

Carbonyl sulfide (OCS): Large-scale distributions over North America during INTEX-NA and relationship to CO₂

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Received 12 July 2007; revised 27 November 2007; accepted 18 February 2008; published 9 May 2008.

[1] An extensive set of carbonyl sulfide (OCS) observations were made as part of the NASA Intercontinental Chemical Transport Experiment–North America (INTEX-NA) study, flown from 1 July to 14 August 2004 mostly over the eastern United States and Canada. These data show that summertime OCS mixing ratios at low altitude were dominated by surface drawdown and were highly correlated with CO₂. Although local plumes were observed on some low-altitude flight legs, anthropogenic OCS sources were small compared to this sink. These INTEX-NA observations were in marked contrast to the early springtime 2001 Transport and Chemical Evolution over the Pacific experiment, which sampled Asian outflow dominated by anthropogenic OCS emissions. To test the gridded OCS fluxes used in past models, the INTEX-NA observations were combined with the sulfur transport Eulerian model (STEM) regional atmospheric chemistry model for a top-down assessment of bottom-up OCS surface fluxes for North America. Initial STEM results suggest that the modeled fluxes underestimate the OCS plant sink by more than 200%.

Citation: Blake, N. J., et al. (2008), Carbonyl sulfide (OCS): Large-scale distributions over North America during INTEX-NA and relationship to CO₂, *J. Geophys. Res.*, 113, D09S90, doi:10.1029/2007JD009163.

1. Introduction

[2] Although carbonyl sulfide (OCS) emissions make up only a small fraction of the total sulfur emitted into the atmosphere compared to sulfur dioxide (SO₂), its comparatively low solubility and long atmospheric lifetime with respect to tropospheric chemistry and photolysis means that a significant fraction should reach the stratosphere. Once in the stratosphere, OCS is oxidized into sulfuric acid and condensed to form stratospheric aerosol [Crutzen, 1976], which is highly effective in reflecting incoming solar radiation back to space, thus enhancing the Earth's albedo [Charlson et al., 1990]. Nevertheless, there are still a great many uncertainties regarding the role played by OCS in the stratosphere [e.g., Chin and Davis, 1995], including an isotope study suggesting that the contribution of OCS to the stratospheric aerosol layer may be relatively minor [Leung et al., 2002]. However, a recent assessment of stratospheric aerosol concluded that in volcanically quies-

cent periods, OCS and SO₂ contribute about equally to the stratospheric sulfur budget [SPARC Scientific Steering Group, 2006].

[3] Sources of OCS include both natural and anthropogenic emissions. OCS is directly emitted from oceans, biomass burning, coal combustion, and industrial emissions, as well as being the product of the oxidation of marine and anthropogenic carbon disulfide (CS₂) [Kettle et al., 2002a]. Oxidation of marine dimethyl sulfide (DMS) may also be a significant (about 10%) though uncertain contributor to atmospheric OCS [Barnes et al., 1994; Arsene et al., 2001; Watts, 2000]. Ice core- and firm ice-derived records suggest that human activities account for approximately 25% of modern atmospheric OCS levels [Aydin et al., 2002]. Past and recent fluctuations are closely related to changing global anthropogenic sulfur emissions [Montzka et al., 2004].

[4] OCS is removed by terrestrial vegetation, soils, photolysis, and reactions with OH and O radicals, resulting in a drawdown of OCS concentration in the boundary layer, which is typically correlated with low CO₂ [Khalil and Rasmussen, 1984; Mihalopoulos et al., 1989; Chin and Davis, 1993; Thornton et al., 1996; Andreae and Crutzen, 1997; Watts, 2000]. Recent work by Montzka et al. [2007] demonstrated substantial losses from the midlatitude Northern Hemisphere (NH) continental boundary layer during the growing season, which in turn appears to drive the OCS seasonality throughout the rest of the NH, consistent with a strong terrestrial vegetation sink. Such a sink may limit the atmospheric residence time of OCS to about

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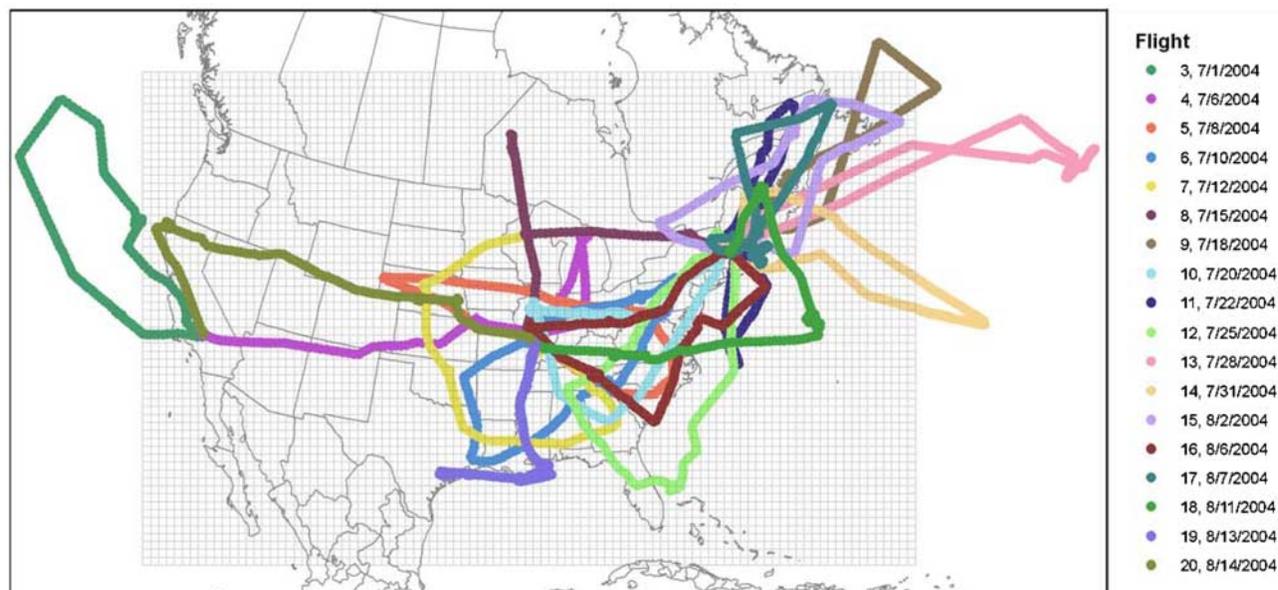


Figure 1. Color-coded map of all DC-8 flight tracks for Intercontinental Chemical Transport Experiment–North America (INTEX-NA) superimposed on the sulfur transport Eulerian model 60 km model domain grid.

2–3 years and also implies a large shortfall in the magnitude of known OCS sources [Xu *et al.*, 2002; Montzka *et al.*, 2007].

[5] The amplitude of the seasonal cycles of OCS and CO₂ are strongly correlated [Montzka *et al.*, 2007], which is consistent with the observation that the uptake of both gases by vegetation follows a common pathway through the stomata [Goldan *et al.*, 1988; Sandoval-Soto *et al.*, 2005]. However, the OCS molecule tends to be irreversibly taken up by photosynthesizing plants, in contrast to CO₂, which is also “exhaled” during respiration [Sandoval-Soto *et al.*, 2005]. Thus further study of atmospheric OCS may provide insight into the mechanisms that control CO₂ sinks, improve the current systematic error in the simulated seasonal flux cycle of the CO₂, and help to better understand the overall carbon cycle [Montzka *et al.*, 2007; Gausepohl *et al.*, 2006].

2. Experiment

[6] During July and August 2004, observations of OCS and other species were made from the NASA DC-8 aircraft during the daytime over North America for the Intercontinental Chemical Transport Experiment–North America (INTEX-NA). A major objective of INTEX-NA was to elucidate the sources, transport, and chemical evolution of air masses on transcontinental/intercontinental scales and their impact on air quality and climate. A particular focus for this study was the quantification and characterization of the inflow and outflow of pollution over North America.

[7] Whole air samples were collected at a frequency of 1 to 5 min and analyzed in the University of California, Irvine (UCI) laboratory utilizing gas chromatography. The sampling, analytical equipment, and procedures were almost identical to those described by Colman *et al.* [2001] and for Transport and Chemical Evolution over the

Pacific (TRACE-P) experiment by Blake *et al.* [2004]. A short description follows.

[8] Air was collected in evacuated 2 L stainless steel canisters aboard the DC-8 and pressurized with a stainless steel (grease-free) bellows pump. Prior to deployment, the canisters were evacuated and subsequently filled with 20 torr (1 torr = 1.332 mbar) of deionized, degassed water to improve the performance of the analytical system and the stability of compounds in the canisters. The canisters were analyzed typically within 1 week of sample collection. Storage tests have shown that OCS is stable (i.e., statistically there was no difference between the first and last samples) in our canisters for storage times of at least 1 week, which is the period when most loss would be expected to occur.

[9] For analysis, each cryogenically preconcentrated sample was partitioned into five different streams, with each stream sent to one of five column-detector combinations optimized for nonmethane hydrocarbons, halocarbons [Blake *et al.*, 2003; Colman *et al.*, 2001], and sulfur gases [Blake *et al.*, 2004]. The combination that was used to quantify the OCS was a DB-5ms column (60 m; ID, 0.25 mm; film, 0.5 μ m) coupled to an HP-5973 mass selective detector quadrupole mass spectrometer. The OCS calibration was performed by reference to a commercial standard (Scott-Marrin), with 5% accuracy, and was the same calibration scale as that employed for the TRACE-P experiment [Blake *et al.*, 2004]. The measurement precision for OCS during INTEX-NA was better than 1%, with a detection limit better than 20 parts per trillion by volume (pptv). OCS was always present above its detection limit.

[10] High-precision in situ measurements of carbon dioxide (CO₂) were made on the DC-8 by a modified Li-COR model 6252 infrared gas analyzer having an accuracy and precision of 0.25 ppmv and 0.07 ppmv, respectively [Vay *et al.*, 1999].

[11] For an overview of the Summer 2004 INTEX-NA project, see *Singh et al.* [2006]. (Data are archived at <http://www-air.larc.nasa.gov>.)

3. Observations

[12] INTEX-NA comprised 17 science flights, during which a total of 2924 whole air samples were collected, covering an area from the eastern Pacific to the western Atlantic United States. The eastern United States was the principal focus (Figure 1). The University of California, Irvine analysis quantified more than 50 different trace gases, including nonmethane hydrocarbons, halocarbons, and alkyl nitrates. However, this paper focuses on the observations of OCS and its relationship to CO₂ during INTEX-NA, with comparison to the Transport and Chemical Evolution over the Pacific observations and initial modeling results.

3.1. Sinks

[13] The INTEX-NA observations, shown as averaged $1^\circ \times 1^\circ$ grid squares (Figure 2) reveal that the lowest mixing ratios of OCS were found at the lowest altitudes, with higher mixing ratios aloft over the western United States. A significant correlation between OCS and CO₂ exists, with an R^2 of 0.69 for OCS versus CO₂ samples collected over the continent (Figure 3). Stronger correlations are found for several individual flights, mostly flown over vegetated regions of the eastern United States. For example, flight 12 was flown on 20 July 2004 and comprised six low-altitude legs, three of which were over the North Atlantic and three over different areas of the eastern United States (Figure 4) and had the highest R^2 value (0.91) for OCS versus CO₂ (Figure 3). The low-altitude legs flown over the ocean during flight 12 showed no significant drawdown (or obvious large enhancement) of either OCS or CO₂ (Figure 5). However, all three legs flown in the continental boundary layer (CBL) showed significant drawdown of both gases (Figure 5).

[14] Trajectories were calculated from exact flight positions for each leg along the DC-8 flight path using a kinematic model [*Fuelberg et al.*, 1996]. According to these trajectories, the air mass sampled during flight 12 over the ocean had spent at least several days in the marine boundary layer (Figure 6), while the air intercepted in the CBL had spent several days at low altitudes over vegetated continental regions of the United States and Canada (Figure 7). These observations serve to illustrate the contrast between the strong sink of OCS and CO₂ at low altitudes for air with a history of terrestrial influence, compared to air masses with principally oceanic influence.

3.2. Comparison With TRACE-P

[15] Because TRACE-P was flown in the Asian 2001 spring season, OCS soil and vegetation sinks were expected to be near seasonal lows [e.g., *Kettle et al.*, 2002b]. For TRACE-P, over the western Pacific, OCS mixing ratios were enhanced by at least 10% in samples collected below 2 km altitude, compared to those collected at 8–10 km (Figure 8a). Similarly, strong gradients were observed for the anthropogenic tracer gas tetrachloroethene (C₂Cl₄) (Figure 8d and in the papers by *Blake et al.* [2003, 2004]) and combustion marker CO (Figure 8b), suggesting

that boundary layer levels of OCS may have been strongly influenced by continental anthropogenic sources during TRACE-P [*Blake et al.*, 2004]. Mean TRACE-P levels of OCS (as well as C₂Cl₄) over the central and eastern Pacific, at altitudes below about 4 km, were significantly lower than those over the western Pacific (Figure 8). This was mainly the result of a diminished influence from continental sources [*Blake et al.*, 2004].

[16] In contrast with the TRACE-P observations, the INTEX-NA OCS and CO₂ data show significant biogenic drawdown near the surface. A mean mixing ratio for OCS below 2 km of 410 pptv accounts for a 10% depletion compared to a mean background value aloft of approximately 450 pptv (Figure 8). The corresponding depletion for CO₂ was about 1.6%.

3.3. Sources

[17] Biomass burning emissions from Alaskan wildfires were sampled over the NW Atlantic off the coast of Newfoundland during flight 9, 18 July 2004 (Figure 1). This plume had been transported rapidly across Canada in about 5 d. The OCS/CO₂ enhancement ratio was approximately $12\text{--}20 \times 10^{-6}$ vol/vol (depending on choice of “background” value), which is at the upper end of the range reported for SE Asian (mostly biomass burning) emissions [*Blake et al.*, 2004; *Thornton et al.*, 1996], but plotted on Figure 3, the samples would not appear as outliers. The corresponding value for the OCS/CO ratio is about 0.09 ($0.07\text{--}0.11$) $\times 10^{-6}$ vol/vol, which is at the lower end of the observations for SE Asia [*Blake et al.*, 2004].

[18] A notable feature of INTEX-NA is the high background concentrations of OCS and CO₂ (>500 pptv OCS) observed at high altitudes (8–10 km) over the Pacific (flight 3) and Atlantic (flight 15) oceans (Figures 1 and 2). These high-altitude enhancements are associated with meteorological back trajectories that originate from Asia [*Liang et al.*, 2007]. Previous observations closer to the Asian continent show that pollution plumes originating from parts of China associated with high levels of coal burning tend to be particularly enhanced in OCS compared to CO [*Blake et al.*, 2004].

[19] Samples with relatively high CO₂ compared to OCS (seen as outliers in Figure 3) were observed during low-altitude planetary boundary layer (PBL) runs over agricultural regions of the Midwest (specifically, Nebraska and Oklahoma) during the early flight hours of flights 4 and 7 (Figure 1). These outliers may represent air masses that were heavily influenced by the nighttime boundary layer. Ozone levels were very low (<40 ppb) for the flight 4 leg, and anthropogenic hydrocarbons were elevated for the flight 7 PBL leg. These air masses appear to have encountered a large respiration and/or anthropogenic source of CO₂ but no (or relatively low) emissions of OCS, differentiating them from the typical daytime PBL sampling during INTEX-NA.

[20] For most INTEX-NA samples collected over the eastern United States, any anthropogenic emissions of OCS and CO₂ appear to have been successfully masked by their colocated biospheric sink. For example, Figure 9 highlights a flight where the low-altitude air originated over the industrial Ohio River (OR) valley [*Hennigan et al.*, 2006]. Sharp spikes of elevated CO₂ and SO₂ were observed at 15.9 h, 17.1 h, and 18.9 h for the fast response

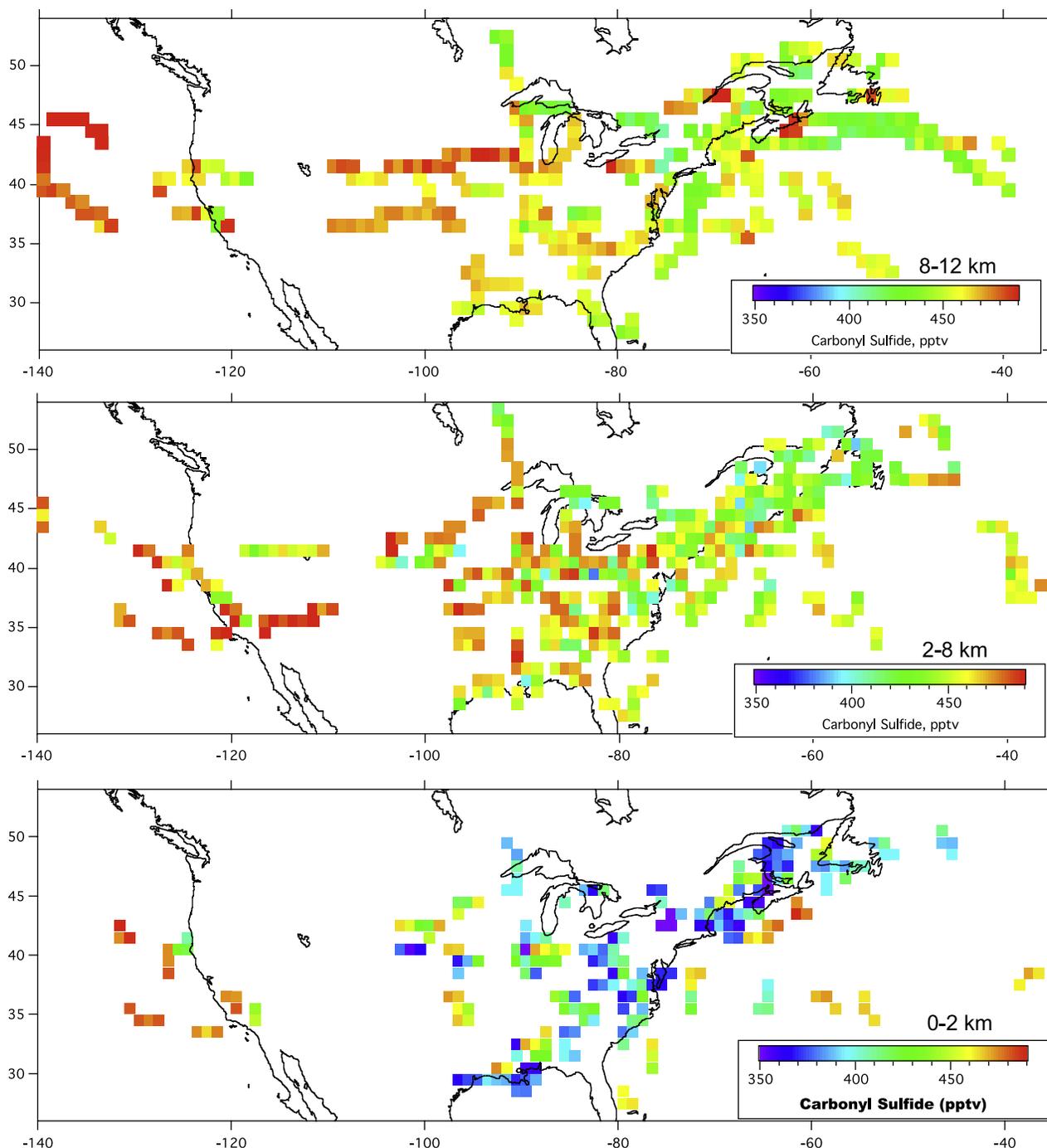


Figure 2. Map of $1^\circ \times 1^\circ$ mean observed carbonyl sulfide (OCS) concentrations for three altitude ranges for all INTEX-NA DC-8 flights (July and August 2004).

results for those gases and were accompanied by some short-term enhancement in the relatively low-resolution OCS mixing ratio data (Figure 9). The region bordering the OR region contains a large number of power plants that burn fossil fuels, primarily coal. Because OCS is a source of SO₂, some of the SO₂ associated with the spike could originate from the oxidation of OCS. However, this SO₂ source is likely insignificant as oxidation of OCS is slow in the boundary layer, and the OR region represents a very

large SO₂ source (roughly 25% of United States point source direct emissions [Hennigan *et al.*, 2006]).

[21] The only OCS emission factor for the type of combustion representative of the OR area in the literature to date was that for a coal-fired power plant, reporting an OCS/CO₂ ratio of 2.3×10^{-6} ($= 0.0049 \text{ g OCS kg}^{-1} \text{ coal burned}$ at the Cherokee Power Plant in Denver, Colorado) [Khalil and Rasmussen, 1984; Chin and Davis, 1993]. Three industrial plumes observed at low altitudes during INTEX-NA had discernable simultaneous peaks of SO₂,

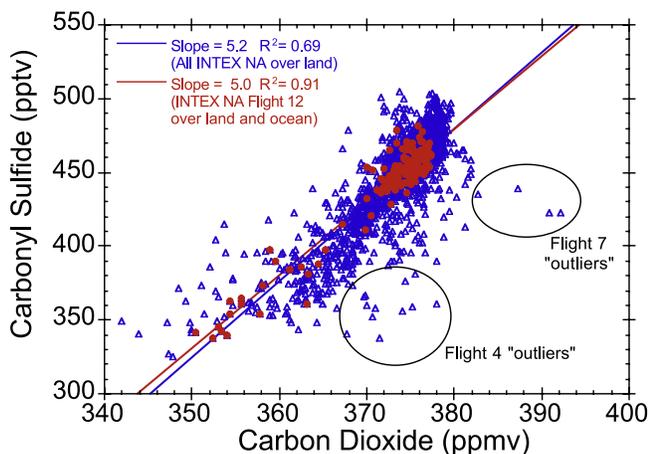


Figure 3. Correlation plot of OCS versus CO₂ for all INTEX-NA DC-8 samples collected over the continent (July and August 2004) and for flight 12, 25 July 2004 (which included samples collected over both ocean and land). The plot also identifies “outlier” points sampled at low altitude over the Midwest (Nebraska and Oklahoma) during flights 4 and 7.

OCS, and CO₂. The $\Delta\text{OCS}/\Delta\text{CO}_2$ values are shown in Table 1, corresponding to a mean $\Delta\text{OCS}/\Delta\text{CO}_2$ enhancement ratio of approximately $5\text{--}7 \times 10^{-6}$ vol/vol. This is significantly lower than the $9\text{--}24 \times 10^{-6}$ vol/vol range for

$\Delta\text{OCS}/\Delta\text{CO}_2$ in air masses originating over China and SE Asia during TRACE-P [Blake *et al.*, 2004], indicating that emission plumes from the OR may be cleaner as the result of the burning of low-sulfur coal and more modern coal-burning technology in the United States.

[22] As stated in section 3.1, the large-scale levels of OCS and CO₂ sampled over the continent appeared to be strongly influenced by the drawdown of both gases to vegetated continental land surfaces. This sink was associated with a typical ratio for ΔOCS versus ΔCO_2 (e.g., from flight 12) of about 5×10^{-6} vol/vol ($R^2 = 0.91$) (Figure 3), so it follows that the industrial plume enhancements with enhancement ratios described above and this drawdown ratio could combine to produce the mean slope of about 5.2×10^{-6} ($R^2 = 0.69$) for the linear best fit for all the INTEX-NA samples collected over the United States (Figure 3). Given this mixture of sources and sinks, we turn to computer modeling of these different OCS components to further interpret these data.

4. Sulfur Transport Eulerian Model (STEM) Model

[23] The STEM regional chemistry model [Carmichael *et al.*, 2003; Campbell *et al.*, 2007] was used for preliminary simulations of OCS on the INTEX-NA domain, driven by available gridded surface fluxes used in previous models [Kettle *et al.*, 2002a] and fixed boundary conditions. The loss of OCS by oxidation with the atmospheric hydroxyl radical was neglected because the reactive lifetime of more

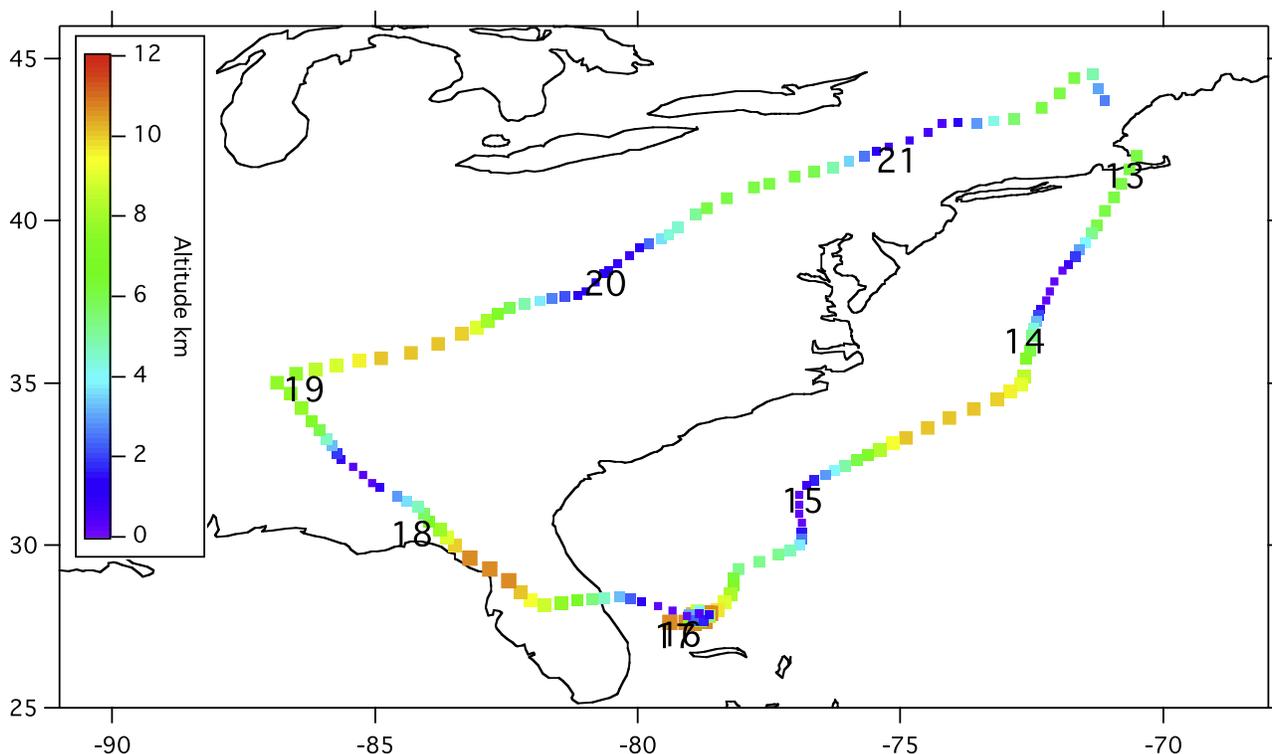


Figure 4. Flight track with color-coded altitude for INTEX-NA DC-8 flight 12, 25 July 2004. Small blue squares correspond to the positions of samples collected during the six boundary layer runs. Black numbers correspond to UTC hour.

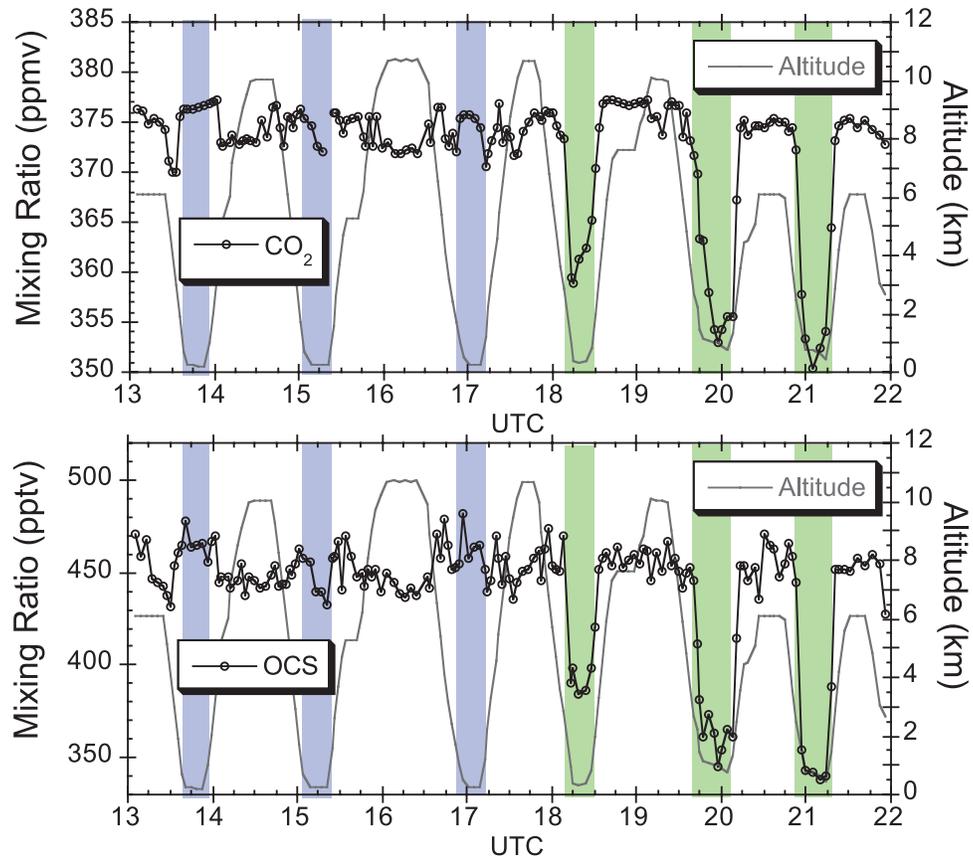


Figure 5. Mixing ratios of OCS and CO₂ and altitude versus UTC hour for INTEX-NA DC-8 flight 12, 25 July 2004. Blue shading highlights marine boundary layer legs, and green shading highlights continental boundary layer legs.

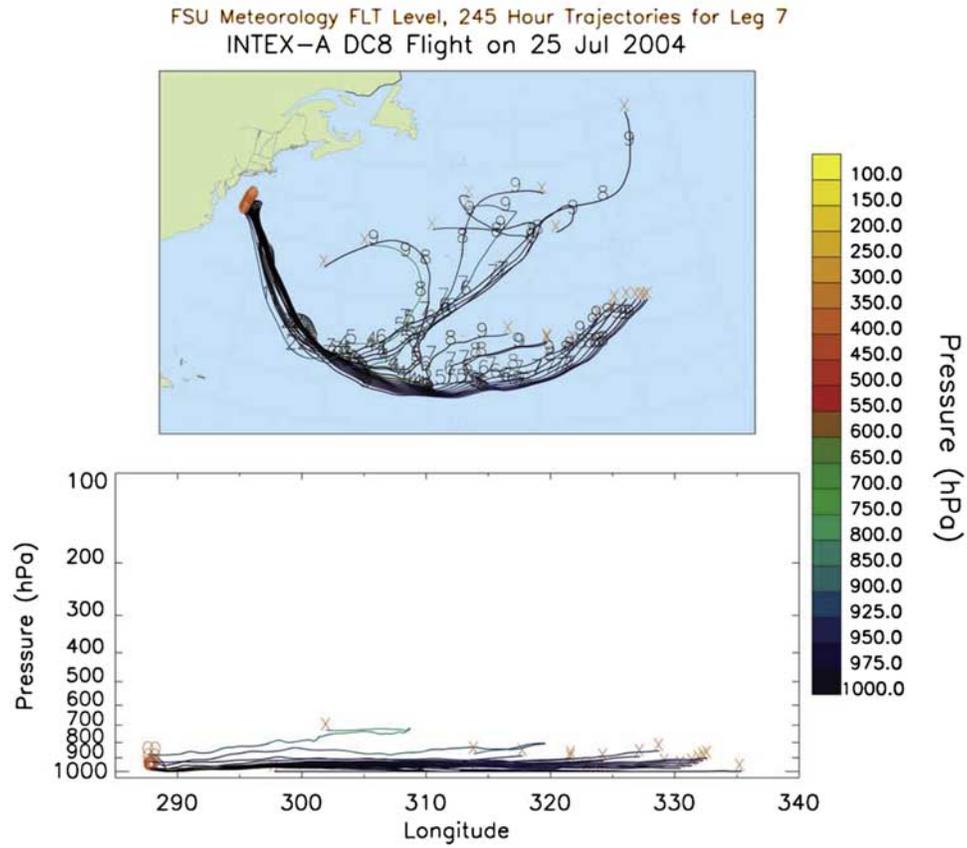


Figure 6. Backward trajectory for the first low-altitude leg during flight 12, flown at about 1310 to 1325 UTC.

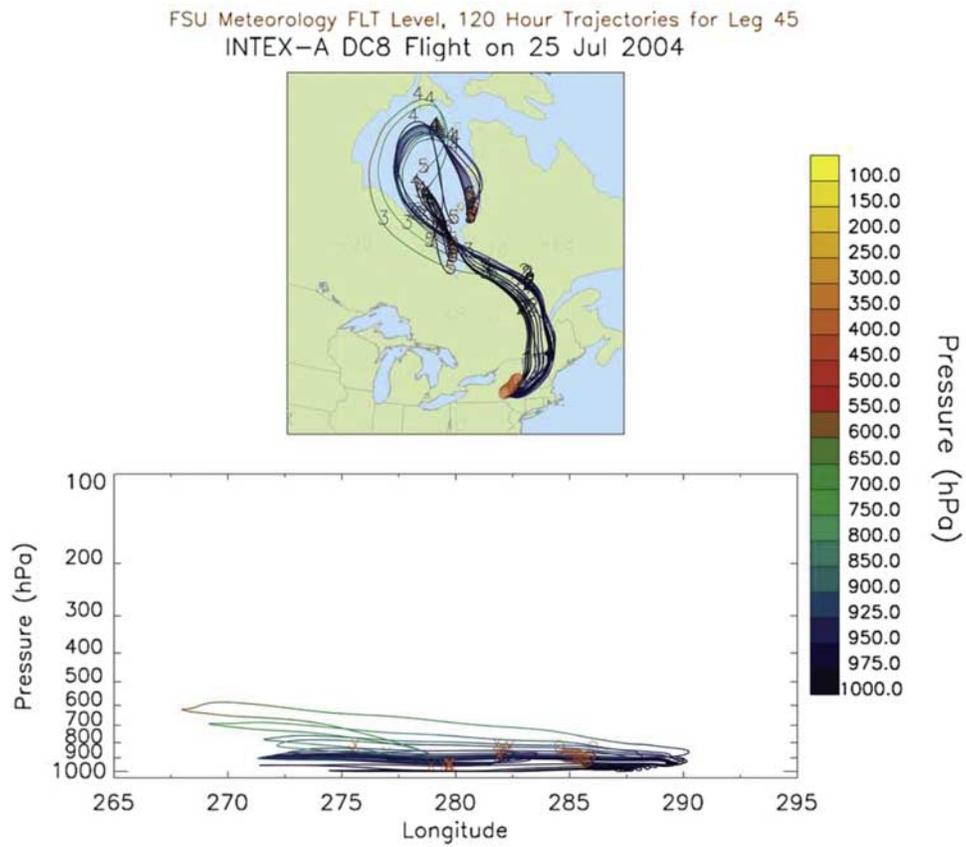


Figure 7. Backward trajectory for the fifth low-altitude leg during flight 12, flown at about 1945 to 2015 UTC.

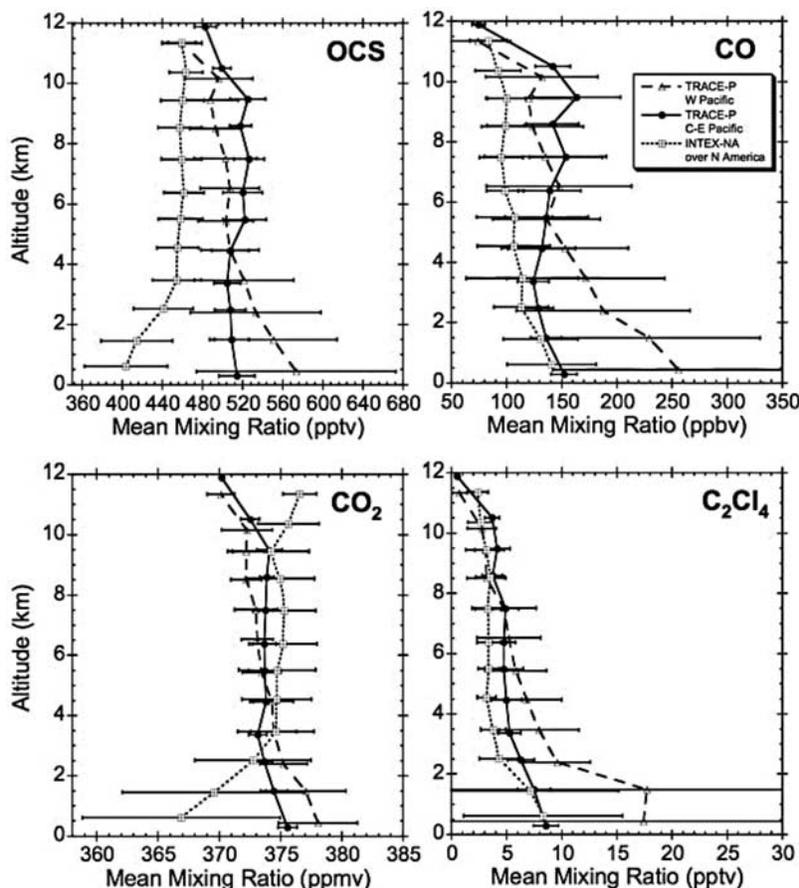


Figure 8. Mean (1 km increments) vertical profiles for OCS, CO, CO₂, and C₂Cl₄. The mean values for INTEX-NA samples collected over the continent are compared to data collected at latitudes >25°N over the western Pacific (<165°E) and central/eastern Pacific (165°E–230°E) during TRACE-P. Error bars represent 1 standard deviation from the mean.

than a year for July in the Northern Hemisphere is much longer than the transport lifetime in the boundary layer of the model domain of several days. The model domain has a 60 km × 60 km grid resolution and 21 vertical sigma layers that extend from the surface up to the 100 hPa level.

[24] The OCS surface fluxes have a monthly time resolution for the following flux components: terrestrial vegetation sink, soil sink, ocean source, anthropogenic source, and reactive sources from oxidized anthropogenic and ocean sources of DMS and CS₂ [Kettle *et al.*, 2002a]. All are 1° × 1° spatial resolution (model domain grid cell is 0.5°), except for ocean OCS flux and ocean OCS flux as oxidized CS₂, which are both at 5° × 5° [Kettle *et al.*, 2002a]. The spatial distributions for these fluxes for July are shown in Figure 10. The magnitude of the soil sink, total anthropogenic source, and ocean source are approximately 43%, 77%, and 8% of the plant sink, respectively. The anthropogenic emissions are concentrated in the eastern portion of the domain because of emissions from large point sources, while the plant and soil sinks are distributed more evenly across the domain. The INTEX-NA flight paths are concentrated over the eastern portion of the domain as well.

[25] Two model runs were completed, with model run A driven by the gridded fluxes and model run B run by the same fluxes but with the plant uptake doubled. The plant uptake was doubled in model run B because recent measurements from plant-scale experiments [Sandoval-Soto *et al.*, 2005] and a global air-monitoring network [Montzka *et al.*, 2007] indicate that the true plant sink may be 200% or more than Kettle *et al.*'s [2002a] estimates of the plant sink. We doubled the plant uptake uniformly in space as an initial investigation of the missing sink. However, future investigations may reveal significant spatial variation in how the sink has been underestimated.

[26] The western boundary condition for the model runs was estimated on the basis of data from the 1 July flight

Table 1. Enhancements Above Local “Background” Values and $\Delta\text{OCS}/\Delta\text{CO}_2$ Ratios for Three Industrial Plumes Observed at Low Altitudes and That Had Discernable Simultaneous Peaks of SO₂, OCS, and CO₂

Flight Number	Approximate UT	ΔCO_2	ΔOCS	$\Delta\text{OCS}/\Delta\text{CO}_2$
10	17.0	2.6	16.5	6.5
16	19.5	2.4	16.5	6.8
11	15.9	6.1	28.8	4.7

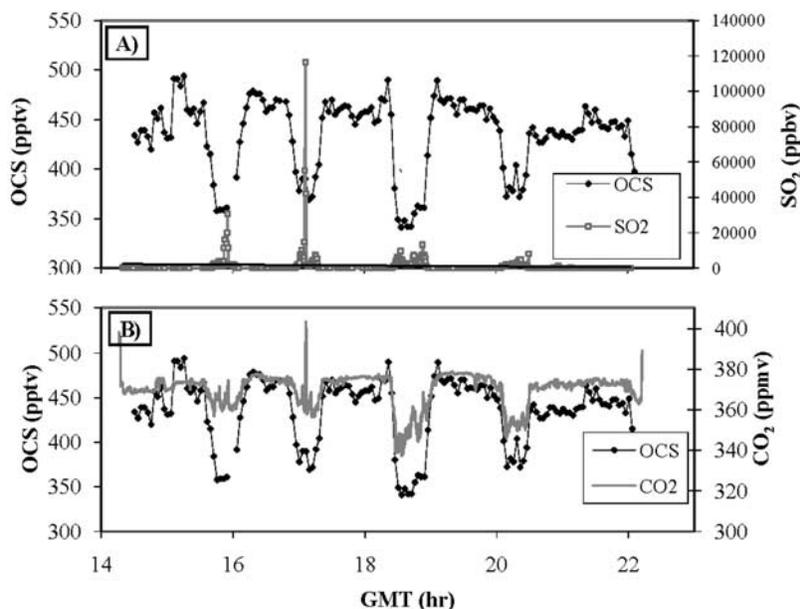


Figure 9. Time series for INTEX-NA DC-8 observations of OCS, SO₂, and CO₂ during flight 10, 20 July 2004. These different species are plotted at different scales.

which took place over the Pacific Ocean. The observed OCS concentration for this flight had a mean of 480 ± 10 pptv, while the mean for all flights was 440 ± 40 pptv. The western model boundary condition is fixed at 480 pptv on the basis of the low variation of the observations over the Pacific. Additional observations and forthcoming results from global transport models should be used for more realistic boundary conditions in future model runs.

[27] Defining the other lateral model domain boundaries is more complicated because of the strong influence by terrestrial sinks. The OCS surface fluxes over Canada shown in Figure 10 suggest that the northern model boundary will be highly varied. These lateral boundaries may best be estimated as space-varying, time-invariant surfaces [Gerbig *et al.*, 2003]. However, for the model runs in this study, the lateral boundaries are fixed at 450 pptv on the basis of the mean INTEX-NA observations to the north and east of the model domain of 450 ± 20 pptv.

[28] The top boundary condition was estimated from high-altitude OCS data. The highest STEM vertical level over the ocean is centered at 13.1 km. The highest altitude for INTEX-NA OCS observations were at 11.9 km. Mean OCS observations above 11 km had a value of 460 ± 10 pptv. A fixed value of 460 pptv is used for the top boundary.

[29] The OCS model error is compared in Figure 11 for model runs A and B. For model run A, the low concentrations of OCS observed in the boundary layer are overestimated by the model. This very large underestimation at the surface was not characteristic of previous model runs when comparing INTEX-NA observations with STEM simulations of CO₂ and CO [Campbell *et al.*, 2007]. Doubling the plant uptake in run B improves the agreement for these low-altitude values; however, considerable overestimation remains. The greatest improvements between run A and run B are made near the surface where the model errors are the largest and the influence of the surface fluxes are dominant. The model performance showed a 15%

reduction in RMS errors between model run A and B, with RMS errors of 37.4 pptv and 31.8 pptv, respectively. As an alternative to increasing the plant sink, we could have increased the soil sink or decreased the anthropogenic sources in order to improve the model performance. However, the plant uptake is thought to be underestimated by a factor of 2 or more [Sandoval-Soto *et al.*, 2005; Montzka *et al.*, 2007], while the uncertainties in the anthropogenic source is much smaller ($\sim 50\%$), and the soil sink may actually be overestimated instead of underestimated [Watts, 2000]. The original Kettle *et al.* [2002a] data suggests that the soil sink was 40% of the plant uptake. Increasing this plant uptake by a factor of 2 or more would make plant uptake the dominant flux for the growing season.

[30] A time series of OCS concentrations compares the observed data to the values obtained from the model runs for the 20 July flight (Figure 12). This flight covers a representative sample of the INTEX-NA flight paths but observes some of the largest drawdown of OCS during the entire experiment. Neither of the model runs captures the depth of the terrestrial sink, even with a doubling of the plant uptake flux. The emissions and model resolutions are too coarse to show the low-altitude, anthropogenic emission spikes. Anthropogenic input from Asia was also shown to influence this flight at high altitudes [Liang *et al.*, 2007], which may account for some of the high-altitude (background) underestimation. Underestimation at high altitudes may also be associated with variability in the background concentrations.

5. Conclusion and Next Steps

[31] Unlike the net Asian OCS source investigated in TRACE-P during winter/spring [Blake *et al.*, 2004], the data presented here suggests that the dominant terrestrial surface OCS flux in the North American summer is the vegetation sink. This sink works effectively and illustrates the large-

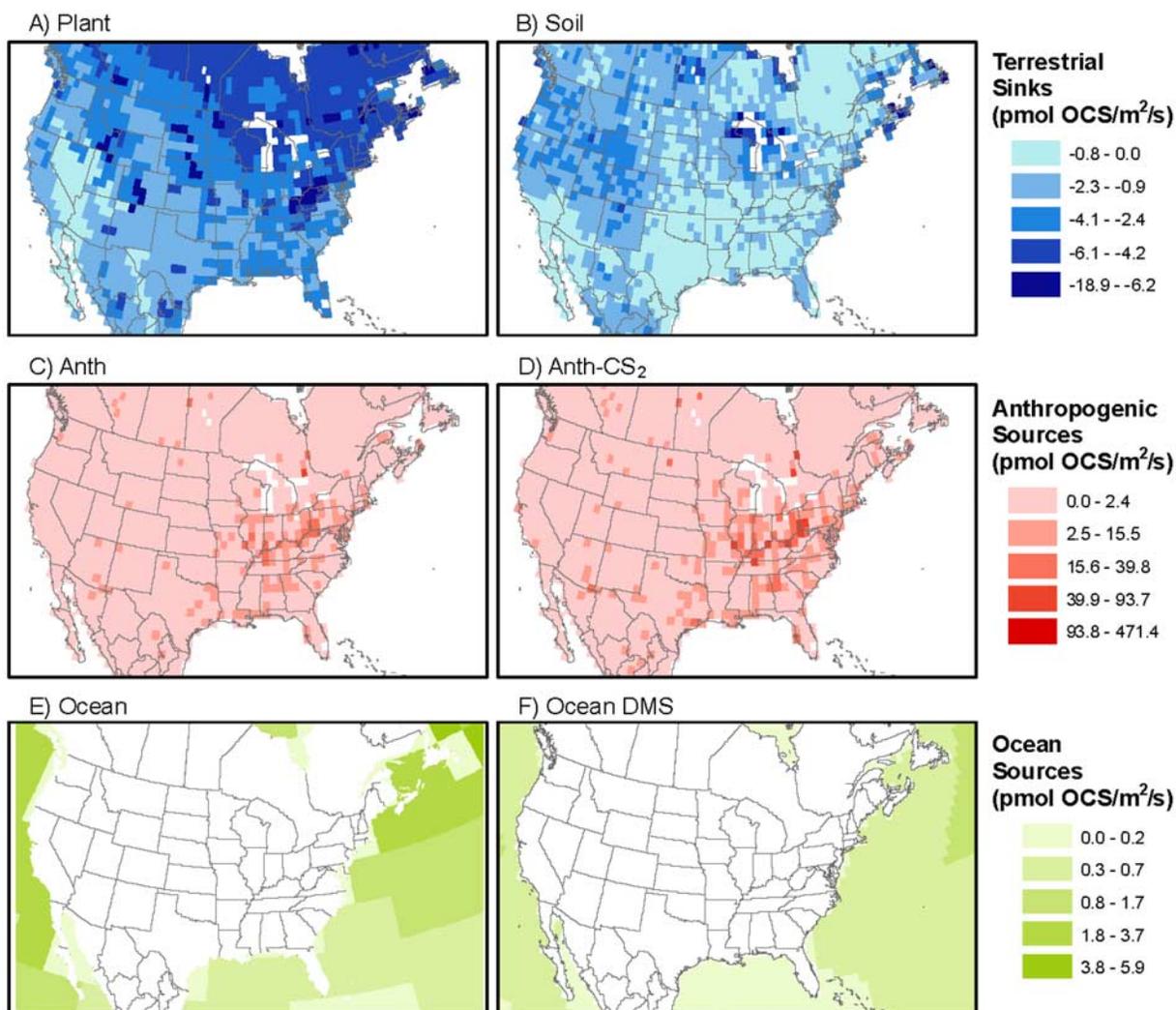


Figure 10. OCS surface fluxes ($\text{pmol OCS m}^{-2} \text{s}^{-1}$) for July over North America from the paper by Kettle *et al.* [2002a, 2002b] including the (a) plant sink, (b) soil sink, (c) anthropogenic source, (d) reactive source of anthropogenic CS₂, (e) ocean source, and (f) reactive source of oceanic dimethyl sulfide (DMS). The oxidized CS₂ ocean source and oxidized DMS anthropogenic source were included in the model but are not plotted here because of their small magnitude.

scale colocated summer drawdown of OCS and CO₂ and how terrestrial sinks dominate during this season at low altitudes over vegetated regions of North America. Initial STEM model results indicate that the current, proposed magnitude of the OCS surface sink may be underestimated by more than 200%.

[32] Further development of the forward OCS model for analysis of the vegetation sink is planned, adding improved boundary conditions, emissions, and chemistry. Large uncertainties in the global sources of OCS may remain as suggested by recent work [Sandoval-Soto *et al.*, 2005; Montzka *et al.*, 2007]. However, atmospheric analysis of OCS may be more promising for regional applications during the growing season, when the OCS plant uptake is dominant over other OCS surface flux components. Furthermore, a combination of OCS and CO₂ analysis could lead to an improved understanding of the terrestrial biosphere sinks.

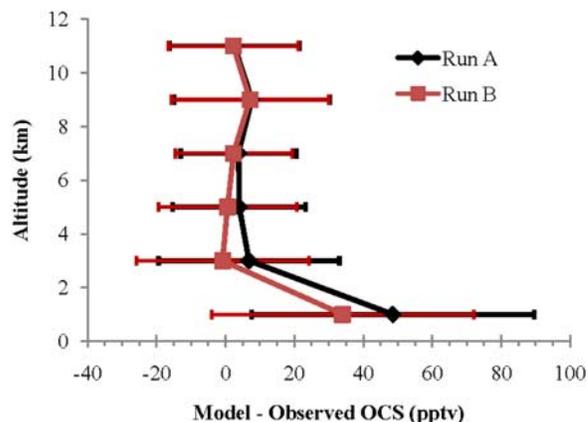


Figure 11. Vertical profile of model error for model run A (driven by gridded fluxes) and model run B (plant uptake increased by a factor of 2) for continental DC-8 flights.

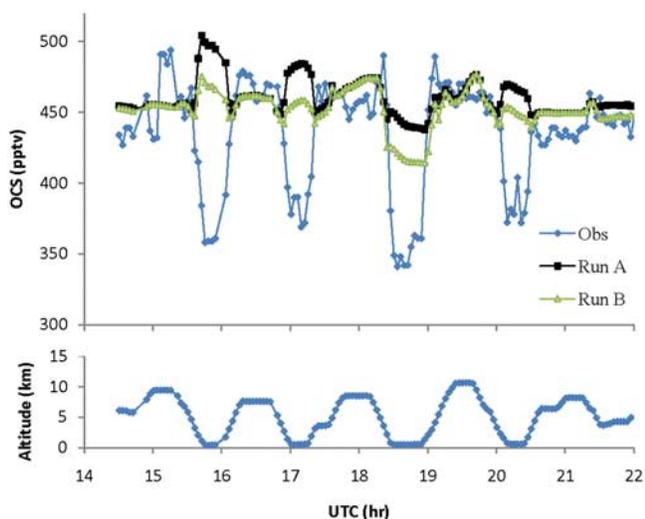


Figure 12. OCS concentrations from observed data and model runs (run A original gridded fluxes, run B gridded fluxes with plant uptake increased by a factor of 2), and flight path altitude for INTEX-NA DC-8 flight, 20 July 2004 (flight 10).

[33] **Acknowledgments.** We wish to thank Barbara Chisholm, Kevin Gervais, Gloria Liu, and Brent Love for their outstanding contributions during the INTEX-NA mission, and we also wish to thank the DC-8 crew and the INTEX support staff. Thanks also to Jack Dibb and Mads Andersen for manuscript suggestions. We gratefully acknowledge funding from the NASA Office of Earth Science Tropospheric Chemistry Program.

References

- Andreae, M. O., and P. J. Crutzen (1997), Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, *Science*, *276*, 1052–1056, doi:10.1126/science.276.5315.1052.
- Arsene, C., I. Barnes, K. H. Becker, and R. Mocanu (2001), FT-IR product study on the photo-oxidation of dimethyl sulfide in the presence of NO_x-temperature dependence, *Atmos. Environ.*, *35*, 3769–3780, doi:10.1016/S1352-2310(01)00168-6.
- Aydin, M., W. J. De Bruyn, and E. S. Saltzman (2002), Preindustrial atmospheric carbonyl sulfide (OCS) from an Antarctic ice core, *Geophys. Res. Lett.*, *29*(9), 1359, doi:10.1029/2002GL014796.
- Barnes, I., H. K. Becker, and I. Patroescu (1994), The tropospheric oxidation of dimethyl sulfide: A new source of carbonyl sulfide, *Geophys. Res. Lett.*, *21*(22), 2389–2392, doi:10.1029/94GL02499.
- Blake, N. J., et al. (2003), NMHCs and halocarbons in Asian continental outflow during the transport and chemical evolution over the Pacific (TRACE-P) field campaign: Comparison to PEM-West B, *J. Geophys. Res.*, *108*(D20), 8806, doi:10.1029/2002JD003367.
- Blake, N. J., et al. (2004), Carbonyl sulfide (OCS) and carbon disulfide (CS₂): Large-scale distributions over the western Pacific and emissions from Asia during TRACE-P, *J. Geophys. Res.*, *109*, D15S05, doi:10.1029/2003JD004259.
- Campbell, J. E., et al. (2007), Analysis of anthropogenic CO₂ signal in ICARTT using a regional chemical transport model and observed tracers, *Tellus, Ser. B*, *59*(2), 199–210, doi:10.1111/j.1600-0889.2006.00239.x.
- Carmichael, G. R., et al. (2003), Regional-scale chemical transport modeling in support of the analysis of observations obtained during the TRACE-P experiment, *J. Geophys. Res.*, *108*(D21), 8823, doi:10.1029/2002JD003117.
- Charlson, R. J., J. Langner, and H. Rodhe (1990), Sulfate aerosol and climate, *Nature*, *348*(22), doi:10.1038/348022a0.
- Chin, M., and D. D. Davis (1993), Global sources and sinks of carbonyl sulfide and carbon disulfide and their distributions, *Global Biogeochem. Cycles*, *7*(2), 321–337, doi:10.1029/93GB00568.
- Chin, M., and D. D. Davis (1995), A reanalysis of carbonyl sulfide as a source of stratospheric background sulfur aerosol, *J. Geophys. Res.*, *100*(D5), 8993–9005, doi:10.1029/95JD00275.
- Colman, J. J., A. L. Swanson, S. Meinardi, B. C. Sive, D. R. Blake, and F. S. Rowland (2001), Description of the analysis of a wide range of volatile

- organic compounds in whole air samples collected during PEM-Tropics A and B, *Anal. Chem.*, *73*, 3723–3731, doi:10.1021/ac10027g.
- Crutzen, P. J. (1976), The possible importance of OCS for the sulfate layer of the stratosphere, *Geophys. Res. Lett.*, *3*(2), 73–76, doi:10.1029/GL003i002p00073.
- Fuelberg, H. E., R. O. Loring Jr., M. V. Watson, M. C. Sinha, K. E. Pickering, A. M. Thompson, G. W. Sachse, D. R. Blake, and M. R. Schoeber (1996), TRACE A trajectory intercomparison 2. Isentropic and kinematic methods, *J. Geophys. Res.*, *101*(D19), 23,927–23,939, doi:10.1029/95JD02122.
- Gausepohl, S. C., A. S. Denning, J. Berry, S. Montzka, I. Baker, and J. Kleist (2006), Assessing the seasonal cycle of simulated photosynthesis using carbonyl sulfide (COS) at a continental mixed forest site, *Geophys. Res. Abstr.*, *8*, 05284.
- Gerbig, C., J. C. Lin, S. C. Wofsy, B. C. Daube, A. E. Andrews, B. B. Stephens, P. S. Bakwin, and C. A. Grainger (2003), Toward constraining regional-scale fluxes of CO₂ with atmospheric observations over a continent: 2. Analysis of COBRA data using a receptor-oriented framework, *J. Geophys. Res.*, *108*(D24), 4757, doi:10.1029/2003JD003770.
- Goldan, P. D., R. Fall, W. C. Kuster, and F. C. Fehsenfeld (1988), Uptake of COS by growing vegetation: A major tropospheric sink, *J. Geophys. Res.*, *93*(D11), 14,186–14,192, doi:10.1029/JD093iD11p14186.
- Hennigan, C., S. Sandholm, S. Kim, R. E. Stickel, L. G. Huey, and R. J. Weber (2006), Influence of Ohio River Valley emissions on fine particle sulfate measured from aircraft over large regions of the eastern United States and Canada during INTEX-NA, *J. Geophys. Res.*, *111*, D24S04, doi:10.1029/2006JD007282.
- Kettle, A. J., U. Kuhn, M. von Hobe, J. Kesselmeier, and M. O. Andreae (2002a), Global budget of atmospheric carbonyl sulfide: Temporal and spatial variations of the dominant sources and sinks, *J. Geophys. Res.*, *107*(D22), 4658, doi:10.1029/2002JD002187.
- Kettle, A. J., U. Kuhn, M. von Hobe, J. Kesselmeier, and M. O. Andreae (2002b), Comparing forward and inverse models to estimate the seasonal variation of hemisphere-integrated fluxes of carbonyl sulfide, *Atmos. Chem. Phys.*, *2*, 343–361.
- Khalil, M. A. K., and R. A. Rasmussen (1984), Global sources, lifetimes and mass balances of carbonyl sulfide (OCS) and carbon disulfide (CS₂) in the Earth's atmosphere, *Atmos. Environ.*, *18*, 1805–1813, doi:10.1016/0004-6981(84)90356-1.
- Leung, F.-Y. T., A. J. Colussi, M. R. Hoffmann, and G. C. Toon (2002), Isotopic fractionation of carbonyl sulfide in the atmosphere: Implications for the source of background stratospheric sulfate aerosol, *Geophys. Res. Lett.*, *29*(10), 1474, doi:10.1029/2001GL013955.
- Liang, Q., et al. (2007), Summertime influence of Asian pollution in the free troposphere over North America, *J. Geophys. Res.*, *112*, D12S11, doi:10.1029/2006JD007919.
- Mihalopoulos, N., B. Bonsang, B. C. Nguyen, M. Kanakidou, and S. Belviso (1989), Field observations of carbonyl sulfide deficit near the ground: Possible implication of vegetation, *Atmos. Environ.*, *23*, 2159–2166, doi:10.1016/0004-6981(89)90177-7.
- Montzka, S. A., M. Aydin, M. Battle, J. H. Butler, E. S. Saltzman, B. D. Hall, A. D. Clarke, D. Mondeel, and J. W. Elkins (2004), A 350-year atmospheric history for carbonyl sulfide inferred from Antarctic firn air and air trapped in ice, *J. Geophys. Res.*, *109*, D22302, doi:10.1029/2004JD004686.
- Montzka, S. A., B. Hall, J. W. Elkins, L. Miller, A. Watson, C. Sweeney, and P. P. Tans (2007), On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO₂, *J. Geophys. Res.*, *112*, D09302, doi:10.1029/2006JD007665.
- Sandoval-Soto, L., M. Stanimirov, M. von Hobe, V. Schmitt, J. Valdes, A. Wild, and J. Kesselmeier (2005), Global uptake of carbonyl sulfide (COS) by terrestrial vegetation: Estimates corrected by deposition velocities normalized to the uptake of carbon dioxide (CO₂), *Biogeosciences*, *2*, 125–132.
- Singh, H. B., W. H. Brune, J. H. Crawford, D. J. Jacob, and P. B. Russell (2006), Overview of the summer 2004 Intercontinental Chemical Transport Experiment—North America (INTEX-A), *J. Geophys. Res.*, *111*, D24S01, doi:10.1029/2006JD007905.
- SPARC Scientific Steering Group (2006), Assessment of stratospheric aerosol properties (ASAP), edited by L. Thomason and T. Peter, *SPARC Rep. 4*, World Meteorol. Organ., Geneva, Switz.
- Thornton, D. C., A. R. Bandy, B. W. Blomquist, and B. E. Anderson (1996), Impact of anthropogenic and biogenic sources and sinks on carbonyl sulfide in the North Pacific troposphere, *J. Geophys. Res.*, *101*(D1), 1873–1881, doi:10.1029/95JD00617.
- Vay, S. A., B. E. Anderson, T. J. Conway, G. W. Sachse, J. E. Collins Jr., D. R. Blake, and D. J. Westberg (1999), Airborne observations of the tropospheric CO₂ distribution and its controlling factors over the South Pacific Basin, *J. Geophys. Res.*, *104*(D5), 5663–5676, doi:10.1029/98JD01420.

Watts, S. F. (2000), The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide, *Atmos. Environ.*, 34, 761–779, doi:10.1016/S1352-2310(99)00342-8.

Xu, X., H. G. Bingemer, and U. Schmidt (2002), The flux of carbonyl sulfide and carbon disulfide between the atmosphere and a spruce forest, *Atmos. Chem. Phys.*, 2, 171–181.

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