Measurements of Atmospheric Carbonyl Sulfide During the NASA Chemical Instrumentation Test and Evaluation Project: Implications for the Global COS Budget

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Atmospheric COS concentrations were measured by three analytical systems during the Chemical Instrumentation Test and Evaluation (CITE 3) project. The three systems all used cryogenic sample preconcentration and gas chromatographic (GC) separation but differed in the method of detection. The FPD system used a flame photometric detector, the MS system used a mass selective detector, and the ECD-S system used a fluorinating catalyst followed by an electron capture detector. With the FPD system, we found a mean COS concentration of 510 ppt over the North Atlantic and 442 ppt over the Tropical Atlantic. With the ECD-S system, we found a mean COS concentration of 489 ppt over the North Atlantic and 419 ppt over the Tropical Atlantic. All three systems registered a latitudinal gradient in atmospheric COS of between 1.6 and 2.0 ppt per degree of latitude, with increasing COS concentrations northward which was similar to the gradient measured by Bingemer et al. (1990). It is difficult to reconcile the measured latitudinal concentration gradient with present theories of the global COS budget since the largest sink of COS is thought to be a flux to land plants, most of which are in the northern hemisphere.

INTRODUCTION

Of all the major sulfur compounds occurring in the atmosphere, carbonyl sulfide (COS) has the greatest mean concentration and the least variability. Since 1975, tropospheric COS measurements from Europe [*Sandalls and Penkett*, 1977], North America [*Maroulis et al.*, 1977], the remote Pacific [*Torres et al.*, 1980; *Johnson and Harrison*, 1986], and the central Atlantic [*Bingemer et al.*, 1990] have all shown COS concentrations to range from 350 to 650 ppt with a mean value near 500 ppt. This homogeneous concentration implies a lifetime of several years or more, at least several orders of magnitude longer than other naturally occurring sulfur compounds. Only anthropogenic SF_6, present at very low concentrations in the atmosphere, <3 ppt [*Zander et al.*, 1991] has a longer lifetime.

Numerous sources of atmospheric COS have been investigated. *Goldan et al.* [1988], reviewing earlier measurements of soil emissions [*Goldan et al.*, 1987; *Lamb et al.*, 1987] estimated a global source of COS to the atmosphere from soils of 1.2 to 3.3 Gmol (10^9 mol) of COS per year. *Johnson and Harrison* [1986] calculated an annual oceanic source of COS to the atmosphere of 3 to 7 Gmol, somewhat less than earlier estimates of 5 to 13 Gmol [*Khalil and Rasmussen*, 1984] and 7.7 Gmol [*Ferek and Andreae*, 1983]. *Crutzen et al.* [1979] estimated that biomass burning contributes 3.3 Gmol of COS annually to the atmosphere. *Khalil and Rasmussen* [1984]

estimated that anthropogenic emissions of COS to the atmosphere ranged from 1 to 5 Gmol/yr. Last, COS appears to be a product of OH-initiated atmospheric oxidation of CS_2. Laboratory studies have found that the CS_2 to COS product ratio is unity so that for each CS_2 molecule emitted into the atmosphere, a molecule of COS will be produced [*Barns et al.*, 1983]. The global source of atmospheric COS from this reaction can be estimated from the calculated global source of atmospheric CS_2. Alternatively, the COS source can be calculated as the mean atmospheric CS_2 concentration divided by the atmospheric lifetime of CS_2. Measurements during the Chemical Instrumentation Test and Evaluation (CITE 3) program [*Johnson and Bates*, this issue; *Bandy et al.*, this issue (*a*), (*b*)] showed that the mean atmospheric CS_2 concentration is lower than previously estimated, as recently noted by *Kim and Andreae* [1987]. A mean atmospheric CS_2 concentration of 1 ppt and lifetime of 10 days [*Barns et al.*, 1983] results in an annual COS source of 5 Gmol of COS. In summary, these proposed sources of atmospheric COS amount to 13 to 23 Gmol/yr.

Only a few sinks of atmospheric COS have been identified. Although the most important climatic consequence of atmospheric COS is its flux to the stratosphere [*Crutzen*, 1976], the estimated flux of approximately 2.5 Gmol/yr [*Turco et al.*, 1980] is small in comparison with the total COS sources. Reaction with OH radical, the major sink for almost all reduced gases in the atmosphere, has been shown to be very slow for COS [*Wahner and Ravishankara*, 1987; *Chen and Lee*, 1986], amounting to only 1.7 to 2.5 Gmol/yr. A proposed sink of atmospheric COS to land plants [*Fall et al.*, 1988; *Taylor et al.*, 1983; *Kluczewski et al.*, 1985] appears to be the

major sink of atmospheric COS, although actual field measurements of this process remain scarce. *Goldan et al.* [1988] estimated the global sink of atmospheric COS to land plants to be 3.3–6.7 Gmol COS per year, using laboratory measurements of the uptake of COS by agricultural plants. The total for these three sinks ranges from 7.5 to 12 Gmol/yr.

A proposed global budget of COS is shown in Table 1. Estimates of the atmospheric lifetime of COS range from 2 to 5 years based on the range of proposed sources. As with other proposed budgets [*Kahlil and Rasmussen*, 1984; *Johnson*, 1985; *Goldan et al.*, 1988], this budget can only be balanced by taking the minimum value for the sources and the maximum value for the sinks. Since the concentrations of COS in the atmosphere are near the values that were recorded in the mid-1970's [*Sandalls and Penkett*, 1977; *Torres et al.*, 1980], it is obvious that the sources and sinks of COS in the atmosphere must be close to steady state.

If the lifetime is comparable to the interhemispheric mixing time of 1 year, a measurable interhemispheric COS concentration gradient should exist, provided the sources and sinks of atmospheric COS do not exactly balance within each hemisphere. Measurement of an interhemispheric or latitudinal gradient of atmospheric COS concentrations can therefore place constraints on possible COS budget estimates.

We present here COS data collected during the NASA CITE 3 program from three different instruments, which all show a COS latitudinal gradient. We discuss the present uncertainties in our understanding of the global cycle of atmospheric COS and compare the results of our measurements with present theories of the atmospheric COS cycle.

MEASUREMENTS

The CITE 3 project occurred in August and September of 1989 with the primary mission of intercomparing a large number of techniques to measure five sulfur gases (H_2S, COS, SO_2, DMS, CS_2) under actual field conditions. Seven flights were conducted over the North Atlantic, and an additional seven flights were conducted over the Tropical Atlantic. Data were also collected on the ferry flights from Wallops Island, Virginia, to Natal, Brazil. An overview of the CITE 3 experiment is given by *Hoell et al.* [this issue]. Although the primary purpose of the experiment was to compare measurement techniques, the resulting field measurements provide a detailed data set for further scientific evaluation.

Three of the instruments on the Electra measured carbonyl sulfide. The electron capture sulfur detector (ECD-S) from the NOAA Pacific Marine Environmental Laboratory is fully described by *Johnson and Bates* [this issue]. Briefly, COS in a 167-mL sample of air was cryogenically enriched and chromatographed on a Carbopack B/1% XE-60/1.5% H_3PO_4 column using nitrogen carrier. After exiting the separation column, sulfur compounds were fluorinated on a silver catalyst with the addition of a low concentration of F_2, then detected in an ECD. For COS the system had a calculated detection limit of 5 ppt, a reproducibility (precision) of 8%, and an accuracy of 12%. The quoted precision is likely a conservative estimate, as the entire set of atmospheric COS concentration measurements from the Tropical Atlantic had a sigma over mean of 2%. Standards contained in aluminum high-pressure cylinders were diluted with zero air and analyzed every 40 to 60 min to calibrate the system. The COS concentrations in the high-pressure cylinders were determined from standards generated using gravimetrically calibrated permeation tubes.

The flame photometric detection (FPD) system is similar to the system used on the GAMETAG project in 1977 and 1978 [*Torres et al.*, 1980; *Maroulis*, 1980]. Briefly, COS in a 810-mL air sample was cryogenically enriched in a 30-cm section of Teflon tubing using liquid argon as a cryogen. The cryogenic loop was warmed with hot water, injecting the sample onto a 0.6-m-long, Porapak Q chromatographic column using 10 mL/min of air as the carrier gas. Following the separation column, the sample stream entered a conventional FPD. For COS the system had an accuracy of 20% and a precision of 10%. The system was calibrated using standards from high-pressure cylinders that were added to the sample line using mass flow controllers. The concentrations of COS in the high-pressure standards were determined using gravimetrically calibrated permeation tubes.

The mass selective (MS) system from Drexel University is fully described elsewhere [*Thornton et al.*, 1990]. Briefly, COS in a 3-L air sample was cryogenically enriched using liquid argon as a cryogen. The cryogenic loop was warmed, injecting the sample onto a 3-m-long, 2-mm ID Teflon column packed with 3% Carbowax 20 M and 1% H_3PO_4 (Supelco Inc., Bellefonte, Pennsylvania) using a He carrier flow of 10 mL/min. Following the separation column, the sample stream entered an Extrel Corp. (Pittsburgh, Pennsylvania) C50-400 quadrupole mass spectrometer. Each sample included

TABLE 1. A Proposed Budget of Atmospheric COS

	Gmol COS per year	Reference
Sources		
Soils	1.2–3.3	*Golden et al.* [1988]
Ocean	3.0–7.0	*Johnson and Harrison* [1986]
Biomass burning	3.3	*Crutzen et al.* [1979]
Anthropogenic emissions	1.0–5.0	*Khalil and Rasmussen* [1984]
CS_2 oxidation	5	*Barns et al.* [1983]
Sum	13–23	
Sinks		
Flux to stratosphere	2.5	*Turco et al.* [1980]
OH reaction	1.5–2.5	*Wahner and Ravishankara* [1987]
Land plants	3.3–6.7	*Golden et al.* [1988]
Sum	7.5–12	

an isotopically labeled internal standard, which was added at the inlet of the Teflon sample line. The concentration of isotopically labeled $CO^{34}S$ in the standard was determined by comparison with standards of $CO^{32}S$ generated from gravimetrically calibrated permeation tubes. For COS the system had an accuracy of 20% and a precision of 5%.

RESULTS

Flight Overlap

Unfortunately, the configuration of each analytical system represented a compromise in order to measure several sulfur compounds. As such, the three systems did not always measure COS. Only on the ferry flights (flights 10 and 11) were all three systems measuring COS. On four flights (4, 13, 14, and 15), COS was measured by only two systems. The remaining flights (5-9, 16-19) had only one system measuring COS, and on flight 10, COS was not measured by any system. Table 2 lists which systems measured COS on each flight.

Flight Data

Time series plots of COS concentrations as measured by the FPD and ECD-S from flight 4 over the North Atlantic are shown in Figure 1 as an example of the individual flight data. It can easily be seen that during each flight there was little correlation between the COS concentration time series of the FPD and the ECD-S. The data points were not collected at exactly the same time, so a direct statistical correlation cannot be made. However, to get an objective estimate of the correlation between the two systems (FPD and ECD-S) for flights 4, 13, 14, and 15 we constructed a least squares fifth-order polynomial fit to each of the two time series of COS concentration measurements. The correlation coefficient between the predicted COS concentrations at regular time intervals (every 0.05 hour) was then calculated. By this method we have found that the correlation coefficient between the FPD and the ECD-S systems for each individual flight was weak and negative, with correlation coefficients ranging from -0.2 to -0.5. The clear conclusion is that during each flight the sample-to-sample variation in the measured concentrations from one or both systems was instrumental and not the result of real atmospheric concentration changes. Apparently, the 5 to 10% precision in the measurements was greater than the
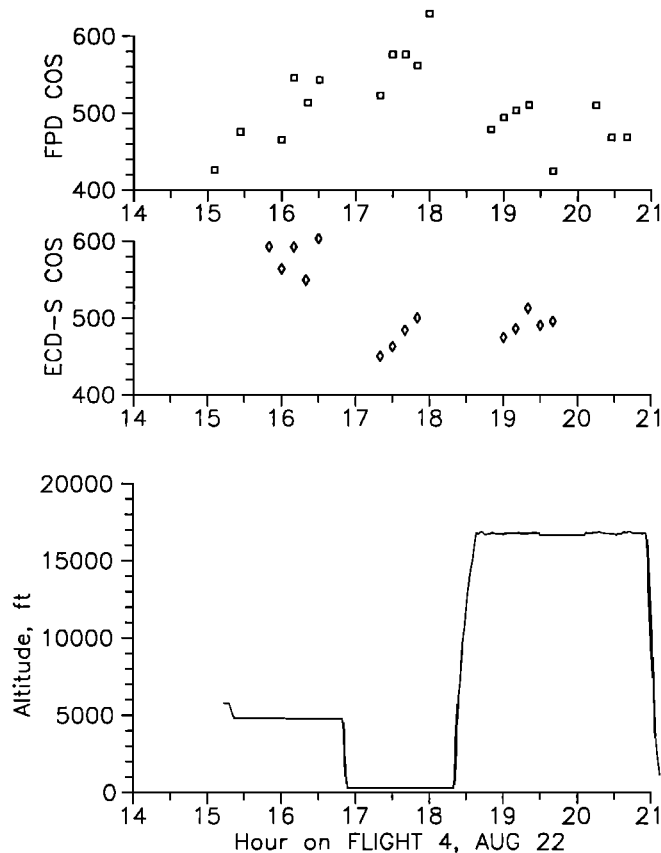

Fig. 1. A time series of the COS measurements from flight 4. The top plot is from the FPD system, the middle plot is from the ECD-S system, and the bottom plot is the aircraft altitude.

atmospheric variations encountered along most of the flight paths.

By a much different method, *Gregory et al.* [this issue] have found significant correlations between the FPD and the ECD-S systems. That method looked at correlations between the concentration record of the two systems in pairs of measurements where the collection periods overlapped in time. Also, and more importantly, *Gregory et al.* also looked at the entire CITE 3 record, not single flights. By finding significant correlations throughout the entire data record, it appears that the

TABLE 2. A Schedule of COS Measurements Showing Which Instrument Measured COS
on the Various Flights, and the Latitude Range of Each Flight

Flight Number	Date	Latitude Range, deg		FPD	MS	ECD-S
		Low	High			
4	Aug. 22	32	38	×		×
5	Aug. 23	33	38			×
6	Aug. 25	37	40			×
7	Aug. 28	38	40			×
8	Aug. 30	31	38			×
9	Aug. 31	36	39	×		
10	Sept. 1	37	40			
11	Sept. 8	13	38	×	×	×
12	Sept. 9	-6	13	×	×	×
13	Sept. 12	-11	-6	×		×
14	Sept. 15	-6	2	×		×
15	Sept. 16	-6	2	×		×
16	Sept. 19	-6	-2	×		
17	Sept. 20	-6	-2	×		
18	Sept. 22	-6	-5	×		
19	Sept. 22	-6	-5	×		

variations in flight-to-flight COS concentrations were real and not instrumental.

We will not duplicate the extensive work of Gregory et al. [this issue] in looking at all of the correlations in the instrumental measurements. However, the data record provides some additional insight into the global cycle of atmospheric COS. If the sample-to-sample variations in the COS record on a particular flight were mostly instrumental noise, and if the instrumental noise was random, then the average of a larger set of data will reduce the instrumental noise by the square root of the sample number.

As most flight tracts included measurement periods near the surface (at altitudes of 300 to 500 ft) as well as at higher altitudes (typically 5000 ft but occasionally higher), we have divided the data set into mean values for each analytical system for each flight at each of two altitudes, below and above 2000 ft. Figure 2 shows these mean values for each system in each of the two altitude bins as functions of flight number.

Several features appear in the flight-to-flight mean COS values. One is a lower amount of variability over the Tropical Atlantic (flights 13–19) as opposed to North Atlantic (flights 4–9). Another feature is the lower amount of COS on flight 6 and higher amounts on flights 4 and 5. The meteorological data and back trajectory analysis are described by Shipham et al. [this issue], who show that air masses encountered on the flight tracks originated 5 days earlier over the North Tropical Atlantic Ocean for flights 4 and 5, over the eastern United States for flights 7 and 8, over northern and central Canada and passing over the eastern United States for flights 6 and 9, and over the central Tropical Atlantic Ocean for flights 13 through 19. If the geographic regions 5 days upwind of the flight track were influencing the measured concentration, then the concentrations associated with these regions can be ranked as North Tropical Atlantic > eastern United States > Canada > central Tropical Atlantic Ocean.

Latitudinal Gradient

The latitudinal gradient of atmospheric COS concentrations was measured on the ferry flight (flights 11 and 12) from Wallops Island, Virginia, to Natal, Brazil (38°N to 6°S). As the primary mission of the flight was to ferry the plane and equipment from Virginia to Brazil, the most fuel- and time-efficient flight path was chosen. This resulted in long flight tracks in the mid-troposphere at altitudes of 12,000 to 16,000 ft. Flight 11 occurred on September 9 from Wallops Island to Barbados (13°N) with a refueling stop in Puerto Rico. Flight 12 continued the following day to Natal with a refueling stop in Cayenne, French Guiana (5°N).

During flight 12 the ECD-S system was not operating under optimal conditions. Under "normal" operation at Wallops Island and at Natal, the module containing the gas chromatography (GC) columns and catalysts was removed from the aircraft so that heat and gas flow could be maintained (which was not allowed on the aircraft for safety reasons). During the overnight stay at Barbados, this was not possible, so that it was many hours into the flight before the system stabilized and reliable measurements could begin. There was also a data gap in the ECD-S record at the beginning of flight 11 resulting from a poisoned fluorination catalyst that required several hours to recover.

Plots of COS concentrations as a function of latitude for each of the three systems are shown in Figure 3 along with simple linear regressions. Although there appeared to be greater variability in the concentration records of the FPD and the ECD-S than in the MS, the gradients registered by each system over the length of the flight path were quite consistent at between 1.60 and 2.02 ppt per degree, with concentrations decreasing southward. The similarity in the measured COS gradients is remarkable in contrast to the lack of correlation
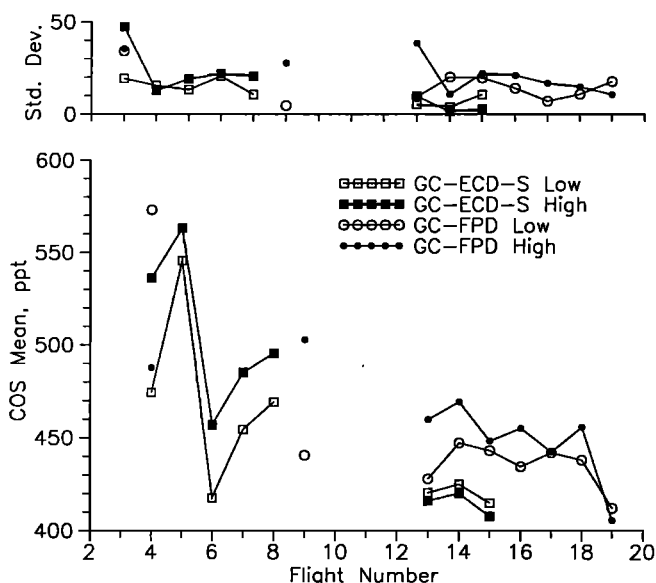

Fig. 2. Plots of the mean and standard deviations for two altitude bins (above 2000 ft, and below 2000 ft) from each flight from each analytical system.
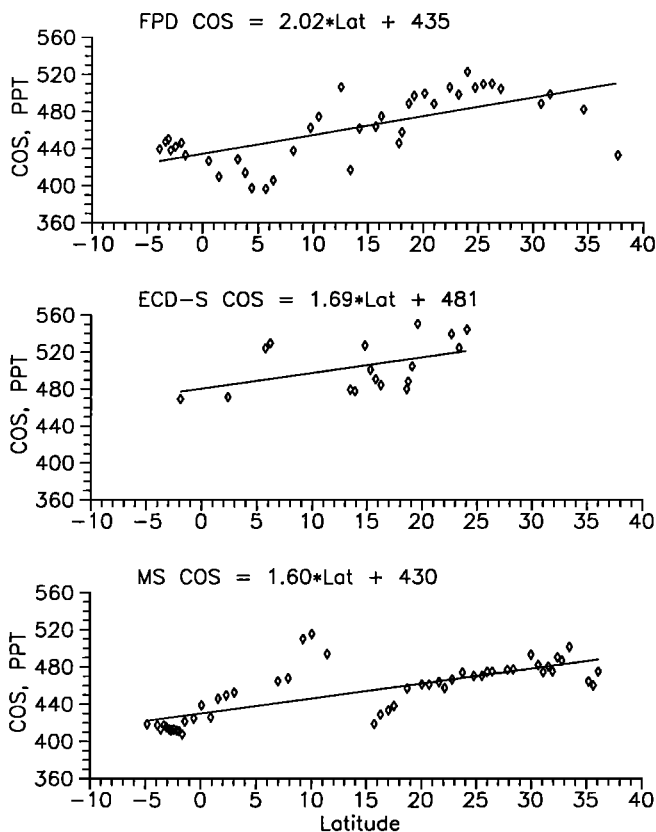

Fig. 3. The latitudinal gradient of COS as measured during the ferry flight (flights 11 and 12) on September 8 and 9, 1991, by (top) the FPD system, (middle) the ECD-S system, and (bottom) the MS system. The lines represent least squares linear fits.

between the COS records of the FPD and the ECD-S during flights over the North Atlantic and Tropical Atlantic. The likely explanation is that the real variation in atmospheric COS concentrations was greater during the ferry flights than during the other flights, which each consisted of measurements in a relatively narrow latitude band.

The latitudinal gradient is also supported in the statistical record of the FPD and ECD-S systems from the flights in the North Atlantic and the Tropical Atlantic. The ECD-S record showed a mean COS concentration of 489 ± 5.7 ppt over the North Atlantic (31°N to 40°N) and 419 ± 0.8 ppt over the Tropical Atlantic (11°S to 2°N), where the indicated limits are the standard error (standard deviation/square root of N). This translates into a latitudinal gradient of 1.77 ppt per degree. The FPD record showed a mean and standard error COS concentration of 510 ± 8.3 ppt over the North Atlantic and 442 ± 2.5 ppt over the Tropical Atlantic, which corresponds to a latitudinal gradient of 1.72 ppt per degree.

Vertical Gradients

A simple vertical gradient for each flight is demonstrated in Figure 2, where the mean COS concentrations from below 2000 and above 2000 ft are shown as a function of flight number for the FPD and ECD-S systems. The ECD-S record shows a vertical gradient with COS concentrations increasing with altitude in the northern hemisphere (flights 4–8) and an opposite gradient (decreasing with altitude) in the data from the Tropics (flights 13–15). Unfortunately, in all overlap flights (4, 13, 14, and 15) the FPD measured a vertical gradient in the opposite direction.

DISCUSSION

The most striking feature in the COS measurements from the CITE 3 project is the latitudinal gradient which was confirmed by all three analytical systems. Previous measurements over the Pacific Ocean have shown little [Torres et al., 1980] or no [Johnson and Harrison, 1986] significant latitudinal gradient. However, a recent study conducted from ship-based measurements over the Atlantic Ocean [Bingemer et al., 1990] revealed a latitudinal gradient of atmospheric COS similar to that presented here. That study found the highest COS concentrations in air that had passed over Europe. Our highest concentrations of COS were in air masses that had traveled westward on the south side of the North Atlantic High. Although our trajectory analysis only goes back 5 days, the air masses may have originated in Europe as well. If this is the case, then a substantial source of atmospheric COS may be located in the European continent. A European source could explain part of the discrepancy between the lack of a COS gradient over the Pacific Ocean and the measured COS gradient over the Atlantic Ocean.

The most direct and important implication of the north-south concentration gradient is that there is a net source of COS in the northern hemisphere and a net sink of COS in the southern hemisphere, with southward transport of atmospheric COS. This distribution of atmospheric COS does not conform to our present understanding of the atmospheric COS budget, in particular with our understanding of the distribution of COS sinks. Most sources of COS are assumed to be nonanthropogenic, the ocean is assumed to be a major source, and the only significant sink is believed to be deposition to land plants (Table 1), which implies that the northern hemisphere sink of COS is at least twice that of the southern hemisphere.

Possible explanations for the measured gradient include the following: (1) Anthropogenic sources are much larger than estimated. (2) Land plants may not be the major sink. Deposition to land plants has been clearly demonstrated in laboratory chambers; however, a recent field study in a Georgia pine forest [Berresheim and Vulcan, 1992] has failed to document COS deposition to land plants. (3) Another sink may be operating, one that is not asymmetric between the hemispheres, as is the proposed land plant sink.

A second feature in the data that was supported by both the FPD and the ECD-S was the higher variability of COS concentrations over the North Atlantic versus the Tropical Atlantic. The variability within each flight is shown in Figure 2 as plots of the standard deviation of the COS concentration measurements for each flight (for each of the two altitude bins). Measurements by the ECD-S showed that the standard deviation of the COS concentrations over the Tropical Atlantic was one-half to one-third that over the North Atlantic. The higher variability seen over the North Atlantic Ocean is consistent with a closer proximity to stronger sources (either associated with land or industrial activity) and stronger sinks such as land plants. The increased variability in North Atlantic atmospheric COS concentrations was also noted by Bingemer et al. [1990].

A final feature in the COS data that was supported mostly by the ECD-S record was that the COS concentrations associated with source regions (defined as the geographical regions 5 days upwind of the particular measurements) were ranked as North Tropical Atlantic > eastern United States > Canada > central Tropical Atlantic Ocean. The ranking of the North Tropical Atlantic and the central Tropical Atlantic are consistent with the general north-south gradient; the ranking of the eastern United States and Canada are not. The surprisingly low concentrations of COS in air that arrived from Canada might be explained by a large sink of COS to the boreal forest in central and northern Canada, which might be expected during the summer growing season. If land plants in the northern hemisphere are indeed the major sink of atmospheric COS, and if the northern boreal forests comprise a large component of this sink, then the concentration of COS in the northern hemisphere should exhibit an annual cycle that may be detectable from a time series of atmospheric COS at a clean northern hemisphere site.

CONCLUSIONS

The latitudinal gradient of COS measured over the Atlantic Ocean during CITE 3 averaged 1.8 ppt per degree, with concentrations increasing northward. This gradient was supported by all three instruments on the ferry flight, and by the two instruments in their mean values from the North Atlantic and Tropical Atlantic flights. This gradient is not consistent with a small anthropogenic source and with land plants being the major sink. However, the variability of COS was greater over the Northern Atlantic Ocean than over the Tropical Atlantic Ocean, consistent with greater sources and sinks in the northern hemisphere. These measurements confirm that our present understanding of the global budget of atmospheric COS is incomplete.

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