

University of Groningen

Annual cycle of the production and fate of DMS and DMSP in a marine coastal system

Kwint, RLJ; Kramer, KJM

Published in:
Marine Ecology Progress Series

DOI:
[10.3354/meps134217](https://doi.org/10.3354/meps134217)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1996

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
Kwint, RLJ., & Kramer, KJM. (1996). Annual cycle of the production and fate of DMS and DMSP in a marine coastal system. *Marine Ecology Progress Series*, 134(1-3), 217 - 224.
<https://doi.org/10.3354/meps134217>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Annual cycle of the production and fate of DMS and DMSP in a marine coastal system

Rik L. J. Kwint^{1,2,*}, Kees J. M. Kramer^{2,**}

¹University of Groningen, Department of Microbiology, PO Box 14, 9750 AA Haren, The Netherlands

²TNO Institute of Environmental and Energy Research and Process Innovation, Department for Ecological Risk Studies, PO Box 57, 1780 AB Den Helder, The Netherlands

ABSTRACT: The production of DMSP by phytoplankton and the fate through the marine system of both DMSP and DMS were followed for a period of 21 mo in the natural environment by studying a Wadden Sea tidal inlet. The major production and emission of DMS appeared to be limited to a period of only 2 mo, which was closely linked to the presence of phytoplankton blooms. The production of DMS in the water column was not well correlated with chlorophyll *a* concentrations or plankton species composition. It was however, found to be closely related to the start of a *Phaeocystis* bloom early in spring. Contrary to our expectations, the senescence phase of this *Phaeocystis* bloom did not result in high DMS accumulation. It is postulated that this phenomenon could be the result of a bacterial consumption which increased with time in combination with a decreasing DMSP-lyase activity of *Phaeocystis*. A simple model, into which the overall DMSP consumption could be introduced, could very well imitate the measured concentrations of DMS in the water column of the natural system studied.

KEY WORDS: Dimethylsulphoniopropionate · Dimethylsulphide · Phytoplankton · Consumption · *Phaeocystis* · Annual cycle

INTRODUCTION

The production of dimethylsulphide (DMS) and its release into the air constitutes one of the most important biogenic sources of sulphur to the atmosphere. It is formed from the precursor DMSP (β -dimethylsulphoniopropionate), which has a presumed osmoregulating or cryoprotecting function in marine algae (Dacey et al. 1987, Gröne & Kirst 1992, Baumann et al. 1994).

In the atmosphere, DMS can be oxidized to non sea salt sulphates and methane sulphonic acid which can be responsible for formation of cloud condensation nuclei, or CCN, which influence cloud formation and the backscattering of solar radiation and, thus, may have an influence on climate (Charlson et al. 1987, Caldeira 1989, Legrand et al. 1991, Malin et al. 1992).

There appears to be no direct correlation between chlorophyll *a* (chl *a*) and DMS concentration in oceanic surface waters (Dacey & Wakeham 1986, Turner et al.

1989, Bürgermeister et al. 1990, Leck et al. 1990). This makes it difficult to predict global DMS quantities by means of biomass estimations from remote sensing data. DMSP is associated with some algal species but there is a wide variation in the potential for algae to produce it. Diatoms are generally considered to be unimportant producers of DMSP, while other algal classes, including Dinophyceae and Prymnesiophyceae, are considered to produce relatively large amounts of DMSP and DMS (Keller et al. 1989, Gibson et al. 1990, Matrai & Keller 1993, 1994, Stefels & van Boekel 1993). Factors which control the release of DMS into the water are not clearly understood, but possible mechanisms are: metabolic excretion, algal senescence and zooplankton grazing activity (Dacey & Wakeham 1986, Nguyen et al. 1988, Belviso et al. 1990, 1993, Stefels & van Boekel 1993, Levasseur et al. 1994). Loss factors for DMSP and DMS from the water column are bacterial consumption of DMS and DMSP, ventilation into the atmosphere and photochemical oxidation of DMS. Sedimentation of particulate DMSP (DMSP_p) can also occur (Brimblecombe & Shooter 1986, Kiene 1990, 1992, Kiene & Service 1991, Belviso et al. 1993, Osinga et al. 1996).

*E-mail: lamr@kribc.tno.nl

**Present address: TERNAPARCEL, PO Box 109, 1860 AK Bergen, The Netherlands

Kwint & Kramer (1995) showed, in several experiments carried out in marine pelagic mesocosms, that a maximum release of DMS occurred directly after a phytoplankton bloom, during the senescence phase. In order to extrapolate these results to larger systems such as the North Sea, we monitored phytoplankton blooms over a period of 21 mo (November 1991 to July 1993), thereby taking in 2 phytoplankton spring blooms in the Marsdiep channel, a tidal inlet of the Dutch Wadden Sea. Our main goal was to see whether predictions are possible on a larger (natural) scale for the release of DMS through this extrapolation, taking into account the seasonal cycle of DMS and DMSP. Due to the length of the monitoring period, the results form a unique data set. In addition, mesocosm experiments were carried out with water from the same location (Kwint & Kramer 1995).

MATERIALS AND METHODS

Samples were collected in the Marsdiep tidal inlet from November 1991 to November 1992 (Series I) and from January to June 1993 (Series II) a few hundred metres off the coast of Den Helder, The Netherlands. Sampling was intended to take place at 10:00 h and at high tide in order to rule out any tidal or diurnal effects. This automatically implied a sampling interval of about 2 wk. After it became clear that changes in DMS concentration could occur very rapidly, the frequency was changed. Sampling was attempted at high tide as often as was logistically possible from the start of the phytoplankton spring bloom in 1993 (March to June).

Water samples were collected in a 10 l bucket that was rinsed thoroughly with seawater prior to sampling. Subsamples for chl *a*, phytoplankton, and DMS and DMSP were immediately taken from this large sample.

Chl *a* subsamples were stored in 1 l polyethylene bottles in the dark, until analysis, which took place within 2 h. One litre samples were filtered over glass fibre filters (Whatman GF/C), extracted with 90% acetone and analyzed on a spectrophotometer according to standard procedures (Parsons et al. 1984).

Samples for the phytoplankton species identification were preserved and stored with Lugol's until further examination. Phytoplankton were identified and counted in a 5 ml Kolkwicz chamber under an inverted microscope. For each sample at least 20 fields were counted (magnification 400×).

Subsamples for the determination DMS and DMSP were taken in 1 l, dark, glass stoppered bottles and stored on ice until further treatment. The samples were treated immediately after returning to the laboratory (usually within 2 h). A subsample of 10 to 25 ml was gently filtered over a Whatman GF/C filter. It was considered important that no pressure or suction was applied in order to minimize interference resulting from damaged cells. DMS was purged from the filtered water sample by using high grade helium. The helium, containing the volatile compounds and water vapour, was dried by means of a Nafion permeation drier (Perma Pure Products, Farmingdale, USA) with nitrogen as the drying gas. After drying, the volatile compounds were collected on a cryogenic trap consisting of a straight glass tube containing Tenax-ta (Chrompack, Middelburg, The Netherlands) according to Kwint & Kramer (1995). After collection, the Tenax tube was closed with Swagelock caps and stored in liquid nitrogen until analysis (adapted from Lindqvist 1989). Storage tests with calibration gas showed that samples can be stored thus for at least 8 wk without detectable change.

To determine the concentration of dissolved DMSP (DMSP_d) a 10 ml subsample from the purged filtrate was placed in a 20 ml vial, which, after addition of 1 ml 10 M NaOH (Dacey & Blough 1987), was immediately closed with a Teflon coated septum. The vials were stored at 4°C until analysis. After hydrolysis by the NaOH, the sample was moved from the vial to the purge vessel in a closed system by means of 2 hypodermic needles and the helium flow (see Fig. 1). The complete sample could be analyzed without any loss of DMS to the gas phase by using this procedure.

A 10 ml unfiltered seawater sample was hydrolysed in a similar way in order to assess the total amount of DMSP + DMS. The DMSP_p concentration was calculated by subtracting the DMS and DMSP_d concentration. Thus in principle DMSP_p consists of all intra cellular DMSP, DMSP adsorbed to detritus and that incorporated into zooplankton and zooplankton faecal pellets.

DMS was analyzed according to Lindqvist (1989) on a Varian 3500 gas-chromatograph equipped with 10 m Poraplot-U capillary (0.53/0.7 mm inside/outside diameter) column (Chrompack) and a photo-ionization detector (10.2 eV, HNU Systems Inc., Newton, MA, USA). Hydrogen was used as the carrier gas. The detection limit was 1.5 pMol

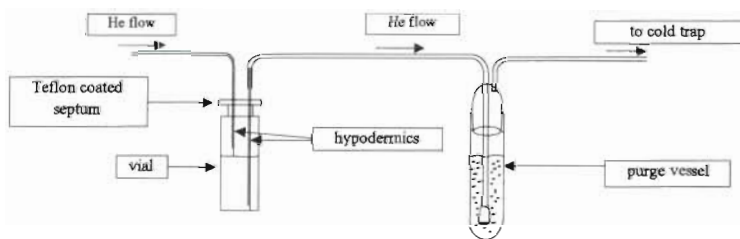


Fig. 1. Diagram of method used to transfer DMSP samples to the normal purge-trap system

DMS. The coefficients of variation (CV) for the DMS analyses for independent analyses were no larger than 5% for samples with a concentration over 100 nM, and 17% for samples with a concentration below this value (Kwint & Kramer 1995).

Fluxes of DMS to the atmosphere were calculated from the water concentrations and from wind speeds (daily averages) obtained from a meteorological station near the sampling site, using the Liss/Slater model (Liss & Slater 1974).

RESULTS AND DISCUSSION

Fig. 2 shows the results for the chl *a* and DMS measurements for both Series I and II. During the winter period, DMS and chl *a* in these coastal waters showed relatively low background values as compared to the spring/summer values (chl *a* about 2.5 $\mu\text{g l}^{-1}$, DMS below 0.5 nM) for both years. Each spring (March), the chl *a* as well as the DMS concentration started to rise and a maximum was reached within 1 mo.

During Series I (1992), maximum chl *a* (20 $\mu\text{g l}^{-1}$) and DMS concentrations (17 nM) coincided. During Series II we found similar values for chl *a* (18 $\mu\text{g l}^{-1}$) and DMS (18 nM) around the same date. The sampling frequency was increased in this period and it was found that a peak in the chl *a* concentration (30 $\mu\text{g l}^{-1}$) preceded the DMS peak by about 5 d. The maximum chl *a* and DMS concentrations in both years (DMS measured in duplicate) appear to be in surprisingly good agreement. Also, the very steep increase in the concentration of DMS was found for both years. Furthermore, these results agree well with the seasonal variations measured by Leck et al. (1990) for spring/summer data in the Baltic Sea and with those measured by Liss et al.

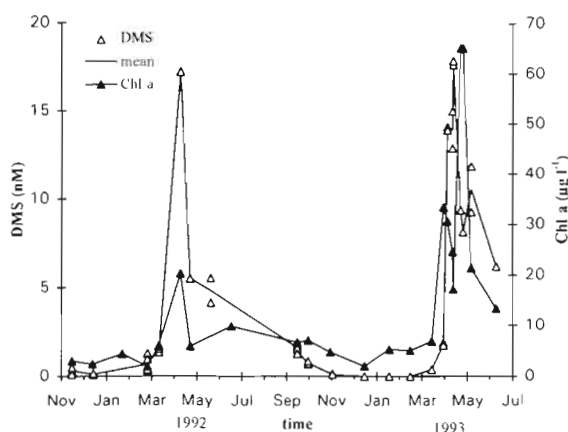


Fig. 2. Seasonal cycle of chlorophyll *a* and DMS in the Marsdiep (The Netherlands) tidal inlet in 1992 (Series I) and 1993 (Series II). Note different scales for DMS and chl *a*

(1994) during a series of cruises in the southern North Sea. Our observations, especially those related to the dynamics of the DMS concentrations, are also in accordance with measurements in enclosure experiments with North Sea plankton (Kwint et al. 1993, Kwint & Kramer 1995, Quist et al. unpubl.). The rapid changes in the DMS concentration mean that the major part of the production of DMS which may escape into the atmosphere is limited to a period of only about 2 mo, i.e. in spring and early summer. The limitation to such a short period of DMS fluxes to the atmosphere has major implications for climate modelling. Obviously the sampling frequency of the first series was not sufficient to cope with the dynamics of the phytoplankton and DMS related processes. For this reason we will focus our attention on the observations made in 1993 (Series II) in this discussion.

Fig. 3 compares the results of the DMS measurements with the calculated flux to the atmosphere during Series II. The flux to the atmosphere appears to follow the same trend as the water concentration. Differences in the ratio between the calculated flux and DMS water concentration can be attributed to differences in wind speed. The wind speeds observed during the measurement period varied but did not change to such an extent that major differences were found. As daily averaged wind speeds were used in these calculations, it would be possible that relatively large deviations would affect the actual daily fluxes. However, the maximum wind speeds encountered in the period of observation never exceeded 6 m s^{-1} . As a result only minor variations in fluxes are to be expected over shorter time scales, since the data are still in the rather horizontal part of the Liss/Slater model (Liss & Slater 1974). Therefore we used an equilibrium model rather than a dynamic model. The latter would have been more appropriate under more variable wind speed conditions.

A comparison between the results obtained by a micro-meteorological measurement (gradient method) and by the Liss/Slater model calculation agreed well, at

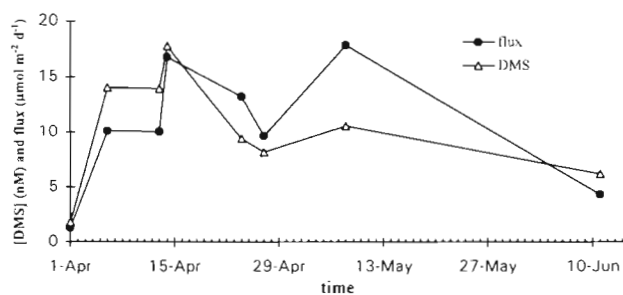


Fig. 3. Comparison of DMS_{winter} concentrations and daily flux $\mu\text{mol m}^{-2} \text{d}^{-1}$ during spring 1993 in the Marsdiep tidal inlet

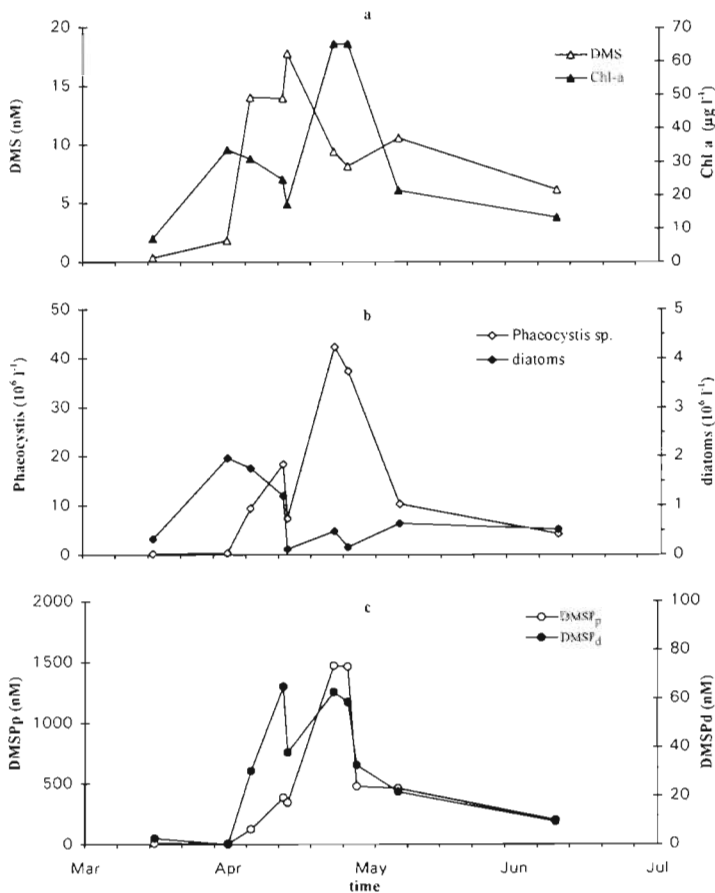


Fig. 4. (a) Development of DMS_{water} concentrations in Series II (1993) along with the development in chl *a* concentrations. (b) Development of diatoms (72% *Skeletonema costatum*, 22% *Nitzschia closterium* and 6% others), along with development in *Phaeocystis* sp. numbers during Series II (note difference in scales). (c) Development of dissolved DMSP concentration (DMSP_d), along with the development in particulate DMSP concentration (DMSP_p) during Series II (note difference in scales for DMSP_p and DMSP_d)

least for the wind speeds observed during these tests (Baart pers. comm.). It is demonstrated in Fig. 3 that the emission of DMS exceeds the background values during a period of only 6 wk. In the period 5 April to 10 May 1994 we observed that the calculated flux of DMS ranged from about 10 to 15 $\mu\text{mol m}^{-2} \text{d}^{-1}$. Assuming that the observations are representative for this period of the year, this implies that phytoplankton activity in these coastal waters during the spring period resulted in a total DMS emission of 0.4 to 0.6 mmol m^{-2} into the atmosphere. The total emission per year was calculated to be about 1.17 $\text{mmol m}^{-2} \text{yr}^{-1}$. According to Andreae & Raemdonck (1983) and Bates et al. (1987) coastal waters in the temperate zone have an emission rate of 1.1 to 1.8 $\text{mmol m}^{-2} \text{yr}^{-1}$. These findings underline the importance of the DMS production during the short spring bloom period.

In order to enhance the resolution of the DMS and chl *a* concentration development in Series II as depicted in Fig. 2, these results are shown in more detail in Fig. 4. Fig. 4a clearly shows that the DMS concentration increases from approximately 2 to 14 nM in only 1 wk. The DMS concentration remained at the same level for another week, with a maximum of approximately 18 nM and then decreased to half this value within 2 wk. The chl *a* development showed 2 successive peaks with an interval of about 2 wk. The highest DMS peak followed the first chl *a* peak only.

The phytoplankton composition during this period is presented in Fig. 4b. After a first diatom bloom (consisting of 72% *Skeletonema costatum*, 22% *Nitzschia closterium* and 6% other diatoms) there was a succession towards *Phaeocystis* sp. (mainly present in colonial form) causing the second peak in chl *a*. It is commonly found in these coastal waters that the initial diatom bloom is succeeded by a *Phaeocystis* development (Gieskes & Kraay 1975, Reid et al. 1990). During our observations the *Phaeocystis* bloom reached a maximum of 42×10^6 cells l^{-1} in about 3 or 4 wk (Fig. 4b), which appears to be a normal value for these waters (Cadée & Hegeman 1991). Along with the development of the *Phaeocystis* cell numbers, a parallel development in DMSP_p could be observed. Diatoms are generally considered not to contain a large amount of DMSP but *Phaeocystis* sp. is known to produce considerable amounts of DMSP (Keller et al. 1989, Liss et al. 1994).

In Fig. 4c the concentrations of DMSP_p and DMSP_d are given. Starting in April, DMSP_d increased from detection limits (0.06 nM) to 65 nM. After an initial drop, the DMSP_d concentration came back to this level, after which it decreased to about 20 nM. DMSP_p rose from 7 to no less than 1500 nM in 4 wk, after which a rapid decrease followed to about 500 nM in a few days. This maximum concentration of DMSP_p is to be considered high for open sea values, but not uncommon in coastal waters with massive plankton (*Phaeocystis*) blooms (Liss et al. 1994, Stefels et al. 1995). The DMSP_p peak coincided with the formation of a peaking of DMSP_d, with a ratio of DMSP_p to DMSP_d of about 20. The DMSP_d production also coincided with the development of the DMS maximum (Fig. 4a). It is known that the early stages of a *Phaeocystis* bloom enhance the transformation of DMSP_d to DMS through the action of a DMSP-lyase (Stefels & van Boekel 1993). It was also demonstrated in that paper that DMS was produced only after the

bloom had peaked (senescence) in (axenic) *Phaeocystis* cultures, which is not consistent with our findings as we did not find a major release of DMS after the *Phaeocystis* bloom.

In order to get some idea about the DMSP_p per unit of biomass, the ratio of $\text{DMSP}_p:\text{chl } a$, along with the $\text{chl } a$ concentration, are shown in Fig. 5a. It is clear that the ratio of $\text{DMSP}_p:\text{chl } a$ changes with the succession of the plankton species, and that this ratio increases steeply with the early development of the *Phaeocystis* bloom. Once the effects of the contribution of the diatoms to the $\text{chl } a$ signal had ceased, a rather constant ratio of $\text{DMSP}_p:\text{chl } a$ of about $20 \text{ nmol } \mu\text{g}^{-1}$ was established. This appears even to be true for the situation where the *Phaeocystis* bloom had passed its maximum. It is well known from the literature that *Phaeocystis* contain a relatively high amount of DMSP (per biovolume) e.g. in comparison to diatoms (Keller et al. 1989, Liss et al. 1993).

This is represented in Fig. 5b. Here the amount of DMSP_p is calculated based on cell densities (Fig. 4b.) and the amounts DMSP_p cell⁻¹ reported in the literature. For diatoms (Keller et al. 1989) and *Phaeocystis* (Quist et al. unpubl.) $17 \text{ fmol cell}^{-1}$ and $34 \text{ fmol cell}^{-1}$ respectively were used (note the difference in scales). It is highly unlikely that the DMSP_p in the diatoms was responsible for the release of DMSP_d observed in Fig. 4c. Otherwise the diatoms should be producing large amounts of DMSP that was immediately excreted without use. The *Phaeocystis* bloom is a resultant of fast growing and decaying cells and it is argued here, that the increase in DMSP_d can be attributed to the activity of *Phaeocystis* alone.

Since the formation of DMS is linked to the existence of DMSP_p , either by direct transformation or via a route involving the formation of DMSP_d , one would expect that a DMSP_p peak would eventually yield a high DMS concentration, potentially much higher than the peak observed after the diatom bloom. Surprisingly, the peak in DMSP_p during the *Phaeocystis* bloom was not followed by a major DMS development.

DMSP_p may be transformed directly to DMS by *Phaeocystis* produced DMSP_p -lyase. Stefels & van Boekel (1993) showed that this process is particularly important in the log-phase of a culture, and not during senescence. This process may have resulted in the relatively small but significant increase in DMS concentration in the initial *Phaeocystis* growth phase. Although some increase could be observed in the formation of DMS after the *Phaeocystis* bloom (Fig. 4a), the amount does not reflect the large amount total DMSP that was potentially available once the *Phaeo-*

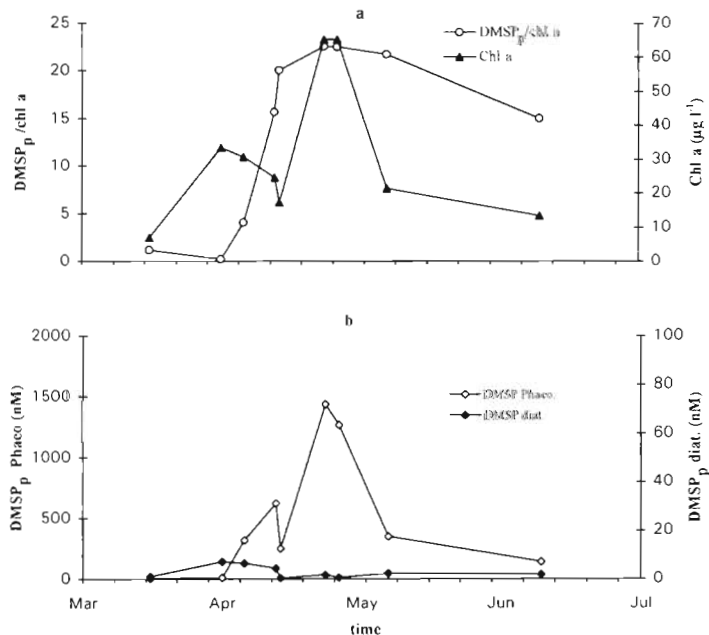


Fig. 5. (a) Comparison of the ratio $\text{DMSP}_p:\text{chl } a$ ($\text{nmol } \mu\text{g}^{-1}$) and the development in $\text{chl } a$ during Series II (note different scales). (b) Development of DMSP_p concentration in *Phaeocystis* sp. and diatom cells (note different scales for *Phaeocystis* sp. and diatoms)

cystis bloom had collapsed in the last week of April. The drop of 1000 nM in DMSP_p concentration (and the drop of 30 nM DMSP_d) in the last week of April was not at all counterbalanced by the 3 nM DMS increase (Fig. 4a) and/or the calculated flux (Fig. 3). A comparison of the DMSP_p loss per m^2 and the calculated sea-air exchange of DMS, assuming an average water depth of 10 m, indicates that the DMS flux consists of only an insignificant fraction in this period: DMSP_p loss = $10 \text{ mmol m}^{-2} \text{ d}^{-1}$, DMS flux = $17 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$.

A link is obviously missing in the step leading from DMSP_p to either DMSP_d or DMS. It is not likely that the sampling frequency applied could have caused a major DMS or DMSP_d peak to be missed considering the width of the DMS peak before the *Phaeocystis* bloom. The missing sink may have been the result of the (bacterial) transformation of DMSP_p directly into sulphur compounds that were not analyzed, export of DMSP_p out of the system, e.g. by sedimentation of the particulate material (phytoplankton, faecal pellets), or by a fast turnover of DMS and DMSP_d .

Physico-chemical processes (photochemical oxidation) are not considered to be very important (Brimblecombe & Shooter 1986). Of course the export of DMSP_p cannot be excluded. However, the Marsdiep tidal inlet, the adjacent coastal waters and the Wadden Sea are turbulent systems, and it is not likely, therefore, that this mechanism can solely account for the export effect observed.

Therefore, either the direct or the indirect bacterial transformations seem to be the most dominant routes of DMS and DMSP conversion. Aerobic routes for DMSP transformation include the direct formation of acrylate and DMS (De Souza & Yoch 1995), the formation of methylmercaptopropionate (MMPA) and the subsequent break down to acrylate and methanethiol, or the DMSP to MPA (mercaptopropionate) route via MMPA (Visscher & Taylor 1994, Quist et al. unpubl.). Furthermore, a rapid utilization of DMS by bacteria could prevent the accumulation of this compound. DMS consuming bacteria (producing sulphate and CO_2 or DMSO) have been isolated (Hansen et al. 1993).

As a result we must assume that the rate of the transformation processes of DMSP_d and DMS to other, not measured, compounds is high. Otherwise we would have detected a large increase in DMS or DMSP_d concentration in the samples upon release by or senescence of the *Phaeocystis*. Due to these fast transformation rates it is difficult to estimate which process and/or route is the most important. Kiene & Service (1991) and Bates et al. (1994) estimate that only a maximum of 30% of the DMSP_d will actually be converted to DMS. Of this DMS pool a major part can be consumed by bacteria (Kiene 1992, Quist et al. unpubl.). The question remains as to why this process of rapid bacterial conversion does not take place during the period when DMS and DMSP accumulate after the diatom bloom. It is postulated here that this may be the result of a change in the bacterial activity and populations.

Bacterial consumption is largely dependent upon the available substrate. For DMS consumers this means that although they will always be present in low densities, the bacterial population will start to increase when sufficient DMS becomes present in the water column (Quist et al. unpubl.). In the initial phase of DMS production, as a result of the diatom senescence, the bacterial population is not yet well

developed. Therefore, a relatively large proportion of the particulate and dissolved DMSP will lead to the formation of DMS (supported by a high DMSP-lyase activity from the initial *Phaeocystis* bloom). The presence of algal exudates enables a bacterial population to develop rapidly. A well developed bacterial population will be more effective in the facultative transformation of DMS and DMSP_d . This may result in a situation which was reflected by our field observations: a DMS peak following a diatom bloom (or following the increase of *Phaeocystis* numbers) and the absence of such high DMS concentrations after the *Phaeocystis* bloom. The existence of such a process was confirmed in a mesocosm experiment where the actual bacterial DMS and DMSP consumption rates were measured, and where numbers of DMS-utilizing bacteria were measured (Quist et al. unpubl.). In order to elucidate the possible role of bacteria in the conversion of DMS(P), a simple model was constructed. Based on a description of the fraction DMSP_p lost from the water column, a curve is fitted assuming a logistic growth curve. This curve is used to simulate bacterial activity during the period of the plankton bloom in the model situation.

The proportion of DMSP_p that is converted (by bacteria) to other sulphur compounds than DMS can be defined as $([\text{DMSP}_p] - [\text{DMS}])/[\text{DMSP}_p]$. This represents a net result as DMS may be well produced but turned over rapidly itself. In Fig. 6 the field data calculated for the Marsdiep channel in April and May are presented. The data points show that not only the overall DMSP_p -loss increases, but also the proportion of DMSP_p lost from the watercolumn until almost 100% of the DMSP_p is consumed at the end of the bloom without DMS accumulation. Assuming a bacterial process, the curve fitted through the field data points in Fig. 6 represents a logistic growth curve not uncommon in microbiology studies, with the equation: $N(t) = K/K^{1 - (t/K)^a}$ (Schlegel & Schmidt 1985), with N representing bacterial numbers, K representing the carrying capacity of the system, a the growth constant and t the time. The simulated growth curve should be considered as a mathematical representation of total loss factors (of which bacterial activity is the major component).

To illustrate our hypothesis that the proportional increase of DMSP consumption is related to bacterial growth more clearly, we apply the logistic increase of DMSP consumption on a curve fitted through the measured DMSP data points in Fig. 7 (solid line, compare with Fig. 4c). When the fraction (percentage) of DMSP_p that is transformed, as identified by the logistic growth curve (dashed line), is subtracted from this DMSP_p curve, a new curve appears that represents that

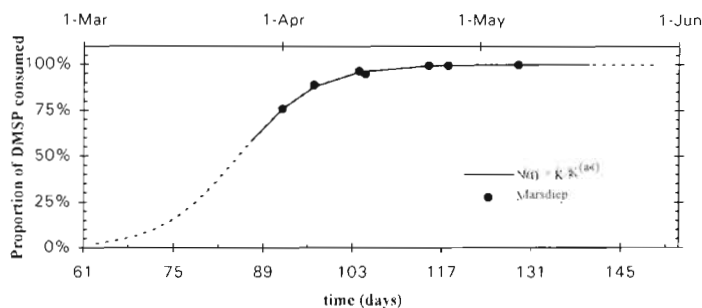


Fig. 6. Proportion of DMSP_p that is lost from the water column without accumulation of DMS (●) in the Marsdiep channel in Series II. A logistic growth curve (for bacteria) is fitted to the collected data (—)

part of the DMSP_p that accumulates as DMS (broken line). When the actually measured concentrations of DMS from the field are added, a good agreement can be observed.

Although our model represents a rather simple and speculative approach, we think that it clearly illustrates the potential effects of varying bacterial activities, resulting in an outcome that reflects our findings in the natural system. It suggests a mechanism where a high density of *Phaeocystis* does not automatically lead to a large production of DMS. Due to the nature of these complex interactions, small shifts in e.g. delayed bacterial activity may easily result in a situation where a massive DMS production follows a *Phaeocystis* bloom, as has been observed before (Liss et al. 1994).

CONCLUSIONS

The idea is emerging that only during special circumstances does the DMS concentration rise above normal background concentrations. Our results indicate that a considerable part (30 to 50%) of the annual emission of DMS over the sea/air interface takes place in the time span of about 6 wk, closely related to the phytoplankton bloom. The DMS concentration is not controlled by the DMS(P) producers alone but by the balance between production and consumption of DMSP and DMS. Small shifts in bacterial activity or populations can lead to either an increase or decrease in the amount of DMS emitted to the atmosphere.

Although our quantitative results were collected in coastal waters, with a dominant role of *Phaeocystis* sp., we feel that the mechanisms involved have a universal application. That the major flux of DMS to the atmosphere may be limited to only a short period could have consequences for climate modelling. Furthermore, the fact that bacterial consumption of DMS and DMSP may play the major role in determining the amount of DMS available for ventilation to the atmosphere makes it difficult to predict whether a climate feedback mechanism (Charlson et al. 1987) exists via DMS formation in the oceans.

Acknowledgements. The authors thank Gerrit Hoornsman, Marijke van der Meer and Henk Verhagen for their technical assistance; and Piet Roele for teaching us to handle the research vessel 'Nauplius II'. This project could not have been carried out without the hospitality of the Department of Analytical Chemistry TNO. Without the expertise of the late Finn 'Bill' Lindqvist in the analysis of DMS and related compounds, none of this would have been possible to achieve. The project was supported by the Dutch government (Ministry of VROM) under contract no. NOLK/026/90.

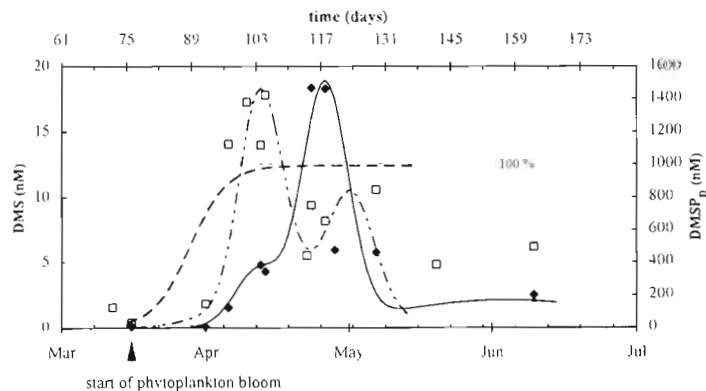


Fig. 7. Graphical representation of bacterial 'loss-factors' for DMS and DMSP. Observed $\text{DMS}_{\text{water}}$ concentrations (\square), DMSP_p concentrations (\blacklozenge), DMSP fitted curve (—), bacterial 'loss factor' (---) and result from subtracting the loss of DMSP_p from the DMSP fit (- - - -) (note different scales for DMS and DMSP_p)

LITERATURE CITED

- Andreae MO, Reamdonck H (1983) Dimethylsulfide in the surface ocean and the marine atmosphere: a global view. *Science* 221:744-747
- Bates TS, Cline JD, Gammon RH, Kelly-Hansen SR (1987) Regional and seasonal variations in the flux of oceanic dimethylsulfide to the atmosphere. *J Geophys Res* 92(C3): 2930-2938
- Bates TS, Kiene RP, Wolfe GV, Matrai PA, Chavez FP, Buck KR, Blomquist BW, Cuהל RL (1994) The cycling of sulfur in surface seawater of the Northeast Pacific. *J Geophys Res* 99(C4):7835-7843
- Baumann MEM, Brandini FP, Staubes R (1994) The influence of light and temperature on carbon-specific DMS release by cultures of *Phaeocystis antarctica* and three antarctic diatoms. *Mar Chem* 45:129-136
- Belviso B, Buat-Menard P, Putaud JP, Nguyen BC, Claustre H, Neveux J (1993) Size distribution of dimethylsulfoniopropionate (DMSP) in areas of the tropical northeastern Atlantic Ocean and the Mediterranean Sea. *Mar Chem* 44: 55-71
- Belviso S, Kim SK, Rassoulzadegan F, Krajka B, Nguyen BC, Mihalopoulos N, Buat-Menard P (1990) Production of dimethylsulfonium propionate (DMSP) and dimethylsulfide (DMS) by a microbial food web. *Limnol Oceanogr* 35(8):1810-1821
- Brimblecombe P, Shooter D (1986) Photo-oxidation of dimethylsulphide in aqueous solution. *Mar Chem* 19(4): 343-354
- Bürgermeister S, Zimmermann RL, Georgii HW, Bingemer HG, Kirst GO, Jansen M, Ernst W (1990) On the biogenic origin of dimethylsulfide: relation between chlorophyll, ATP, organismic DMSP, phytoplankton species, and DMS distribution in Atlantic surface water and atmosphere. *J Geophys Res* 95(D12):20607-20615
- Cadée GC, Hegeman J (1991) Historical phytoplankton data of the Marsdiep. *Hydrobiol Bull* 24(2):111-118
- Caldeira K (1989) Evolutionary pressures on planktonic production of atmospheric sulphur. *Nature* 337:732-734
- Charlson RJ, Lovelock JE, Andreae MO, Warren SG (1987) Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* 326:655-661
- Dacey JWH, Blough NV (1987) Hydroxide decomposition of

- dimethylsulfoniopropionate to form dimethylsulfide. *Geophys Res Lett* 14(12):1246–1249
- Dacey JWH, King GM, Wakeham SG (1987) Factors controlling emission of dimethylsulphide from salt marshes. *Nature* 330:643–645
- Dacey JWH, Wakeham SG (1986) Oceanic dimethylsulfide: production during zooplankton grazing on phytoplankton. *Science* 233:1314–1316
- De Souza MP, Yoch DC (1995) Purification and characterization of dimethylsulfoniopropionate lyase from an *Alcaligenes*-like dimethyl sulfide-producing marine isolate. *Appl Environ Microbiol* 61(1):21–26
- Gibson JAE, Garrick RC, Burton HR, McTaggart AR (1990) Dimethylsulfide and the alga *Phaeocystis-pouchetii* in Antarctic coastal waters. *Mar Biol* 104:339–346
- Gieskes WWC, Kraay GW (1975) The plankton spring bloom in Dutch coastal waters of the North Sea. *Neth J Sea Res* 9: 166–196
- Gröne T, Kirst GO (1992) The effect of nitrogen deficiency, methionine and inhibitors of methionine metabolism on the DMSP contents of *Tetraselmis subcordiformis* (Stein). *Mar Biol* 112:497–503
- Hansen TA, Quist P, Van Der Maarel MJEC, Dijkhuizen L (1993) Isolation of marine dimethylsulfide-oxidizing bacteria. In: Restelli G, Angeletti G (eds) *Dimethylsulphide: oceans, atmosphere and climate*. Int Symp Proc Belgirate. Kluwer Acad. Publ, Dordrecht, p 37–42
- Keller MD, Bellows WK, Guillard RRL (1989) Dimethyl sulfide production in marine phytoplankton. In: Saltzman ES, Cooper WJ (eds) *Biogenic sulfur in the environment*. ACS Symposium series 393. American Chemical Society, Washington, DC, p 167–182
- Kiene RP (1990) Dimethyl sulfide production from dimethylsulfoniopropionate in coastal seawater samples and bacterial cultures. *Appl Environ Microbiol* 56(11): 3292–3297
- Kiene RP (1992) Dynamics of dimethyl sulfide and dimethylsulfoniopropionate in oceanic water samples. *Mar Chem* 37:29–52
- Kiene RP, Service SK (1991) Decomposition of dissolved DMSP and DMS in estuarine waters: dependence on temperature and substrate concentration. *Mar Ecol Prog Ser* 76:1–11
- Kwint RLJ, Kramer KJM (1995) DMS production by plankton communities. *Mar Ecol Prog Ser* 121:227–237
- Kwint RLJ, Kramer KJM, Baart AC, Verhagen HLM (1993) The production of dimethylsulfide by a plankton community: a mesocosm experiment. In: Restelli G, Angeletti G (eds) *Dimethylsulphide: oceans, atmosphere and climate*. Int Symp Proc Belgirate. Kluwer Acad Publ, Dordrecht, p 53–62
- Leck C, Larsson U, Bågander LE, Johansson S, Hajdu S (1990) Dimethyl sulfide in the Baltic Sea: annual variability in relation to biological activity. *J Geophys Res* 95(C3): 3353–3363
- Legrand M, Feniet-Saigne C, Saltzman ES, Germain C, Barkov NI, Petrov VN (1991) Ice-core record of oceanic emissions of dimethylsulphide during the last climate cycle. *Nature* 350:144–146
- Levasseur M, Keller MD, Bonneau E, D'Amours D, Bellows WK (1994) Oceanographic basis of a DMS-related Atlantic cod (*Gadus morhua*) fishery problem: blackberry feed. *Can J Fish Aquat Sci* 51:881–889
- Lindqvist F (1989) Sulfur-specific detection in air by photoionization in a multiple detector gas chromatographic system. *J High Res Chrom* 12:628–631
- Liss PS, Malin G, Turner SM (1993) Production of DMS by marine phytoplankton. In: Restelli G, Angeletti G (eds) *Dimethylsulphide: oceans, atmosphere and climate*. Int Symp Proc Belgirate. Kluwer Acad Publ, Dordrecht, p 1–14
- Liss PS, Malin G, Turner SM, Holligan PM (1994) Dimethyl sulphide and *Phaeocystis*: a review. *J Mar Syst* 5:41–53
- Liss PS, Slater PG (1974) Flux of gases across the air-sea interface. *Nature* 247:181–184
- Malin G, Turner SM, Liss PS (1992) Sulfur: the plankton/climate connection. *J Phycol* 28:590–597
- Matrai PA, Keller MD (1993) Dimethylsulfide in a large scale coccolithophore bloom in the Gulf of Maine. *Cont Shelf Res* 13(8/9):831–843
- Matrai PA, Keller MD (1994) Total organic sulfur and dimethylsulfoniopropionate in marine phytoplankton: intracellular variations. *Mar Biol* 119:61–68
- Nguyen BC, Belviso S, Mihalopoulos N, Gostan J, Nival P (1988) Dimethyl sulfide production during natural phytoplanktonic blooms. *Mar Chem* 24(2):133–142
- Osinga R, Kwint RLJ, Lewis WE, Kraay GW, Lont JD, Lindeboom HJ, van Duyl FC (1996) Production and fate of dimethylsulfide and dimethylsulfoniopropionate in pelagic mesocosms. The role of sedimentation. *Mar Ecol Prog Ser* 131:275–286
- Parsons RT, Maita Y, Lalli CM (1984) *Determination of nutrients, chlorophylls and total carotenoids: spectrophotometric method. A manual of chemical and biological methods for seawater analysis*. Pergamon Press, Oxford, p 3–25, 101–111
- Reid PC, Lancelot C, Gieskes WWC, Hagmeier E, Weichart G (1990) Phytoplankton of the North Sea and its dynamics: a review. *Neth J Sea Res* 26(2/4):295–331
- Schlegel HG, Schmidt K (1985) *General microbiology*. Univ Press, Cambridge, p 190–197
- Stefels J, Dijkhuizen L, Gieskes WWC (1995) DMSP-lyase activity in a spring phytoplankton bloom off the Dutch coast, related to *Phaeocystis* sp. abundance. *Mar Ecol Prog Ser* 123:235–243
- Stefels J, Van Boekel WHM (1993) Production of DMS from dissolved DMSP in axenic cultures of the marine phytoplankton species *Phaeocystis* sp. *Mar Ecol Prog Ser* 97: 11–18
- Turner SM, Malin G, Liss PS (1989) Dimethyl sulfide and (dimethylsulfonio)propionate in European coastal and shelf waters. In: Saltzman ES, Cooper WJ (eds) *Biogenic sulfur in the environment*. ACS symposium series 393. American Chemical Society, Washington, DC, p 183–201
- Visscher PT, Taylor BF (1994) Demethylation of dimethylsulfoniopropionate to 3-mercaptopropionate by an aerobic marine bacterium. *Appl Environ Microbiol* 60(12): 4617–4619

This article was submitted to the editor

Manuscript first received: April 4, 1995

Revised version accepted: November 27, 1995