DMSP synthesis and exudation in phytoplankton: a modeling approach

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ABSTRACT: In the marine environment, phytoplankton are the fundamental producers of dimethylsulfoniopropionate (DMSP), the precursor of the climatically active gas dimethylsulfide (DMS). DMSP is released by exudation, cell autolysis, and zooplankton grazing during phytoplankton blooms. In this study, we developed a model of phytoplankton DMSP and DMS production allowing quantification of the exudation rates of these compounds during different growth phases. The model was tested on published data from axenic cultures of *Prorocentrum minimum* and *Phaeocystis* sp.; DMSP exudation rates vary considerably between the 2 species. Model results show that *P. minimum* exudes around 1 % d^{-1} of its DMSP quota during the latent, exponential and senescent phases. This is comparable to the average exudation rate estimated from previous laboratory experiments. However, *Phaeocystis* sp. exudes from 3 to 11 % d^{-1} of its DMSP quota. For this species, DMSP exudation rates apparently show an inverse relationship with the population growth rate. The maximum DMSP exudation rate in *Phaeocystis* sp. is 10 times higher than previously reported DMSP or DMS exudation rates. Our results suggest that exudation may be as important as cell autolysis in the release of DMSP during *Phaeocystis* sp. blooms. We conclude that exudation should be incorporated in models of DMS cycling in the marine environment. Moreover, our results for *Phaeocystis* sp. suggest that a low and constant exudation rate, as sometimes used in models, is not suitable for all conditions.

KEY WORDS: DMS · DMSP · Exudation · Synthesis · *Phaeocystis* · Model

INTRODUCTION

Over oceanic regions, the release of marine dimethylsulfide (DMS) to the atmosphere is thought to play an important climatic role by increasing the scattering of solar radiation and by providing cloud condensation nuclei. Dimethylsulfoniopropionate (DMSP), the DMS precursor, is synthesized by many macroalgae and phytoplankton. It has been suggested that DMSP acts as an osmolyte (Vairavamurthy et al. 1985, Dickson & Kirst 1987), a cryoprotectant (Kirst et al. 1991) and a methyl

donor (Ishida 1968). Cell quotas of DMSP are highly variable among species (Keller et al. 1989). Prymnesiophytes and dinoflagellates have a high intracellular DMSP concentration compared to diatoms. DMSP quotas vary also through the algal growth cycle (Stefels & van Boekel 1993, Matrai & Keller 1994) and may be influenced by nitrate (Turner et al. 1988, Groene & Kirst 1992, Keller & Korjeff-Bellows 1996) and phosphate limitation (Stefels & van Boekel 1993). DMSP is released into seawater mainly during senescence or the latter phase of blooms (Matrai & Keller 1993), most likely via cell autolysis (Nguyen et al. 1988, Kwint & Kramer 1995) and zooplankton grazing (Dacey & Wakeham 1986, Cantin et al. 1996). Phytoplankton may also exude DMSP, but DMSP

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liberation by phytoplankton is usually attributed to cell autolysis. Exudation is rarely considered as a DMSP liberation mechanism. In seawater, DMSP may be either demethylated by bacteria without any production of DMS or enzymatically cleaved to DMS by phytoplankton (Stefels & van Boekel 1993, Wolfe & Steinke 1996) or bacterial (Kiene & Bates 1990, Kiene 1992) DMSP-lyase. The 3 main sinks of DMS are: consumption by bacteria, photo-oxidation into dimethylsulphoxide (DMSO; Brimblecombe & Shooter 1986, Kieber et al. 1996) and ventilation to the atmosphere.

The multitude of interacting mechanisms makes modeling appropriate to study DMS dynamics and to evaluate the DMS flux to the atmosphere. Gabric et al. (1993) modified a nitrogen-based model by adding DMS-related processes to reproduce the evolution of DMS concentrations in seawater during a phytoplankton bloom. Lawrence (1993) modeled DMS dynamics both in the ocean and in the atmosphere. In his model, the food web was oversimplified, and Lawrence pointed out the lack of knowledge about DMS processes in the marine environment. Van den Berg et al. (1996b) modified a coupled physical-phytoplankton model, the FYFY model (van den Berg et al. 1996a), developed for the southern North Sea, by adding DMS-related processes. The FYFY model simulates 6 phytoplankton classes, 1 grazer size and bacteria. Their results showed, among other things, the importance of *Phaeocystis* DMSP-lyase on DMS flux to the atmosphere. These models improved our understanding of DMS dynamics, mainly by synthesizing present information and pointing towards areas where better understanding is needed. An ultimate goal of modeling DMS dynamics is to evaluate the impact of an anticipated climatic warming on DMS production and the possible feedback strength of the cooling effect induced by DMS emission. However, uncertainties in DMSP production, DMS production, and DMS sinks limit our capability to evaluate such feedback mechanisms.

This modeling study focuses on DMSP synthesis and DMSP release by phytoplankton during the growth cycle. In a minireview, Malin & Kirst (1997) stressed the lack of DMSP releasing rates by organisms and particularly by phytoplankton. Only 3 rates of DMS production by phytoplankton can be extracted from different laboratory studies and uncertainties remain about them. Dacey & Wakeham (1986) and Vairavamurthy et al. (1985) estimated that the daily percentage of the DMSP quota exuded as DMS into seawater was 0.3 and 1.4% for the dinoflagellates *Gymnodinium nelsoni* and *Hymenomonas carterae*, respectively. The rate given for *G. nelsoni* is probably underestimated due to bacterial DMS consumption. The third rate present in the literature is from Vetter & Sharp (1993), who grew an axenic culture of the centric diatom *Skele-*

tonema costatum and estimated a DMS production rate of 10 to 40 fg S(DMS) cell^{-1} d^{-1}. In these 3 studies, the reported release product by the different phytoplankton species is DMS. However, it has not been investigated whether or not these species synthesize DMSP-lyase. The presence of DMS in these cultures may have resulted from phytoplankton DMSP-lyase production or from the activity of possible bacterial contaminants. Bacteria may have consumed DMS and therefore caused DMS exudation rates to be underestimated.

The goal of the present study was to model DMSP synthesis and DMSP exudation by marine phytoplankton. To study these processes it is essential to use axenic phytoplankton cultures to eliminate DMSP and DMS losses due to bacterial consumption. The data from 2 published axenic culture studies were used to constrain the model. These 2 studies dealt with 2 important DMSP producers (Keller et al. 1989), the dinoflagellate *Prorocentrum minimum* and the prymnesiophyte *Phaeocystis* sp. *P. minimum* has a wide distribution, forming large blooms in temperate and subtropical waters bordering the North Pacific (Russia, China, Japan, Canada), the east and south coasts of the USA, the NE Atlantic, the North Sea and the Mediterranean Sea (Grzebyk & Berland 1996). *Phaeocystis* sp. is known to produce DMSP-lyase (Stefels & van Boekel 1993) and is an important player in the DMS cycle. *Phaeocystis* forms large blooms in the North Sea (Veldhuis & Admiraal 1987, van Boekel et al. 1992, Turner et al. 1996), the Arctic (Wassmann et al. 1990, Matrai & Vernet 1997) and the Antarctic (Gibson et al. 1988, Crocker et al. 1995), where it has been associated with the highest DMS concentrations ever measured in the oceans (Gibson et al. 1988, Crocker et al. 1995).

EXPERIMENTAL DATA AND MODELING APPROACH

We used data from Matrai & Keller (1994) and Stefels & van Boekel (1993), who grew axenic cultures of *Prorocentrum minimum* and *Phaeocystis* sp., respectively. Both species were grown in 1 l flasks. *P. minimum* was grown in K-medium (Keller et al. 1987) at 18°C with a light intensity of 166.1 µE m^{-2} s^{-1} in a 14 h light:10 h dark cycle. *Phaeocystis* sp. was grown in a medium described by Veldhuis & Admiraal (1987), with the exception that nitrate was the only nitrogen source. The culture was maintained at 10°C with a light intensity of 85 µE m^{-2} s^{-1} in a 14 h light:10 h dark cycle. Changes in nutrient concentrations were not measured in either study, but nitrogen limitation was expected for *P. minimum* and phosphorus limitation for *Phaeocystis* sp. More details on the materials and methods are available in the respective papers.

Cultures were reported to be axenic, preventing bacterial consumption of DMSP and DMS. The losses by ventilation and photo-oxidation were thought to be low but they were not evaluated. The published data used in this study were carefully selected to include only samples obtained through gravity or low pressure filtration, thus minimizing artifacts due to cell rupture. Measurements of the DMS fraction in the *Phaeocystis* sp. culture did not necessitate filtration, circumventing the filtration artifact. Certain data sets were not used because of evidence of bacterial contamination or ambiguity in the data. Admittedly the data sets we used to test the model were small, but they were the most reliable published. We assume in our modeling work that there were no DMS sinks in the cultures, i.e. no ventilation, photo-oxidation or bacterial consumption. If, in fact, DMS sinks occurred in the cultures, the conclusions of this work remain uncompromised and the different rates given in this paper would then be underestimates.

In this study, it is assumed that *Prorocentrum minimum* and *Phaeocystis* sp. exude DMSP. The particulate DMSP ($DMSP_p$) and the dissolved DMSP ($DMSP_d$) concentrations were measured in the *P. minimum* culture. In the *Phaeocystis* sp. culture, the $DMSP_p$, the $DMSP_d$ and the DMS concentrations were measured. However, the $DMSP_d$ concentrations were null. The *Phaeocystis* sp. results are slightly different from those published by Stefels & van Boekel (1993) due to *a posteriori* corrections. The absence of $DMSP_d$ in the *Phaeocystis* sp. culture was probably due to the DMSP-lyase produced by this species. The DMSP-lyase, probably located on the exterior of the cell, would rapidly cleave the DMSP exuded by *Phaeocystis* sp. into DMS.

Existing DMS models are modified nitrogen- or carbon-based models. Our modeling strategy was to use a model based on phytoplankton cell numbers to simulate DMS dynamics. This approach was chosen for 3 reasons: firstly, intracellular nitrogen and carbon concentrations are not constant throughout the growth cycle of phytoplankton (Parsons et al. 1984); secondly, N:S and C:S ratios are not constant through the growth cycle (Cuhel et al. 1984, Vetter & Sharp 1993, Matrai & Keller 1994); and thirdly, the temporal changes of the particulate organic nitrogen and carbon were not measured in the *Phaeocystis* sp. culture.

MODEL DEVELOPMENT

We developed equations to model DMSP synthesis and exudation based on processes and rates described in the literature. We began with the simplest model and initial parameters taken from the literature, when available.

Variations in algal cell numbers. The temporal change in algal cell numbers was simulated with a logistic equation. Since nutrient depletion was not followed and since the light was saturating in the batch cultures, we could not model the nutrient or light dependence of the phytoplankton population growth. The growth of the phytoplanktonic population is determined by:

$$\frac{d(CELL)}{dt} = R \cdot CELL \cdot \frac{(K - CELL)}{K} \quad (1)$$

where CELL is cell numbers (cells l^{-1}), t is time (d), R is the maximum specific growth rate (d^{-1}), and K is the carrying capacity of the cultures (cells l^{-1}). To simulate the decrease in cell numbers during the senescent phase, we added a mortality term to the equation of temporal changes in cell numbers through time:

$$\frac{d(CELL)}{dt} = R \cdot CELL \cdot \frac{(K - CELL)}{K} - m \cdot CELL \quad (2)$$

where m (d^{-1}) is the specific mortality rate.

In our modeling work, the ratio g/g_{max} is used as an index of growth limitation, where g (cells l^{-1} d^{-1}) represents the realized population growth rate, described by Eq. (1), and g_{max} (cells l^{-1} d^{-1}) is the maximal population growth rate. Prior to reaching the inflection point of the growth curve (where the derivative of Eq. 1 is zero; Day 10 and 12 for *Prorocentrum minimum* and *Phaeocystis* sp., respectively), the microalgae are assumed to grow at maximal rates, unlimited by either light or nutrients. The ratio g/g_{max} is set at 1 for this part of the culture cycle. After the inflection point, growth limitation is assumed to occur, and g/g_{max} is computed for each time step by dividing the growth rate calculated from Eq. (1) (normalized by cell numbers) by the maximum rate attained at the inflection point.

DMSP synthesis. To model DMSP synthesis, we assigned a DMSP synthesis rate to each phytoplankton cell. This is represented by the following equation:

$$\frac{d(DMSP_t)}{dt} = \rho_{syn} \cdot CELL \quad (3a)$$

where $DMSP_t$ is the total amount of DMSP synthesized (µmol DMSP l^{-1}) in the culture, ρ_{syn} is the cellular synthesis rate (µmol $DMSP_p$ cell^{-1} d^{-1}) and CELL (cells l^{-1}) is calculated by Eq. (2). To model the $DMSP_t$, we used a parameterization simulating maximal DMSP synthesis, when cells are growing fast and duplicating, and minimal DMSP synthesis, when cell growth becomes limited. Thus, we set the DMSP synthesis rate dependent on the relative growth rate:

$$\rho_{syn} = \max\left[S_{MIN}, S_{MAX} \left(\frac{g}{g_{max}} \right)^A \right] \quad (3b)$$

The expression $\max[S_{MIN}, S_{MAX} \cdot (g/g_{max})^A]$ means that ρ_{syn} is set as the maximal value between S_{MIN} and $S_{MAX} \cdot (g/g_{max})^A$. S_{MIN} (µmol DMSP$_p$ cell^{-1} d^{-1}) and S_{MAX} (µmol DMSP$_p$ cell^{-1} d^{-1}) are constants representing respectively the minimum and maximum DMSP synthesis rate per cell, and A (dimensionless) is a species-specific coefficient for DMSP synthesis. The constant A represents the sensitivity of DMSP synthesis to variations in the population growth rate; a high A value indicates a strong response of the DMSP synthesis rate to a change in algal growth rate.

Particulate and dissolved DMSP pools. In an axenic culture, the temporal changes in the DMSP$_p$ pool result from the balance between DMSP synthesis, exudation and cellular autolysis, as given by the following equation:

$$\frac{d(DMSP_p)}{dt} = \rho_{syn} \cdot CELL - \rho_{exu}\ CELL \cdot QUOTA$$
$$- m \cdot CELL \cdot QUOTA \qquad (4)$$

The first term on the right-hand side of Eq. (4) is DMSP synthesis as defined by Eq. (3a). The second term represents the loss by exudation, where ρ_{exu} (d^{-1}) is the specific exudation rate and QUOTA (µmol DMSP cell^{-1}) is the instantaneous ratio of DMSP$_p$ to cell number. The third term represents the amount of DMSP released in seawater via mortality (autolysis).

The accumulation of DMSP$_d$ is the sum of DMSP released by exudation and by autolysis:

$$\frac{d(DMSP_d)}{dt} = \rho_{exu} \cdot CELL \cdot QUOTA$$
$$+ m \cdot CELL \cdot QUOTA \qquad (5)$$

Parameters are the same as in Eq. (4).

The model was applied to the experimental data. The parameters were obtained through manual iterations to minimize differences between experimental and modeled results as expressed by Eq. (6) (below). A mathematical tool was used to evaluate the model misfit of the experimental results. The misfit was expressed as the average percentage of model error:

% model error =

$$\frac{\displaystyle\sum_{t=0:n}\left(\left|\frac{DMSP_{pe}(t)-DMSP_{pm}(t)}{DMSP_{pe}(t)}\right| + \left|\frac{DMSP_{de}(t)-DMSP_{dm}(t)}{DMSP_{de}(t)}\right| \right)}{2n} \times 100 \quad (6)$$

where $DMSP_{pe}(t)$ and $DMSP_{pm}(t)$ are the experimental and modeled values of DMSP$_p$ at time t, $DMSP_{de}(t)$ and $DMSP_{dm}(t)$ are the experimental and modeled values of DMSP$_d$ at time t and n is the number of observations. A percentage-based index was selected as a way to give similar weights to small and large experimental values. This prevents errors on large values from determining total error. A percentage of 0 from Eq. (6) represents a perfect fit while a value of 100% signifies

that the model simulates the experimental results with an average error of 100%. The model is coded with the software Matlab (The Mathworks Inc., Natick, MA, USA) and is solved by finite differences with time steps of 14 min, determined by trial and error to be the optimal interval to get accurate numerical solutions.

MODEL RESULTS

Algal cell numbers

The adjustment of the model parameters, related to temporal changes in algal cell numbers (Eq. 2), to the experimental data resulted in the values presented in Table 1 for K, R and CELL(0) (i.e. cell number at $t = 0$). We fixed m at 0 until maximum cell number was reached (Day 16 for both species), then a null growth rate and a constant mortality rate (Table 1) were imposed in order to reproduce the temporal changes of cell numbers (Fig. 1) throughout the cultures.

DMSP synthesis

Adjusting the model DMSP synthesis parameters (Eqs. 3a & 3b), S_{MIN}, S_{MAX} and A, to minimize differences between experimental and modeled results led to the values presented in Table 1. The sum of the experimental values of DMSP$_p$, DMSP$_d$ and DMS represented the total DMSP (DMSP$_t$) synthesized in the cultures (circles in Fig. 2). The accurate reproduction of experimental DMSP$_t$ concentrations by the model provided the basis to model further transfers from the intracellular DMSP to the dissolved DMSP.

Particulate and dissolved DMSP pools

Different formulations for the parameters of Eqs. (4) & (5) were tested (Figs. 3 & 4) to reproduce the measured DMSP$_p$ and DMSP$_d$ pools (DMS for *Phaeocystis* sp.). The simplest assumption is that cell mortality (autolysis) is the only source of DMSP$_d$. This was tested by setting ρ_{exu} at 0 d^{-1} (see Eqs. 4 & 5). Figs. 3A & 4A show that such a parameterization overestimated the particulate fraction and underestimated the dissolved fraction. This parameterization yielded a model error of 34% and 58% for *Prorocentrum minimum* and *Phaeocystis* sp., respectively. Therefore, exudation had to be included to accurately reproduce experimental results. A constant exudation rate of 1% of the DMSP quota per day was then used in the model ($\rho_{exu} = 0.01$ d^{-1}). Such an exudation rate is the only one suggested in the literature (Dacey & Wakeham 1986). Gabric et al. (1993)

Table 1. Model variables and parameters used to simulate DMSP and DMS production by *Prorocentrum minimum* and *Phaeocystis* sp.

Symbol	Description	Units	*P. minimum*	*Phaeocystis* sp.
Variables				
t	Time	d^{-1}		
CELL	Cell numbers	cells l^{-1}		
g	Realized growth rate	cells l^{-1} d^{-1}		
$DMSP_t$	Concentration of $DMSP_t$	μM		
$DMSP_p$	Concentration of $DMSP_p$	μM		
ρ_{syn}	DMSP synthesis rate	μmol DMSP cell^{-1} d^{-1}		
$DMSP_d$	Concentration of $DMSP_d$	μM		
DMS	Concentration of DMS	μM		
ρ_{exu}	DMSP exudation rate	d^{-1}		
Parameters				
K	Carrying capacity	cells l^{-1}	200×10^6	300×10^6
R	Maximal potential growth	d^{-1}	0.45	0.48
CELL(0)	Initial cell number	cells l^{-1}	2.8×10^6	1.5×10^6
m_{expo}	Mort. rate in expo. phase	d^{-1}	0	0
m_{sene}	Mort. rate in sene. phase	d^{-1}	0.018	0.18
g_{max}	Max. realized growth rate	cells l^{-1} d^{-1}	22.4×10^6	35.4×10^6
S_{MIN}	Min. synthesizing rate	μmol $DMSP_p$ cell^{-1} d^{-1}	8.4×10^{-9}	0.67×10^{-9}
S_{MAX}	Max. synthesizing rate	μmol $DMSP_p$ cell^{-1} d^{-1}	53.8×10^{-9}	4.8×10^{-9}
A	Specific coef. of synthesis	Dimensionless	10	1.6
QUOTA(0)	Initial DMSP quota	μmol $DMSP_p$ cell^{-1}	46.9×10^{-9}	10.0×10^{-9}
E_{MIN}	Min. exudation constant	d^{-1}	0.01	0.03
E_{MAX}	Max. exudation constant	d^{-1}	0.01	0.11

used this value to simulate DMSP exudation by phytoplankton. This parameterization reproduced experimental $DMSP_p$ and $DMSP_d$ results for *P. minimum* in exponential phase and gave a slight misfit in late senescent phase (Fig. 3B). This simulation led to a model error of 15%. Other parameterizations were attempted to decrease the model error for *P. minimum* results, but the improvement was small (model error of 12%) relative to the complexity induced in the equations by

these changes. Thus, we consider a constant exudation rate of 1% of the DMSP quota per day to be appropriate to reproduce exudation by *P. minimum*.

In contrast to *Prorocentrum minimum*, the utilization of a constant exudation rate of 1% d^{-1} of the DMSP quota was not appropriate to simulate exudation by *Phaeocystis* sp. (Fig. 4B). Model results using such an exudation rate led to considerable overestimation of experimental $DMSP_p$ and considerable underestimation of DMS. The model error for this simulation was 44%. As previously explained, DMS was measured in the *Phaeocystis* sp. culture since this species produces DMSP-lyase. To improve our reproduction of *Phaeocystis* sp. experimental results, an optimization of ρ_{exu} was carried out to minimize the model error index. It was found that a ρ_{exu} of 0.036 d^{-1} (Fig. 4C) satisfactorily modeled the experimental $DMSP_p$ and DMS values during latent and exponential phases. However, the model still overestimated experimental results for $DMSP_p$ and underestimated experimental results for DMS production during the senescent phase. This simulation reduced the model error to 21%. The model error cannot be decreased further using the equations presented here.
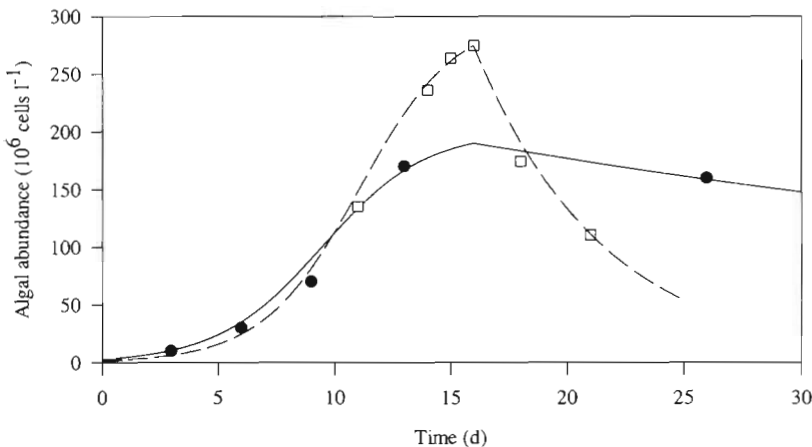

Fig. 1. Temporal variations of the abundance of 2 axenic cultures of *Prorocentrum minimum* and *Phaeocystis* sp., grown by Matrai & Keller (1994) and Stefels & van Boekel (1993), respectively. (□, — — —) Experimental and modeled values, respectively, for *Phaeocystis* sp. (●, ———) Experimental and modeled values, respectively, for *P. minimum*
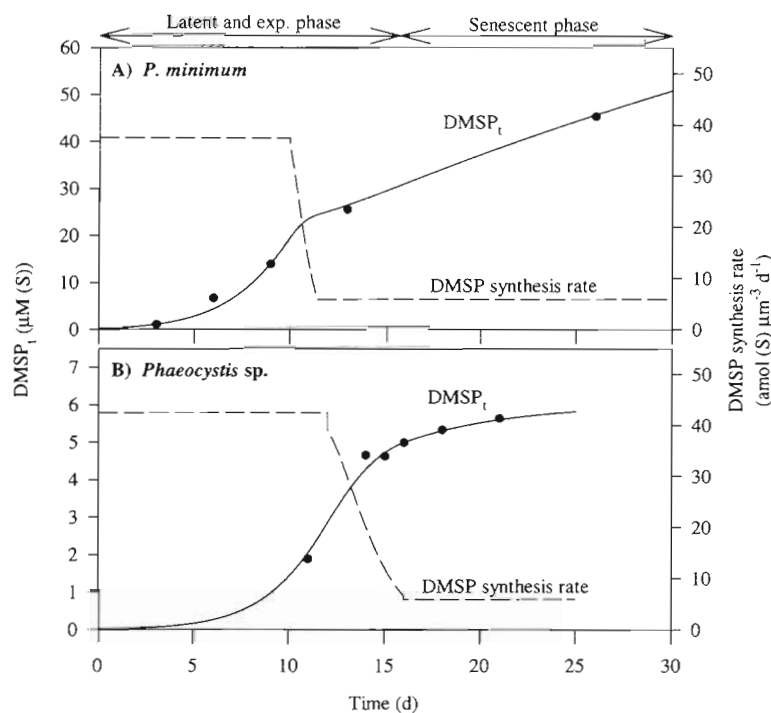
Fig. 2. Accumulation of the total DMSP synthesized (DMSP$_t$) and temporal changes of DMSP synthesis rates during 2 axenic cultures of (A) *Prorocentrum minimum* and (B) *Phaeocystis* sp. (●) Experimental values of DMSP$_t$, (———) modeled DMSP$_t$ and (— — —) DMSP synthesis rates
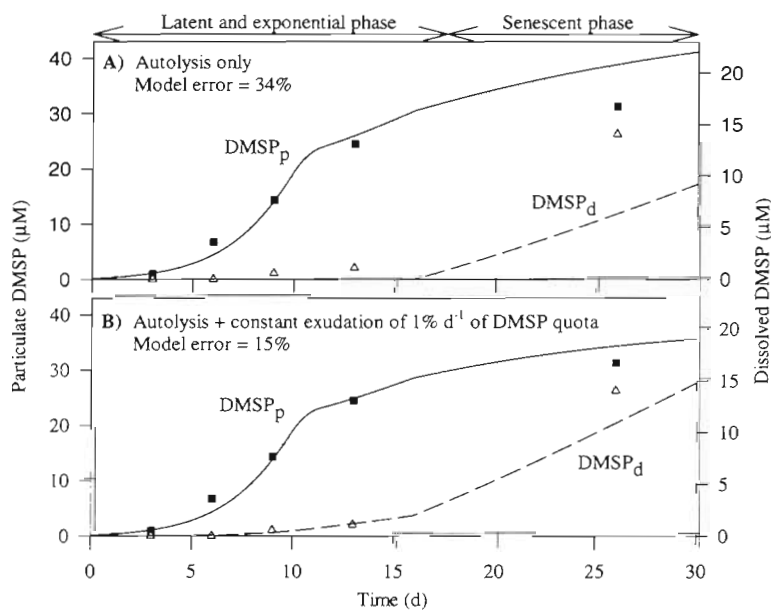

Fig. 3. Model simulations representing different possibilities of DMSP$_d$ release by *Prorocentrum minimum*. Symbols represent experimental results and lines modeled results (■: DMSP; △: DMSP$_d$). Model errors represent the sum of relative differences between experimental and modeled results for DMSP$_p$ and DMSP$_d$

These results suggest that exudation rates are higher during the senescent phase than during the exponential growth phase. Such a concept has already been used in modeling carbon flux in a pelagic environment. Baretta et al. (1988) simulated a continuous base excretion rate plus additional excretion when the phytoplankton growth rate was decreasing due to nutrient limitation. Some field and laboratory studies support this possibility. Matrai & Keller (1993) reported very high DMSP$_d$ values in the older parts of a coccolithophore bloom. Other studies (Nguyen et al. 1988, Stefels & van Boekel 1993, Kwint & Kramer 1995) reported higher DMS production in the senescent phase of blooms than during the initial phase, but they did not investigate whether this higher DMS production was due to autolysis or exudation.

In order to simulate a greater DMS exudation in the senescent phase, the exudation rate (ρ_{exu}) was taken to vary with the population growth rate, as suggested by Baretta et al. (1988), following the equation:

$$\rho_{exu} = \max\left[E_{MIN}, E_{MAX} \cdot \left(\frac{g_{max} - g}{g_{max}} \right) \right] \quad (7)$$

where E_{MIN} (d^{-1}) and E_{MAX} (d^{-1}) are constants representing the minimum and maximum exudation rates, respectively. As previously mentioned, ρ_{exu} was set to E_{MIN} during the latent phase and early exponential phase. Adjustment of E_{MIN} and E_{MAX} to minimize the model error for *Phaeocystis* sp. resulted in values of 3% and 11%, respectively (Fig. 4D). These model results represented a better simulation of the releasing mechanisms in the latent, exponential and senescent phases. The model error was 13%. However, there was still a discordance between experimental and modeled results in the early senescent phase, as reflected in the DMSP$_p$ and DMS values on Day 16 (Fig. 4D). Since this deviation was found for both DMSP$_p$ and DMS, and the time of appearance of the DMSP$_p$ peak was not reproduced by the model, we considered this disparity worthy of investigation. Further structural changes to the model were made by simulating a burst of exudation in the early senescent phase. Such parameterization improved the fit between experimental and modeled results (not shown) and
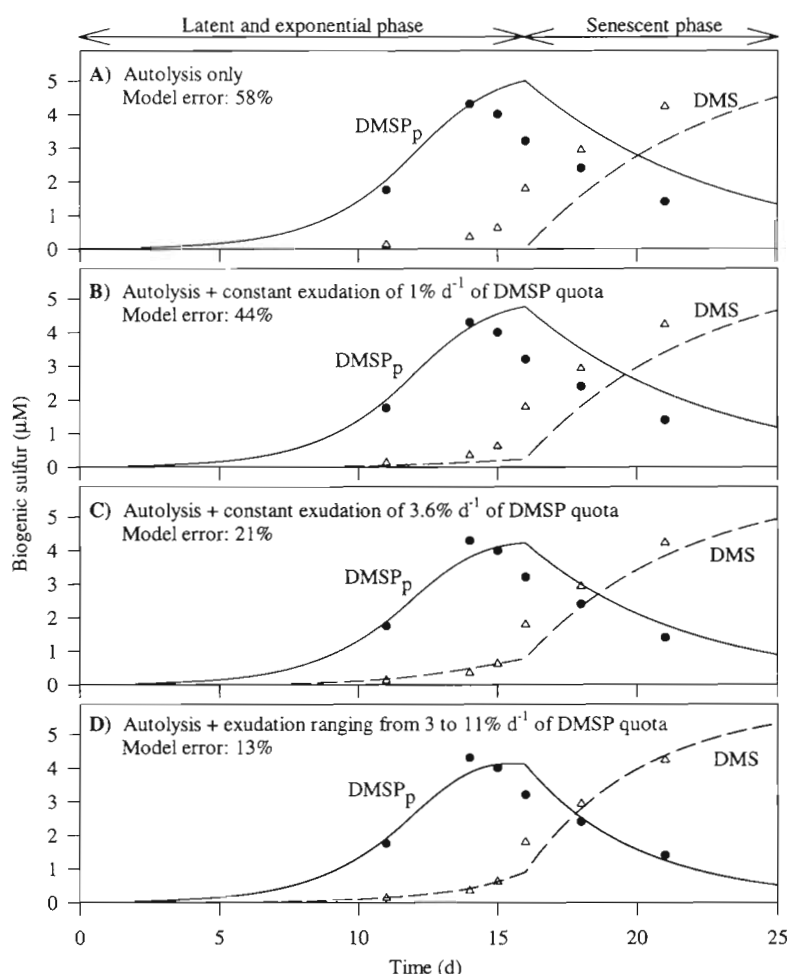
Fig. 4. Model simulations representing different possibilities of DMS release by *Phaeocystis* sp. Symbols represent experimental results and lines modeled results (•: DMSP$_p$; △: DMS). Model error represents the relative difference between experimental and modeled results for DMSP$_p$ and DMS

mum. Since *P. minimum* is about 10 times larger than *Phaeocystis* sp. (1437 µm^3 cell^{-1} compared to 113 µm^3 cell^{-1}, respectively), simulated DMSP quotas, synthesis and exudation rates are presented on a cell volume basis in Table 2. DMSP quotas and synthesis rates were very similar for the 2 species. However, the DMSP exudation rate in *Phaeocystis* sp. was 1 order of magnitude higher than the one for *P. minimum*. Our results, showing a high exudation rate for *Phaeocystis* sp., and this species' known capability to cleave DMSP into DMS (Stefels & van Boekel 1993) reinforce its key role in the DMS cycling in seawater. Keller & Korjeff-Bellows (1996) noted that prymnesiophytes, in general, have high levels of DMSP$_d$ in the culture medium.

DMSP synthesis

The usual method utilized to model DMSP$_p$ is to associate a constant DMSP quota to phytoplankton biomass (Gabric et al. 1993, van den Berg et al. 1996b). This method was not used for 3 reasons: firstly, the DMSP quota varies through time in the phytoplankton cultures used for this work; secondly, DMSP quotas are known to vary under nutrient limitation (Turner et al. 1988, Groene & Kirst 1992, Keller & Korjeff-Bellows 1996); and thirdly, the DMSP$_t$ measured in the cultures continued to increase after the maximum cell number was reached (Fig. 2). Such features cannot be reproduced with a constant DMSP quota. We cannot really study the transfer mechanisms between the DMSP pools without first reproducing the total DMSP synthesized in the cultures.

According to the results of our model, the DMSP synthesis rate varied by 1 order of magnitude through the growth cycle. As shown in Fig. 2, the simulated DMSP synthesis rates were maximal from the latent to mid-exponential growth phases, decreased sharply during the second half of exponential phase and remained low thereafter. One interesting feature is that to simulate the experimental data, the decrease in the modeled DMSP synthesis rate had to occur a few days before the maximum of algal cell numbers was reached. This decrease in DMSP synthesis began soon after the decrease in the population growth rate. These model results suggest that the decrease of DMSP synthesis is associated with physiological stress situations, such as

decreased the model error to 8%. However, such changes led to greater complexity and to a much more species-specific model. These 2 disadvantages and the absence of a theoretical explanation for such phenomena do not justify the small improvement in the data fit. Considering the available data, the optimal method to simulate the DMSP exudation by *Phaeocystis* sp. is to use a growth-rate-dependent equation to simulate low exudation in healthy growing conditions and higher exudation in limiting growth conditions.

INTERPRETATION OF MODEL RESULTS

Comparison between the two species

Our results show that the main difference between the 2 species is the high exudation rate by *Phaeocystis* sp. compared with the low rate by *Prorocentrum mini-*

Table 2. DMSP quotas and characteristics per cellular volume for *Prorocentrum minimum* and *Phaeocystis* sp.

Variable	Units	*P. minimum*	*Phaeocystis* sp.
DMSP quota	fmol (S) μm^{-3}	0.03 – 0.15	0.08 – 0.14
DMSP synthesis	fmol (S) μm^{-3} d^{-1}	0.006 – 0.037	0.006 – 0.042
DMSP exudation	fmol (S) μm^{-3} d^{-1}	0.0003 – 0.0015	0.003 – 0.015

Table 3. Percentage of the algal DMSP quota exuded per day determined during laboratory studies or utilized in modeling studies

Phytoplankton	% of DMSP quota exuded (d^{-1})	Source
Gymnodinium nelsoni	0.3	Dacey & Wakeham (1986)
Hymenomonas carterae	1.4	Vairavamurthy et al. (1985)
Prorocentrum minimum	1	Present study
Phaeocystis sp.	3–11	Present study
Modeling studies		
Phytoplankton community	1.85	Gabric et al. (1993)
Phytoplankton community	None	Lawrence (1993)
Phytoplankton community	None	van den Berg et al. (1996b)

nutrient or light limitation, which reduce the phytoplankton population growth rate. Physiological studies are necessary to understand the underlying processes. In these cultures, the decrease in DMSP synthesis rates during the late exponential phase was probably related to nitrogen limitation for *Prorocentrum minimum* (Matrai & Keller 1994) and to phosphorus limitation for *Phaeocystis* sp. (Stefels & van Boekel 1993). It is unlikely that sulfur limitation occurred during the experiments since sulfate was in excess in the culture medium (Matrai & Keller 1994).

Magnitude of DMSP exudation

The results of the model show that DMSP exudation rates vary significantly between species and may be approximately 10 times higher than previously reported (Table 3). The exudation rate for *Prorocentrum minimum* found in this study (1% d^{-1} of the DMSP quota) is comparable to the other exudation rates reported in the literature. However, the exudation rate for *Phaeocystis* sp. ranged from 3 to 11% d^{-1} of the DMSP quota. Dacey & Wakeham (1986) calculated that 0.3% d^{-1} of the DMSP quota of *Gymnodinium nelsoni* was released as DMS in seawater (Table 3). Vairavamurthy et al. (1985) reported that 1.4% of the DMSP quota was exuded daily as DMS in the culture of the prymnesiophyte *Hymenomonas carterae*. The presence of DMS in these cultures suggests that either *G. nelsoni* and *H. carterae* produce

DMSP-lyase or that the cultures were contaminated by bacteria after a few days. The presence of bacteria would have lowered the measurements of the exudation rates, but this possible underestimation cannot be quantified. In our modeling approach, it was assumed that no DMSP or DMS sinks occurred in the cultures. If such sinks occurred, the concentrations of DMSP and DMS measured would be underestimated. Under this circumstances the exudation rates obtained in this study would be underestimated as well.

Current DMS models neglect or underestimate phytoplankton exudation (Table 3). Gabric et al. (1993) modeled a 9 species phytoplankton community including *Phaeocystis* sp. They used a constant DMSP exudation rate of 1% d^{-1} of the DMSP quota. They also attributed a DMS exudation rate of 0.85% d^{-1} of the DMSP quota to all species of the community. Thus every species released both DMSP and DMS, for a total exudation equaling 1.85% of the DMSP quota. Lawrence (1993) and van den Berg et al. (1996b) ignored exudation in their model. DMSP and DMS releases were attributed exclusively to cell autolysis and grazing. These 2 releasing mechanisms may represent, under certain circumstances, the major factors of DMSP release in seawater. However, neglecting algal exudation could frequently lead to large underestimations of DMSP release into seawater.

The physiological reason for phytoplankton release of DMSP is unknown. That phytoplankton release dissolved organic matter has been demonstrated. Based on a literature review, Baines & Pace (1991) obtained an average percent of extracellular release of 13% of total carbon fixation. DMSP may represent more than 10% of the organic carbon present in certain species of phytoplankton (Matrai & Keller 1994). DMSP could belong to the metabolites exuded. In the case of *Phaeocystis*, the exudation of DMSP and its conversion to DMS and acrylic acid, through DMSP-lyase, may allow this species to benefit from the antibiotic properties of acrylic acid (Davidson & Marchant 1987), although the effectiveness of the properties is still under debate. Ledyard et al. (1993) reported that bacteria may grow on the acrylic acid concentrations found in natural environments. However, new evidence reported by Noordkamp et al. (1998) suggests that acrylic acid may reach very high concentrations (a few mM) inside the mucus holding *Phaeocystis* colonies together. This

could have an antibiotic effect in protecting the polysaccharide mucus. In such circumstances the exuded DMS could simply be a by-product.

Robustness of the results: a numerical experiment

The way the model is structured may overemphasize the importance of exudation. It is possible that the simulation of the same experimental data with a different approach, for example simulating the phytoplankton abundance with an approximation of the carbon biomass instead of the cell numbers, could have led to different exudation rates. The structure of the base model we used may have underestimated cell mortality (autolysis) during the exponential and senescent phases. Mortality was not included in the simulations of the exponential phase (Table 1), assuming that culture conditions were optimal for phytoplankton growth during this period. However, mortality may have occurred during this period since cell counts in the culture represented net growth (growth minus mortality). In our base model, the mortality rate during senescence was set to reproduce the decrease in cell numbers measured in both cultures. This rate may have been underestimated since the population may have still been growing, at a reduced rate, during senescence. Since the cultures were axenic, no regeneration of organic matter occurred. However, the phytoplankton may have grown on amino nitrogen (Wheeler et al. 1977) and on organic phosphorus compounds (Nalewajko & Lean 1980) released by algal autolysis. Duplicating cells in the senescent phase could thus theoretically explain the increase of $DMSP_t$ observed during this period (Fig. 2), even in the absence of continued DMSP synthesis.

The model was modified to investigate the impact of higher phytoplankton mortality during the exponential and senescent phases. This investigation was done for both *Prorocentrum minimum* and *Phaeocystis* sp., but only the data from the *Phaeocystis* sp. culture are presented. In the *Phaeocystis* sp. culture, the maximal DMSP release during the exponential phase was $3\% \, d^{-1}$ of the $DMSP_t$. Assuming that this release was entirely from autolysis, the autolysis rate was set at $3\% \, d^{-1}$ and the exudation rate at $0\% \, d^{-1}$ (Table 4). This increase of the autolysis rate required slight modifications of the carrying capacity (K), the initial cell number [CELL(0)], the initial DMSP quota [QUOTA(0)] and the maximal synthesis rate (S_{MAX}) to correctly simulate experimental cell numbers and $DMSP_t$ (Fig. 5A). The mortality rate during the senescent phase was increased from 18 to 22%. A population growth rate equivalent to 15% of the maximal realized growth rate (g_{max}) was required in the senescent phase to compensate for increased mortality. Such simulations of population growth in the senescent phase represent cell duplication in the culture. These cell duplications are assumed to produce the $DMSP_t$ increase observed during the senescent phase of cultures (Fig. 5A). A constant DMSP quota, equal to that on Day 15, was attributed to each newly replicated cell. A null DMSP synthesizing rate was then attributed to cells carried over from the exponential phase, now assumed to be inactive (no growth). This new way to simulate the $DMSP_t$ increase during the senescent phase necessitated a population growth rate as high as 15% of the maximal population growth rate.

The same model modification for *Prorocentrum minimum* necessitated a growth rate, for the senescent phase, equivalent to 70% of g_{max} (not shown). Such a high growth rate is unlikely to occur in *P. minimum* cultures during the senescent phase, but a growth rate equivalent to 15% of g_{max} may be possible in the case of *Phaeocystis* sp. Therefore, we cannot preclude the possibility that a fraction of the $DMSP_t$ increase occurring during the senescent phase (Fig. 2) resulted from continuous cell duplication, balanced by higher mortality. However, it is unlikely that such high growth rates occurred in the senescent phase of axenic cultures with no nutrient regeneration.

The utilization of a higher mortality rate (Table 4) in the model leads to more $DMSP_d$ liberated by autolysis. A lower exudation rate may then reproduce the $DMSP_d$ and DMS concentrations observed in the cultures. Fig. 5B

Table 4. Model parameters used to simulate DMSP and DMS production by *Phaeocystis* sp. in the base model, and in the models with continuous cell duplication (Fig. 5) and applied to the mesocosm data (Fig. 6). Symbols are the same as in Table 1

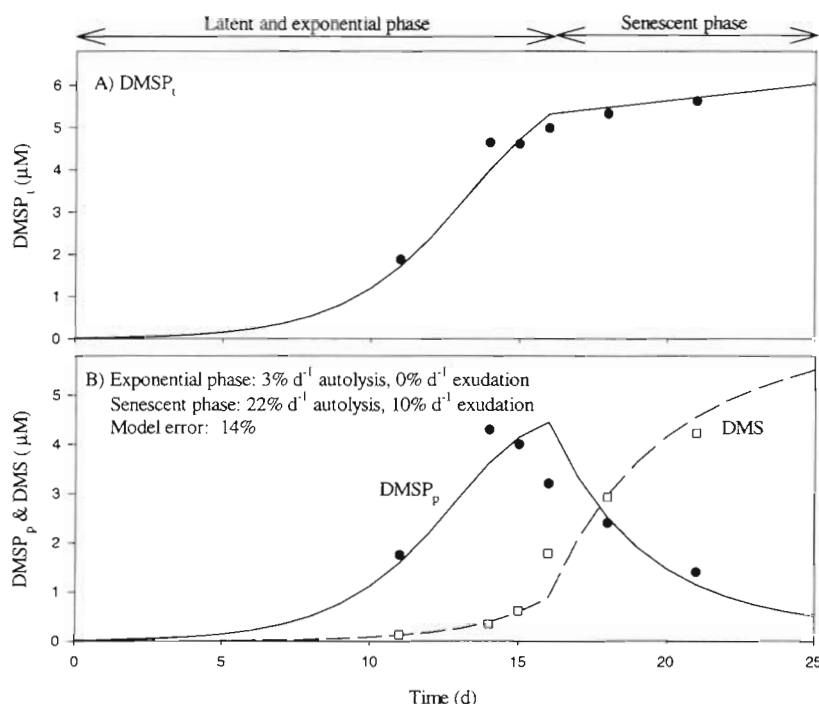| Symbol	Units	Base	Continuous duplication	Mesocosm
K	cells l^{-1}	300×10^6	335×10^6	110×10^6
R	d^{-1}	0.48	0.48	0.46
CELL(0)	cells l^{-1}	1.5×10^6	1.7×10^6	1.6×10^6
m_{expo}	d^{-1}	0	0.03	0
m_{sene}	d^{-1}	0.18	0.22	0.15
g_{max}	cells $l^{-1} \, d^{-1}$	33.4×10^6	39.5×10^6	12.5×10^6
S_{MIN}	µmol $DMSP_p$ cell^{-1} d^{-1}	0.67×10^{-9}	0	0.67×10^{-9}
S_{MAX}	µmol $DMSP_p$ cell^{-1} d^{-1}	4.8×10^{-9}	4.4×10^{-9}	4.8×10^{-9}
A	Dimensionless	1.6	1.6	1.6
QUOTA(0)	µmol $DMSP_p$ cell^{-1}	10.0×10^{-9}	9.0×10^{-9}	10.0×10^{-9}
E_{MIN}	d^{-1}	0.03	0.00	0.03
E_{MAX}	d^{-1}	0.11	0.10	0.11

Fig. 5. Numerical experiment where a higher mortality rate was used to verify the impact on DMSP synthesis and DMSP exudation. (A) Temporal changes in DMSP$_t$, the increase in DMSP$_t$ during senescent phase is exclusively due to newly replicated cells. (B) Temporal changes in DMSP$_p$ and DMS

rable with the values found in the literature (Vairavamurthy et al. 1985, Dacey & Wakeham 1986). Even such an apparently low DMSP exudation rate may be important in nature. The ratio between DMSP$_p$ and DMSP$_d$ in the natural environment may be as high as 20:1 (Kwint & Kramer 1996). Under these circumstances, 1 d of DMSP$_d$ exudation at a rate of 1% d^{-1} would represent 20% of the DMSP$_d$ pool. DMSP$_d$ exudation even by species with low exudation may therefore prove to be a significant source of extracellular DMSP in nature.

Phaeocystis sp. exudation: a major contributor to DMS release in seawater

Results presented in Fig. 4 show that the utilization of an exudation rate of 1% d^{-1} of the DMSP quota, such as presented in the literature, may underestimate the DMSP release (autolysis and exudation) by Phaeocystis sp. by as much as 44% on average. Our modeling strategy simulated the experimental data with a mean error of 13% (Fig. 4D). To achieve this we used (1) a higher DMSP exudation rate for Phaeocystis sp. and (2) a higher exudation rate for the senescent phase than for the exponential phase. Higher DMS production in the senescent phase of blooms than during the initial phase has previously been reported (Nguyen et al. 1988, Matrai & Keller 1993, Stefels & van Boekel 1993, Kwint & Kramer 1995). This has usually been attributed to cell autolysis (Nguyen et al. 1988, Kwint & Kramer 1995). Autolysis certainly plays an important role, but this mechanism was not sufficient in our model results to explain the accumulation of dissolved DMSP and DMS in the cultures. Exudation must also be taken into account.

Applying our model to a Phaeocystis sp. bloom in a mesocosm

Synchronization between maximum DMS concentration and Phaeocystis sp. cell numbers was observed in mesocosm studies (Kwint et al. 1996). Results from our exudation model may reproduce some aspects of this phenomenon. Kwint et al. (1996) observed that the peak of DMS did not correspond to the senescent phase of the Phaeocystis sp. bloom, but

shows the results from the new simulation for Phaeocystis sp. As in the original model, the whole DMSP content of autolysing cells was transferred to the DMS pool. The DMSP exudation rate was optimized to fit the experimental results as described in 'Model results: Particulate and dissolved DMSP pools'. The simulation results (Fig. 5B) show that if maximal cell autolysis during the exponential phase and cell duplication during the senescent phase are taken into account, the inclusion of DMSP exudation is not necessary to reproduce the experimental results for the exponential phase. However, a DMSP exudation rate of 10% d^{-1} must be used to reproduce experimental values for the senescent phase. In a recent laboratory study, Noordkamp et al. (1998) reported that both excretion and cell lysis contribute to the production of acrylate, cleaved from DMSP upon excretion, in stationary phases of axenic cultures of Phaeocystis. These results agree with ours, suggesting that DMSP is liberated both by exudation and by cell lysis.

Importance of exudation by Prorocentrum minimum, a low exudation species

Our estimated DMSP exudation rate for Prorocentrum minimum of 1% d^{-1} of its DMSP quota is compa-

was always synchronized with maximum cell numbers. They observed that zooplankton abundance peaked before the DMS maximum and concluded that grazing had no direct relation to the accumulation of $DMSP_d$ and DMS in the mesocosm. Phytoplankton autolysis is unlikely to have produced the DMS peak, since the latter was synchronized with the maxima of cell numbers. Osinga et al. (1996) worked on the same data set and rejected the possibility that the DMS peak was caused by a mass sedimentation event followed by massive lysis at the bottom of the mesocosm.

The application of our model to this data set shows that DMSP exudation may explain a significant part of the DMS peak observed to be simultaneous with the algal biomass maximum. Our model simulates axenic monospecific cultures, while the mesocosms include the whole pelagic community. However, the blooms in

the mesocosms were largely dominated by *Phaeocystis* sp. (Kwint et al. 1996), allowing us to apply our model to the mesocosm data.

The parameters related to the temporal changes in the algal cell numbers (Table 4; third column) were modified to approximate the rise in cell numbers up to the bloom maximum (Fig. 6A). The simulation was stopped when the maximal cell number was reached. Population growth led to a rise in $DMSP_p$ up to the bloom maximum (Fig. 6B). There were high frequency variations in the $DMSP_p$ concentrations, but we did not expect or intend to simulate perfectly these temporal changes since other phytoplankton species, grazers, and bacteria interacted in the mesocosms. The use of a low and constant DMSP exudation rate (1% d^{-1}, as suggested in the literature) resulted in the simulated DMS concentration represented by the dashed line in Fig. 6C. Subtracting bacterial DMS consumption as measured by Kwint et al. (1996) (23 nM d^{-1} averaged for the *Phaeocystis* sp. bloom period) led to null values (not shown). On Day 14 (DMS maximum), the simulated DMS concentration produced by the 1% d^{-1} exudation rate accounted for 18% of the DMS concentration measured in the mesocosm when no bacterial consumption was considered, and 0% when bacterial consumption of DMS was considered. Applying the model with the variable exudation rates as found in this study for *Phaeocystis* sp. generated the DMS concentrations represented by the solid line in Fig. 6C. On Day 14, the simulated DMS concentrations represented 76% of the DMS measured when no bacterial consumption was considered, and 35% when it was considered.

The data in the shaded area in Fig. 6 may be interpreted as a burst of exudation when the population growth became nitrogen limited. During this last day of population growth the $DMSP_p$ concentration dropped from ~2400 to ~600 nM, while the DMS concentration increased from ~25 to ~425 nM. As for the simulation of the laboratory data on *Phaeocystis* sp. ('Model results: Particulate and dissolved DMSP pools'), the $DMSP_p$ and the DMS concentrations in the mesocosm would be better modeled by the introduction of a burst of exudation synchronized with growth limitation.
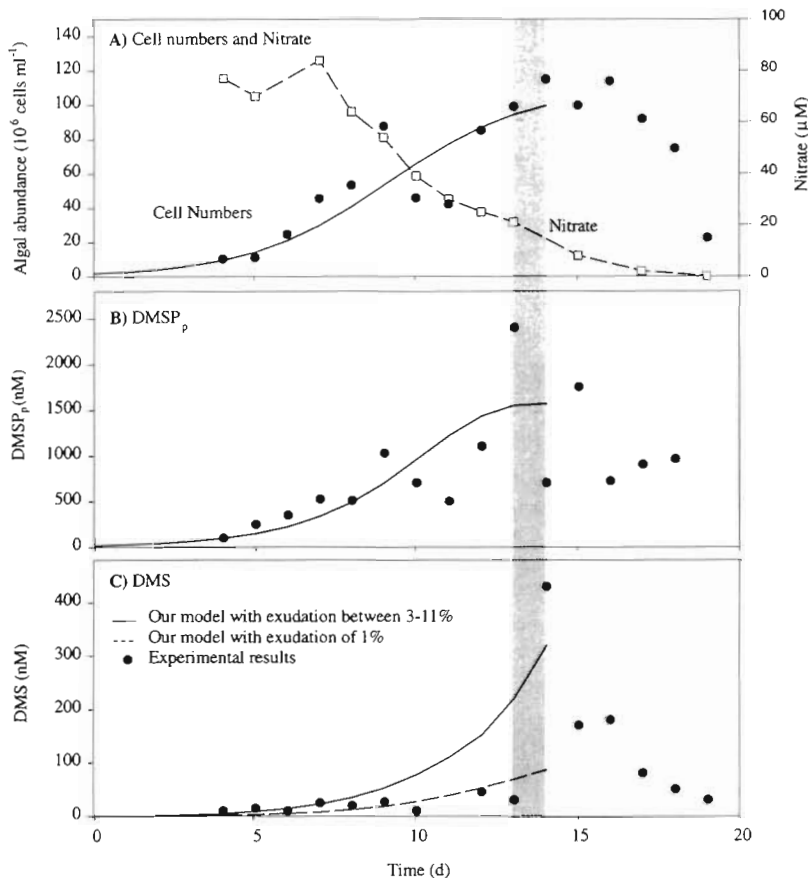

Fig. 6. Model results when applied to a mesocosm experiment (Kwint et al. 1996). Symbols represent experimental results while solid lines represent model results. The dashed line in (A) links measured nitrate concentrations. The dashed line in (C) represents model DMS concentrations. The modeled DMS concentrations would be lower if bacterial consumption had been taken into account (see 'Interpretation of model results: Applying our model to a *Phaeocystis* sp. bloom in a mesocosm'). The shaded area represents a putative massive exudation of $DMSP_d$ (converted to DMS) by the phytoplankton

Importance of considering exudation by *Phaeocystis* sp. in modeling *in situ* conditions

Kwint & Kramer (1996) suggested that high DMS fluxes to the atmosphere seem to occur over short periods of weeks. *Phaeocystis* sp. blooms can potentially result in important DMS releases to the atmosphere. Van den Berg et al. (1996b) showed in a modeling experiment the importance of DMSP-lyase, synthesized by *Phaeocystis* sp., on the overall DMS concentration in seawater and on the DMS flux to the atmosphere over the North Sea. Little attention has been paid to DMSP exudation. However, Wassmann et al. (1990) suggested a sequence of events during *Phaeocystis pouchetii* blooms in the Barents Sea by which nutrient depletion induced heavy exudation in the upper layer of the water column followed by massive sedimentation and autolysis out of the euphotic layer. Under such circumstances, exudation is the main DMSP-releasing mechanism in surface water since autolysis is mostly confined to the deeper layer.

The model developed by van den Berg et al. (1996b) is the most advanced in simulating annual marine DMS dynamics in the natural environment. They pointed out 2 main periods during which the model fails to reproduce the field observations. One of them is an overestimation by the model of the total DMS concentrations in April, and the other is an underestimation in May and June. The phytoplankton bloom simulated by the FYFY model is in exponential growth in April and in senescence in May. We suggest that the utilization of a variable exudation rate, simulating low exudation during the exponential phase and strong exudation during the senescent phase, as we developed in this study, would decrease the discrepancy encountered by van den Berg et al. (1996b) between modeled and measured DMS concentrations.

Conclusion

This paper emphasizes the importance of considering DMSP exudation in DMSP-releasing mechanisms. In this study, only 2 species of phytoplankton were examined with relatively small data sets. There is certainly a need for data on other species and more accurate knowledge of the physiological mechanisms underlying exudation. Our work indicated that *Phaeocystis* sp. deserves special attention in this regard. In the modeling exercise of simulating both data sets on *Phaeocystis* sp., the laboratory and the mesocosm, the utilization of a quick and large release of DMSP at the end of the exponential phase would have led to better simulation of the data. Such a large release could help to explain observations on the synchronization of maximum chlorophyll with DMS concentrations (Kwint & Kramer 1996, Kwint et al. 1996).

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