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On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO_2

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[1] Measurements of carbonyl sulfide (COS) from a global air-monitoring network over multiple years suggest that atmospheric mixing ratios of COS are strongly influenced by terrestrial vegetation in the Northern Hemisphere (NH) and by the oceans in the Southern Hemisphere (SH). The annual mean NH mixing ratio estimated from results at seven surface sites during 2000.2–2005.2 was 476 ± 4 ppt, or slightly less than the mean of 491 ± 2 ppt derived from results at three surface sites in the SH. The lowest annual mean mixing ratios were measured at low-altitude continental sites in the midlatitude and high-latitude NH. Mixing ratios undergo substantial seasonal variations at nearly all sites across the globe; the largest seasonal variations are observed at the NH sites having the lowest annual means. There is little coherence in the seasonality in the NH and SH, suggesting that the COS seasonality is driven by different processes in each hemisphere. These seasonal changes cause the NH/SH ratio, as estimated from the available surface data, to vary regularly from 0.91 ± 0.01 to 1.04 ± 0.02 across a year; the annual mean NH/SH ratio was 0.97 ± 0.01. Results from over 160 aircraft profiles regularly collected at eight sites over the continental United States throughout an entire year reveal substantial vertical gradients for COS mixing ratios that vary with season. While similar mixing ratios are observed throughout the NH troposphere during January–April (up to 8 km above sea level (asl)), during the growing season substantially reduced mixing ratios are observed in the boundary layer above the continental United States (defined here as <2 km asl). The surface and aircraft results for COS show strong similarities to atmospheric CO_2, though both the amplitude of seasonal variations measured at Earth's surface and the observed vertical gradients during the growing season are 5–6 times larger for COS than for CO_2 on a relative basis. A qualitative analysis of the results in light of known sources and sinks suggests (1) that terrestrial uptake, most likely due to photosynthetically active vegetation, dominates the seasonality observed throughout the Northern Hemisphere at a rate that is about 5 times greater than estimates based upon scaling net primary production by mean, ambient air mixing ratios of COS to CO_2, (2) the oceans dominate the seasonality observed in the Southern Hemisphere, and (3) biomass burning has a small influence on the seasonality observed for COS in the extratropics of both hemispheres.

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1. Introduction

[2] Carbonyl sulfide (COS) was first detected and measured in the atmosphere over 30 years ago [*Hanst et al.*, 1975; *Sandalls and Penkett*, 1977]. It is the most abundant sulfur-containing trace gas in the atmosphere and accounts for a substantial portion of the sulfur in the stratospheric aerosol layer [*Ko et al.*, 2003; *Notholt et al.*, 2006]. Despite the abundance of atmospheric COS measurements, especially from periodic campaigns, the available data have not allowed a coherent picture of the atmospheric distribution, seasonality, and interannual variability for this trace gas across the Northern or Southern hemispheres [*Notholt et al.*, 2006]. Furthermore, available measurements are difficult to reconcile with known sources and sinks. A 3-D modeling study [*Kjellström*, 1998] suggests mixing ratios in the SH should be larger than in the NH, though some observations

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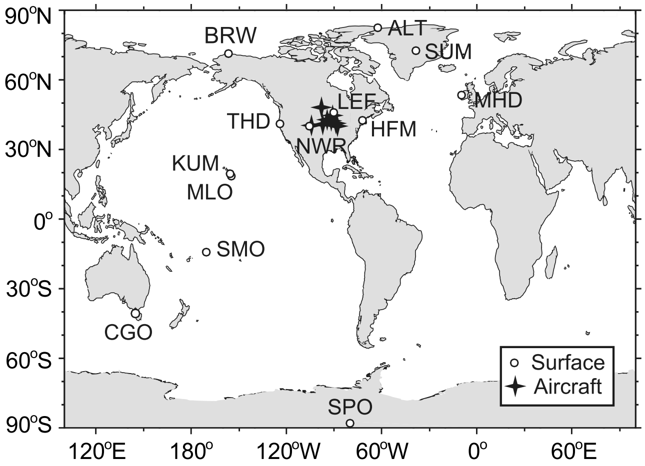

Figure 1. Locations at which ground-based samples are collected in paired glass or electropolished stainless steel flasks multiple times per month (circles). Flask sampling has been ongoing at most sites since 2000, though the period of sampling is shorter at Trinidad Head, United States (THD), Mace Head, Ireland (MHD), and Summit, Greenland (SUM). Aircraft flask samples were regularly collected above the locations indicated by black crosses from September 2004 through November 2005; during a typical flight, up to 12 individual flasks were filled at regular intervals up to an altitude of 8 km above sea level (asl). See text for additional details.

have revealed a substantial gradient of opposite sign [*Bingemer et al.*, 1990; *Johnson et al.*, 1993; *Griffith et al.*, 1998].

[3] A recent analysis of COS sources and sinks suggests that atmospheric COS should undergo seasonal variations primarily as a result of seasonality in vegetative uptake and oceanic emissions [*Kettle et al.*, 2002a, 2002b]. Other sources and sinks of COS also change seasonally, such as emissions from biomass burning and uptake by soils, but variations in these fluxes are estimated to be less than one-third as large as seasonality in fluxes from the oceans and vegetative uptake [*Kettle et al.*, 2002a].

[4] The oceans and vegetation have an opposing influence on atmospheric COS seasonality; emissions from oceans and uptake by vegetation both peak during summer months [*Ulshöfer et al.*, 1995; *Weiss et al.*, 1995; *Kettle et al.*, 2002a]. Atmospheric measurements ought to provide some constraints on the relative magnitude of these processes and their seasonality, but the available data have not provided a clear picture of how background surface mixing ratios of COS in the NH vary across broad scales in response to these offsetting fluxes [*Kettle et al.*, 2002b]. An analysis of multiyear, long-path absorbance measurements suggested that they were consistent with the current understanding of the atmospheric COS budget, though constraints on the relative magnitude of vegetative uptake and ocean-related emissions were not possible [*Kettle et al.*, 2002b]. Seasonally varying uptake that is consistent with the influence of vegetation can be observed in ambient mixing ratios close to forested regions [*Xu*, 2000; *Xu et al.*, 2002], though the influence of this loss on broader scales is not obvious. In one ship-based study, temporarily reduced mixing ratios of COS were accompanied by lower amounts of CO_2 in air originating from over the Asian continent, presumably as a result of vegetative uptake of both gases [*Thornton et al.*, 1996]. At other times, however, enhanced COS mixing ratios have been observed downwind of the Southeast Asian and North American continents [*Thornton et al.*, 1996; *Bingemer et al.*, 1990; *Notholt et al.*, 2000; *Xu et al.*, 2001; *Blake et al.*, 2004]. Such elevations are often attributed to the influence of anthropogenic activity, and coal or biomass burning.

[5] The uptake by vegetation has been recognized for many years as a dominant sink for atmospheric COS [*Brown and Bell*, 1986; *Goldan et al.*, 1988; *Kjellström*, 1998; *Kettle et al.*, 2002a; *Xu et al.*, 2002; *Sandoval-Soto et al.*, 2005]. Substantial uptake of COS by vegetation is expected because it undergoes rapid hydrolysis by enzymes present in leaf water that are involved in the initial stages of photosynthesis: carbonic anhydrase, rubisco, and PEP carboxylase [*Protoschill-Krebs and Kesselmeier*, 1992; *Protoschill-Krebs et al.*, 1996]. Furthermore, in pure water the hydrolysis of COS is primarily irreversible [*Elliot et al.*, 1989], in contrast to CO_2 for which hydrolysis is readily reversible. Studies with radioactively labeled sulfur in COS show that sulfur taken up as COS by vegetation becomes incorporated into plant amino acids and proteins [*Brown et al.*, 1986; *Kluczewski et al.*, 1985]. The uptake of COS and CO_2 by photosynthetically active vegetation is modulated by the activity of these enzymes and by leaf stomatal conductance [*Kesselmeier and Merk*, 1993; *Gillon and Yakir*, 2001; *Sandoval-Soto et al.*, 2005; *Yonemura et al.*, 2005].

[6] In order to provide additional information for assessing the influence of different processes on the abundance, distribution, and variability of atmospheric COS, we made measurements of atmospheric COS at multiple surface sites across the globe for over 5 years and from samples collected onboard aircraft above fixed locations in the continental United States throughout an entire year. The results provide a coherent picture of the atmospheric distribution and seasonal variation for COS in both hemispheres. The predominant features of the observations are qualitatively consistent with known sources and sinks of COS and their seasonal variability. A comparison of the seasonality and vertical gradients between COS and CO_2, along with other considerations, indicate that the loss of COS to vegetation is substantially larger than can be estimated directly from scaling net primary productivity (NPP) by the ratio of global mean mixing ratios of COS and CO_2.

2. Experimental Procedure

2.1. Ground-Based, Ambient Air Measurements of COS

[7] Since early 2000, we have measured COS from flasks filled with ambient air at multiple sites in both hemispheres (Figure 1): from glass flasks (2 L) filled at South Pole (SPO, 90°S, 2866 m above sea level or m asl); from glass and electropolished stainless steel (SS) flasks (2.5–3 L) filled at Cape Grim, Australia (CGO, 40.4°S, 144.6°W, 94 m asl) and American Samoa (SMO, 14.2°S, 170.6°W, 77 m asl); and from electropolished SS flasks (2.5–3 L) filled at Mauna Loa, United States (MLO, 19.5°N, 155.6°W, 3397 m asl), Cape Kumukahi, United States (KUM, 19.5°N,

154.8°W, 3 m asl), Niwot Ridge, United States (NWR, 40.0°N, 105.54°W, 3475 m asl), Wisconsin, United States (LEF, 45.9°N, 90.3°W, 868 m asl—inlet is 396 m above ground on a tall tower), Harvard Forest, United States (HFM, 42.5°N, 72.2°W, 340 m asl, inlet is 29 m above ground), Barrow, United States (BRW, 71.3°N, 155.6°W, 11 m asl), and Alert, Canada (ALT, 82.5°N, 62.3°W, 210 m asl). Pressurized samples also have been collected in electropolished SS flasks since 2002 at Trinidad Head, United States (THD, 41.0°N, 124.1°W, 120 m asl) and Mace Head, Ireland (MHD, 53.3°N, 9.9°W, 42 m asl), and in glass flasks since mid-2004 at Summit, Greenland (SUM, 72.6°N, 38.4°W, ~3200 m asl). At all sites samples are collected as paired flasks 1 to 5 times per month. They are filled to absolute pressures between 300 kPa and 350 kPa in SS flasks and at ~175 kPa in glass flasks. The total number of flask pairs collected at surface sites through 2005 is approximately 2070. From each of the flasks sampled, two aliquots are analyzed in the NOAA/ESRL/GMD's (formerly NOAA/CMDL) Boulder laboratories with gas chromatography and mass spectrometry detection. The median replicate injection precision for COS at ambient levels with our instrumentation is 0.4% (n ~ 3000); 95% of the time it is <1.3% (i.e., <6.3 ppt). We discard results when paired flasks disagree by more than 6.3 ppt; this accounts for 15% of all samples collected. The mean delay between sampling and analysis in the surface-based results presented here was 11 ± 6 days at most NH sites (it was 36 ± 10 days at ALT), 20 ± 9 days at CGO and SMO, and 114 ± 84 days at SPO.

[8] Because sample flasks are collected without any chemical drying agents in line, tests were conducted to ascertain the possible influence of hydrolysis on COS mixing ratios in air stored in stainless steel flasks for extended periods. Real air spiked with up to 5 cm^3 of deionized and distilled liquid H_2O (neutral pH) showed losses of only 2% over a 35-day period in a 3-L flask pressurized to 350 kPa. Flasks spiked with substantially less water, or amounts more similar to those expected from sampling humid ambient air at remote sites, showed much smaller losses. In separate tests, the instrument response to COS has been found to be independent of CO_2 mixing ratios across the range 0–700 ppm CO_2. Additional details regarding sampling, stability of COS in glass flasks, analysis, standardization (data are referenced to the NOAA-2004 COS scale), and instrument linearity are provided elsewhere [*Montzka et al.*, 2004].

2.2. Ground-Based Sampling Protocols, Data Filtering and Handling

[9] Most flasks are filled when the wind is from a predefined "clean air" sector, though no effort was made to remove the fraction of samples collected under nonbackground meteorological conditions. At coastal sites, this clean air sector was over the ocean, not the land. Results from about 1% of all sample pairs collected have been eliminated from consideration on the subjective basis that they were not representative of background air. These samples were collected from SPO (n = 2), CGO (n = 3), SMO (n = 10), and THD (n = 4). All results from other sites are considered in this analysis (provided the pair agreement was <6.3 ppt, see above). Flasks are generally filled over a few minutes time at these sites within 2 hours of local noon. Hemispheric mean mixing ratios are calculated for the lower atmosphere from monthly means at selected stations or groups of stations with cosine of latitude weighting of atmospheric boxes encompassing different site groupings in the following manner: $SH_{mean} = [SPO \times 0.408 + CGO \times 0.770 + SMO \times 0.974]/[0.408 + 0.770 + 0.974]$, and $NH_{mean} = [(KUM + MLO) \times 0.970/2 + (LEF + NWR + HFM) \times 0.751/3 + (BRW + ALT) \times 0.402/2]/[0.970 + 0.751 + 0.402]$. The sites were grouped by latitude to incorporate low- and high-altitude sites in the NH boxes, where possible. Results from THD, MHD, and SUM are not incorporated into these hemispheric means because the measurement record at these sites did not span the entire measurement period. A global mean mixing ratio is estimated for the lower atmosphere from the mean of the hemispheric means.

2.3. Aircraft-Based, Ambient Air Measurements of COS

[10] From September 2004 to November 2005 approximately 1800 additional air samples were collected in glass flasks from monthly aircraft flights at eight sites across the midwestern United States (Figure 1): BGI (42.82°N, 94.41°W), BNE (40.80°N, 97.18°W), CAR (40.37°N, 104.30°W), DND (48.14°N, 97.99°W), FWI (44.66°N, 90.96°W), HIL (40.07°N, 87.91°W), OIL (41.28°N, 88.94°W), and RIA (42.40°N, 91.84°W). The total number of flights conducted above these sites over this period was 162. During a flight, up to 12 glass flasks are collected at different altitudes as the aircraft descended in a spiral from ~8 km asl to the surface over a 30-min period. All flasks are first flushed and then pressurized over a few seconds period to 275 kPa with a diaphragm pump (EPDM or Viton diaphragm). Flights were typically conducted within 3 hours of 11:00 local standard time. Flasks are shipped to Boulder and analyzed typically within 1 to 2 weeks after sampling (median delay = 9 days; 95% of the time the delay before analysis was <15 days). In contrast to flasks sampled from ground-based stations, only a single aliquot is analyzed from each aircraft flask. Tests concerning the integrity of COS in sample pumps, flasks, and ancillary equipment suggest that atmospheric COS is reliably sampled on the aircraft sampling platform.

2.4. Measurements of CO_2

[11] Independent samples are routinely collected on a weekly basis by the Carbon Cycle Greenhouse Gas Group of NOAA/ESRL/GMD in Boulder, CO at all the ground-based stations where COS measurements were made except THD and HFM [*Conway et al.*, 1994, 2004]. In the same aircraft flasks that are analyzed for carbonyl sulfide, CO_2 is also measured by the NOAA/ESRL/GMD Carbon Cycle Greenhouse Gas Group. Data for CO_2 at HFM were obtained with in situ instrumentation; these data were kindly provided by Harvard University (W. Munger, personal communication, 2005).

3. Results

3.1. Annual Mean Mixing Ratios

[12] Over 5 full years of measurements reveal annual mean mixing ratios of COS at ground-based stations across the globe that range from 440 to 500 ppt (Figure 2 and Table 1). The highest annual mean mixing ratios of carbonyl sulfide

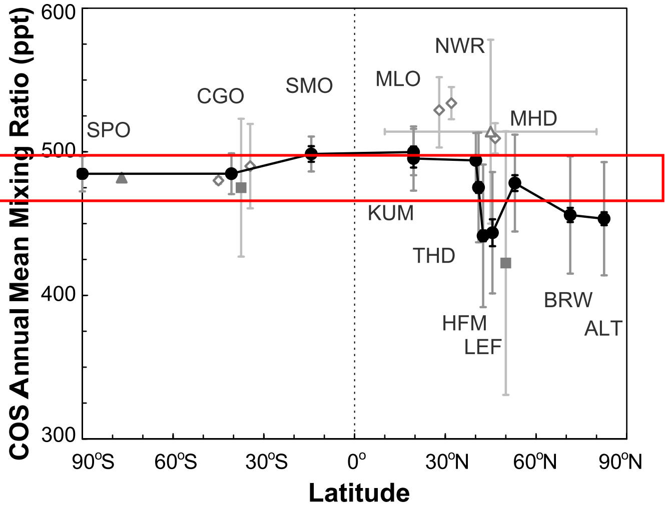

Figure 2. Annual mean mixing ratios for carbonyl sulfide (COS) at surface stations (solid black and gray symbols) and from aircraft or long-path absorbance through the troposphere (open symbols). Annual means from up to 5 years of data collected at NOAA ground-based sampling stations (solid black circles connected by lines) are compared to results from previous work: ground-based studies (gray solid triangle at 77°S represents near-surface firn data from *Sturges et al.* [2001]; gray squares at 37.5°S from *Milhalopoulos et al.* [1991] and at 50°N from *Xu* [2000]) and aircraft data from a range of latitudes in the Northern Hemisphere (open triangle from *Bandy et al.* [1992]) or free tropospheric means from Fourier Transform Infrared (FTIR) absorbance (open diamonds at 45°S and 34.5°S from *Griffith et al.* [1998]; at 28°N from *Schneider* [2002]; at 32°N and 46.5°N from *Mahieu et al.* [2003] and *Rinsland et al.* [2002]). The error bars displayed indicate 1 standard deviation of all measurements and include seasonal variations. The smaller, darker error bars displayed on the NOAA results show 1 standard deviation of the five annual means determined for the years 2000.2–2005.2 at most sites (only 3 years at THD, 41.0°N and only 2 years at MHD, 53.3°N) (at some sites, this interannual variability is smaller than the symbol).

are observed in the tropics and subtropics of both hemispheres (between ±20° latitude). In the SH, only slightly lower mixing ratios are observed at the higher-latitude sites CGO (40°S) and SPO (90°S). Reduced annual means are also observed at higher latitudes in the NH, but this decline is substantially enhanced north of 40°N. Although mixing ratios at higher-latitude coastal sites (THD and MHD) are only slightly lower than observed at similar latitudes in the SH, much lower COS mixing ratios are measured in the NH at low-altitude continental (HFM and LEF) and arctic coastal sites (BRW and ALT) north of 41°N. Annual surface means at these NH sites are up to 45 ppt lower than observed at similar latitudes in the SH.

[13] Annual mean mixing ratios have also been determined for COS during a single year from samples collected onboard aircraft above eight, midcontinental sites in the United States (Figure 3 and Table 1). The results suggest annual means in the free troposphere above the U.S. continent that are slightly higher than those observed at NWR (3.5 km asl), a high-altitude surface site at which free tropospheric air is typically sampled. In aircraft samples collected predominantly within the continental boundary layer (defined here as <2 km asl), annual mean mixing ratios measured were 23–50 ppt lower than observed in the free troposphere (5–8 km asl).

3.2. Seasonality Observed for Atmospheric Carbonyl Sulfide

[14] The surface-based and aircraft-based measurements also reveal that mixing ratios of COS undergo pronounced and regular seasonal variations at nearly all locations sampled in this study (Figure 4). The smallest seasonal variation amplitudes are observed at SH sites. Results from the mid-to-high latitude SH sites (CGO at 40°S and SPO at 90°S), for example, show consistent sinusoidal variations with amplitude 8% (peak to peak; Table 1). Peak mixing ratios are observed at these sites in Austral summer (February) and minima are measured in Austral winter (August). At the tropical station SMO (14°S), seasonal changes are less apparent owing to a much higher sample-to-sample variability (range = ±7%). Despite the enhanced variability at SMO, however, maximum and minimum mixing ratios at SMO generally occur during a similar time of year as observed at CGO and SPO (Figure 4).

[15] Results from NH sites are also characterized by consistent seasonal variations, but these variations are substantially larger than observed in the SH. Seasonal variations in the NH have peak-to-peak amplitudes ranging from 9 to 33% of the measured annual means (Table 1). The largest seasonal variation amplitudes are observed at low-altitude, continental sites exhibiting the lowest annual means (LEF and HFM) (Figures 4 and 5 and Table 1). Slightly smaller and delayed seasonal changes are measured in the arctic (BRW and ALT), and annual means at these sites are slightly higher than observed at LEF and HFM. Substantially smaller and further delayed variations are measured at high-altitude continental (NWR) and oceanic (MLO) sites and in the marine boundary layer (KUM). Annual means at these three sites are the highest measured in the NH (494–500 ppt; Table 1). Seasonality and annual means observed at the coastal midlatitude sites THD and MHD are intermediate between those observed at NWR and arctic sites. Results at THD, however, exhibit even higher sample-to-sample variability than SMO.

[16] Results from a year of flasks collected onboard aircraft at sites above the continental United States also show substantial seasonal variations for COS at all altitudes, though the amplitude of these variations varies with altitude (Figure 6a). In samples collected predominantly within the free troposphere (above 2 km asl), the observed seasonality is similar in phase and magnitude to that observed at the high-altitude surface sites NWR and MLO. In samples collected below 2 km asl, the amplitudes of seasonal variability for COS are substantially enhanced.

[17] Despite the large differences in annual means and seasonal variation amplitudes at different sites in the NH, similar mixing ratios of COS are observed throughout the entire NH during February, March, and April (Figures 5 and 7). During each of these months the full range of monthly mean mixing ratios measured at all NH surface sites is typically less than 30 ppt. This consistency is also

Table 1. Carbonyl Sulfide (COS) Mixing Ratios in the Troposphere[a]

Site	Latitude, Longitude	Measurement Period	Mean Mixing Ratio (1 s.d.[b])	Mean Seasonal Amplitude, Peak to Peak, as Winter and Spring Minus Summer and Fall (1 s.d.), ppt[b]	Amplitude/Mean
		Northern Hemispheric Surface Sites			
ALT	82N, 62W	2000.2–2005.2	456 (2)	116 (14)	25%
BRW	71N, 156W	2000.2–2005.2	456 (5)	121 (9)	27%
SUM[c,d]	73N, 38W	2004.5–2005.2	461 (n.a.)	n.a.	
MHD[d]	53N, 10W	2001.4–2005.2	478 (8)	102 (18)	21%
LEF	46N, 90W	2000.2–2005.2	444 (8)	128 (20)	29%
HFM	43N, 72W	2000.2–2005.2	441 (8)	147 (10)	33%
NWR	40N, 106W	2000.2–2005.2	494 (3)	63 (14)	13%
THD[d]	41N, 124W	2002.2–2005.2	475 (8)	118 (15)	25%
MLO	20N, 156W	2000.2–2005.2	500 (3)	47 (9)	9%
KUM	20N, 155W	2000.2–2005.2	495 (6)	69 (8)	14%
		Continental U.S. Aircraft Profiles at Eight Sites (km Above Sea Level)			
0–2[d]		2000.4–2005.7	480	103	22%
2–4[d]		2000.4–2005.7	502	62	12%
4–6[d]		2000.4–2005.7	508	57	11%
6–8[d]		2000.4–2005.7	515	74	14%
		Southern Hemispheric Surface Sites			
SMO	14S, 171W	2000.2–2005.2	498 (4)	−40 (8)	8%
CGO	40S, 145W	2000.1–2005.2	484 (2)	−40 (1)	8%
SPO[e]	90S, 102E	2000.4–2005.1	486 (2)	−38 (6)	8%
		Aggregated Means for 2000.2–2005.2			
NH surface			476 (4)	78 (6)	16%
SH surface			491 (2)	−34 (7)	7%
Global surface			484 (2)	50 (4)	10%

[a] Aircraft results are from flights above eight sites in the continental United States situated between 40–48°N and 89–104.3°W as described in the experimental section. Units for COS mixing ratios are pmol mol^{-1}, or ppt by mole; n.a. indicates data not available. ALT: Alert, Canada; BRW: Barrow, United States; SUM: Summit, Greenland; MHD: Mace Head, Ireland; LEF: Wisconsin, United States; HFM: Harvard Forest, United States; NWR: Niwot Ridge, United States; THD: Trinidad Head, United States; MLO: Mauna Loa, United States; KUM: Cape Kumukahi, United States; SMO: American Samoa; CGO: Cape Grim, Australia; SPO: South Pole; NH: Northern Hemisphere; and SH: Southern Hemisphere.

[b] One standard deviation of the available annual means or five annual cycles (≤5, depending upon site).

[c] Not a full year of data.

[d] Data from these sites are not included in the calculation of hemispheric means.

[e] Data covers only 4 years at this site, because no results were obtained in mid-2001.

apparent in samples collected from aircraft above the continental United States: from January to April of 2005, COS mixing ratios at the lowest altitudes (<2 km asl) were typically within 10 ppt of those measured at higher altitudes (2–4 km, 4–6 km, and 6–8 km) (Figure 6a).

[18] In late spring as the NH growing season begins, however, large gradients develop across the NH in which reduced COS mixing ratios are first observed at continental sites and later appear at arctic sites and in the free troposphere. These surface gradients can approach 140 ppt (30%) and persist through the summer and much of the fall season (Figures 5 and 7). The earliest and largest springtime declines in COS mixing ratios are observed in the NH at low-altitude, continental sites (LEF and HFM). The onset of this seasonal decline at LEF and HFM (in May) roughly coincides with a gradient developing for COS between the boundary layer and free troposphere over the continental United States, with reduced mixing ratios observed in the continental boundary layer (<2 km asl) (Figure 6).

[19] The phase of the observed seasonality in the NH is much different than is observed in the SH (Figure 4). Mixing ratios at NH sites peak during April–June (spring), and minima occur between August–October (late summer to early fall). The unique timing of regular seasonal variations in the different hemispheres becomes particularly apparent by considering hemispheric surface means derived with results

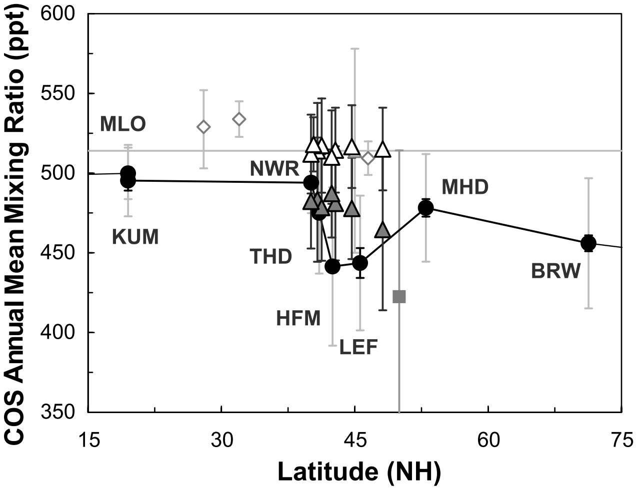

Figure 3. Annual mean mixing ratios for COS from eight aircraft sampling sites over the midcontinental United States (September 2004–August 2005) binned by altitude above sea level and compared to Northern Hemisphere (NH) annual means displayed in Figure 2. Mean mixing ratios at sampling altitudes less than 2 km asl are indicated as solid triangles, and those sampled at between 5 and 8 km asl are indicated as open triangles. Other symbols are as described in Figure 1.

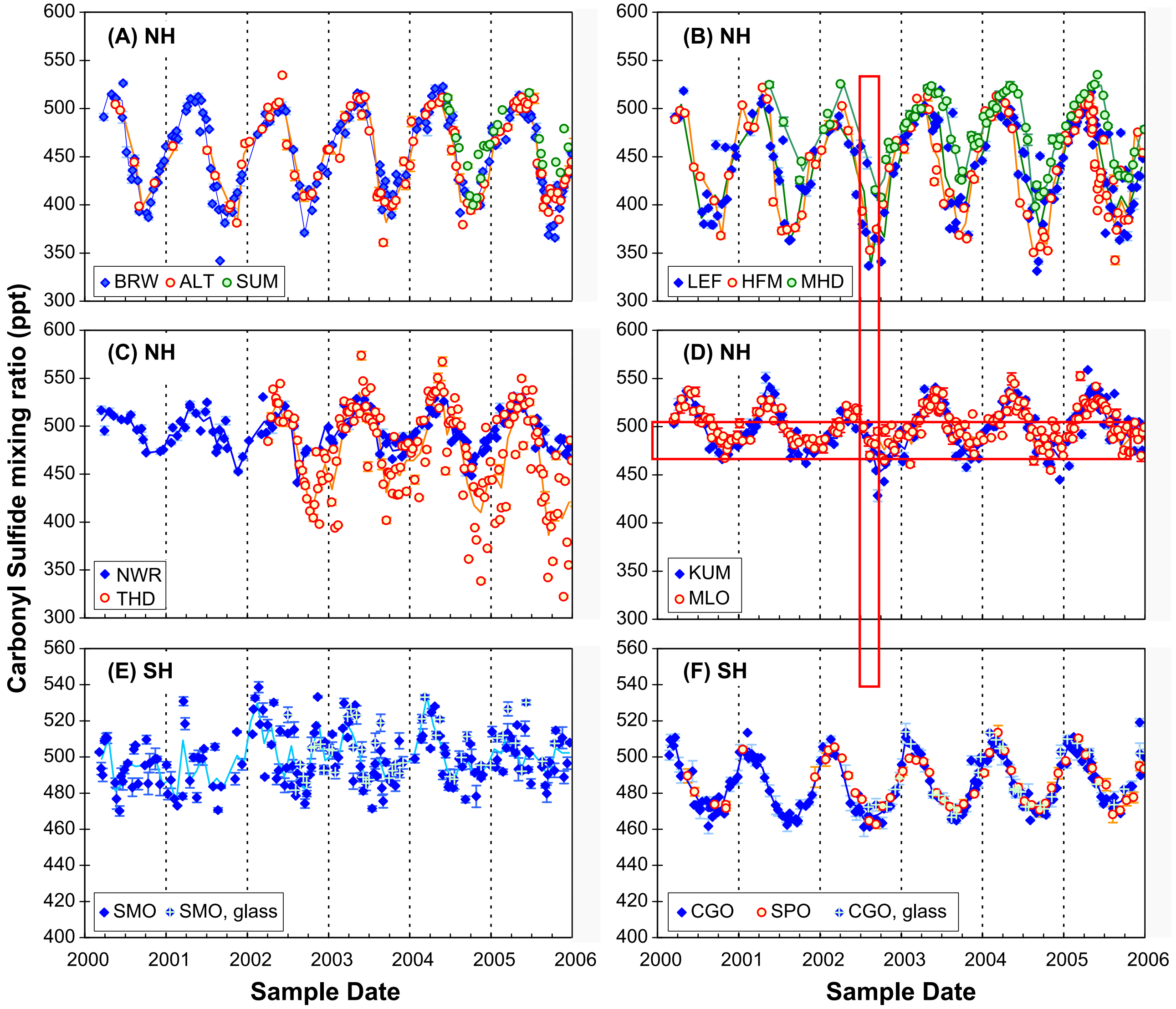

Figure 4. COS mixing ratios measured at ground-based sampling sites throughout the globe. Each point represents a single flask pair mean; error bars are 1 standard deviation of the individual flask results. Monthly means (lines) are estimated from the flask pair means. (a–d) Results from the NH; (e and f) Southern Hemisphere (SH) results (note the vertical scale is expanded in these SH panels).

from individual sites (Figure 8a). Maximum and minimum hemispheric mixing ratios in the NH lag those in the SH by 1 to 2 months only. This implies that different processes dominate the observed seasonality in the two hemispheres; one would expect the variations to be approximately 6 months out of phase if the same process were driving the seasonal changes in both hemispheres (see, for example, CH_3CCl_3 results from *Montzka et al.* [2000]). Seasonal variation in hemispheric transport does not influence this conclusion appreciably given the observed magnitude and phasing of the mixing ratio gradients for COS in the tropics.

[20] The ground-based flask measurements can be aggregated to estimate a lower-atmosphere SH mean mixing ratio for COS of 491 ± 2 ppt, a lower-atmosphere NH mean of 476 ± 4, and a lower-atmosphere global mean mixing ratio of 484 ± 2 ppt (Table 1; uncertainties represent 1 s.d. of five annual means from 2000.2–2005.2). These hemispheric means suggest that the annual mean COS mixing ratio near Earth's surface in the NH was ~3% lower than in the SH during this 5-year period (NH/SH = 0.97 ± 0.01; the uncertainty given here represents 1 s.d. of five annual hemispheric mean ratios). Given that the results suggest the presence of steep gradients of COS across latitudes, longitudes, and altitudes in the NH, the accuracy of hemispheric means and the NH/SH ratio derived from a few measurement sites depends critically on the location of those sites. For example, the annual mean NH/SH ratio at Earth's surface becomes 1.00 if results from LEF and HFM are not included. Furthermore, the aircraft results presented here suggest that an annual mean NH/SH ratio calculated with results from the free troposphere over the continents might be greater than 1.00.

[21] The unique phasing of COS mixing ratio variability in the two hemispheres results in a mixing ratio gradient

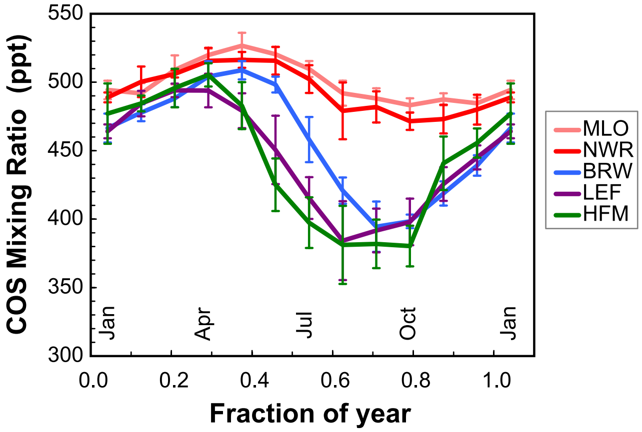

Figure 5. Monthly mean COS mixing ratios from selected NH ground-based sampling stations averaged over the entire measurement period (2000–2005). Uncertainties represent 1 standard deviation of the monthly means measured in the different years.

across the equator that changes sign seasonally. The dependence of this gradient on season may help explain in part the wide range of COS mixing ratio gradients observed between the hemispheres in past reports [*Notholt et al.*, 2006]. The NH/SH ratio calculated from the NOAA surface data varies from 0.91 ± 0.01 to 1.04 ± 0.02 across a year (Figure 8b; the uncertainty given here represents 1 s.d. of results from five annual periods). Given that spatial gradients in the NH are large, the magnitude of seasonal changes in the NH to SH ratio also depends upon which sites are included in the calculation. The pattern of seasonality in this ratio, however, is more robust; COS mixing ratios are generally higher in the SH from August–March, and they are higher in the NH from April–June (Figure 8b).

3.3. Long-Term Trends in Global Surface Means of Carbonyl Sulfide

[22] Previous reports have indicated a slow decline in COS mixing ratios in both the NH and SH since the 1980s [*Rinsland et al.*, 2002; *Mahieu et al.*, 2003; *Montzka et al.*, 2004]. No consistent trend is discernable for COS mixing ratios during 2000.2–2005.2 at any individual ground-based site; the full range for 12-month running means over this period was 1.6% for the SH, and 2.9% for the NH.

4. Discussion

4.1. Annual Mean Mixing Ratios

[23] Regular and periodic sampling of air at multiple surface sites across the globe and from aircraft over the continental United States has revealed a nonuniform distribution and repeatable seasonal changes in atmospheric mixing ratios of COS. These results allow the influence of sources and sinks on atmospheric COS to be assessed on broad scales, especially when the results are considered on an annual mean basis. In both hemispheres the highest surface means are observed toward the equator (Figure 2). This pattern suggests stronger sources or weaker sinks in equatorial latitudes of both the Northern and Southern hemispheres when compared to higher latitudes, perhaps as a result of biomass burning [*Notholt et al.*, 2003] or enhanced photochemical oxidation of reduced sulfur gases (CS_2 and $(CH_3)_2S$) (Table 2). The substantial hemispheric asymmetry observed for COS at the surface at higher latitudes implies the presence of a substantial sink for COS in the NH. The particularly low mixing ratios observed at low-altitude, continental surface sites and within the

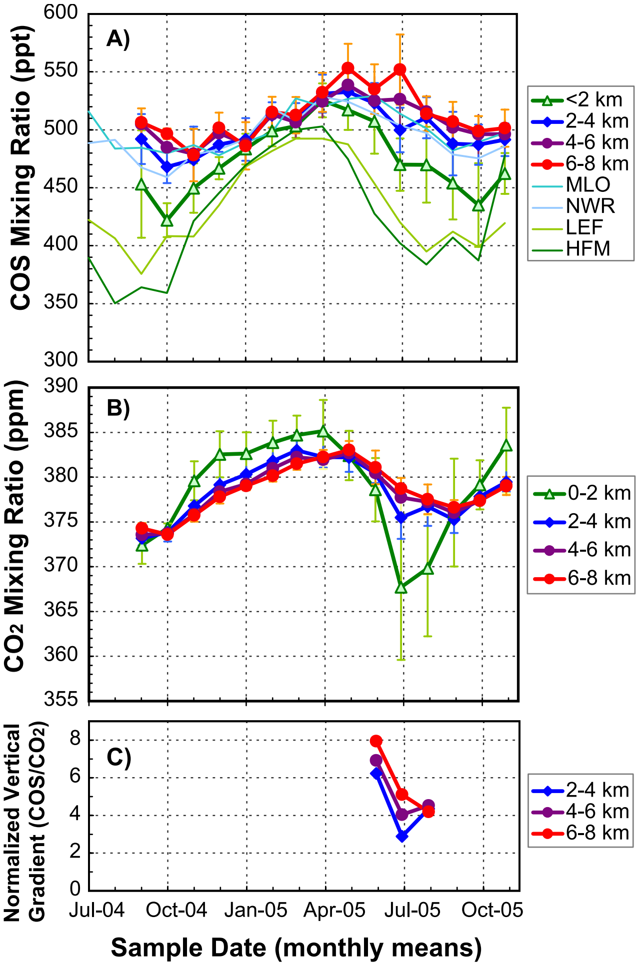

Figure 6. (a) A comparison between COS mixing ratios measured at surface sites (thin lines) to those measured from aircraft (symbols connected with thick lines) over the continental United States as a function of sampling date. Available aircraft results from all eight continental sampling stations were binned by month and altitude (see legend); the error bars shown represent ±1 standard deviation of the mean mixing ratio for each altitude bin. The median number of aircraft samples at each bin for each month was typically 23–29. (b) Results for CO_2 from the same aircraft samples considered in Figure 6a. (c) The ratio of the normalized vertical COS gradient to the normalized CO_2 gradient determined from aircraft data appearing in Figures 6a and 6b for months when boundary layer mixing ratios of CO_2 are depleted compared to the free troposphere (as, for example, $[(X_{COS,\,6-8\,km} - X_{COS,\,<2\,km}) / (X_{CO2,\,6-8\,km} - X_{CO2,\,<2\,km})] \times (X_{CO2,\,6-8\,km}/X_{COS,\,6-8\,km})$). The different colors indicate the enhancements observed for COS and CO_2 within different altitude bins relative to samples collected below 2 km asl.

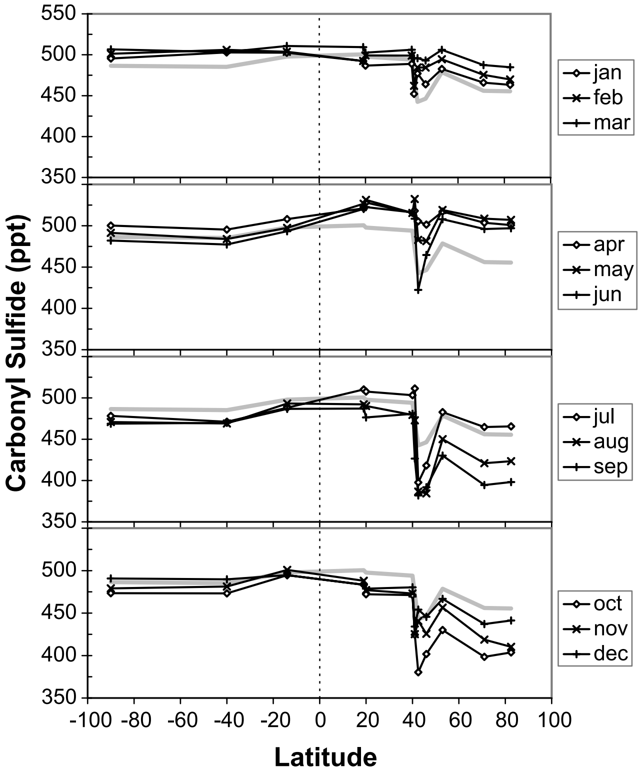

Figure 7. The mean latitudinal distribution of COS ambient air mixing ratios as a function of month throughout the available measurement period. This represents the years 2000.2–2005.2 for all sites except THD (data available only since early 2002) and MHD (data available only since early 2003). The annual mean at each site is also shown for reference (gray line).

continental boundary layer from aircraft imply that this sink arises from uptake by terrestrial ecosystems.

[24] When considered alone or with annual means published previously, the observations suggest the presence of strong spatial gradients in annual mean COS mixing ratios at sites in the NH but only weak spatial gradients in the remote SH (Figure 2) [*Milhalopoulos et al.*, 1991; *Bandy et al.*, 1992; *Mahieu et al.*, 2003; *Griffith et al.*, 1998; *Xu*, 2000; *Sturges et al.*, 2001; *Rinsland et al.*, 2002; *Schneider*, 2002]. The aircraft data reveal substantial vertical gradients in annual mean mixing ratios of COS in the lower 8 km of the troposphere above the central North American continent (Figure 3). These results suggest that the large gradients observed in the NH between annual means measured at continental surface sites such as NWR and LEF (or HFM) may stem in large part from differences in sampling elevation and the substantial mixing ratio gradients observed for COS between the planetary boundary layer and the free troposphere. The high-altitude site NWR (3.5 km asl) is above the continental boundary layer most of the time, and COS mixing ratios at this site are elevated when compared to results from samples regularly collected within the forested, continental boundary layer (LEF at 0.87 km asl and HFM at 0.34 km asl).

[25] The results obtained from flasks collected by aircraft in the free troposphere are consistent with free tropospheric means observed at a similar latitude above the Jungfraujoch at 45.6°N for the period 1997–2001 (mean = 509 ppt, s.d. of five annual means = 5 ppt; *Mahieu et al.* [2003]) (Figure 3). This consistency supports the findings of *Griffith et al.* [1998], who reported that free tropospheric mixing ratios in the NH were 20% higher than observed in the SH. The cause for elevated mixing ratios in the NH free troposphere has not been explicitly identified, though oxidation of enhanced amounts of reduced sulfur gases may contribute. *Notholt et al.* [2003] recently noted enhanced mixing ratios of COS in the tropical upper troposphere that they attributed to the influence of biomass

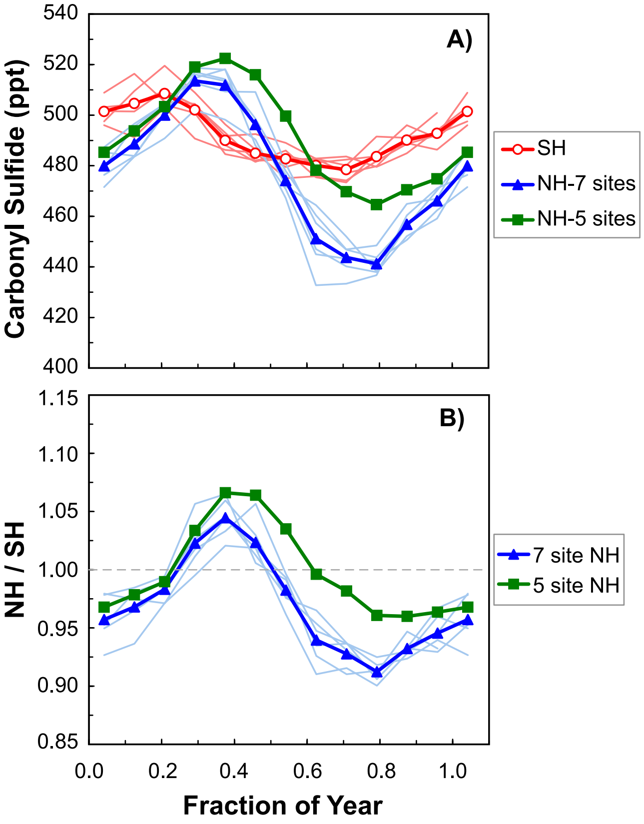

Figure 8. (a) Hemispheric mean mixing ratios derived from seven NH sites (blue triangles), a subset of these NH sites (five sites, green squares), and three SH sites (red circles) as a function of season. Results from individual years are displayed as the lighter colored lines, and the mean from all years are shown as the darker lines with symbols. Only the mean result is shown for the five NH site means for clarity. Hemispheric means were derived as described in the experimental section; the two additional sites included in the seven site NH means were the continental sites Wisconsin, United States (LEF) and Harvard Forest, United States (HFM). (b) The ratio of hemispheric means displayed in Figure 8a as a function of season. Results for individual years (light blue lines) and the means from all years (dark blue line with triangles) are calculated with the seven-site NH means. The mean ratios for all years calculated from five NH sites (LEF and HFM not included) is also displayed (green line with squares).

Table 2. Net Sources and Sinks of Carbonyl Sulfide and Implied Atmospheric Lifetime[a]

	Low	High
Net Sources		
Oceanic, COS	−110	190
Oxidation of Oceanic CS_2 and DMS	149	330
Anthropogenic, as COS	32	96
Oxidation of anthropogenic CS_2	58	170
Biomass burning[b]	68	144
Other (wetland, soils...)	13	119
Net Sinks		
Vegetation[c]	730	1500
Soils	74	180
OH oxidation	82	110
COS photolysis (stratosphere)	11	21
O atom oxidation	5	16
Totals and Lifetime Estimate		
Total of sources	210	1049
Total of sinks	902	1827
Implied lifetime (years)	3	1.5

[a] Adapted from *Kettle et al.* [2002a] but with adjustments to biomass burning and vegetative fluxes as described in the text. The global lifetime estimate is calculated from the stated total sinks and a mean global mixing ratio of 480 ppt (8.5 × 10^{10} moles of COS in the atmosphere). Units for sources and sinks of carbonyl sulfide are 10^9 g S.

[b] Low end of stated range is consistent with estimates from *Chin and Davis* [1993], *Nguyen et al.* [1995], and global fire emissions of CO [*Duncan et al.*, 2003] combined with additional CO combustion sources [*Andreae and Merlet*, 2001] and the molar COS/CO emission ratio of *Nguyen et al.* [1995]. The high end is from *Andreae and Merlet* [2001]. A mean of these four estimates gives an annual global flux of 89 Gg S yr^{-1}.

[c] Corresponds to 3 and 6 times net primary productivity × (X_{COS}/X_{CO2}) as estim [illegible] see also con [illegible]

table has sandoval-soto low and high (not kettle) as 730-1500

burning, though it is not known if this source is biased into one hemisphere over the other.

[26] In the SH, annual means at all three sampled sites are within 14 ppt (3%), and the annual means observed at these sites are quite similar to those published previously from samples collected at the surface or from firn air [*Milhalopoulos et al.*, 1991; *Sturges et al.*, 2001], and from within the free troposphere [*Griffith et al.*, 1998].

4.2. Seasonality Observed for Atmospheric Carbonyl Sulfide

[27] Our ground-based data suggest that COS undergoes a substantial, coherent seasonal variation in both the Northern and Southern hemispheres, but with a phase in these hemispheres that is very different.

4.2.1. Seasonality Observed for COS in the Southern Hemisphere

[28] The consistency observed for mixing ratios and seasonality at CGO and SPO, which are situated in very different local environments, suggests that COS mixing ratios vary coherently throughout the mid-to-high-latitude Southern Hemisphere. This conclusion is supported by free tropospheric means measured above Wollongong, Australia (34.4°S) during 1996–1997, which showed a similar annual mean and a similarly phased seasonality [*Griffith et al.*, 1998] (Figure 3).

[29] The dominant flux of COS and the flux undergoing the largest seasonal variation in the SH is related to oceanic processes (Figure 9a) [*Kettle et al.*, 2002a]. Other SH fluxes are believed to be smaller and more constant over a year. Enhanced oceanic emissions of COS and other gases (CS_2 and $(CH_3)_2S$) that rapidly photooxidize to produce COS are expected during summer because COS and CS_2 are photochemically produced in the aqueous phase from dissolved organic matter [*Kettle et al.*, 2002a; *Weiss et al.*, 1995; *Ulshöfer et al.*, 1995]. For CS_2 this aqueous source, and ultimately the production of COS, is thought to be enhanced in the tropics. Direct emission of COS from the ocean, however, is estimated to be more important at higher

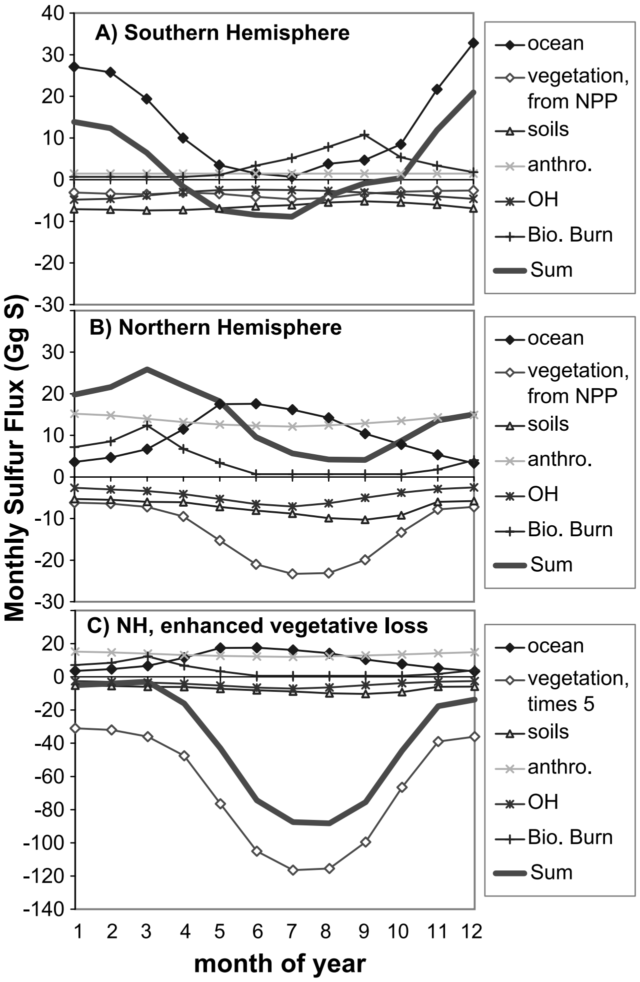

Figure 9. (a and b) COS fluxes by hemisphere and month (Gg S $month^{-1}$) as estimated by *Kettle et al.* [2002a] but with revisions to fluxes associated with biomass burning. The influence of seasonality in biomass burning has been added here on the basis of a global annual COS flux from burning of 89 Gg S yr^{-1} (see Table 2) and the assumption that the seasonality in COS fluxes is identical to that of CO from fires [*Duncan et al.*, 2003]. (c) Same as Figure 9b, but with fluxes to vegetation derived from net primary productivity (NPP) (as given by *Kettle et al.* [2002a]) multiplied by a factor of 5 (see text) (note scale change compared to Figures 9a and 9b). This factor is within the range suggested by *Sandoval-Soto et al.* [2005], who proposed vegetative losses for COS that are 3 to 6 times greater than derived by *Kettle et al.* [2002a] from scaling NPP by (X_{COS}/X_{CO2}).

latitudes because hydrolysis is reduced in colder waters [*Kjellström*, 1998; *Kettle et al.*, 2002a]. The phase of the atmospheric variations observed in mid-to-high latitudes of the SH (peak in the summer; Figures 4f and 8a) are qualitatively consistent with the analysis of *Kettle et al.* [2002a], which suggests that the oceans dominate the seasonal variability for COS. This consistency suggests that the SH observations provide a clear picture of how the oceans influence atmospheric COS.

[30] Biomass burning is believed to be a smaller source of COS than the oceans in the SH, though large uncertainties in the magnitude and interannual variability of this source remain (Figure 9a and Table 2) [*Chin and Davis*, 1993; *Nguyen et al.*, 1995; *Kettle et al.*, 2002a]. On the basis of the correlation observed between COS and CO emissions from burning, COS emissions from this source are expected to peak in the SH during August–September [*Duncan et al.*, 2003]. COS mixing ratios at CGO and SPO are at a minimum during this time of year, suggesting that biomass burning contributes much less than other fluxes (i.e., the ocean) to the observed COS seasonality at these SH sites (Figure 4f).

[31] The influence of biomass burning may explain a portion of the irregular seasonality observed at SMO, specifically the elevated mixing ratios sometimes observed at this site during the high-burning months of August and September (Figure 4e). The high sample-to-sample variability, however, suggests that local sources or sinks may be influencing results from SMO more than at other sites. Results from Amsterdam Island (37°S) during the late 1980s exhibited even higher sample-to-sample variability (on the order of ±15%) than observed at SMO, but no clear seasonality was apparent [*Milhalopoulos et al.*, 1991].

[32] Seasonal movements in tropical convergence zones near SMO can result in air that has a strong NH character reaching SMO. Results for longer-lived trace gases that we measure concurrently with COS from these same flasks and that have large, persistent, interhemispheric differences (HCFCs, HFCs, etc., data not shown) suggest that this influence peaks during January–April. Although the COS mixing ratios at SMO are typically enhanced then, mixing ratios at MLO and KUM are generally similar or lower than those measured at SMO during these months. This suggests that seasonal variation in transport across the equator is not the primary cause of elevated mixing ratios at SMO during January–April.

4.2.2. Seasonality Observed for COS in the Northern Hemisphere

[33] The NOAA observations suggest that an entirely different process dominates the seasonal changes observed for atmospheric COS throughout the Northern Hemisphere. Variations in the amplitude and timing of the seasonality at NH sites drive the strong, annual mean mixing ratio gradients observed there. Sites at which lower annual means are measured exhibit the largest seasonal variation amplitudes (Figure 5). The largest amplitude variations are observed at low-altitude, forested continental sites. It appears that differences in COS seasonal variation amplitudes and phasing at these NH sites are determined by the degree to which air sampled at these sites is influenced by the continental boundary layer at midlatitudes. These results imply that a substantial, seasonally varying, continental-based surface sink drives the seasonal variations observed for atmospheric COS throughout much of the NH. Low-altitude sites removed from this influence show somewhat smaller seasonal changes (BRW and ALT). Furthermore, mixing ratios at sites not situated within the continental boundary layer (NWR, MLO, KUM, THD, MHD, and aircraft results from above 2 km asl) exhibit even smaller monthly mean, seasonal variation amplitudes that are lagged even further behind those observed at LEF and HFM.

[34] Despite these differences, similar COS mixing ratios and seasonal variations are observed throughout the year in the NH free troposphere (consider data from NWR, MLO, and aircraft above 2 km asl in Figure 6a). The data suggest that free-tropospheric mixing ratios in the NH vary in a coherent and consistent manner throughout much of the NH, and that free tropospheric air above the continent is largely decoupled from the continental boundary layer during the growing season. The results also demonstrate that the timing of seasonal changes in the NH is substantially different than observed in the SH, even at locations far removed from continental boundary-layer influences.

[35] In a study of seasonal variations in COS fluxes, *Kettle et al.* [2002a] determined that multiple processes are expected to influence the seasonal variations of carbonyl sulfide in the NH atmosphere (Figure 9b). They noted that the largest single NH flux, and the one undergoing the largest variation seasonally, is uptake by vegetation. Vegetative uptake of COS peaks during the NH growing season, precisely when substantially reduced mixing ratios are observed over the continental United States (Figures 4–7). The NH flux undergoing the second largest variation seasonally was estimated to be production from the ocean, though the phase of this flux is opposite to that needed to explain the observed atmospheric seasonality. Given the differences in open ocean area, coastal ocean area, and ocean productivity between the NH and SH, and an understanding of how COS fluxes vary across these regimes, *Kettle et al.* [2002a] estimated that seasonal changes in ocean flux from the NH might be only half as large as those in the SH (a range of $\sim$15 Gg S yr^{-1} compared to $\sim$30 Gg S yr^{-1}) (see Figures 9a and 9b). As a result, one would expect the influence of the NH oceans on COS seasonality to be about half as large as it is in the SH. Other fluxes vary seasonally by lesser amounts, such as production from biomass burning, the direct and indirect (via atmospheric oxidation of CS_2, primarily) emission of COS by anthropogenic activities, loss to soils, and oxidation by the atmospheric hydroxyl radical.

[36] Carbonyl sulfide is taken up by vegetation because it undergoes rapid hydrolysis by enzymes present in leaf water that are involved in the initial stages of photosynthesis [*Protoschill-Krebs and Kesselmeier*, 1992; *Protoschill-Krebs et al.*, 1996]. Furthermore, the affinity for carbonic anhydrase to catalyze the hydrolysis of COS is substantially greater than for the hydration of CO_2 [*Protoschill-Krebs et al.*, 1996]. Many past estimates of the magnitude of COS uptake by vegetation [*Goldan et al.*, 1988; *Kjellström*, 1998; *Kettle et al.*, 2002a] are based upon scaling NPP by the atmospheric mean mixing ratio of COS (X_{COS}) relative to CO_2 (i.e., NPP × (X_{COS}/X_{CO2})). When estimated in this way, the uptake flux of COS to vegetation in the NH is calculated

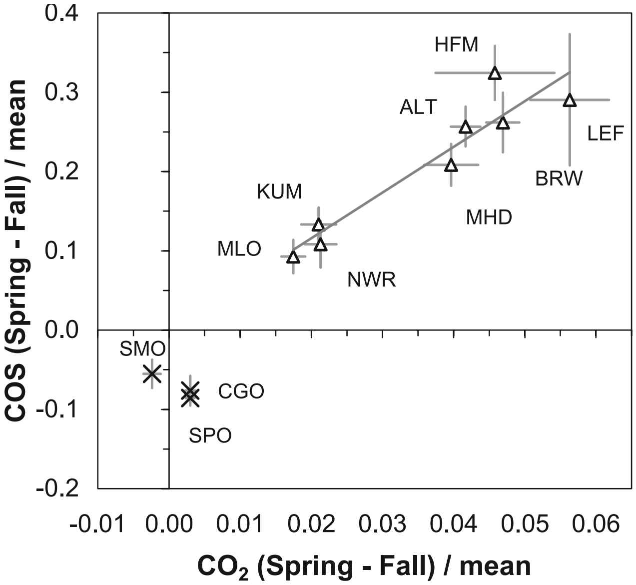

Figure 10. The relationship between relative seasonal amplitudes observed for COS and CO_2 ambient air mixing ratios at Northern Hemispheric sites (triangles) and Southern Hemispheric sites (crosses). Peak-to-peak seasonal variations (winter and spring minus summer and fall) were estimated from 5 years of data and normalized to annual means measured at each individual site. Orthogonal regression of the Northern Hemispheric results alone yielded a slope of 6 ± 1 and a regression r^2 of 0.9. A similarly high regression correlation coefficient is obtained if the regression is performed on absolute seasonal variation amplitudes.

to be only slightly larger (30%) than oceanic emissions [*Kettle et al.*, 2002a] (Figure 9b). Furthermore, because the oceanic source and vegetative sink have similar magnitudes in the NH but amplitudes of nearly opposite phase in this calculation, a larger seasonal variation in total COS fluxes and atmospheric mixing ratios would be expected in the SH (Figures 9a and 9b) [*Kettle et al.*, 2002a, 2002b].

[37] By contrast, our observational data for COS reveal substantially larger seasonal variations in the NH than in the SH, and a fairly coherent phase throughout the NH that is consistent with uptake by vegetation dominating other fluxes. If other fluxes of COS are indeed small and relatively invariant, the results suggest that in the NH the seasonality of vegetative uptake is substantially larger than seasonal variations in oceanic fluxes. Furthermore, the observations imply that the absolute magnitude of the vegetative sink is substantially larger than estimated from NPP × (X_{COS}/X_{CO2}).

4.2.3. Comparisons Between Atmospheric Observations of COS and CO_2

[38] The role of vegetative uptake on influencing the seasonality of COS can be further explored by examining the seasonality of atmospheric CO_2. The amplitudes of seasonal CO_2 mixing ratio variations at sites throughout the NH are determined largely by seasonal changes in terrestrial Net Ecosystem Production (or NEP, where NEP = NPP − (Heterotrophic Respiration)) [*Erickson et al.*, 1996; *Randerson et al.*, 1997]. The largest seasonal changes are observed for CO_2 at sites influenced most strongly by terrestrial vegetation where photosynthesis varies substantially across the seasons. This same pattern is observed for COS; the seasonal amplitudes observed for COS mixing ratios at different sites are strongly correlated (r^2 = 0.9) to those observed for CO_2 (Figure 10). This correlation is not observed for most other gases, though a weak correlation is observed between CO_2 and gases with known surface sinks such as H_2 (r^2 = 0.75, n = 7 sites) and CH_3Cl (r^2 = 0.5, n = 9 sites) (data not shown). The strong correlation observed between COS and CO_2 suggests that a similar process dominates the seasonal variations observed for these gases. Our understanding of sources and sinks of both COS and CO_2 suggests that this process is most likely uptake by terrestrial vegetation during photosynthesis.

[39] The comparison between seasonal amplitudes of COS and CO_2 mixing ratios at surface sites also suggests that the net uptake of COS during the growing season is many times larger than net uptake of CO_2 when considered on a relative basis. The orthogonal regression slope of the seasonal amplitude relationship between COS and CO_2 is 6 ± 1 (Figure 10). While seasonal changes in NEP lead to seasonal variations in CO_2 mixing ratios of up to 5.5% (peak-to-peak), the relative seasonal changes observed throughout the NH for COS are 6 times larger.

[40] The measurements of COS and CO_2 from aircraft samples suggest that the variations observed for COS throughout the NH are driven by continental processes. Profiles for these gases show a similar pattern of reduced mixing ratios in the continental boundary layer during the NH growing season (Figure 6). However, while reduced mixing ratios of CO_2 during the NH growing season represent a balance between vegetative uptake and total respiration (i.e., NEP), the percentage reduction in COS mixing ratio is 4–6 times (5.5 ± 1.6) larger during June–August (calculated relative to mixing ratios measured at 4–8 km asl) (Figure 6c). The enhanced surface uptake implied for COS relative to CO_2 from the aircraft profiles is similar to the magnitude of enhanced seasonality observed for COS relative to CO_2 on a hemispheric scale. This similarity suggests that continental uptake by vegetation could be largely responsible for the hemispheric-wide seasonality observed for COS in the NOAA data presented here.

[41] The relationship between COS and CO_2 fluxes on smaller scales has been studied during multiple seasons above a temperate zone spruce forest in Germany [*Xu et al.*, 2002]. In this work, COS uptake was also enhanced relative to CO_2, by a factor of 10 ± 1.7 ppt COS/ppm CO_2. This corresponds to a relative uptake of COS that is 7–8 times larger than CO_2 (assuming ambient mixing ratios of 480 for COS and 370 for CO_2), which is similar to the enhancements observed in COS seasonality and vertical gradients on broader scales in the NOAA data presented here. Ancillary measurements of photosynthetically active radiation and H_2O suggested that the observed COS uptake was primarily from vegetation undergoing photosynthesis [*Xu et al.*, 2002].

[42] An understanding of why the relative uptake rate of COS by vegetation might be enhanced compared to CO_2 by factors of 5 to 8 is possible from a consideration of laboratory studies of deposition velocities (the net flux normalized to ambient concentrations) of COS relative to

CO_2 and the large influence respiration has on the net flux of CO_2 to vegetation. Leaf- and branch-scale experiments of crops and trees undergoing active photosynthesis show an enhanced deposition velocity for COS relative to CO_2. Though a range of deposition velocities has been measured to crops and trees by different investigators, the mean deposition velocity ratio ($V_{d,\ (COS/CO2)}$) in plants studied to date is between 2 and 3 [*Sandoval-Soto et al.*, 2005]. When $V_{d,\ (COS/CO2)}$ is weighted by NPP and aerial extent appropriate for plant types found in different ecosystems, a mean V_d ratio of 2.1–2.4 can be estimated for the globe or for extratropical, NH biomes (calculated from data given by *Sandoval-Soto et al.* [2005]).

[43] One might expect COS uptake to be enhanced over CO_2 because the affinity for carbonic anhydrase to catalyze the hydrolysis of COS is substantially greater than for CO_2 [*Protoschill-Krebs et al.*, 1996]. This reaction, however, is not the rate limiting step in carbon assimilation by vegetation. The carbonic anhydrase-catalyzed hydration of CO_2 is fast enough so that most CO_2 entering leaf stomata will undergo hydration, especially in high latitudes of the NH [*Gillon and Yakir*, 2001]. Given that COS and CO_2 have similar free-air diffusivities and aqueous solubilities, it is likely that a similar fraction of COS molecules entering leaf stomata will undergo rapid hydrolysis and that the gross, enzyme-catalyzed hydrolysis rate of COS and CO_2 by vegetation are similar when considered on a relative basis (normalized to their respective mean atmospheric mixing ratios).

[44] The enhanced relative net uptake of COS compared to CO_2 in leaf- and branch-scale experiments likely arises because the net uptake of CO_2 results from the activity of the slower enzyme rubisco (in C_3 plants) instead of the rapid and irreversible hydrolysis of COS that is catalyzed by carbonic anhydrase. Although CO_2 becomes rapidly hydrated by carbonic anhydrase upon entering a leaf stomate, this reaction is readily reversible and only facilitates the transport of CO_2 to the enzymes responsible for carbon uptake and assimilation. As a result, the net uptake of COS and CO_2 on the leaf scale are determined by the resistances associated with transporting these gases to the different enzymes (to the leaf, into the stomate, and into the mesophyllic region of the leaf) plus the activity of these different enzymes. Because the activity of carbonic anhydrase is much faster than rubisco, and the rates of transport for both gases are likely comparable or slower than this enzyme activity, the relative uptake of CO_2 and COS can vary with stomatal conductance, availability of enzymes for reaction, and other variables. In C_4 plants, for example, a faster enzyme is associated with carbon assimilation (PEP-CO), so one might expect a smaller relative enhancement of COS uptake compared to CO_2.

[45] A factor of three enhancement in relative uptake of COS over CO_2 in leaf- and branch-scale studies would be roughly consistent with irreversible hydrolysis of COS and the paradigm for CO_2 interactions with C_3 vegetation: whereas most of the CO_2 entering a leaf undergoes hydration catalyzed by carbonic anhydrase, the plant assimilates or takes up only about one-third of this CO_2. The remaining two-thirds of the CO_2 ultimately diffuses back to the atmosphere with its oxygen isotopes reset by the leaf water [*Francey and Tans*, 1987; *Farquhar et al.*, 1993].

[46] The uptake of COS by vegetation on the landscape scale is likely enhanced additionally relative to CO_2 because respiration reduces net fluxes of CO_2 substantially; COS emissions from vegetation, however, are small [*Kettle et al.*, 2002a; *Sandoval-Soto et al.*, 2005]. The relative magnitudes of respiration and gross carbon uptake, and their seasonal variability has been derived from field measurements in many biomes across the NH [*Falge et al.*, 2002]. These flux studies suggest that the gross uptake of CO_2 by terrestrial vegetation, or Gross Primary Production (GPP), is about 3 times larger than net CO_2 uptake (NEP) during the growing season (June–September). Hence we expect that the relative uptake of COS is as much as 3 times larger than CO_2 owing to this influence alone. That COS is responding to influences other than NEP is also implied by the timing of the seasonality; the later minimum observed for COS indicates that the draw down is not proportional to net ecosystem uptake, which has an earlier phasing (Figure 6).

[47] Considering that the net uptake of COS on leaf and branch scales is 2 to 3 times faster than CO_2 and that respiration diminishes net CO_2 uptake by vegetation by an additional factor of about 3 during the growing season, an annual vegetative uptake flux for COS that is 6 to 9 times larger than expected for CO_2 can be estimated on the basis of small-scale laboratory and field flux studies [$(2\text{ to }3) \times 3 = 6\text{ to }9$]. This enhancement is similar to that implied from the relationship observed between COS and CO_2 seasonal amplitudes throughout the NH (Figure 10), and suggests that the enhanced seasonality and vertical gradients observed for COS in the NH may be reasonably explained by terrestrial vegetative uptake.

[48] On an annual basis, gross uptake of carbon by terrestrial vegetation (as GPP) is thought to be about 2 times larger than NPP [*Prentice et al.*, 2001]. Accordingly, an estimate of COS annual loss to vegetation that is derived by NPP × (X_{COS}/X_{CO2}) may be small by a factor of 4 to 6 [$(2\text{ to }3) \times 2$].

[49] An enhanced uptake of COS by vegetation has important implications relevant to the interpretation of the current atmospheric measurements and for providing insight into important biogeochemical processes. First, it suggests that uptake by vegetation is by far the dominant flux controlling the seasonal variations of COS throughout much of the Northern Hemisphere (Figure 9c). Such a large loss to vegetation would explain why the influence of the oceans on the seasonality in atmospheric COS mixing ratios is not readily apparent in the NH. It also suggests that the COS flux to vegetation is substantially larger than other fluxes, such as uptake by soils. Though *Watts* [2000] suggested that soils could be a more important sink for COS than uptake by vegetation, this estimate was based upon vegetative uptake being scaled by NPP. If such a scaling underestimates actual vegetative losses by a factor of 4–6, an updated consideration of soil losses [*Kesselmeier et al.*, 1999; *Kettle et al.*, 2002a] suggests that uptake by soils may be <10% of vegetative losses. This conclusion supports the observations of *Xu et al.* [2002] and *Steinbacher et al.* [2004] who found, in a study covering multiple seasons, that only 1% of the total uptake flux of COS at a particular temperate zone spruce forest was accounted for by soil losses.

[50] Second, a large sink of COS suggests that its lifetime is substantially shorter than the 6 years suggested by scaling vegetative losses by NPP × (X_{COS}/X_{CO2}) [e.g., *Kettle et al.*,

2002a]. A shorter lifetime is implied by the substantial gradients observed above the continent between the boundary layer and the free troposphere, and by previous work suggesting much larger vegetative losses of COS [*Xu et al.*, 2002; *Sandoval-Soto et al.*, 2005]. A rough estimate of the COS lifetime can be calculated on the basis of our understanding of the gross flux of CO_2 to vegetation, as estimated by an analysis of ^{18}OCO [*Francey and Tans*, 1987]. Such considerations suggest that roughly one-third of all atmospheric CO_2 becomes hydrated by carbonic anhydrase each year. Given that the diffusivity of COS is similar to CO_2 and that COS becomes hydrolyzed rapidly by carbonic anhydrase, an upper limit to the partial lifetime of COS owing to vegetative uptake of about 3 years is implied. When combined with losses to soils and the stratosphere, a lifetime for COS on the order of 2.5 years can be calculated (Table 2).

[51] Third, the much shorter lifetime implied for COS from the observations and considerations discussed above indicates that sources of COS throughout the globe are substantially underestimated. Global COS emission magnitudes in recent reports range from between 150 and 970 Gg S yr^{-1} [*Watts*, 2000; *Kettle et al.*, 2002a]; an enhanced biomass burning source suggested here increases that range to 210–1049 Gg S yr^{-1} (Table 2). Given that the atmospheric burden of COS has not changed substantially over the past 5 years, a factor of 4–6 increase in uptake by vegetation suggests a shortfall in COS sources of up to 800 Gg S yr^{-1}. Such a discrepancy is quite large, considering the extensive studies attempting to constrain COS fluxes from the ocean, land, vegetation, human activity and biomass burning. Despite this effort, however, large uncertainties on source magnitudes of COS remain. The main source of COS is currently believed to be the oxidation of dimethyl sulfide (DMS), a gas emitted predominantly from natural ecosystems and for which global emission magnitudes are poorly constrained. Furthermore, the yield of COS in this reaction (0.7 ± 0.2%) perhaps has a substantial uncertainty as it has not been measured under ambient conditions and was found to be dependent upon NO_x levels [*Barnes et al.*, 1994].

[52] The flux of COS from biomass burning also has large uncertainties. Mean emission magnitudes between 66 and 144 Gg S yr^{-1} have been suggested elsewhere, and the uncertainty quoted on these fluxes can be greater than a factor of 2 [*Chin and Davis*, 1993; *Nguyen et al.*, 1995; *Andreae and Merlet*, 2001]. Some of this uncertainty relates to uncertainty in annual CO emissions from burning; additional uncertainty arises because the emission ratio of COS to CO or CO_2 has not been thoroughly studied. The data presented here may provide some constraints on the magnitude of the biomass-burning source of COS relative to other sources. The lack of any visible enhancement in SH mixing ratios during the dominant biomass burning season (August–October) argues for a biomass-burning source in the SH that is small compared to oceanic fluxes. Furthermore, large interannual variations in Boreal fires have been noted during August of 2002 and May of 2003, and their influence on mixing ratios of CO in the high Northern Hemisphere has been detected [*Kasischke et al.*, 2005]. These were substantial perturbations to the CO budget: CO emissions in August of 2002 were 80 Gg, or 2 to 3 times larger than in other months of 2002. Mean NH CO emissions from burning during August are typically <10 Gg [*Duncan et al.*, 2003]. Despite this substantial perturbation in burning rates during this time, the anomalies in COS are <3%, or small compared to the observed seasonal variations, and therefore to the flux of COS to vegetation.

[53] Finally, the suggestion that the loss of COS from the atmosphere is dominated by uptake to vegetation in a manner similar to CO_2 during photosynthesis implies that studies of COS may provide unique insights into carbon uptake by photosynthesis. This is especially true because emissive fluxes of COS from vegetation are much smaller on a relative basis than those of CO_2 from respiration. The results imply that regional and broad-scale variations in Northern Hemispheric COS may be responding primarily to changes in Gross Primary Productivity. Accordingly, studies of COS may be able to provide unique insight into rates of GPP as has been envisioned through the study of ^{18}O of CO_2 [*Francey and Tans*, 1987].

5. Conclusions

[54] Results from a multiyear, ground- and aircraft-based air sampling network have provided new insights into the distribution and seasonality of atmospheric COS in the lower atmosphere, constrains on the magnitude and seasonal variation of its predominant fluxes, and the identification of striking similarities among the broad-scale seasonality and gradients observed for atmospheric COS and CO_2:

[55] 1. The highest annual mean mixing ratios of COS are observed at Earth's surface at sites closest to the equator in both hemispheres. Though only slightly reduced annual means are measured at higher latitudes in the SH, substantially reduced annual means are observed at higher NH latitudes. The lowest annual means are observed at forested sites situated within the continental boundary layer. Elevated mixing ratios are also observed in the NH, free troposphere.

[56] 2. Coherent seasonal variations are observed for atmospheric COS in both hemispheres, but the seasonality in the two hemispheres arises from the predominant influence of different processes. This seasonality causes the hemispheric difference, as estimated from the sampled surface sites, to change sign over a year. In the SH, the observations are consistent with this seasonality being driven by variations in oceanic fluxes of COS and its precursors. The seasonality throughout the NH appears to be driven primarily by substantial losses from the midlatitude, continental boundary layer during the growing season, and this signal propagates to the rest of the NH atmosphere (higher and lower latitudes, and to the free troposphere) with some delay. These results are consistent with a strong influence of terrestrial vegetation on the distribution and seasonality of COS in the NH. Biomass burning appears to play a smaller role in influencing seasonal changes in COS compared to SH oceans and NH terrestrial vegetation.

[57] 3. Strong similarities were noted in the timing and amplitude of seasonal variations between COS and CO_2, though the gradients observed for COS between the continental boundary layer and free troposphere above multiple, central North American sites were 4–6 times larger than observed for CO_2, on an averaged, relative basis. The enhanced uptake rates implied for COS over terrestrial ecosystems from these data likely explain the enhanced

atmospheric mixing ratio seasonality observed for COS at all NH sites: the relative seasonal variation amplitudes for COS at NH sites are highly correlated to those observed for CO_2, but are 6 ± 1 times larger on a relative basis. The enhanced uptake of COS over CO_2 is qualitatively explained by our current understanding of the interaction of these trace gases with photosynthetically active vegetation.

[58] 4. The large vegetative sink implied by these results suggests a fairly short atmospheric lifetime for COS of about 2.5 years and a large shortfall in the magnitude of known COS sources.

[59] 5. The results suggest that the distribution and seasonality of COS throughout most of the Northern Hemisphere is driven primarily by vegetative uptake in a mechanism parallel to the uptake of CO_2 during photosynthesis. It follows that studies of COS may provide unique constraints on carbon assimilation by the terrestrial biosphere that are independent of the influence of respiration. Specifically, because COS is not emitted in copious amounts by vegetation, as is CO_2, studies of COS may provide direct insights into gross carbon fluxes to vegetation in a manner similar to that envisioned by studying ^{18}O of CO_2.

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