Production of dimethylsulfoxoniumpropionate and dimethylsulfide in intertidal sediment ecosystems.
van Bergeijk, S.A.

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DMS emissions from a sedimental microbial ecosystem subject to diel variations of oxic and anoxic conditions: a simple mathematical model

Hugo A. van den Berg, Henk M. Jonkers, Stef A. van Bergeijk, Sebastiaan A.L.M Kooijman

This modelling study relates dimethyl sulfide (DMS) emission from a microbial mat to the flux of dimethylsulfoniopropionate (DMSP) that is exuded into the interstitial space of the mat by phototrophs. DMSP may be either cleaved or demethylated. Only cleavage results in the production of DMS, which itself is further oxidized or escapes from the mat. The fate of DMSP depends on the functional group composition of the mat, the physiological characteristics of these groups, and the eco-physiological conditions oxic/anoxic and light/dark, which both vary in a diel cycle. These three factors are accounted for in a mathematical model of a microbial mat typical of the Wadden Islands of The Netherlands and Germany. Model simulations quantify increased DMS production under alkaline stress as well as additional DMSP loads.

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Introduction

Laminated marine and estuarine sedimental microbial ecosystems - 'microbial mats' - typically make up the top few millimeters of a sediment (Stal et al. 1985, Stal 1991, Van Gemerden 1993, Van den Ende & Van Gemerden 1994, De Zwart & Kuenen 1995, Stal 1995). They contain carbon dioxide fixing microorganisms, both phototrophs and chemotrophs (Van Gemerden 1993). Oxic conditions prevail in the top layer of the mat, as a result of oxygenic photosynthesis, carried out by cyanobacteria or unicellular eukaryotes (Van den Ende & Van Gemerden 1994). Each night these oxic conditions are displaced by anoxic conditions. Photosynthesis has then ceased, and diffusion of oxygen from the atmosphere into the mat is too slow to keep up with the physiological activity in the mat (Visscher 1992). Consequently, anaerobic processes such as fermentation and sulfate reduction dominate the mat's biochemistry at night. In the early hours of the morning, the situation is once more reversed as oxygenic photosynthesis resumes and the mat becomes oxic again, from the top downwards.

This diel cycle of oxic/anoxic conditions is reflected in the carbon exchange with the atmosphere. A net carbon dioxide fixation flux occurs during daylight, while there is probably a net loss flux at night. The latter flux, however, is generally smaller than the gain. As a result, the amount of organic matter in the sediment steadily increases; when the cells die, a portion of their biomass is decomposed, while the remainder is buried in the underlying sediment (Van Gemerden 1993).

The diel oxic/anoxic cycle also affects the breakdown of dimethylsulfoniopropionate (DMSP), which is produced by phototrophs, presumably as an osmolyte (Vairavamurthy et al. 1985, Dickson & Kirst 1987). When the phototrophic cells die or become exposed to an osmotic shock (such as a rain shower), DMSP is released into the interstitial space of the mat (Dickson & Kirst 1986; Ch. 3, 4). The compound may be broken down through a number of biochemical processes, most of which are catalysed by the various groups of microorganisms in the mat. These biotransformations are summarized in Figure 7.1. An important DMSP derivative is dimethyl sulfide (DMS), a volatile sulfur compound, which may be broken down further, but which may also diffuse from the mat into the atmosphere.

Our aim in this study is to quantify the turnover of DMSP in a microbial mat. Attention is focussed on two points. The first is the production of DMS (DMSP demethylation versus DMSP cleavage); the second point is DMS clearance (microbial consumption versus diffusive emission to the atmosphere). We formulate a model which is applied to a number of perturbations in environmental regimes. The model takes into account the daily oxic/anoxic cycle. It is a two-compartment model with autonomously time-varying compartment sizes.

Conceptual and mathematical model development is presented in Section 'Model development'. Slurry experiments, carried out to obtain information about degradation rates in microbial mats, are presented in Section 'Slurry experiments'.
Model simulations, sensitivity analysis and numerical results of ecological disturbances are presented in Section 'Simulations'.

Figure 7.1. Biotransformations of DMSP in a microbial mat. Each arrow corresponds to a biotransformation. DMSO: dimethylsulfoxide; MSH: methanethiol; MMPA: methylmercaptopropionate; MPA: mercaptopropionate.

**Model development**

A full account of the geophiology of DMSP in a microbial mat might accommodate all of the biotransformations depicted in Figure 7.1. Quantitative data on the kinetics of most of these processes are all but lacking, however. Therefore, the geochemistry accounted for in the model is restricted to just two compounds, DMSP and DMS. The processes which play a role in the biotransformations of these two substances are listed in Table 7.1.

Table 7.1. Biotransformations of DMSP and DMS.

<table>
<thead>
<tr>
<th>Process</th>
<th>Reactants</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSP exudation</td>
<td>DMSP&lt;sub&gt;intr&lt;/sub&gt;</td>
<td>DMSP</td>
</tr>
<tr>
<td>DMS exudation</td>
<td>DMS&lt;sub&gt;intr&lt;/sub&gt;</td>
<td>DMS + CH&lt;sub&gt;3&lt;/sub&gt;=CHOO⁻ + H&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>DMSP cleavage</td>
<td>DMSP</td>
<td>DMS + CH&lt;sub&gt;3&lt;/sub&gt;=CHOO⁻ + H&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>DMSP demethylation (AHe)</td>
<td>A + DMSP</td>
<td>MMPA + CH&lt;sub&gt;3&lt;/sub&gt;A</td>
</tr>
<tr>
<td>DMSP demethylation (SRB)</td>
<td>½ SO₄&lt;sup&gt;2-&lt;/sup&gt; + DMSP</td>
<td>MMPA + HCO₃⁻ + ½ HS⁻ + 1½ H&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>DMS oxidation (PSB)</td>
<td>H₂O + DMS</td>
<td>DMSO + 2[H]</td>
</tr>
<tr>
<td>DMS oxidation (AHe)</td>
<td>5 O₂ + DMS</td>
<td>2 HCO₃⁻ + SO₄&lt;sup&gt;2-&lt;/sup&gt; + 4 H&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>DMS oxidation (SRB)</td>
<td>1½ SO₄&lt;sup&gt;2-&lt;/sup&gt; + DMS</td>
<td>2 HCO₃⁻ + 2½ HS⁻ + 1½ H&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>DMS oxidation (Meth)</td>
<td>1½ H₂O + DMS</td>
<td>½ HCO₃⁻ + HS⁻ + 1½ CH₄ + 1½ H&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

The following abbreviations are used to denote physiological groups: AHe: Aerobic heterotrophs; PSB: Purple sulfur bacteria; SRB: Sulfate-reducing bacteria; Meth: Methanogens.

‘A’ in DMSP demethylation denotes the methyl acceptor.

MMPA: methylmercaptopropionate; DMSO: dimethylsulfoxide; DMSP<sub>intr</sub> indicates DMSP in the intracellular space of oxygenic phototrophs.
Sedimental microbial ecosystems feature a rich spatial heterogeneity (Visscher 1992). A crude way to capture some of this spatial heterogeneity is a two-way split into a top and a bottom compartment. These compartments are referred to here as ‘oxic’ and ‘anoxic’ (but the connotation should be to all of the relevant conditions that are typical of the top and bottom compartments). A diagram of the model with its two compartments is given in Figure 7.2. The two compartments are taken to be well-mixed. The depth of the boundary between the oxic and the anoxic compartment will be assumed to be time-varying. Thus, the compartments have volumes which are not constant in time.

Model specification

The object to be modelled is a microbial mat with area $A$ and depth $d$. Interstitial concentrations of DMSP and DMS are tracked in order to describe DMS emission rates from the mat under various conditions. The metabolic activities of the following physiological groups are taken into account: oxygenic phototrophs; aerobic heterotrophs (including chemolithotrophs); purple sulfur bacteria; sulfate reducing bacteria; and methanogens.

By assumption, $A$ is small enough to discard heterogeneity along the ‘horizontal’ axes. The mat is a box of volume $Ad$, divided into an ‘oxic’ top layer and an ‘anoxic’ bottom layer. The boundary between these two layers is located at a depth $z(t)$. Thus, the oxic layer has a thickness $z(t)$ and a volume $Az(t)$, while the anoxic layer beneath the oxic layer has a thickness $(d-z(t))$ and a volume $A(d-z(t))$. 
The following function is employed to describe the movement of the oxic/anoxic boundary:

\[
\frac{z(t)}{d} = z^* + \frac{\Delta z}{4} \left(1 + \cos(t - \phi)\right)^2
\]  

(1)

with parameters \(z^*, \Delta z, \text{and } \phi\). A graph of this function is given in Figure 7.3, with \(z^*/d=0.01, \Delta z/d=0.5\). The parameter \(z^*\) represents the minimal thickness of the oxic layer. The parameter \(\Delta z\) represents the amplitude of the diel movement of the oxic/anoxic boundary. The parameter \(\phi\) represents a phase shift. At \(t=\phi\), the boundary is located at a depth \((z^* + \Delta z)\); in the present model, this time of day is taken to be 1.30 p.m.

![Figure 7.3](image)

**Figure 7.3.** Diel pattern of oxic and anoxic conditions in a microbial mat. Abscissa is time of day, from midnight to midnight. Ordinate represents the depth axis, with the mat surface on top. The heavy line depicts the movement of the oxygen null isopleth in a microbial mat on the Frisian island of Texel (adapted from Visscher & Van den Ende (1994). The thin line graphs the function used in the present paper to describe this movement. This function is given in Equation 1.

DMSP and DMS levels in the interstitial space of the mat are assumed to be replenished at a constant rate by DMSP exudation and DMS exudation carried out by oxygenic phototrophs. It is assumed that these exudation processes are compensated for by synthesis of intracellular DMSP in these organisms.

The model comprises four state variables:

1. \(P_{ox}(t)\): the quantity of DMSP in the oxic layer, divided by \(A\);
2. \(P_{an}(t)\): the quantity of DMSP in the anoxic layer, divided by \(A\);
3. \(D_{ox}(t)\): the quantity of DMS in the oxic layer, divided by \(A\);
4. \(D_{an}(t)\): the quantity of DMS in the anoxic layer, divided by \(A\).

Note that \(P_{ox}(t)/z(t)\) represents the concentration of DMSP in the oxic layer. Similarly, \(P_{an}(t)/(d-z(t))\) represents the concentration of DMSP in the anoxic layer. DMS concentrations are given by \(D_{ox}(t)/z(t)\) and \(D_{an}(t)/(d-z(t))\).

Four kinds of fluxes affect these state variables: gain fluxes due to exudations from the oxygenic phototrophs; gain and loss fluxes due to biotransformations; passive fluxes due to diffusive exchanges with the surrounding of the mat; and ‘shift’ fluxes due to the movement of the oxic/anoxic boundary. The latter two kinds require a few words of explanation.
Passive fluxes

Both DMSP and DMS may diffuse through the boundary between the mat and atmosphere above the mat. In this model, only diffusion of DMS out of the mat is taken into account, in the form of a term

\[- \kappa_D \frac{D_{ox}(t)}{z(t)}\]

in the kinetics of \(D_{ox}(t)\) (recall that \(D_{ox}(t)/z(t)\) is a concentration), where \(\kappa_D\) is an effective mass transfer coefficient. DMS concentrations in the surrounding of the mat are taken to be nil, so that diffusive imports of DMS do not figure in the model. The scope of the present model is restricted to a fully emersed mat, where passive exchanges of DMSP between mat and ambient be ignored.

Boundary ‘shift’ fluxes

The continual repartitioning of the space within the mat into an oxic compartment and an anoxic compartment is represented by the time-varying depth of the boundary \(z(t)\). Simply as a result of this repartitioning, exchanges between the oxic and anoxic quantities occur. The magnitude of these fluxes clearly depends on the rate of change of \(z(t)\); as the boundary progresses downwards, particles shift from the diminishing anoxic layer into the oxic layer. Then, as the oxic layer once again retreats, a reverse shift occurs.

At this point, it is convenient to introduce a function \(z'(t)\) of time, defined as follows:

\[z'(t) = \frac{d}{dt} z(t)\]  

(2)

Thus, \(z'(t)\) gives the rate of change of \(z(t)\).

The shift flux should be the product of \(z'(t)\), \(A\), and the concentration at the boundary. A simple and natural choice for this boundary concentration is to take the oxic concentration when the oxic layer is decreasing, and to take the anoxic concentration when the anoxic layer is decreasing.

To implement these considerations, consider first the case where \(z'(t) < 0\) (the oxic layer is decreasing). The boundary flux then amounts to \(P_{ox}(t)z'(t)/z(t)\) for DMSP, and to \(D_{ox}(t)z'(t)/z(t)\) for DMS. Thus, a term \(P_{ox}(t)z'(t)/z(t)\) is added to the kinetics of \(P_{ox}(t)\), while a term \(-P_{ox}(t)z'(t)/z(t)\) is added to the kinetics of \(P_{an}(t)\) (note that the latter is a gain term, for \(z'(t)\) is negative).

When the anoxic layer is decreasing, \(z'(t) > 0\), the boundary flux term in the kinetics of \(P_{ox}(t)\) is given by

\[P_{an}(t) \frac{z'(t)}{d - z(t)}\]
while this term appears with a minus sign in the kinetics of $P_{\text{m}}(t)$. At points in time
where $z'(t) = 0$, there are no boundary fluxes. The 'shift' DMSP fluxes may be
denoted $\Phi_{P}(t)$, defined as $P_{\text{ox}}(t)z'(t)/z(t)$ for $z'(t) \leq 0$ and as $P_{\text{m}}(t)z'(t)/(d-z(t))$ for
$z'(t) > 0$. For DMS fluxes, the analogous term $\Phi_{D}(t)$ is introduced, defined as
$D_{\text{ox}}(t)z'(t)/z(t)$ for $z'(t) \leq 0$ and as $D_{\text{m}}(t)z'(t)/(d-z(t))$ for $z'(t) > 0$.

**Metabolic conversions**

The concentrations of DMSP and DMS change continually as a result of the
active biotransformations. When different conditions (oxic, anoxic, light) are taken
into account, it is found that the nine biotransformations listed in Table 7.1 need to
be represented as 12 distinct processes. These are listed in Table 7.2, together with
representative parameter values for a microbial mat as found on the Wadden Islands
of The Netherlands and Germany. All DMS accounted for in the present model
derives from DMSP. It has been found that DMS can also arise from other sources,
such as methoxylated aromatic compounds (Bak et al. 1992). In the present model it
is assumed that those additional transformations contribute very small to DMS
fluxes in comparison to the DMSP-derived flux, and may therefore be ignored.

By way of example, the derivation of a kinetics term for one such process will
now be outlined. Consider an oxic process which is rate-limited by the
concentration of DMSP. Recall that this concentration is given $P_{\text{ox}}(t)/z(t)$.
The process is assumed to depend on this concentration according to the familiar
Michaelis-Menten type hyperbola, with a saturation constant $K$. The rate at which
the process proceeds at DMSP concentrations very much larger than the saturation
constant can be conceived as a product of two factors. The first factor is the
maximum rate per unit biomass, denoted by $v_i$. The second factor is the quantity of
biomass which is 'devoted to' the process at hand, and which is, moreover, exposed
to the oxic condition. Denote the quantity of biomass devoted to the process per
unit mat volume by $\rho_i$. On the assumption that this biomass is distributed uniformly
along the depth axis of the mat, the biomass exposed to the oxic condition is given as
$\rho_i A z(t)$. Thus the maximum rate, divided by $A$, is just $v_i \rho_i z(t)$. The rate term in the
above system of differential equations thus becomes

$$
\frac{P_{\text{ox}}(t)/z(t)}{K_i + P_{\text{ox}}(t)/z(t)} v_i \rho_i z(t)
$$

Terms for anoxic processes are derived analogously.

The biomass in natural mats is not uniformly distributed, contrary to the
assumption underlying the present model. However, it is becoming increasingly
clear that separation of functional groups into several layers at varying depths is far
from strict (e.g. Visscher 1992, Van den Ende et al. 1997). A generalization of these
recent findings for the sake of model clarity seems therefore legitimate.
### Table 7.2. Parameter values.

<table>
<thead>
<tr>
<th>Oxic/anoxic boundary kinetics</th>
<th>$\phi$</th>
<th>$d$</th>
<th>$z^*$</th>
<th>$\Delta z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMS loss to ambient</td>
<td>$K_D$</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metabolic conversions</td>
<td>$v_i$</td>
<td>$K_i$</td>
<td>$\rho_i$</td>
<td>$v_i \rho_i / K_i$</td>
</tr>
<tr>
<td>1 DMSP exudation</td>
<td>OL</td>
<td>$5.04 \times 10^{-6}$</td>
<td>-</td>
<td>3.75</td>
</tr>
<tr>
<td>2 DMS exudation</td>
<td>OL</td>
<td>$1.008 \times 10^{-6}$</td>
<td>[1]</td>
<td>3.75</td>
</tr>
<tr>
<td>3 DMSP cleavage</td>
<td>OA</td>
<td>$4.32 \times 10^{-2}$</td>
<td>[2]</td>
<td>3.75</td>
</tr>
<tr>
<td>4 DMSP cleavage</td>
<td>O</td>
<td>$7.20 \times 10^{-1}$</td>
<td>[3]</td>
<td>0.75</td>
</tr>
<tr>
<td>5 DMSP cleavage</td>
<td>OAL</td>
<td>$7.20 \times 10^{-2}$</td>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td>6 DMSP cleavage</td>
<td>A</td>
<td>$1.44 \times 10^{-1}$</td>
<td>[5]</td>
<td>0.45</td>
</tr>
<tr>
<td>7 DMSP demethylation</td>
<td>O</td>
<td>1.44</td>
<td></td>
<td>0.75</td>
</tr>
<tr>
<td>8 DMSP demethylation</td>
<td>A</td>
<td>$2.88 \times 10^{-1}$</td>
<td>[6]</td>
<td>0.90</td>
</tr>
<tr>
<td>9 DMS oxidation</td>
<td>OAL</td>
<td>$7.20 \times 10^{-1}$</td>
<td>[7]</td>
<td>0.15</td>
</tr>
<tr>
<td>10 DMS oxidation</td>
<td>O</td>
<td>$1.44 \times 10^{-1}$</td>
<td>[8]</td>
<td>0.75</td>
</tr>
<tr>
<td>11 DMS oxidation</td>
<td>A</td>
<td>$2.88 \times 10^{-1}$</td>
<td>[10]</td>
<td>0.015</td>
</tr>
<tr>
<td>12 DMS oxidation</td>
<td>A</td>
<td>$1.44 \times 10^{-2}$</td>
<td>[11]</td>
<td>0.045</td>
</tr>
</tbody>
</table>


Processes are carried out by the following physiological groups: Oxygenic phototrophs: $i=1,2,3$; Aerobic heterotrophs: $i=4,7,10$; Purple sulfur bacteria: $i=5,9$; Sulfate-reducing bacteria: $i=6,8,11$; Methanogens: $i=12$

- Conditions: O: oxic; A: anoxic; OA: both in the oxic and in the anoxic layers; OL: only in the oxic layer, and only between 7 a.m. and 7 p.m. OAL: in both layers, but only between 7 a.m. and 7 p.m.

- $\phi$ in d (day); $d$, $z^*$, and $\Delta z$ in m; $K_D$ in m d$^{-1}$; $V_i$ in mol d$^{-1}$ (g cell protein)$^{-1}$; $K_i$ in mol m$^{-3}$; $\rho_i$ in (g cell protein) m$^{-3}$

- $V_2$, $V_6$, $K_6$, $K_{10}$, $K_{11}$, $K_{12}$ were taken directly from the reference.

- $V_3$, $V_4$, $V_9$, $V_{10}$, $V_{11}$, $V_{12}$ were calculated from data provided by the reference.

- $V_1$, $V_5$, $V_7$, $V_8$, $K_5$, $K_7$, $K_{17}$, $K_{13}$ are 'guesstimates'.


- $V_7$ and $K_7$ are supported by Taylor & Gilchrist (1991); $V_5$ and $K_5$ are supported by Jonkers et al. (1998a).

- $\rho_i$'s were based on most-probable-number (MPN) counts and photopigment content (chlorophyll a and Bchlrophyll a) in microbial mats (De Wit et al. 1989, Visscher 1992, Van den Ende & Van Gemerden 1994) and MPN counts of DMSP and DMS degrading bacteria (Jonkers et al. 2000).

- $\rho_i$'s for sulfate-reducing bacteria involved in DMS oxidation and DMSP demethylation and cleavage were based on the relative numbers of species known to utilize these degradation pathways (Tanimoto & Bak 1994, Van der Maarel et al. 1996a, Van der Maarel et al. 1996b).

- Estimates for oxic/anoxic boundary kinetics were based on Visscher & Van den Ende (1994).
Differential equations

Collecting the terms corresponding to passive fluxes, boundary ‘shift’ fluxes, and biotransformations, we find that the kinetics of DMSP and DMS is described in our model by the following system:

\[
\begin{align*}
\frac{d}{dt} P_{ox}(t) &= \Phi_P(t) + \rho_1 z(t) - \sum_{i=3,4,5,7} \frac{P_{ox}(t) v_1 \rho_i z(t)}{K_i z(t) + P_{ox}(t)} \\
\frac{d}{dt} P_{an}(t) &= -\Phi_P(t) - \sum_{i=3,5,6,8} \frac{P_{an}(t) v_1 \rho_i (d - z(t))}{K_i (d - z(t)) + P_{an}(t)} \\
\frac{d}{dt} D_{ox}(t) &= \Phi_D(t) - \kappa D \frac{D_{ox}(t)}{z(t)} + v_2 \rho_2 z(t) + \sum_{i=3,4,5} \frac{P_{ox}(t) v_1 \rho_i z(t)}{K_i z(t) + P_{ox}(t)} - \sum_{i=9,10} \frac{D_{ox}(t) v_1 \rho_i z(t)}{K_i z(t) + D_{ox}(t)} \\
\frac{d}{dt} D_{an}(t) &= -\Phi_D(t) + \sum_{i=3,5,6} \frac{P_{an}(t) v_1 \rho_i (d - z(t))}{K_i (d - z(t)) + P_{an}(t)} - \sum_{i=9,11,12} \frac{D_{an}(t) v_1 \rho_i (d - z(t))}{K_i (d - z(t)) + D_{an}(t)}
\end{align*}
\]

where the index \( i \) ranges over the twelve metabolic conversion processes listed in Table 7.2. Representative parameter values for a microbial mat as found on the Wadden Islands of The Netherlands and Germany are also given in Table 7.2. A number of the parameter values in this table are ‘guesstimates’. These values were arrived at by comparing kinetic parameters over a range of substances in the functional group concerned. To assess how this guesswork affects the results of the simulations, a sensitivity analysis was performed.

The terms for \( i = 1,2,5,9 \) are set to zero for \( t<7/24 \text{ d} \) and \( t>19/24 \text{ d} \) (that is, at ‘night’). These terms correspond to the activities of phototrophs, which require light to carry out the biotransformations expressed by these terms.

When the hyperbolic rate dependences are linearized, Equation 3 becomes:

\[
\begin{align*}
\frac{d}{dt} P_{ox}(t) &= \Phi_P(t) + \phi_1 z(t) - \lambda_{ox} P_{ox}(t) \\
\frac{d}{dt} P_{an}(t) &= \Phi_P(t) - \lambda_{an} P_{an}(t) \\
\frac{d}{dt} D_{ox}(t) &= \Phi_D(t) - \kappa D \frac{D_{ox}(t)}{z(t)} + \phi_2 z(t) + \eta_{ox} \lambda_{ox} P_{ox}(t) - \lambda_{ox} D_{ox}(t) \\
\frac{d}{dt} D_{an}(t) &= -\Phi_D(t) + \eta_{an} \lambda_{an} P_{an}(t) - \lambda_{an} D_{an}(t)
\end{align*}
\]

These expressions contain a number of ‘lumped’ parameters, which are defined in Table 7.3: \( \phi_1 \) and \( \phi_2 \) are production flux parameters; the four \( \lambda \)-type parameters are pure rate parameters. The partitioning coefficients \( \eta_{ox} \) and \( \eta_{an} \) are important. These
express the portion of DMSP which ends up, after microbial degradation, as Table 7.3. Lumped parameters.

<table>
<thead>
<tr>
<th>Definition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>light</td>
<td>dark</td>
</tr>
<tr>
<td>( \phi_1 = v_1 \rho_1 )</td>
<td>( 1.89 \times 10^5 )</td>
</tr>
<tr>
<td>( \phi_2 = v_2 \rho_2 )</td>
<td>( 3.78 \times 10^6 )</td>
</tr>
<tr>
<td>( \lambda_{ox} = \sum_{i=3,4,5,7} \frac{v_i \rho_i}{K_i} )</td>
<td>( 1.58 \times 10^2 )</td>
</tr>
<tr>
<td>( \lambda_{an} = \sum_{i=3,5,6,8} \frac{v_i \rho_i}{K_i} )</td>
<td>( 5.60 \times 10 )</td>
</tr>
<tr>
<td>( \lambda_{ox} = \sum_{i=9,10} \frac{v_i \rho_i}{K_i} )</td>
<td>( 5.10 )</td>
</tr>
<tr>
<td>( \lambda_{an} = \sum_{i=9,11,12} \frac{v_i \rho_i}{K_i} )</td>
<td>3.05</td>
</tr>
<tr>
<td>( \eta_{ox} = \frac{\sum_{i=3,4,5,7} v_i \rho_i / K_i}{\sum_{i=3,4,5,7} v_i \rho_i / K_i} )</td>
<td>0.316</td>
</tr>
<tr>
<td>( \eta_{an} = \frac{\sum_{i=3,5,6,8} v_i \rho_i / K_i}{\sum_{i=3,5,6,8} v_i \rho_i / K_i} )</td>
<td>0.538</td>
</tr>
</tbody>
</table>

\( \phi \) s in mol d\(^{-1}\) m\(^{-3}\); \( \lambda \) s in d\(^{-1}\)
\( \eta \) s are mol S in DMS per mol S in DMSP
Terms marked * are omitted for the 'dark' values

DMS. In other words, these two parameters compare the importance of DMSP cleavage with respect to total microbial DMSP breakdown (cleavage plus demethylation).

**Slurry experiments**

To determine degradation rates of DMSP and DMS, slurry experiments were done with sediment collected in August 1996 at two different sites in the Bassin d'Arcachon (France): Île aux Oiseaux (station A) and Pointe de Causseyre (station L). The sediment of station A consists of fine sand and clay and is mostly covered with seagrass. The sediment of station L is much more sandy and was covered with low numbers of diatoms at the moment of sampling. (For a more detailed description of the Bassin d'Arcachon, see (Caumette et al. 1996). Samples were taken during low tide from the upper layer (ca. 1 cm) of the sediment. The sediment of
station A was filtered with a coarse sieve to remove the seagrass. Slurries were prepared by mixing the sediment with seawater in a ratio of ca. 1:5 (w:v). Then 40 ml of slurry was put in 160-ml glass vials which were closed with butyl rubber stoppers and crimp seal caps. For light and oxic conditions the vials were incubated on a shaking incubator at about 40 μmol photons m⁻² s⁻¹; for dark and anoxic conditions the vials were wrapped with aluminum foil and purged with nitrogen gas for about 30 minutes. In the experiments, either DMS ('DMS addition') or DMSP ('DMSP addition') was added. Both were added through the rubber stoppers in a final concentration of 50 μmol l⁻¹ slurry. DMS was determined gas chromatographically by headspace analysis (Van Bergeijk & Stal 1996). To determine DMSP, samples of 1 ml were taken from the slurries with a syringe through the rubber stoppers. DMSP was measured indirectly, as DMS, after alkaline hydrolysis.

Equation 4 was simultaneously fitted to the data, using the least-sum-of-squares criterion, and with the diffusion, ‘shift’, and exudation terms set to zero, as these terms do not apply in the experimental situation. A background term was added to the DMSP concentration in order to account for DMSP that shows up in the analysis although it was not biologically available in the slurry. This term was estimated as a ‘nuisance parameter’. Initial conditions were taken to be the average of the experimental values at t=0. The parameter estimates which were obtained are shown in Table 7.4. Curves corresponding to these estimates are shown in Figure 7.4, together with the experimental data.

Table 7.4. Parameter estimates for slurry experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>λ_P (h⁻¹)</th>
<th>λ_D (h⁻¹)</th>
<th>η</th>
</tr>
</thead>
<tbody>
<tr>
<td>St. A, light-oxic</td>
<td>0.368 (0.169)</td>
<td>0.107 (0.013)</td>
<td>0.323 (0.107)</td>
</tr>
<tr>
<td>St. A, dark-anoxic</td>
<td>0.0847 (0.0301)</td>
<td>0.0095 (0.0021)</td>
<td>0.865 (0.110)</td>
</tr>
<tr>
<td>St. L, light-oxic</td>
<td>0.140 (0.0336)</td>
<td>0.0326 (0.0044)</td>
<td>0.845 (0.096)</td>
</tr>
<tr>
<td>St. L, dark-anoxic</td>
<td>0.0359 (0.0054)</td>
<td>0.0041 (0.0012)</td>
<td>0.627 (0.066)</td>
</tr>
</tbody>
</table>

Values in parentheses are estimated standard deviations.

Simulations

Procedures

Equation 4 was solved numerically for the parameter values listed in Tables 2 and 3, using a Runge-Kutta fourth order scheme (Burden & Faires 1989), with a step size of 0.0005 d. A stationary cycle was obtained by simulating diel cycles until the relative distance between the values of the four state variables at the beginning and the end of a simulated day was smaller than 10⁻⁶. This relative distance was computed by taking for each state variable its value at the beginning and at the end of a simulated day, dividing the difference between these values by the ‘beginning’ value,
thus obtaining four relative change values (one for every state variable), and, finally, taking the square root of the squared relative change values.

To compute the mean emission rate of DMS from the mat, a fifth state variable was added which accumulated the diffusive efflux of DMS.

Stationary cycle

A stationary diel cycle in the model mat was computed. Figure 7.5 shows the time course of the interstitial DMSP and DMS concentrations during this cycle, in the oxic layer as well as in the anoxic layer, for the parameter values listed in Table 7.3 with $\kappa_D$ from Table 7.2. The mean DMS emission flux during this cycle
Figure 7.5. Diel pattern of DMSP and DMS concentrations in the oxic and anoxic layers of the microbial mat model, during a stationary diel cycle. A: DMSP concentration in the oxic layer; B: DMSP concentration in the anoxic layer; C: DMS concentration in the oxic layer; D: DMS concentration in the anoxic layer. Concentrations in μmol m$^{-2}$. This cycle serves as the 'benchmark' cycle. The solution of the linearized system (Eq. 4) was virtually identical to the solution of the original non-linear system (Eq. 3) for this benchmark cycle.

Sensitivity analysis

To gauge the influence of the parameter values on the mean DMS emission, stationary cycles were computed for altered parameter values. The parameters were altered one at a time, keeping all others at the benchmark values listed in Table 7.3.

The oxic DMSP turnover rate $\lambda_{ox}$ was set at various values ranging from zero to well over the benchmark value. The mean DMS emission flux did not appear to be

DMS emissions: a mathematical model
sensitive to this parameter in the neighbourhood of the benchmark value of Table 7.3. Indeed, only at oxic DMSP turnover rate values much below this standard value did the emission flux become markedly lower than the benchmark value of 0.0147 μmol m$^{-2}$ d$^{-1}$ (Figure 7.6A).

The anoxic DMSP turnover rate $\lambda_{an}$ was also set at various values ranging from zero to well over the benchmark value. It appeared that the mean DMS emission flux is not critically dependent on the anoxic DMSP breakdown rate (Fig. 7.6B; both the ‘light’ and the ‘dark’ values of $\lambda_{an}$ were set at the value plotted on the abscissa in this graph).

The oxic DMS turnover rate $\lambda_{ox}$ was set at various values ranging from zero to over ten-fold the ‘light’ benchmark value (Table 7.3). It turned out the mean DMS emission flux decreases with an increasing oxic DMS breakdown rate (Fig. 7.6C; both the ‘light’ and the ‘dark’ values of $\lambda_{ox}$ were given the value plotted on the abscissa in this graph). Among the four lumped rate parameters, $\lambda_{ox}$ was found to be the most critical as regards the mean DMS emission flux.

The mean DMS emission flux was also found to decrease with an increasing anoxic DMS breakdown rate $\lambda_{an}$ (Fig. 7.6D; both the ‘light’ and the ‘dark’ values of $\lambda_{an}$ were given the value plotted on the abscissa in this graph). However, the benchmark value is in the region where the mean DMS emission is hardly affected by changes of $\lambda_{an}$. Therefore, the DMS emission flux is not very sensitive to $\lambda_{an}$ in the neighborhood of the benchmark value (Table 7.3).

Sensitivity with respect to the partitioning coefficients was also evaluated. Both were set at values ranging from zero to one. As one would expect, the mean DMS emission flux increases with an increasing oxic partitioning coefficient $\eta_{ox}$ (Fig. 7.7A; both the ‘light’ and the ‘dark’ values of $\eta_{ox}$ were given the value plotted on the abscissa in this graph). The oxic partitioning coefficient $\eta_{ox}$ increases as DMSP demethylation by aerobic heterotrophs becomes quantitatively less important in the DMSP diagenesis of the mat. In this respect, this physiological group plays a key role in the mat’s behavior as a DMS ‘plant’. The anoxic partitioning coefficient $\eta_{an}$ on the other hand, did not appear to be critical with respect to the mean DMS emission flux (Fig. 7.7B; both the ‘light’ and the ‘dark’ values of $\eta_{an}$ were given the value plotted on the abscissa in this graph).

Finally, the DMS mass transfer coefficient $k_{l/D}$ was set at various values. It was found that this parameter affects the mean DMS emission flux markedly (Fig. 7.7C). If the present benchmark value is an overestimate, the DMS efflux might be much smaller than the benchmark value of 0.0147 μmol m$^{-2}$ d$^{-1}$. 

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Figure 7.6. Model sensitivity analysis. Graphs show mean DMS emission over the stationary diel cycle as a function of a model parameter, Equation 4. Other parameter values are kept at the benchmark values of Tables 2 and 3. Both 'light' and 'dark' values are set at the value plotted here on the abscissa. A: oxic DMSP breakdown rate; B: anoxic DMSP breakdown rate; C: oxic DMS breakdown rate; D: anoxic DMS breakdown rate. Emission rates in \( \mu \text{mol m}^{-2} \text{d}^{-1} \).

**Altered DMS emission in perturbed mats**

A number of ecological 'what if' questions may be put to the model. Five such questions will presently be considered here.

**Increasing exudation rates.** Increased irradiation may lead to an increased exudation of DMSP and DMS by the oxygenic phototrophs. Dimensional analysis of system Equation 4 reveals that the mean DMS efflux will increase by a factor \( \alpha \) when both exudation rates (\( \dot{\phi}_1 \) and \( \dot{\phi}_2 \)) are multiplied by that factor \( \alpha \) (this result no longer holds when \( \alpha \) becomes so large that the linear approximations to the hyperbolic responses in Equation 3 are no longer valid).
Figure 7.7. Model sensitivity analysis. Graphs show mean DMS emission over the stationary diel cycle as a function of a model parameter, Equation 4. Other parameter values are kept at the benchmark values of Tables 2 and 3. Both 'light' and 'dark' values are set at the value plotted here on the abscissa. A: oxic partitioning coefficient; B: anoxic partitioning coefficient; C: mass transfer coefficient. Emission rates in μmol m$^{-2}$ d$^{-1}$.

**Shifts in physiological group compositions.** The composition of the mat may alter as regards the relative propensities of the various physiological groups. The biomass densities, expressed by the $p$ parameters, then change. The effects of such changes depend on the contributions made by the various groups to the lumped parameters listed in Table 7.3. For the benchmark setting of Table 7.3, the most influential groups are found to be the oxygenic phototrophs and the aerobic heterotrophs. The former group is responsible for DMSP and DMS exudation. As noted in the preceding paragraph, DMS efflux is directly proportional to the exudation fluxes carried by the oxygenic phototrophs (provided that the ratio $\phi_1 / \phi_2$ remains the
same). The aerobic heterotrophs, too, have already been noted for their key role in determining the oxic partitioning coefficient $n_{\text{ox}}$.

Together, the aerobic heterotrophs and the purple sulfur bacteria give $\lambda_{\text{ox}}^P$ its large value. However, as long as this value remains above $\sim 40$ d$^{-1}$, changes in contributing biomass densities do not much affect the mean DMS emission flux.

The most critical lumped rate parameter in the sensitivity analysis proved to be $\lambda_{\text{ox}}^D$. This parameter is composed of about equal contributions of purple sulfur bacteria and aerobic heterotrophs. In sum, it appears that the mat’s DMS production is most sensitive to changes in the biomass density of the oxygenic phototrophs and the aerobic heterotrophs, followed by the purple sulfur bacteria.

**Osmotic stress: continuous DMSP load.** Osmotic stress may occur regularly throughout the diel cycle, causing the oxygenic phototrophs to release intermittently some of their DMSP into the interstitial space. Such osmotic stress may be modelled as a continuous extra DMSP flux, proportionally distributed over the oxic and anoxic layers. Figure 7.8 shows the stationary cycle results for a number of continuous DMSP load fluxes. This graph is nearly linear. Thus, one may infer a partitioning coefficient of $\sim 0.16$ (S in DMS per S in DMSP) for the additional loads; this number expresses the fraction of the load that escapes as DMS.

![Figure 7.8. Mean DMS emission over the stationary diel cycle as a function of DMSP load (Eq. 4). Parameter values are kept at the benchmark values of Tables 2 and 3.](image)

The stationary diel patterns of DMS emission from the model mat, at a number of load values in the same range as the abscissa of Figure 7.8, are shown in Figure 7.9. There appears to be a shift in maximum DMS efflux from 3 p.m. towards noon, as the load value increases.
Alkaline stress: oxic knockout. Microbial mats tend to be poorly carbonate buffered, as a result of carbonate diffusion limitation; intense photosynthetic activity (carbon dioxide fixation) in such systems leads to alkaline stress (Visscher & Van Gemerden 1991a). Changes in the pH value of the interstitial fluid lead to a diminished activity of the microbes which carry out the ‘oxic’ processes in the present model (De Zwart & Kuenen 1995). Such alkaline stress may be modelled by multiplying the \( v_i \) values for ‘oxic’ processes (Table 7.2) by a ‘knock-out’ factor, and recomputing the lumped parameters defined in Table 7.3. Figure 7.10A shows the stationary cycle results for a number of oxic knock-out factors.

The nearly proportional behaviour exhibited in this graph means that oxic knock-out is dominated by the diminished exudation rates. However, inasmuch as alkaline stress usually arises as a result of intensive photosynthetic activity, it seems plausible that exudation rates remain at the benchmark value (or become even higher). Figure 7.10B shows what happens when the exudation rates are exempted from oxic knock-out. The exudation rates \( \phi_1 \) and \( \phi_2 \) have been kept at their benchmark values in these simulations. Oxic knock-out in this case tends to increase DMS emission from the mat (except at ‘severe’ knock-out factors below ~ 0.1). This result is consistent with simulation results reported by (De Zwart & Kuenen 1995).

Eutrophic stress: continuous DMSP load at anoxic conditions. The mat may become covered by rotting algae, which cause the entire mat to become anoxic and which, moreover, exude a considerable DMSP load. Such eutrophic stress may be modelled by assigning the ‘anoxic’ values in Table 7.3 to the ‘oxic’ parameters,
adding a continuous extra DMSP flux, proportionally distributed over the oxic and
anoxic layers, and, finally, setting the exudation rates \( \dot{\phi}_1 \) and \( \dot{\phi}_2 \) to zero.
Dimensional analysis shows that the mean DMS emission rate is directly
proportional to the imposed DMSP load. Simulations indicate a partitioning
coefficient of \( \sim 0.21 \) (S in DMS per S in DMSP) for the eutrophic loads; this number
expresses the fraction of the load that escapes as DMS.

Discussion
The present model gives a quantitative description of DMS emission from a
microbial sedimental ecosystem in response to various ecological influences, such as
osmotic stress, alkaline stress, and eutrophic stress. The model shows how
physiological characteristics at the level of individual functional groups can be
aggregated into a simple model of the microbial mat. The sensitivity analysis
presented here should be helpful in assessing differences between maps of various
functional group compositions, as regards their DMSP biotransformation behaviour.

Atmospheric DMS has been implicated in a climatic feedback mechanism
(Charlson et al. 1987, De Zwart & Kuenen 1992, Williams 1996). Briefly, through a
number of intervening processes, DMS is ultimately involved in the formation of
clouds. An increase of cloudiness is thought to adversely affect the activity of the
marine and estuarine unicellular organisms. Inasmuch as the production of DMS is
among those activities, a regulatory feedback cycle is thus thought to arise. The link
between solar irradiance and biotic DMS production is quite uncertain (Charlson et
al. 1987; see also Lawrence 1993). Models of the type proposed in this paper can
quantify the role of microbial mats in this link.
The transfer fluxes of DMS and DMSP between the oxic layer and anoxic layer are represented in the present model as boundary ‘shift’ fluxes. Because the two compartments are assumed to be well-mixed, the concentration profiles have a step shape. They are constant within each of the two layers, with a discontinuous ‘jump’ at the oxic-anoxic transition. In reality, the concentration profiles have a more smooth shape, leading to concentrations at the oxic-anoxic boundary that are intermediate between the oxic and anoxic values. Consequently, the ‘shift’ fluxes in the present model are either an overestimation or an underestimation of the true ‘shift’ transfer between the two layers, depending on whether the boundary shifts in the direction of the higher or the lower of the two concentrations. On the other hand, exchange by diffusion is unaccounted for in the present model. It is not difficult to show that the over/underestimation error in the shift flux and the error arising from the neglect of diffusion always act in opposite directions, tending to counteract one another. Hence, one might regard the shift flux error as a crude model of diffusive exchanges. The error increases as the concentration difference between the two layers increases, which ties in with its proposed role as a simulacron of intrasedimental diffusion. It may well be the case that true diffusion of DMS within the sediment proceeds much slower or much faster than in the present crude model. In that case, an additional explicit diffusion term should be added to the model. An experimental observation which would prompt the inclusion of such a term would be a marked emission of DMS during the night, a phenomenon that is not observed in the present model.

A substantial portion of the parameters in Table 7.2 are ‘guesstimates’, which is rather discouraging given that the Wadden Island microbial mat is a much-studied ecosystem and that the present model is comparatively simple. The problem is inherent in any effort to describe the behavior of a microbial ecosystem in terms of the constituent organisms. All relevant data on these constituents must be available in order to obtain a reliable integrated model. As it stands, the present model falls short of this requirement. The sensitivity analysis, however, showed mean DMS emission to be most sensitive to the rate parameter $\lambda_{\text{ox}}$, which was computed from available data. Thus, so long as the remaining rate parameters are within the correct order of magnitude (say), the model’s description of DMS emission may be rather fair.

To check this, we compared the lumped parameters of our benchmark with the parameters derived from the slurry experiments, Table 7.4. The values were found to compare quite well: except for the degradation rates of DMSP ($\lambda_{\text{ox}}$ and $\lambda_{\text{an}}$), all parameters were in the same order of magnitude. The $\lambda_{\text{ox}}$ and $\lambda_{\text{an}}$ values obtained from the data of the slurry experiment of station L were markedly lower than the benchmark values. There are two possible explanations for this. Firstly, the microbial biomass of the sediments from station L might have been much lower than the biomass in the microbial mats which our model aims to represent.
Secondly, the 'guesstimates' for $\lambda_{ox}$ and $\lambda_{an}$ may be well off the mark. Especially the value for the oxic demethylation of DMSP (Table 7.2) seems to be very high. This value could not be taken directly from the literature, which demonstrates the problem we had with collecting the data necessary for our model. But although $\lambda_{ox}$ and $\lambda_{an}$ might have been overestimated, this hardly has an effect on the DMS emission which is predicted by the model, as was already mentioned above (see also Fig. 7.6A, B).

The present model relates DMS emission from a microbial mat to functional group composition (the physiological make-up of the mat), as well as to various types of ecological alterations. The model's primary outputs are time courses of DMS and DMSP in the interstitial fluid of the sediment in the oxic (top) layer and the anoxic (bottom) layer, DMS emission rates, and partitioning coefficients for additional DMSP loads. It would be instructive to compare the simulated time profiles with experimental ones. Unfortunately, in situ tracking of DMSP and DMS concentrations in microbial mats is difficult to achieve in practice. Reliable in situ measurements of DMS concentrations are presently not available, due to the persistent DMSP-lyase activity of microbial mat samples. Sampling causes mechanical disturbance which results in release of DMS from DMSP-producing primary producers (Wolfe et al. 1997). The subsequent lysis of the released DMS results in an overestimation of the DMS concentration. Inhibitors which completely block the DMSP-lyase activity and leave the DMSP and DMS concentrations unchanged are presently not available (Kiene 1988, Visscher et al. 1994). Moreover, the patchy distribution of organisms involved in DMSP production and turnover in microbial mats contributes to further inaccuracy in the determination of DMS and DMSP concentrations. To overcome these problems, the sediment was slurried in previous research. Slurries were preincubated for a certain period in order to obtain a homogeneous slurry in which any DMSP that is initially present is largely consumed (Kiene 1988, Visscher et al. 1994). The obvious drawback of this method is that the in situ microbial composition and related processes are disturbed or altered. (Visscher et al. 1995) found that slurry-based concentrations were over two orders of magnitude larger than pore water-based measurements. The values in the benchmark cycle of this paper are again about two orders of magnitude lower, meaning that exudation rates in our model may be too low, or that the breakdown rates may be too fast; the latter possibility is also suggested by the results of the slurry experiments, Table 7.4.

Physiological properties of the constituent biota and fluctuating abiotic conditions combine to produce the eco-metabolism of a microbial mat. The model presented and analyzed here captures the essentials of these interactions in order to describe DMSP metabolism at the ecosystem level, and predict increased DMS emissions under various ecological disturbances.