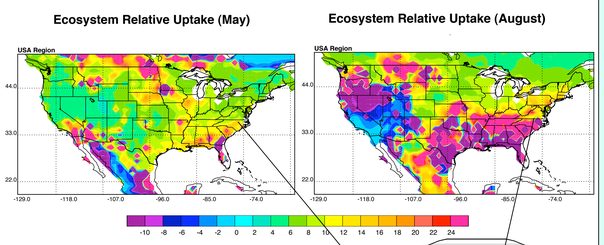
$$\mathrm{GPP} = -\frac{\mathrm{NEE} \cdot \mathrm{ERU}}{2.2}$$

$$\mathrm{RECO} = \mathrm{NEE} - \mathrm{GPP}$$

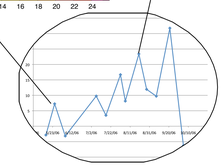
- Ecosystem Relative Uptake measured in the atmosphere over the NACP region is similar to that predicted from measurements of GPP and NEE of the dominant ecosystems of the region. Therefore, the atmospheric measurements can be inverted used to infer RECO (ecosystem respiration) and GPP at a regional scale.

Regional and Seasonal Changes

ERU calculated from GPP and NEE predicted by SiB show regional and seasonal differences in the balance of RECO and GPP. Atmospheric measurements of ERU should reflect this variation.



- ERU from atmospheric profiles at CMA (N. Carolina) show the expected seasonal pattern of change.



Caveattes

- Flask measurements don't adequately sample atmospheric "noise." Continuous measurements from tall towers would be better.
- The assumption that COS uptake is 2.2 times GPP is probably too simplistic.
- Boundary conditions and large-scale advection need to be accounted for.

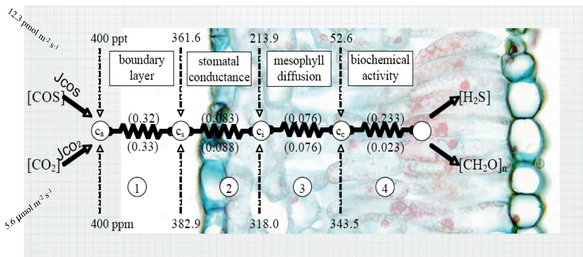
The Next Steps

- We have incorporated a parameterization for COS uptake by leaves and soils into SiB 3.
- We have coupled SiB 3 simulated surface fluxes from the land into a global atmospheric transport model - PCTM - that is also being used for assimilation of carbon cycle fluxes.
- We have made preliminary adjustments to the accepted global budget to a larger land surfaces sink.

Mechanism of Upatke

•**Biochemistry**: uptake of COS is by a hydrolysis reaction catalyzed by carbonic anhydrase (CA), located in the chloroplasts of leaves and in micro-organisms in the soil. Diffusion to the sites of reactions plays a major role in regulating the rate of uptake. The major control of soil diffusion is by water content, and that of the leaf is regulated by the stomata - which in turn tend to co-vary with the rate of photosynthesis.

carbonic anhydrase
$COS + H_2O \rightleftharpoons H_2S + CO_2$

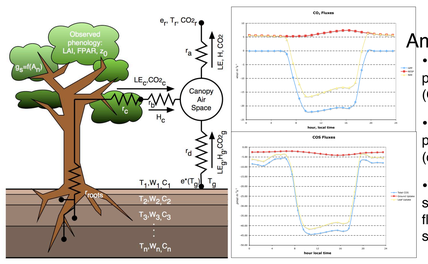


$$J_{\mathrm{leaf}} = [\mathrm{COS}]_a \cdot \left[\frac{1.106}{g_b} + \frac{1.162}{g_s} + \frac{2.10}{g_i} + \frac{1}{k \cdot P_s}\right]^{-1}$$

$$J_{\mathrm{soil}} = \mathrm{resp_het} \cdot \mathrm{k_soil} \cdot f(\mathrm{wfrac})$$

Implementation in SiB - 3.0

SiB-3.0 is a land-surface model that includes the biochemistry and biophysics of CO_2 uptake and respiration. It has been extensively tested at various scales from the leaf to the globe - for CO_2. The parameterization for COS has not yet been tested.



Amazon Forest

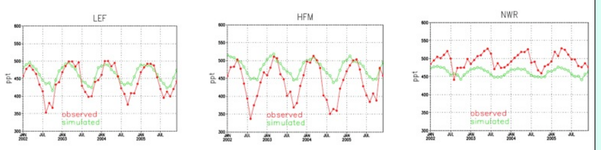
- Leaf COS uptake parallels photosynthesis (GPP)
- Soil COS uptake is anti-parallel to respiration (opposite sign).
- Temperature and water stress responses of COS fluxes assumed to be similar to CO_2.

Global Scale Simulations

- SiB-3.0-COS was used to simulate fluxes of CO_2 and COS hourly at 1x1 degree grid, globally for 2000-2005 .
- These land surface fluxes were provided to PCTM.
- To account for the effect of COS depletion near the surface, these fluxes were scaled linearly by the ratio of COS concentration in the lowest model layer to that used in the simulation.
- Initially, estimates of ocean, anthropogenic and atmospheric chemistry fluxes were based on Kettle et al., (2002).
- Observed winds from the NASA-Geos-4 reanalysis were used to drive the transport.
- The Simulated concentrations at grid cells corresponding to sampling locations we extracted for comparison to observations.

Results

- Initial simulations with the Kettle et al., fluxes in PCTM match the background concentration fairly well but draw-down at continental sites is too small.

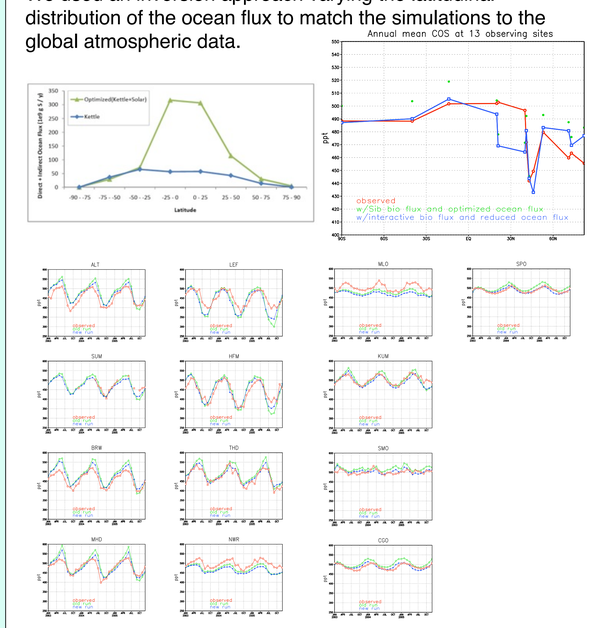


- The new estimates of plant and soil uptake of COS are 3 fold larger and differently distributed than those used by Kettle et al.
- New sources are need to balance the budget, and we postulate an additional ocean flux.

(unit = 1.0e+09 g Sulfur)

Sources	K2002	This Study
Direct COS Flux from Oceans	39	39
Indirect COS Flux as DMS from Oceans	81	81
Indirect COS Flux as CS_2 from Oceans	156	156
Direct Anthropogenic Flux	64	64
Indirect Anthropogenic Flux from CS_2	116	116
Indirect Anthropogenic Flux from DMS	0.5	0.5
Biomass Burning	11	136
Additional Ocean Flux		600
Sinks		
Destruction by OH Radical	-94	-101
Uptake by Canopy	-238	-738.2
Uptake by Soil	-130	-355.8
net total	5.5	-2.5

We used an inversion approach varying the latitudinal distribution of the ocean flux to match the simulations to the global atmospheric data.



The largest remaining errors are at the high elevation sites, MLO and NWR. Further calibration of the global budget and the parameterization of COS exchange in SiB are in order before proceeding with inversions.

Conclusions

- Top-down measurements of ecosystem relative uptake of COS and CO_2 over the mid-continent of N. America agrees with bottom-up estimates based on ecosystem studies.
- Seasonal changes in ERU predicted from simulations of NEE and GPP are observed with atmospheric profiles.
- Parameterization for COS exchange by the land surface have been incorporated into the carbon cycle model, SiB-3.
- New simulations of the surface uptake of COS were obtained and other terms of the global budget were revised to balance the global budget and optimize concentrations.
- The model does a reasonable job of matching the seasonal variation in atmospheric concentration at most background atmospheric sites, but more calibration work is needed.
- Large vertical gradients in COS between the boundary layer and free troposphere observed over the continents, are predicted by the model.
- Simultaneous measurements of CO_2 and COS could provide improved constraints on 4-d data assimilation of carbon cycle processes,
- Advances in measurement technology and studies of COS exchange at the leaf, soil and ecosystem scales are needed to realize this potential.

References

Baker, I.T., A.S. Denning, L. Prihodko, K. Schaefer, J.A. Berry, G.J. Collatz, N.S. Suits, R. Stockli, A. Philpott, O. Leonard, 2007: Global Net Ecosystem Exchange (NEE) of CO2, Available on-line [http://www.daac.ornl.gov] from Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, Tennessee, U.S.A.

Blake, N. J., J. E. Campbell, S. A. Vay, H. E. Fuelberg, S. Meinardi, F. S. Rowland, and D. R. Blake. 2008. Carbonyl sulfide (OCS): Large scale distributions over North America during INTEX-NA and relationship with CO_2. *J. Geophs Res.*:doi:10.1029/2007JD009163.

Campbell, J.E. Carmichael, G.R., Chai, T., Mena-Carrasco, M., Tang, Y., Blake, D.R., Blake, N.J., Vay, S.A.7. Collatz, G.J., Baker, I., Berry, J.A., Montzka, S.A., Sweeney, C., Schnoor, J.L.1, Stanier, C.O 2008. Photosynthetic Control of Atmospheric Carbonyl Sulfide During the Growing Season. *Science* **322**, 1085-1089.

Kawa, R.S., D.J. Erickson III, S. Pawson and Z. Zhu. 2002. Global CO2 transport simulations using meteorological data from the NASA data assimilation system *J. Geophs. Res*. **109**, D18312, doi: 10.1029/2004JD004554

Kettle, A.J, U. Kuhn, M. von Hobe, J. Kesselmeier and M.O.Andreae. 2002. Global budget of atmospheric carbonyl sulfide: Temporal and spatial variation of the dominant sources and sinks. *J. Geophs. Res*. **107,** D46558, doi:10. 1029/2002187.

Montzka, S.A., P.Calvert, B.D.Hall, J.W.Elkins, T.J. Conway, P.P.Tans, and C.Sweeney. 2007. On the global distribution, seasonality and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO2. *J. Geophs. Res*. **112**, D09302, doi:10.1029/2006JD007665.

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