MODELLING EMISSIONS OF DMS FROM THE OCEAN, AT A EUROPEAN SCALE

Susannah.Grice@aeat.co.uk, James.Sturman@aeat.co.uk, Chris.Dore@aeat.co.uk, Mike Woodfield@aeat.co.uk

AEA Energy and Environment, The Gemini Building, Harwell IBC, Didcot OX11 0QR

ABSTRACT

To be written

I INTRODUCTION

Objective

The objective of this work is to improve and apply existing methods for estimating emissions of dimethylsulfide (DMS) from the ocean at a European scale. This is being done as part of the NatAir project, which aims to improve methodologies for quantifying natural and biogenic emissions to the atmosphere across Europe (XXX Reference to overview/special edition XXX).

A number of global estimates of total sea surface DMS emissions have been made in the past (e.g. Erickson, 1990, Tarrason et al., 1995). These have been calculated using a range of different modelling approaches. However, generally they have been applied at a relatively coarse spatial resolution (e.g. 1° x 1° latitude and longitude) compared to the 10 km x 10 km spatial resolution that has been used in this study.

The DMS emission estimates calculated in this study are both highly spatially and temporally resolved. More specifically, emission maps of DMS have been generated for the NATAIR extent, which includes the Baltic Sea, the Black Sea, the Mediterranean Sea, a section of the North Atlantic Ocean and a section of the Caspian Sea). The emission estimates have been generated at daily resolution for four years: 1997, 2000, 2001 and 2003. Annual emission totals are also presented by summing the daily estimates.

There is currently no suitable SNAP[1] or NFR[2] code for DMS emissions from the oceans, although the emissions estimated here are regarded as being attributable to the NATAIR extent, and have not been assigned to specific countries.

Background

Dimethylsulfide (DMS) is produced biologically and photochemically in ocean surface waters. It is then emitted into the atmosphere via sea-air gas exchange. Rapid oxidation of DMS then follows, leading to the formation of SO_2 and methane sulphonic acid (MSA) (Bates et al., 1992; Kettle et al., 1999). SO_2 can be further oxidized, leading to the formation of sulphate particles which can act as condensation nuclei (CN)>. Consequently, emissions of DMS are not only of relevance for the global biogeochemical sulphur cycle, but also (through cloud formation) may

[1] SNAP- "Selected Nomenclature for Reporting". A reporting format previously used for submissions to the LRTAP Convention, and a structure still favoured by many emission inventory compilers.
[2] NFR- "Nomenclature For Reporting". The reporting format currently used for submissions to the LRTAP.

alter the radiation budget of the earth (Charlson et al., 1987; Kettle et al., 1999; Yoon and Brimblecombe, 2002).

At high latitudes there is a pronounced seasonal cycle of seawater DMS concentration, showing a maximum in summer and minimum in winter (Kouvarkis and Mihlopoulos, 2002; Kettle et al., 1999). This corresponds to the seasonal cycle observed in measurements of atmospheric condensation nuclei, non-sea-salt sulphate and MSA.

A weaker seasonal cycles has been measured at lower latitudes (where there is larger annual average flux in spite of the smaller surface area). Whilst at the equator, there is almost no seasonal variation at all, despite the larger surface area (Kettle et al., 1999).

Recent measurements in the Mediterranean Sea have evaluated the biogenic contribution of sulphur to the atmospheric total non-sea-salt SO_4^{2-} concentration to between 0.6% and 28.3% (Mihalopoulos et al., 1997; Ganor et al., 2000).

II APPROACH/ METHOD

Available Modelling Approaches
The flux of DMS from the sea to the atmosphere can be modelled as a function of:

- The chemical potential of DMS at the sea-atmosphere interface (i.e. the difference between DMS concentrations in the water at the sea surface and DMS concentrations in the air just above it).
- Wind induced turbulence in the upper ocean (Kettle and Andreae, 2000).

However, the relationship between these variables is not well understood and therefore several different modelling approaches have been developed in a attempt to parameterise this emission mechanism and estimate fluxes (Kettle and Andreae, 2000). In particular, wind induced turbulence in the upper ocean, which is a kinetic constraint on the rate of flux, has been problematic to characterise. A frequently used concept is that of a "piston velocity"- the velocity with which gas diffuses across the air-sea interface in the stagnant film model. The piston velocity is proportional to the molecular diffusivity of the gas in sea water, and inversely proportional to the thickness of the stagnant film across which it travels. The piston velocity is also a function of wind speed and there are different approaches to parameterising this relationship.

The literature gives two different approaches used in parameterising the piston velocity. The earlier approach, for example used by Liss and Merlivat (1986) and Wanninkof (1992) expresses piston velocity as a function of wind speed and sea surface temperature (SST). However, failure to verify the relationship between piston velocity and wind speed has lead to alternative efforts to find a better parameterisation. This has included parameterisations of piston velocity as a function of surface roughness or wave average slope. For example, Erikson (1993) assumed a different transfer rate for areas with and without white cap coverage and Frew (in Kettle and Andreae, 2000) used satellite remote sensing images to obtain a flux using mean square wave slope.

Model Selection
From the range of models available in the literature (see Kettle and Andreae (2000) for a discussion of many of these), the semi-empirical model of Liss and Merlivat (1986) has been adopted for use here. Reasons for selecting this model include the following.

First, Liss and Merlivat's (1986) model explicitly represents three different wind speed regimes in the equations to calculate the piston velocity. These wind speed regimes are used as a proxy for different sea surface conditions, whereby the three model equations have been parameterised separately to best represent emissions from the sea surface for different possible conditions. This would seem to be more physically realistic than one equation covering all conditions, since it is likely that the exact mechanisms leading to DMS emissions from the sea will vary across a range wind speeds and sea surface conditions. The behaviour of the model under different wind speed regimes will be discussed further in the uncertainty analysis.

Second, the input data required in Liss and Merlivat's (1986) model equations are 10m wind speed (i.e. the wind speed at 10m above the sea surface) and SST data. These are relatively straightforward parameters to obtain, and suitable MM5 meteorological data has been provided for this study (Heiko Pfeiffer pers. Comm. 2006). Model equations relying on a more complex, and possibly less certain, set of input data would introduce further uncertainties to the model results. With both wind speed data and SST data, the uncertainties are well known and sensitivity analysis can then be used to test the impact of these uncertainties on the model results. It has therefore been possible to obtain a good understanding of the uncertainties introduced to the modelling through the input data using Liss and Merlivat's (1986) model.

Furthermore, one of the aims of this study was to produce spatially disaggregated DMS emissions, consideration must be given to the availability of spatially disaggregated input data (the MM5 meteorological data meeting the needs of the Liss and Merlivat model).

Since none of the models in the literature have been shown to produce consistently more reliable results than others, it was considered appropriate not to introduce further uncertainty through using a model with more complex input parameters. Although it should be appreciated that, as stated above, all available model parameterisations are considered to include significant levels of uncertainty in representing emissions of DMS.

Further discussion of the pros and cons of using this input data at the scale (spatial and temporal) for which the model has been run is presented in the uncertainty analysis section.

Model Equations

The model equations used in this work are presented below. These have been taken from Liss and Merlivat (1986) unless otherwise stated.

The flux (F) of DMS from the sea surface into the atmosphere in the model has been expressed as:

$$F = K_w \Delta C \qquad \text{(equation 1)}$$

where K_w is the piston velocity and ΔC is the difference between the DMS concentration in the water and air at the sea-atmosphere interface. ΔC can be calculated using equation 2:

$$\Delta C = (C_a/H)-C_w \qquad \text{(equation 2)}$$

where C_a is the atmospheric concentration, C_w is the concentration of DMS in the water and H is Henry's constant. However, since relative to the seawater concentrations of DMS, atmospheric concentrations tend to be negligible, equation 2 is simplified to:

$$\Delta C = -C_w \qquad \text{(equation 3)}$$

The piston velocity (K_w) has been modelled using three wind speed regimes, each representing different sea surface conditions with a semi empirical equation. These are:

Smooth surface regime (0-3.6 m s^{-1})

$$K_w = e_1(Sc_r/Sc)^{2/3}|U_{10}| \qquad \text{(equation 4)}$$

Rough surface regime (3.6-13 m s^{-1})

$$K_w = e_2(Sc_r/Sc)^{1/2}(|U_{10}|-3.6)+e_3(Sc_r/Sc)^{2/3} \qquad \text{(equation 5)}$$

Breaking wave regime (>13 m s^{-1}).

$$K_w = e_4(|U_{10}|-13)(Sc_r/Sc)^{1/2}+e_5(|U_{10}|-3.6)(Sc^r/Sc)^{1/2}+e^6(Sc_r/Sc)^{2/3} \qquad \text{(equation 6)}$$

where the constants are presented in Table 1. Sc is the non-dimensional Schmidt number of CO_2 at SST (see equation 7). This is the ratio of the absolute viscosity of seawater to the diffusivity of DMS in water. It is a function of SST (T) and has been calculated in the modelling presented here using the equation of Saltzman et al (1993):

$$Sc = 2674.0-147.12T+3.726T^2-0.038T^3 \qquad \text{(equation 7)}$$

Table 1: Constants used in equations 4, 5 and 6

Constant	Value
e_1	0.17
e_2	2.85
e_3	0.612
e_4	5.9
e_5	2.679
e_6	0.612
Sc_r [1]	600

[1] Schmidt number for CO_2 at 20ºC

Applying the Model to a European Scale

Figure 1 shows the European NatAir extent with the ocean area divided into 5 distinct sea areas. The spatial resolution at which the modelling has been carried out is 10 km x 10 km grid squares. In order to run the model at this scale, relatively fine resolution input data is needed. Details of the input data used in this analysis are given below:

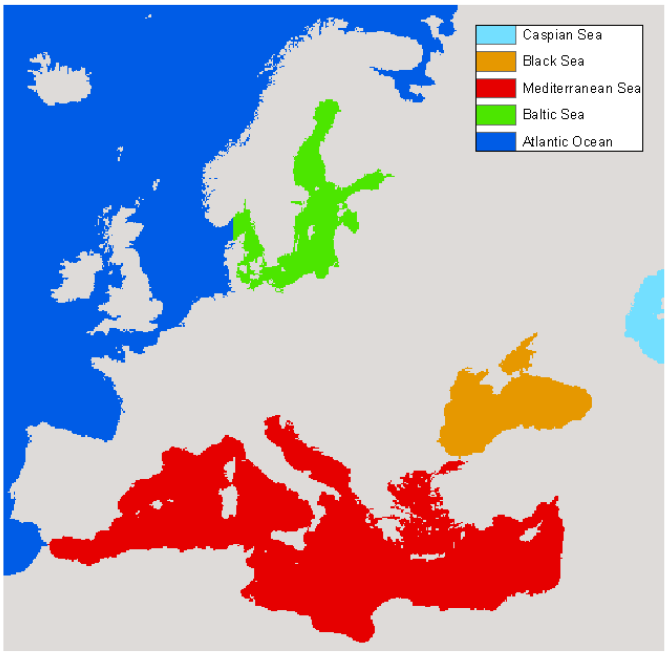
- MM5 meteorological data (24 km x 24 km) including 10m wind speed data and SST data
- Seawater DMS concentration data (1 x 1° latitude-longitude) from http://dss.ucar.edu/datasets/ds289.2. as described in Kettle and Andreae (2000)

The MM5 meteorological data was transformed to the NatAir grid (10 x 10 km resolution) using an area weighted averaging approach.

To generate mapped seawater DMS concentration data, the points coverage downloaded from the above website was transformed to a grid (50 km x 50 km) using an inverse distance weighted mean method- whereby each grid square has been calculated to be the same value as the point to which the centre point of the grid square is nearest. No seawater DMS concentration data are available for the black sea in the database describe in Kettle and Andreae (2000). Therefore we have taken the mean sea water DMS concentration in Eastern Mediterranean Sea and applied this across the Black Sea. A discussion of the implications of this assumption is given in the uncertainty analysis.

The temporal resolution that the model has been run at is a one day time step. This is because, although a shorter time step would have been preferable to capture wind speed variability, the SST data was only available at a daily time step and seawater DMS concentration grids were only available as a monthly average. The model has been run over four years: 1997, 2000, 2001 and 2003.

Figure 1: Marine area covered by the NatAir extent



III RESULTS

Figure 2 shows maps of modelled DMS emissions across the NatAir model domain for 1997, 2000, 2001 and 2003. Total emissions for this area for these years are presented in Table 2, along with total emissions for each sea area identified in Figure 1. Table 3 presents details of the average annual emission per grid square for these different sea areas. Figure 3 shows daily emission totals for each sea area identified.

Figure 2: Modelled DMS emissions maps (kg yr^{-1} $gridsquare^{-1}$)

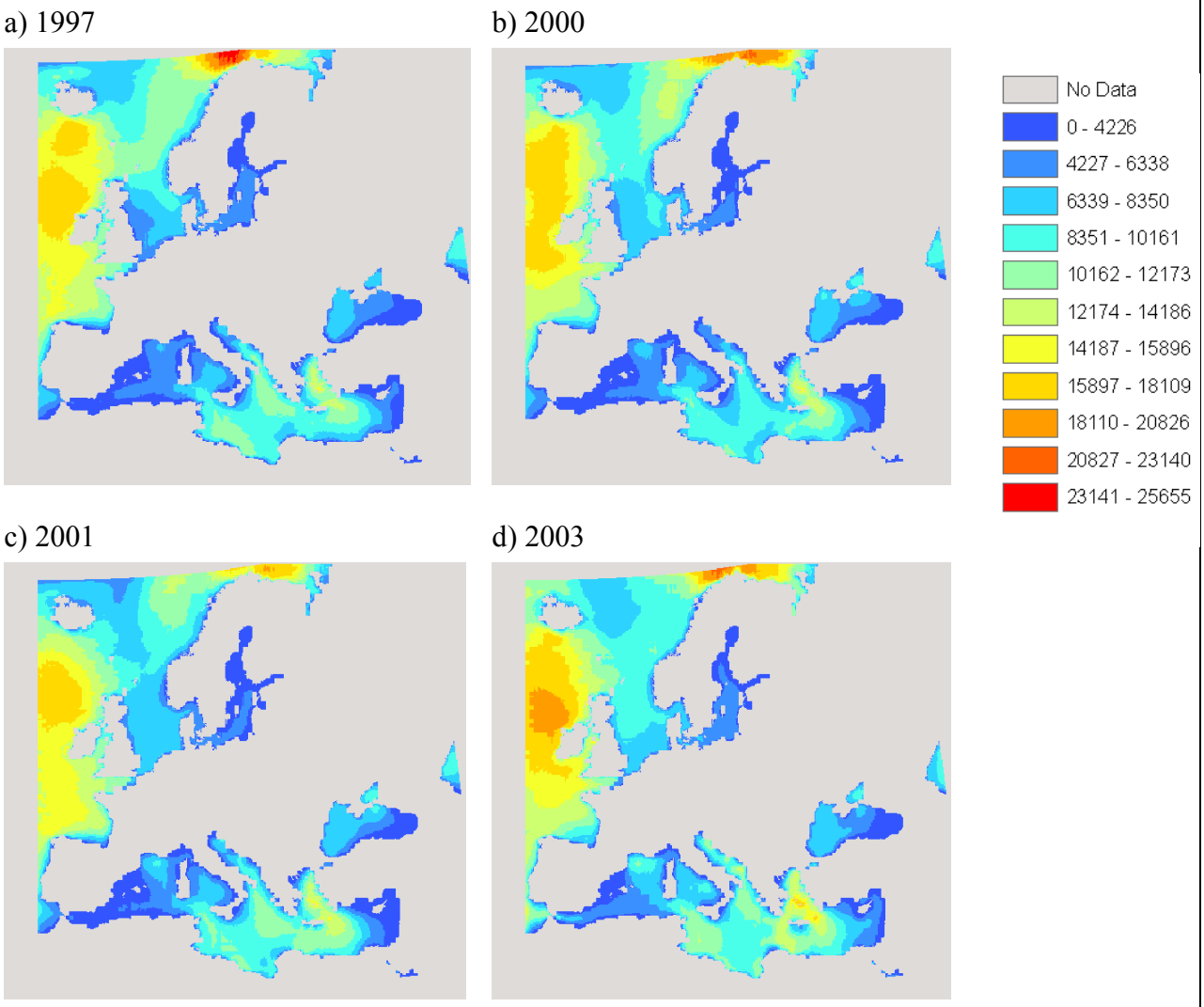


Table 2: DMS emissions within the NatAir extent (Gg/year)

Year	Total emission across NatAir grid	Caspian Sea	Black Sea	Mediterranean Sea	Baltic Sea	Atlantic Ocean
1997	698.4	6.3	21.2	166.1	16.1	488.6
2000	673.9	5.2	23.7	156.4	15.1	474.5
2001	662.3	5.1	24.6	170.6	14.5	447.3
2003	727.7	5.2	23.2	192.5	17.6	488.7

Table 3: Average DMS emission per grid square for different sea areas within the NatAir extent (kg/year)

Year	Total emission across NatAir grid	Caspian Sea	Black Sea	Mediterranean Sea	Baltic Sea	Atlantic Ocean
1997	8932.0	80.8	270.7	2124.7	205.7	6248.0
2000	8617.4	66.4	303.0	2000.7	193.0	6068.7
2001	8469.5	64.8	314.9	2181.3	185.4	5720.3
2003	9306.1	66.8	297.3	2462.2	224.9	6249.7

In all four years, the greatest total emissions of DMS, and the greatest emissions of DMS per grid square were modelled to occur in the section of the Atlantic Ocean covered by the NatAir model domain. Figure 2 shows that there was significant spatial variability within this area of the Atlantic in terms of the total emission per grid square. Two areas of particularly high emissions were evident for all four years in the North Atlantic. These were the sea area off the Northern most tip of Norway and the sea area running from just south of Iceland down to the Bay of Biscay off the west coast of France. Parts of the Eastern Mediterranean were also modelled to have had relatively high emissions per grid square, especially in 2003.

In terms of total emissions of DMS, 2003 had the greatest total of the four years modelled across the NatAir model domain, followed by 1997 and then 2000. Modelled total emissions in 2001 were 92% of the total emissions of DMS in 2003.

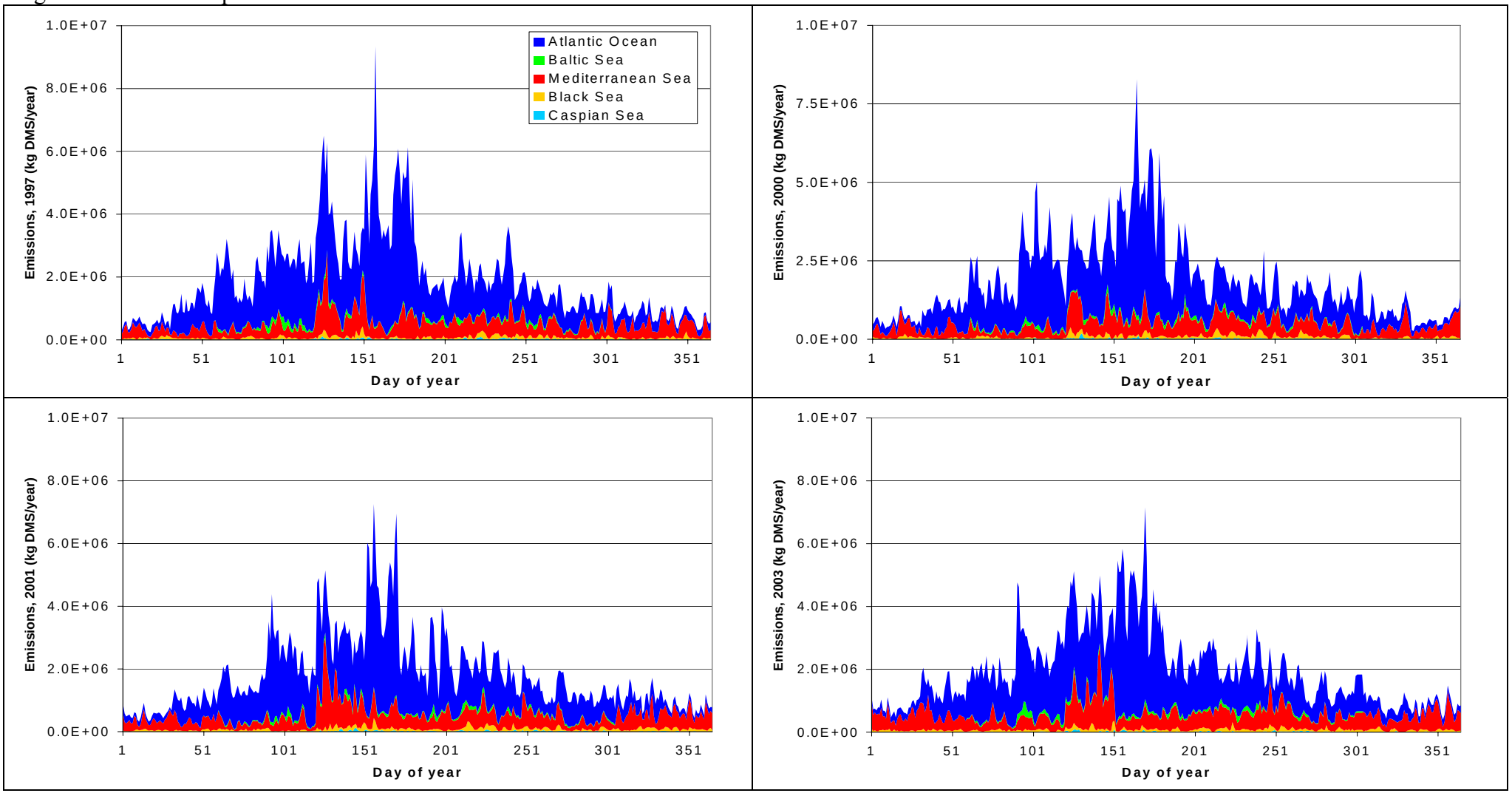
Figure 3 shows that in terms of temporal variability throughout the year, emissions from the section of the North Atlantic Ocean covered by the NatAir model domain tended to be highest in the first half of the year, with emissions typically dropping to very low levels by November, December and January compared with spring and early summer emissions. There was less evidence of seasonality in the other four sea areas considered in this analysis. However, emissions totals per day in the first four months of the year were generally lower for these four sea areas than in the rest of the year for all years modelled.

Figure 3 also shows how the relative contributions of emissions from each sea area to the total modelled emission varied throughout the year for all four years considered. The relative make up of total emissions tended to be dominated by emissions from the Atlantic. However, in January and December each year, the majority of DMS emissions were modelled as coming from the Mediterranean, rather than the Atlantic Ocean.

The seasonality of the total emissions are strongly influenced by the seasonality in the Atlantic Ocean for all years considered, because the vast majority of total emissions were modelled to come from the area of the Atlantic Ocean included in the model domain.

The seasonality in the results described above broadly agrees with observations from the literature. For example, Savoie and Propspero (1989) observed pronounced seasonal cycles at high latitudes in methane sulpfonic acid concentrations (produced exclusively by the atmospheric oxidation of DMS). At lower latitudes they observed a weaker seasonal cycle with none at all at equator. The section of the Atlantic Ocean included here is the covers the highest latitudes in the model domain and also displays the strongest seasonality. In the Mediterranean, which covers the lowest latitudes, there is the least evidence of seasonality in our model results.

Figure 3: Time series plots of emissions of DMS



Comparison with other Large Scale Emissions Estimates

Global annual DMS flux estimates range from 15 to 38.5 Tg S yr^{-1} and are presented in Table 4.

Table 4. Comparison of global DMS fluxes from the ocean (Kettle and Andreae, 2000)

Investigation	Annual DMS Flux (Tg S yr-1)
Nguyen et al. (1978)	26
Andreae and Raemdonck (1983)	38.5
Bates et al. (1987)	16
Andreae (1990)	19 – 54
Burgermeister et al.(1990)	24.8 - 28.3
Erickson (1990)	15
Staubes and Georgii (1993)	26.8
Tarrason et al. (1995)	15.5
Putaud and Nguyen (1996)	17 – 21
Kettle and Andreae (2000)	15 – 33

The sea area of the NATAIR extent represents approximately 5% of the global sea coverage, and the NATAIR emission estimates of DMS represent approximately 3% of the global estimates given in Table 1. There are a number of reasons why this difference may arise.

Grid cells in the NATAIR extent are not expected to give a good representation of the global average. This is because the sea areas in the NATAIR coverage are relatively sheltered compared to e.g. the whole of the Atlantic and the Pacific Oceans. As a result the wind speed (and hence average DMS emissions) are expected to be lower in the NATAIR extent than a typical global average for a marine location. The impact of sheltering on the emissions is clearly evident in Figure 2. The NATAIR extent also includes a limited range of latitudes, and whilst a range is included, this is not expected to be representative of a global marine coverage.

The modelling work has been conducted at a relatively high temporal resolution (daily). However, averaging the wind speed data to daily will have an impact on the emission estimates, and will tend to under represent the emissions, because the relationship with wind speed is non-linear. This is considered in more detail in Section IV Uncertainties.

IV UNCERTAINTIES

Model Equations

One of the greatest sources of uncertainty for any DMS modelling study lies in the approach adopted to model the piston velocity (K_w). As discussed in the method section, the piston velocity is very difficult to parameterise in a model (hence the numerous modelling approaches available in the literature). Therefore significant uncertainty is introduced to the model results.

In the model equations used in this study, wind speed has been used as a proxy for near surface kinetic energy. There is clearly is not a perfect relationship between wind speed and near surface kinetic energy so this approach does have some inherent draw backs. However, these two variables should be highly correlated such that when 10m wind speeds are high, near surface kinetic energy will also increase. A major source of uncertainty arises here because there may be other factors, such as sea currents, which affect the near surface kinetic energy as well as the wind speed.

Uncertainties specific to the model equations adopted in this study also include the use of wind speed to select which of the three different model equations should be used: smooth surface, rough surface or breaking wave regimes. While it is clearly the case that higher winds do result in rougher seas, it is not clear whether the cut off between sea surface conditions will always occur at the exact wind speeds defined in the equations. However, the advantages of this approach are that by using three different semi-empirical equations to represent DMS emissions from different surface conditions, the model should be better representing the emissions occurring than if only one equation was used. Therefore, one potential avenue for future work might be to consider alternative methods to classify which surface regime is dominating the area modelled.

Table 5 shows for all sea area grid squares across the 365 (or 366 in 2000) days modelled each year, the percentage of squares modelled using each equation. This shows that the rough surface regime (3.6-13 ms^{-1}) dominated the model runs, with generally less than 5% of grid squares modelled using the breaking wave regime (>13ms^{-1})

Table 5. For 365 (366 in 2000) days, the percentage of grid squares modelled using each model equation (%)

	Smooth surface regime (<3.6 m/s)	Rough surface regime (3.6-13m/s)	Breaking wave regime (>13m/s)
	equation 4	equation 5	equation 6
1997	23.3	72.2	4.5
2000	24.5	70.8	4.7
2001	23.6	72.6	3.7
2003	21.7	73.7	4.6

Input Data

Seawater DMS Concentration Maps

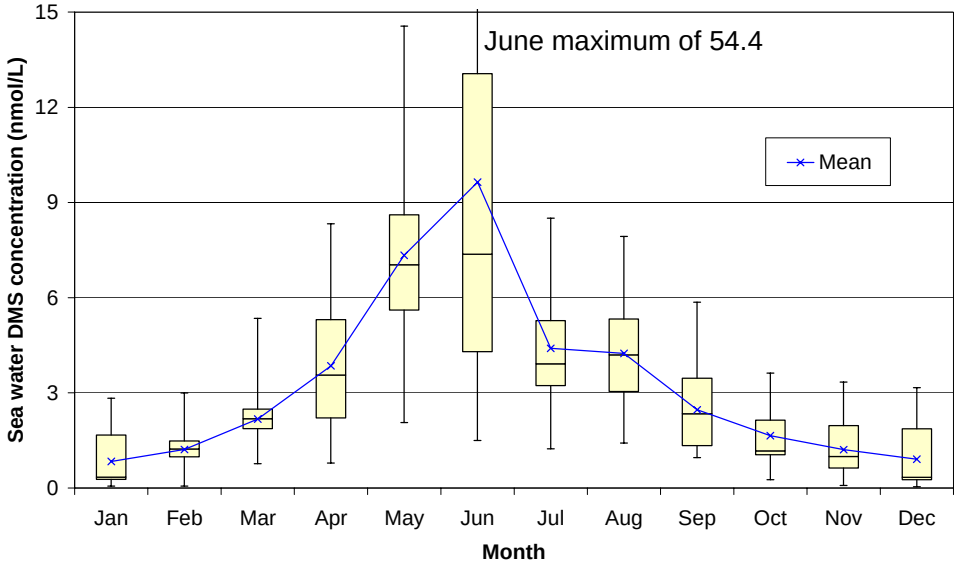
The seawater DMS concentration dataset has a number of uncertainties associated with it. First, it has quite a coarse temporal resolution (monthly) compared with the other input data (daily). This means that changes throughout the month in seawater DMS concentration are not represented in the modelling. This coarse temporal resolution is necessary however, because the DMS dataset was constructed from a fairly sparsely populated (in time and location) set of field studies (Kettle and Andreae, 2000). It was also created using studies from multiple years, and the same set of monthly maps has been used for each year modelled. We have therefore been unable to represent the temporal variability between years and in terms of attempting to model future trends in DMS emissions (using 2003 meteorological data to represent future warmer years), this has presented difficulties.

Attempts were made to correlate seawater DMS concentrations with SSTs to enable a correction factor to be used for future years. However, no significant relationship was found and it is likely that a number of factors interact in a complex system to determine seawater DMS concentrations. So, more detailed analysis, extended to considered a range of extra factors (e.g. nutrient availability), would be required to allow the estimation of DMS concentrations (and hence emissions) for future years.

Additionally, no seawater DMS concentration data was available for the Black Sea. In order to estimate emissions across the entire seawater area within the NatAir extent, it has therefore been necessary to estimate seawater DMS concentrations in the Black Sea. This has been done by applying the average concentration across the Eastern Mediterranean to all grid squares within the Black Sea. The assumption inherent in taking this approach to populate the Black Sea area with sea water DMS concentration data is that the two sea areas, which although geographically close are separated by land, will have broadly similar concentrations. However, no field studies to test this assumption have been carried out so significant uncertainties have been introduced.

The box-whisker plot in Figure 4 shows summary statistics for each of the 12 monthly seawater DMS maps used as input data. The 'whiskers' show the minimum and maximum mapped seawater DMS concentration for each month, while the 'boxes' show the 25th, 50th and 75th percentiles of the mapped seawater DMS concentration data. This plot shows that the seawater DMS concentrations were lowest from October to February, with the highest concentrations found in May and June. June was a particularly high month with the very highest concentrations an order of magnitude greater than most of the rest of the year.

Figure 4. Box whisker plot of seawater DMS concentrations



Wind speed Maps

The model has been run using daily average wind speed. However, obviously wind speed varies on a much shorter time scale. Therefore, it is likely that using the daily average wind speed will under-predict emissions as the peak wind speeds, which would cause the most significant emissions, will be smoothed out by the averaging of the meteorological data. Further discussion of the implications of this is presented with the sensitivity analysis below.

The spatial resolution of the MM5 meteorological data also introduces uncertainties into the method. This is because particularly in coastal regions, there may be intra-grid square variability in terms of wind speeds and therefore emissions. Additionally, at the land-sea interface, where there are grid squares containing both land and sea, these have not been

modelled. Omission of these grid squares is unlikely to have a significant impact upon the total emission estimate for the entire grid extent. However, for users of the spatially disaggregated map data, it may have a more significant impact. This is particularly the case for concentration modelling over land as these are the most relevant grid squares.

SST Maps

The model has been run using daily average SST data. This is likely to vary on a less rapid time step than wind speed data, although changes in the levels of solar radiation reaching the sea will cause SST to show a strong diurnal pattern. However, assuming that the daily input data used is representative of daily SST, using daily values is likely represent seasonal variability in SST well.

The SST maps are produced at the same spatial resolution as the 10m wind speed maps, so similar issues related to spatial resolution will apply with the SST input data set as the wind speed data set (see above for details of this).

Sensitivity Analysis

Figures 5 and 6 show sensitivity analysis of the model equations for a range of conditions typical of the model runs for 1997, 2000, 2001 and 2003. In understanding these graphs it is important to note that up to three quarters of grid squares modelled at a daily resolution were modelled using equation 2 (3.6-13ms^{-1}). Only up to 5% were modelled using equation 3 (>13ms^{-1}). Therefore although the greatest emissions per grid square would be generated in the wind speed regime of >13ms^{-1}, total emissions in our model runs are likely to be dominated by wind speeds in the range of equation 2 (3.6-13ms^{-1}).

Figure 5. Sensitivity analysis of the model equations to sea water DMS concentrations (nmol/L) for a range of wind speeds with a SST of 10°C

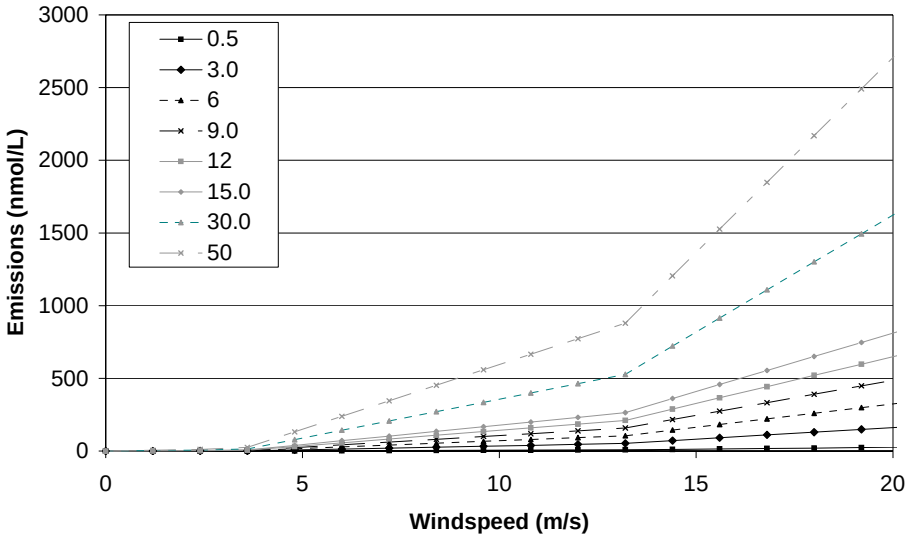
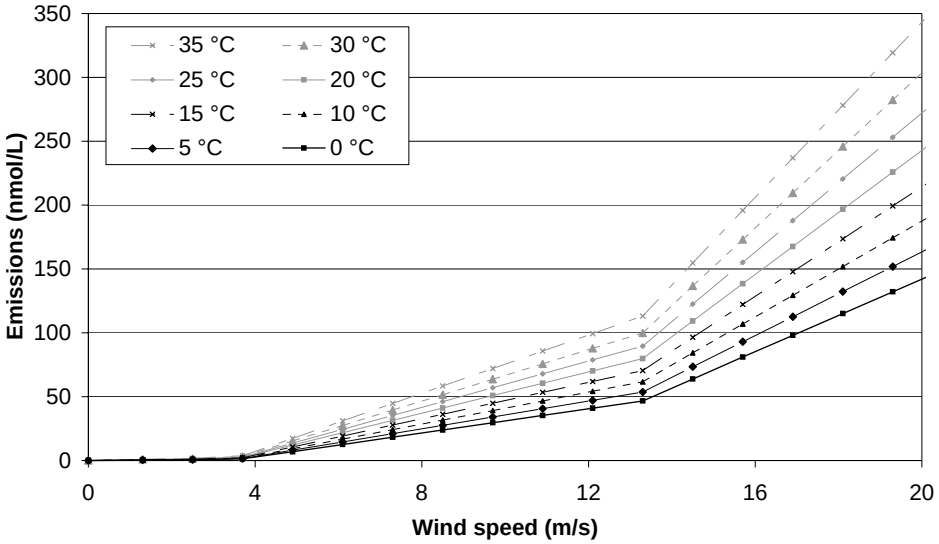


Figure 6. Sensitivity analysis of the model equations to SST for a range of wind speeds with a sea water DMS concentrations of3.5nmol/L



V CONCLUSIONS AND OUTLOOK

DMS emission estimates for the NATAIR domain have been generated at fine spatial and temporal scales (10 km x 10km and daily). Whilst the emission estimates are high in uncertainty, the total annual estimates of DMS emissions show good agreement with the data available from the literature.

Both spatial and temporal variations have been investigated. The Atlantic Ocean has been shown to be the most significant source in terms of emissions per grid cell, and the effects of sheltering is clearly evident across the NATAIR domain.

A simple sensitivity analysis has been conducted to characterise the impacts of wind speed, sea surface temperature, and DMS concentration as input parameters.

It has not been possible to investigate the impact of future climate conditions on the DMS emissions in any detail. This is due to the limited availability of DMS concentration data. However, it is possible to speculate that increased nutrient input to the sea may give rise to increased DMS concentrations in coastal zones, which would result in increased emissions. In addition, changes to general meteorological conditions (increased temperatures and more variable wind speeds) are likely to increase emissions of DMS.

Future work is likely to bring improvements to various aspects of the semi-empirical models. However, the DMS concentration dataset is currently sparse, making it difficult to obtain a good understanding of the spatial and temporal variability that occurs. Improving this measurement dataset will be expensive and time consuming.

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