

Controls of dimethyl sulphide in the Bay of Bengal during BOBMEX-Pilot cruise 1998

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The air-sea exchange is one of the main mechanisms maintaining the abundances of trace gases in the atmosphere. Some of these, such as carbon dioxide and dimethyl sulphide (DMS), will have a bearing on the atmospheric heat budget. While the former facilitates the trapping of radiation (greenhouse effect) the latter works in the opposite direction through reflectance of radiation back into space by sulphate aerosols that form from oxidation of DMS in atmosphere. Here we report on the first measurements made on DMS in the Bay of Bengal and the factors regulating its abundance in seawater. Phytoplankton alone does not seem to control the extent of DMS concentrations. We find that changes in salinity could effectively regulate the extent of DMSP production by marine phytoplankton. In addition, we provide the first ever evidence to the occurrence of DMS precursor, DMSP, in marine aerosols collected in the boundary layer. This suggests that the marine aerosol transport of DMSP will supplement DMS gaseous evasion in maintaining the atmospheric non-sea salt sulphur budget.

1. Introduction

The oceans emit 20% of sulphur to the marine boundary layer in the form of DMS (Rodhe 1999), which is a non-sea salt sulphate compound. Marine phytoplankton produces DMSP for the maintenance of osmotic pressure between the cell fluid and the surrounding seawater (Liss *et al* 1993). Once released into seawater, through cell lysis or zooplankton grazing, DMSP is decomposed to DMS and acrylic acid. The DMS thus produced, being less soluble, escapes to the atmosphere where it is susceptible to photochemical degradation. The importance of DMS and its climatological implications invited the attention of those studying the boundary layer. The Indian Ocean is the least studied in this respect (Kettle *et al* 1999). The surface mixed layer in the bay of Bengal is maintained through the combined effects of wind forcing and fresh water run-off (Shetye and Gouveia 1998). The rivers from the Indian subcontinent drain about 1.6×10^3 km³ of water into the bay annually. The strong vertical stratification, resulting from the low salinity lens

at the surface, reduces effective upward transport of nutrients across the pycnocline (Rao *et al* 1994). Consequently, the column primary production is less in the Bay of Bengal than in the Arabian Sea (Qasim 1977). In addition, the bay is well known to be a highly turbulent region, particularly during monsoons. Therefore, it is important to understand the dynamics of gases of climatic importance in this region and their air-sea fluxes. For instance, atmospheric carbon dioxide is stated to find a sink in the Bay of Bengal (Kumar *et al* 1996) while the Arabian Sea is a perennial source (Sarma *et al* 1998). In the present attempt we try to understand the factors regulating DMS production in the bay.

2. Material and methods

2.1 Measurements of water column parameters

Data were collected during the Bay of Bengal Monsoon Experiment (BOBMEX) Pilot Cruise,

Keywords. Dimethyl sulphide; air-sea exchange; BOBMEX; Bay of Bengal; aerosols.

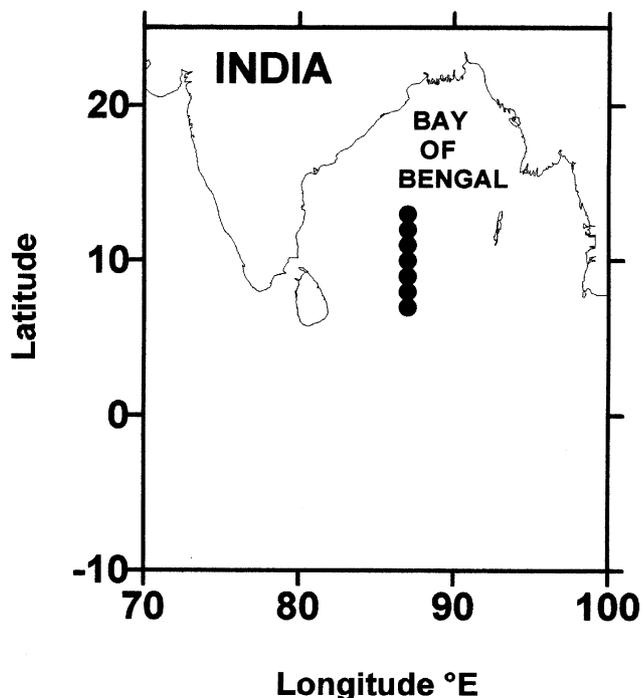


Figure 1. Locations of stations occupied during the BOB-MEX-Pilot cruise in the Bay of Bengal.

October – November 1998, on board ORV Sagar Kanya. Station locations are shown in figure 1. A Sea-Bird CTD system was used along with a rosette to collect water samples from the upper 250 m of the water column. Temperature, salinity and chlorophyll data were obtained through the use of respective sensors. Water samples were analyzed for oxygen, nitrate, chlorophyll, DMS and DMSP. Oxygen and

nitrate were analyzed by photometry. A SKALAR Autoanalyser was used in nitrate analysis. Chlorophyll samples, collected at selected stations, were processed on board and analyzed in the shore-based laboratory. These chlorophyll results were used to calibrate those obtained from the fluorescence sensor attached to the CTD system. DMS analysis was done through purging and cryogenic trapping technique (Turner *et al* 1990). Immediately upon sampling DMS samples were preserved at 4°C in dark glass bottles. Samples were analyzed within 24 hrs after sampling. The eluted DMS, under warm (~ 80°C) conditions, was detected on a HP Gas Chromatograph equipped with Chromosil 330 separator column and Flame Photometric Detector. The precision of DMS analysis was found to be 8–10%. Samples for DMSP were immediately subjected to alkali hydrolysis (Turner *et al* 1990) during which it decomposed to DMS. Since the samples were not filtered our DMSP values represent total (dissolved + particulate) concentrations in water. Subsequently, DMSP was quantified in terms of DMS. Sea-to-air fluxes of DMS were calculated based on the formulations given by Turner *et al* (1996). Wind speeds were measured on board. For the purpose of sea-to-air flux calculations, DMS in the atmosphere was assumed to be zero since its concentration in air is about three orders of magnitude lower than that in seawater (Turner *et al* 1996; Andreae and Crutzen 1997).

2.2 Aerosol measurements

Aerosol samples were collected at variable heights above the sea level on board the ship. Polycarbonate

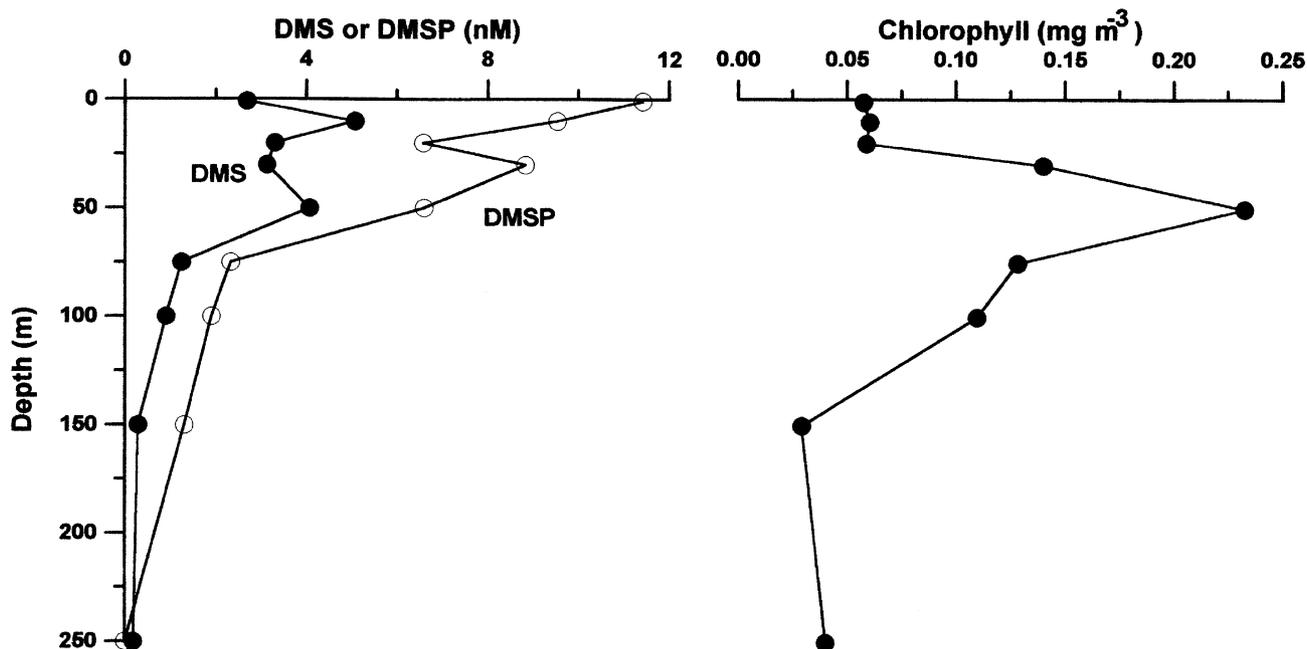


Figure 2. Vertical profiles of DMS, DMSP and chlorophyll at 7°N in the Bay of Bengal.

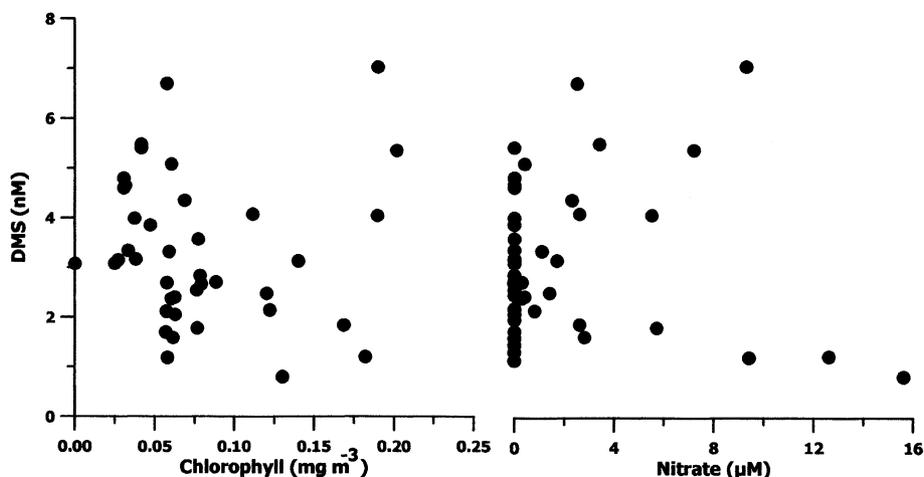


Figure 3. Relationships for DMS with chlorophyll and nitrate in the upper 30 m of the study region.

membrane filter papers of $0.4\ \mu\text{m}$ pore size and 47 mm diameter were used to collect aerosols under vacuum. A Millipore pump with constant vacuum was used and the volume of air filtered was calculated. Immediately upon sampling the filter paper was transferred to the purging unit where it was first subjected to DMS analysis. Upon completion of DMS analysis, alkali was added to the filter paper and purging continued during which DMSP, on the filter, was quantitatively converted to DMS. Thus produced DMS was analysed as detailed above.

3. Results and discussion

3.1 Controls of DMS in water column

The concentrations of DMS and DMSP were higher in the upper 50 m and decreased to near zero levels at 250 m (figure 2). DMS and DMSP vertical profiles resembled mirror images in surface layers (upper 50 m) but are not necessarily so always. This is because of the fact that DMSP can be decomposed by phytoplankton and bacterial lyases in addition to photolysis (Andreae and Crutzen 1997). Moreover, DMS not only undergoes photolytic and bacterial decomposition but can also escape to atmosphere. The relations between vertical profiles of these reduced sulphur compounds and chlorophyll were not complementary (figure 2). For instance, although the chlorophyll was lower at the surface both DMS and DMSP were higher. When chlorophyll reached maximum the abundance of DMSP began to decrease. Figure 3 depicts relationships for DMS with chlorophyll and nitrate. In concurrence with the vertical trends there was no specific quantitative relation between DMS and chlorophyll. Similarly, nitrate also did not exhibit any clear relation with DMS. The extent of production of DMSP is proposed to decrease under nitrogen available conditions (Liss *et al* 1993). However, recent

laboratory experiments revealed non-dependence of DMSP levels on nitrate availability (Keller *et al* 1999). Relation between nitrate and DMSP in the Bay of Bengal was poor. Our present observations (figure 3) concur well with the laboratory results of Keller *et al* (1999).

As chlorophyll and nutrients did not exhibit any control on DMS we attempted to find if physico-chemical properties have any role to play. For this purpose we used salinity since this property shows large horizontal gradients in the surface layer of the Bay of Bengal than temperature. Salinity was positively related to chlorophyll but negatively to DMSP (figure 4). These contrasting relations could be explained by vertical variations in these parameters. While salinity and chlorophyll usually increase from surface to the base of the mixed layer the DMSP maximum occurs closer to the surface in the Bay of Bengal.

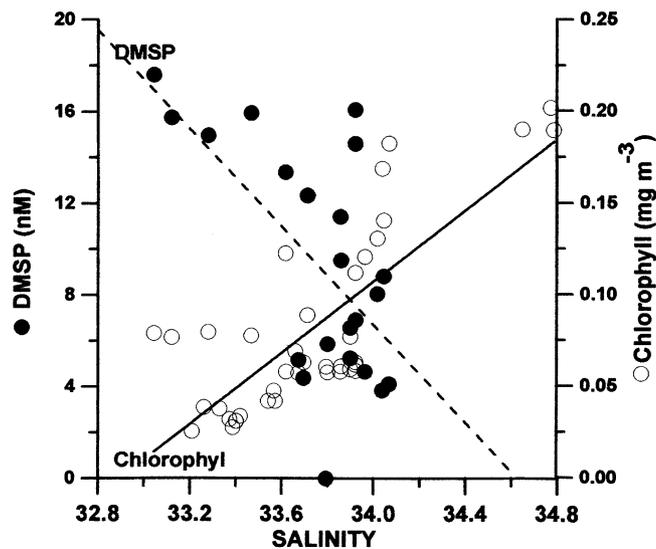


Figure 4. Relationships for salinity with DMSP and chlorophyll in the upper 30 m of the study region. Solid line is the least square regression for chlorophyll and the dashed one for DMSP.

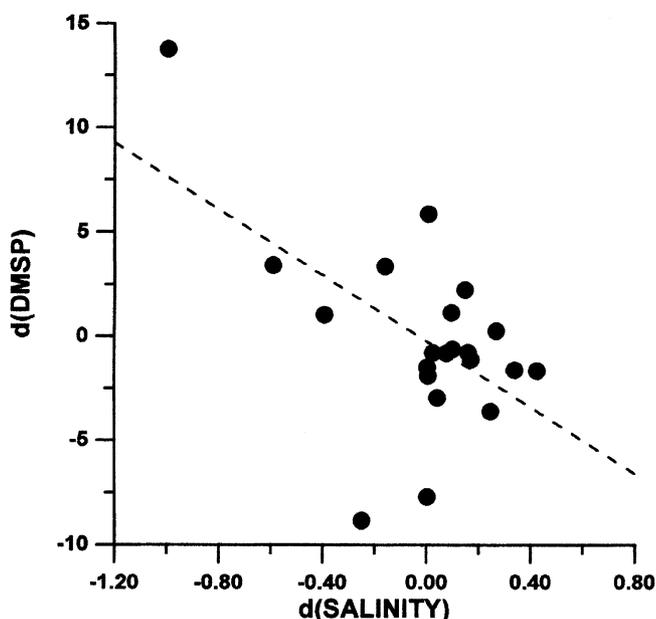


Figure 5. Relation between differences, horizontally or vertically between two depths or locations, in salinity and DMSP.

3.2 Hypothesis

Here, besides the above, we offer an alternative explanation. In spite of the low chlorophyll at lower salinities the higher abundance of DMSP could imply that this osmolyte production is favoured by higher osmotic pressure imbalance between phytoplankton cell fluid and the surrounding seawater medium. This may be justified from the fact that the phytoplankton acclimatized to a salinity of 35 will undergo physiological changes when salinity drops thus producing more osmolyte, DMSP. If this alternative explanation is valid we should find an inverse relation between differences in salinity and DMSP. Figure 5 reveals a negative linear relation between the two proving the fact that a drop in salinity indeed leads to higher production of DMSP. The salinity, therefore, appears to have a control on the production of DMSP, which in turn controls the DMS abundance in the bay.

3.3 Sea-to-air transport of DMS and DMSP

Sea-to-air exchange of DMS will depend on the intensity of wind and DMS concentration in surface seawater. In the present study surface DMS concentrations ranged between 1.4 and 4.65 nM with an average of 2.82 nM. The evaluated DMS fluxes varied from 0.16 to 10.93 $\mu\text{mol S m}^{-2} \text{d}^{-1}$. The highest DMS flux occurred at 8°N (figure 6) where the wind speed was the strongest (8.6 m s^{-1}). The average gaseous efflux during the study period is found to be 1.6 $\mu\text{mol S m}^{-2} \text{d}^{-1}$. Table 1 presents the results of DMS and DMSP in marine aerosols. The results clearly indicate DMSP and DMS occurrence in aerosols. Their concen-

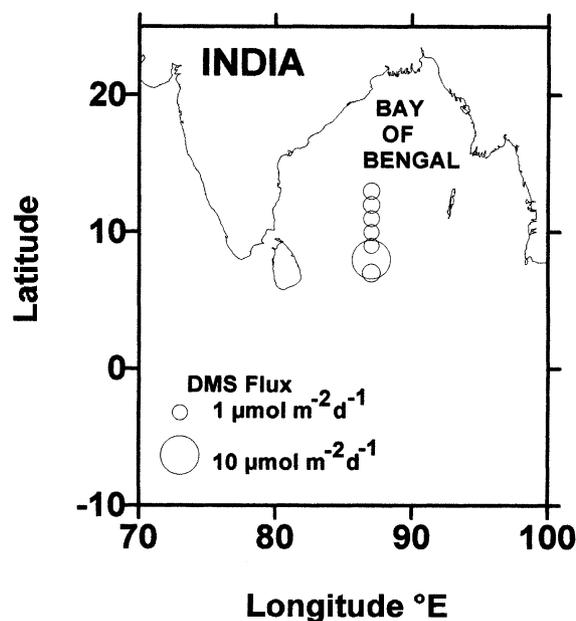


Figure 6. Latitudinal variations in sea-to-air fluxes of DMS in the Bay of Bengal.

Table 1. Concentrations of DMSP and DMS in marine aerosols.

S. No.	Height above sea level (m)	Aerosol DMS pmol m^{-3}	Aerosol DMSP pmol m^{-3}
1	1–2 ^a	0	0.795
2	2.6 ^b	0.504	0
3	6.85 ^b	0.796	1.066
4	2.6 ^c	0	0
5	6.85 ^c	0	0
6	2.6 ^d	0	4.042
7	2.6 ^e	0	0.455
8	4.7 ^e	1.441	0
9	6.85 ^e	0	0
10	1–2 ^f	0	0
11	6.85 ^g	0	0.418
12	6.85 ^h	0.597	0.836

Superscripts in col. 2 indicate the heights of sampling at a given location.

tration levels are comparable to DMS concentrations in marine air. Non-detectable levels in table 1 imply that the ejected DMSP and DMS might have been lost from aerosols to air or at least converted to a different and undetectable form. Given the fact that these compounds are susceptible to bacterial decomposition and photolytic oxidation these will be short lived in the atmosphere. The effect of wind speed on DMSP in aerosols cannot be assessed at present. This mechanism, however, could be very important for non-sea salt sulphate budget in the atmosphere. This transport mechanism could be all the more important in the North Indian Ocean since this region experiences strong winds during southwest monsoon and climatic disturbances.

4. Conclusions

Results obtained in this study suggest that the changes in salinity play a major role in the production of DMSP by phytoplankton, which in turn controls the abundance of DMS in seawater. In addition to the diffusive DMS evasion, DMSP (along with DMS) is shown to be ejected to the atmosphere through aerosols thereby forming a new transport pathway.

Acknowledgements

We thank the Director, NIO, for the facilities and the Departments of Ocean Development, and Science and Technology, New Delhi, for financial support. The first and third authors acknowledge the CSIR support through fellowships. This is NIO contribution number 3553.

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