Calculation of DMS surface water concentrations and fluxes to the atmosphere from chlorophyll $a$ data?

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A new simple model to calculate the DMS surface water concentration from chlorophyll \( a \) data is presented. The total DMSP concentration is calculated from the chlorophyll \( a \) data using DMSP/chl \( a \) ratios that were measured in the field, taking succession of dominant algal species into account. DMS concentrations are then calculated from these DMSP concentrations using a non-linear ‘loss’ curve. Validation of the model with measured North Sea and open ocean DMS data from the literature showed a remarkably good agreement. Application of the model to literature chlorophyll \( a \) data resulted in a prediction of monthly averaged DMS\(_{\text{water}}\) concentrations for the North Sea and North Atlantic Ocean. From the DMS concentrations the sea-air fluxes of these areas are calculated, which are compared with literature flux data.

**INTRODUCTION**

Dimethylsulphide (DMS) is an important trace gas, as it is the most important biological source of atmospheric sulphur (Malin et al. 1992, Bates et al. 1993). It is formed from the phytoplankton metabolite \( \beta \)-dimethylsulphoniopropionate (DMSP). After ventilation into the atmosphere DMS can be oxidized to form methane sulphonic acid and finally sulphate, which has a considerable effect on the acidity of rainwater (Laane et al. 1989, Malin et al. 1992, Mihalopoulos et al. 1993). The sulphate also has a direct backscattering effect on solar radiation and an indirect effect through the formation cloud condensation nuclei (CCN) that increase the global cloud albedo (Charlson et al, 1987, Holligan, 1992, Malin et al. 1992). Charlson et al. (1987) postulated the hypothesis that a possible climate feedback mechanism may be based on the formation of DMS. When the atmospheric CO\(_2\) concentration rises and the global temperature increases, phytoplankton production may also enhance. As a consequence the production of DMS may increase proportionally with the phytoplankton, which, due to the climate effect mentioned above, will decrease the enhanced greenhouse effect. The DMSP concentration in seawater shows seasonal fluctuations which correlate well with algal densities of certain species (Keller et al. 1989, Leck et al. 1990, Matrai & Keller 1994). During algal blooms high concentrations of DMSP and DMS are observed (Leck et al. 1990, Malin et al. 1993, Crocker et al. 1995). This is especially the case when algae such as *Phaeocystis* sp. or *Emiliania huxleyi* are the dominant species (Matrai & Keller 1993, Liss et al. 1994). Algal blooms may thus have pronounced effects on the annual global production and sea-air exchange of DMS.

In an attempt to predict the DMS concentrations in the water column, and hence the fluxes to the atmosphere, several approaches have been followed. The first approach assumes a linear correlation of chlorophyll \( a \) (chl \( a \)) versus DMS concentrations. If chl \( a \) data, e.g. obtained by remote sensing, could be translated into estimations of DMS concentrations in global surface ocean waters, it should be possible to refine the ideas of the climatic feedback mechanism. However, in numerous cases a (linear) correlation
between chl $a$ and DMS concentration in water has been disappointingly poor. Table I gives an overview of these linear correlations reported for various field surveys.

Table I. Comparison of linear correlations between chl $a$ and DMS concentrations in surface waters

<table>
<thead>
<tr>
<th>$r^2$</th>
<th>$n$</th>
<th>Reference</th>
<th>area considered</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.67</td>
<td>135</td>
<td>Barnard et al. (1982)</td>
<td>Atlantic</td>
</tr>
<tr>
<td>0.53</td>
<td>225</td>
<td>Andreae &amp; Raemdonck (1983)</td>
<td>Pacific</td>
</tr>
<tr>
<td>0.58</td>
<td>29</td>
<td>Cline &amp; Bates (1983)</td>
<td>Eq. Pacific</td>
</tr>
<tr>
<td>0.57</td>
<td>166</td>
<td>Andreae &amp; Barnard (1984)</td>
<td>Atlantic</td>
</tr>
<tr>
<td>-0.17</td>
<td>51</td>
<td>Andreae &amp; Barnard (1984)</td>
<td>Sargasso Sea</td>
</tr>
<tr>
<td>ne</td>
<td>--</td>
<td>Holligan et al. (1987)</td>
<td>Coastal North Sea &amp; Atlantic</td>
</tr>
<tr>
<td>ne</td>
<td>--</td>
<td>Turner et al. (1988)</td>
<td>Coastal North Sea &amp; Atlantic</td>
</tr>
<tr>
<td>0.3</td>
<td>&gt;1000</td>
<td>Andreae (1990)</td>
<td>open oceans</td>
</tr>
<tr>
<td>0.06</td>
<td>--</td>
<td>Leck et al. (1990)</td>
<td>Baltic Sea time series</td>
</tr>
<tr>
<td>0.89</td>
<td>14</td>
<td>Leck et al. (1990)</td>
<td>Baltic Sea transect</td>
</tr>
<tr>
<td>0.583</td>
<td>158</td>
<td>Malin et al. (1993)</td>
<td>NE. Atlantic</td>
</tr>
<tr>
<td>0.356</td>
<td>30</td>
<td>Crocker et al. (1995)</td>
<td>Southern Ocean</td>
</tr>
<tr>
<td>0.03-0.3</td>
<td>34</td>
<td>Watanabe et al. (1995)</td>
<td>N.E. Pacific</td>
</tr>
</tbody>
</table>

The poor correlation should not necessarily be surprising, as the release of DMS is a function of both production and consumption of DMSP (Turner et al. 1988, Cooper & Matrai 1989, Gröne 1995, Kwint & Kramer 1996b).

A second approach tries to understand the complexity of the aquatic ecosystem. Although we may understand the production of DMSP by phytoplankton and macrophytes, the factors controlling the concentration of DMS in the water column are not yet clearly understood. They consist of a complex web of interactions which includes zooplankton grazing, algal senescence, algal and bacterial DMSP lyase enzyme activity, chemical and microbial transformation of DMS(P) and processes like sedimentation (Dacey & Wakeham 1986, Nguyen et al. 1988, Belviso et al. 1990, De Souza & Yoch 1995, Kwint & Kramer 1995, Stefels et al. 1995).

To allow prediction of the DMS concentrations, the web of interactions has to be well understood, and hence ecological modelling has been applied (e.g Gabric et al. 1993). These methods try to simulate the development of a phytoplankton bloom, to which is linked the production of DMSP and the resulting DMS. This has lead to several
publications where the fluxes of DMS(P) are described qualitatively and quantitatively (Kiene & Bates 1990, Kiene 1992, Bates et al. 1994, Kwint et al. 1996, chapter 7). However, the predictive value of such models is somewhat limited as the estimation of fluxes for each route of DMS(P) transformation in the model spans a rather wide range. When we applied the model by Gabric et al. (1993) to explain our experiments, we were unable to simulate a DMS peak preceding the chl a maximum as we observed in the field (Kwint et al. 1997). This indicates that imperfections in the modelling approach still exist, and extension to a complete annual cycle, and to more than one plankton species may be required.

On the other hand, all models (and field observations) agree that of the total amount DMSP produced by phytoplankton only a small fraction becomes available as DMS in the water column (estimates range from 0.4 to 10%). This indicates that the processes that attribute to DMS(P) consumption, or the loss, may be very important (Kiene 1992, Bates et al. 1994, Kwint et al. 1996).

The method we like to present here, involves a non-linear correlation between chl a and DMS, assuming a loss of DMS(P) increasing with time. In a survey, conducted in the Marsdiep tidal inlet (The Netherlands, see Figure 1) over a period of 18 months, Kwint & Kramer (1996b) found that the production of DMS in relation to the chl a could only be understood, when the loss of DMS(P) was described in terms of the production of DMSP by phytoplankton and an increasing loss of DMSP to sulphur compounds, other than DMS. It is also possible that the observed increasing loss from DMSP was caused by an increase in the (bacterial) metabolisation of DMS (Kwint et al. 1997).

The most important loss factors for DMS from surface waters are bacterial degradation and transformation, photo-oxidation, and sea-air exchange to the atmosphere (Brimblecombe & Shooter 1986, Kiene 1992, Bates et al. 1994).

Loss of DMSP may be through bacterial transformation (demethylation, Taylor & Gilchrist 1991, Kwint et al. 1997), and sedimentation of phytoplankton cells containing DMSP, or by sedimentation in the form of zooplanktonic faecal pellets (Wolfe 1992, Kwint et al. 1996, Osinga et al. 1996a). Considering that most of these processes are biological in nature, it is not realistic to assume that they are all constant in time.

In this paper we present a new and simple model approach, the increasing loss method. This method allows us to calculate the DMS concentration in the water column based on only the concentration chl a, species composition, the species specific DMSP/chl a ratio, and the calculated loss of DMS(P) as function of time. The method will be demonstrated in a number of different areas of the North Sea and the north Atlantic Ocean, areas that range from highly productive coastal waters to oligotrophic open ocean, hence also different typical species distributions. The
calculated DMS concentrations will be compared with available literature data on field measurements.

The development of the model follows the following lines:

First approach will be the application of the loss curve, obtained in the field at one location (Marsdiep) to Dutch coastal waters, eastern UK coastal waters and southern central North Sea. Secondly, after a discussion on the shape of the loss curve, optimized curves will be used to predict the DMS production for these respective areas. It will be shown that extrapolation to other, less productive waters is feasible, and hence a calculation of DMS(water) concentrations for the northern Atlantic can be performed. From the calculated DMS(water) concentrations, the fluxes of DMS to the atmosphere will be calculated for these areas, which will be shown in relation to data from literature.

MATERIALS AND METHODS
Description of the model
The basic principle of the new model is derived from Kwint & Kramer (1996b). Based on a series of data for DMS and DMSP in the field, collected over 18 months, the DMS(P) loss was defined as:

\[ \% \text{loss} = 100 \times \frac{(\text{DMSP} - \text{DMS})}{\text{DMSP}} \]  

(1)

A line was fitted through these resulting data points. This curve was assumed to have a sigmoidal form, fitted by iterative process using the equation:

\[ N(t) = N_0 \times \frac{K}{(N_0 + (K-N_0))(a.t)} \]  

(2)

commonly used in microbiology (Schlegel & Schmidt 1985), the \( N \) representing the DMSP loss, \( K \) the carrying capacity of the system (100% loss of DMSP), \( a \) the ‘growth’ constant and \( t \) the time in days. This simulated growth (= % loss) curve should be considered as a mathematical representation of the total loss, including all processes involved in the loss of DMSP and DMS from the water column.

This is not unrealistic as several biological processes involved in the degradation and transformation of DMS(P), thus of the total loss, may show a similar profile:

- an increase of microbial conversion of DMSP and DMS is enhanced as a result of the adaptation of the population of DMS(P) consuming bacteria, when DMS(P) concentrations become elevated (Kwint et al. 1997);

Figure 1. Map of the southern North Sea, with a division in different areas, based on hydrodynamical characteristics (NSTF, 1993). Arrow indicates the Marsdiep tidal inlet.
• the activity of the phytoplanktonic DMSP-lyase enzyme will decrease during the aging of the phytoplanktonic bloom (Stefels & Van Boekel 1993), leading to a decreased direct production of DMS with time;

• the zooplankton grazing activity will increase over the season (Reid et al. 1990) and hence the loss of DMSP due to sedimentation of faecal pellets (Kwint et al. 1996) or due to (bacterial) metabolisation of DMSP and DMS in the zooplankton gut will increase as well (Wolfe 1992);

• a considerable part of the DMSP ingested by unicellular grazers is not converted to DMS (Wolfe et al. 1994); as the grazing efficiency increases with time, following the algal bloom, it is expected that the loss will increase with time as well.

The characteristics of the curve are given in Table III.

As one loss curve may not be sufficient to describe the DMS concentration (see discussion), for each area the original curve was optimized by matching the calculated and measured DMS concentrations. In an iterative process the \( a \) and \( N_0 \) in the formula mentioned above were adapted, \( K \) was kept constant.

The new model was applied to different water masses defined for the North Sea (Figure 1), and the northern Atlantic Ocean. The definition of the North Sea areas follows the definition of typical water masses, based on hydrodynamic observations and modelling (NSTF 1993). They can be characterized as follows. Area 4, Dutch coastal zone, is a highly eutrophic area with a major influence of river Rhine input. The Area 3b, English coast, is a less productive coastal zone, while the Area 7b consists of central North Sea waters with a considerably lower production.

The area of the north Atlantic Ocean was defined according to two zones: 55-59°N and 59-63°N, boarded by the continents. For the area 55-65°N, 0-20°W, data on DMS(P) and chl \( a \) were available (Malin et al. 1993).

In our model calculation the following sources were applied.

For chl \( a \) we used the data for 1989 of Joint & Pomroy (1993) in the North Sea (Areas 4, 3b and 7b), for the area west of the Shetland Islands data from Longhurst et al. (1995), and for the two north Atlantic zones data from Gieskes & Kraay (1980), Veldhuis et al. (1993) and Longhurst et al. (1995).

The description of the species distribution and the periods of their presence, as assumed in our calculations in the respective areas, was defined according to Gieskes & Kraay (1980), Reid et al. (1990) and Veldhuis et al. (1993), as summarized in Table II.
Table II. DMSP/Chl a ratios (µmol.mg⁻¹) used in the model. Ratios are based on: Keller et al. (1989), Malin et al. (1993) and Kwint et al. (1997).

<table>
<thead>
<tr>
<th></th>
<th>Months</th>
<th>DMSP/Chl a (µmol.mg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Coastal North Sea</td>
<td></td>
<td></td>
</tr>
<tr>
<td>diatoms</td>
<td>Jan-Mar, Oct-Dec</td>
<td>2.5</td>
</tr>
<tr>
<td>intermediate</td>
<td>Apr</td>
<td>12</td>
</tr>
<tr>
<td><em>Phaeocystis</em> sp.</td>
<td>May-Sept</td>
<td>25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>• Open North Sea and Atl. Ocean</th>
<th>Months</th>
<th>DMSP/Chl a (µmol.mg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>diatoms</td>
<td>Jan-Mar, Sep-Dec</td>
<td>2.5</td>
</tr>
<tr>
<td>intermediate</td>
<td>Apr, May</td>
<td>20</td>
</tr>
<tr>
<td><em>Emiliania huxleyi</em></td>
<td>Jun-Aug</td>
<td>100</td>
</tr>
</tbody>
</table>

The species specific DMSP/chl a ratio was obtained from Keller et al. (1989), Malin et al. (1993) and Kwint et al. (1997).

The measured concentrations of DMS(water) in the North Sea come from Liss et al. (1993b). These data were obtained during the same cruises as for the chl a data. The DMS_water data for the north Atlantic come from Malin et al. (1993) and the compilation by Tarrasón et al. (1995).

All data (chl a, DMS) were characterized in monthly averages, the standard deviations of chl a for each area were subject to the same calculations.

The procedure of the calculation of the [DMS] by our model is as follows.

From the chl a monthly averages the amount of DMSP produced is calculated as function of time using the ratios of DMSP/chl a, defined per species, and taking the succession into account (Table II).

The calculated monthly averaged DMSP concentrations were then subjected to the loss curve. The remaining fraction was considered as the average DMS concentration in that particular month for the area considered. The following equation was used:

\[
[DMS]_{month} = [DMSP]_{month} \times (100 - \% \text{ loss})_{month}
\]
Calculation of sea-air DMS fluxes

The method of flux calculation is based on Liss & Merlivat (1986). They describe the flux of DMS to the atmosphere with the equation:

\[ F = K_w \times C_w \]  

with \( F \) as the flux, \( C_w \) as the concentration of DMS in the surface water and \( K_w \) as the transfer velocity of the DMS. The DMS concentration in air can be neglected. The \( K_w \) is dependent on water temperature via the Schmidt number (Saltzman et al. 1993) and windspeed. There appear to be three wind regimes: smooth surface (1st windspeed class), rough surface (2nd windspeed class) and breaking waves (3rd windspeed class) (Turner et al. 1996), with increasing efficiency in transfer. As the wind speeds in the

![Figure 2](image)

Figure 2. Monthly averages for chl a (Joint & Pomroy 1993), together with the calculated DMSP concentrations (top row of graphs), calculated DMS concentrations, together with the measured DMS concentrations (middle row of graphs) (Liss et al. 1993b) and the increasing loss curve used to calculate the DMS (bottom graph). P values originate from paired t tests. For further explanations, see text.
highest class have a relatively large impact on the $K_w$, but usually a low abundance, it was found to be necessary to calculate a weighted average for the windspeed. Daily windspeed and temperature information was obtained from the Royal Dutch Meteorological Institute. For each area considered the geographical centre was taken as representative. Daily noon wind speed data were used. These data were sub-divided into the three classes: $w \leq 3.6$ m s$^{-1}$ (0-3 Bft), $3.6 < 13$ m s$^{-1}$ (3-6 Bft) and $w \geq 13$ m s$^{-1}$ (6-12 Bft), and a frequency distribution of each windspeed class was made. In this way a daily weighted average windspeed for each month in 1989 could be calculated, which could thus be transferred to daily weighted $K_w$'s per month.

RESULTS & DISCUSSION

Application of the model to several North Sea areas

The results of the calculation of the [DMS] from chl $a$ data are summarized in Figure 2. The top row of graphs displays the monthly average chl $a$ concentrations for each sector in the southern North Sea from February to October 1989, next to the calculated monthly average DMSP concentrations. Error bars in these figures represent standard deviations.

From these DMSP results, the proportion of DMSP lost was subtracted, using the information from the loss curve, presented in the bottom graph. This resulted in the calculated DMS water concentrations (middle row of graphs). They are presented together with the monthly averaged DMS field observations (Liss et al. 1993b).

The calculated and measured concentrations of DMS compare very well. Application of a paired t-test (p value's in Figure 2) showed a good agreement for the Dutch coastal zone and the area 7b, the southern part of the central North Sea ($p = 0.9194$ and...
For the English coastal zone the agreement is slightly less (p = 0.7534). The agreement was in all cases better than the linear correlations calculated by other authors (see Table I).

The loss curve used, is the sigmoidal curve fitted for the Marsdiep. The use of one typical loss curve, which was obtained from a rather atypical spot along the Dutch coast, may not be universally applicable. One may assume differences when going to less productive waters and/or changes in species composition.

In order to assess the validity of the loss curve as depicted in Figure 2, the curve was recalculated for each area considered, based on matching of the DMS calculated and measured and varying the \( N_0 \) and \( a \) in equation (2).

The results are shown in Figure 3, the characteristics of the loss curves are presented in Table III.

Table III. Characteristics of the different loss curves for each sector in the southern North Sea

<table>
<thead>
<tr>
<th></th>
<th>Marsdiep</th>
<th>Dutch coast</th>
<th>English coast</th>
<th>southern central North Sea</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_0 )</td>
<td>0.73</td>
<td>0.74</td>
<td>0.86</td>
<td>0.87</td>
</tr>
<tr>
<td>( a )</td>
<td>0.014</td>
<td>0.014</td>
<td>0.0034</td>
<td>0.00067</td>
</tr>
</tbody>
</table>

We observed that for the Dutch coastal zone, no major change occurred, the shape of the new loss curve for this area has a similar shape as the original curve from the Marsdiep. Obviously the average interactions in this area are about similar to those in the spot sampling area, the Marsdiep tidal inlet. The increase in p-value (p = 0.9983) is the result of the iterative matching process. However, when going to the English coastal zone and to the southern central North Sea areas we see a marked change. Firstly, the fit (obviously) improves (to p = 0.8848 and p = 0.9092, respectively), but also the shape of the loss curves changed. Where the Dutch coast curve rises from 60 to 98% in the period February - October, the English coast curve rises from 85 to 92% and the central North Sea curve from 87 - 89 %, each for the same period.

It is clear from the bottom graphs in Figure 3 that there is a trend of flattening of the loss curves going from highly productive waters like the Dutch coastal area to the less productive part of the North Sea. This trend indicates, that in less productive oligotrophic waters there seems to be a more or less constant loss of DMSP from the water column of about 88%.

This trend in flattening out of the loss curve from highly productive waters to less productive waters is consistent with the idea that in eutrophic waters the increase in
production at the start of the spring plankton bloom is rather fast, while in oligotrophic waters the differences between summer and winter are less pronounced. As a result of the steep increase in eutrophic waters, the biological processes dependent on the primary/DMSP production (e.g. zooplankton grazing, bacterial transformation) will also be enhanced, but they will require some time for adaptation. In the end their consumption may be much more efficient. In less productive waters the differences are smaller, adaptation may be a lesser requirement (Colebrook 1979, Reid et al. 1990).

We observed that for the areas considered in the North Sea one curve could be used (Figure 2), but that regional differences exist (Figure 3). Extrapolation of the loss curve to other, highly productive areas (eutrophic coastal zones, upwelling areas, polar seas), may therefore become problematic, as the shape of the curve needs to be validated for each area. However, the extrapolation may be possible for open oligotrophic (oceanic) waters as the loss seems to become about constant in these areas. A constant loss of DMSP would, assuming one dominant phytoplankton species, indicate a linear relation with chl a. This seems in contrast with the observations presented in Table 1. It should be mentioned, however, that in this table the open ocean results in general provide better correlations than the comparisons for eutrophic coastal (or mixed) observations.

Figure 4. DMS surface water concentrations obtained from Tarrasón et al. (1995), compared with concentrations calculated from chl a data using our model for the North Atlantic Ocean, continental shelf area (top graph) and open area (middle graph) and for the entire North Sea area (bottom graph). P values originate from paired t tests.

Calculation of the DMS water concentration for the North Atlantic
Assuming that for open ocean waters the constant loss of DMS(P) of 88% is realistic for a larger area than the central North Sea, we may extrapolate this to the north Atlantic waters.
We validated our model for this area with DMSP and DMS data collected in a coccolithophore bloom in the period June-July 1987 (Malin et al. 1993). The results of our calculations are compared with the measured data for this area (Table IV).

Table IV. Average surface seawater concentration (with standard deviations) of Chl a, particulate DMSP and DMS according to measurements by Malin et al. (1993) (left) and calculated using our model (right). For further explanation see text.

<table>
<thead>
<tr>
<th></th>
<th>Malin et al. (1993)</th>
<th>this work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chl a (mg.m⁻³)</td>
<td>1.04 ± 0.62</td>
<td>1 ± 0.67</td>
</tr>
<tr>
<td>DMSPₚ (µmol.m⁻³)</td>
<td>96.7 ± 47.4</td>
<td>100 ± 67.6</td>
</tr>
<tr>
<td>DMS (µmol.m⁻³)</td>
<td>12.0 ± 12.4</td>
<td>12 ± 8.1</td>
</tr>
</tbody>
</table>

Our calculated [DMS] of 12 µmol DMS m⁻³ agrees remarkably well with the value of 12.0 µmol DMS m⁻³ measured. The high standard deviation for the calculated [DMS] are the result of the standard deviations found in the chl a (n = 2500) data set. Apparently the standard deviation for the measured [DMS] (n = 158) is higher. We like to stress that the good agreement in the average (per month) is of more importance than the difference in the standard deviations.

In an attempt to validate our model further, we compared our calculated DMS concentrations for two north Atlantic zones with the measured DMS concentrations, as reviewed by Tarrasón et al. (1995). The results of this comparison are presented in Figure 4.

In our calculations again a loss of 88% of the total amount of DMSP was assumed, while the remaining 12% was considered to be DMS. Our model gives a good agreement between calculated and measured data in the open ocean area (p = 0.7353, paired t test). The agreement in the ‘shelf and coastal regions’ area, as defined by Tarrasón et al. (1995), is considerably less (p = 0.3982). We should realize, however, that this area consists of both open ocean and coastal seas in the Tarrasón data set, and that we used the cross Atlantic zones defined before. The comparison between our calculated results and the measured data for the entire North Sea area, compare again very well(p = 0.8727).

Figure 5. DMS sea-air fluxes from the North Atlantic from Tarrasón et al. (1995), Lawrence (1993) and this study in the zone 59-63 °N (top graph) and 55-59 °N (bottom graph), for further explanation see text.
Calculation of DMS fluxes from the North Atlantic

Based on our calculated [DMS] we predicted the sea/air exchange for the north Atlantic and the (total) North Sea. The results are presented in Figure 5, together with the calculated DMS fluxes as presented by Lawrence (1993) and Tarrasón et al. (1995). Our calculations generally predict a considerably larger flux of DMS to the atmosphere than is assumed in the literature. The values for the more northern zone (top graph) are higher than for the more southern zone (bottom graph). The high fluxes calculated by Lawrence (1993) for the winter period in this area are inconsistent with our calculations and the calculations by Tarrasón et al. (1996). The values of Lawrence represent the combined data for the Atlantic and the Pacific however. In contrast, the calculations reported by Bates et al. (1987a) for the Pacific (50-65 °N) being 1.4 µmol DMS m⁻² d⁻¹ for the winter period and 6.57 µmol DMS m⁻² d⁻¹ for the summer period compare well with our values for the Atlantic (55-59 °N) of 1.67 and 5.02 µmol DMS m⁻² d⁻¹ respectively.

The discrepancy that appears to exist between our calculated fluxes and those from the literature can partly be explained by the methods used for the flux calculations. We used Kw values based on daily wind speed measurements and hence a daily weighted Kw for every month. Other authors in the review of Lawrence (1993) use averaged Kw’s for the summer months May to October and for the winter months November to April, differences in the outcome of calculated fluxes are inevitable. Using an overall average will overestimate the influence of the lowest speed class and underestimate the influence of the highest speed class on the Kw.

Figure 6. DMS fluxes to the atmosphere, using DMS surface water concentrations calculated from chl a data using our model and Kw’s from Turner et al. (1996) (white columns, summer Kw = 2.69 cm.hr⁻¹, winter Kw = 9.4 cm.hr⁻¹), Bates et al. (1987a) (shaded columns summer Kw = 6.58 cm.hr⁻¹, winter Kw = 8.83 cm.hr⁻¹), and daily weighted Kw’s for each month (dark columns) for the North Atlantic Ocean.

59-63 °N (top graph), 55-59 °N (middle graph) and the North Sea (bottom graph).
Tarrasón et al. (1995) used six hourly measured wind speeds from the year 1988 to calculate the \(K_w\)'s and fluxes of DMS to the atmosphere, while we used 24 hourly measured wind speeds (noon) for the year 1989.

In order to show the effect of the approaches used for the selection of the \(K_w\) values, we simulated our calculations, based on DMS data produced by our model, but using the \(K_w\)'s from Turner et al. (1996) of 2.69 cm h\(^{-1}\) (summer) and of 9.4 cm h\(^{-1}\) (winter), and Bates et al. (1987a), 6.58 and 8.83 cm h\(^{-1}\) respectively. In Figure 6 the results of the three observations are shown.

For the three area's observed, no significant difference between our calculations and those using the \(K_w\) from Bates et al. (1987a) is observed (One way ANOVA, \(p > 0.05\)). Between our approach and that using the \(K_w\) from Turner et al. (1996) there is a significant difference, however (One way ANOVA, \(p < 0.01\)). It is clear that by using different established ways to calculate the flux of DMS to the atmosphere, large variations in the fluxes may be introduced.

**CONCLUSIONS**

The relatively simple model that is presented here, may make it possible to calculate DMS water concentrations for large areas of open, low productive waters using chl \(a\) data, assuming a constant loss of DMS(P) to other sulphur compounds than DMS of 88%. As the majority of the worlds oceans consist of low productive waters, the model may provide simple means in the calculation of the global standing stock of DMS and its variations over the seasons.

For more productive waters our model seems to work as well. It appears, however, that regional differences are observed, and that the loss curve needs to be defined and validated for these regions.

It is demonstrated that the estimation of DMS fluxes is highly dependent on the method of flux calculation, especially where the wind speed data are introduced in the calculation of the transfer velocity (\(K_w\)).