



## Global 3-D model analysis of the seasonal cycle of atmospheric carbonyl sulfide: Implications for terrestrial vegetation uptake

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[1] We use a global 3-D simulation of atmospheric carbonyl sulfide (COS) to interpret observations at a network of surface sites. We aim to identify the primary factors underlying observed seasonal variations and to constrain COS uptake by terrestrial vegetation. Model simulations are based on a recent estimate of global COS fluxes, with closure between sources and sinks. We find that the dominant influences on seasonal variation of COS are terrestrial vegetation uptake in the northern extratropics, and ocean fluxes in the southern extratropics. Simulations underestimate the amplitude of the observed seasonal cycle in the northern hemisphere, particularly at terrestrial sites, indicating that COS uptake by terrestrial vegetation has been underestimated in recent budgets. Fitting the observed seasonal variation at northern hemisphere sites in the model requires a doubling of the global vegetation sink to  $\sim 490 \text{ Gg S y}^{-1}$ , while fitting the southern hemisphere data suggests a reduction of  $\sim 50 \text{ Gg S y}^{-1}$  in the southern extratropical ocean source. Balancing these changes in COS fluxes requires an additional source ( $\sim 235 \text{ Gg S y}^{-1}$ , equivalent to 40% of identified sources) missing from present budget estimates. Discrepancies between annual mean observations and simulated concentrations, derived from our best estimates of seasonal fluxes, are largest in the tropics, suggesting an underestimate of COS sources at these latitudes. **Citation:** Suntharalingam, P., A. J. Kettle, S. M. Montzka, and D. J. Jacob (2008), Global 3-D model analysis of the seasonal cycle of atmospheric carbonyl sulfide: Implications for terrestrial vegetation uptake, *Geophys. Res. Lett.*, 35, L19801, doi:10.1029/2008GL034332.

### 1. Introduction

[2] Atmospheric mixing ratio measurements of carbonyl sulfide (COS) show strong seasonal correlations with  $\text{CO}_2$  at northern hemisphere surface sites; this is attributed to the dominant influence of terrestrial vegetation uptake during the growing season for both species [Montzka et al., 2007]. Carbonyl sulfide is hydrolyzed within the leaf by the primary enzymes involved in  $\text{CO}_2$  assimilation [Protoschill-Krebs and Kesselmeier, 1992]. It has been suggested that observed

atmospheric variations of COS have the potential to provide ‘top-down’ constraints on rates of gross carbon assimilation by terrestrial plants and hence on Global Primary Productivity (GPP) [Montzka et al., 2007].

[3] Uptake by vegetation has been long recognized as a major sink for atmospheric COS [Goldan et al., 1988], but recent estimates differ by up to a factor of 6 [Xu et al., 2002; Sandoval-Soto et al., 2005]. There also remain large uncertainties on other components of the atmospheric COS budget [Watts, 2000; Montzka et al., 2007]. Successful exploitation of the observed seasonal correlations between COS and  $\text{CO}_2$  as constraints on gross carbon uptake (GPP) requires improved quantification of COS uptake by vegetation and of the COS budget, as well as identification of the different processes governing seasonal COS variability. In this study we simulate the seasonal atmospheric variation of COS with a 3-D global atmospheric chemical transport model (GEOS-Chem CTM [Suntharalingam et al., 2004]) in combination with recent estimates of COS flux distributions [Kettle et al., 2002]. Simulations are evaluated against atmospheric measurements from the global surface NOAA-ESRL network of Montzka et al. [2007]. We aim to identify the dominant factors underlying observed seasonal variations and to constrain the magnitude of COS uptake by terrestrial vegetation.

### 2. COS Fluxes to the Atmosphere

[4] Atmospheric COS measurements show no discernible trend since 2000 implying that sources and sinks are currently in balance [Montzka et al., 2007]. Early attempts to characterize the global COS budget reported an excess of identified sources over sinks [Chin and Davis, 1993]. Recent studies have revised flux estimates and closed the budget within the large range of uncertainties [Watts, 2000; Kettle et al., 2002]. In Table 1 we present the budget of Kettle et al. [2002], along with suggested revisions by Montzka et al. [2007].

[5] The major identified sources are from industrial activity and the ocean [Chin and Davis, 1993; Watts, 2000]. These include direct emissions and indirect contributions from carbon disulfide ( $\text{CS}_2$ ) and dimethyl sulfide (DMS) oxidation [Kettle et al., 2002]. Biomass burning and anoxic soils provide smaller sources [Watts, 2000; Nguyen et al., 1995]. The main sinks are uptake by plants and soils, oxidation by OH and stratospheric photolysis [Chin and Davis, 1993; Watts, 2000]. Kettle et al. [2002] (hereinafter referred to as K2002) provided a spatially and seasonally resolved representation of the major fluxes (Figure 1). According to K2002, primary influences on northern hemisphere seasonal variations are vegetation uptake and ocean DMS oxidation. Plant uptake displays a summertime max-

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**Table 1.** Recent Estimates of Global Atmospheric COS Budget ( $\text{Gg S y}^{-1}$ )

	<i>Kettle et al.</i> [2002] Mean (Range) <sup>a</sup>	<i>Montzka et al.</i> [2007] Revisions	This Study Revisions <sup>b</sup>
SOURCES			
Ocean (direct and indirect)	280 (40–520)		230
Anthropogenic (direct and indirect)	180 (90–266)		
Biomass burning	70 (30–110)	68–144	
Anoxic soils and wetlands	26 (12–112)		
Total Sources	555 (170–1010)	210–1049	505
SINKS			
Plant uptake	238 (210–270)	730–1500	490
Oxic soils	130 (74–180)		
Atmospheric loss (oxidation, photolysis)	120 (96–147)		
Total Sinks	490 (380–597)	902–1827	740

<sup>a</sup>Modification to K2002: biomass burning estimate is from the global total of *Nguyen et al.* [1995].

<sup>b</sup>Revised ocean estimate of this study is based on reductions to southern extra-tropical fluxes alone (see text).

imum (coincident with timing of maximal stomatal opening during the growing season), while the DMS oxidation source peaks in May–July driven by higher marine productivity. These two fluxes act in opposition to modulate northern hemispheric COS variations. The southern hemisphere COS seasonal cycle is primarily driven by the ocean source, which peaks in the austral summer.

### 3. Methods

[6] We use the GEOS-Chem atmospheric CTM (v 7.03) driven by assimilated meteorological data from the NASA Goddard Earth Observing System (GEOS-3). The meteorological data have a horizontal resolution of  $1^\circ \times 1.25^\circ$  and 55 vertical levels and a temporal resolution of 6 hours. The horizontal resolution was degraded to  $2^\circ \times 2.5^\circ$  for computational efficiency in this study. The COS simulation is based on the gridded flux inventories of K2002 with modifications listed below. It is driven by meteorological data for the year 2001, with a 3 year spin-up.

[7] Details of individual process parameterizations for COS fluxes are presented by K2002. Here we only discuss representation of terrestrial vegetation uptake and ocean fluxes. K2002 represent COS uptake by plants based on  $\text{CO}_2$  assimilation by terrestrial vegetation [*Goldan et al.*, 1988; *Chin and Davis*, 1993]. This approach defines the COS flux as a product of the  $\text{CO}_2$  flux scaled by the ratio of ambient atmospheric mixing ratios of COS and  $\text{CO}_2$ .

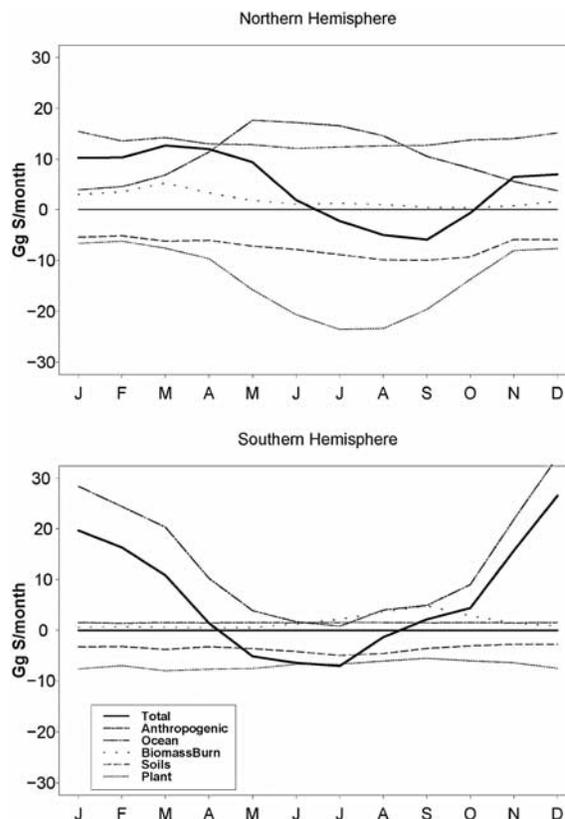
$$\text{Flux}_{\text{COS}} = \text{Flux}_{\text{CO}_2} \times \frac{[\text{COS}]}{[\text{CO}_2]} \quad (1)$$

K2002 use normalized Net Primary Productivity (NPP) distributions as a proxy for  $\text{CO}_2$  uptake, and assume similar atmosphere to plant uptake resistances (or deposition velocities,  $V_d$ ) for  $\text{CO}_2$  and COS. These assumptions are a likely source of error [*Sandoval-Soto et al.*, 2005], and are discussed further in section 4.

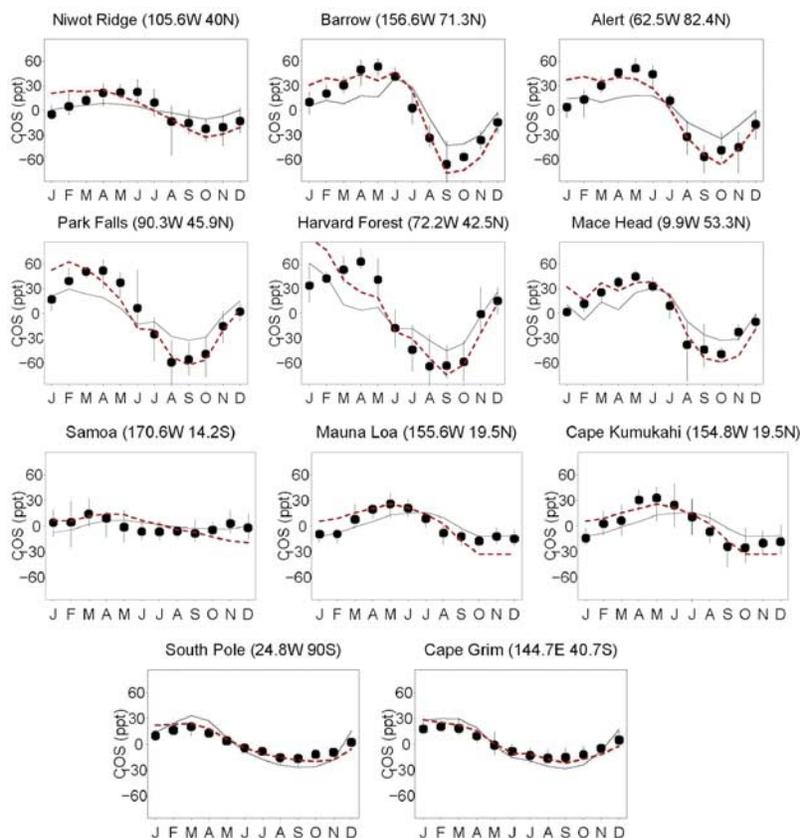
[8] K2002 derive oceanic COS fluxes using an upper ocean photochemical model. COS from DMS oxidation is estimated from the DMS flux distribution of *Kettle and Andreae* [2000] (annual DMS flux of 22 Tg S) in combi-

nation with a molar conversion factor derived from *Barnes et al.* [1994].

[9] Our simulation includes seasonally varying biomass burning (unaccounted for in K2002) based on the monthly climatology of *Duncan et al.* [2003] and scaled to the global estimate of *Nguyen et al.* [1995] (mean annual COS flux of 70 Gg S). We compute tropospheric oxidation of COS by



**Figure 1.** Seasonal variation of COS fluxes from K2002 aggregated for northern and southern hemispheres. Biomass burning variation is based on the work by *Duncan et al.* [2003]. The black solid line represents the sum of the separate components.



**Figure 2.** Monthly COS mixing ratio anomalies (relative to annual mean) at surface sites. Black circles represent averages of the monthly mean observed anomalies for the years 2001–2005, and associated error bars represent the maximum to minimum range. The following model simulations are shown: (a) K2002 fluxes (solid line); (b) “Increased Sink” (dashed line).

OH using the temperature dependent rate constant of *Atkinson et al.* [1997] and monthly mean OH fields (for year 2001) [*Park et al.*, 2004]. Our modified K2002 budget used in GEOS-Chem is summarized in Table 1.

[10] Surface flask measurements of COS have been made on a regular basis since early 2000 at 3 southern and 10 northern hemisphere sites [*Montzka et al.*, 2007]. In this analysis we use the data for years 2001–2005.

#### 4. Results

[11] Figure 2 compares monthly mixing ratio anomalies at each site for observations (black circles) and the model simulation using the K2002 fluxes of Table 1 (solid line). Anomalies are calculated by subtracting annual mean values for each year from the monthly means. Observations at northern hemisphere sites show a distinct seasonal pattern with maxima in March–May and minima in August–October consistent with terrestrial biospheric uptake during the growing season. Seasonal amplitudes range from 30 to over 70 ppt and are largest at forested sites.

[12] The K2002 simulation underestimates the seasonal amplitude at northern hemisphere sites, particularly in forested regions (e.g., by more than 30 ppt at Park Falls and Harvard Forest). Simulations driven by meteorological data for other years (1999–2000) also show similar under-

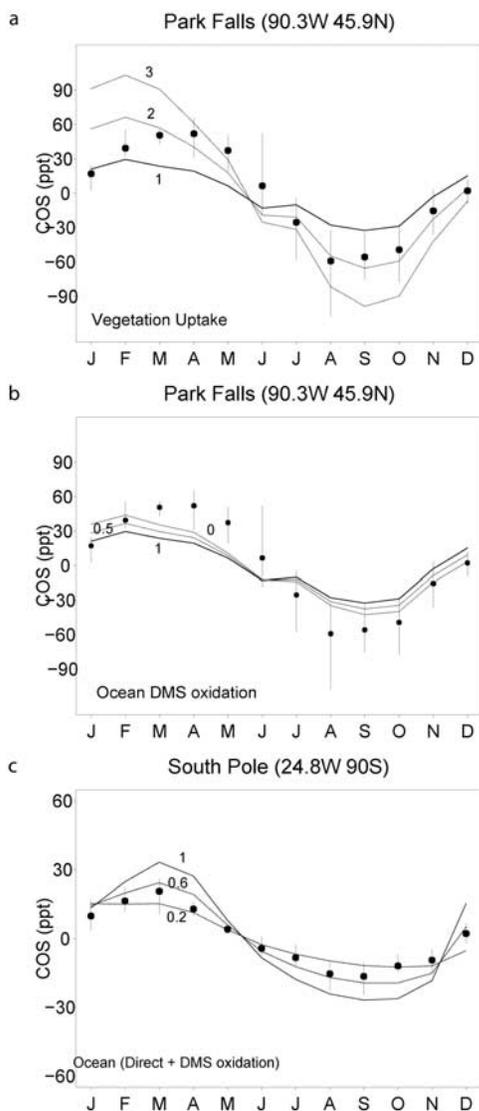
estimates of observed amplitudes at these sites. This suggests a general underestimate of the terrestrial biospheric COS sink. No such model bias is found in simulated  $\text{CO}_2$  at the same sites [*Suntharalingam et al.*, 2004] suggesting that model transport error is unlikely to be responsible for the discrepancy.

[13] Higher estimates for plant COS uptake ( $730\text{--}1480\text{ Gg S y}^{-1}$ ) have been estimated from field and laboratory studies [*Xu et al.*, 2002; *Sandoval-Soto et al.*, 2005]. These estimates are 3–6 times larger than the K2002 values. *Sandoval-Soto et al.* [2005] note a preferential uptake of COS over  $\text{CO}_2$  implying a higher deposition velocity ( $V_d$ ) for COS. Their estimate for plant uptake of COS

$$Flux_{COS} = Flux_{CO_2} \times \frac{[COS]}{[CO_2]} \times \frac{V_{d,COS}}{V_{d,CO_2}} \quad (2)$$

accounts for this difference in  $V_d$ , and also uses Gross Primary Productivity (GPP) as a more appropriate proxy for  $\text{CO}_2$  assimilation by the plant. The K2002 estimates for plant COS uptake (equation 1) assumed the same  $V_d$  for COS and  $\text{CO}_2$ , and used NPP (approximately half the magnitude of GPP) for the  $\text{CO}_2$  flux uptake, yielding smaller flux magnitudes.

[14] We find an increase in modeled vegetation uptake improves representation of the seasonal cycle at northern



**Figure 3.** Sensitivities of simulated COS to changes in the following: (a) vegetation uptake; (b) ocean DMS oxidation flux; (c) aggregated southern ocean direct and DMS oxidation flux. The factor by which each flux is changed (relative to K2002) is shown on the respective model curves. Black circles represent observed monthly mean mixing ratio anomalies (for 2001–2005) at the specific site.

hemisphere sites. Figure 3a presents a sensitivity analysis at Park Falls. Doubling of plant uptake produces good representation of the observed amplitude, while increase by a factor of 3 overestimates it. To estimate the optimal increase in vegetation uptake consistent with observations, we use minimization of the root mean squared error (RMSE) between model ( $xm$ ) and observed ( $xobs$ ) monthly concentrations.

$$RMSE = \sqrt{\frac{\sum_{y=2001}^{2005} \sum_{mo=1}^{12} (xobs_{mo,y} - xm_{mo})^2}{N}} \quad (3)$$

$N$  is the total number of monthly observations for the years considered (2001–2005). We evaluate the RMSE for a

range of simulations that systematically increase plant uptake; the ‘best’ model representations are those with lowest RMSE values. The RMSE is estimated for northern hemisphere sites of Harvard Forest, Park Falls, Barrow, Alert and Mace Head, as vegetation fluxes are likely to be the dominant influence on seasonal variability here [Montzka *et al.*, 2007]. Simulations that increase the seasonally varying plant uptake by factors of 1.9 to 2.2 (to 460 – 530 Gg S  $y^{-1}$ ) produce the lowest RMSEs and improved representation of the seasonal cycle. This top-down constraint supports the recommendation for a larger sink from terrestrial vegetation. Our estimate is, however, smaller than the 3–6 times increase suggested by recent studies [Sandoval-Soto *et al.*, 2005; Xu *et al.*, 2002], and Figure 3a indicates that increases of this magnitude overestimate observed amplitudes.

[15] The oceanic COS source from DMS oxidation peaks in spring-summer muting the influence of vegetation uptake in the northern hemisphere. We find, however, in sensitivity simulations (Figure 3b), that the impact at terrestrial sites is small; even a complete suppression of this source does not enable simulated amplitudes to match observations. This does not preclude a smaller role for COS from oceanic DMS oxidation; we discuss this later in the context of the southern hemisphere sites.

[16] Observed seasonal variation in the southern hemisphere is of smaller amplitude (19 – 22 ppt at South Pole and Cape Grim) and displays a maximum in January–March and a minimum in August–October (Figure 2). This is consistent with a pattern of seasonal variation driven by direct ocean fluxes and ocean DMS oxidation, which both peak in the summer [Kettle *et al.*, 2002]. Modeled monthly anomalies based on K2002 (solid line, Figure 2) agree in phase, but show a small overestimate in amplitude ( $\sim 8$  ppt) suggesting an excess of modeled ocean sources at these latitudes. An intercomparison of DMS climatologies by Belviso *et al.* [2004] finds the Kettle and Andreae [2000] distribution, from which the K2002 fluxes are derived, high by more than a factor of 2 in the southern extratropics. K2002 also note significant uncertainties in their estimates of ocean COS fluxes arising from poorly constrained quantum yields of COS in the underlying photochemical model.

[17] Figures 3c illustrates that reduction of the southern extratropical ocean fluxes that display distinct seasonal variation (i.e., aggregated direct and DMS oxidation flux) improves simulation of the seasonal observations. We aggregate these fluxes as their simulated seasonal signatures are similar. We estimate the optimal flux reduction in southern ocean fluxes by evaluating the RMSE at the southern sites South Pole and Cape Grim for changes in this aggregated flux. The K2002 ocean  $CS_2$  oxidation flux is predominantly aseasonal with minimal impact on the simulated seasonal cycle, and hence not included in this analysis. We limit the flux reduction to 30°S–90°S, as Belviso *et al.* [2004] note that the Kettle and Andreae [2000] DMS distribution displays the most significant discrepancies here.

[18] Minimum RMSE values are obtained with a reduction of  $\sim 50$  Gg S  $y^{-1}$  equivalent to  $\sim 60\%$  of the southern extratropical ocean flux. This is within the uncertainty bounds on ocean fluxes estimated by K2002, but yields discernible improvement in the model simulation. We derive an improved model representation of the observed

seasonal cycles in both hemispheres ('Increased Sink' scenario: Figure 2) with an increase in COS vegetation uptake from 238 Gg S  $y^{-1}$  to 490 Gg S  $y^{-1}$  and a decrease in southern ocean fluxes of 50 Gg S  $y^{-1}$ .

## 5. Implications for Global Budget

[19] The revised estimates of COS fluxes demanded by seasonal constraints have important implications for current estimates of the global COS budget. The K2002 budget was balanced within the limits of stated uncertainties. For a doubling of plant uptake (to  $\sim 490$  Gg S  $y^{-1}$ ) and reduction in southern ocean fluxes (by 50 Gg S  $y^{-1}$ ) the revised annual mean estimates of global sinks and sources are 740 Gg S and 505 Gg S, representing an  $\sim 40\%$  imbalance (mean excess of sinks over sources of 235 Gg S  $y^{-1}$ ).

[20] Atmospheric COS measurements show no recent trend hence the increased sink demanded by the observed seasonal cycle must be balanced by additional sources or reduced estimates of sinks. Annual mean concentration residuals (i.e., model minus observed values) for the 'Increased Sink' scenario show the largest deficits in the tropics (average deficit for tropical sites of  $-44$  ppt in comparison to  $-36$  ppt and  $-38$  ppt for southern and northern extratropical sites respectively). This suggests a possible underestimate of sources at these latitudes. Likely candidates, with predominantly tropical sources, include biomass burning and oceanic CS<sub>2</sub> oxidation. Montzka *et al.* [2007] propose a larger biomass burning source of 89 Gg S  $y^{-1}$  (range 68–144 Gg S  $y^{-1}$ ) which also accounts for the contribution from biofuel combustion. This higher flux likely accounts for some of the missing source, but is insufficient to close the budget on its own.

[21] According to K2002, almost 70% of the oceanic flux from CS<sub>2</sub> oxidation has its origins between 30°S and 30°N. While the K2002 ocean fluxes represent an advance over previous estimates, uncertainties remain large and current understanding of marine COS cycling is poor [Preiswerk and Najjar, 2000; Ulshofer and Andreae, 1998]. Additional work is needed to elucidate the relevant processes and improve quantification of COS from CS<sub>2</sub> and DMS oxidation. Other potential candidates include COS fluxes from coastal and estuarine areas [Uher, 2006] currently unaccounted for in the open ocean parameterizations of K2002.

[22] Smaller tropical sinks may also play a role in closing the budget. The soil flux was previously characterized as a net source [Goldan *et al.*, 1988; Castro and Galloway, 1991; Chin and Davis, 1993]. Current understanding designates soils a net sink and some studies suggest a significantly smaller role for this flux (e.g.,  $<1\%$  of the plant uptake [Xu *et al.*, 2002; Steinbacher *et al.*, 2004]). The K2002 soil flux is based on extrapolation of a single study of northern mid-latitude arable soils [Kesselmeier *et al.*, 1999]. Improved quantification of this sink requires measurements encompassing different soil types and conditions, particularly from the tropics.

[23] A trial 'Balanced Budget' scenario, constructed to close the budget with an additional tropical COS source of 235 Gg S  $year^{-1}$  (distributed aseasonally and uniformly between 30°S and 30°N) in conjunction with the fluxes of the 'Increased Sink' scenario, reduces annual mean concen-

tration residuals close to zero at all latitudes (i.e., to average values of 1.5 ppt for southern high latitude sites, 3.2 ppt for tropical sites and 0.7 ppt for northern high latitude sites). The corresponding modeled seasonal anomalies do not differ significantly from those of the 'Increased Sink' scenario. This also represents an improvement over the original K2002 simulation. While the 'Balanced Budget' simulation does not identify the specific missing sources, it indicates that increased sources and/or reduced sinks in the tropics satisfy much of the atmospheric observational constraints. Determination of the extent to which the atmospheric measurements can identify the optimal combination of individual sources and sinks requires a formal inverse analysis.

[24] In summary, our global 3-D model interpretation of atmospheric observations confirms that terrestrial vegetation uptake dominates seasonal variations in the northern hemisphere, while ocean fluxes are the main influence in the southern hemisphere. A simulation with doubling of vegetation uptake (to 490 Gg S  $y^{-1}$ ) and reduction in southern extratropical ocean fluxes (of 50 Gg S  $y^{-1}$ ) improves the model representation of observed seasonal variation in both hemispheres. Balancing this requires a large COS source ( $\sim 235$  Gg S  $y^{-1}$ ) missing from present budget estimates.

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