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## Assessment of dimethylsulfide sea-air exchange rate

Jean-Philippe Putaud<sup>1</sup> and Ba Cuong Nguyen

Centre des Faibles Radioactivités, Laboratoire Mixte Centre National de la Recherche Scientifique - Commissariat à l'Energie Atomique, Gif-sur-Yvette, France

**Abstract.** The concentrations of dimethylsulfide (DMS) in surface seawater and in the atmosphere at three heights above sea level (1, 6, and 20 m) were measured in June 1992 in the Atlantic Ocean south of the Azores Islands (34–37°N, 23–26°W) at stations of the "Surface of Oceans: Fluxes and Interactions With the Atmosphere" cruise (SOFIA). Simultaneous meteorological and micrometeorological measurements were also made. Sea surface temperature and wind speed were used to estimate sea-air exchange coefficients, according to two parameterizations of the piston velocity  $K_w$  reported by *Liss and Merlivat* [1986] and by *Smethie et al.* [1985]. The *Liss and Merlivat*'s [1986] parameterization leads to values of  $K_w$  smaller by 40% on average than *Smethie et al.*'s [1985] parameterization, the difference depending on wind speed.  $K_w$  values were used to calculate the DMS flux from an air-sea exchange model, with DMS concentrations measured in and above the seawater. Friction velocity, air temperature and heat flux were used to compute the eddy diffusion coefficient  $K_z$  as a function of altitude. In the cases where the DMS concentration decreased between 1 and 6 m, DMS flux in the 1–6 m layer was calculated from  $K_z$  and DMS atmospheric gradients according to the gradient-transfer approach. DMS flux values obtained from the sea-air exchange model and from the gradient-transfer approach appear to be significantly correlated ( $R=0.7$ ,  $n=15$ ). The slopes of regressions suggest that the *Liss and Merlivat*'s [1986] and *Smethie et al.*'s [1985] parameterizations of  $K_w$  both lead to DMS sea-air fluxes lower than that calculated by the gradient-transfer approach by a factor of  $1.6$  to  $1.9 \pm 0.5$  and  $1.1$  to  $1.4 \pm 0.4$ , respectively.

### Introduction

Numerous field measurements performed over various oceanic and coastal areas have shown dimethylsulfide (DMS) to be the major volatile sulfur species emitted at the seawater-atmosphere interface, representing almost 90% of gaseous sulfur produced by biogenic sources (see a review by *Bates et al.* [1992]). DMS emissions could therefore play a significant role in the global sulfur cycle. Moreover, atmospheric oxidation products of DMS (mainly  $\text{SO}_2$ ,  $\text{CH}_3\text{SO}_3\text{H}$  and  $\text{H}_2\text{SO}_4$ ) are thought to contribute to the formation of cloud condensation nuclei (CCN), the population of which may affect the stratiform cloud layer albedo [*Bates et al.*, 1987b; *Charlson et al.*, 1987]. DMS production resulting mainly from plankton activity [*Dacey and Wakeham*, 1986; *Keller et al.*, 1989; *Nguyen et al.*, 1988; *Belviso et al.*, 1991] may depend on some meteorological parameters, such as solar radiation, as suggested by *Bates et al.* [1987b]. Therefore a feedback loop could involve DMS production and atmospheric albedo over oceans [*Charlson et al.*, 1987]. Nevertheless, recent estimates [*Bates et al.*, 1992] indicate that anthropogenic emissions of gaseous sulfur (mainly  $\text{SO}_2$ ) nowadays largely exceed natural emissions on a global scale. But uncertainties in estimates of global DMS flux rate still exist [see, e.g. *Andreae*, 1986], and

refinements in its evaluation are needed to determine the potential climatic impact of DMS over oceanic areas, and particularly in the southern hemisphere, where DMS emission is still thought to be the principal sulfur source.

The use of the sea-air exchange model described by *Liss and Slater* [1974] has been the method classically employed to estimate the DMS sea-air flux [see, e.g., *Bates et al.*, 1987a, 1992; *Berresheim*, 1987; *Leck and Rodhe*, 1991; *Nguyen et al.*, 1990, 1992]. In this method, the sea-air flux is assumed to be equal to the product of an exchange coefficient across the interface and the concentration gradient between surface seawater and the atmosphere. Attempts to balance local sulfur budgets by using this method indicated that DMS sea-air fluxes did not match with the measured or estimated deposition fluxes of DMS oxidation products by a factor of at least 2 [*Berresheim*, 1987; *Nguyen et al.*, 1992]. Although this kind of budget is subject to large uncertainties, at least partially due to long-range transport and exchanges of sulfur compounds between the troposphere and stratosphere, these imbalances suggest that the uncertainty on DMS sea-air flux estimates could be a factor of 2, mainly due the estimation of the sea-air exchange coefficients. A similar result has been obtained by *Erickson* [1989], who found that when averaged over a range of global wind speeds, the exchange coefficient determined from *Liss and Merlivat*'s [1986] parameterization should be multiplied by a factor of 1.8 to give a global  $^{14}\text{CO}_2$  flux consistent with the global oceanic  $^{14}\text{C}$  inventory.

In this paper, two different parameterizations of exchange coefficients are used to estimate DMS sea-air flux using an sea-air exchange model based on simultaneous DMS and meteorological parameter measurements performed in the Atlantic Ocean. These estimates are compared with DMS flux

<sup>1</sup>Now at European Commission, Joint Research Centre, Environment Institute, Atmospheric Process Unit, Ispra, Italy.

values calculated using the gradient-transfer approach, based on an eddy diffusion coefficient computed from meteorological parameters and atmospheric DMS gradients in the 1-20 m layer. These two independent methods are compared to assess the estimates of DMS ocean-to-atmosphere flux.

## Experimental Procedure

Surface seawater and atmospheric samples were collected in June 1992 on board R/V *Le Suroît* during the "Surface of Oceans: Flux and Interactions With the Atmosphere" (SOFIA) experiment in the south of São Miguel Island (Azores), between 34°N and 38°N, and 23°W and 27°W (Figure 1). About 60 mL of surface seawater were sampled every 6 hours (0000, 0600, 1200 and 1800 LT) from the sea surface temperature (SST) measurement bucket, using a polypropylene syringe. The seawater samples were immediately injected through a GF/F glass fiber filter into a bubbler, where DMS was extracted by helium bubbling at a flow rate of 100 mL/min, and concentrated in a cryogenic trap at -90°C before being analyzed by gas chromatography with flame photometric detection [Nguyen *et al.*, 1990]. The accuracy of the analysis is estimated to be about 10%.

Atmospheric samples were simultaneously collected at 1 and 6 m above sea level (asl), 3 m in front of the bow of the ship, and at 20 m asl from the signal mast, only when the ship was heading into the wind, with a velocity smaller than 2 knots (3.7 km/h). If the level of the lowest air sampling inlet was well controlled using a floater, the altitudes of the 6 m and 20 m intakes were not corrected from the pitching of the ship. It should also be noted that these sampling conditions did not totally exclude risks of atmospheric profile disturbance by the ship, particularly over the bridge, at 20 m asl [Weill *et al.*, 1994]. About 25 L samples were collected within 5 min by compressing air into stainless steel canisters twice a day when possible, once before the sunrise and once around noon, a few minutes before or after the seawater sampling. In total, 29 vertical profiles of DMS concentrations were measured. The analysis of the air samples was performed within 3 hours after sampling, letting compressed atmospheric samples expand through the cryogenic trap. The subsequent analysis was the same as for seawater samples [Nguyen *et al.*, 1990]. The detection limit was about 0.4 nmol m<sup>-3</sup> for this experiment.

The accuracy of the analysis is estimated to be about 10%, and several tests performed on board indicated that the standard deviation for three analyses of the same sample was less than 3%.

SST was measured every 3 hours using a standard bucket to sample seawater, with an accuracy of ±0.1°C. Comparing to other SST measurements performed on board, a possible bias of less than 0.3°C has been estimated, which does not imply a large uncertainty in fluxes and drag coefficients, taking into account the low wind speed observed during the experiment (Figure 2d). Standard meteorological and turbulent measurement of wind speed, air temperature and humidity were performed from an instrumented mast equipped with a sonic anemometer on the foredeck of the ship at 15 m above sea level. The turbulent measurements provided fluxes and the corresponding parameterizations to be used with meteorological measurements. Bulk parameterizations were used by Dupuis *et al.* [1996] to assess the wind stress  $\tau$  and the latent heat flux  $H$  from which friction velocity ( $u^*$ ) and surface value of the virtual temperature flux ( $\langle w'\theta' \rangle$ ) were determined:

$$\tau = \rho C_d (U-U_s) = -\rho u^*{}^2$$

$$H = \rho c_p C_H (U-U_s)(T_s-T) = \rho c_p \langle w'\theta' \rangle$$

where  $\rho$  is the density of air,  $c_p$  is the specific heat of air,  $w'$  and  $\theta'$  represent fluctuations in vertical wind speed and temperature, and  $U$ ,  $T$ ,  $U_s$  and  $T_s$  are mean values of horizontal wind speed and temperature at height  $z$  and surface, respectively. Dupuis *et al.* [1996] estimated that the  $u^*$  and  $\langle w'\theta' \rangle$  values obtained from this method are within 20% of values calculated using the inertial dissipation method described by Large and Pond [1981, 1982].

## Results

DMS concentrations in surface seawater ranged from 0.3 to 1.5 nmol L<sup>-1</sup> (Figure 2a), with an average of 0.82 ± 0.30 nmol L<sup>-1</sup>. Although the mean DMS concentration was slightly lower during the second leg than the first (0.68 versus 0.90 nmol L<sup>-1</sup>), the same feature could be observed in DMS distribution, i.e., a kind of channel in a SW-NE direction where DMS concentrations were significantly lower than to the north and south (Figure 1a and 1b). SST variations recorded during the

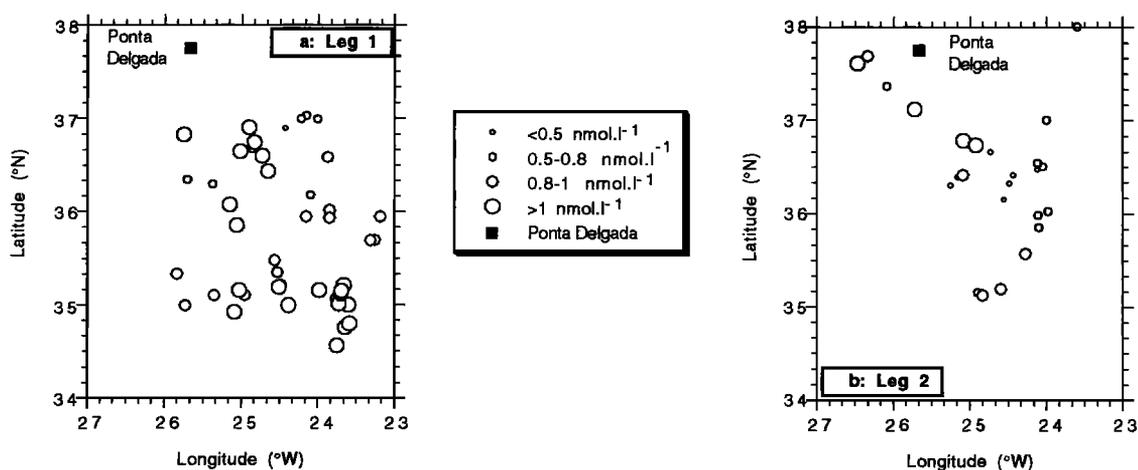
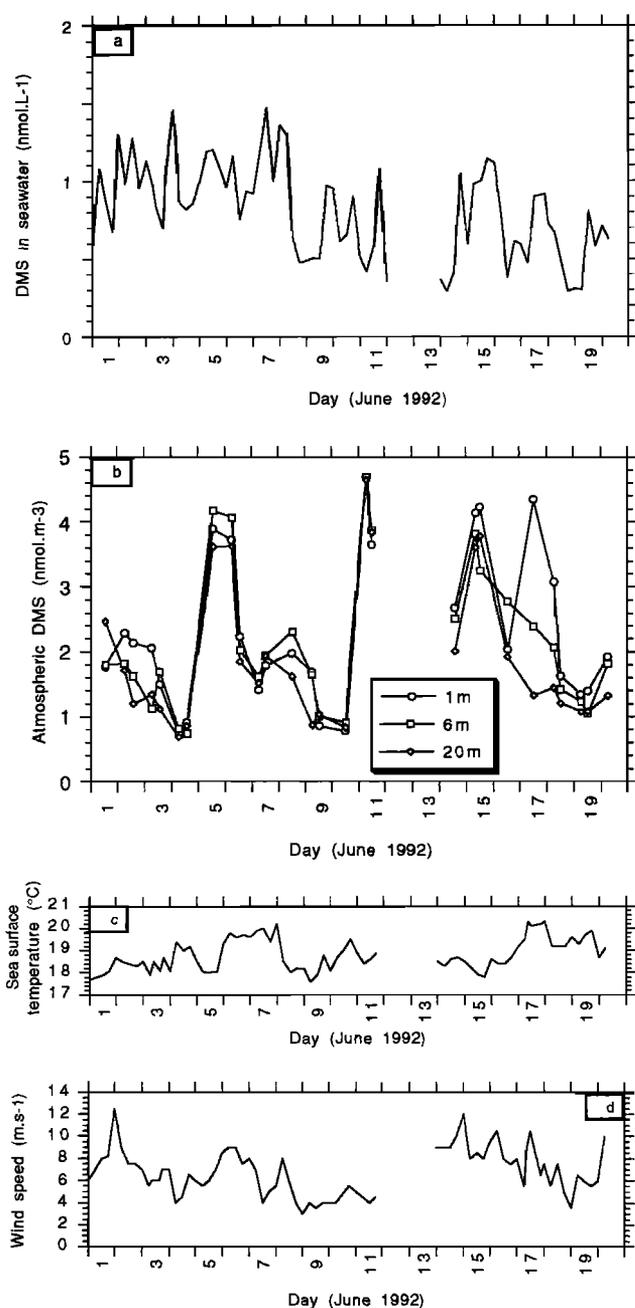


Figure 1. Study area and DMS concentrations in surface seawater.



**Figure 2.** (a) Variations of DMS concentrations in surface seawater, (b) atmospheric DMS concentrations at 1, 6 and 20 m above sea level, (c) sea surface temperature and (d) wind speed.

cruise presented the same kind of feature, with warmer waters around the southwest part and the center of the studied area. The increase of DMS concentration in cold sectors of fronts, as already observed by *Holligan et al.* [1987] could therefore at least partially explain the variations in DMS seawater concentrations reported here. DMS concentrations measured during this experiment are consistent with those measured by *Bürgermeister et al.* [1990] in the same area in April 1987 (range 0.9-1.9 nmol L<sup>-1</sup>), but quite smaller than the average of about 2.2 nmol L<sup>-1</sup> calculated for 35°N in the Pacific Ocean from a model by *Bates et al.* [1987a]. The lack of chlorophyll level measurements or phytoplankton population

determination during this cruise prevents us from proposing an explanation of the discrepancy between our measurements and the seawater DMS concentrations predicted by this model.

DMS concentrations in the atmosphere ranged from 0.7 to 4.9 nmol m<sup>-3</sup> at 1 and 6 m above sea level and from 0.7 to 5.2 nmol m<sup>-3</sup> at 20 m above sea level (Figure 2b). However, the averages on 29 series of three samples collected at 1, 6, and 20 m were 2.4, 2.2, and 2.0 nmol m<sup>-3</sup>, respectively. These values are significantly higher than those observed by *Bürgermeister et al.* [1990] in this area (0.05-0.8 nmol m<sup>-3</sup>). This difference cannot be explained because there is no available information on the meteorological conditions (particularly wind speed) during that experiment. DMS atmospheric concentrations were generally smaller in the afternoon than before sunrise. The mean ratios of the afternoon to morning concentrations observed on the same days were 0.85±0.26, 0.88±0.27, and 0.82±0.32 (*n* = 11) at 1, 6 and 20 m levels, respectively. If we assume that the DMS sea-air flux was on average similar early in the morning and soon after midday, this decrease denotes a faster oxidation of DMS during the day than during the night. Except in three cases, atmospheric concentrations at the three levels were strongly correlated (Figure 2b). Among the 29 atmospheric DMS profiles obtained during this experiment, 13 did not present a decrease in DMS concentration between 1 and 6 m, as well as nine between 6 and 20 m. For the situations where a negative gradient of DMS was observed, the decrease ranged from 0.8 to 58% (median 17%) and from 0.2 to 61% (median 14%) in the 1-6 m and 6-20 m layers, respectively. It should be noted that taking into account the accuracy (10%) and precision (better than ±3%) of atmospheric DMS measurements, the uncertainty on a DMS gradient is about 15%.

## Discussion

### Estimates of DMS Flux From a Sea-Air Exchange Model

The gas exchange between air and water is commonly described by a film model where the transport close to the interface is governed by molecular diffusion, and chemical reactions both in the liquid and gas phase have a negligible effect on the transport [*Aneja and Overton*, 1990]. Therefore, according to the first Fick's law, the gas flux  $F_i$  is proportional to the concentration gradient in each layer:

$$F_i = -D_i \partial C_i / \partial z \quad (1)$$

where  $D_i$  is the coefficient of molecular diffusion of the gas in the layer *i* material.

Writing (1) for each of the air and water films, and assuming that the transport of the gas across the interface is in steady state [*Liss and Slater*, 1974], we obtain for a gas sparingly soluble and little reactive (i.e., the gas phase resistance to transport is negligible compared to the water phase resistance)

$$F = -K_w (C_a / H - C_w) \quad (2)$$

where  $K_w$  is defined as the sea-air transfer coefficient or piston velocity and  $H$  is the Henry's constant.

For DMS,  $H$  (nmol L<sup>-1</sup> air / nmol L<sup>-1</sup> water) can be calculated as a function of the sea surface temperature ( $T$ ) [*Dacey et al.*, 1984]:

$$H = [\exp(12.64 - 3547/T)]/RT \quad (3)$$

with  $T$  in kelvins, and  $R$  being perfect gas constant ( $0.082 \text{ atm mol}^{-1} \text{ K}^{-1}$ ).

During our experiment, SST ranged from  $16.8^\circ\text{C}$  to  $20.2^\circ\text{C}$  (Figure 2c), corresponding to  $H$  values between 0.065 and 0.072. Comparison between DMS concentrations in the atmosphere at 1 m above sea level ( $C_a$ ) and DMS concentrations in surface seawater ( $C_w$ ) measured simultaneously shows that during this experiment, the term  $C_a/H$  was always smaller than  $C_w$  (ratio in the range 0.01–0.17, mean 0.05,  $n=28$ ). This indicates that seawater was always supersaturated in DMS with respect to the atmosphere but that DMS concentration in the atmosphere can in some circumstances significantly affect DMS sea-air flux.

**Liss and Merlivat's parameterization of  $K_w$  ( $K_w$ (L&M)).** Three relationships giving the variations with wind speed of  $K_w$  for  $\text{CO}_2$  at  $20^\circ\text{C}$  have been proposed by *Liss and Merlivat* [1986], based on field data sets reported by *Wannikhof et al.* [1985] and results of wind tunnel studies reported by *Broecker and Siems* [1984]. At other temperatures, or for other gases, these expressions of  $K_w$  have to be adjusted taking into account a Schmidt number power dependence of  $-2/3$  for lower wind speeds and  $-1/2$  for the higher ones. The Schmidt number ( $Sc$ ) is defined as  $Sc = \nu/D$ , where  $\nu$  is the kinematic water viscosity and  $D$  the molecular diffusivity of the gas in seawater (both in  $\text{cm}^2 \text{ s}^{-1}$ ), which are both functions of SST. Then  $K_w$  ( $\text{cm h}^{-1}$ ) for DMS at a temperature  $T$  can be estimated by

$$K_w = 0.17A(T)^{-2/3} u \quad (4)$$

for  $0 < u < 3.6 \text{ m s}^{-1}$

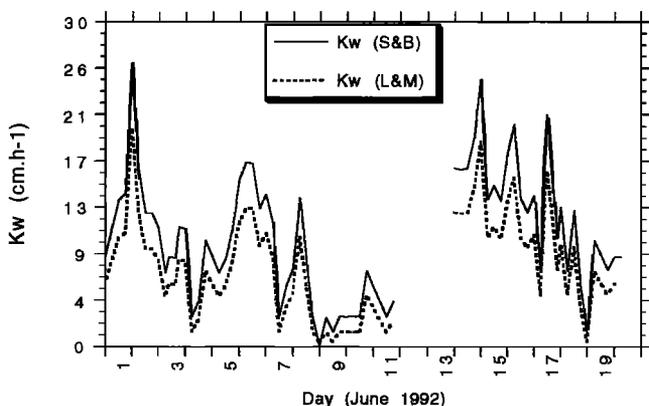
$$K_w = 0.17A(T)^{-2/3} u + 2.68A(T)^{-1/2} (u - 3.6) \quad (5)$$

for  $3.6 < u < 13 \text{ m s}^{-1}$ , and

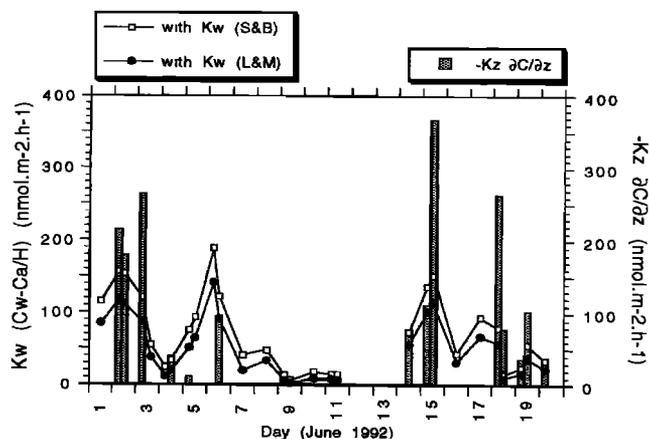
$$K_w = 0.17A(T)^{-2/3} u + 2.68A(T)^{-1/2} (u - 3.6) + 3.05A(T)^{-1/2} (u - 13) \quad (6)$$

for  $u > 13 \text{ m s}^{-1}$ , where  $u$  is in  $\text{m s}^{-1}$  and  $A(T) = Sc_{\text{DMS}}(T)/Sc_{\text{CO}_2}(293)$  is the dimensionless ratio between the Schmidt number of DMS at temperature  $T$ , and the Schmidt number of  $\text{CO}_2$  at  $20^\circ\text{C}$  ( $=595$ ) [*Liss and Merlivat*, 1986].

From the DMS Schmidt number ( $Sc_{\text{DMS}}$ ) determined recently by *Saltzman et al.* [1993] and (4) and (5), we



**Figure 3.** Variations of sea-air exchange rates calculated from parameterizations proposed by *Liss and Merlivat* [1986] (L&M), and by *Smethie et al.* [1985] and *Bates et al.* [1987a] (S&B).



**Figure 4.** Variations of DMS flux estimated from the gradient-transfer approach and from a sea-air exchange model according to *Liss and Merlivat's* [1986] (L&M) and *Smethie et al.'s* [1985] (S&B) parameterizations of  $K_w$  (see text).

calculated  $K_w$ (L&M) values for DMS ranging from 0.2 to  $20 \text{ cm h}^{-1}$  (mean 7.2, Figure 3).

**Smethie et al.'s parameterization of  $K_w$  ( $K_w$ (S&B)).** Another parameterization of  $K_w$  is based on the correlation between the radon piston velocity and wind speed observed by *Smethie et al.* [1985] in the Atlantic Ocean, and fitted to take into account results of laboratory experiments which indicated that piston velocity reaches 0 for wind speed  $\approx 3 \text{ m s}^{-1}$  [*Broecker et al.*, 1978; *Wannikhof et al.*, 1985]. For DMS,  $K_w$  was calculated by *Bates et al.* [1987a] from radon piston velocities, assuming that exchange coefficients vary with the Schmidt number to the power  $-1/2$  [*Holmen and Liss*, 1984; *Ledwell*, 1984]. Then  $K_w$  ( $\text{cm hr}^{-1}$ ) can be estimated by

$$K_w = 2.75 (u-3) (Sc_{\text{DMS}})^{-1/2} / (1.12 \cdot 10^{-2} / 1.14 \cdot 10^{-5})^{-1/2} \quad (7)$$

for  $u \geq 3 \text{ m s}^{-1}$ , where units are the same as in (4) and (5).

From (7), we obtained  $K_w$ (S&B) exchange coefficients in the range  $0\text{--}26 \text{ cm h}^{-1}$  (mean 10.1, Figure 3), on average 40% higher than  $K_w$ (L&M) values estimated by (4) and (5).

The data reported here confirm the situation usually encountered, where variations in DMS seawater concentrations were relatively small (factor of 5) compared with those from transfer velocities (a factor of  $>100$ ). According to (2), the DMS sea-air flux was therefore controlled by the sea-air exchange rate rather than by the amount of DMS available at the ocean surface. Using (2) with  $K_w$  and DMS concentrations determined for the same time, we obtained estimates of DMS sea-air flux plotted on Figure 4, ranging from 2 to  $140 \text{ nmol m}^{-2} \text{ h}^{-1}$  (mean  $49 \text{ nmol m}^{-2} \text{ h}^{-1} = 1.2 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ ) or from 6 to  $190 \text{ nmol m}^{-2} \text{ h}^{-1}$  (mean  $69 \text{ nmol m}^{-2} \text{ h}^{-1} = 1.7 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ ), according to *Liss and Merlivat's* [1986] and *Smethie et al.'s* [1985] parameterization of  $K_w$ , respectively. These values are significantly smaller than the estimates by *Erickson et al.* [1990] for this area in July ( $\approx 4.5 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ ) calculated from a model based on the correlation between DMS flux and incident solar radiation observed by *Bates et al.* [1987b]. This discrepancy is due to differences in both the seawater DMS and the sea-air exchange coefficients taken into account. First, the DMS concentration in seawater observed during this experiment was almost three times lower than the

mean value of 2.3 nmol L<sup>-1</sup> estimated by *Bates et al.* [1987a] for summer at 35°N in the Pacific Ocean. Second, in their calculation of DMS flux *Erickson et al.* [1990] used the  $K_w$  values estimated from *Liss and Merlivat's* [1986] formulae multiplied by a factor of 1.8, resulting of the comparison between globally averaged *Liss and Merlivat's* [1986] air-sea exchange rates of CO<sub>2</sub> and oceanic <sup>14</sup>CO<sub>2</sub> fluxes assessed from the <sup>14</sup>C budget [*Erickson, 1989*].

#### DMS Flux From the Gradient-Transfer Approach

In the gradient-transfer approach, it is assumed that turbulence causes a positive flux of parameter  $X$  ( $F_x$ ) down the atmospheric gradient of  $X$  concentration, at a rate which is proportional to the magnitude of the gradient by similarity with transfer in laminar flows. For a simple vertical diffusion model, assuming that advection does not affect significantly the profiles and that the system is stationary, this can be written

$$F_x(z) = -K_z(z) \partial X(z)/\partial z \quad (8)$$

where  $z$  is the altitude (meters) and  $K_z$  is the eddy diffusion coefficient (m<sup>2</sup> s<sup>-1</sup>) for compound  $X$ .

For DMS, assuming that the contribution of atmospheric oxidation in the DMS vertical profile is negligible with respect to the contribution of eddy diffusion (this assumption will be discussed below), we can write

$$F_{\text{DMS}}(z) = -K_z(z) \partial[\text{DMS}]/\partial z \quad (9)$$

The vertical transport evaluation was based on the assumption made by *Thompson and Lenschow* [1984, p. 4789] that the eddy diffusion coefficient " $K_z(z)$  is not affected by chemical reactions and that the dimensionless gradient for mass transfer is equal to that of temperature.".  $K_z(z)$  can therefore be described by [*Businger et al., 1971*]

$$K_z(z) = u^* k z [0.74 (1-9z/L)^{-1/2}]^{-1} \quad z/L < 0 \quad (10)$$

with  $L = u^*{}^3 \langle T \rangle / kg \langle w'\theta' \rangle$  where  $u^*$  is the surface velocity (m s<sup>-1</sup>),  $k$  is the dimensionless von Karman constant (0.35),  $L$  is the Monin-Obukhof length (meters),  $\langle T \rangle$  is the mean atmospheric temperature (kelvins),  $g$  is the gravitational acceleration (m s<sup>-2</sup>), and  $\langle w'\theta' \rangle$  is the kinematic surface virtual temperature flux (K m s<sup>-1</sup>), which was always >0 ( $\text{SST} > T_{\text{air}}$ ) during periods where negative DMS gradients were observed (Table 1).

It should be noted that another analytic form for  $K_z$  has been proposed [*Dyer and Bradley, 1984*], which would have led to  $K_z$  values smaller by less than 15% for the range of  $z/L$  values encountered during this experiment (-0.01 to -0.3). Additional uncertainty on the determination of  $K_z$  results from the uncertainties in the  $u^*$  values which was determined with a  $\pm 10\%$  accuracy (A. Weill, personal communication, 1993).

Considering that only a positive DMS sea-air flux is realistic, equation (9) is consistent only with negative

**Table 1.** Physical Parameters and DMS Gradients Used to Compute DMS Fluxes From the Gradient-Transfer Approach in the 1-6 m Atmospheric Layer.

Day, Time	$w'\theta'$ K m s <sup>-1</sup>	$u$ m s <sup>-1</sup>	$u^*$ m s <sup>-1</sup>	$Ri$	$L$ m	$K_z$ , m <sup>2</sup> s <sup>-1</sup>	$\partial c/\partial z$ nmol m <sup>-1</sup>	$-K_z \Delta c/\Delta z$ nmol m <sup>-2</sup> s <sup>-1</sup>
02, 0600	0.02513	9.0	0.341	-0.0207	-116.36	0.643	-0.093	5.97 x 10 <sup>-2</sup>
02, 1200	0.00605	7.5	0.278	-0.0080	-262.77	0.488	-0.101	4.95 x 10 <sup>-2</sup>
03, 0600	0.00646	5.5	0.205	-0.0284	-98.10	0.395	-0.186	7.34 x 10 <sup>-2</sup>
03, 1200	0.00611	6.0	0.222	-0.0193	-132.44	0.413	0.040	
04, 0600	0.00960	4.0	0.160	-0.1351	-31.52	0.386	0.015	
04, 1200	0.00324	4.5	0.170	-0.0261	-111.62	0.321	-0.034	1.09 x 10 <sup>-2</sup>
05, 0600	0.00162	5.5	0.202	-0.0041	-380.31	0.349	-0.008	2.94 x 10 <sup>-3</sup>
05, 1200	-0.00184	6.0	0.219	0.0101	423.37	0.344	0.058	
06, 0600	0.02050	9.0	0.340	-0.0165	-142.69	0.628	0.070	
06, 1200	0.01258	9.0	0.339	-0.0095	-230.72	0.601	-0.041	2.46 x 10 <sup>-2</sup>
07, 0600	0.01548	7.0	0.561	-0.0307	-85.31	0.513	0.040	
07, 1200	0.00414	4.0	0.155	-0.0532	-66.42	0.317	0.031	
08, 1200	0.00739	6.0	0.223	-0.0238	-110.10	0.423	0.067	
09, 0600	0.00449	4.0	0.155	-0.0588	-61.19	0.322	-0.009	2.74 x 10 <sup>-3</sup>
09, 1200	0.00029	3.5	0.135	0.0031	-627.53	0.228	0.030	
10, 1200	0.00056	3.0	0.064	-0.6104	-34.78	0.151	0.027	
11, 0600	0.00041	4.5	0.167	0.0019	-859.73	0.281	0.001	
11, 1200	-0.00344	4.0	0.147	0.0578	68.66	0.162	0.045	
14, 1200	0.00342	9.0	0.338	-0.0015	-837.61	0.568	-0.034	1.92 x 10 <sup>-2</sup>
15, 0600	0.00190	8.0	0.297	-0.0007	-1,020.78	0.497	-0.062	3.10 x 10 <sup>-2</sup>
15, 1200	0.00010	8.5	0.317	0.0017	-22,643.11	0.521	-0.195	1.02 x 10 <sup>-1</sup>
16, 1200	0.00095	8.0	0.297	0.0006	-2,036.64	0.492	0.149	
17, 1200	0.00586	10.5	0.403	-0.0019	-834.62	0.678	-0.389	2.64 x 10 <sup>-1</sup>
18, 0600	0.00272	5.5	0.203	-0.0094	-228.72	0.360	-0.203	7.30 x 10 <sup>-2</sup>
18, 1200	0.01289	7.5	0.279	-0.0195	-125.28	0.522	-0.042	2.17 x 10 <sup>-2</sup>
19, 0600	0.01041	6.5	0.241	-0.0260	-100.23	0.464	-0.022	1.02 x 10 <sup>-2</sup>
19, 1200	0.00802	6.0	0.223	-0.0259	-102.33	0.427	-0.067	2.86 x 10 <sup>-2</sup>
20, 0600	0.00738	6.0	0.223	-0.0238	-110.60	0.422	-0.022	9.40 x 10 <sup>-3</sup>

gradients of DMS in the atmosphere. Actually, in 13 and 8 of the 29 atmospheric DMS profiles obtained, DMS concentrations did not decrease between 1 and 6 m asl (Table 1) and 6 and 20 m (data not shown), respectively. As a numerical simulation of the air flowing around the ship *Le Suroît* [Weill *et al.*, 1994] shows possible strong perturbations at 20 m asl, where atmospheric samples were collected, the DMS concentrations observed at this level will be considered only when they present a significant gradient compared to the DMS concentrations observed at 6 m height. This same simulation shows only weak perturbations of the air flow 2 m in front of the ship at 1 and 6 meters asl. However several other reasons could explain positive atmospheric DMS gradients within this layer. Although no physical or meteorological criterion was found to disregard the profiles with such gradients, it is very likely that nonstationary states and/or advection of air masses from areas presenting different DMS emission rates could lead to positive atmospheric DMS gradients. In the following discussion, only the 16 cases where a decrease in DMS concentrations was observed between 1 and 6 m will be considered and assumed to proceed from a simple vertical turbulent diffusion.

DMS flux in the 1-6 m layer was first calculated for these 16 cases by computing an average value of  $K_z$  between the two altitudes  $z_1$  and  $z_2$  ( $K_{z1-z2}$ ) from (10) by

$$K_{z1-z2} = 1/(z_2-z_1) \int K_z(z) dz$$

that is

$$K_{z1-z2} = 1/(z_2-z_1) 0.35u^*/0.74 [f(z_2)-f(z_1)] \quad (11)$$

with

$$f(z) = 2z/3\beta (1 + \beta z)^{3/2} - 4/15\beta^2 (1 + \beta z)^{5/2}$$

where

$$\beta = -9/L$$

From (11), we obtained average values of  $K_z$  between 1 and 6 m ( $K_{1-6}$ ) ranging from 0.32 to 0.47  $m^2 s^{-1}$  (Table 1), consistent with values previously reported [see, e.g. *Nguyen et al.*, 1984]. From these values, negative DMS gradients observed between 1 and 6 m, and using (9), we calculated DMS fluxes ranging between 10 and 367  $nmol m^{-2} h^{-1}$  (Figure 4), with a mean value of 125  $nmol m^{-2} h^{-1}$  (3.0  $\mu mol m^{-2} d^{-1}$ ).

$K_{6-20}$  was also calculated from the equation (11) to be between 0.8 and 3.0  $m^2 s^{-1}$ . DMS flux in the 6-20 m layer was obtained by the same method as for the 1-6 m layer and found to range from 0.1 to 720  $nmol m^{-2} h^{-1}$ . Comparing DMS fluxes calculated from the same profile in the 1-6 m and 6-20 m layers, in only four cases are these values within  $\pm 30\%$ , i.e. within the uncertainties on the flux values. This suggests that the DMS flux was generally not constant throughout the 1-20 m layer, although DMS oxidation was unlikely to play a significant role in DMS flux decrease between sea surface and 20 m asl during this experiment. Indeed, the timescale of diffusion between 1 and 20 m ( $t = h^2/4K_z$ ) [McKeene *et al.*, 1990] was in the range 0.6-2.3 min (mean 1.1 min), which is very short with respect to the DMS atmospheric lifetime estimated at 12-36 hours [Andreae *et al.*, 1988; Bates *et al.*, 1990]. The difference observed in the DMS flux between these two layers could be due to a contribution of positive or negative DMS advection flux, which could be significant compared with the local sea-air flux, at least in the 6- to 20- m layer.

For the four situations where DMS flux was similar in the 1-6 m and 6-20 m layers, the whole DMS profile (Figure 5a) can be exploited to get an estimate of DMS flux through the 1- to 20- m atmospheric layer, without considering mean values for  $K_z$ . Indeed, from equation (9) we obtained:

$$\partial[DMS]/\partial z = -F_{DMS}(z)/K_z(z) \quad (12)$$

As  $F_{DMS}$  can be considered as constant between 1 and 20 m height in these four situations, an analytical form of  $[DMS](z)$  can be established by integrating (12):

$$[DMS](z) = -0.74 F_{DMS} / 0.35 u^* g(z) + A \quad (13)$$

where

$$g(z) = \ln \{ [(1 + \beta z)^{1/2} + 1] / [(1 + \beta z)^{1/2} - 1] \}$$

and A is a constant of integration.

Therefore  $F_{DMS}$  could be estimated from the slope of the plots representing  $-0.35 u^*[DMS](z)/0.74$  versus  $g(z)$  presented on Figure 5b. It appears that (13) can adequately reproduce these four profiles since the coefficient of linear regressions are all  $R^2 \geq 0.99$ . The values of DMS flux calculated by this method are similar ( $\pm 20\%$ ) to the values calculated for the same time from (9) in the 1-6 m layer, which indicates that averaging  $K_z$  in this layer can lead to reliable estimates of DMS flux. Taking into account the accuracy of  $u^*$  determination ( $\pm 10\%$ ), the uncertainty introduced in using  $K_z$  values averaged between 1 and 6 m height ( $\pm 20\%$ ), and the uncertainty on DMS gradient determination ( $\pm 15\%$ ), DMS

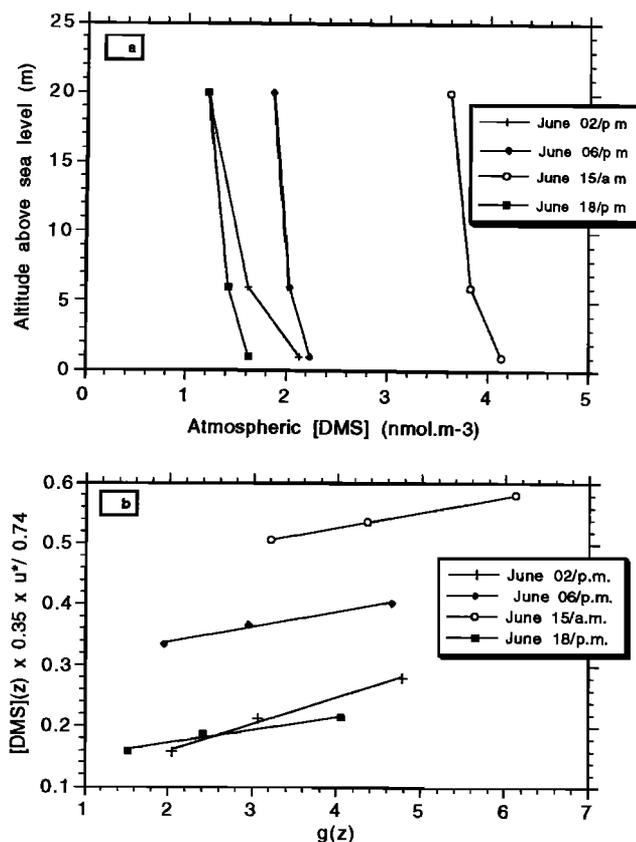


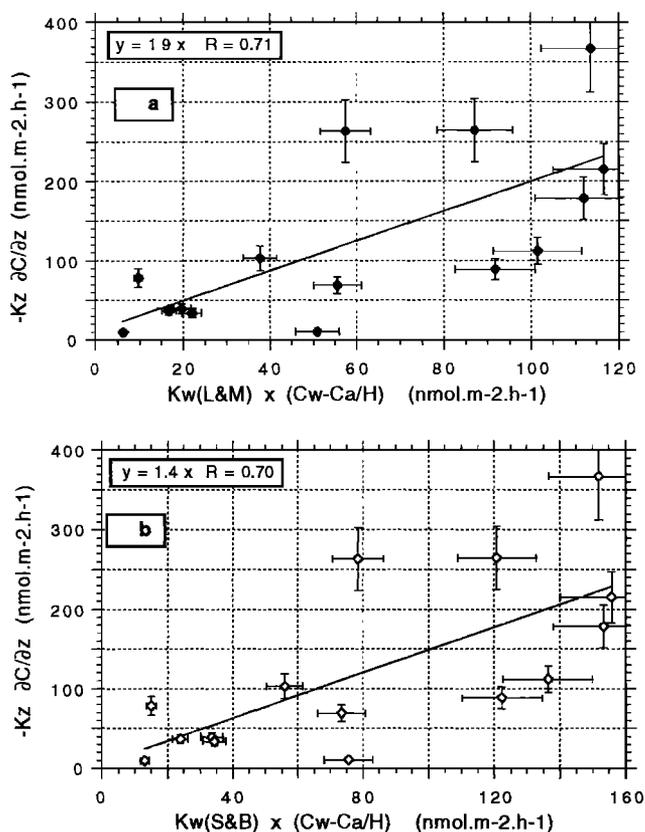
Figure 5. (a) DMS profiles presenting a constant DMS flux with height in the 1-20 m layer and (b) compared with their analytical form deduced from the gradient-transfer approach.

fluxes obtained by the gradient method present, however, a overall uncertainty of  $\pm 45\%$ .

### Comparison

As discussed above, DMS flux is generally not constant throughout the 1-20 m atmospheric layer. It seems therefore more reliable to compare the DMS sea-air flux estimated from the sea-air exchange model to the atmospheric DMS flux calculated by the gradient-transfer approach in the lowest atmospheric layer considered during this experiment, i.e., the 1-6 m layer. DMS fluxes calculated for the same times by these 2 different methods have been plotted on Figures 6a and 6b for  $K_w$  values calculated from *Liss and Merlivat* [1986] (equations (4)-(5)) and *Smethie et al.* [1985] (equation (6)), respectively. Error bars represent only uncertainties on DMS measurements and gradients. DMS fluxes calculated by the sea-air exchange model with both  $K_w$  parameterizations are correlated with those calculated by the gradient-transfer approach ( $R=0.71$  and  $R=0.70$ ,  $n=15$ ). Thus, although DMS gradients generally did not present the expected decrease and despite the uncertainties in  $K_z$  determination ( $\pm 45\%$ ), the gradient-transfer approach can in some situations be used to estimate DMS fluxes which are closely related to those calculated by the classical sea-air exchange model.

The values of  $F_{DMS}$  calculated by the gradient method were a factor of about 1.9 higher than that calculated by using  $K_w$  parameterized by *Liss and Merlivat* [1986] : a  $t$  test indicates



**Figure 6.** Relationships between DMS flux calculated from the gradient-transfer approach and from an sea-air exchange model with sea-air exchange coefficients calculated (a) from *Liss and Merlivat*'s [1986] and (b) from *Smethie et al.*'s [1985] parameterizations.

that the probability for the slope of the regression (Figure 6a) to be in the range  $1.9 \pm 0.5$  is 99.7% (intercept not significantly different from 0). It should be noted that the mean ratio between DMS fluxes estimated from the sea-air exchange model and from the gradient method would have been reduced to 1.6 if the other parameterization of  $K_z$  proposed by *Dyer and Bradley* [1984] had been used. These results are in good agreement with *Erickson*'s findings that  $K_w$  values estimated from *Liss and Merlivat*'s [1986] parameterization could be underestimated by a factor of 1.8 [*Erickson*, 1989] or that air-sea exchange coefficients are enhanced over neutral stability values in situations of air-sea thermal stability (*Erickson*, 1993), which were the conditions observed at the times for which our DMS flux values are calculated.

$F_{DMS}$  calculated by the gradient method were about 1.4 times higher than that based on the parameterization of  $K_w$  described by *Smethie et al.* [1985]. A  $t$  test indicates here that the probability for the slope of the regression (Figure 6b) to be outside the range  $1.4 \pm 0.4$  is only 0.4% and that the intercept is once more not significantly different from 0. The other parameterization of  $K_z$  proposed by *Dyer and Bradley* [1984] would have led to a slope of only 1.1. Therefore, using an sea-air exchange model with the parameterization of  $K_w$  described by (7) very probably leads to an underestimate of DMS sea-air flux by 10-40%. The most recent estimate for global DMS sea-air flux [*Bates et al.*, 1992] is  $0.48 \pm 0.33$  Tmol/yr ( $15 \pm 10$  Tg S/yr), with only 30% of the uncertainty coming from regional average estimates of DMS concentrations in seawater. If the correlation (Figure 6b) resulting from data obtained with wind speed in the range  $3-10$  m  $s^{-1}$  could be extrapolated to higher wind speeds, mainly observed in the southern hemisphere, the global DMS sea-air flux could be reevaluated to  $0.53-0.67$  Tmol/yr ( $17-21$  Tg S/yr), with an uncertainty of  $\pm 0.11-0.14$  Tmol/yr ( $3.5-4.5$  Tg S/yr).

The validity of these results is of course dependent on the reliability of the gradient-transfer approach to determine DMS fluxes. Although the significant correlations observed (Figures 6a and 6b) could be considered as an evidence of this assumption, large uncertainties ( $\pm 45\%$ ) are introduced in DMS flux calculation from the gradient method. More accuracy in DMS flux calculation should be achieved in using the eddy correlation or eddy accumulation methods during specifically planned experiments, allowing performance of high-frequency or high-accuracy atmospheric DMS measurements.

### Conclusion

DMS atmospheric profiles observed in the 1-20 m layer over the Atlantic Ocean in June 1992 cannot be generally interpreted as resulting from a simple vertical eddy diffusion, although photochemistry was unlikely to significantly affect DMS gradients. In many occurrences, explanations can be suggested such as stable conditions preventing turbulence generation by buoyancy in some cases and possible fast vertical transport in other cases. Advection of air masses from neighboring areas where DMS emission was significantly different could also contribute to the observed atmospheric DMS concentrations, particularly at 20 m height. Therefore the gradient-transfer approach can only be used to determine fluxes in situations that fulfill the assumptions on which it is based, especially the condition of horizontal homogeneity.

Indeed, only four among the 29 profiles performed in the 1-20 m atmospheric layer could be fitted by an analytical form deduced from the gradient-transfer approach and assuming a constant DMS flux in this layer. These fluxes compare well ( $\pm 20\%$ ) with the estimates of DMS flux in the 1-6 m layer calculated using averaged values of eddy diffusion coefficient between these two levels. The 15 values of DMS flux calculated by the gradient-transfer approach in cases where a decrease in DMS was observed in the 1-6 m layer were compared with DMS sea-air flux values obtained from the sea-air exchange model for the same instant. These DMS fluxes estimated by two completely independent methods show a significant correlation ( $R = 0.7$ ,  $n=15$ ), with intercept not significantly different from 0. The slopes of the regressions indicate that the gradient-transfer approach lead to estimates of DMS flux higher by a factor of 1.6-1.9 and 1.1-1.4 than the use of the parameterization of the sea-air exchange coefficient by *Liss and Merlivat* [1986] and *Smethie et al.* [1985], respectively. This confirms the suggestion of *Erickson et al.* [1990] that  $K_w$  values estimated from *Liss and Merlivat's* [1986] parameterization could be underestimated by a factor of 1.8. Taking into account that the most recent estimate of global DMS oceanic flux ( $0.48 \pm 0.33$  Tmol/yr, i.e.  $15 \pm 10$  Tg S/yr) reported by *Bates et al.* [1992] was based on *Smethie et al's* [1985] parameterization of  $K_w$ , this figure could be reevaluated by 10-40%. However, large uncertainties introduced in the DMS flux calculation by the gradient approach method ( $\pm 45\%$ ) prevent these results being considered as definitive.

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- B.C. Nguyen, Centre des Faibles Radioactivités, CNRS, Av. de la Terrasse, F-9118 Gif-sur-Yvette cedex, France. (e-mail: bacuong@saclay cea.fr)
- J.-P. Putaud, Joint Research Centre, TP 460, I-21020 Ispra (Va), Italy. (e-mail: jean.putaud@jrc.it)

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