CO-OPERATIVE PROGRAMME FOR MONITORING
AND EVALUATION OF THE LONG RANGE
TRANSMISSION OF AIR POLLUTANTS IN EUROPE

BIOGENIC SULPHUR EMISSIONS
FROM THE NORTH ATLANTIC OCEAN

Leonor Tarrason

METEOROLOGICAL SYNTHESIZING CENTRE - WEST
THE NORWEGIAN METEOROLOGICAL INSTITUTE
P.O.BOX 43-BLINDERN, N-0313 OSLO 3, NORWAY
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Leonor Tarrason
CORRIGENDUM

Please note the following corrections to the EMEP/MSC-W manuscript: "Biogenic Sulphur Emissions from the North Atlantic Ocean" (Note 3/91).

Page 14: The caption for Table 2 should be "Comparison of emission budgets for sulphur dioxide for 1988, in $10^9$ g as S."

Page 15: The caption for Figure 9 should be "Estimated yearly emissions of SO$_2$ from the North Atlantic Ocean. Year: 1988. Units: 100 tonnes as S."

Enclosed is the figure corresponding the 1988 yearly emission of SO$_2$ from the North Atlantic Ocean in 100 tonnes as SO$_2$. 
Corrigendum: Estimated yearly emission of SO₂ from the North Atlantic Ocean.

Year: 1988. Units: 100 tonnes as SO₂
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PREFACE AND ACKNOWLEDGEMENTS

This note presents an emission budget for biogenic sulphur from the North Atlantic Ocean. The calculation is based upon the production of dimethyl sulphide (DMS) observed over the North Atlantic because DMS is considered to be the main source of gaseous sulphur over the ocean. The emissions are presented on a monthly basis. The introduction of seasonal variations is an important characteristic of the presented emission budget that claims to reproduce the observed seasonality of DMS production over the ocean.

This work would not have been possible without the collaboration of Dr. S. Turner from the School of Environmental Sciences at University of East Anglia. Special thanks to Professor P. Liss for his support and suggestions. The author is grateful to Professor A. Eliassen and Dr. T. Iversen for valuable discussions.

The calculations presented in this note have used meteorological data provided by ECMWF, Shinfield Park, Reading, Berkshire, U.K.
1. INTRODUCTION

Oceans play an important role in the global biochemical sulphur cycle and are a major source for the sulphate aerosol found in the marine troposphere. Dimethyl sulphide (DMS) has been identified as the main source of gaseous sulphur over the ocean. This compound accounts for more than 95% of the observed reduced sulphur in surface ocean waters (Cline and Bates, 1983) and is produced from the biological activity of phytoplankton. DMS is emitted to the atmosphere by sea-air exchange and is subsequently photooxidized to methanesulphonic acid (MSA) and sulphur dioxide (SO$_2$), and further to particulate sulphate (SO$_4^{2-}$). This aerosol is the major component of non-sea-salt marine sulphate and an important contributor to the acidity of natural precipitation. It also appears to act as cloud condensation nuclei (CCN), thereby affecting the cloud droplet size, cloud albedo and consequently, the radiative balance of the earth (Charlson et al., 1987; Bates et al., 1987).

In this context, budgets of DMS fluxes to the atmosphere are necessary both to establish the relative importance of natural and anthropogenic emissions to the chemistry of precipitation and to analyse the potential role of DMS as a climate regulating substance.

The first attempts to estimate the emissions of reduced sulphur from the ocean to the atmosphere were based on mass balance calculations. In 1963, Eriksson proposed a global yearly emission of 288·10$^{12}$ gS a$^{-1}$. This value was considerably reduced by Granat et al. (1976) who, also on the basis of mass balance for the total atmospheric budget of sulphur, calculated a global emission of 32·10$^{12}$ gS a$^{-1}$. Andreae and Raemdonck (1983) presented the first calculation based on observations of DMS concentrations over the ocean. Their estimate of 39·10$^{12}$ gS a$^{-1}$ has served as reference in several studies including natural emissions from the ocean. The importance of seasonal variations in the oceanic production of DMS was first indicated by Bates et al. (1987) who argued that former estimates of the global DMS fluxes to the atmosphere had biased towards the more productive summer season. They distinguished between summer (from May to October) and winter season (from November to April) and based their calculations on area-weighted analyses of DMS concentrations over the North Pacific Ocean. They estimated a global flux of 16·10$^{12}$ gS a$^{-1}$ which is in agreement with recent mass balance calculations (Kritz, 1982).

Observations of DMS contents in seawater indicate a significant seasonal variation in the biological production over the ocean. Maximum concentrations occur during the spring season while minimum concentrations have been observed during winter. The difference between spring and winter seasons appears to be larger and more pronounced at higher latitudes. So, for example, over the North Sea, there is a pronounced maximum in spring, a minor maximum in autumn and almost no DMS production during winter (Turner et al., in prep.).

The purpose of this study is to provide a description of DMS production over the North Atlantic Ocean that includes both seasonal and regional variations and that can be used in acid deposition models. Special attention is given to the North Sea, since the biological productivity and the geographical position of that area makes it particularly important as a potential contributor to the acid deposition levels over Europe.
2. DESCRIPTION OF METHODS

2.1 Calculation of DMS fluxes: sea-air exchange

The flux density of gases across the sea-air interface is usually estimated by assuming that the flux is proportional to the product of the concentration difference across the interface and a first order exchange coefficient:

\[ F = \Delta C \cdot K_w \]  \hspace{1cm} (1)

where \( \Delta C \) is the concentration difference that produces the flux and \( K_w \) is the transfer velocity. \( \Delta C \) is defined as the difference between the equilibrium concentration in water with respect to the concentration of the gas in air at 10m, \( C_a \cdot H^{-1} \), and the actual concentration in water, \( C_w \):

\[ \Delta C = C_a \cdot H^{-1} - C_w \]  \hspace{1cm} (2)

and \( H \) is Henry's Law constant.

For the case of DMS, the concentrations in marine air are at least two orders of magnitude below the concentrations in equilibrium with seawater (Barnard et al., 1982) implying that \( C_w \gg C_a \cdot H^{-1} \), and \( \Delta C \approx C_w \). In other words, the sea surface is supersaturated with DMS which results in a net flux of DMS directed towards the atmosphere. Once released to the atmosphere, the steady state concentration of DMS is kept quite low by rapid reaction with hydroxyl radicals. The sea-to-air flux may therefore be estimated as the product of the exchange velocity, \( K_w \), and the observed DMS concentrations in seawater, \( C_w \).

\[ F = C_w \cdot K_w \]  \hspace{1cm} (3)

2.1.1. DMS concentrations, \( C_w \)

DMS concentrations in seawater are available from different observational campaigns. The main characteristic of the observed DMS concentrations is its patchiness. This is a consequence of its biological origin which makes spatial extrapolation difficult. Studies of chlorophyll distributions over the ocean have been suggested as a possible method for mapping DMS production areas. However, this method can be inaccurate because the ratios between chlorophyll and DMS productions are not well known. Significant DMS production seems to be associated with very specific phytoplankton species, p.e. coccolithophore (Malin et al., in prep.) so that highly productive phytoplankton areas do not necessarily correspond to high DMS concentrations. At present, the mapping of DMS over the ocean is made through a classification of different production areas, based on area averages of the observations.
This study distinguishes 3 different production areas over the North Atlantic Ocean (see Figure 1) and considers them subject to different seasonal variations:

a) open ocean areas (lower production, smoother seasonal variations)
b) shelf and coastal regions (larger production, more pronounced seasonal variations)
c) the North Sea

There are no coherent field studies of the seasonality of DMS concentrations in the North Atlantic Ocean, neither for the open ocean nor for shelf or coastal areas. However, at the Bermuda Workshop on N and S Cycling in the NAO Atmosphere (April, 1990) an attempt was made to collate all field observations (at different latitudes and months) to derive a best estimate for a generalized seasonal cycle for DMS concentrations (Johnson et al., submitted). The adopted concentrations are shown in Figures 2 a) and b) where the curves indicate the possible ranges of uncertainty in the determination of a seasonal cycle from the analysed data.

**Figure 1.** Adopted division of the North Atlantic Ocean.  
a) open ocean  
b) shelf and coastal regions  
c) North Sea
The North Sea is studied separately because of its high productivity and its closeness to North Western Europe. The seasonal cycle for the North Sea has been produced by Dr. S. Turner on the basis of all cruise observations collected in the area by their research group at the University of East Anglia (Turner et al., in prep) and is given in Figure 2 c). The uncertainty margins in this case correspond to the 75% and 25% percentiles from observations.
2.1.2. The Transfer Velocity, $K_w$

The transfer velocity on sea-air exchange is usually considered a function of the kinetic viscosity, molecular diffusivity, wind speed and seawater temperature. Different models and experimental approaches have been used to describe the gas transfer process. A short description of these can be found in Liss and Merlivat (1986).

The transfer velocities used in the present study are calculated with the empirical law of Liss and Merlivat. This law represents a good synthesis of the different available estimates and is based on lake and wind-tunnel experiments. It considers the transfer velocity as a function of the wind speed and distinguishes three types of roughness regimes (see figure 3). The figure shows Liss and Merlat's idealised dependence of the transfer velocity with the wind speed and compares it with results from other techniques. The transfer velocities calculated with isotopic analysis techniques ($^{222}$Rn and $^{14}$C) are generally larger than the values suggested by Liss and Merlivat and show very little dependence with the wind fields (Bates et al., 1987; Liss and Merlivat, 1986). Recent experiments using dual tracer techniques (Watson et al., 1991) seem to confirm the dependence with the wind fields that is suggested in Liss and Merlivat's parameterization.

In numerical terms, the three roughness regimes are distinguished as follows:
\[ K_w = 0.17 \cdot u \quad \text{for} \quad u \leq 3.6 \quad \text{(Smooth Surface Regime)} \]  
\[ K_w = 2.85 \cdot u - 9.65 \quad \text{for} \quad 3.6 < u \leq 13.0 \quad \text{(Rough Surface Regime)} \]  
\[ K_w = 5.90 \cdot u - 49.30 \quad \text{for} \quad u > 13.0 \quad \text{(Breaking Wave Regime)} \]

where "u" represents the wind speed at 10m and is given in m s\(^{-1}\), and \( K_w \) is given in cm h\(^{-1}\). This parameterization is valid for a gas with Schmidt number \( Sc=600 \) at 20°C and has to be corrected in accordance with the Schmidt number of the gas under consideration.

The Schmidt number, \( Sc \), measures the ratio between the transfer coefficients in water for momentum (the kinematic viscosity, \( \nu \)) and mass (the molecular diffusivity, \( D \)). The adopted parameterization establishes that for a smooth surface regime (\( u \leq 3.6 \) m/s), the dependence of the transfer velocity with the Schmidt number is proportional to \( Sc^{-2/3} \) (in agreement with boundary layer models, which seem to work correctly under calm conditions). For larger wind speeds, the dependence is assumed to be \( K_w \propto Sc^{1/2} \). For a given gas, the Schmidt number decreases with temperature which implies that the transfer velocity is enhanced as temperature increases. The Schmidt number for DMS has been calculated at different temperatures and has been introduced to modify equations (4), (5) and (6). It can be noted that the transfer velocities calculated in this way are non-linear functions of the wind fields and the surface temperature.

**Figure 3.** Liss and Merlivat’s (1986) transfer velocity estimate (solid line) compared to results from other methods.

In this study, transfer velocities are calculated every 6 hours from the actual wind fields and the sea surface temperatures. Six-hourly DMS fluxes are then calculated according to equation (3) and the results accumulated into monthly values. Because of the non-linear dependence of \( K_w \) with the meteorological conditions, the fluxes calculated in this way are expected to be more accurate than the ones deduced from climatological analysis. The calculated monthly fluxes do not necessarily correspond to the values that would result from an averaged wind and temperature field.
2.2. Photooxidation of DMS

The mechanisms involved in the photochemistry of DMS in air are still under discussion. However, it is generally agreed that the main products of DMS photooxidation are sulphur dioxide, SO₂ (further oxidized to particulate sulphate) and methanesulfonic acid, MSA. Recent studies of Yin et al. (1990) indicate that SO₂ is the principal product of DMS photooxidation, although the actual yield of SO₂ can be reduced in presence of high concentrations of NOx. The NOx mixing ratios that these authors consider that would affect the production of SO₂ from DMS are 0.12-18 ppm for NO and 0.02-0.03 ppm for NO₂. These values are well above the normal levels usually observed above coastal areas. The observed ranges over Europe are normally 15 ppt < NO < 7ppb, and 70 ppt < NO₂ < 12 ppb (Iversen et al., 1990). For this reason, the production of SO₂ from DMS is considered in this study to be 66%, in agreement with Yin et al. experiments in presence of "low" NOx concentrations.

Figure 4 shows a very simplified photooxidation mechanism for dimethylsulphide. Because the lifetime of DMS is considered to be approximately 14 hours (Warneck, 1988), the present estimation of the monthly biogenic fluxes of sulphur does not involve any further chemistry of DMS than a simple yield to sulphur dioxide and methane sulphonic acid.

![Figure 4. Simplified atmospheric photooxidation of dimethylsulphide](image)

A question that remains under discussion is the further evolution of MSA. Some authors (Warneck, 1988) suggest that MSA associated with the marine aerosol is rapidly oxidized to sulphuric acid. Yin et al. propose instead an oxidation pathway through CH₃SO₃, a precursor of MSA. In any case, there seems to be a mechanism responsible for the production of particulate sulphate from DMS other than the oxidation of sulphur dioxide. This implies that the acidification levels derived from the oxidation of SO₂-only might underestimate the effect of DMS in the chemistry of precipitation.
3. RESULTS

DMS fluxes have been calculated for the meteorological conditions of 1988. Wind fields at 10m and surface temperatures are 6-hourly analyses from the European Center for Medium-Range Weather Forecasting (ECMWF), given with a spatial resolution of 150x150 km².

Figure 5 shows the accumulated yearly fluxes of DMS from the North Atlantic area under consideration. The emission is given in $10^3$ tonnes of S per grid square per year. The spatial distribution of the biogenic emissions corresponds with the initial distinction between production areas, so that coastal areas have larger yearly emissions than open sea areas. The large emission regions east of Canada and south of Iceland are a consequence of the meteorological conditions, in contrast to coastal areas at lower latitudes.

**Figure 5.** Spatial distribution of the calculated DMS yearly emissions from the North Atlantic Ocean. Year: 1988. Units: $10^3$ tonnes S per grid square per year.
The effect of meteorology in the calculation of fluxes is illustrated in detail in Figure 6. This figure shows how the seasonal variation of DMS fluxes relates to the variation of seawater concentrations and of the monthly averaged meteorological conditions. The meteorology effect is described by calculating the monthly fluxes in the case of a constant monthly concentration of DMS in water of 3.06 nmol S l\(^{-1}\) (the yearly average). This is an indication of the effect of the monthly averaged exchange velocities. DMS fluxes follow primarily the seasonal variation in oceanic production, although the actual importance of the fluxes is weighted by the effect of meteorology. For instance, weaker winds around Irafoss (Iceland) during May '88 justify the displacement of maximum DMS fluxes to April '88, while maximum concentrations in water occured during May.

![Meteorological Effect](image)

**Figure 6.** Seasonal variation of DMS fluxes in relation to the seasonal variation of concentrations in water and the effect of meteorology. Values for a single gridpoint near Irafoss, Iceland. Note that each curve is expressed in different units: fluxes in mgS m\(^{-2}\)month\(^{-1}\) and concentrations in nmol S l\(^{-1}\).

The seasonal variation of DMS fluxes over the North Sea is given in Figure 7. Monthly fluxes are integrated over the North Sea area (~ 600,000 km\(^2\)). The North Sea emissions show a pronounced seasonality with maximum emissions during May and an important secondary maximum during late summer. The secondary maximum is a consequence of the meteorological conditions of 1988 which enhanced the importance of the late summer concentration maximum. The yearly DMS flux from the North Sea is estimated to 32.2 \(\times\) 10\(^6\) gS a\(^{-1}\). However, the uncertainties associated with the area averaged DMS concentrations in water imply a range of variation in the yearly fluxes between 12.9 and 39.1 \(\times\) 10\(^6\) gS a\(^{-1}\).
Figure 7. Seasonal variation of DMS fluxes integrated over the North Sea. The curves indicate uncertainty ranges derived from the estimation of the DMS concentrations in water.

Figure 8. Seasonal variation of DMS fluxes integrated over the North Atlantic Ocean. The curves indicate uncertainty ranges derived from the estimation of the DMS concentrations in water.
Figure 8 shows the seasonal variation for the total North Atlantic area under consideration (~ 35,000,000 km²). Maximum DMS emission months are April, May and June. The autumn secondary maximum in oceanic production does not appear in this average. Averaging the seasonal variation over different production areas and different meteorological conditions, tends to reduce the importance of the secondary maximum. The yearly flux integrated over the North Atlantic is estimated to be 1569·10⁹ gS a⁻¹. The uncertainty range derived from the estimation of the DMS concentration fields corresponds to a factor of 2 variation in the North Atlantic yearly fluxes, with a maximum estimate to 3610·10⁹ gS a⁻¹ and a minimum estimate to 649·10⁹ gS a⁻¹.

A yearly flux of 1569·10⁹ gS corresponds to an averaged flux over the North Atlantic of ~ 130 μgS m⁻² day⁻¹ ( = 4.06 μmolS m⁻² day⁻¹ ). Extrapolation of this averaged flux to the total oceanic surface would yield a global flux of sulphur of ~15·10¹² gS a⁻¹ which coincides quite well with the 16·10¹² gS a⁻¹ estimated by Bates et al. (1987). Table 1 compares results from the North Atlantic and North Pacific seasonal studies. The yearly averages are quite similar and therefore give similar results for the global DMS flux. However, the two studies show certain differences in their seasonal analysis. Table 1 shows how the area weighted averaged concentrations used for the North Atlantic are larger than the North Pacific averages. At the same time, the exchange velocities calculated for the present study are, on average, about 30% smaller than the transfer velocities used by Bates et al. That difference could have been expected since these authors use exchange velocities based in the ²²²Rn deficit experimental technique.

<table>
<thead>
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<th>Table 1. Comparison of results between two different studies.</th>
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<tbody>
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<td>NORTHERN PACIFIC</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>SUMMER</td>
</tr>
<tr>
<td>Area Weighted Averages</td>
</tr>
<tr>
<td>DMS conc. in seawater (μmol S l⁻¹)</td>
</tr>
<tr>
<td>Kₑ exchange velocities (m day⁻¹)</td>
</tr>
<tr>
<td>DMS fluxes (μmol S m⁻² day⁻¹)</td>
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Global values for DMS emissions

<table>
<thead>
<tr>
<th>μmol S m⁻² day⁻¹</th>
<th>g S a⁻¹</th>
</tr>
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<tbody>
<tr>
<td>4.25</td>
<td>16·10¹²</td>
</tr>
<tr>
<td>4.04</td>
<td>15·10¹²</td>
</tr>
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The SO$_2$ yearly emissions have been derived from the DMS yearly fluxes by considering that 66% of the emitted DMS is subsequently oxidized to sulphur dioxide. Consequently, the same seasonal variations depicted in Figures 7 and 8 are valid for the SO$_2$ emissions.

The emissions in Figure 9 (see next page) are expressed in the EMEP domain. The calculated SO$_2$ yearly emissions are similar to the emission of 2·$10^3$ tonnes as SO$_2$ per year per grid square that is used by the EMEP model (Iversen et al., 1990). However, the monthly variations of the calculated budget can introduce significant changes. A significant amount of the SO$_2$ biogenic emission takes place during special months and the emissions are then well above the year average. Table 2 shows how during the month of maximum biogenic emission (that is, May) the SO$_2$ emission over the North Sea can be larger than the Norwegian anthropogenic emission. During winter the biogenic emissions are considerably smaller.

The introduction of monthly variations in the biogenic emission from the North Atlantic ocean modifies the ratio of anthropogenic vs. natural emissions and consequently, it is expected to affect the deposition values over Western Europe.

<table>
<thead>
<tr>
<th>Emission area</th>
<th>SO$_2$ Emission</th>
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<tbody>
<tr>
<td>Denmark</td>
<td>121.00</td>
</tr>
<tr>
<td>Ireland</td>
<td>76.00</td>
</tr>
<tr>
<td>Norway</td>
<td>33.00</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>1832.00</td>
</tr>
<tr>
<td>Int. trade, North Sea</td>
<td>87.00</td>
</tr>
<tr>
<td>North Sea (DMS)</td>
<td>21.20</td>
</tr>
<tr>
<td>North Atlantic (DMS)</td>
<td>1035.50</td>
</tr>
</tbody>
</table>
Figure 9. Estimated yearly emission of SO$_2$ from the North Atlantic Ocean. Year: 1988
Units: 100 tonnes as SO$_2$. 

4. CONCLUSIONS

The calculation of DMS fluxes to the atmosphere is subject to considerable uncertainties, primarily related to the spatial distribution of DMS concentrations in water and also to the description of the sea-air exchange processes. In this study the uncertainty ranges have been considered in terms of the variations associated with the description of the seasonal cycles of DMS production over the ocean. These variations introduced an uncertainty factor of 2 in the calculated yearly fluxes from the North Atlantic Ocean. The given uncertainty ranges and the global flux calculation of $15 \cdot 10^{12}$ gS a$^{-1}$ are within the limits of other current estimates of biogenic fluxes from the ocean.

The monthly accumulated DMS fluxes to the atmosphere have been derived from the distinction of three production areas with different seasonal cycles and for the meteorological conditions of 1988. The introduction of the actual meteorological conditions in the calculation of the sea-air exchange has allowed the identification of a large emission area south of Iceland. The effect of the meteorology is also shown to be important for the determination of the seasonal cycle of DMS emissions to the atmosphere.

DMS emissions for the North Sea and the rest of the North Atlantic Ocean have been presented on a monthly basis. This seasonal description of biogenic emissions responds to the natural cycle of DMS production over the oceans and it is expected to modify the relative importance of biogenic contribution to the acidification levels over Europe.

A budget for North Atlantic SO$_2$ emissions has been estimated by assuming a constant 66% production yield of SO$_2$ from DMS. The introduction of MSA in the emission budgets is left as an option, that would depend on the photochemistry adopted by every particular model. It should be noted, however, that the omission of MSA in the biogenic budgets can underestimate the oceanic contribution to the acidity of precipitation.

The inter-annual variation of the DMS fluxes has not been explicitly considered in the present study. It is expected that the particular meteorological conditions of the different years can alter the distribution the maximum emission areas and affect the seasonal cycle. However, the uncertainty associated with the distribution of DMS concentrations in seawater is large in comparison with the expected effect of inter-annual variations, so that the presented 1988 budget might be considered representative for the different years.
REFERENCES


Malin, G., Turner, S., Liss, P., Holligan, P. and Harbour, D. Production of Dimethylsulphide and Dimethylsulphoniopropionate in the North East Atlantic during the summer coccolithophore bloom, in preparation.


