Short-term variability in marine atmospheric dimethylsulfide concentration

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Abstract. Dimethylsulfide (DMS) concentrations measured twice per hour in marine boundary layer air at the Cape Grim baseline station exhibit high variability over timescales as short as several hours. Major sources of this variability are identified as a diurnal cycle associated with the daytime destruction of DMS by reaction with hydroxyl radical, and a strong dependence upon wind speed, with high DMS concentrations at high wind speeds. The wind speed dependence was found to be broadly consistent with the wind speed dependence proposed by Liss and Merlivat [1986] for 10 m wind speed in the range 3.6 to 13 m s^{-1} .

Introduction

The major natural source of reactive sulfur to the global atmosphere is believed to occur in the form of dimethylsulfide (DMS) emissions from biological activity in the surface waters of the global oceans [Bates et al., 1992; Spiro et al., 1992]. However estimates of the total DMS emissions from the global oceans are difficult to make from representative measurements, since these have not been made over all of the globe [Bates et al., 1987, 1992]. Accordingly, estimates have usually been made by combining measured and assumed data on surface water DMS concentrations with a sea-air transfer velocity that is a function of wind speed, and Schmidt number (the ratio of kinematic viscosity of seawater and DMS diffusivity in seawater).

The wind speed dependence of transfer velocity is thought to be large for wind speeds above about 4 m s^{-1} so uncertainty in this dependence is potentially one limiting factor in determining the accuracy with which global DMS emission fluxes may be calculated [Erickson et al., 1990; Bates et al., 1992; Spiro et al., 1992; Bates et al., 1993], especially since one of the most widely used parameterisations, that of Liss and Merlivat [1986], has not been rigorously tested on DMS [Liss and Merlivat, 1986; Watson et al., 1991].

Once DMS is in the marine atmosphere the rate at which it is oxidised to the aerosol products that may have a role in climate regulation [Charlson et al., 1987] is a linear function of DMS concentration. Thus the factors influencing not just

DMS flux but also DMS concentration must be understood if quantitative assessment and modelling of the hypothesised DMS-sulfate aerosol-cloud albedo climate feedback are to be carried out [Lawrence, 1993]. As discussed above we can expect the wind speed dependence of DMS sea to air transfer to be one such factor, along with a diurnal variability in DMS concentration associated with a diurnal cycle in DMS oxidation, which in clean air in summer should be dominated by daytime reaction with hydroxyl radical.

Here we discuss data on DMS air concentration measured at relatively high frequency (twice per hour) over an 18 day period in summer at the Australian baseline station at Cape Grim. Variance in the data record is investigated for evidence of diurnal variability and dependence on wind speed, with the parameterisation given by Liss and Merlivat [1986] for transfer velocity as a function of windspeed providing a convenient (though not the only available) framework for assessment of the latter.

DMS and Wind Speed Data

DMS and wind speed data were obtained from 1st-18th December 1993 at an altitude of approximately 110 m above sea level at the Cape Grim atmospheric observatory ($40^{\circ} 41'S$, $144^{\circ} 41'E$), located at the apex of the Cape, which juts out into the Southern Ocean in a southwesterly direction.

The wind speed data were obtained as hourly mean values derived from 1 minute averages recorded from the observatory's Vaisala WAA-15 anemometer. DMS data were obtained twice per hour from 4 litre air samples using an automated gas-chromatograph/sulfur-chemiluminescence detector system employing a cryogenically cooled sample trap after water and oxidant removal [Kittler et al., 1992]. Calibration was by injection of a known quantity of methylethylsulfide, as an internal standard. Analytical imprecision, determined using several different permeation tubes operated as both internal and external standards, was no worse than $\pm 10\%$ over the normal range of atmospheric DMS concentrations. Figure 1 contains a time series plot of the DMS data from 1st to 18th December 1993, presented as hourly means.

Data Analysis

The variance evident in Figure 1 can be shown to have at least two major sources, variance associated with the diurnal photochemical cycle that produces daytime removal

Figure 1. Time series of hourly mean DMS concentrations measured at Cape Grim, Tasmania, in December 1993, derived from two measurements per hour.

(oxidation) of DMS, and variance at less regular timescales associated with changing meteorological conditions, especially changes in wind speed.

We consider first the variations in atmospheric DMS concentration occasioned by changes in sea-air transfer resulting from variation of wind speed. For this we require a conceptual framework linking wind speed and DMS sea-air transfer. One convenient and much used parameterisation is provided by Liss and Merlivat [1986], who suggested a non-linear dependence of gas transfer velocity on wind speed represented by a linear piecewise continuous function. The middle linear segment, covering the 10 metre wind speed range 3.6 to 13 m s⁻¹, covers the wind speed range encountered during our experimental period.

Figure 2 contains a plot of purely "marine" DMS data (a total of 181 hourly means) stratified and averaged according to 1 m s⁻¹ hourly mean wind speed bins. Note that these data correspond strictly to hours in which wind direction was directly off the Southern Ocean (190° < wind direction < 280°). Note also that the wind speeds used have been scaled to the usual 10 m reference altitude [Liss and Merlivat, 1986] from the 110 m measurement altitude, on the assumption that air

Figure 2. Observed (points) and predicted (line) wind speed dependence of DMS concentration in "marine" air at Cape Grim in December 1993. The single point on the predicted line corresponds to the mean "marine" DMS concentration, 2.2 nmole m⁻³, plotted against the corresponding mean wind speed derived from these 181 hourly data, 9.4 m s⁻¹.

sampled at this level over the Cape originated at 30 m altitude over the open ocean [Baines and Murray, 1994]. A standard logarithmic wind profile with drag coefficient, C_D expressed in terms of 10 m wind speed, U_{10} , as

$$C_D = (0.75 + 0.067U_{10})/1000 \quad (1)$$

was employed, yielding an average decrease of 5% in wind speed going from 30 m to 10 m.

The data in Figure 2 clearly exhibit a very strong dependence of DMS concentration on wind speed. However interpretation of these concentration data in terms of DMS transfer velocities requires a knowledge of DMS air-sea flux, not air concentration. We use a simple atmospheric box model and the Liss and Merlivat [1986] parameterisation to make this connection, while at the same time providing an evaluation of the variance in DMS concentration caused by the diurnal oxidation cycle.

Atmospheric removal of DMS from the marine boundary in summertime (December) conditions should be dominated by reaction with hydroxyl radical [Thompson et al., 1994]. We modelled this daily removal of DMS using a very simple boundary layer box model in which OH concentration is calculated from just the few central reactions involved in the O₃ - CH₄ - CO photo-oxidation cycle, as shown in Table 1. The justification for using this small reaction set is the fact that under the low NO_x /low NMHC conditions encountered in the very clean air masses over the Southern Ocean these few reactions dominate the OH formation and removal processes, an assertion that has been borne out by the ability of this simple model to account for the major features of the seasonal and diurnal and cycles of O₃ and H₂O₂ at Cape Grim [Ayers et al., 1992].

As applied here to simulated DMS removal during the experimental period the box model employs climatological mean data for December at Cape Grim for input parameters such as temperature, humidity, O₃, CH₄ and CO concentration, as described by Bentley and Ayers [1991]. The actinic fluxes used to drive the photochemistry were scaled to 60% of the clear-sky values to approximate the reduction in boundary layer solar irradiance caused by the ubiquitous marine stratus clouds present for much of the experimental period. This value was derived from a comparison of previously published values for daily global solar exposure at Cape Grim in December [Forgan, 1994], of 22.6 MJ m⁻² compared with the theoretical value for a clear sky (transmissivity 0.8) of 36.0 MJ m⁻². Boundary layer

Table 1. Simple kinetic scheme used in boundary layer box model. For details see Bentley and Ayers [1991] and Ayers et al., [1992]

O ₃ + hν → O(¹ D) + O ₂	J1
O(¹ D) + H ₂ O → 2OH·	K2
O(¹ D) → O(³ P)	K3
CO + OH· → H· + CO ₂	K4
CH ₄ + OH· → CH ₃ · + H ₂ O	K5
O ₃ + OH· → HO ₂ · + O ₂	K6
H· + O ₂ → HO ₂ ·	K7
CH ₃ · + O ₂ → CH ₃ O ₂ ·	K8
HO ₂ · + O ₃ → OH· + 2O ₂	K9
HO ₂ · + NO → OH· + NO ₂	K10
CH ₃ O ₂ · + NO → CH ₃ O· + NO ₂	K11
2HO ₂ · → H ₂ O ₂ + 2O ₂	K12
2CH ₃ O ₂ · → products	K13
HO ₂ · + CH ₃ O ₂ · → CH ₃ OOH + O ₂	K14
H ₂ O ₂ + hν → 2OH·	J2
CH ₃ OOH + hν → OH· + CH ₃ O·	J3
H ₂ O ₂ → dry deposition	K15
CH ₃ OOH → dry deposition	K16

Figure 3. Solid lines : modelled and observed overall (hourly) average diurnal cycle in DMS concentration at Cape Grim in December 1993. Dashed line : complementary wind speed averages.

depth, H , was assumed to be 1000m, based on the potential temperature profiles from December 1986 recorded near Cape Grim by Berresheim et al. [1990].

The time dependence of the diurnal variations in DMS concentration in the atmospheric boundary layer may then be expressed as resulting from a balance between the DMS flux into the boundary layer from the ocean, and DMS removal from the boundary layer may via reaction with OH and entrainment into the lower troposphere above the boundary layer :

$$\frac{d[\text{DMS}]}{dt} = \frac{F_{\text{DMS}}}{H} - K[\text{OH}][\text{DMS}] + \frac{E_v([\text{DMS}_t] - [\text{DMS}])}{H} \quad (2)$$

where F_{DMS} is the surface flux of DMS into the boundary layer, K is the 1st order rate constant for reaction of OH with DMS, E_v is the boundary layer-lower troposphere entrainment velocity (set to 0.0035 m s^{-1} ; Ayers and Galbally, 1995), and $[\text{DMS}_t]$ is the concentration of DMS in the lower troposphere, just above the boundary layer. Based on aircraft profiles of DMS concentration measured near Cape Grim in December 1986 $[\text{DMS}_t]$ was set to 10% of the boundary layer concentration [Berresheim et al., 1990].

Equation 2 was solved for F_{DMS} according to the constraint that the modelled 24 hour average DMS concentration was required to equal the average concentration observed during the field experiment (2.5 nmol m^{-3} , see Figure 1). An F_{DMS} value of $3.3 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ resulted, which yields the model-predicted diurnal cycle shown in Figure 3, where the average diurnal cycle derived from the 18 days of measured DMS data is also plotted. For maximum representativeness and equal weighting of all hours in this overall comparison the observed DMS data were not selected according to wind direction, so include both "marine" air masses arriving directly off the Southern Ocean, as well as "modified marine" air masses which had a short fetch (up to a few km) over the coastline either side of the Cape, so >800 data points underlie the "observed" curve.

The correspondence between the two curves in Figure 3 suggests that the model provides a satisfactory means of using observed atmospheric DMS concentrations to derive a self-consistent estimate of the DMS sea-air flux needed to balance the observed diurnal DMS loss. This then provides the necessary tool to enable investigation of the wind speed dependence of DMS sea-air transfer, via analysis of the observed wind speed dependence of atmospheric DMS concentration. The agreement between the observed and modelled average diurnal cycles also gives some confidence

that the ratio of the maximum /minimum concentration extremes, 1.7, derived from the model curve is representative of the fractional variance in concentration contributed by the DMS oxidation process. To confirm that diurnal variations in wind speed cannot be the cause of the observed diurnal variation in DMS concentration Figure 3 includes a plot of the complementary average wind speed data.

Results

We note first that the wind speed range encountered during the measurement period extends little beyond the middle linear segment of the Liss and Merlivat [1986] transfer coefficient parameterisation, covering the 10 metre wind speed range 3.6 to 13 m s^{-1} . Thus we are essentially testing the appropriateness of a single linear relationship, making it permissible to obtain an initial nexus between DMS concentration and wind speed by taking a simple average of both DMS concentration and wind speed across the whole experimental period. In other words, the DMS flux deduced by requiring equality between the modelled and the observed daily mean DMS concentrations, as done to produce the modelled result in Figure 3, can be associated with the mean wind speed that occurred during the measurement period, 9.4 m s^{-1} . This provides an initial point at which all three of DMS concentration, wind speed, and (a model-derived value of) F_{DMS} are defined.

Values of DMS concentration at other wind speeds may then be predicted from equation 2, using this initial estimate of F_{DMS} at 9.4 m s^{-1} , on the assumption that seawater DMS concentration is constant, and that F_{DMS} scales with variation in wind speed according to the Liss and Merlivat [1986] specification of transfer coefficient as a function of wind speed.

This approach was carried out both for the complete data set, and for the purely "marine" data set upon which the points in Figure 2 were based. The difference between the two sets of results was not significant in comparison with the significant level of "noise" on the observational data, which is evident in Figure 2. The computed wind speed dependence of DMS concentration is compared with the observational data in Figure 2, with the computed line derived as explained above from our simple boundary layer model with the DMS flux scaled from the initially defined "average" point. To do this, we used the Schmidt number scaling recommended by Liss and Merlivat [1986] to adapt their parameterisations from CO_2 to DMS, utilising a value of 1336 for the DMS Schmidt number at 285.8 K [Saltzman et al., 1990]. Considering the fact that a number of simplifying assumptions underlie our analysis, including the implicit assumption of a constant oceanic DMS concentration during our measurement period, the observed data points and computed curve in Figure 2 show a level of agreement that lends some credibility to the use of the Liss and Merlivat [1986] parameterisation, and confirms the importance of variations in wind speed as the major source of variance in DMS air concentration data during our experimental period.

Further Comments

It is important to acknowledge that other parameterisations for the variation of exchange coefficient with wind speed may be found in the literature, for example the quadratic parameterisation due to Wanninkhof [1992], as discussed by Bates et al. [1993]. Our choice of the Liss and Merlivat [1986] parameterisation was in part due to its linear form over most of the wind speed range of our measurements, which facilitated simple arithmetic averaging

of the data to produce an initial flux/wind speed point. At low wind speeds the scatter shown by the data points in Figure 2 is such that our data cannot provide useful discrimination between alternative formulations. At the higher wind speeds in Figure 2 it seems unlikely that the Liss and Merlivat [1966] parameterisation could be low by as much as the 77% discussed by Bates et al. [1993]. However we hesitate to use our results to draw quantitative conclusions about different parameterisations since a number of the assumptions underlying our analysis, especially the assumption of constant oceanic DMS concentration over the 18 days of our experiment, cannot be directly verified, making a formal uncertainty analysis impossible.

Finally, we acknowledge the very recent paper of Andreae et al. [1994] whose methods differed considerably from those used here, but whose conclusions (with some minor qualifications) were very similar to those reached here: Andreae et al. [1994] found day/night variability due to atmospheric DMS oxidation produced concentration variability of a factor of 1.5 to 3; the major source of variance in air concentration was due to variations in sea-air transfer resulting from variations in wind speed; and current air-sea transfer parameterisations do a reasonably good job of describing the latter process.

Summary and Conclusions

A simple model of DMS removal in the marine atmospheric boundary layer by reaction with OH and entrainment into the lower troposphere has been shown to reproduce well the diurnal cycle of DMS measured at Cape Grim in December 1993. The systematic daily variation in concentration due to the diurnal cycle was deduced to have an average day/night amplitude of a factor of 1.7.

The model was then used to predict the wind speed dependence of atmospheric DMS concentration in marine air according to the parameterisation of sea-air gas exchange proposed by Liss and Merlivat [1986]. Agreement between the predicted and observed wind speed dependence of atmospheric DMS concentration was sufficiently good to confirm that variation in sea-air transfer was a larger source of variance in atmospheric DMS concentration, which ranged over a factor of 4 for wind speed variations from around 4 to 16 m s⁻¹.

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