

Carbon disulfide in the North Atlantic and Pacific Oceans

Huixiang Xie and Robert M. Moore

Department of Oceanography, Dalhousie University, Halifax, Nova Scotia, Canada

Abstract. Carbon disulfide (CS_2) was determined in surface waters of the North Atlantic and Pacific Oceans. The mean concentrations (and ranges) of CS_2 in open ocean waters were 13.4 (7.8–26.1) $\mu\text{M S}$ (picomol sulfur per liter) for the North Atlantic and 14.6 (7.2–27.5) $\mu\text{M S}$ for the Pacific. The concentrations in the coastal waters of the North Atlantic averaged 26.4 $\mu\text{M S}$ and ranged from 17.9 to 40.4 $\mu\text{M S}$. Warm waters generally contained higher levels of CS_2 than did cold waters. All the study areas were found to be supersaturated in CS_2 relative to the atmosphere based on calculations from published CS_2 mixing ratios in the marine boundary layer and their Henry's law constants. Sea-to-air fluxes of CS_2 were estimated using exchange velocities for spot and climatological wind speeds. The global oceanic flux extrapolated from this study is 0.18 $\text{Tg CS}_2 \text{ yr}^{-1}$ and in the range 0.13–0.24 $\text{Tg CS}_2 \text{ yr}^{-1}$. It is suggested that microbial processes, photochemical reactions, and phytoplankton activity are potential sources for oceanic CS_2 .

1. Introduction

Carbon disulfide is considered to be a minor sulfur-bearing constituent in the global sulfur budget [Wine *et al.*, 1981; Kim and Andreae, 1987; Andreae, 1990]. However, the importance of this reduced sulfur species is recognized by its potential role as a major precursor for atmospheric carbonyl sulfide (OCS), which indirectly affects Earth's climate and environment through its involvement in the formation of stratospheric sulfate aerosols [Crutzen, 1976; Barns *et al.*, 1983; Khalil and Rasmussen, 1984; Hofmann, 1990; Chin and Davis, 1993]. As a result of cloud transportation and its relatively long lifetime (~1 week) compared with other reactive reduced sulfur species, such as dimethyl sulfide, methyl mercaptan, and dimethyl disulfide (minutes to hours), CS_2 is also probably a significant contributor to sulfur dioxide in the middle and upper troposphere [Chatfield and Crutzen, 1984].

Since the first seawater measurements of CS_2 made by Lovelock [1974], the ocean has been on the list of candidates as sources for atmospheric CS_2 . Kim and Andreae [1987, 1992] measured CS_2 in the midlatitudes of the North Atlantic and arrived at an oceanic emission rate of 0.26 $\text{Tg CS}_2 \text{ yr}^{-1}$. In an expedition to the Antarctic region, Staubes and Georgii [1993] failed to detect the existence of CS_2 for most of their water samples, probably owing to a high instrumental detection limit (13 $\mu\text{M S}$) (picomol sulfur per liter). Although a number of workers [Bandy *et al.*, 1982; Jørgensen and Okholm-Hansen, 1985; Turner and Liss, 1985; Wakeham *et al.*, 1987] reported sporadic measurements in coastal, saline marsh, or estuarine waters, the work of Lovelock [1974] and Kim and Andreae [1987, 1992] remains the only reasonably well documented field CS_2 analysis, particularly for the open ocean.

In 1995 and 1996, we determined CS_2 in the high latitudes of the North Atlantic and in the Pacific Ocean from 40°N to

40°S. The purposes of these studies are to expand the current CS_2 data set and thus improve its ocean-to-atmosphere flux estimate and to better characterize the biogeochemical processes responsible for CS_2 production in seawater. Results from surface water measurements are presented here.

2. Methods

Measurements were made during three cruises covering the areas of Labrador Sea (Figure 1a), northeast Atlantic off Ireland (Figure 1b), and the Pacific Ocean (Figure 1c). The Labrador Sea survey was carried out on the Canadian Scientific Ship (CSS) *Hudson* in July 1995, the northeast Atlantic voyage was on the British Royal Research Ship (RRS) *Challenger* from early June to early July 1996, and the Pacific expedition was conducted on the National Oceanic and Atmospheric Administration Ship (NOAAS) *Discoverer* in October and November 1995.

Water was taken using either a submersible pump (*Hudson* cruise) or 1-L stainless steel Knudsen bottles equipped with Teflon seals (*Challenger* cruise) or 10-L Niskin bottles (*Discoverer* cruise). Surface water was also intermittently collected with a galvanized bucket. Prior to the field trip, the Knudsen bottles were checked for CS_2 contamination. This involved filling the bottles with deionized water (Nanopure UV) and analyzing aliquots of this water at an interval of ~2 hours. None of the bottles showed contamination for a tested period of ~12 hours. The difference in CS_2 concentrations between the bucket samples and the samples from the Knudsen bottles was within 5%. Samples from the pump or the Niskin bottles were cross-checked against those from the bucket and no significant differences between the three methods were observed. Subsamples were drawn into 100-mL ground glass syringes and stored in a covered seawater tank or a bucket of seawater. They were analyzed within 6 hours, with no significant storage artifacts detected.

Analysis was performed using gas chromatography-mass spectrometry interfaced with a purge-trap technique. Moore *et al.* [1996] describe the details of this system. In summary, a 40-mL sample was purged for 12 mins with an ultrahigh pu-

Copyright 1999 by the American Geophysical Union.

Paper number 1998JC900074.
0148-0227/99/1998JC900074\$09.00

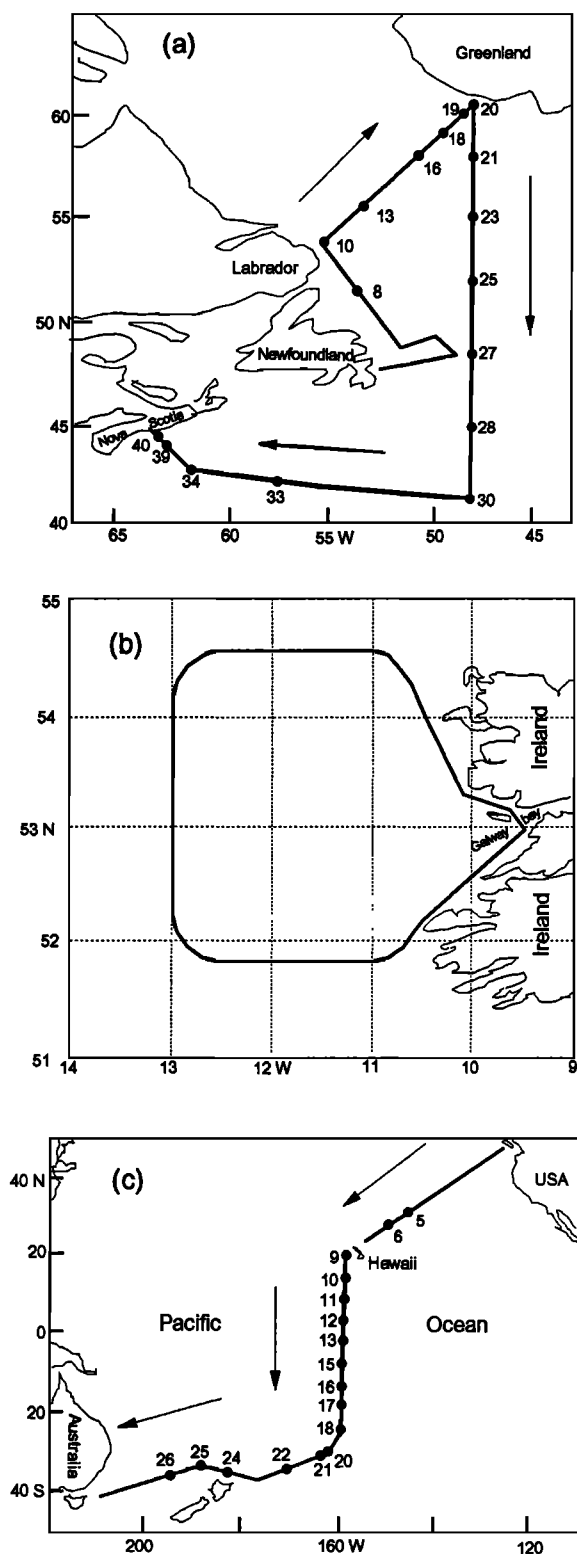


Figure 1. Location maps showing (a) cruise track and station positions of CSS *Hudson*, 1995; (b) investigated area (framed solid lines) by RRS *Challenger*, 1996; and (c) cruise track and station positions of NOAA *Discoverer*, 1995.

urity (UHP) helium stream (40 mL min^{-1}). CS_2 and other volatiles from the purge stream were cryotrapped into a stainless steel tube, subsequently desorbed, and then transported by a stream of UHP helium (5 mL min^{-1}) to a DB-624 column for

separation. The eluted components were detected using a VG MD800 mass selective detector. Reanalysis of stripped water samples showed no detectable CS_2 . The precision of this method was evaluated by sequentially measuring six replicates of a water sample collected at 100 m at a station during the *Challenger* cruise. The relative standard deviation was 1.4% at a 10 pM S level. The detection limit of the system, defined either as the amount of CS_2 corresponding to a peak area of twice the instrumental noise or as 3σ of 17 blanks determined during the *Challenger* cruise, was 1.5 pM S .

For the *Hudson* cruise a liquid standard was gravimetrically prepared by injecting a known amount of pure CS_2 into a known amount of ethylene glycol. Calibrations were made by analyzing a series of water samples containing varying amounts of the standard. For the *Challenger* and *Discoverer* cruises, measurements were calibrated using a gravimetrically produced gas standard containing 1.49 parts per million by volume (ppmv) of CS_2 in UHP nitrogen stored in a 29.5-L Aculife-treated aluminum cylinder. Calibration curves were constructed by injecting volumes of the standard between 10 and $50 \mu\text{L}$ via a septum port using Hamilton syringes. The liquid and gas standards were checked against each other, and no difference exceeding the analytical uncertainty was observed.

Determinations of methyl chloride, methyl bromide, methyl iodide, and isoprene were also made. Results of methyl chloride from the *Hudson* and *Discoverer* cruises have been reported by Moore *et al.* [1996].

3. Results and Discussion

3.1. Surface Concentrations

Relative to the open oceans, higher concentrations of CS_2 were observed in coastal waters (Table 1), as reported by previous studies [Lovelock, 1974; Kim and Andreae, 1987, 1992]. The concentration in nearshore waters off Nova Scotia and Greenland averaged 25.8 pM S , similar to the concentration of 27.1 pM S observed in waters near or in Galway Bay, Ireland. These values were almost twice as high as those from the open ocean waters.

The mean concentrations of CS_2 in the open oceans were fairly constant, whereas the concentration ranges for the *Hudson* ($7.8\text{--}26.1 \text{ pM S}$) and *Discoverer* ($7.2\text{--}27.5 \text{ pM S}$) cruises were much greater than those for the *Challenger* cruise ($8.3\text{--}17.6 \text{ pM S}$) (Table 1), probably because of wider ranges of biological and physical properties spanned by the *Hudson* and *Discoverer* transects. To test for possible relationships between CS_2 concentration and biological or physical parameters, we plotted CS_2 concentration, chlorophyll *a* level and sea surface temperature along cruise tracks and found no simple correlations (Figures 2-4). However, it was obvious that, in

Table 1. CS_2 Concentrations in Surface Waters

Surveyed Area	Concentration, pM S
Coastal Waters	
Labrador Sea	25.8 (17.9-34.5)
Northeast Atlantic	27.1 (19.9-40.4)
Open Ocean Waters	
Labrador Sea	13.4 (7.8-26.1)
Pacific Ocean	14.6 (7.2-27.5)
Northeast Atlantic	12.2 (8.3-17.6)

Concentrations are mean values with ranges in parentheses.

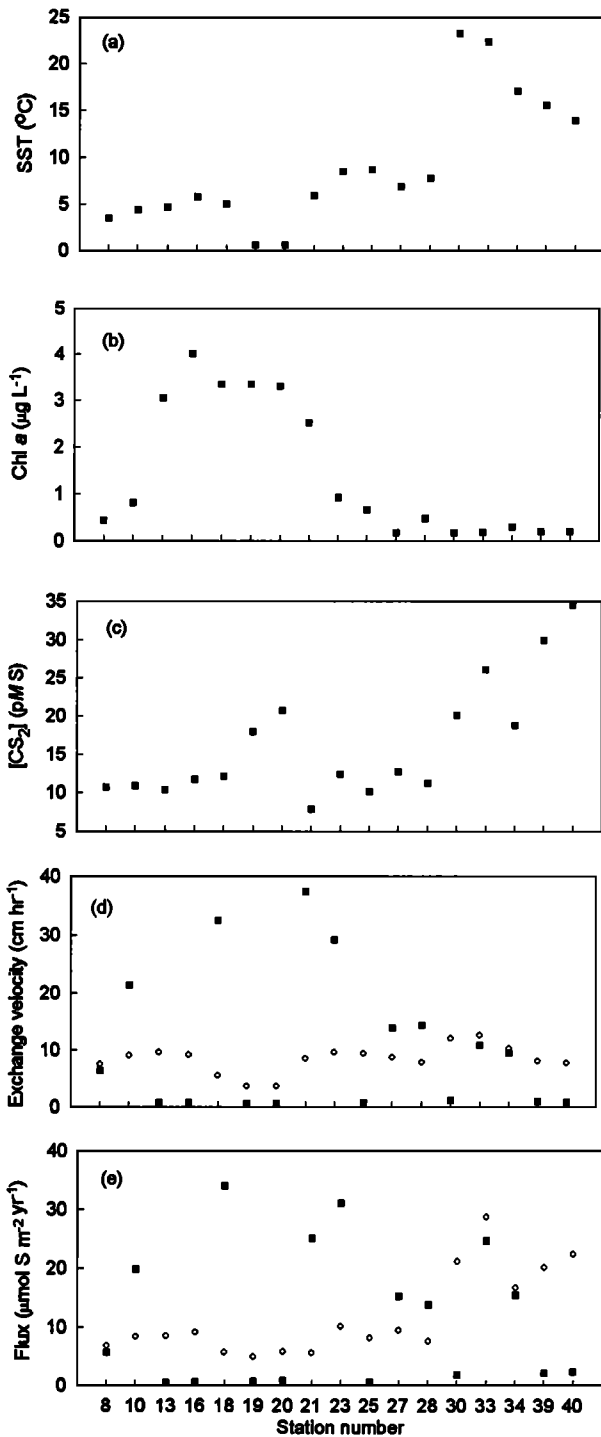


Figure 2. Surface data along the *Hudson* cruise track. (a) sea surface temperature (SST); (b) chlorophyll *a*; (c) concentration of CS₂; (d) exchange velocities from the Wanninkhof [1992] relationship using spot wind speed (solid squares) and climatological wind speed (open circles); and (e) flux estimates of CS₂ using exchange velocities in figure 2d, with solid squares from spot wind speed and open circles from climatological wind speed.

the open oceans, warm waters were more enriched with CS₂ than cool waters. This was strongly evidenced by more than a doubling of the CS₂ concentration when the *Hudson* traversed from the cool Labrador Sea waters into the warm Gulf

Stream waters (stations 30 and 33 in Figure 2). Kim and Andreae [1987] also reported elevated CS₂ levels in the Gulf Stream. Excluding the coastal areas, the broad data set embracing all the three cruises displays a positive linear correlation between CS₂ concentration and temperature ($[CS_2] = 7.2 + 0.39 t$, $r = 0.584$, $n = 57$, where t is temperature in degrees Celsius, r is correlation coefficient, and n is number of samples). No such relationship exists between CS₂ and chlorophyll.

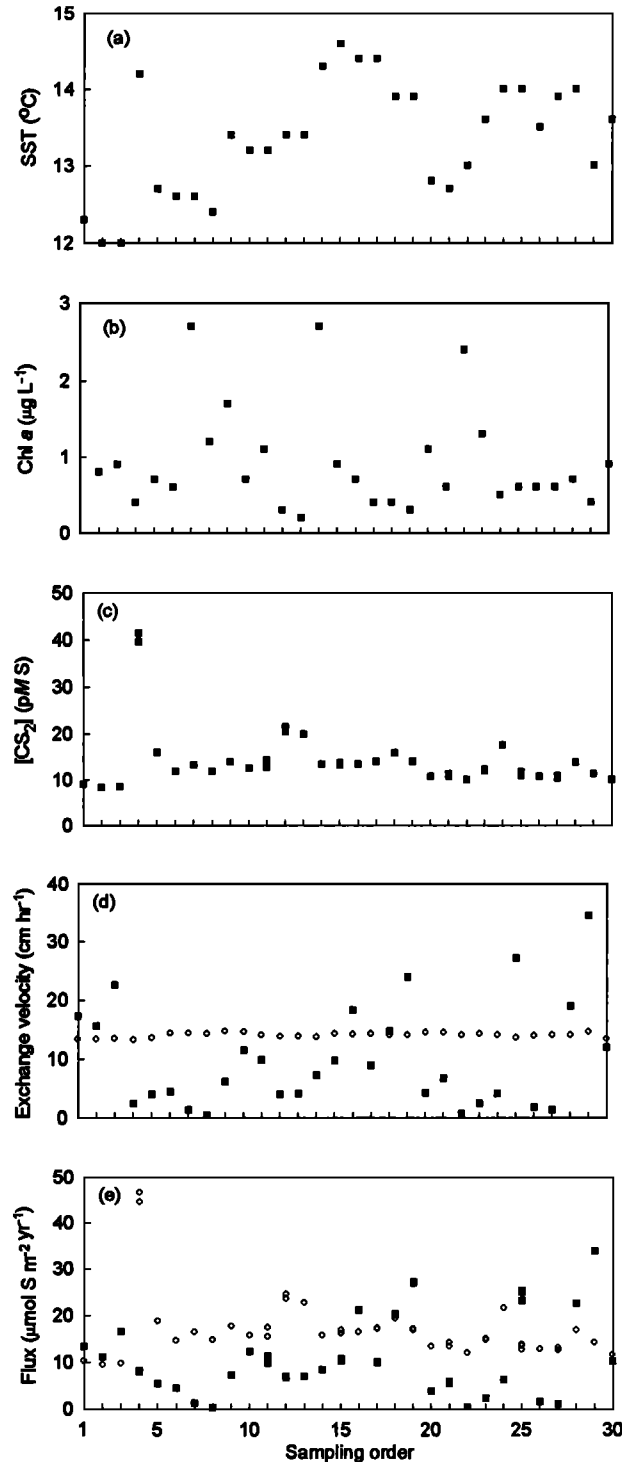


Figure 3. Same as Figure 2, but along the *Challenger* cruise track

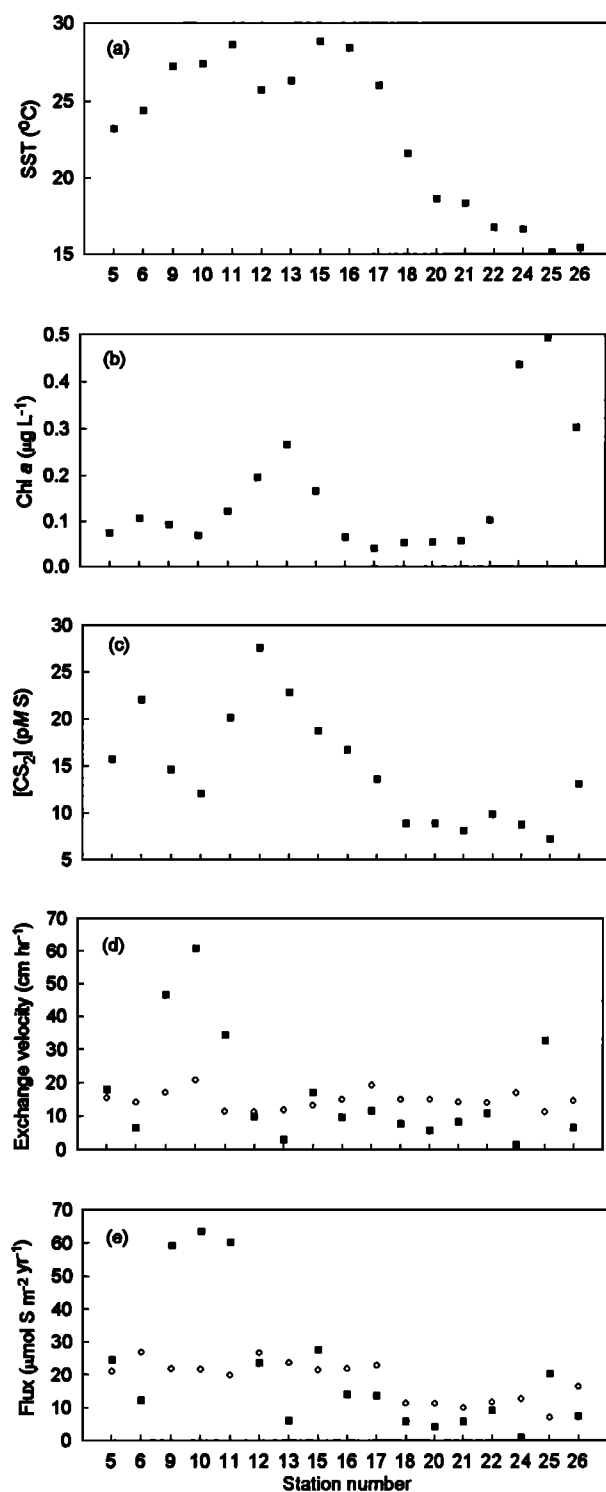


Figure 4. Same as Figure 2, but along the *Discoverer* cruise track.

3.2. Flux Estimates

The saturation ratio (SR) of CS_2 is defined as

$$SR = C_{g,eq} / C_g$$

$$SR = H C_1 / C_2$$

where $C_{g,eq}$ is the atmospheric CS_2 concentration in equilibrium with seawater, C_1 and C_2 are water phase and air phase

concentrations of the compound, respectively; and H is the dimensionless Henry's law constant. Using the Henry's law constants provided by Elliott [1989] and assuming the atmospheric mixing ratio of CS_2 to be 2 parts per trillion by volume (pptv) in the marine boundary layer over the open ocean and 10 pptv over coastal waters [Kim and Andreae, 1987; Bandy et al., 1993; Johnson and Bates, 1993; Thornton and Bandy, 1993], we found a mean saturation ratio of 41 in the range from 6 to 124. De Bruyn et al. [1995] also measured the Henry's law constants for CS_2 , and their values are, on average, 41% larger than those from Elliott [1989] in the range 5°–25°C. Thus the saturation ratio would be accordingly 41% higher had we used the Henry's law constants from De Bruyn et al. [1995]. It is therefore evident that all the investigated waters were highly supersaturated in CS_2 .

Estimates of CS_2 flux across the sea-air interface were made using the laminar layer model of Liss and Slater [1974] expressed as

$$F = k (C_1 - C_g / H)$$

$$F = k C_1 (1 - 1 / SR) \quad (1)$$

where k is the exchange velocity and other terms are defined as above. A number of formulas are available addressing the relationship between the exchange velocity and wind speed [Liss and Merlivat, 1986; Wanninkhof, 1992; Erickson, 1993], and substantial differences exist in the value of k yielded from these formulas. The Wanninkhof relationship is normalized to the global measurements of $^{14}CO_2$, and fitted to wind speed on a quadratic dependence:

$$k = 0.31 u^2 (Sc / 660)^{-0.5} \quad (2)$$

or

$$k = 0.39 u_{av}^2 (Sc / 660)^{-0.5} \quad (3)$$

where u is a spot measurement of wind speed in meters per second, u_{av} is a long-term averaged wind speed, and Sc is the Schmidt number for CS_2 at the appropriate temperature. Sc is the ratio of the kinematic viscosity of seawater to the diffusion coefficient of CS_2 . The kinematic viscosity of distilled water was obtained using its dynamic viscosity [Sengers and Waston, 1986] and density [Lide, 1996]; the diffusion coefficient of CS_2 in distilled water was derived from the relationship of Wilke and Chang [1955]. The two terms were converted to values in seawater using the methods given by Wanninkhof [1992]. We fitted Sc of CS_2 to a temperature relationship of $Sc = 3377.8 - 221.71 t + 6.9370 t^2 - 0.08751 t^3$ ($r^2 = 0.9999$, $n = 301$), where t is temperature in degrees Celsius.

The relationship of Liss and Merlivat [1986] (herein after referred as to LM) expresses the exchange velocity as a function of wind speed in three linear segments,

$$k = 0.17 u, u \leq 3.6 \quad (4)$$

$$k = 2.85 u - 9.65, 3.6 < u \leq 13 \quad (5)$$

$$k = 5.9 u - 49.3, u > 13. \quad (6)$$

The three equations are normalized to a gas with $Sc = 600$, and corrections need to be made if $Sc \neq 600$. Specifically, $k \propto Sc^{-2/3}$ for $u \leq 3.6$ m s⁻¹ and $k \propto Sc^{-1/2}$ for higher wind speeds [Liss and Merlivat, 1986]. It is suggested that short-term wind speeds are more appropriate than long-term averaged wind

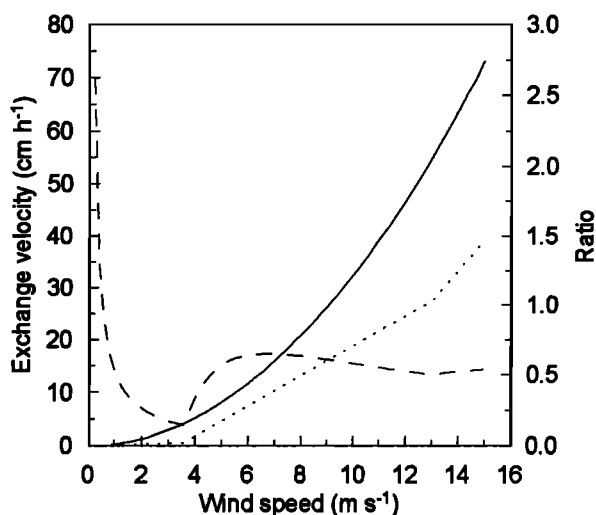


Figure 5. Exchange velocity as a function of wind speed. Solid line is from the Wanninkhof [1992] relationship (see equation (2)) dotted line is from the Liss and Merlivat [1986] relationship, and dashed line is the ratio of the dotted line to the solid line.

speeds for the LM equations [Wanninkhof, 1992]. The LM approach is based on the results from tracer experiments conducted on small lakes and from wind-wave tank studies [Wanninkhof, 1992, and reference therein]. Recent dual tracer experiments implemented on sea [Watson *et al.*, 1991; Liss *et al.*, 1993] provided support for the LM predictions, although the double-tracer technique is suspected to yield low exchange velocities at high wind speeds [Wanninkhof, 1992, and reference therein].

Figure 5 compares the relationship of LM with that of Wanninkhof. With the exception of extremely low wind speeds (≤ 0.5 m s⁻¹), the LM relationship gives significantly lower exchange velocities than the Wanninkhof relationship. In a wind speed range 1-15 m s⁻¹, the average exchange velocity derived from the LM relationship is 46% lower than that obtained from the Wanninkhof formulation.

We estimated CS₂ fluxes using exchange velocities from either (2), (3), or (4)-(6) and the Henry's law constants from Elliott [1989]. Spot wind speeds, recorded concurrently with sampling of water samples, were taken for (2) and (4)-(6), and climatological wind speeds were used for (3). The climatological wind speeds were extracted from the Comprehensive Ocean-Atmosphere Data Set (COADS) (1946-1989). Moore and Webb [1996] and Moore *et al.* [1996] discussed the advantages and disadvantages of adopting spot or climatological wind speed. The exchange velocities and fluxes derived from

(2) and (3) are plotted along cruise tracks (Figures 2-4). As expected, the exchange velocity and flux calculated from the climatological wind speeds are less variable than those from the spot wind speeds. Table 2 summarizes flux estimates for the three cruises. In the coastal regions where we sampled, fluxes obtained from spot wind speeds are much smaller than those from climatological wind speeds, indicating that the spot wind speeds in these areas were greatly biased toward low values. To a lesser extent, this also happens in the open NE Atlantic. By contrast, in the open ocean of the Labrador Sea and the Pacific, the fluxes derived from the spot wind speeds are slightly greater than those from the climatological wind speeds. Consistent with Figure 5, the LM relationship yields significantly lower fluxes than the Wanninkhof formulation. The mean flux derived from the former is only 29% of that from the latter for the coastal waters and 57% for the open ocean. The lower percentage for the coastal waters is mainly a result of the lower wind speeds encountered during the field investigations. The spot wind speed measured for the coastal waters averaged 2.9 m s⁻¹ and ranged from 2.0 to 4.4 m s⁻¹, while the mean spot wind speed for the open ocean was 6.9 m s⁻¹ with 79% of the individual wind speeds above 4.0 m s⁻¹. As shown in Figure 5, the ratio of the exchange velocity from the LM relationship to that from the Wanninkhof formulation is much lower at a wind speed of ~ 3 m s⁻¹ than at ~ 7 m s⁻¹, which obviously exerts similar effects on the fluxes derived from these two relationships. We also calculated the fluxes using the Henry's law constants from De Bruyn *et al.* [1995]. The results were essentially identical to those obtained using the constants from Elliott [1989]. This is not surprising because the atmospheric concentration of CS₂ is negligible compared with that in equilibrium with seawater, no matter which set of Henry's law parameterizations is chosen to compute the equilibrated concentrations. Therefore the term in (1) that involves the ratio C_g / HC_1 (i.e., $1 / SR$) can actually be ignored in the flux calculation.

Two methods have been employed to extrapolate our flux estimates to the global oceans. Following the procedures of Bates *et al.* [1987] and Mihalopoulos *et al.* [1992], the first method separates the ocean into coastal and open sea areas and further divides the open sea into five latitudinal regions. Each region is assigned a unit area flux obtained from our measurements in the corresponding region. The calculated regional fluxes and other related data are shown in Table 3. The unit area flux gradually decreases poleward, except in the subtropical regions, where it is smaller than in the temperate waters. This may reflect the seasonal variations of CS₂ flux since most of the measurements in the subtropical areas were made in austral spring while all the field surveys in the temperate latitudes took place in boreal summer. The contribu-

Table 2. Flux Estimates of CS₂ in the Investigated Oceans

Surveyed Area	Exchange Velocity From Wanninkhof [1992]		Exchange Velocity From Liss and Merlivat [1986]
	SWS	CWS	SWS
		Coastal Waters	
Labrador Sea	1.6 (0.8-2.5)	13.4 (5.0-22.4)	0.4 (0.2-0.6)
Northeast Atlantic	7.2 (6.7-8.0)	30.8 (22.7-45.6)	2.4 (1.0-3.1)
		Open Ocean Waters	
Labrador Sea	12.9 (0.6-31.1)	11.3 (5.6-28.7)	7.3 (0.1-15.9)
Pacific Ocean	21.0 (1.0-63.6)	18.0 (6.9-26.9)	11.8 (0.2-34.0)
Northeast Atlantic	11.2 (0.4-33.8)	15.0 (9.6-21.5)	6.4 (0.1-16.9)

Fluxes (in $\mu\text{mol m}^{-2} \text{yr}^{-1}$) are mean values with ranges in parentheses. SWS is spot wind speed and CWS is climatological wind speed.

Table 3. Flux Estimates of CS₂ in the Global Oceans Using Method 1

Region	Latitude, degree	Area, 10 ¹² m ²	Unit Flux, μmol S m ⁻² yr ⁻¹	Flux, Tg CS ₂ yr ⁻¹
Equatorial	0-5	32	25.1	0.030
Tropical	5-20	92	21.4	0.075
Subtropical	20-35	77	14.2	0.042
Temperate	35-50	67	16.8	0.043
Subarctic	50-65	48	13.5	0.025
Coastal	0-50	49	20.8	0.039
Total		365		0.25

Area data are from *Bates et al.* [1987], except for the coastal waters, which are from *Andreae* [1986].

tion of CS₂ evasion from each region to the atmosphere results from a combination of the unit area flux and the area for that region, ranking the tropical oceans as a main contributor and the subarctic areas as a minor one. CS₂ flux from coastal regions is comparable with that from the subtropical or temperate waters. The annual oceanic flux is thus estimated to be 0.25 Tg CS₂.

The second method is based on our observation that CS₂ flux is strongly related to sea surface temperature (Figure 6). Figure 6 includes all the open ocean flux data from the three cruises, using (2) for calculating exchange velocities. The increase in flux with water temperature is a coupled consequence of the positive correlation found between CS₂ concentration and water temperature and the inverse relationship between the Schmidt number and water temperature. We have grouped the open ocean into three types of waters by temperature, specifically, waters below 10°C, between 10° and 20°C, and above 20°C. Areas of these waters are 12-month averages estimated from the COADS monthly mean sea surface temperature data. In a fashion analogous to that in the first method, a unit area flux is assigned to each type of water. The estimated global flux is 0.24 Tg CS₂ yr⁻¹ (Table 4), in good agreement with the result of the first method. This agreement is not surprising since the regional subdivisions of the world ocean in method 1 basically reflect the general patterns of the surface ocean temperature.

The magnitude of our flux estimate will decrease to ~0.13 Tg CS₂ yr⁻¹ if we use the LM equations for calculating the exchange velocities. Since there is no consensus on which rela-

tionship is more accurate, the best estimate from this study is defined as the average of the fluxes derived from the two relationships, the value being 0.18 Tg CS₂ yr⁻¹ with a range from 0.13 to 0.24 Tg CS₂ yr⁻¹. *Kim and Andreae* [1987] reported the sea-to-air flux of CS₂ to be 0.26 (0.13-0.52) Tg CS₂ yr⁻¹ based on the measurements in the mid-latitudes of the North Atlantic. *Chin and Davis* [1993] tried to improve this estimate by taking into account the seasonal and diurnal variation in the flux and arrived at a value of 0.18 (0.09-0.36) Tg CS₂ yr⁻¹. Therefore the flux estimate from this work agrees well with that obtained by *Chin and Davis* [1993], but it is 31% less than that yielded by *Kim and Andreae* [1987]. Our estimate represents 32% (23-42%) of the total annual CS₂ emission to the atmosphere derived by *Chin and Davis* [1993].

Seasonal variations in CS₂ flux were not taken into account in our estimates owing to lack of data with complete seasonal coverage in the visited ocean areas. In particular, no seawater measurements of CS₂ have ever been made in winter months, making it hard to further refine the flux estimates. Moreover, in the flux calculation, it is implicitly assumed that the concentration of CS₂ is not affected by wind speed. As pointed out by *Moore et al.* [1996] in dealing with the case of methyl chloride, this is not true if a high wind speed persists for such a time that the resulting elevated flux cannot be sustained simply because the loss terms overtake the production processes in a water column, inevitably resulting in a decrease in CS₂ concentration. It is, however, difficult to quantify the uncertainty of this effect in the estimates of CS₂ flux we have made, as we do not have a quantitative knowledge of the in situ loss and production processes.

None of the present flux estimates is large enough to match predictions from atmospheric models, which suggest an oceanic source of the order of ~10 Tg CS₂ yr⁻¹ [*Rodhe and Isaksson*, 1980; *Wine et al.*, 1981; *Chatfield and Crutzen*, 1984; *Toon et al.*, 1987]. These models utilized ~30 pptv of atmospheric CS₂ at ground level [*Sandalls and Penkett*, 1977; *Maroulis and Bandy*, 1980; *Bandy et al.*, 1981, 1986], which has been proved to be inappropriately high for unpolluted marine air. A more recent and generally accepted mixing ratio of CS₂ in remote marine boundary layer is a few parts per trillion by volume [*Kim and Andreae*, 1987; *Bandy et al.*, 1993; *Johnson*

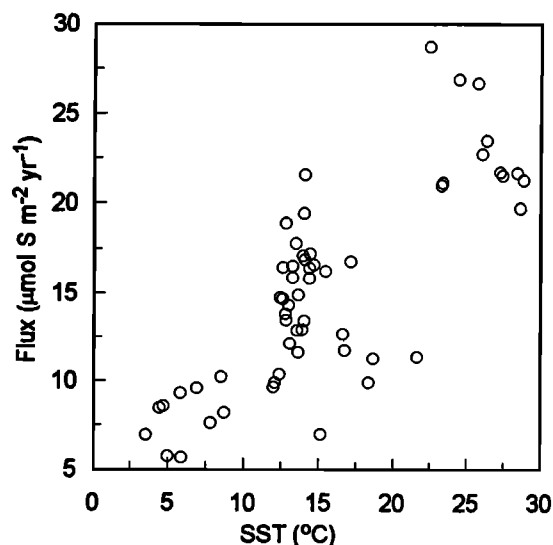


Figure 6. Flux of CS₂ versus sea surface temperature (SST). See detailed description in text.

Table 4. Flux Estimates of CS₂ in the Global Oceans Using Method 2

Temperature, °C	Area, 10 ¹² m ²	Unit flux, μmol S m ⁻² yr ⁻¹	Flux, Tg CS ₂ yr ⁻¹
≤10	77	8.0	0.023
10-20	75	14.4	0.041
>20	164	22.1	0.138
Coastal	49	20.8	0.039
Total	365		0.24

and Bates, 1993; Thornton and Bandy, 1993], which would lead to much lower modeled fluxes.

3.3. Sources of Oceanic CS₂

Previous studies [Kim and Andreae, 1987, 1992; Chin and Davis, 1993] and this work have indicated that the ocean is an important source for atmospheric CS₂. However, the processes that produce CS₂ in marine waters remain poorly understood. In this section we try to summarize the current knowledge about sources of this compound within the ocean.

Andreae [1986] suggested that bacteria-mediated fermentation and reaction of H₂S with organic matter may produce CS₂ in anoxic aquatic environments. This proposition explains well the high concentrations of CS₂ found in sediment pore waters, stagnant bays, coastal wetlands, and salt marshes where anaerobic microbial processes predominate [Lovelock, 1974; Bandy et al., 1982; Wakeham et al., 1987]. It is also supported by the observation that a strong concentration gradient of CS₂ coincided with an O₂-H₂S transition zone in a stratified coastal salt pond [Wakeham et al., 1987]. Diffusion from underlying sediments is probably responsible for high concentrations of CS₂ observed in the deep ocean [Kim and Andreae, 1992; Xie et al., 1998]. However, a sedimentary source alone is insufficient to account for vertical profiles that are characterized by either pronounced, high surface concentrations or subsurface peaks [Kim and Andreae, 1992; Xie et al., 1998]. Processes other than microbial activities in sediments must account for these observations.

Xie et al. [1998] reported photochemical production of CS₂ in the northeast Atlantic off Ireland. The average apparent quantum yield spectrum indicates that the solar UV radiation (290-380 nm) is most effective at inducing formation of CS₂, with visible light having little effect. Photoproduction rate of CS₂ is positively correlated with absorptivity at 350 nm, suggesting that this production is probably mediated by colored dissolved organic matter (CDOM). Coastal waters dominated by terrestrial CDOM are thought to be more photochemically reactive than open ocean waters mainly containing marine CDOM [Kieber et al., 1990; Dister and Zafiriou, 1993]. Higher concentrations of CS₂ observed in coastal waters relative to the open ocean seem to be caused by enhanced photoproduction as well as larger diffusional input from underlying sediments in coastal areas. The potential photoproduction of CS₂ in world oceans extrapolated from the Xie et al. [1998] study is 0.49 Tg CS₂ yr⁻¹, which alone could account for the estimated ocean sources as presented above. Nevertheless, as discussed by Xie et al., it is not a simple matter to extrapolate from a small region, sampled in one season, to the global ocean.

Little attention has been paid to the possibility of a marine algal source, perhaps because Lovelock [1974] reported no release of CS₂ from the algal species he examined. Unfortunately, Lovelock did not reveal any details of the species tested and the experimental conditions employed. Unialgal cultures done in our laboratory have demonstrated that some species of phytoplankton are capable of producing a significant amount of CS₂ [Xie et al., 1998]. The organisms that we have tested included *Chaetoceros calcitrans*, *Phaeodactylum tricoratum*, *Phaeocystis* sp., *Porphyridium purpureum*, *Synechococcus* sp., and *Isochrysis* sp.. Three of these six species, namely, *Chaetoceros calcitrans*, *Phaeodactylum tricoratum*, and *Phaeocystis* sp., were identified to be significant

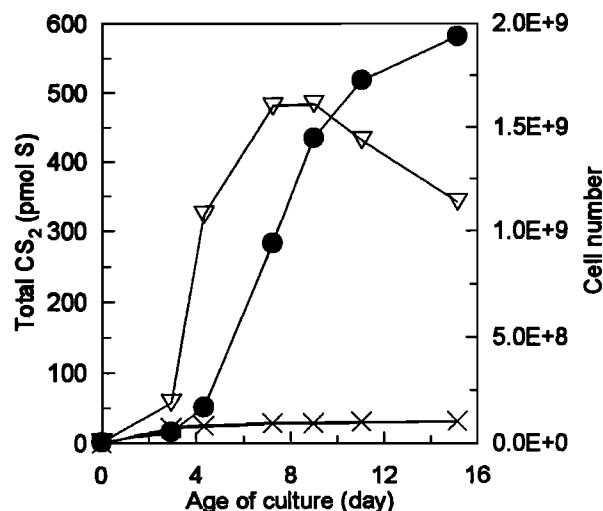


Figure 7. Change of total amount of CS₂ with time in a unialgal and axenic culture of *Chaetoceros calcitrans* incubated under cool-white fluorescent light and temperature-controlled (18°C) conditions. Circles are total CS₂ in the culture, crosses are total CS₂ in the cell-free control, and triangles are total cell number in the culture.

producers of CS₂. Figure 7 shows the total amount of the sulfur compound as a function of time in the *C. calcitrans* culture. Accumulation of CS₂ mainly occurred during cell growth and leveled off at senescence. Our experimental evidence indicated that cool-white fluorescent light, which was used for incubating the cultures, is essentially incapable of inducing CS₂ photoproduction. Thus the production of the compound in these cultures was more likely associated with biological processes.

A direct algal source is also supported by depth profiles obtained in the North Pacific central gyre (Figure 8). A notable feature of these profiles is the coexistence of the CS₂ and chlorophyll *a* maxima within the density gradient at the base of the mixed layer. The maximum in CS₂ occurred below 50 m. Photoproduction should be of little significance for formation of the subsurface CS₂ peak because of depletion of UV radiation at depth. As suggested by Moore et al. [1995] and Taguchi et al. [1988], the deep chlorophyll maximum was probably due to the abundant photosynthetic pigments produced by low-light-adapted algal cells held in the stabilized layers. These algal species might be able to emit CS₂ that was trapped within the pycnocline because of suppressed vertical mixing.

Figure 8 also shows that CS₂ concentration dropped rapidly below the subsurface maximum. However, the compound was detectable even at our maximum sampling depth of ~300 m. In particular, the profile of station 9 showed fairly high concentrations (~20 pM S) at 200 and 300 m. The likelihood of a sampling artifact at these two depths is small, because the same bottles were used to collect samples for other stations that showed much lower concentrations below 200 m. Vertical profiles reported in previous studies [Kim and Andreae, 1992; Xie et al., 1998] indicate that CS₂ is present throughout the water column and that highly pronounced concentration of the compound in deep waters is not a rare phenomenon. In order to maintain the presence of CS₂ in deep waters, physical transport and/or dark production must exist to compensate for

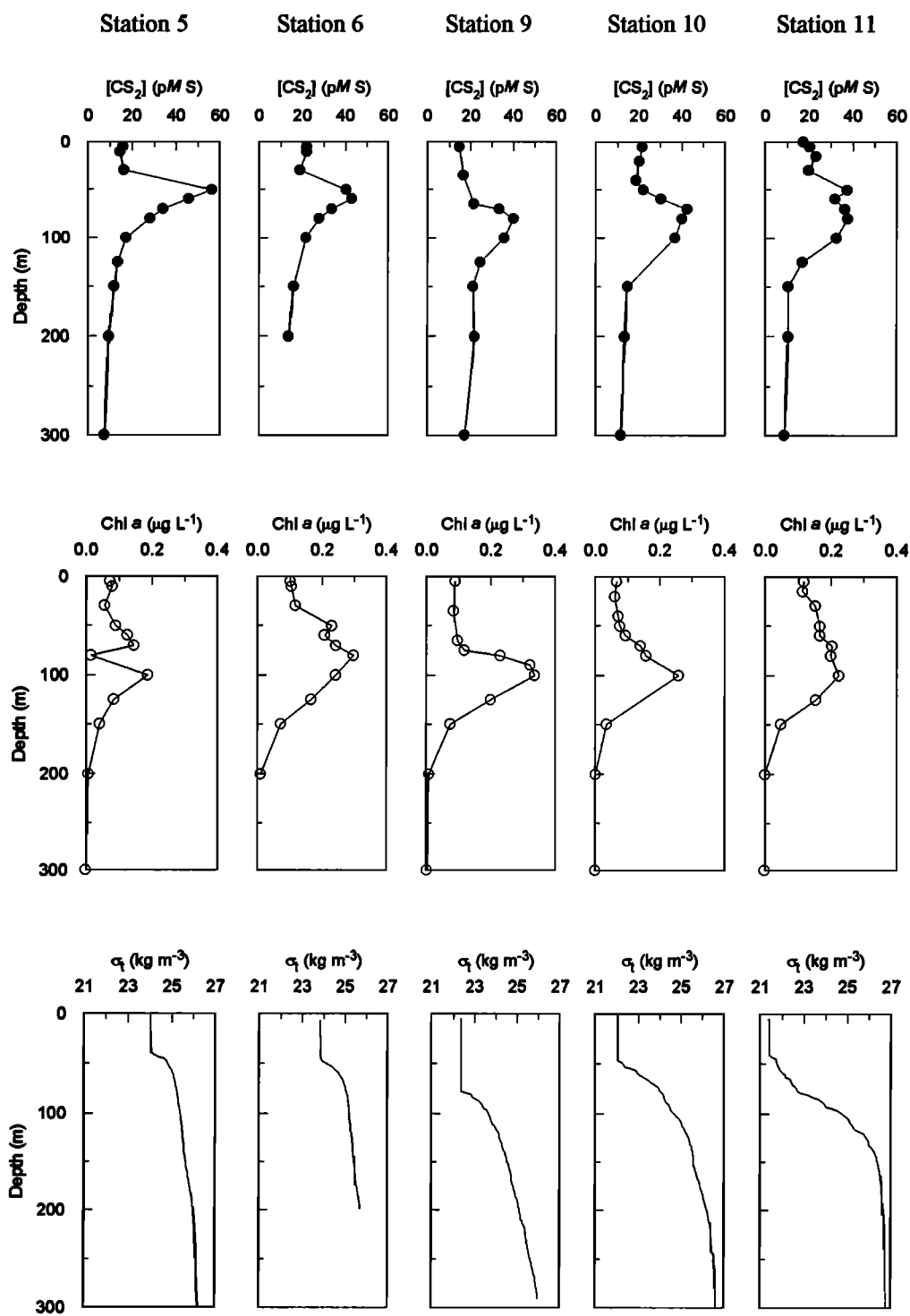
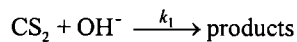
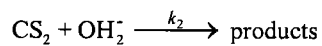


Figure 8. Depth profiles of CS_2 (solid circles), chlorophyll a (open circles), and σ_t (solid lines) obtained during the *Discoverer* cruise in the North Pacific.

loss due to hydrolysis and its reaction with the hydrogen peroxide conjugate base HO_2^- [Elliott, 1990]:

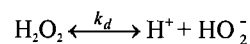


($k_1 = 1.0 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, room temperature)



($k_2 = 20.4 \text{ M}^{-1} \text{ s}^{-1}$, room temperature).

The concentration of HO_2^- can be derived from the acid dissociation [Evans and Uri, 1949]



($k_d = 2 \times 10^{-12}$)

The concentration of H_2O_2 below the euphotic zone is of the order of a few nanomoles per liter [Palenik and Morel, 1988;

Sikorski and Zika, 1993]. Assuming that $[H_2O_2] = 10 \text{ nM}$ and $pH = 8.2$, we estimated the chemical destruction rate in the deep water (200-300 m) at station 9 to be $\sim 1.0 \text{ pM S yr}^{-1}$. Diffusional input to the deep water from the overlying CS_2 enriched layer (the subsurface maximum) was estimated to be in the range $0.6\text{-}10 \text{ pM S yr}^{-1}$ using the vertical concentration gradients of CS_2 at station 9 and the vertical mixing coefficients reported by Ledwell *et al.* [1993] ($350 \text{ m}^2 \text{ yr}^{-1}$) and Li *et al.* [1984] ($5400 \text{ m}^2 \text{ yr}^{-1}$). Thus, physical transport alone could balance the destruction due to hydrolysis and reaction with hydrogen peroxide. It is unknown whether or not a dark process that produces CS_2 exists in oxic aquatic environments. Several groups [Radford-Knoery and Cutter, 1994; Flöck and Andreae, 1996] reported dark production of OCS under naturally occurring oxic conditions. The possibility of a similar dark production of CS_2 cannot be excluded as similar pathways have been found for the production of CS_2 [Xie *et al.*, 1998] and OCS [Ferek and Andreae, 1984] in surface waters (photochemically) and sediments (through anaerobic microbial processes) [Lovelock, 1974; Cutter and Radford-Knoery, 1993].

4. Summary

This study, for the first time, presents the results of CS_2 measurements in the open oceans of the Pacific and the subarctic Atlantic. CS_2 concentrations are higher in coastal and warm waters than in the open ocean and cool waters, respectively. All the investigated regions are greatly supersaturated in CS_2 with respect to the atmosphere, and thus act as a source for atmospheric CS_2 . Our best flux estimate is $0.18 \text{ Tg } CS_2 \text{ yr}^{-1}$ with a range from 0.13 to $0.24 \text{ Tg } CS_2 \text{ yr}^{-1}$, making up 32% (23 to 42%) of annual CS_2 input to the atmosphere obtained by Chin and Davis [1993]. Major uncertainties in the flux estimate arise from the choice of the formula for calculating exchange velocity, the restricted spatial and temporal coverage of the data, and the assumption made in the flux computation that the concentration of CS_2 is independent of wind speed. Processes that significantly contribute to formation of oceanic CS_2 include anaerobic bacterial activities, UV-induced photochemical transformations of CDOM, and possible release from biological activity. Diffusional input from surface waters and sediments could account for the presence of this compound in the intermediate and deep ocean.

Acknowledgments. The authors wish to thank S. Niven for his technical support and assistance in sampling and analysis. We thank all the scientists, officers, and crew aboard CSS *Hudson*, NOAA's *Discoverer*, and RRS *Challenger*. This work was supported by NSERC Strategic and Operating Grants to R. M. Moore and by NERC (UK) Thematic Programme ACSOE. The work was conducted while H. Xie was holding an Izaak Walton Killam Memorial Scholarship at Dalhousie University.

References

- Andreae, M. O., The ocean as a source of atmospheric sulfur compounds, in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Menard, pp. 331-362, D. Reidel, Norwell, Mass., 1986.
- Andreae, M. O., Ocean-atmosphere interactions in the global biogeochemical Sulfur Cycle, *Mar. Chem.*, **30**, 1-29, 1990.
- Bandy, A. R., P. J. Maroulis, L. Shalaby, and L. A. Wilner, Evidence for a short tropospheric residence time for carbon disulfide, *Geophys. Res. Lett.*, **8**, 1180-1183, 1981.
- Bandy, A. R., P. J. Maroulis, B. Bonsang, and C. A. Brown, Emissions of sulfur gases to the atmosphere from estuaries and coastal areas, in *Estuarine Comparisons*, edited by V. S. Kennedy, pp. 303-312, Academic, San Diego, Calif., 1982.
- Bandy, A. R., T. L. Bandy, O. Youngbluth, and T. L. Owens, Trace gas measurements from tethered balloon platforms, *J. Atmos. Oceanic Technol.*, **3**, 581-584, 1986.
- Bandy, A. R., D. C. Thornton, and J. E. Johnson, Carbon disulfide measurements in the atmosphere of the western North Atlantic and the northwestern South Atlantic Oceans, *J. Geophys. Res.*, **98**, 23,449-23,457, 1993.
- Barns, I., K. H. Becker, E. H. Fink, A. Reimer, F. Zabel, and H. Niki, Rate constant and products of the reaction $CS_2 + OH$ in the presence of O_2 , *Int. J. Chem. Kinet.*, **15**, 631-645, 1983.
- Bates, T. M., J. D. Cline, R. H. Gammon, and S. R. Kelly-Hansen, Regional and seasonal variations in the flux of oceanic dimethylsulfide to the atmosphere, *J. Geophys. Res.*, **92**, 2930-2938, 1987.
- Chatfield, R. B., and P. J. Crutzen, Sulfur dioxide in remote oceanic air: Cloud transport of reactive precursors, *J. Geophys. Res.*, **89**, 7111-7132, 1984.
- Chin, M., and D. D. Davis, Global sources and sinks of OCS and CS_2 and their distribution, *Global Biogeochem. Cycles*, **7**, 321-337, 1993.
- Crutzen, P. J., The possible importance of COS for the sulfate layer of the stratosphere, *Geophys. Res. Lett.*, **3**, 73-76, 1976.
- Cutter, G. A., and J. Radford-Knoery, Carbonyl sulfide in two estuaries and shelf water of the western North Atlantic Ocean, *Mar. Chem.*, **43**, 225-233, 1993.
- De Bruyn, W. L., 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.
- Dister, B., and O. C. Zafiriou, Photochemical free radical production rates in the eastern Caribbean, *J. Geophys. Res.*, **98**, 2341-2352, 1993.
- Elliott, S., The solubility of carbon disulfide vapor in natural aqueous systems, *Atmos. Environ.*, **23**, 1977-1980, 1989.
- Elhott, S., Effect of hydrogen peroxide on the alkaline hydrolysis of carbon disulfide, *Environ. Sci. Technol.*, **24**, 264-267, 1990.
- Erickson, D. J., III, A stability dependent theory for air-sea gas exchange, *J. Geophys. Res.*, **98**, 8471-8488, 1993.
- Evans, M. G., and N. Uri, The dissociation constant of hydrogen peroxide and the electron affinity of the HO_2 radical, *Trans. Faraday Soc.*, **45**, 224-230, 1949.
- 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.
- Hofmann, D. J., Increase in the stratospheric background sulfuric acid aerosol mass in the past 10 years, *Science*, **248**, 996-1000, 1990.
- Johnson, J. E., and T. S. Bates, Atmospheric measurements of carbonyl sulfide, dimethyl sulfide, and carbon disulfide using the electron capture sulfur detector, *J. Geophys. Res.*, **98**, 23,411-23,421, 1993.
- Jørgensen, B. B., and B. Okholm-Hansen, Emission of biogenic sulfur gases from a Danish estuary, *Atmos. Environ.*, **19**, 1737-1749, 1985.
- Khalil, M. A. K., and R. A. Rasmussen, Global sources, lifetimes and mass balances of carbonyl sulfide (OCS) and carbon disulfide in the Earth's atmosphere, *Atmos. Environ.*, **18**, 1805-1813, 1984.
- Kieber, R. J., X. Zhou, and K. Mopper, Formation of carbonyl compounds from UV induced photodegradation of humic substances in natural waters: Fate of riverine carbon in the sea, *Limnol. Oceanog.*, **35**, 1503-1515, 1990.
- Kim, K.-H., and M. O. Andreae, Carbon disulfide in seawater and the marine atmosphere over the North Atlantic, *J. Geophys. Res.*, **92**, 14,733-14,738, 1987.
- Kim, K.-H., and M. O. Andreae, Carbon disulfide in the estuarine, coastal and oceanic environments, *Mar. Chem.*, **40**, 179-197, 1992.
- Ledwell, J. R., A. J. Watson, and C. S. Law, Evidence for slow mixing across the pycnocline from an open-ocean tracer-release experiment, *Nature*, **364**, 701-703, 1993.

- Li, Y. H., T. H. Peng, W. S. Broecker, and H. G. Ostlund, The average vertical mixing coefficient for the oceanic thermocline, *Tellus, Ser. B*, **36**, 212-217, 1984.
- Lide, D. R., *Handbook of Chemistry and Physics*, 77th ed. CRC Press, Boca Raton, Fla., 1996.
- Liss, P. S., and L. Merlivat, Air-sea gas exchange rates: Introduction and synthesis, in *The Role of Air-Sea Exchange in Geochemical Cycling*, edited by P. Buat-Menard, pp 113-129, 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.
- Liss, P. S., A. J. Watson, M. I. Liddicoat, G. Malin, P. D. Nightingale, S. M. Turner, and R. C. Upstill-Goddard, Trace gases and air-sea exchange, *Philos. Trans. R. Soc. London, Ser. A*, **343**, 531-541, 1993.
- Lovelock, J. E., CS₂ and the natural sulfur cycle, *Nature*, **248**, 625-626, 1974.
- Maroulis, P. J., and A. R. Bandy, Measurements of atmospheric concentrations of CS₂ in the eastern United States, *Geophys. Res. Lett.*, **7**, 681-684, 1980.
- Mihalopoulos, N., B. C. Nguyen, J. P. Putaud, and S. Belviso, The oceanic source of carbonyl sulfide, *Atmos. Environ., Part A*, **26A**, 1383-1394, 1992.
- Moore, L. R., R. Goericke, and S. W. Chisholm, Comparative physiology of *Synechococcus* and *Prochlorococcus*: Influence of light and temperature on growth, pigments, fluorescence and absorptive properties, *Mar. Ecol. Prog. Ser.*, **116**, 259-275, 1995.
- Moore, R. M., and M. Webb, The relationship between methyl bromide and chlorophyll *a* in high latitude ocean waters, *Geophys. Res. Lett.*, **23**, 2951-2954, 1996.
- Moore, R. M., W. Groszko, and S. Niven, Ocean-atmosphere exchange of methyl chloride: Results from NW Atlantic and Pacific Ocean studies, *J. Geophys. Res.*, **101**, 28,529-28,538, 1996.
- Palenik, B., and F. M. M. Morel, Dark production of H₂O₂ in the Sargasso Sea, *Limnol. Oceanogr.*, **33**, 1606-1611, 1988.
- Radford-Knoery, J. R., and G. A. Cutter, Biogeochemistry of dissolved hydrogen sulfide species and carbonyl sulfide in the western North Atlantic Ocean, *Geochim. Cosmochim. Acta*, **58**, 5421-5431, 1994.
- Rodhe, H., and I. Isaksen, Global distribution of sulfur compounds in the troposphere estimated in a height/latitude transport model, *J. Geophys. Res.*, **85**, 7401-7409, 1980.
- Sandalls, F. J., and S. A. Penkett, Measurements of carbonyl sulfide and carbon disulphide in the atmosphere, *Atmos. Environ.*, **11**, 197-199, 1977.
- Sengers, J. V., and J. T. Watson, Improved international formulations for the viscosity and thermal conductivity of water substances, *J. Phys. Chem. Ref. Data*, **15(4)**, 1291-1300, 1986.
- Sikorski, R. J., and R. G. Zika, Modeling mixed-layer photochemistry of H₂O₂: Optical and chemical modeling of production, *J. Geophys. Res.*, **98**, 2315-2328, 1993.
- Staubes, R., and H.-W. Georgii, Biogenic sulfur compounds in seawater and the atmosphere of the Antarctic region, *Tellus, Ser. B*, **45B**, 127-137, 1993.
- Taguchi, S., G. R. Ditullio, and E. A. Laws, Physiological characteristics and production of mixed layer and chlorophyll maximum phytoplankton populations in the Caribbean Sea and western Atlantic Ocean, *Deep Sea Res., Part A*, **35**, 1363-1377, 1988.
- Thornton, D. C., and A. R. Bandy, Sulfur dioxide and dimethyl sulfide in the central Pacific troposphere, *J. Atmos. Chem.*, **17**, 1-13, 1993.
- Toon, O. B., J. F. Kasting, R. P. Turco, and M. S. Liu, The sulfur cycle in the marine atmosphere, *J. Geophys. Res.*, **92**, 943-963, 1987.
- Turner, S. M., and P. S. Liss, Measurements of various sulphur gases in a coastal marine environment, *J. Atmos. Chem.*, **2**, 223-232, 1985.
- Wakeham, S. G., B. L. Howes, J. W. H. Dacey, R. P. Schwarzenbach, and J. Zeyer, Biogeochemistry of dimethyl sulfide in a seasonally stratified coastal salt pond, *Geochim. Cosmochim. Acta*, **51**, 1675-1684, 1987.
- Wanninkhof, R., Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, **97**, 7373-7382, 1992.
- Watson, A. J., R. C. Upstill-Goddard, and P. S. Liss, Air-sea gas exchange in rough and stormy seas measured by a dual tracer technique, *Nature*, **349**, 145-147, 1991.
- Wilke, C. R., and P. Chang, Correlation of diffusion coefficients in dilute solutions, *AIChE J.*, **1**, 264-270, 1955.
- Wine, P. H., W. L. Chameides, and A. R. Ravishankara, Potential role of CS₂ photooxidation in tropospheric sulfur chemistry, *Geophys. Res. Lett.*, **8**, 543-546, 1981.
- Xie, H., R. M. Moore, and W. L. Miller, Photochemical production of carbon disulphide in seawater, *J. Geophys. Res.*, **103**, 5635-5644, 1998.
- Xie, H., M. G. Scarratt, and R. M. Moore, Carbon disulfide production in laboratory cultures of marine phytoplankton, *Atmos. Environ.*, in press, 1998.

R. M. Moore and H. Xie, Department of Oceanography, Dalhousie University, Halifax, N.S., Canada B3H 4J1. (xie@is2.dal.ca)

(Received June 1, 1997; revised July 1, 1998; accepted October 3, 1998.)