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Measurements of carbonyl sulfide (COS) in surface seawater and marine air, and estimates of the air-sea flux from observations during two Atlantic cruises

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Abstract. Carbonyl sulfide (COS) was measured in surface seawater and in marine air during two Atlantic cruises of the R/V *Polarstern* between Bremerhaven, Germany, and Cape Town, South Africa. The cruises took place in the fall of 1997 and in the summer of 1998. The concentration of COS showed clear diurnal, seasonal, and latitudinal variations, as did its saturation ratio. The concentration of dissolved COS averaged 14.7 pmol L^{-1} and 18.1 pmol L^{-1} for the fall and summer cruises, respectively. On most days, seawater was undersaturated in COS during the late night and early morning but was supersaturated during the rest of the day, implying that the ocean can act as both a source and a sink for COS on the same day. The COS content in seawater was correlated significantly with the global radiation, the CH_3SH concentration, and the seawater temperature. The air-sea flux of COS from the open Atlantic Ocean was estimated using exchange coefficients calculated according to Erickson's stability dependent model for air-sea gas exchange. The largest COS flux into the atmosphere occurred in productive regions (the Benguela Current, the West African upwelling area, and the northeastern Atlantic) during the warmer seasons. A small net oceanic uptake of COS was found in the Benguela Current during the southern winter. The average open ocean fluxes were 13.5 nmol COS m^{-2} d^{-1} and 28.6 nmol COS m^{-2} d^{-1} for the two cruises, respectively. A global open ocean source of 0.10 Tg COS yr^{-1} is extrapolated from the measured data. The atmospheric mixing ratio of COS averaged 474±33 and 502±38 pptv for the fall and summer cruises, respectively, and had no significant interhemispheric gradient.

1. Introduction

Carbonyl sulfide (COS) is the most abundant sulfur-containing gas in the atmosphere and is uniformly distributed in the troposphere with an average mixing ratio of 500±100 pptv. Owing to its long tropospheric lifetime of 2-7 years [*Khalil and Rasmussen,* 1984; *Johnson and Harrison,* 1986; *Chin and Davis,* 1993, 1995; *Griffith et al.,* 1998], it can be transported from the troposphere into the stratosphere. The photolysis and subsequent oxidation of stratospheric COS has been proposed as the main source of nonvolcanic stratospheric aerosol [*Crutzen,* 1976]. This was supported by early modeling studies [*Sze and Ko,* 1979; *Turco et al.,* 1980] and has been confirmed by COS measurements in the stratosphere [*Engel and Schmidt,* 1994]. However, this view has been challenged by more recent modeling results [*Chin and Davis,* 1995; *Weisenstein et al.,* 1997; *Kjellström,* 1998], which show that the modeled net COS flux into the stratosphere is at least 2 times smaller than the estimates of the amount of sulfur required to sustain the background stratospheric aerosol level. Stratospheric aerosol plays an important role in the Earth's radiation budget as well as providing a surface for heterogeneous reactions causing ozone destruction [*Toon and Pollack,* 1982; Lacis et al., 1992; *Rodriguez et al.,* 1991; *Solomon et al.,* 1993].

Emissions from oceans and soils, the photooxidation of CS_2, and biomass burning are believed to be the major sources of atmospheric COS, and uptake by terrestrial vegetation is considered the major sink. Budget estimates show that the total COS source could exceed the total sink by a factor of 2 [*Khalil and Rasmussen,* 1984; *Chin and Davis,* 1993]. This is inconsistent with the absence of any significant secular trend for the atmospheric COS content as indicated by measurements of COS mixing ratios in the troposphere and lower stratosphere [*Bandy et al.*, 1992; *Mihalopoulos et al.*, 1991; *Rinsland et al.*, 1996] and of total column COS [*Rinsland et al.*, 1992; Griffith et al., 1998]. Therefore it is likely that in the current budgets either the sources are overestimated or the sinks are underestimated or both.

Recent studies have revealed the necessity of revising the estimates of the soil and ocean sources. It has been shown that earlier chamber studies that used sulfur-free synthetic air as sweep gas resulted in artificial fluxes due to artificial gradients of sulfur gas imposed on the soil/air system [*Castro and Galloway,* 1991]. While studies using sulfur-free air [*Adams et al.*, 1981; *Goldan et al.*, 1987; *Lamb et al.*, 1987; *MacTarggart et al.*, 1987; *Staubes et al.*, 1989] always showed emission of COS from the soil, more recent measurements with a sweep gas containing ambient levels of COS showed a deposition of COS to the soil [*Castro and Galloway,* 1991; *De Mello and Hines,* 1994; *Kuhn et al.*, 1998]. It has been suggested by *Andreae and Crutzen* [1997] that soils should be considered a global sink of COS rather than a source.

COS is produced in surface seawater by both photochemical and nonphotochemical reactions and is removed from seawater by hydrolysis, downward mixing, and exhalation. Experimental and model studies show that the dominant source of dissolved COS is photoproduction while the main sink is hydrolysis [*Uher,* 1994; *Najjar et al.*, 1995; *Ulshöfer et al.*, 1996]. The balance between COS production from dissolved biological precursors and loss processes due to hydrolysis, downward mixing, and air-sea exchange causes geographical, seasonal, and diurnal variations in the concentration and saturation ratio of COS in seawater and in the air-sea flux. The global marine source of COS was initially estimated at 0.4-0.9 Tg yr^{-1} [*Rasmussen et al.*, 1982; *Ferek and Andreae,* 1983; *Mihalopoulos et al.*, 1992] on the basis of data showing that practically all ocean regions studied were supersaturated with COS. However, this database for global extrapolation was biased toward conditions suiting high COS production, i.e., low latitudes, warmer seasons, and biologically productive areas. The discovery of large-scale uptake of COS by the open ocean during winter [*Weiss et al.*, 1995; *Ulshöfer et al.*, 1995] and the improvement of models for the marine COS cycle have led to a substantial downward revision of global and regional estimates of the COS air-sea flux. It has been suggested by *Weiss et al.* [1995] that the open ocean is a weak sink for COS. Taking into consideration this open ocean sink, the total marine emission of COS to the atmosphere is estimated by *Ulshöfer and Andreae* [1998] to be 0.15 Tg COS yr^{-1}. These revisions have lead to substantial changes in estimates of the global COS budget as well as of the distribution of the COS sources and sinks between the Northern and Southern Hemispheres. They need to be confirmed by further studies on air-sea and air-soil exchange.

Since the estimated lifetime of tropospheric COS exceeds the interhemispheric transport time of ~ 1 year, a large interhemispheric gradient could only exist if the COS sources and sinks showed a strong imbalance between both hemispheres. According to the most recent COS budgets of *Chin and Davis* [1993] and *Andreae and Crutzen* [1997], CS_2 oxidation appears to be the largest source of atmospheric COS. Nearly 60% of atmospheric CS_2 is believed to be emitted by anthropogenic sources [*Chin and Davis,* 1993]. Since these sources are mainly located in the Northern Hemisphere, a higher level of atmospheric COS is to be expected there, assuming that the other sources and sinks are approximately balanced between the hemispheres. Significantly higher COS levels were observed in the Northern Hemisphere by *Bingemer et al.* [1990], *Johnson et al.* [1993], and *Griffith et al.* [1998], suggesting a large contribution from anthropogenic sources in the Northern Hemisphere. Other measurements [*Torres et al.*, 1980; *Johnson,* 1985; *Staubes-Diederich,* 1992], however, found either a small enhancement in the COS mixing ratio of the Northern Hemisphere or none at all. At present, there is no convincing explanation for this discrepancy.

In this paper we present measurements of the spatial and temporal variations in atmospheric and marine COS during two Atlantic cruises of the German research vessel *Polarstern.* The mechanisms of COS production and decay are discussed based on their relationship to some of the parameters involved. The air-sea flux of COS along the cruise track is estimated and then extrapolated to obtain the potential contribution of the global open oceans to atmospheric COS.

2. Experimental

Marine air was collected in 4.5 L sample bags made of Tedlar PVF film (50 mm, Du Pont). To prevent contamination of the samples by sea spray and emission from the ship, the air was drawn at a rate of ~ 2 L min^{-1} from the crow's nest (~25 m above see level (asl)) to the top of the ship's bridge using a Teflon diaphragm pump (N86 KTE, KNF Neuberger). A well defined 0.2 L min^{-1} flow was used to fill the sample bag, while the remainder of the air flow from the pump was vented. The sampling interval was 15 min for a sample volume of ~ 3 L. After sampling, the air samples were normally analyzed within 30 min. Laboratory tests show that samples can be stored in the bags for more than 10 hours without any significant change in the COS content.

A Weiss-type seawater equilibrator (Figure 1) from the Max Planck Institute for Chemistry [*Bange et al.*, 1996] was used to obtain the saturation ratio (SR= $C_{\text{equilibrated air}}/C_{\text{ambient air}}$) and concentration of dissolved COS. This instrument, made entirely of Teflon, equilibrates the headspace air (~20 L) above a water surface with a continuous flow of 20 L min^{-1} of incoming seawater. The incoming seawater is sprayed through a nozzle into the headspace. The headspace air is cir-

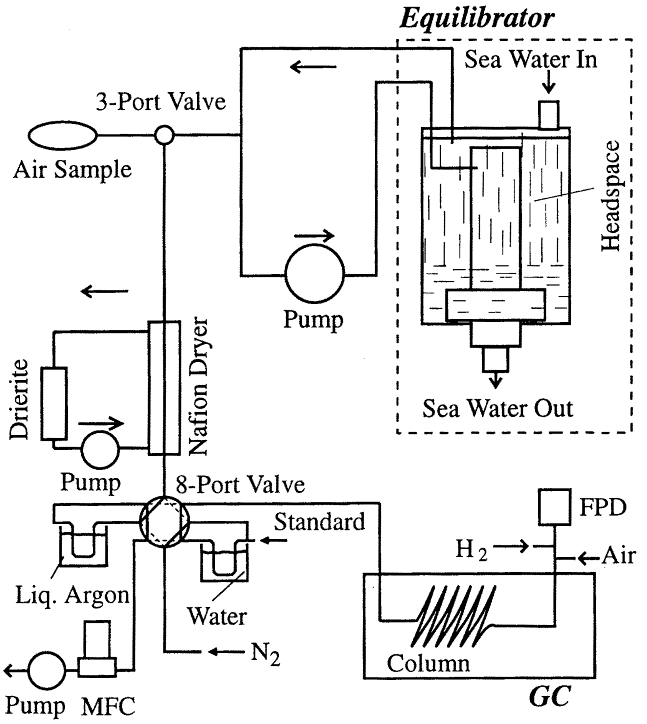

Figure 1. Gas chromatograph-based system for the analysis of air samples from Tedlar bags and from the headspace of a seawater equilibrator

culated at 5 L min^{-1} using a Teflon pump. The equilibrator is described in detail by *Butler et al.* [1988], *Bange et al.* [1996], and *Johnson* [1999]. Seawater was pumped from the intake in the "crossbeam-rudder-space" 5 m below surface by the ship's water pump. The residence time of water in the pumping system is ~ 2 min. In order to avoid stress or rupture of alga cells, seawater was not filtered. Comparison of the seawater temperature measured at the intake to that measured at the bow showed no significant difference, indicating a rapid exchange of seawater between the sampling location and the surroundings. The temperature of the seawater inside the equilibrator was measured using a calibrated digital thermometer. A slight warming of less than 0.7°C as compared to the seawater temperature at 5 m depth was observed. This has been taken into account in calculating the seawater COS concentrations.

Sulfur-containing gases were measured in the air from Tedlar bags and the headspace of the seawater equilibrator using the analytical system depicted in Figure 1. Ambient air or headspace air, selected using a three-port valve, was transferred at a rate of 60 mL min^{-1} through a silanized capillary glass loop (20 cm length, filled with 2 cm glasswool) immersed in liquid Argon (-186°C). To prevent the formation of ice in the glass loop, water vapor was removed by passing the sample through a Nafion dryer. Samples were enriched for 5-8 min. Typical sample volumes were 0.3-0.6 L. Upon switching the eight-port valve and warming the glass loop to room temperature, the trapped gases were injected into a gas chromatograph (GC, HP 5710A, Hewlett Packard) equipped with a flame photometric detector (FPD, Tracor). Sulfur-containing gases were separated on a 1.52 m × 3.175 mm Teflon column packed with Carbograph 1SC (Alltech). The chromatograph was programed to hold the sample at 40°C for 2 min followed by a heating phase in which the temperature was increased to 60°C at a rate of 16°C min^{-1}. The oven was then held at this temperature for 4 min. Nitrogen (99.999%, Messer Griesheim) was used as carrier gas at a flow rate of ~ 20 mL min^{-1}. Chromatograms were acquired and processed by an E-Lab chromatography system (OMS-Technology).

The analytical system was calibrated by the injection of a standard gas mixture into one of the glass loops, using a gas tight Teflon/glass syringe (Precision Sampling Corp.). The standard gas mixture was produced using permeation tubes (Valco VICI) kept at 30.0±0.1°C in a permeation dilution device. The permeation rates were determined by weighing the tubes about once a month with an electronic balance (Sartorius). The permeation rate of COS was 79.4±7.3 ng min^{-1} with no significant temporal trend ($>1\sigma$) over a period of 18 months. During the cruise in 1998 a CH_3SH permeation tube with a permeation rate of 71.3±2.5 ng min^{-1} was used for calibration. As no such tube was available during the cruise in 1997, we calibrated the CH_3SH peaks indirectly using the COS calibration curves and taking into consideration the different sensitivity of the system to COS and to CH_3SH. Calibration of the GC was carried out on all observational days during the cruises except October 20, 1997. However, owing to a leak in the permeation system which was not discovered until October 25, 1997, the calibrations on the first few days of the cruise in 1997 yielded incorrect values. As a result, all samples analyzed prior to that date could only be evaluated on the basis of the calibration curves from October 25, 1997. This could have led to a larger uncertainty for the data obtained during the first 8 days of this cruise. Since the subsequent daily calibrations agreed to better than 10%, we believe that the inherent uncertainty should not be significantly larger than 10%, assuming that our GC/FPD worked stably during the entire cruise.

On the basis of the reproducibility of the standard samples, we estimate the analytical precision for COS to be 3%. The overall precision of this method was better than 8%, based on the relative standard deviation of the COS mixing ratios of the air samples. However, for the reason mentioned above, the uncertainty of the data between October 17 and 24, 1997, could be somewhat larger.

Meteorological and oceanographical parameters were monitored by the ship's sensors. Wind speed and direction were measured at 37 m asl on both the port and starboard sides of the ship. Air temperature and humidity were measured at 27 m asl on the port and starboard sides of the ship. Only signals from the windward sensor were used. Seawater temperature and salinity were

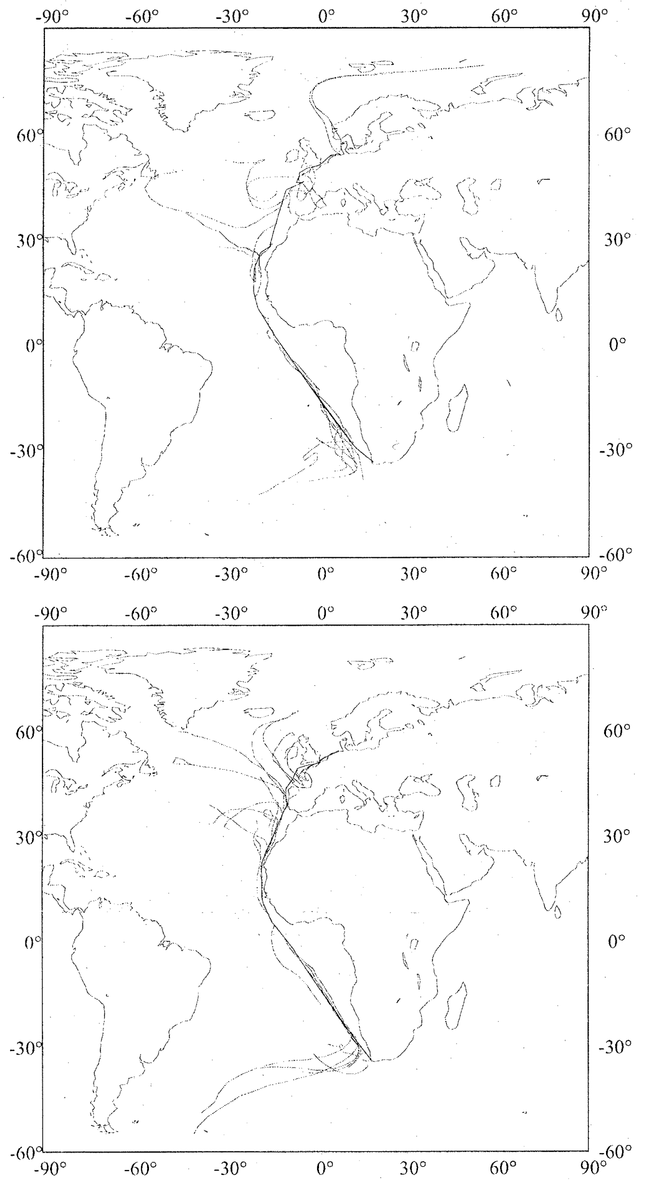

Figure 2. Cruise tracks and 108-hour backward air trajectories for air parcels arriving at sea level for the cruises (top) *ANT-XV/1* and (bottom) *ANT-XV/5*.

measured at the bow. The ship's position was determined by the Global Positioning System (GPS). The ship's data used in this paper are averaged over 30 min.

3. Results and Discussion

3.1. Cruises

Measurements of COS in marine air and surface seawater were made aboard the R/V *Polarstern* during the cruises *ANT-XV/1* (from Bremerhaven, Germany, to Cape Town, South Africa; October 15 to November 7, 1997) and *ANT-XV/5* (from Cape Town, South Africa, to Bremerhaven, Germany; May 26 to June 21, 1998). Figure 2 shows the cruise tracks for the two voyages and 108-hour backward trajectories as provided by the German Weather Service for air parcels arriving at 0000 UTC each day at sea level at the ship's position. During both cruises the ship sailed on the open ocean most of the time and passed through the North Atlantic Current, the Canary Current, the Equatorial Counter Current, the South Equatorial Current, and the Benguela Current. The backward trajectories indicate that the air masses had not been directly affected by the continents for at least 4-5 days prior to sampling, except on October 18 and 19, 1997, when air was advected from southern Europe (Spain and France). The Intertropical Convergence Zone (ITCZ) was located around 10°N and 5°N for the two cruises, respectively.

3.2. Seawater COS

COS concentrations in surface seawater were derived from the COS mixing ratios measured in the headspace of the equilibrator. The Henry's law constant and its temperature dependence according to *Johnson and Harrison* [1986] were used in the calculation. The dimensionless Henry's law constant H is given by

$$\ln(H) = 12.722 + \frac{3496}{T}, \qquad (1)$$

where T is the seawater temperature in K. Changes in H due to the slight warming of seawater in the equilibrator have been corrected for. The concentration and saturation ratio (SR) of COS in seawater and the global radiation (the solar radiation received from a solid angle of 2π steradian on a horizontal surface, *World Meteorological Organization (WMO)* [1996]) are plotted in Figure 3 for both cruises. As can be seen in the plots, the concentration and SR of seawater COS showed strong latitudinal and diurnal variation. The COS concentration ranged from 3.7 to 57.1 pmol L^{-1} during *ANT-XV/1* and from 3.0 to 182.5 pmol L^{-1} during *ANT-XV/5*. Enhanced marine levels of COS was observed in areas of high biological productivity, particularly during the warmer seasons, for example, in the Benguela Current in November, in the Northeast Atlantic in June and in the West African upwelling area. Pronounced diurnal cycles of dissolved COS and its saturation ratio were observed each day, with afternoon maxima and early morning minima. The diurnal cycle was especially pronounced on sunny days. An important feature of the saturation ratio profile is that the saturation ratio decreased to a level of undersaturation (SR<1.0) during the late night and early morning on most observational days, i.e., surface seawater takes up COS from the atmosphere during this period of the day. Although undersaturation of seawater COS has been observed during winter by *Weiss et al.* [1995] in the subtropical gyres and in temperate regions of the Pacific and by *Ulshöfer et al.* [1995] in the temperate North Atlantic, there have been no previous reports of such undersaturation as an almost regular diurnal feature of temperate and equatorial ocean waters during summer. Our data indicate that nocturnal COS undersaturation may occur regularly in Atlantic Ocean waters, even during the warmer seasons and in productive regions, enabling seawater to act as a sink for atmospheric COS during the late night and early morning. These measurements indicate that a further downward revision of the estimated net COS emission from the oceans may be necessary.

Figure 4 shows the normalized diurnal variations in the concentration of COS in seawater and in global radiation averaged along the cruise tracks. The diurnal cycle of dissolved COS is consistent with previous field observations [*Andreae and Ferek,* 1992; *Weiss et al.,* 1995]. Dissolved COS has a minimum in the early morning, increases rapidly after sunrise, and peaks around 1500 local time. The intensity of global radiation reaches its maximum at 1200 local time. There is a time lag of ~ 3 hours between the peak of the normalized COS concentration and that of the intensity of global radiation. During the daytime, dissolved COS is mainly produced by photochemical reactions and is removed by hydrolysis, downward mixing, and exhalation from seawater. After sunrise, the concentration of seawater COS increases because COS is produced more rapidly than it is removed. The photoproduction rate of seawater COS approaches its maximum around noon, but the concentration of dissolved COS does not, as the production rate still exceeds the removal rate. The concentration of dissolved COS peaks ~ 3 hours later (i.e., at around 1500), when the rate of production is balanced by the loss rate. Therefore the time lag observed is caused by the overall balance between the production and removal of dissolved COS.

The diurnal peak-to-peak amplitude of dissolved COS is correlated with the daily mean global radiation, which

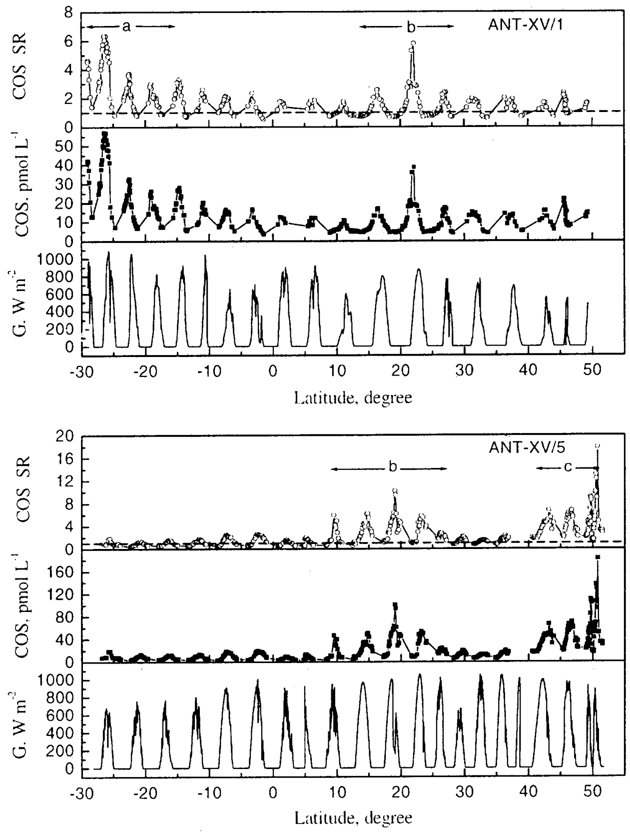

Figure 3. Concentration and saturation ratio of COS in seawater and the global radiation during the cruises *ANT-XV/1* (October 15 to November 7, 1997) and *ANT-XV/5* (May 26 to June 21, 1998). The dashed horizontal lines represent equilibrium (SR=1). The approximate positions of the Benguela Current, the West African upwelling area, and the Northeast Atlantic region are marked by a, b, and c, respectively.

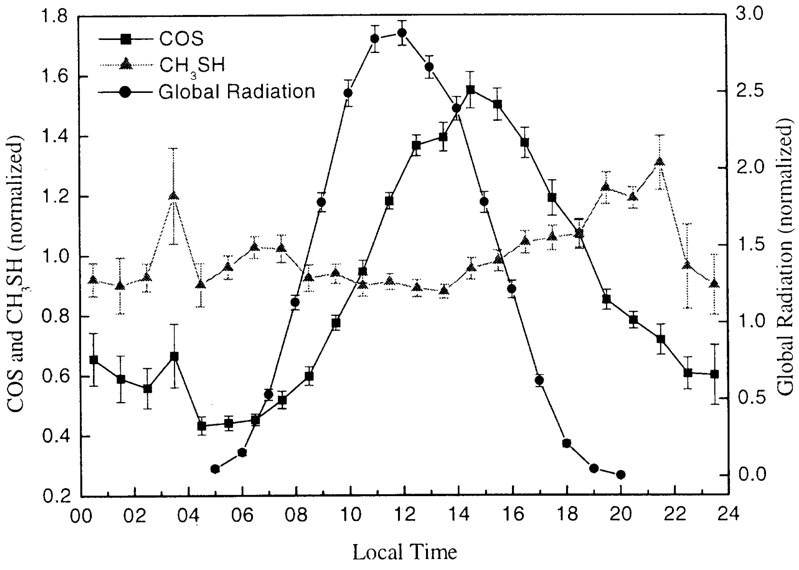

Figure 4. Diurnal variations in the concentration of dissolved COS and of CH_3SH and in global radiation during *ANT-XV/1* and *ANT-XV/5*. The individual data points are normalized to the daily mean values and then averaged over all observational days. The error bars indicate one standard error of the mean.

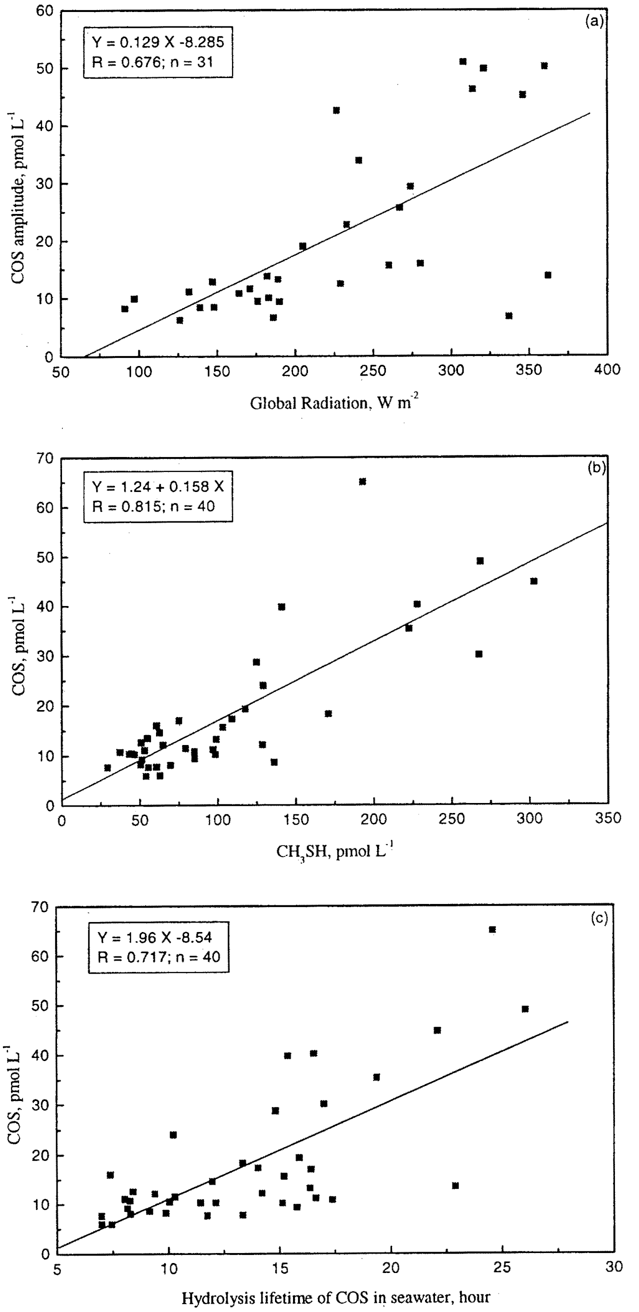

Figure 5. Correlation (a) between the COS peak-to-peak amplitude and global radiation, (b) between the daily mean COS and CH_3SH concentrations, and (c) between the daily means of the COS concentration and of the hydrolysis lifetime of COS in seawater. The lines show the least squares fit to the data. The regression parameters are shown in the corresponding boxes.

may be used as a proxy for incident solar radiation and UV flux (Figure 5a). This result is in accordance with other laboratory and field results which support the theory of COS photoproduction [*Ferek and Andreae,* 1984; *Uher,* 1994; *Zepp and Andreae,* 1994; *Ulshöfer et al.,* 1996; *Flöck and Andreae,* 1996].

CH_3SH has been proposed as a potential precursor to COS in seawater by *Ulshöfer et al.* [1996] and *Flöck and Andreae* [1996]. During incubation experiments with natural seawater, they observed an inverse relationship between the concentrations of COS and CH_3SH. *Pos et al.* [1998] proposed a sulfur-centered radical (thiyl or sulfhydryl) as the key sulfur intermediary in COS production based on mechanistic studies in seawater. Our measurements provide the first field evidence to support this view.

In almost all chromatograms of headspace samples, a CH_3SH peak was clearly identified. We are confident that the CH_3SH signal is not an artifact from the sampling system for the following reasons: (a) no substantial changes in the concentrations of COS and CH_3SH were observed after cleaning the system, which was usually done every 2 or 3 days during the cruises; (b) the diurnal cycle of the CH_3SH signal (see Figure 4) cannot be explained by production in the sampling system since the major physical parameters in the laboratory system (temperature, radiation) underwent no diurnal cycle. A direct calibration of CH_3SH was not possible during *ANT-XV/1*, as no CH_3SH permeation tube was available. The CH_3SH peaks from this cruise were therefore calibrated indirectly, using the COS calibration curves from the same day. Because the FPD is more sensitive to COS than to CH_3SH, this nonspecific calibration was then corrected for the sensitivity difference between COS and CH_3SH. The correction factor was derived from the COS and CH_3SH calibration curves obtained during the *ANT-XV/5* cruise, when direct simultaneous calibrations were conducted for both compounds. We used the Henry's law constant for CH_3SH given by *De Bruyn et al.* [1995] for the calculation of the seawater CH_3SH concentration. The concentration of dissolved CH_3SH was found to be 3-16 times higher than COS in the same water samples. The CH_3SH concentration varied inversely to COS during daylight (Figure 4), implying that COS was produced during the same photochemical process in which CH_3SH was destroyed. The relative diurnal amplitude of CH_3SH was smaller than that of COS, suggesting longer time constants for the sources and sinks of seawater CH_3SH. After eliminating the diurnal signal in the data by averaging over 24 hours, the resulting daily means of COS and CH_3SH are correlated at a highly significant level ($R = 0.815, n = 40$, Figure 5b) along the cruise tracks. The correlation between the two compounds suggests that CH_3SH is a key factor in the formation of COS in surface seawater.

Although other organosulfur compounds, such as glutathione (GSH), 3-mercaptopropionic acid (3-MPA), cysteine (CYS), may also act as COS precursors, as indicated by incubation experiments with synthetic seawater [*Flöck et al.,* 1997], there have as yet been no reports on the relationship between these compounds and COS in natural seawater. Future attempts to clarify this relationship would be worthwhile and would help improve our understanding of the formation mechanism of COS in seawater.

In addition to being produced photochemically, COS can also be produced in the dark. However, dark production normally only contributes a small amount (<30%) to COS formation and does not influence the COS diurnal cycle [*Ulshöfer et al.,* 1996; *Flöck and Andreae,* 1996]. Hydrolysis is the dominant sink for COS in seawater, causing the concentration of dissolved COS to decay to its nocturnal minimum. The hydrolysis rate constant can be calculated using theoretical equations or from experiment data. We obtained an average hydrolysis lifetime of 9.8 hours with a range between 4.8 and 15.5 hours by neglecting the dark production and applying an exponential fit of the nighttime decay of COS to our data from the nights of October 23 to 26, 1997. This hydrolysis lifetime compares well to theoretic values of 4.0-13.4 hours calculated using the models of *Elliot et al.* [1989] and *Radford-Knoery and Cutter* [1994] and implies a major role of hydrolysis in the removal of seawater COS. Furthermore, hydrolysis also seems to be one of the key factors controlling the large-scale geographical distribution of seawater COS. Figure 5c shows the significant correlation between the daily means of the COS concentration and of the hydrolysis lifetime of COS in seawater. Since each data point represents both a temporal and a spatial average, the observed correlation suggests that hydrolysis exerts a major influence on the concentration of dissolved COS. Further factors are the UV light intensity and concentrations of precursors.

3.3. COS Air-Sea Flux

As previously shown in Figure 3, the COS saturation ratio in surface seawater showed large latitudinal, seasonal, and diurnal variations. The calculated COS SR varied from 0.5 to 6.3 with an average of 1.8 during the cruise *ANT-XV/1* and from 0.4 to 17.9 with an average of 2.0 during the cruise *ANT-XV/5*.

In order to estimate the net contribution of the Atlantic waters to the atmospheric COS cycle, we calculated the COS air-sea flux F using the model of *Liss and Slater* [1974]:

$$F = k_w \left(C_w - \frac{C_a}{H} \right) = k_w \frac{C_a}{H} (\mathrm{SR} - 1), \qquad (2)$$

where C_a and C_w are the concentrations of COS in the atmosphere and in seawater, respectively, k_w is the air-sea exchange coefficient or piston velocity, H is Henry's law constant for COS in atm L mol^{-1}, and SR is the saturation ratio of COS. The dependence of H on water temperature has been well established by *Johnson and Harrison* [1986] (equation (1)). H varies by less than a factor of 2 over the normal range of seawater temperatures. The air-sea exchange coefficient k_w can be highly variable, and its dependence on atmospheric and oceanic conditions, such as wind speed, boundary layer stability, surfactants, bubbles, etc., has not yet been satisfactorily quantified. Nevertheless, several empirical models are available for calculating k_w. Three models developed by *Liss and Merlivat* [1986] (LM86), *Wanninkhof* [1992] (W92), and *Erickson* [1993] (E93) have been employed by various authors to estimate the COS air-sea flux [*Mihalopoulos et al.,* 1992; *Weiss et al.,* 1995; *Ulshöfer et al.,* 1995; *Ulshöfer and Andreae,* 1998]. The LM86 and W92 models only consider the influence of wind speed on k_w, whereas the E93 model takes into account both wind speed and thermal stability, which is a function of the temperature difference ($\Delta\theta$) between sea surface and air. Although there is no current consensus as to which model provides the best flux estimate, *Erickson* [1989] suggested that LM86 underestimates the k_w values. This was confirmed by *Putaud and Nguyen* [1996] in a study on dimethyl sulfide (DMS) air-sea exchange using micrometeorological techniques. Since the marine boundary layer was thermally unstable most of the time during the two cruises, we have only used the E93 stability dependent model for calculating k_w in this work.

The E93 model was developed on the basis of the "whitecap" model of *Monahan and Spillane* [1984], who assume a close relationship between the exchange coefficient and the whitecap coverage. The air-sea exchange coefficient k_w is expressed as

$$k_w = k_m (1 - W) + k_t W, \qquad (3)$$

where k_m and k_t are coefficients representing the conditions for a nonwhitecap area and for a turbulent whitecap area, respectively, and W is the fraction of the sea surface covered by whitecaps. W is proportional to the rate of energy input to a specified ocean area and depends on surface wind speed (V) and the local drag coefficient (C_D), which is itself a function of V and $\Delta\theta$. Details about the stability dependent model are described by *Erickson* [1993 and references therein]. In the current paper, wind speed and air and seawater temperatures for the calculation of W are taken from the measurements by the ship's sensors during the two cruises. Air temperature was measured at 27 m asl, seawater temperature at 5 m depth. Wind speed measured at 37 m asl was converted to that at 10 m asl using a logarithmic wind profile and the neutral drag coefficient of *Trenberth et al.* [1989].

Two sets of k_m and k_t values are available for (3). One set was derived by *Monahan and Spillane* [1984] based on radon data from projects Geochemical Ocean Sections Study (GEOSECS) and Transient Tracers in the Ocean (TTO). Another set of coefficients ($k_m = 5.0$ cm h^{-1} and $k_t = 1300$ cm h^{-1}) was derived in E93 and attempts to bring the low wind speed results into better agreement with observations while maintaining a global area weighted k_w value of 20.9 cm h^{-1} for CO_2. In this work the latter set of k_m and k_t values is used to calculate k_w for radon. The k_w values for radon were converted to k_w for COS using the relation:

Table 1. Statistics of the COS Measurements and Flux Estimates for the Open Atlantic Ocean During the Cruises in October-November 1997 and May-June 1998[a]

Parameter	October-November 1997	May-June 1998
n[b]	301	392
C_w[c], pmol L^{-1}	14.8±11.4	18.1±16.1
SR	1.8±1.2	2.0±1.6
H, atm L mol^{-1}	61.3±9.7	59.8±10.4
Sc[d]	543±95	562±107
W_s, m s^{-1}	5.4±2.4	7.5±2.9
$\Delta\theta$[e], K	0.9±0.8	1.3±1.9
k_w[f], m d^{-1}	2.1±0.7	3.7±2.8
$F_{\rm COS}$, nmol m^{-2} d^{-1}	13.4±19.5	28.6±47.8

[a] Statistics are given in mean$\pm 1\sigma$.

[b] Data obtained near the English Channel (north of 48°N) are excluded to remove the effect of shelf water.

[c] C_w was derived from the COS mixing ratio measured in the headspace air of the equilibrator. The Henry's law constant calculated using the empirical function of *Johnson and Harrison* [1986] was used for the derivation.

[d] Empirical equations, as given by *Siedler and Peters* [1986] were used for calculating the kinematic viscosity of seawater. The molecular diffusivity COS at 25°C is 1.94×10^{-5} cm^2 s^{-1} [*Sharma*, 1965]. The temperature dependence of the gas diffusivity reported by *Himmelblau* [1964] was used to calculate the COS diffusivity at other temperatures.

[e] Here $\Delta\theta$ is derived from the air temperature measured at 27 m asl and the seawater temperature measured at 5 m depth.

[f] The exchange coefficient was estimated using the stability dependent model [*Erickson,* 1993].

$$k_{\rm COS} = k_{\rm Rn}\left[\frac{Sc_{\rm COS}}{Sc_{\rm Rn}}\right]^{n} \qquad (4)$$

with the power dependence of the Schmidt number Sc (the ratio of the kinematic viscosity to the molecular diffusivity of a gas) as proposed by *Liss and Merlivat* [1986] and *Jähne et al.* [1987]:

$$n = -\frac{1}{2} \text{ for } V \geq 3.6 \text{ m s}^{-1}; \; n = -\frac{3}{4} \text{ for } V < 3.6 \text{ m s}^{-1}.$$

$Sc_{\rm Rn}$ was calculated using the temperature function given by *Erickson* [1993]. A set of empirical equations given by *Siedler and Peters* [1986] was used for calculating the kinematic viscosity of seawater. The molecular diffusivity of COS at 25°C is 1.94×10^{-5} cm^2 s^{-1} [*Sharma,* 1965]. The temperature dependence of the gas diffusivity as reported by *Himmelblau* [1964] was used for calculating the COS diffusivity at the other temperatures.

The estimated k_w values, as well as the COS fluxes and other related parameters for the two cruises, are listed in Table 1. The large deviations of these flux estimates are mainly due to the strong diurnal and latitudinal variation in the concentration of COS in seawater. Figure 6 shows the regional and seasonal variations in the COS air-sea flux. The largest COS emissions were observed in the productive regions of the summer hemisphere, i.e., in the Benguela Current in November and in both the Northeast Atlantic and the West African upwelling area in June. A small deposition flux (5.1 nmol COS m^{-2} d^{-1}) existed even in the productive Benguela Current during the southern winter. As shown in Table 1, the mean flux values for both cruises are positive, indicating a net COS emission from the ocean; however, there is a large variability associated with these values. By extrapolating our flux estimates for low and middle latitudes and the fluxes for the high latitudes (subpolar and polar) given by *Weiss et al.* [1995] to the global open oceans, we obtain a global open ocean source of 0.10 Tg COS yr^{-1}. This value should be considered as an upper limit since our measurements did not cover the high winter, when stronger deposition could occur, as shown by *Ulshöfer et al.* [1995]. Nevertheless, our flux estimate suggests that the global open ocean is probably a small source of atmospheric COS, rather than the minor sink suggested by *Weiss et al.* [1995]. On a global scale, the major COS emission of the ocean most likely occurs from coastal and shelf regions [*Weiss et al.,* 1995; *Ulshöfer and Andreae,* 1998].

3.4. Atmospheric COS

The latitudinal distribution of COS in the marine atmosphere is plotted in Figure 7. The COS mixing ratio averaged 474±33 and 502±38 pptv for the two cruises, respectively. During both cruises, the latitudinal distribution of atmospheric COS was more uniform than that obtained on other cruises with similar instrumentation [*Bingemer et al.,* 1990; *Staubes-Diederich,* 1992]. Nev-

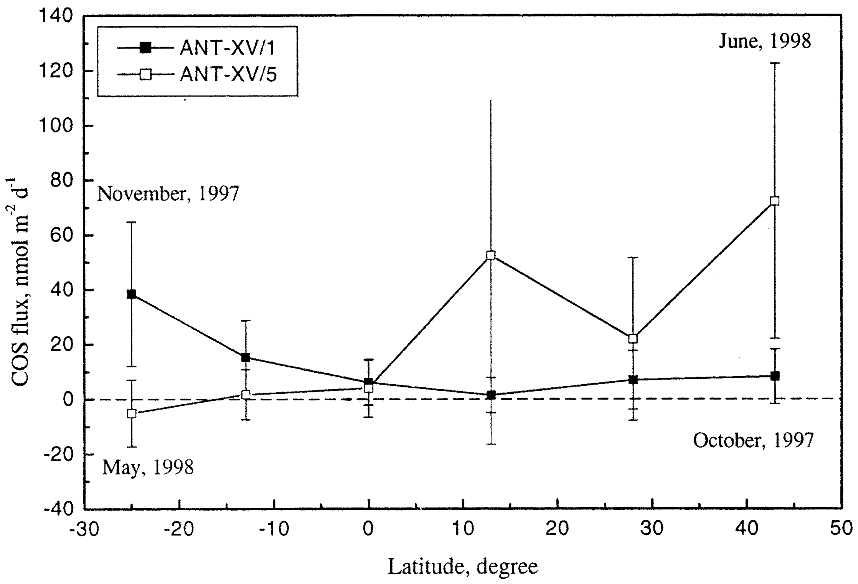

Figure 6. Regional and seasonal variation in the estimated COS air-sea flux during the two cruises. The dashed line represents zero flux. The error bars indicate one standard deviation from the mean values.

ertheless, it does have some characteristic features. The COS level in the subtropical and temperate regions was significantly lower than that observed in the equatorial and tropical regions. A similar distribution, i.e., a steep rise of the COS mixing ratio from the northern subtropical Atlantic toward the equator, was also observed by *Staubes-Diederich* [1992] in the fall of 1988. This author attributed the observed maximum near the equator to the transport of continental air from Africa. The backward trajectories in Figure 2 do not indicate any direct transport of air from the African continent to the ship during our measurements. However, it is possible that the tropospheric level of COS in the equatorial and the tropical bands were enhanced during the cruises by continental COS sources, such as biomass burning. According to remote observations of the European Space Agency (ESA), the seasonal distribution of the global number of fires peaked around September-October of 1997 and had a secondary maximum in May of 1998, with the latitudinal distribution peaking between 20°S and 20°N (see http://shark1.esrin.esa.it/ionia/FIRE/). As the tropical land surface may act both as a source

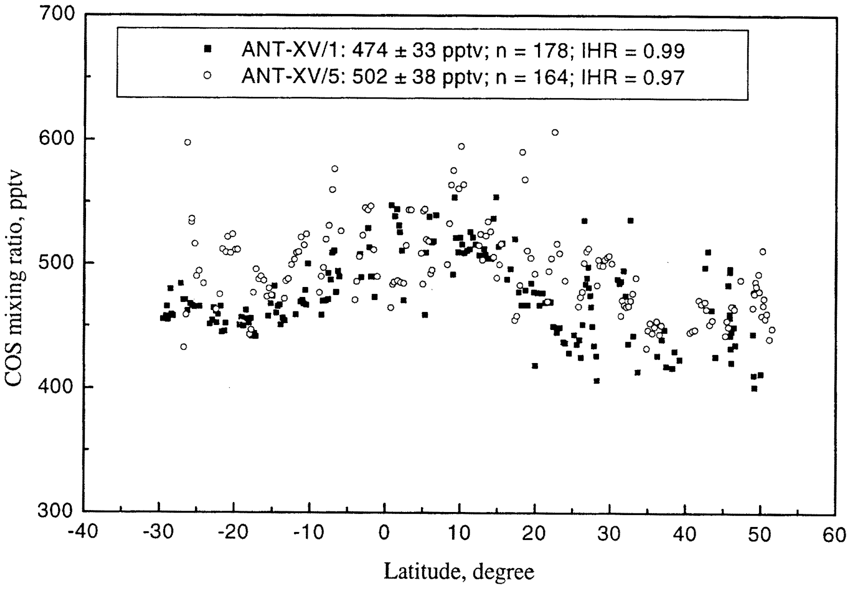

Figure 7. Latitudinal distribution of the COS mixing ratio in the marine boundary layer during the cruises *ANT-XV/1* and *ANT-XV/5*. The ITCZ was used to define the boundary of the air masses from the two hemispheres in the calculation of the interhemispheric ratio.

(biomass burning) and as a sink (assimilatory uptake) of atmospheric COS, this interpretation remains highly speculative. Enhanced levels of COS in the boundary layer have been observed during aircraft sampling of regional biomass burning plumes over tropical Africa [*Bingemer et al.,* 1992] and over the western Pacific Ocean after long range transport from southeast Asian fires [*Thornton et al.,* 1996]. *Thornton et al* [1996] also reported depletion of COS in air of continental origin owing to loss of COS to vegetation.

Interhemispheric ratios (IHR = $M_{\mathrm{NH}}/M_{\mathrm{SH}}$) of atmospheric COS in the range of 0.92-1.25 have been reported by other authors [*Torres et al.,* 1980; *Johnson,* 1985; *Bingemer et al.,* 1990; *Staubes-Diederich,* 1992; *Johnson et al.,* 1993; *Griffith et al.,* 1998]. It has been suggested that higher IHRs are caused by larger anthropogenic emissions in the Northern Hemisphere [*Bingemer et al.,* 1990; *Johnson et al.,* 1993]. Taking the ITCZ as the tropospheric boundary between the air masses of both hemispheres we obtain an IHR of 0.99 for the cruise *ANT-XV/1* and 0.97 for the cruise *ANT-XV/5.* Taking into consideration the standard errors of the mean for both hemispheres, these IHR values are not significantly different from unity, at the confidence level of 95%.

The IHR values in this work and those of 0.92 reported by *Johnson* [1985] and 0.96 and 0.99 by *Staubes-Diederich* [1992] do not support the idea of a significant contribution of industrial sources in the Northern Hemisphere to atmospheric COS levels. Nevertheless, it does not necessarily mean that such a contribution does not exist. As *Griffith et al.* [1998] point out, in situ measurements of IHR from cruises involve a change of season between hemispheres. On the basis of stationary long-term measurements of total column COS, averaging over several years and all seasons, Griffith et al. [1998] derive a mean IHR in the range 1.1-1.2. This robust estimate of IHR allows for significant anthropogenic emission in the Northern Hemisphere.

The variability in the IHR values derived from in situ measurements may be caused mainly by seasonal and geographical variations in the major sources and sinks of atmospheric COS. Ocean emission is highly dependent on the season, as shown by the data from this work and from *Weiss et al.* [1995]. Owing to the seasonality in plant physiology, the uptake of atmospheric COS by vegetation may have a seasonal variation, as does the CO_2 assimilation, especially in the middle and high latitudes. In addition, both the ocean source and the vegetation sink of COS may not be equally distributed between the hemispheres because of the asymmetric distribution of the ocean and vegetated areas between the two hemispheres [see *Bates et al.,* 1992]. Recent measurements suggest that soil represents a sink for atmospheric COS [*Kuhn et al.,* 1999]. *Watts* [2000] recently estimated a soil sink of 0.92 Tg COS yr^{-1} with an uncertainty of 85%. It is not known whether this sink also undergoes a seasonal variability or not. There is very little information about the temporal and geographical distributions of chemical COS sources (i.e., the oxidation of CS_2 and DMS). More studies on COS sources and sinks with emphasis in their temporal and spatial variations are needed. In view of the highly complex variability in time and space of all the major parameters involved, tests of the compatibility between the observed distributions of atmospheric COS and budget estimates are probably only possible in modeling studies.

4. Conclusions

Measurements during two Atlantic cruises showed strong spatial and temporal variations in the concentration of dissolved COS and its saturation ratio. Our data indicate that COS undersaturation exists in the low and midlatitudinal Atlantic waters, but it occurs regularly only during periods with no or little sunlight. Field evidences for a relationship between the concentrations of COS and CH_3SH in natural ocean water were presented for the first time. The significant correlation between the daily means of the COS concentration and of the hydrolysis lifetime of COS in seawater indicates the important role of hydrolysis in controlling the geographical distribution of COS in seawater. COS air-sea fluxes, estimated using the flux model of *Liss and Slater* [1974] and the stability dependent model of *Erickson* [1993] for the exchange coefficient, show strong regional and seasonal variations. The largest COS emissions were observed in productive regions in the warmer seasons. A small net deposition was found in the Benguela Current during the southern winter. On the basis of our fluxes for low and middle latitudes and the fluxes for high latitudes from *Weiss et al.* [1995], we estimate the upper limit for the global open ocean source for COS to be 0.10 Tg COS yr^{-1}, suggesting that the open ocean makes only a minor contribution to the budget of atmospheric COS. The COS measurements showed a relatively uniform latitudinal distribution in the marine atmosphere, with mixing ratios of 474±33 and 502±38 pptv for the 1997 and 1998 cruises, respectively. The mixing ratio of atmospheric COS showed several characteristic features in its latitudinal distribution, i.e., an enhanced level in the equatorial and tropical regions and lower levels in the subtropical and temperate regions. However, no significant interhemispheric gradient was observed, arguing against any significant contribution of industrial sources in the Northern Hemisphere.

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References

Adams, D. F., S. O. Farwell, M. R. Pack, and E. Robinson, Biogenic sulfur gas emissions from soils in eastern and southern United States, *J. Air Pollut. Control. Assoc.*, *31,* 1083-1089, 1981.

Andreae, M. O., and P. J. Crutzen, Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, *Science, 276,* 1052-1058, 1997.

Andreae, M. O., and R. J. Ferek, Photochemical production of carbonyl sulfide in seawater and its emission to the atmosphere, *Global Biogeochem. Cycles, 6,* 175-183, 1992.

Bandy, A. R., D. C. Thornton, D. L. Scott, M. Lalevic, E. E. Lewin, and A. R. Driedger III, A time series for carbonyl sulfide in the northern hemisphere, *J. Atmos. Chem., 14,* 527-534, 1992.

Bange, H. W., S. Rapsomanikis, and M. O. Andreae, The Aegean Sea as a source of atmospheric nitrous oxide and methane, *Mar. Chem., 53,* 41-49, 1996.

Bates, T. S., B. K. Lamb, A. Guenther, J. Dignon, and R. E. Stoiber, Sulfur emissions to the atmosphere from natural sources, *J. Atmos. Chem., 14,* 315-337, 1992.

Bingemer, H. G., S. Bürgermeister, R. L. Zimmermann, and H.-W. Georgii, Atmospheric COS: Evidence for a contribution anthropogenic sources?, *J. Geophys. Res., 95,* 20,617-20,622, 1990.

Bingemer, H. G., M. O. Andreae, T. W. Andreae, P. Artaxo, G. Helas, D. J. Jacob, N. Mihalopoulos, and B. C. Nguyen, Sulfur gases and aerosols in and above the equatorial African rain forest, *J. Geophys. Res., 97,* 6207-6217, 1992.

Butler, J. H., J. W. Elkins, C. M. Brunson, K. B. Egan, T. M. Thompson, T. J. Conway, and B. D. Hall, Trace gases in and over the West Pacific and East Indian Oceans during the El Niño Southern Oscillation event of 1987, *Data Rep. ERL ARL-16,* 104 pp., Nat. Oceanic and Atmos. Admin., Air Resource Lab, Silver Spring, Md., 1988.

Castro, M. S., and J. N. Galloway, A comparison of sulfur-free and ambient air enclosure techniques for measuring the exchange of reduced sulfur gases between soils and the atmosphere, *J. Geophys. Res., 96,* 15,427-15,437, 1991.

Chin, M., and D. D. Davis, Global sources and sinks of OCS and CS_2 and their distributions, *Global Biogeochem. Cycles, 7,* 321-337, 1993.

Chin, M., and D. D. Davis, A reanalysis of carbonyl sulfide as a source of stratospheric background sulfur aerosol, *J. Geophys. Res., 100,* 8993-9005, 1995.

Crutzen, P. J., The possible importance of CSO for the sulfate layer of the stratosphere, *Geophys. Res. Lett., 3,* 73-76, 1976.

De Bruyn, W. J., E. Swartz, J. H. Hu, J. A. Shorter, P. Davidovits, D. R. Worsnop, M. S. Zahniser, and C. E. Kolb, Henry's law solubilities and Setchenow Coefficients for biogenic reduced sulfur species obtained from gas-liquid uptake measurements, *J. Geophys. Res., 100,* 7245-7251, 1995.

De Mello, W. Z., and M. E. Hines, Application of static and dynamic enclosures for determining dimethyl sulfide and carbonyl sulfide exchange in sphagnum peatlands: Implications for the magnitude and direction of flux, *J. Geophys. Res., 99,* 14,601-14,607, 1994.

Elliot, S., E. Lu, and F. S. Rowland, Rates and mechanisms of the hydrolysis of carbonyl sulfide in natural waters, *Environ. Sci. Technol., 23,* 458-461, 1989.

Engel, A., and U. Schmidt, Vertical profile measurements of carbonylsulfide in the stratosphere, *Geophys. Res. Lett., 21,* 2219-2222, 1994.

Erickson, D. J., III, Variations in the global sea-air transfer velocity field of CO_2, *Global Biogeochem. Cycles, 3,* 37-41, 1989.

Erickson, D. J., III, A stability dependent theory for air-sea gas exchange, *J. Geophys. Res., 98,* 8471-8488, 1993.

Ferek, R. J., and M. O. Andreae, The supersaturation of carbonyl sulfide in surface waters of the Pacific Ocean off Peru, *Geophys. Res. Lett., 10,* 393-396, 1983.

Ferek, R. J., and M. O. Andreae, Photochemical production of carbonyl sulphide in marine surface waters, *Nature, 307,* 148-150, 1984.

Flöck, O. R., and M. O. Andreae, Photochemical and non-photochemical formation and destruction of carbonyl sulfide and methyl mercaptan in ocean waters, *Mar. Chem., 54,* 11-26, 1996.

Flöck, O. R., M. O. Andreae, and M. Dräger, Environmentally relevant precursors of carbonyl sulfide in aquatic systems, *Mar. Chem., 59,* 71-85, 1997.

Goldan, P. D., W. C. Kuster, D. L. Albritton, and F. C. Fehsenfeld, The measurement of natural sulfur emissions from soil and vegetation: Three sites in the Eastern United States revisited, *J. Atmos. Chem., 5,* 439-467, 1987.

Griffith, D. W. T., N. B. Jones, and W. A., Matthews, Interhemispheric ratio and annual cycle of carbonyl sulphide (OCS) total column from ground-based solar FTIR spectra, *J. Geophys. Res., 103,* 8447-8454, 1998.

Himmelblau, D. M., Diffusion of dissolved gases in liquids, *Chem. Rev., 64,* 527-550, 1964.

Jähne, B., K. O. Münnich, R. B. A. Dutzi, W. Huber, and P. Libner, On the parameters influencing air-water gas exchange, *J. Geophys. Res., 92,* 1937-1949, 1987.

Johnson, J. E., The role of the oceans in the atmospheric cycle of carbonyl sulfide, Ph.D. dissertation, Univ. of Washington, Seattle, 1985.

Johnson, J. E., Evaluation of a seawater equilibrator for shipboard analysis of dissolved oceanic trace gases, *Anal. Chim. Acta, 99,* 119-132, 1999.

Johnson, J. E., and H. Harrison, Carbonyl sulfide concentrations in the surface waters and above the Pacific Ocean, *J. Geophys. Res., 91,* 7883-7888, 1986.

Johnson, J. E., A. R. Bandy, D. C. Thornton, and T. S. Bates, Measurements of atmospheric carbonyl sulfide during the NASA Chemical Instrument Test and Evaluation Project: Implications for the global COS budget, *J. Geophys. Res., 98,* 23,443-23,448, 1993.

Khalil, M. A. K., and R. A. Rasmussen, Global sources, lifetimes and mass balances of carbonyl sulfide (OCS) and carbon disulfide (CS_2) in the Earth's atmosphere, *Atmos. Environ., 18,* 1805-1813, 1984.

Kjellström, E., A three-dimensional global model study of carbonyl sulfide in the troposphere and the lower stratosphere, *J. Atmos. Chem., 29,* 151-177, 1998.

Kuhn, U., C. Ammann, A. Wolf, F. X. Meixner, M. O. Andreae, and J. Kesselmeier, Carbonyl sulfide exchange on an ecosystem scale: Soil represents a dominant sink for atmospheric COS, *Atmos. Environ., 33,* 995-1008, 1999.

Lacis, A., J. Hansen, and M. Sato, Climate forcing by stratospheric aerosols, *Geophys. Res. Lett., 19,* 1607-1610, 1992.

Lamb, B., H. Westberh, G. Allwine, L. Bamesberger, and A. Guenther, Measurement of biogenic sulfur emission from soil and vegetation: Application of dynamic enclosure methods with Natusch filter, and GC/FPD analysis, *J. Atmos. Chem., 5,* 417-437, 1987.

Liss, P. S., and L. Merlivat, Air-sea gas exchange rates: Introduction and system, in *The Role of Air-Sea Exchange in Geochemical Cycling,* edited by P. Buat-Menard, pp. 113-127, D. Reidel, Norwell, Mass., 1986.

Liss, P. S., and P. G. Slater, Flux of gases across the air-sea interface, *Nature, 247,* 181-184, 1974.

MacTarggart, D. L., D. F. Adams, and S. O. Farwell, Measurement of biogenic sulfur emissions from soils and vegetation using dynamic enclosure methods: Total sulfur gas emission via MFC/FD/FPD determinations, *J. Atmos. Chem., 5,* 417-437, 1987.

Mihalopoulos, N., J. P. Putaud, B. C. Nguyen, and S. Belviso, Annual variation of atmospheric carbonyl sulfide in the marine atmosphere in the southern Indian Ocean, *J. Atmos. Chem., 13,* 73-82, 1991.

Mihalopoulos, N., B. C. Nguyen, J. P. Putaud, and S. Belviso, The oceanic source of carbonyl sulfide (COS), *Atmos. Environ., 26,* 1383-1394, 1992.

Monahan, E. C., and M. C. Spillane, The role of oceanic whitecaps in air-sea gas exchange, in *Gas Transfer at Water Surfaces*, edited by W. Brutsaert and G.H. Jirka, pp. 495-503, D. Reidel, Norwell, Mass., 1984.

Najjar, R. G., D. J. Erickson III, and S. Madronich, Modeling the air-sea fluxes of gases formed from the decomposition of dissolved organic matter: Carbonyl sulfide and carbon monoxide, in *Role of Nonliving Organic Matter in the Earth's Carbon Cycle*, edited by R. G. Zepp and Ch. Sonntag, pp. 107-132, John Wiley, New York, 1995.

Pos, W.H., D. D. Riemer, and R. G. Zika, Carbonyl sulfide (OCS) and carbon monoxide (CO) in natural waters: Evidence of a coupled production pathway, *Mar. Chem., 62,* 89-101, 1998.

Putaud, J. P., and B. C. Nguyen, Assessment of dimethylsulfide sea-air exchange rate, *J. Geophys. Res., 101,* 4403-4411, 1996.

Radford-Knoery, J., and G. A. Cutter, Biogeochemistry of dissolved hydrogen sulfide and carbonyl sulfide in the western North Atlantic Ocean, *Geochim. Cosmochim. Acta, 58,* 5421-5431, 1994.

Rasmussen, R. A., M. A. K. Khalil, and S. D. Hoyt, The oceanic source of carbonyl sulfide (OCS), *Atmos. Environ., 16,* 1591-1594, 1982.

Rinsland, C. P., R. Zander, E. Mahieu, P. Demoulin, A. Goldman, D. H. Ehhalt, and J. Rudolph, Ground-based infrared measurements of carbonyl sulfide total column abundance: Long-term trends and variability, *J. Geophys. Res., 97,* 5995-6002, 1992.

Rinsland, C. P., et al., Trends of OCS, HCN, SF_6, $CHClF_2$ (HCFC-22) in the lower stratosphere from 1985 and 1994 atmospheric trace molecule spectroscopy experiment measurements near 30°N latitude, *Geophys. Res. Let., 23,* 2349-2352, 1996.

Rodriguez, J. M., M. K. W. Ko, and N. D. Sze, Role of heterogeneous conversion of N_2O_5 on sulphate aerosols in global ozone loses, *Nature, 352,* 134-137, 1991.

Sharma, M. M., Kinetics of reactions of carbonyl sulphide and carbon dioxide with amines and catalysis by Brønsted bases of the hydrolysis of COS, *Trans. Faraday Soc., 61,* 681-688, 1965.

Siedler, G., and H. Peters, Properties of sea water, in *Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology, vol. 3: Oceanography,* edited by J. Sündermann, pp. 233-264, Springer-Verlag, New York, 1986.

Solomon, S., R. W. Sanders, R. R. Garcia, and J. G. Keys, Increased chlorine dioxide over Antarctica caused by volcanic aerosols from Mount Pinatubo, *Nature, 363,* 245-248, 1993.

Staubes, R., H.-W. Georgii, and G. Ockelmann, Flux of COS, DMS, and CS_2 from various soils in Germany, *Tellus, Ser. B, 41,* 305-313, 1989.

Staubes-Diederich, R., Verteilung von Dimethylsulfid, Carbonylsufid und Schwefelkohlenstoff in Ozean und mariner Atmosphäre, Ph.D. thesis, J. W. Goethe Univ., Frankfurt am Main, Germany, 1992.

Sze, N. D., and M. K. W. Ko, CS_2 and COS in the stratospheric sulphur budget, *Nature, 280,* 308-310, 1979.

Thornton, D. C., A. R. Bandy, and B. W. Blomquist, Impact of anthropogenic and biogenic sources and sinks on carbonyl sulfide in north Pacific troposphere, *J. Geophys. Res., 101,* 1873-1881, 1996.

Toon, O. B., and J. B. Pollack, Stratospheric aerosols and climate, in *The Stratospheric Aerosol Layer*, edited by R.C. Whitten, pp. 121-146, Springer-Verlag, New York, 1982.

Torres, A. L., P. J. Maroulis, A. B. Goldberg, and A. R. Bandy, Atmospheric COS measurements on project GAMETAG, *J. Geophys. Res., 85,* 7357-7360, 1980.

Turco, R. P., R. C. Whitten, O. B. Toon, J. B. Pollack, and P. Hamill, COS, stratospheric aerosol and climate, *Nature, 283,* 283-285, 1980.

Trenberth, K. E., W. G. Large, and J. G. Olson, The effective drag coefficient for evaluating wind stress over the oceans, *J. Clim., 2,* 1507-1516, 1989.

Uher, G., Photochemische Produktion von Carbonyl Sulfid (COS) im Oberflächenwasser der Ozeane: Prozeßstudien und ein empirisches Modell, Ph.D. thesis, Univ. of Mainz, Mainz, Germany, 1994.

Ulshöfer, V. S., and M. O. Andreae, Carbonyl sulfide (COS) in the surface ocean and the atmospheric COS budget, *Aquatic Geochem., 3,* 283-303, 1998.

Ulshöfer, V. S., G. Uher, and M. O. Andreae, Evidence for a winter sink of atmospheric carbonyl sulfide in the northeast Atlantic Ocean, *Geophys. Res. Lett., 22,* 2601-2604, 1995.

Ulshöfer, V. S., O. R. Flöck, G. Uher, and M. O. Andreae, Photochemical production and air-sea exchange of carbonyl sulfide in the eastern Mediterranean Sea, *Mar. Chem., 53,* 25-39, 1996.

Wanninkhof, R., Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res., 97,* 7373-7382, 1992.

Watts, S. F., The mass budgets of carbonyl sulfide, dimethyl sulfide, carbon disulfide and hydrogen sulfide, *Atmos. Environ., 34,* 761-779, 2000.

Weisenstein, D. K., G. K. Yue, M. K. W. Ko, N. D. Sze, J.M. Rodriguez, and C.J. Scott, A two-dimensional model for sulfur species and aerosols, *J. Geophys. Res., 102,* 13,019-13,035, 1997.

Weiss, P. S., J. E. Johnson, R. H. Gammon, and T. S. Bates, Reevaluation of the open ocean source of carbonyl sulfide to the atmosphere, *J. Geophys. Res., 100,* 23,083-23,092, 1995.

World Meteorological Organization (WMO), *Guide to Meteorological Instruments and Methods of Observation*, 6th ed., Geneva, 1996.

Zepp, R. G., and M. O. Andreae, Factors affecting the photochemical production of carbonyl sulfide in sea water, *Geophys. Res. Lett., 21,* 2813-2816, 1994.

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