Assessing the Flux of Different Volatile Sulfur Gases to the Atmosphere

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Abstract

Reduced sulfur gases and optical properties were measured in the upper ocean during an Atlantic Meridional Transect (AMT) cruise of the RRS *James Clark Ross* from England to the Falkland Islands in 1998. Sea surface concentrations of carbonyl sulfide (COS) exhibited a pronounced diel variation at low latitudes but no diel cycle at mid and high latitudes possibly because of oceanic fronts and the longer hydrolysis time constant in cold water. The highest COS concentrations were observed in coastal and upwelling areas. CS_2 concentrations varied less than those of COS, and the highest concentrations were found in the North African upwelling area with decreasing concentrations both northward and southward of this maximum. Dimethylsulfide (DMS) had the largest concentrations in the upper ocean, but methyl mercaptan (CH_3SH) was an important reduced sulfur species in some coastal and upwelling areas. This may be associated with high bacterial growth rates. Colored dissolved organic matter (CDOM) fluorescence and absorbance also exhibit the highest values in coastal and upwelling areas and the lowest values in the southern subtropical gyre. The results suggest that carbon disulfide (CS_2) outgassed from the oceans and oxidised in the atmosphere may represent a larger source of COS to the atmosphere than the direct flux of COS across the sea-air interface.

1 Introduction

The sources and sinks of the volatile reduced sulfur compounds (dimethylsulfide (DMS), carbonyl sulfide (COS), carbon disulfide (CS_2), methyl mercaptan (CH_3SH), hydrogen sulfide (H_2S), and dimethyl disulfide (DMDS)) have been fairly well identified [*Watts*, 2000]. DMS is produced in the oceans through lyase cleavage of dimethylsulfoniopropionate (DMSP), an osmolyte that is produced within the cells of certain phytoplankton species and is released to the water column through zooplankton grazing, diffusion, and viral infection [*Andreae and Crutzen*, 1997; *Kiene et al.*, 2000]. DMS is lost from the upper ocean through photochemical oxidation [*Brimblecombe and Shooter*, 1986; *Kieber et al.*, 1996; *Brugger et al.*, 1998] and surface outgassing. CH_3SH is also produced from DMSP in a pathway that competes with DMS production, and is rapidly lost from the water column by assimilation into sulfur-containing amino acids, reduction to H_2S, adsorption to colored dissolved organic matter (CDOM) [*Kiene et al.*, 2000], photochemical oxidation [*Flöck and Andreae*, 1996], and surface outgassing. COS is produced mostly photochemically in the upper ocean by the interaction of ultraviolet light with CDOM, and is lost from the upper ocean through hydrolysis and surface outgassing. The principal source of CS_2 is probably photochemical production from CDOM [*Xie et al.*, 1998], but it may have a significant biological source in certain regions [*Xie et al.*, 1999]. *Kim and Andreae* [1987] note that CS_2 in seawater is stable on time scales of days, and *Elliott* [1990] notes that the CS_2 turnover time with respect to hydrolysis and aqueous phase oxidation by hydrogen peroxide may extend to years. It is probable that surface outgassing is the main sink for CS_2 from the water column [*Kettle and Andreae*, 2000]. H_2S is produced mainly from the hydrolysis of COS, from particulate organic material and possibly by marine algae [*Watts*, 2000; *Andreae et al.*, 1991]. It is oxidized in oxygenated seawater with a half-life of from 2–50 hours, and the interaction of its sources and sinks is such that it has a diurnal cycle with a maximum just before dawn [*Andreae*, 1990]. The production and flux of DMDS has been observed in large quantities from coastal wetlands [e.g., *Cooper et al.*, 1987; *de Mello et al.*, 1987], freshwater lakes [e.g., *Richards et al.*, 1991], and possibly from a marine coastal environment [*Turner and Liss*, 1985], but it has not been reported in the open ocean, and its oceanographic source is probably negligible.

For most of these reduced gases, the production and flux is currently difficult to quantify. The biological source and sink terms for DMSP, DMS, CH_3SH and DMDS make it difficult to extrapolate expedition or laboratory measurements to a global scale. The global sources and sinks of COS and CS_2 are better constrained, but still depend on the spatial and temporal distribution of colored dissolved organic matter (CDOM), and this is subject to a lot of uncertainty. The calculation of the sea-air flux of all volatile species from conventional piston velocity parameterizations using the concentrations across the sea-air interface is not known with great accuracy [*Jähne and Haußecker*, 1998].

This paper reports the upper ocean concentrations of a series of volatile sulfur species (COS, CH_3SH, DMS, and CS_2) which were measured during an Atlantic meridional transect from England to the Falkland Islands in Sept.-Oct., 1998. The fluxes of these gases were determined from a conventional piston velocity parameterization using in situ wind speed measurements. The results suggest a reassessment of the dissolved sulfur flux from the oceans to the atmosphere.

2 Methods

A series of measurements were collected during the Atlantic Meridional Transect (AMT-7) of the RRS *James Clark Ross* in Sept.-Oct., 1998 [*Aiken et al.*, 2000]. These measurements included a series of reduced sulfur gases, optical properties of discrete water samples, and ancillary measurements. They are summarized in Table 1 and the noon locations of the ship are shown in Figure 1.

2.1 Reduced Sulfur Gas Measurements

Upper ocean and atmospheric measurements of reduced gas species were made using a flame photometric detector within an automated preconcentration analysis system, previously described by *Ulshöfer* [1995]. Upper ocean measurements were made by sampling from the headspace gas (400 mL of air drawn through a cold trap at 200 mL/min) of a Weiss equilibrator that was continuously supplied with seawater at a rate of approximately 24-30 L minute^{-1} from the ship's uncontaminated intake system mounted below the keel of the ship at approximately 6 m depth (the total residence time of seawater in the ship's plumbing was approximately 1-2 minutes). The gas phase headspace mixing ratios were converted to upper ocean concentrations using the Henry law coefficients (from the Internet compilation of *Sander* [1996]; http : //www.mpch − mainz.mpg.de/ sander/res/henry.html; reproduced in Table 2) and the continuous equilibrator temperature measurements measured with a thermocouple (PMC corporation, KX-PC/PC-24; 0.01°C precision; *Rhee*, 2000; made available by T. S. Rhee, 1999). The atmospheric measurements were made through approximately 90 m of 1/4" teflon tubing with the intake mounted at approximately 18 m above sea level on the foremast of the ship. There was no scrubber on the inlet to remove ozone from the atmosphere sample, and this suggests that only the atmospheric concentrations of COS could be measured reliably [*Hofmann et al.*, 1992]. Water collected in certain sections of the tubing, especially during a storm that was encountered north of the Falkland Islands, but model calculations indicate that the COS in atmospheric air samples that were drawn through this water did not remain in the liquid phase long enough to be depleted through hydrolysis. Samples were measured at an interval of 30 minutes for most of the cruise from England to Montevideo and at an interval of 20 minutes from Montevideo to the Falkland Islands. Three equilibrator headspace measurements were followed by one atmospheric measurement in a sequence which was repeated for the entire cruise.

The system had been built expressly to determine oceanic and atmospheric concentrations of COS. However, on previous expeditions (e.g., *Ulshöfer* [1995]; *von Hobe et al.* [1999]), peaks in the chromatogram for the equilibrator headspace were observed for CH_3SH, DMS, CS_2, and possibly DMDS in certain coastal regions. During the Atlantic meridional transect, calibrations were performed approximately every 2-3 days for COS, CH_3SH, and CS_2 [*Kettle*, 2000] using thermostatted permeation devices with a mass change history extending over two years. A series of post-cruise calibrations were also carried out for COS, CH_3SH, DMS, and CS_2 at the Max Planck Institute for Chemistry in Mainz, Germany. These revealed that the slopes of the calibration graphs of the logarithm of the photomultiplier voltage versus the logarithm of the trapped mass (for COS, DMS, and CS_2) were parallel and offset from each other at a fixed ratio. This enabled the DMS peaks in the chromatogram to be calibrated after the end of the cruise using the calibration information from COS and CS_2.

It was not clear whether a Weiss equilibrator could be used to quantitatively measure the upper ocean concentration of CH_3SH, DMS, and CS_2. All previous measurements of these gases have been made using purge and trap systems. A number of possible problems have been identified in using this equilibrator technique for the measurement of these gases in seawater. For example, there was the possibility of the correlation of successive measurements where the retention of a sulfur gas in the cold trap from one measurement would influence the next measurement (i.e., the problem of significant non-zero blank values). However, the possibility of blank contamination in individual measurements was ruled out in laboratory tests wherein air passed through a filter unit (consisting of cartridges of molecular sieve and activated charcoal) resulted in chromatograms with no peaks at the eluting times of COS, CH_3SH, DMS, and CS_2, and other tests with the highest purity helium carrier gas (99.9999%) also showed no sample contamination. In the actual time series measurements, an artifact of this type would have been apparent as a systematic change in the three successive equilibrator headspace gas measurements which followed every atmospheric measurement. No such trend was observed, and this suggests that the equilibrator headspace measurements presented here were not subject to an artefact associated with the sampling sequence. It appears that the apparatus design wherein the cold trap is heated to temperatures over 100 °C higher than the boiling point of the least volatile gas (CS_2) was sufficient to eliminate a hypothesized blank problem.

For DMS, the physical treatment of the water sample could have influenced the measured seawater concentration [e.g., *Turner et al.*, 1990]. However, previous investigations into the influence of prefiltering on the ultimate DMS concentrations measured for seawater samples have reported conflicting sampling artefacts introduced by the filtering procedure [e.g., *Barnard et al.*, 1982; *Andreae and Barnard*, 1984; *Turner et al.*, 1990], and other studies have reported no significant differences between filtered and unfiltered samples [e.g., *Andreae and Barnard*, 1983; *Kiene*, 1992]. This suggests that the physical treatment of the seawater sample may not be important. This possible problem was recognized by *Groszko and Moore* [1998] for halocarbons, which are also produced within phytoplankton cells. Their experiments show no difference in concentration between different equilibrator techniques and only a small difference in concentration between equilibrator and purging techniques, probably due to an error in the solubility parameterization. There might also be an error in the solubility parameterizations for the organic sulfur gases, but it is likely to be much smaller than the range of concentrations that is reported. Finally, the equilibrator measurements that are reported in this paper are consistent to other purge and trap measurements reported at similar times of year and locations.

Algal growth on the inside of the equilibrator could have produced reduced sulfur gases that could have contaminated the equilibrator headspace samples [*Johnson*, 1999]. A thin layer of reddish slippery substance was found coating the inside surfaces when the equilibrator was opened for cleaning in Lisbon and Montevideo. The substance was wiped away with a paper towel, and the inside surfaces were rinsed with HCl solution. No investigations have been reported on the growth rate of algae on the inside of Weiss equilibrators made from Teflon, or its impact on the measurement of reduced sulfur gases. However, the level 1 model of *Johnson* [1999] was reworked to include a production term inside the equilibrator and, even using the highest aqueous DMSP turnover rate measured by *Kiene* [1996] and 100% conversion into DMS, the possible contribution due to fouling is calculated to be negligible.

Another possible problem with using an equilibrator for CH_3SH, DMS, and CS_2 measurements is the time for the the dissolved gas in seawater to equilibrate with the headspace air (Table 3). The equilibration time is a particular concern because the headspace concentrations are forced out of equilibrium every 20 minutes when a 0.5 L air sample is drawn from the headspace and replaced with ambient air taken from outside the equilibrator (which is depleted in CH_3SH, DMS, and CS_2). The theoretical equilibration time (τ) for the Weiss equilibrator is given by the following equation from *Johnson* [1999]:

$$\tau = \frac{V_a}{LQ\epsilon} \tag{1}$$

where V_a is the volume of air in the equilibrator (approximately 21 L), L is the Ostwald solubility coefficient, Q is the flow rate of water through the equilibrator (24-30 L/minute), and ϵ is a dimensionless constant specific for the equilibrator. *Johnson* [1999] has evaluated ϵ for two different gases to be between 0.3-0.4. Using the conservative value of 0.3, the calculated equilibration times for COS, CS_2, CH_3SH, and DMS (shown in Table 3) are 4.9, 1.9, 0.5, and 0.2 minutes, respectively. A brief literature survey of equilibrator measurements [*Butler*, 1989; *Butler et al.*, 1995; *Lobert et al.*, 1995; *Johnson*, 1999; *Pszenny et al.*, 1999] has shown that the Weiss equilibrator has been used for species with even longer equilibration times. Assuming a worst case scenario where there are no sulfur compounds initially in the headspace air, then at the end of one 20 minute sampling period, the headspace mixing ratios would be almost at the equilibrium mixing ratios for COS, CS_2, CH_3SH, and DMS. The COS headspace mixing ratio should be even closer to the equilibrium value because the atmospheric air which is drawn into the headspace of the equilibrator typically has a concentration of ca. 500 ppt.

Another problem associated with the Weiss equilibrator standing in the sunlight on deck is the possibility of atmospheric reactions (with hydroxyl radical, in particular) in the headspace air, which would serve to deplete the headspace mixing ratios of CH_3SH, DMS, and CS_2 before measurement. In this regard, the chemical lifetime of the trace species should be longer than the sampling and equilibration times. Table 3 shows the chemical lifetime of the different species with respect to oxidation by hydroxyl radical (assuming high average daily OH concentrations in the marine boundary layer of 5×10^6 molec cm^{-3}; Mark Lawrence, private communication, 2000) ranges between about 1.7 hours for CH_3SH to 5 years for COS. The usual OH concentrations in the free atmospheric boundary layer were probably in the range 0.7–5.0 $\times 10^6$ molec cm^{-3} for most of the meridional transect [*Lawrence et al.*, 1999]. The headspace of the equilibrator was shielded from the direct light of the sun by superstructure of the ship and by shading of the translucent teflon walls of the equilibrator (Figure 2 shows that the teflon walls admitted about 1% of the solar irradiance in the visible and ultraviolet portions of the spectrum.) The OH radical concentrations inside the equilibrator would probably have been reduced still further by the impact of water spray on the concentrations of ozone, HO_2, and OH. At night, the OH radical concentration would have decreased to negligible levels and the chemical lifetimes of CS_2, CH_3SH, and DMS would have been much longer than the sampling time.

2.2 Discrete Optical Measurements

The optical properties of discrete seawater samples were measured about twice per day. Samples were drawn into 250 mL brown Nalgene bottles (which had been acid rinsed) from the ship's uncontaminated seawater supply and were subsequently transferred to quartz optical cells for absorbance and fluorescence measurements. Absorbance measurements were performed first on both filtered (using a Whatman GF/F glass fiber filter 47 mm in diameter, heated overnight at 450°C) and unfiltered samples followed by fluorescence measurements on unfiltered water samples only. Absorbance of water samples was measured in a 10 cm cell with quartz windows using a Shimadzu UV1500 double beam spectrophotometer (the ship's on board milli-Q water was used as a reference). Absorbance spectra were recorded from 200-900 nm, and the average signal from 550-650 nm was subtracted following the procedure used by *Green and Blough* [1994] to account for differences in the refractive index between the seawater standard and the milli-Q water reference. The list of files and times and locations of sampling are shown in Table 7.

Fluorescence of water samples was measured in a 1 cm quartz cell on a Shimadzu 160 instrument. Emission spectra were measured with a 10 nm bandpass for the following excitation wavelengths: 254, 270, 290, 300, 310, 320, 330, 345, 360, and 370 nm. The fluorescence seawater samples were not filtered to reduce the risk of introducing contamination (following the investigation of *Determann et al.* [1994]). *Chen and Bada* [1992] report no difference in the fluorescence between filtered and non-filtered seawater samples. The list of files and times and locations of sampling are shown in Table 8.

2.3 Ancillary measurements

The ship was equipped with automated instrumentation to collect data at one minute intervals for air temperature, wind speed and direction, barometric pressure, insolation, upper ocean temperature and salinity. In addition, the following measurements were collected at six hour intervals and relayed to the United Kingdom Meteorological Office (UKMO): air temperature, dew point temperature, sea surface temperature (hull mounted sensor), barometric pressure, cloud cover (estimated visually), and wind speed and direction (estimated using Beaufort scale or from underway instrumentation). Except for wind speed, these two meteorological data sets were collected with different instrumentation. Upper air temperature and upper air dew point temperature were collected and sent to the UKMO approximately every two days.

These data sets were used to calculate heat and momentum fluxes along the cruise track. Long-wave radiation was calculated from the bulk formula of *Fung et al.* [1984] using the continuous recording of air and sea surface temperature and the 6 hour measurements for dew point temperature and cloud cover. The wind stress, sensible heat, and latent heat were calculated using the iterative procedure of *Large and Pond* [1981] using the continuous underway data set.

The upper ocean density and optical charactistics were sampled with CTD and expendable bathythermograph (XBT) probes. The CTD measured vertical profiles of temperature and salinity, phytoplankton fluorescence, transmission coeffient at 660 nm, and downwelling irradiance in the range of photosynthetically available radiation (PAR, in the spectal range 400-700 nm). CTD measurements were taken approximately once per day, and the temperature structure of the upper ocean was also measured approximately every six hours with an XBT.

Underway chlorophyll *a* concentration ($\mathrm{mg\,m^{-3}}$) was measured during the transect with a Turner (A-10) fluorometer setup following *Welschmeyer* [1994] to allow for chlorophyll *a* detection in the presence of chlorophyll *b* and phaeopigments. Samples for chlorophyll *a* concentration were filtered onto 25 mm diameter GF/F (pore size 0.7 μm) filters, extracted overnight (12-24 hours) in 10 mL of 90% acetone at 4°C. Chlorophyll *a* concentration was determined fluorometrically.

Satellite and remote weather information was also available to complement the information collected during the cruise. Total column ozone information was extracted for each day during the cruise. Satellite-determined chlorophyll a estimates were obtained for 8-day average browse images available from the SeaWiFS project. Finally, 5-day back trajectories were obtained with the HYSPLIT program available from the Internet at http : //www.arl.noaa.gov/ready.html. For some days, especially at low latitudes (where there was vertical motion up to the stratosphere), the HYSPLIT program could not calculate the full 5 day back trajectories. Figure 1 shows days where the longest back trajectories were available (i.e., none with less than a 3.75 day history).

2.4 Flux Calculation

An air-sea exchange gas flux model was formulated on the basis of three gas exchange models proposed by *Liss and Merlivat* [1986], *Wanninkhof* [1992], and *Nightingale et al.* [2000]. According to *Liss and Merlivat* [1986], the flux (F) of gas across the ocean interface is proportional to the difference in the gas concentrations across the air-water interface (ΔC) and the piston velocity (K_w):

$$F = K_w \Delta C \tag{2}$$

where ΔC is expressed as:

$$\Delta C = LC_a - C_w \tag{3}$$

where C_a is the concentration in the atmosphere, C_w is the concentration in the water, and L is the Ostwald solubility coefficient. For COS, measurements from many expeditions indicate that concentrations in the lower atmosphere and upper ocean are comparable over most regions of the ocean and that the atmospheric term in the flux equation can not be neglected. The atmospheric mixing ratios are taken as a daily average from the cruise measurements. For DMS (e.g., *Liss et al.*, 1993), CS_2 (e.g., *Kim and Andreae*, 1987), and CH_3SH (no reported measurements in the atmosphere other than flux chamber measurements; shorter atmospheric lifetime than DMS) the upper ocean was highly supersaturated with respect to the overlying atmosphere, and the atmospheric concentrations could be neglected. The piston velocities were calculated according to the parameterizations of *Liss and Merlivat* [1986] (abbreviated LM86) *Wanninkhof* [1992] (abbreviated W92), and *Nightingale et al.* [2000] (abbreviated NEL00) model. The piston velocities were scaled using Schmidt number ratios. These were obtained from *Saltzmann et al.* [1993] for DMS (the effect of salinity was neglected). For COS, CH_3SH, and CS_2, the Schmidt number was calculated as the ratio of the kinematic viscosity of seawater (with units of square length divided by time) to the diffusivity of the gas in seawater (with units of square length divided by time). Viscosity was obtained from tabulated values from *Riley and Skirrow* [1975] , which were divided by the density of seawater (from *Gill* [1982]) to convert to kinematic viscosity for use in the Schmidt number equation. The diffusivity of COS, CH_3SH, and CS_2 in water was calculated from an empirical equation of *Wilke and Chang* [1954] and *Hayduk and Laudie* [1974]. (The molar volumes for use in this equation have been tabulated in Table 4.) Details of the flux calculations for these gases are presented by *Kettle* [2000].

3 Results

3.1 Oceanographic Situation Along the Cruise Track

The insolation (Figure 3a), integrated insolation (Figure 3b), and cloud cover (Figure 3d) records show that partially cloudy skies were encountered during most of the cruise, and no particular section of the cruise track was noted as having particularly higher or lower insolation than any other sections. Wind speeds were generally high as the ship travelled across the Bay of Biscay from England and decreased from the latitude of Portugal to the North African upwelling area (Figure 3e). Moderate to high wind speeds were encountered between the equator and the Tropic of Capricorn and decreased somewhat during the seven days before Montevideo was reached. The wind speeds were low when the ship left Montevideo, but a wind storm was encountered during the leg toward the Falkland Islands. Surface heat loss (Figure 3c) was high from the surface to approximately 20°S and the highest heat loss values were observed during the wind storm between Montevideo and the

Falkland Islands. In the Northern Hemisphere, the wind speed was generally low.

The time series of temperature profiles (Figure 4b) show that the depth of the mixed layer was fairly shallow (less than 50 m) between England and the North African upwelling area. The largest vertical temperature gradients were observed in the vicinity of the North African upwelling area. Between about 0° and 20°S (i.e., in the South Atlantic subtropical gyre in regions of elevated surface heat loss (Figure 3c)) the depth of the upper oceanic boundary layer depth was about 150 m. The temperature profiles in the segment of the transect between Montevideo and the Falkland Islands are characterized by much subsurface structure and reversed temperature gradients. One of the effects of the wind storm may have been enhanced horizontal advection and interleaving of water masses.

The upper ocean salinity structure (Figure 4c and 4d) shows some important differences with respect to the temperature structure in that a region of reduced sea surface salinity was observed in the tropics between about 20°S and 20°N. The shallow salt water lens in the tropics is due to enhanced convective rainfall in the area of the Intertropical Convergence Zone [*Aiken et al.*, 2000]. This halocline structure acts to inhibit deep mixing in this region in the same manner as investigated by *Price* [1979].

The optical and biological properties are consistent with previous meridional transect studies. A one year time history (important in the investigation of certain biologically-derived tracers with long turnover times) of sea surface chlorophyll *a* concentration (from SeaWiFS remotely sensed data) is shown in Figure 5 for every pixel location along the AMT-7 cruise track. The lowest chlorophyll *a* concentrations are observed in the North Atlantic subtropical gyre between Portugal and the North African upwelling area and in the South Atlantic subtropical gyre between the Equator and Montevideo. The highest ocean color chlorophyll *a* concentrations are found at the highest latitudes in both hemispheres, in the coastal regions near Lisbon and Montevideo, and in the North African upwelling area. There was good agreement between remotely sensed chlorophyll *a* estimates and in situ chlorophyll *a* concentrations (Figure 6a; see also *Kettle* [2000]). The beam attenuation coefficient at 660 nm (Figure 6b) and the diffuse attenuation coefficient for PAR (Figure 6c) show less light penetration in regions of higher chlorophyll a concentration, suggesting that much of the light attenuation at longer visible wavelengths is related to phytoplankton populations in the water column.

In situ determinations of the ultraviolet absorption coefficient and fluorescence (Figure 7) show general similarities with the sea surface chlorophyll a and the beam attenuation coefficient at visible wavelengths. A plot of the ultraviolet absorption coefficient of seawater at 300 nm versus the natural logarithm of sea surface chlorophyll a concentration shows a regression coefficient (r) of 0.68 using SeaWiFS chlorophyll a concentration (Figure 8) and a regression coefficient (r) of 0.67 using the in situ chlorophyll a concentration. The relationship between the two quantities is described by:

$$\begin{array}{ll} a_g(300\mathrm{nm}) = 0.429(0.021) + 0.079(0.011)\log_{\mathrm{e}}(C_{Sea}) & \text{for SeaWiFS chlorophyll } a \\ a_g(300\mathrm{nm}) = 0.399(0.017) + 0.072(0.010)\log_{\mathrm{e}}(C_{situ}) & \text{for in situ chlorophyll } a \end{array} \tag{4}$$

where C_{Sea} is the SeaWiFS chlorophyll a concentration estimate (in mg m^{-3}), C_{situ} is the in situ chlorophyll a concentration estimate (in mg m^{-3}), and a_g is the CDOM absorption coefficient (in m^{-1}).

3.2 Concentrations of Reduced Sulfur Gases

The COS atmospheric mixing ratios (Figure 9a) in this expedition are similar to previous measurements. Most of the atmospheric mixing ratios are in the range 140-1150 ppt with an average (one standard deviation) of 540±160 ppt and a mode (from Figure 10e, Table 5) at approximately 480 ppt. The mixing ratios in the current investigation are similar to the range of published values in the compilations of *Chin and Davis* [1995], and to other reports of marine boundary layer mixing ratios presented by *Johnson and Harrison* [1986] (508 ± 84 ppt), *Bingemer et al.* [1991] (609 ± 96 ppt for the northern hemisphere and 460 ± 46 ppt for the southern hemisphere), and *Weiss et al.* [1995] (470 ± 55 ppt and 442 ± 31 ppt for Pacific meridional transects in 1993 and 1994, respectively). The highest atmospheric boundary layer mixing ratios in the North African upwelling area are approximately the same as the extreme values reported by *Chin and Davis* [1995]. The COS mixing ratios in this cruise show a general north-south general gradient across the Atlantic Ocean which has previously been noted by *Bingemer et al.* [1991]. As well, atmospheric concentrations approaching the coast of South America show several diurnal cycles. Back trajectory analysis (Figure 1) indicates that the atmospheric circulation exhibited a lot of cyclonic activity in this region, and that some of the air masses that passed over the ship may have come from South America. It is therefore not possible to discount the possibility that the diurnal cycles in atmospheric mixing ratio may have been due to advection instead of a diurnal variation in the sea-air flux, in the same manner as has been observed by *Wilkniss et al.* [1978] for CO boundary layer mixing ratios near the coast of New Guinea.

The upper ocean COS concentrations (Figure 9b) show very clear diurnal cycles, especially in the South Atlantic tropical gyre regions. These results are consistent with the measurements made at low and mid latitudes by previous investigators [*Ferek and Andreae*, 1984; *Mihalopoulos*, 1989; *Andreae and Ferek*, 1992; *Ulshöfer*, 1995; *Ulshöfer et al.*, 1995; *Weiss et al.*, 1995; *Ulshöfer et al.*, 1996; *von Hobe et al.*, 1999]. Upper ocean concentrations increased near the coasts off Lisbon and Montevideo and in the North African upwelling area. A clear diurnal cycle was not observed during high wind conditions between Montevideo and the Falkland Islands. Previous reports suggest that diurnal cycles in COS concentration do not usually occur at very high latitudes or at mid-latitudes during winter [*Staubes et al.*, 1990; *Staubes and Georgii*, 1993; *Ulshöfer et al.*, 1995]. This is probably due to low photochemical COS production, long hydrolysis lifetime, and deep mixing in these areas.

Upper ocean CS_2 measurements show a characteristic trend with a maximum at the North African upwelling area and a steady decrease toward the north and south (Figure 9c). Concentrations ranged from 1.5–150 pM for the entire cruise with an average of 11 pM and a mode at 5.5 pM (see Figure 10d, Table 5). *Kim and Andreae* [1987] reported coastal concentrations of CS_2 in the range 5-240 pM and open ocean concentrations in the range 10–80 pM for a series of cruises off the eastern United States. *Xie and Moore* [1999] reported surface concentrations in the range 15-80 pM for cruises in the North Atlantic and Pacific Oceans. *Staubes et al.* [1990] measured upper ocean CS_2 concentrations between about 7 pM (the detection limit) to 190 pM along an Atlantic meridional transect from Germany to Brazil. In a Southern Ocean summer cruise, *Staubes and Georgii* [1993] found that open ocean CS_2 concentrations were below the detection limit (7 pM) of their instrument. The concentrations obtained in this experiment are therefore consistent with measurements by previous research groups. Diurnal cycles in the sea surface concentration (in phase with the solar cycle) were observed especially at low latitudes. The magnitude of the diurnal variation is much smaller than for the sea surface COS concentration, and this result could suggest a much weaker sink for CS_2 than for COS.

The sea surface DMS concentration (Figure 11b, Table 5) shows constant values in the open ocean at low and mid latitudes and somewhat elevated concentrations in coastal regions and regions of upwelling. The concentrations range mostly from about 0.2–5.9 nM during the cruise with an average of 2.0 nM. The frequency distribution of measurements (Figure 10c) is very similar in shape to what has previously been reported by *Kettle et al.* [1999] with a mode in the frequency histogram at approximately 1.6 nM. The time series shows higher concentrations at high southern latitudes, in coastal areas, and in the North African upwelling area. Lower concentrations were found in the subtropical gyre of the South Atlantic Ocean. These results are mostly consistent with previous measurements reported from a large database of measurements which are shown overplotted on Figure 11b [*Kettle et al.*, 1999; available on the internet at http://dss.ucar.edu/datasets/ds289.2/]. With respect to the atmospheric DMS measurements, the DMS peak in the chromatograms were almost always near the detection limit of the apparatus (consistent with the results obtained during other research campaigns). However, when the ship crossed the Falkland Islands shelf, the atmospheric DMS mixing ratios appeared to increase from the detection limit to over 1000 ppt. It is difficult to quantify the DMS mixing ratios specifically because the air intake was not fitted with an ozone scrubber and DMS was subject to ozone degradation in the cold trap. Probably the actual atmospheric DMS mixing ratios were higher than indicated by the chromatogram peaks. The 5-day back trajectory analysis (Figure 1b) shows that the air mass over the vessel at the end of the cruise had originated at the coast of Antarctica where previous expeditions have reported very high oceanic concentrations (e.g., *DiTullio and Smith*, 1995; *Turner et al.*, 1995). Similar high atmospheric concentrations have been noted by Jean Sciare for an extended time series on Amsterdam Island (private communication, 2000).

The sea surface CH_3SH concentration was nearly constant (near 300 pM) in the open ocean regions of the transect but increased dramatically in localized areas in the North African upwelling area, in the coastal region near Montevideo, and in the cruise segment between Montevideo and the Falkland Islands (shown in Figure 11a). Some segments of the record also show a weak diurnal cycle out of phase with the solar cycle, which might be due to photochemical destruction in surface waters (as has already been suggested by *Flöck and Andreae* [1996]). The average concentration obtained during the cruise was 420 pM and the mode in the concentration distribution is at 160 pM (Figure 10b, Table 5). Only *Kiene* [1996] has presented quantitative information about the concentration of CH_3SH in seawater (0.3–0.7 nM in the Gulf of Maine). Other studies have reported the existence of CH_3SH without providing specific concentrations. For example, *Andreae and Barnard* [1984] first report the existence of CH_3SH in the upper ocean, but they could not quantify the concentrations due the absence of appropriate standards. However, they estimate that the concentrations of CH_3SH were much smaller than those of DMS. A similar report was made by *Berresheim* [1987], who also could not quantify the aqueous phase concentrations of CH_3SH, but estimated that it amounted to a few percent of the measured DMS concentration. *Leck et al.* [1990] state that the sum of the CS_2 and CH_3SH concentrations constitutes approximately 10% of the total volatile sulfur observed during a transect in the Baltic Sea. All of these measurements were made at high latitudes and are consistent with the results reported for the current investigation. This report suggests that CH_3SH may constitute an important component of the total volatile sulfur pool in upwelling regions and at low latitudes.

Kiene et al. [2000] state that DMS and CH_3SH are produced from DMSP in a competing biological degradation pathway. The formation of CH_3SH is the favored pathway because it can be more easily incorporated into bacterial sulfur amino acids (methionine, cysteine and homocysteine) than is possible with DMS. In spite of being the favored DMSP degradation product, CH_3SH usually has a lower concentration in the upper ocean because of its high biological and chemical reactivity [*Kiene*, 1996; *Kiene et al.*, 2000]. During the Atlantic meridional transect, the ratio of the concentration of DMS to CH_3SH was approximately 10 in the seawater around northern Europe (see Figure 12) and reached about 30 during the cruise segment from Lisbon to the North African upwelling area. However, the ratio decreased to approximately 2 in the North African upwelling area, then increased in the South Atlantic subtropical gyre, and decreased again to about 1 in the coastal region near Montevideo. The variation in ratio of the concentrations of DMS to CH_3SH is difficult to explain. *Kiene et al.* [2000] propose that the determining factor of whether DMS or CH_3SH is produced from DMSP depends on the demand of bacterioplankton for CH_3SH in amino acid synthesis. The disproportionately high CH_3SH concentrations in the North African upwelling area and in the coastal regions near Montevideo may be an indication of unusually high bacterial growth rates, which cause the DMSP in the water column to be degraded mainly to CH_3SH. However, the disproportionately high CH_3SH concentrations may also be due to spatial differences in the the relative rates of disappearance of CH_3SH and DMS [*Kiene*, 1996]. At this time, it is not possible to determine whether the variation in the ratio of the concentrations of CH_3SH and DMS is due to differences in the production or the destruction terms.

3.3 Fluxes

Time series sea-air flux estimates of COS, CH_3SH, DMS, and CS_2 are presented in Figure 13 using the NEL piston velocity. The COS flux time series shows a clear diurnal cycle in the tropical regions with flux out of the ocean during the daytime and a flux into the ocean during the night. The average of all COS flux calculations is slightly positive (i.e., net flux out of the ocean), but the mode in the frequency distribution diagram (Figure 14) is slightly negative, indicating that there are large areas where the net COS flux is into the ocean. The fluxes calculated using the W92 piston velocity parameterization was approximately twice as great as that using the LM86 and the NEL00 parameterization was approximately in between.

The calculated CS_2 flux shows interesting features. The time series profile (Figure 13d) does not show the pronounced diurnal variability at low latitudes that was apparent for COS. The fluxes are highest at the North African upwelling area and decrease further north and south. Higher fluxes are predicted for the region between Montevideo and the Falkland Islands, mostly due to the intense winds in the region. The frequency histogram (Figure 14) reveals that the flux estimates using NEL00 are distributed approximately log-normally with an average of 0.0398 μmol m^{-2} day^{-1} and a mode of 0.0166 μmol m^{-2} day^{-1} (Table 6). The CS_2 flux is thus estimated to be higher than that of COS. If 0.81 mole of COS are produced for every mole of CS_2 consumed in the atmospheric oxidation process [*Chin and Davis*, 1993], then the results suggest that oceanic source of COS from CS_2 oxidation may be larger than the direct flux of COS across the the sea surface. These results are consistent with the estimates and uncertainty of oceanic flux presented by *Watts* [2000].

Time series of DMS (Figure 13c) and CH_3SH (Figure 13b) fluxes are very similar to each other with somewhat elevated values in upwelling and coastal regions and lower fluxes in the subtropical gyres. The highest fluxes for these species were observed along the cruise segment from Montevideo to the Falkland Islands during a wind storm. A plot of the histogram distributions reveals that the fluxes are distributed approximately log-normally. The average fluxes for DMS and CH_3SH using NEL00 are calculated to be 6.7 and 2.3 μmol m^{-2} day^{-1} respectively (Table 6). The ratio of the flux of DMS to CH_3SH (Figure 14) is not constant but varies spatially similar to the upper ocean concentrations. In most regions, DMS appears to be the dominant reduced sulfur gas being emitted to the atmosphere, but in the North African upwelling area and in the coastal region approaching Montevideo, the fluxes of DMS and CH_3SH may have been approximately equal. This may have implications for the atmospheric chemistry of the marine boundary layer as the atmospheric oxidation of CH_3SH is much faster than that of DMS (Table 3).

4 Conclusion

The Atlantic meridional transect of the RRS *James Clark Ross* in Sept.-Oct., 1998 revealed much about the spatial distribution of the reduced sulfur gases and optical properties in the Atlantic Ocean. The profile of discrete sea surface fluorescence obtained on this cruise is consistent with the results obtained by *Determann et al.* [1994], with somewhat higher values at the equator and in coastal regions. The discrete measurements of CDOM absorbance show similar features to the fluorescence data. Neither the results of *Determann et al.* [1994] nor the results of this publication suggest that the oceanic optical properties vary much on spatial scales less than 100 km, except perhaps in the North African upwelling area. The CDOM absorption coefficient shows good correlation with upper ocean SeaWiFS chlorophyll a concentrations.

Averaged over the entire cruise, the COS concentrations in the atmosphere and ocean were near equilibrium, and the peak in the flux frequency histogram was actually at a slightly negative value. The calculated flux of CS_2 was somewhat higher than that of COS. This is somewhat different from the estimates of *Watts* [2000], but is still consistent with the published values within the stated range of uncertainty. DMS concentrations measured with the Weiss equilibrator agreed with the database concentrations of *Kettle et al.* [1999]. It was confirmed that DMS represents the greatest flux of reduced sulfur over most regions of the ocean, but CH_3SH may be an important reduced sulfur species in localized upwelling regions and coastal areas where bacterial growth rates are high. As has been suggested by *Kiene et al.* [2000], it seems that CH_3SH may be more important in understanding the cycling of reduced sulfur in the upper ocean than was previously thought.

Understanding the distribution of the volatile organic sulfur gases and optical properties may be achieved with future modelling investigations. Already, modelling investigations have been used to investigate the spatial and temporal distributions of nonmethane hydrocarbons [*Plass-Dülmer et al.*, 1993] H_2O_2 [*Sikorski and Zika*, 1993], CO [*Kettle*, 1994, 2000], COS [*Ulshöfer*, 1995], and dissolved organic carbon [*Anderson and Williams*, 1999]. Similar modelling exercises hold the promise of being able to further understand the spatial and temporal distributions of CS_2, CH_3SH, and DMS.

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References

Aiken, J., N. Rees, S. Hooker, P. Holligan, A. Bale, D. Robins, G. Moore, R. Harris, and D. Pilgrim, The Atlantic Meridional Transect; overview and synthesis of data, *Prog. Oceanogr.*, *45*, 257–312, 2000.

Anderson, T. R., and P. J. L. Williams, A one-dimensional model of dissolved organic carbon cycling in the water column incorporating combined biological-photochemical decomposition, *Global Biogeochem. Cycles*, *13*, 337–349, 1999.

Andreae, M. O., The ocean as a source of atmospheric sulfur compounds, in *The Role of Air-Sea Exchange in in Geochemical Cycling*, edited by P. Buat-Menard, pp. 331–362. D. Reidel Publishing Company, 1986.

Andreae, M. O., Ocean-atmosphere interactions in the global biogeochemical sulfur cycle, *Mar. Chem.*, *30*, 1–29, 1990.

Andreae, M. O., and W. R. Barnard, The marine chemistry of dimethylsulfide, *Mar. Chem.*, *14*, 267–279, 1984.

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.

Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson Jr., J. A. Kerr, J. A. Rossi, and J. Troe, Evaluated kinetic, photochemical and heterogeneous data for atmospheric chemistry: Supplement V, IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry, *J. Phys. Chem. Ref. Data*, *26*, 521–1011, 1997.

Barnard, W. R., M. O. Andreae, W. E. Watkins, H. Bingemer, and H.-W. Georgii, The flux of dimethylsulfide from the ocean to the atmosphere, *J. Geophys. Res.*, *87*, 8787–8793, 1982.

Bates, T. S., K. C. Kelly, and J. E. Johnson, Concentrations and fluxes of dissolved biogenic gases (DMS, CH_4, CO, CO_2) in the Equatorial Pacific during the SAGA 3 experiment, *J. Geophys. Res.*, *98*, 16969–16977, 1993.

Bates, T. S., K. C. Kelly, J. E. Johnson, and R. H. Gammon, Regional and seasonal variations in the flux of oceanic carbon monoxide to the atmosphere, *J. Geophys. Res.*, *100*, 23093–23101, 1995.

Bates, T. S., K. C. Kelly, J. E. Johnson, and R. H. Gammon, A reevaluation of the open ocean source of methane to the atmosphere, *J. Geophys. Res.*, *101*, 6953–6961, 1996.

Berresheim, H., Biogenic Sulfur Emissions from the Subantarctic and Antarctic Oceans, *J. Geophys. Res.*, *92*, 13245–13262, 1987.

Bingemer, H. G., S. Bürgermeister, R. L. Zimmermann, and H.-W. Georgii, Atmospheric OCS: Evidence for a contribution of anthropogenic sources, *J. Geophys. Res.*, *95*, 20617–20622, 1990.

Brimblecombe, P., and D. Shooter, Photo-oxidation of dimethylsulfide in aqueous solution, *Mar. Chem.*, *19*, 343–353, 1986.

Brugger, A., D. Slezak, I. Obernosterer, and G. J. Herndl, Photolysis of dimethylsulfide in the northern Adriatic Sea: Dependence on substrate concentration, irradiance and DOC concentration, *Mar. Chem.*, *59*, 321–331, 1998.

Butler, J. H., J. W. Elkins, T. M. Thompson, and K. B. Egan, Tropospheric and dissolved N_2O of the west Pacific and east Indian Oceans during the El Nino Southern Oscillation event of 1987, *J. Geophys. Res.*, *94*, 14865–14877, 1989.

Butler, J. H., J. W. Elkins, T. M. Thompson, and B. D. Hall, Oceanic consumption of CH_3CCl_3: Implication for tropospheric OH, *J. Geophys. Res.*, *96*, 22347–22355, 1991.

Butler, J. H., J. M. Lobert, S. A. Yvon, and L. S. Geller, The distribution and cycling of halogenated trace gases between atmosphere and ocean, *Berichte zur Polarforschung*, *168*, 27–40, 1995.

Chen, R. F., and J. L. Bada, The fluorescence of dissolved organic matter in seawater, *Mar. Chem.*, *37*, 191–122, 1992.

Chin, M., and D. D. Davis, Global sources and sinks of OCS and CS_2 and their distributions, *J. Geophys. Res.*, *7*, 321–337, 1993.

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

Cooper, D. J., W. Z. de Mello, W. J. Cooper, R. G. Zika, E. S. Saltzman, J. M. Prospero, and D. L. Savoie, Short-term emission variability in biogenic sulphur emissions from a Florida *Spartina Alterniflora* Marsh, *Atmos. Environ.*, *21*, 7–12, 1987.

Dacey, J. W. H., S. G. Wakeham, and B. L. Howes, Henry's law constants for dimethylsulfide in freshwater and seawater, *Geophys. Res. Lett.*, *11*, 991–994, 1984.

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 Śetchenow coefficients of biogenic reduced sulfur species obtained from gas-liquid uptake measurements, *J. Geophys. Res.*, *100*, 7245–7251, 1995.

de Mello, W. Z., D. J. Cooper, W. J. Cooper, E. S. Saltzman, R. G. Zika, D. L. Savoie, and J. M. Prospero, Spatial and diel variability in the emissions of some biogenic sulfur compounds from a Florida *Spartina Alterniflora* Coastal Zone, *Atmos. Environ.*, *21*, 987–990, 1987.

Determann, S., R. Reuter, P. Wagner, and R. Willkom, Fluorescent matter in the eastern Atlantic Ocean. Part 1: method of measurement and near-surface distribution, *Deep-Sea Res.*, *41*, 659–675, 1994.

DiTullio, G. R., and W. O. Smith Jr., Relationship between dimethylsulfide and phytoplankton pigment concentration in the Ross Sea, Antarctica, *Deep Sea Res.*, *42*, 873–892, 1995.

Elliott, S., The effect of hydrogen peroxide on the alkaline hydrolysis of carbon disulfide, *Environ. Sci. Technol.*, *24*, 264–267, 1990.

Ferek, R. J., and M. O. Andreae, Photochemical production of carbonyl sulfide 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.

Fung, I. Y., D. E. Harrison, and A. Lacis, Andrew, On the variability of the net longwave radiation at the sea surface, *Rev. Geophys. Space Phys.*, *22*, 177–193, 1984.

Gill, A. E., *Atmosphere-Ocean Dynamics.* Academic Press, New York, 1982.

Green, S. A., and N. V. Blough, Optical absorption and fluorescence properties of chromophoric dissolved organic matter in natural waters, *Limnol. Oceanogr.*, *39*, 1903–1916, 1994.

Groszko, W., and R. M. Moore, A semipermeable membrane equilibrator for halomethanes in seawater, *Chemosphere*, *36*, 3083–3092, 1998.

Hayduk, W., and H. Laudie, Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions, *AIChEJ*, *20*, 611–615, 1974.

Hofmann, U., R. Hofmann, and J. Kesselmeier, Cryogenic trapping of reduced sulfur compounds using a Nafion drier and cotton wadding as an oxidant scrubber, *Atmos. Environ., Part A*, *26*, 2445–2449, 1992.

Jackowski, A. W., Vapor-liquid equilibria in binaries composed of methanol, methanethiol, and 2-thiapropane, *Pol. J. Chem.*, *54*, 1765–1773, 1980.

Jähne, B., and H. Haussecker, Air-water gas exchange, *Annu. Rev. Fluid Mech.*, *30*, 443–468, 1998.

Jerlov, N. G., *Optical Oceanography.* Elsevier Publishing Company, Amsterdam, 1976.

Johnson, J. E., Evaluation of a seawater equilibrator for shipboard analysis dissolved oceanic trace gases, *Anal. Chim. Acta*, *395*, 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.

Kettle, A. J., *A Model of the Temporal and Spatial Distribution of Carbon Monoxide in the Mixed Layer.* Thesis, Massachusetts Institute of Technology, 1994.

Kettle, A. J., Comparison of different dynamical models to predict the upper ocean concentration of a photochemical tracer as a function of depth and time, *Mar. Freshwater Res.*, *51*, 289–304, 2000a.

Kettle, A. J., *Extrapolations of the Flux of Dimethylsulfide, Carbon Monoxide, Carbonyl Sulfide, and Carbon Disulfide from the Oceans*, Ph.D. thesis, York University, 2000b.

Kettle, A. J., *et al.*, A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude and month, *Global Biogeochem. Cycles*, *13*, 399–444, 1999.

Kieber, D. J., J. Jiao, R. P. Kiene, and T. S. Bates, Impact of dimethylsulfide photochemistry on methyl sulfur cycling in the equatorial Pacific Ocean, *J. Geophys. Res.*, *101*, 3715–3722, 1996.

Kiene, R. P., Production of methanethiol from dimethylsulfoniopropionate in marine surface waters, *Mar. Chem.*, *54*, 69–83, 1996a.

Kiene, R. P., Turnover of dissolved DMSP in the estuarine and shelf waters of the northern Gulf of Mexico, in *Biological and Environmental Chemistry of DMSP and Related Sulfonium Compounds*, edited by R. P. Kiene, P. T. Visscher, M. D. Keller, and G. D. Kirst, pp. 337–349. Plenum Press, New York, 1996b.

Kiene, R. P., L. J. Linn, and J. A. Bruton, New and important roles for DMSP in marine microbial communities, *J. Sea Res.*, *43*, 1–1, 2000.

Kim, K.-H., and M. O. Andreae, Carbon disulfide in seawater and the marine atmosphere over the North Atlantic, *J. Geophys. Res.*, *92*, 14733–14738, 1987.

Large, W. G., and S. Pond, Open ocean momentum flux measurements in moderate to strong winds, *J. Phys. Oceanog.*, *11*, 324–336, 1981.

Lawrence, M. G., P. J. Crutzen, P. J. Rasch, B. E. Eaton, and N. M. Mahowald, A model for studies of tropospheric photochemistry: Description, global distributions, and evaluation, *J. Geophys. Res.*, *104*, 26245–26277, 1999.

Leck, C., U. Larsson, L. E. Bågander, S. Johansson, and S. Hajdu, Dimethyl sulfide in the Baltic Sea: Annual variability in relation to biological activity, *J. Geophys. Res.*, *95*, 3353–3363, 1990.

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. B. Menard, pp. 113–127. D. Reidel Publishing Company: Berlin, 1986.

Liss, P. S., A. J. Watson, M. I. Liddicoat, G. Malin, P. D. Nightgale, S. M. Turner, and R. C. Upstill-Goddard, Trace gases and air-sea exchanges, *Phil Trans R. Soc. Lond. A*, *343*, 534–541, 1993.

Lobert, J. M., T. J. Baring, J. H. Butler, S. A. Montzka, R. C. Myers, and J. W. Elkins, OATXC 92: Ocean/Atmosphere eXchange of Trace Compounds 1992, Tech. rep., Climate Monitoring and Diagnostics Laboratory, Boulder, Colorado, 1995.

Mihalopoulos, N., B. C. Nguyen, and S. Belviso, Carbonyl sulfide concentrations in the surface waters and above the Indian Ocean, in *Proc. 28th Liège International Astrophysical Colloquium*, edited by J. C. G. P. J. Crutzen, and R. Zander, pp. 477–486. 1989, Université de Liège, Institut d'Astrophysique, Cointe-Ougcée, Belgique.

Nightingale, P. D., G. Malin, C. S. Law, A. J. Watson, P. S. Liss, M. I. Liddicoat, J. Boutin, and R. C. Upstill-Goddard, In situ evaluation of air-sea exchange parameterizations using novel conservative and volatile tracers, *Global Biogeochem. Cycles*, *14*, 373–388, 2000.

Plass-Dülmer, C., A. Khedim, R. Koppmann, F. J. Johnen, and H. Kuosa, Emissions of light nonmethane hydrocarbons from the Atlantic into the atmosphere, *Global Biogeochem. Cycles*, *7*, 211–228, 1993.

Price, J. F., Observations of a rain-formed mixed layer, *J. Phys. Oceanogr.*, *9*, 643–649, 1979.

Pszenny, A. A. P., R. G. Prinn, G. Kleiman, and X. Shi, Nonmethane hydrocarbons in surface waters, their sea-air fluxes and impact on OH in the marine boundary layer during the First Aerosol Characterization Experiment (ACE 1), *J. Geophys. Res.*, *104*, 21785–21801, 1999.

Rhee, T. S., *The process of air-water gas exchange and its application*, Ph.D. thesis, Texas A and M University, 2000.

Richards, S. R., C. A. Kelly, and J. W. M. Rudd, Organic volatile sulfur in lakes of the Canadian Shield and its loss to the atmosphere, *Limnol. Oceanogr.*, *36*, 468–482, 1991.

Riley, J. P., and G. Skirrow, *Chemical Oceanography*, vol. 2. Academic Press, London, 2 edn., 1975.

Saltzman, E. S., D. B. King, K. Holmen, and C. Leck, Experimental determination of the diffusion coefficient of dimethylsulfide in water, *J. Geophys. Res.*, *98*, 16,481–16,486, 1993.

Sander, R., Henry's Law Constants (Solubilities), 1996, http://www.mpch-mainz.mpg.de/ sander/res/henry.html.

Seiler, W., The influence of the biosphere on the atmospheric CO and H_2 cycles, in *Environmental Biogeochemistry and Geomicrobiology, volume 3*, edited by W. E. Krumbein, pp. 773–810. Ann Arbor Science Publishers, 1978.

Sikorski, R. J., and R. G. Zika, Modeling mixed-layer photochemistry of H_2O_2: 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*, *45*, 127–137, 1993.

Staubes, R., H.-W. Georgii, and S. Burgermeister, Biogenic sulfur compounds in seawater and the marine atmosphere, in *Physical-Chemical Behavior of Atmospheric Pollutants, Proceedings of the European Symposium*, pp. 686–692. 1990.

Turner, S. M., P. D. Nightingale, W. Broadgate, and P. S. Liss, The distribution of dimethyl sulphide and dimethylsulphoniopropionate in Antarctic waters and sea ice, *Deep Sea Res.*, *42*, 1059–1080, 1995.

Ulshöfer, V. S., *Photochemische Produktion von Carbonylsulfid im Oberflaechenwasser der Ozeane und Gasaustausch mit der Atmosphaere*, Ph.D. thesis, Ruprecht-Karls-Universitaet, Heidelberg, 1995.

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. Floeck, 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.

von Hobe, M., A. J. Kettle, and M. O. Andreae, Carbonyl sulphide in and over seawater: summer data from the northeast Atlantic Ocean, *Atmos. Environ.*, *33*, 3503–3514, 1999.

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.

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*, 23083–23092, 1995.

Welschmeyer, N. A., Fluorometric analysis of chlorophyll *a* in the presence of chlorophyll *b* and phaeopigments, *Limnol. Oceanogr.*, *36*, 1985–1992, 1994.

Wilke, C. R., and P. Chang, Correlation of diffusion coefficients in dilute solutions, *AIChEJ*, *1*, 264–270, 1955.

Wilkniss, P. E., R. A. Lamontagne, R. E. Larson, and J. W. Swinnerton, Atmospheric trace gases and land and sea breezes at the Sepik River coast of Papua New Guinea, *J. Geophys. Res.*, *83*, 3672–3674, 1978.

Xie, H., and R. M. Moore, Carbon disulfide in the North Atlantic and Pacific Oceans, *J. Geophys. Res.*, *104*, 5393–5402, 1999.

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. Scarrat, and R. M. Moore, Carbon disulfide production in laboratory cultures of marine phytoplankton, *Atmos. Environ.*, *33*, 3445–3453, 1999.

Zandler, M. E., J. A. Watson Jr., and H. Eyring, Application of significant structure theory to the correlation of thermodynamic properties of CO_2, COS, and CS_2 in terms of the respective molecular parameters, *J. Phys. Chem.*, *72*, 2730–2737, 1968.