Can Carbonyl Sulfide Provide Constraints to Gross Terrestrial Photosynthesis?

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1) Abstract:

The atmospheric burden of carbon dioxide (CO_2) increases at variable rates from year to year in part because of variability in carbon uptake and release by the terrestrial biosphere. Improving our understanding of this interaction and the factors that influence it are crucial for developing a predictive understanding of atmospheric CO_2 in the future. Unfortunately, the tools available for studying independently the response of respiration and photosynthesis to changes in climate are limited.

We have suggested recently that carbonyl sulfide may help in this regard (Montzka *et al*., 2007). Uptake by vegetation represents the main loss mechanism for atmospheric carbonyl sulfide (COS). COS undergoes rapid hydrolysis by carbonic anhydrase and rubisco, the same enzymes involved in the initial stages of carbon assimilation by vegetation. The influence of this uptake is readily observed in the spatial and temporal distribution of atmospheric COS in the Northern Hemisphere. COS is unique, however, because it is not emitted in large quantities from vegetation as is CO_2 during respiration. This critical fact suggests that large-scale features observed for COS may be responding primarily to spatial and temporal variations in terrestrial photosynthesis. Although this hypothesis is supported by the measurement data obtained to date, the influence of non-vegetative COS fluxes is poorly constrained. Here we investigate the observations we have made over the past 8 years to assess the relationships between COS and CO_2 as a function of time and space, and the extent to which non-vegetative processes influence atmospheric COS over North America.

2) Background:

Carbonyl sulfide is the most abundant and persistent sulfur containing gas in the atmosphere. Its persistence is determined primarily by the rate at which it is hydrolyzed by vegetation via the same enzymes that catalyze photosynthetic uptake of CO_2.(Protoschill-Krebs *et al*., 1996).
Recent chamber studies and atmospheric data have pointed to the dominance of vegetative loss of COS (Sandoval-Soto *et al*., 2005; Montzka *et al*., 2007), and they suggest that this loss is more directly related to gross photosynthesis rather than net primary production.

Other losses, such as uptake by the oceans and soils, also are significant, though their magnitudes remain uncertain. Emission from the ocean, anthropogenic activity, atmospheric photo-oxidation of reduced sulfur gases such as $(CH_3)_2S$ and CS_2, and biomass burning dominate sources (Kettle *et al*., 2002).

Global Budget (10^9 g S yr^{-1})

Oceanic	– 110 to 190
Ocean DMS oxidation	120 to 190
Ocean CS_2 oxidation	29 to 140
Anthro. CS_2 oxidation	58 to 170
Direct anthro. Emission	32 to 96
Biomass burning	68 to 144
COS & CS_2 soil flux	13 to 119
Total sources:	**210 to 1049**
Vegetation	– 730 to –1500
Uptake by soils	– 74 to –180
Loss by hydroxyl	– 82 to –110
COS photolysis	– 11 to – 21
Total sinks:	**– 897 to – 1827**
Sum	**– 1601 to 152**

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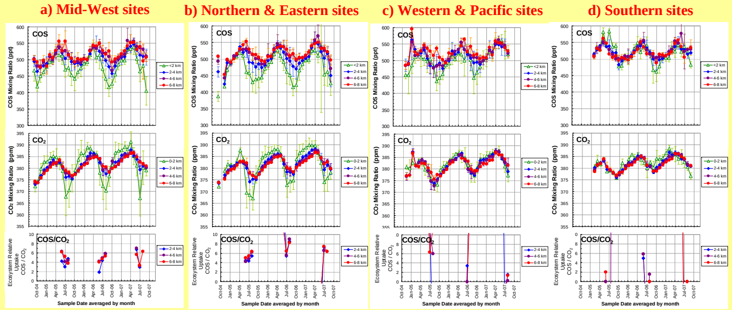
E. Campbell

References:

Kettle *et al*., *J. Geophys. Res*., *107*, 4658, 2002.
Protoschill-Krebs *et al*., *Atmos. Environ*., *30*, 3151-3156, 1996.
Montzka *et al*., *J. Geophys. Res*., *112*, D09302, 2007.
Sandoval-Soto *et al*., *Biogeosciences*, 2, 125-132, 2005.

3) Measured seasonal variations and vertical gradients over North America for COS and CO_2:

a) Mid-West sites | b) Northern & Eastern sites | c) Western & Pacific sites | d) Southern sites

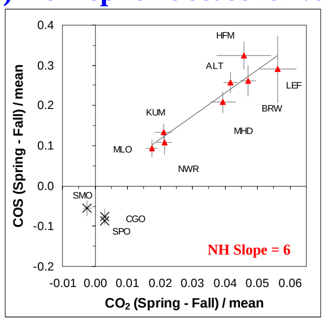


Illinois, Iowa, Nebraska—Corn-belt, agriculture intensive | Non-agricultural, 6 sites—(Royal blue on map) | Hawaii, Vancouver, and California | Texas, Oklahoma, and South Carolina

These data show:

- Strong seasonal variations at all sites for both COS and CO_2.
- Vertical gradients that are largest during the growing season and at Mid-West (**panel a**) and Northern & Eastern sites (**panel b**), with reduced COS and CO_2 mixing ratios measured in the planetary boundary layer (**< 2 km**).
- A larger reduction in COS mixing ratios in the boundary layer during the growing season (relative to higher altitudes) when compared to CO_2 by factors of 3 to 9, at Mid-West (**panel a**) and Northern & Eastern (**panel b**) sites (bottom panels in all figures, the **ecosystem-scale relative uptake (ERU)** calculated as: $[(COS_{6\text{-}8km} - COS_{0\text{-}2km})/COS_{6\text{-}8km}] / [(CO_{2,\,6\text{-}8km} - CO_{2,\,0\text{-}2km})/CO_{2,\,6\text{-}8km}]$. Do the differences between the Mid-West and North/Eastern sites reflect the preponderance of C_3 (trees) vs C_4 (corn and temperate grasses) photosynthesis? COS exhibits reduced boundary-layer mixing ratios through October often, is this because of continued vegetative uptake, or do soils contribute?
- Smaller gradients and ill-defined ecosystem relative uptake values of COS vs CO_2 at Western & Pacific (panel c) and Southern sites (panel d).

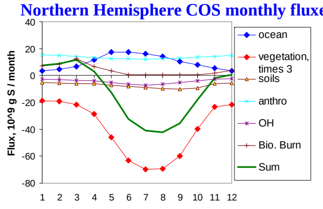
4) Hemispheric seasonal variations for COS and CO_2:



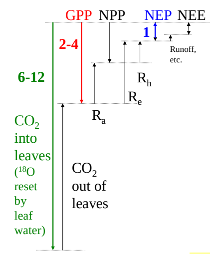
The amplitude of seasonal variations measured for COS and CO_2 at different surface sites across the Northern Hemisphere (NH) are strongly correlated, though **on a relative basis those observed for COS are 6±1 times larger than CO_2** (Montzka et al., 2007).

The similarity between the ecosystem relative uptake (ERU) observed for COS *vs*. CO_2 over continents and the relative seasonal amplitude of COS *vs*. CO_2 implies that **the continental-based uptake observed in the aircraft samples likely drives the hemispheric-wide seasonal changes observed for COS. Budget studies** (rescaled to COS loss being proportional to Gross Primary Production) **suggest that the process responsible for COS uptake over the continents is most likely photosynthesis.**

Northern Hemisphere COS monthly fluxes

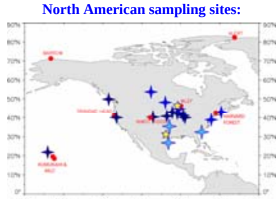


An analysis of COS fluxes in the Northern Hemisphere (NH) with plant uptake scaled by 3 times NPP and biomass burning as estimated in Montzka *et al*. (2007) (**Adapted from Kettle *et al*., 2002**).

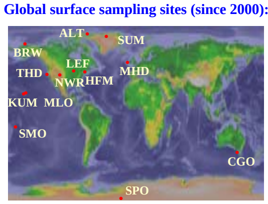


Flask Sampling Network:

North American sampling sites:



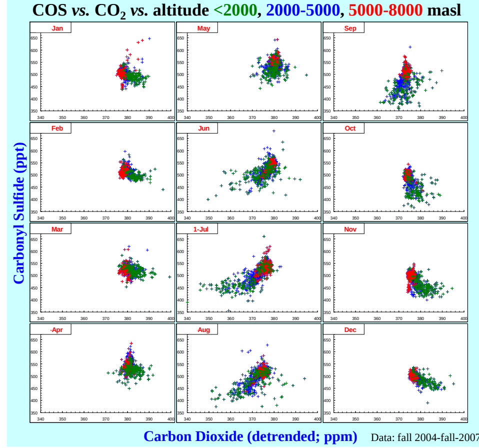
Global surface sampling sites (since 2000):



Average flask sampling frequency (since 2004 for aircraft profiles):
Aircraft profiles 1 to 4 times per month (12 flasks/profile)
2 to 3 samples per week at tower sites (often as pairs)
2 to 4 per month at surface sites (paired flasks)

5) COS *vs*. CO_2 in samples collected from aircraft over North America:

COS *vs*. CO_2 *vs*. altitude <2000, 2000-5000, 5000-8000 masl



During most of the winter and spring, samples with enhanced mixing ratios of CO_2 are generally accompanied by reduced COS mixing ratios. This relationship begins to change as the growing season develops in late spring and reduced levels of CO_2 are accompanied by reduced mixing ratios of COS in low-altitude samples. This relationship holds in samples from June-August. During the fall, however, the range of CO_2 mixing ratios increases while those measured for COS stays about the same.

Although uptake by vegetation strongly influences both COS and CO_2, there are other influences that affect these gases and any correlation between them:
Factors affecting the relationship between Carbon Dioxide and CO_2:

COS	CO_2
C_3 *vs*. C_4 photosynthesis	C_3 *vs*. C_4 photosynthesis
Soil uptake	Respiration emission
Ocean flux	Fossil fuel combustion
Burning emission	
Anthropogenic emission	

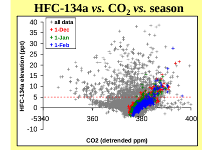
Photosynthesis (C_3 *vs*. C_4): plants incorporating different photosynthesis pathways (C_3 *vs*. C_4) use CO_2 with different efficiency and this could cause spatial variability in the Ecosystem Relative Uptake (ERU) of COS *vs*. CO_2. This may explain why the observed ERUs above Mid-West sites (ERUs of 3-6) where much corn is grown (a C_4 plant) are somewhat smaller than observed at Northern & Eastern sites where C_3 plants are more plentiful (ERUs of 5–9) **(see Figures in #3)**.

The role of non-vegetative influences may be assessed with concurrent measurements of other gases, for example tracers of biomass burning, fossil fuel combustion, anthropogenic pollution, and the influence of oceans and soils:

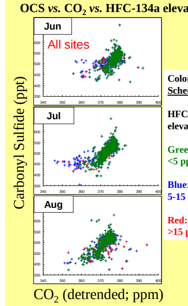
5a) Fossil fuel combustion (CO_2) and anthropogenic COS emission:

HFC and HCFC measurements conducted concurrently show fairly high correlations with CO_2 during wintertime and may provide a means to minimize or remove air samples substantially influenced by fossil fuel combustion and anthropogenic COS emission:

HFC-134a *vs*. CO_2 *vs*. season

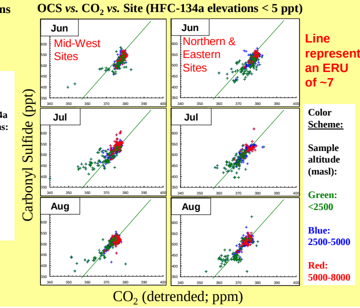


OCS *vs*. CO_2 *vs*. HFC-134a elevations



Color Scheme:
HFC-134a elevations:
Green: <5 ppt
Blue: 5-15 ppt
Red: >15 ppt

OCS *vs*. CO_2 *vs*. Site (HFC-134a elevations < 5 ppt)



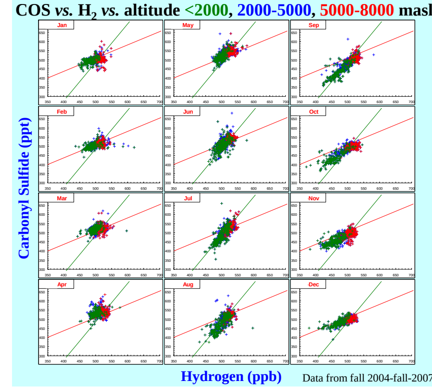
Line represents an ERU of ~7

Color Scheme:
Sample altitude (masl):
Green: <2500
Blue: 2500-5000
Red: 5000-8000

5b) On the influence of soils on COS over North America: can H_2 measurements provide insights?

COS is known to undergo carbonic-anhydrase catalyzed hydrolysis in soils. How much does this contribute to reduced COS in the boundary layer? Do COS soils losses confound the signal from vegetative uptake?

COS *vs*. H_2 *vs*. altitude <2000, 2000-5000, 5000-8000 masl



The main sink for atmospheric H_2 is destruction by soils—this is why reduced mixing ratios of H_2 are generally observed at lower elevations in these samples. COS exhibits a fairly strong correlation with H_2 in most months, as it too has a strong surface-based loss. **The correlation between COS and H_2 is not constant** over the year however; the correlation slope is enhanced by a factor of 3 during the summer months compared to wintertime (**green line** *vs*. **red line**) perhaps as a result of the additional vegetative loss of COS during summer. The enhanced slope is observed through Sept. and Oct., long after the COS *vs*. CO_2 summer correlation has broken down, perhaps implying that vegetative uptake of COS (and CO_2) persists through these months.

5c) On the influence of the oceans…

Budget analyses of varying COS fluxes in the Southern Hemisphere (SH) suggest that SH seasonality may provide an accurate picture of ocean influences on COS. If so, it suggests that the NH ocean influences COS seasonality much less than NH vegetation, though it is not possible to discern yet how much the ocean influences the COS-CO_2 relationships observed over North America. Fairly large vertical gradients are observed for COS above Vancouver—are they from oceanic processes or from air transported recently from over the Canadian continent?

5d) On the influence of biomass burning…

Biomass burning is a known source of COS, though enhancements in background COS mixing ratios were minimal during 2003, a year of enhanced burning and Northern Hemispheric CO mixing ratios (data not shown).

6) Conclusions and Questions:

a) COS exhibits seasonal variations and vertical gradients over North America consistent with a seasonally varying, surface-based sink:
* the gradients are most pronounced during the growing season.
* the gradients are pronounced above mid-continental and eastern sites more than at western, pacific, and southern sites.

b) The magnitudes of seasonality and summer vertical gradients observed for COS are roughly consistent with their main cause being the gross flux into plants during photosynthesis:
***** ratios for the Ecosystem Relative Uptake COS/CO_2 of 4 to 12.
* COS seasonal variations that are 6 times larger than CO_2 (relative basis).
* Correlation slopes for COS vs CO_2 during the growing season of ~7.

c) A correlation develops between COS and CO_2 during the growing season, with reduced mixing ratios of both gases being observed in the planetary boundary layer. In an attempt to minimize anthropogenic influences on these gases, the data were selected for near-background mixing ratios of HFC-134a.

d) Hydrogen, a gas with a strong soil sink, may allow constraints on soil losses of COS independent of vegetative uptake. Large seasonal changes are observed in the COS vs H_2 correlation slope, perhaps because of the additional vegetative uptake of COS during the growing season.

e) With continued studies to better understand the fluxes of COS to the atmosphere, **COS may be able to provide an independent means of assessing regional and interannual variations in terrestrial phtosynthesis independent of the influences of respiration.**

f) Concurrent measurements of a wide suite of other trace gases in these samples (COS, HFCs, HCFCs, CH_3I, $CHBr_3$, Benzene, CO) should improve our understanding of atmospheric CO_2.