Chapter 4

Variability in Dimethyl Sulphide Species

As the DMS and its compounds are biogenic in origin their concentrations in seawater would be highly variable depending on day-night and physico-chemical conditions, biological domains and atmospheric forcings. The present chapter discusses variations in the distributions of DMS and DMSP in the Indian Ocean. Changes in concentrations can be treated in various ways. In this attempt variability is treated in terms of vertical, spatial and temporal changes in properties.

4.1 Vertical distributions

Both DMS and DMSP showed very clear trends in their vertical distributions. For instance, concentrations of DMS were very low in waters deeper than 200 m in the Indian Ocean (Fig. 4.1), which is also the case with DMSP. Therefore, DMS sampling was restricted to the top 200 m of water column for detailed study. Vertical distributions of DMS and DMSP in the coastal and open ocean waters of the Arabian Sea (AS) and in the Central Indian Ocean (CIO) are shown in Fig. 4.1. In the coastal waters of the Arabian Sea (76°E, 10.19°N) maximal concentrations of DMS and DMSP were found at shallow depths. In the present study the highest values of 525 nM of DMS and 916 nM of DMSP were found, respectively, at a station off Candolim and at a location off Mangalore (10.19°N, 76°E, SK148). In the open Arabian Sea (65°E, 18°N), a DMSP maximum of 15.5 nM occurred at 10 m whereas the
Fig. 4.1 Vertical distributions of DMS and DMSP in different domains of the Indian Ocean.
peak DMS of 1.7 nM was found at the sea surface. Therefore, depths of occurrence of maximal levels of DMS and DMSP not necessarily coincide at all stations but the higher abundances mostly occurred closer to the surface. The DMS and DMSP concentrations rapidly decreased to undetectable levels below about 120m. Similar behaviors were observed in their vertical distributions in the coastal and open ocean waters of the Bay of Bengal. In the Central Indian Ocean, however, peaks in DMS (9.7 nM of DMS at 41 m) and DMSP (DMSP maximum of 31.3 nM) were found around a depth of 40 m (Fig. 4.1). Further, DMS and DMSP levels were detectable up to 150 – 175 m. This occurrence of DMS at deeper depths is unique to the central regions of the Indian Ocean (because of deep mixed layers) and contrasts with that in the Arabian Sea and the Bay of Bengal.

The vertical distributions of DMS and DMSP in the Indian Ocean were similar to that reported elsewhere in the world Oceans. Andreae and Barnard [1984] reported maximum concentrations of DMS closer to surface in the Atlantic Ocean. Holligan et al. [1987] also observed higher concentrations of DMS in the top 50 m of the water column that in some cases coincided with higher chlorophyll. Maximal DMS concentrations have been found between 30 and 75 m in the South China Sea [Yang et al., 1999]. Our results are in good agreement with that of Hatton et al. [1999] who observed highest DMS and DMSP concentrations in the 20 - 45 m range of the central and western Arabian Sea.
4.2 Spatial variations

Fig. 4.2 depicts the variation of DMS in the Arabian Sea, along a section near 15°N (off Goa), during January, July, October and December of 1998. Very clear coastal to open ocean trends were observed. In January (winter), the DMS concentrations varied between 6 nM and 12 nM within 50 m of the water column near the coast but between 200 and 400 km away from the shore the concentrations ranged between 2 and 4 nM before increasing to 10 nM further offshore. During the summer (July 1998) DMS values were higher near the bottom of coastal waters (29 nM) that decreased towards the open ocean. Features similar to those in summer were seen October 1998 when DMS concentration levels near the coast varied between 15 and 40 nM while in offshore waters these were low. In December 1998 coastal DMS concentrations were around 30 nM but decreased offshore. Thus in the eastern Arabian Sea high DMS concentrations were found closer to the coast.

Fig. 4.3 exhibits zonal variations of DMS in the Bay of Bengal. Near Paradip (86.87°E, 19.98°N) DMS concentrations varied between 0.5 and 3.3 nM in coastal waters that showed little change with increasing distance from the coast. Similar features were noticed off Chennai as well. Here, DMS varied from 0.5 to 3.2 nM. Thus the zonal variability trends of DMS were contrasting between the Arabian Sea (with clear inshore-offshore gradients) and the Bay of Bengal (with no significant variation).

In the Central Indian Ocean a different scenario is seen. Fig. 4.4 depicts the variation of DMS in the Central Indian Ocean observed during the
Fig. 4.2. Longitudinal variation of DMS off Goa in different seasons.
Fig. 4.3. Variations in DMS and DMSP off the coasts of Paradip (a,b (SK147A); c (SK147B)) and Chennai (d (SK147B)).
Fig. 4.4. Variations in DMS in the Central Indian Ocean during FFP - 98 and IFP - 99 of the INDOEX Experiment.
INDOEX cruises of 1998 and 1999. High DMS concentrations (0.1 to 13.9 nM) were observed between 5°S and 15°S in 1999 (Fig. 4.4b). These were observed as pockets between surface to 75 m with detectable concentrations up to 100 to 150 m. While away from these latitudes viz. between 0° and 5°S, and 15°S and 20°S DMS concentrations, in the same depth range, as mentioned above varied between 1 and 5 nM. DMS levels were lower in 1998 with strong latitudinal gradients (Fig. 4.4a).

Thus DMS in the Indian Ocean exhibits very high spatial variability. Besides the strong vertical variability DMS in the Indian Ocean exhibited very significant spatial variability in which higher concentrations were observed near to the coast and lower concentrations in the open Ocean. Further, DMS concentrations on an average, all the data points put together in respective areas, showed a gradual increase from the Bay of Bengal 1.8 nM to the central Indian ocean 2.2 nM to the Arabian Sea 5.5 nM.

4.3 Temporal variations

4.3.1 Diurnal variation

A time series station (7°N, 87°E) was occupied in the Bay of Bengal for 40 hours during which DMS concentrations showed distinct variations. At the beginning of the time series (3.30 AM) abundances were marked with lower DMS and high DMSP concentrations. Towards late afternoon the situation reversed when higher DMS and lower DMSP levels occurred (Fig. 4.5). However DMS exhibited lower concentrations on the following day while DMSP was low during the intervening night (14-26 hrs). Higher DMSP
Fig. 4.5. Variations in salinity, nitrate, DMSP and DMS at the time series station (7°N, 87°E) during the BOBMEX Pilot Experiment. Zero hours refer to 03.30 AM on 30 October 1998.
concentrations were again observed towards the end (~7.30 PM on the following day) of the experiment. The high DMSP during the beginning of the time series could be due to intense grazing activity by the zooplankton [Dacey and Wakeham, 1986; Wolfe and Steinke, 1996], which leads to the subsequent increase in DMS on the following day. These features reveal that DMSP did not exhibit consistent day-night variations. Chlorophyll a was found to exhibit diurnal variability with maximum values occurring around late afternoon. The secondary DMS maximum of ~3.5 nM (at 50 m) coincided with the chlorophyll a maximum. The DMS concentrations during the time series observations varied from 0.2 to 5.1 nM with an average of 1.8 nM in the upper 100 m, whereas DMSP ranged from 1.4 to 17.6 nM with a mean value of 7.2 nM. DMS showed maximum concentrations around the late afternoon but this trend was not consistent, as the maximum was not observed on the following late afternoon. In addition to this DMS and DMSP maximal concentrations were decoupled from each other.

4.3.2 Variability during a cyclone

A long-term time series experiment (spanning over a month) was undertaken in the Bay of Bengal at 17.5° N and 89° E during the summer monsoon of 1999. The experiment was carried out in two phases wherein weather and oceanographic conditions were remarkably different between the two. Phase I (SK147A) was atmospherically more convective than phase II (SK147B). Variations in DMS, chlorophyll a and UV radiation are shown in Fig. 3.9. Surface as well as MLD averaged chlorophyll levels showed marked
variations. The highs in chlorophyll correspond to the lows in UV radiation thereby exhibiting inverse relation between the two. This relation was observed during both the phases, but phase I shows distinct inverse relation which is not so evident in phase II. The DMS variability was found to be very high during phase I in response to intense atmospheric convection. Phase I shows spikes in surface as well as MLD averaged DMS. In comparison to phase I, phase II does not show any such spikes in DMS. Stress is considered to be one of the reasons for enhanced DMS production [Keller, 1998]. Intense convection results in rough sea states and rapid changes in physico-chemical conditions, which may have led to higher DMSP production by phytoplankton, which in turn results in higher DMS production. During phase I surface DMS varied between 1.5 and 5.5 nM with an average of 3 nM, while in phase II it varied between 1 and 5.3 nM again with an average of 3 nM. The column DMS (0-200 m) in phase I ranged between undetectable levels and 6.3 nM with an average value of 1.4 nM and in phase II it varied from below detection limits to 5.3 nM with a mean of 1.2 nM.

4.3.3 Seasonal variation in waters off Goa

4.3.3.1 Off-Candolim

Data obtained through periodic sampling along a small transect (~13 km) off the Candolim coast (Goa) enabled us find the extent of seasonal variability in DMS and DMSP. During the premonsoon (March) season of 2000 (Fig. 4.6a) concentrations of DMS and DMSP varied, respectively, from 0.3 to 6.1 nM with an average value of 2.5 nM and between 3.2 and 38.7 nM.
Fig. 4.6a. Variations in oxygen, nitrate, DMS and DMSP off Candolim in Goa on 30/3/2000
with a mean of 12.1 nM. A repeat observation in March 2001 (Fig. 4.6b) showed even lower concentrations of DMS and DMSP. DMS varied between undetectable levels and 1 nM while DMSP occurred between undetectable levels and 3 nM. Nitrate concentrations, however, were higher in March 2001 (Fig. 4.6b) than in March 2000 (Fig. 4.6a). Fig. 4.6a suggests a positive relation between nitrate and DMS production during organic matter regeneration in coastal sediments. However, DMSP is negatively related to nitrate distribution (Fig. 4.6a,b). These conditions were found to change in SW monsoon (Fig. 4.6c,d). On 12th September 2000 the surface oxygen varied between 140 and 190 µM whereas its concentrations reduced by 8 - 9 times at depths ~ 10 m. Substantial nitrite was observed wherever there was a fall in the oxygen levels indicating active upwelling and biological activity. DMS and DMSP are, in general, higher at surface because of intense biological activities at surface. Within three weeks the conditions (Fig. 4.6d) were found to be quite different with relatively higher oxygen but only traces of nitrate. These conditions indicate the consumption of nitrate during the intense biological production when oxygen is produced in the water column. Such intense photosynthetic fixation and the presence of traces of nitrate seems to have aided higher production of DMSP (9-113 nM) and DMS (13-132 nM). The DMS levels found in these coastal waters in 29 September 2000 are about 100 times more than that occurred in March 2001. On the other hand, the highest values for DMS were detected very close to the coast in November (1999). A maximal DMS of 525 nM was observed (Fig. 4.6e).
Fig. 4.6b. Variations in oxygen, nitrate, DMS and DMSP off Candolim in Goa on 28/3/2001.
Fig. 4.6c. Variations in oxygen, nitrate, DMS and DMSP off Candolim in Goa on 12/9/2000
Fig. 4.6d. Variations in oxygen, nitrate, DMS and DMSP off Candolim in Goa on 29/9/2000
Nitrate was below detection limits
$H_2S$ was found

Fig. 4.6e. Variations in oxygen, nitrate, DMS and DMSP off Candolim in Goa on 11/11/1999.
Surface oxygen was very high (221 μM) indicating very high photosynthetic activity at the surface. The steep gradient in oxygen, between the surface and bottom (<μM) in these shallow waters, together with the presence of hydrogen sulphide and undetectable nitrate indicates intense biological activity including intense microbial degradation of organic matter. DMS levels ranged from 6 nM to 525 nM while DMSP varied between 8 nM and 339 nM. Coinciding with this trend extremely high DMSP values were found in the same season in Zuari estuary (~419nM) and in western continental marginal waters off Mangalore (~916 nM). Thus, DMS varied from ~0.1 nM in premonsoon season to 525 nM in fall-intermonsoon (or post-SW monsoon) season exhibiting a variability by 5000 times in coastal waters of Goa. Such behavior could be occurring in many places along the west coast of India since the oceanographic conditions are nearly the same.

4.3.3.2 Dona Paula Bay

Both surface and bottom DMS and DMSP concentrations, at a location in Zuari estuary in Goa (Fig. 2.2) showed periodic changes (Fig. 4.7). Surface DMS and DMSP showed higher values during December 1999, February and April (only DMS), July and November 2000. Bottom DMS and DMSP also showed almost similar trends. The highest DMS values were observed in April and July. During June to September the surface DMS varied between 0.3 and 12.8 nM with an average value of 5.8 while surface DMSP varied from 1 to 419.5 nM with an average value of 111.4 nM. Bottom DMS varied from undetectable to 28.3 nM with an average value of 8.5 nM while bottom DMSP
Fig. 4.7. Monthly variations in DMS and DMSP in the Zuari estuary.
varied between 1.4 and 190.6 nM with a mean of 50.5 nM. In general, DMS and DMSP peaks followed phytoplankton and chlorophyll peaks with a lag of one month except during July - August (Fig. 4.8). Nearly 99% of the phytoplankton consisted of diatoms between June and August except in July when diatoms contributed to ~85% with the remaining largely present in the form of dinoflagellates (Fig. 4.9). Chlorophyll $a$ also exhibited peak levels in July. These data reveal species dependency of DMS and DMSP and that dinoflagellates contribute significantly to the production of these sulphur compounds. Enhanced DMS and DMSP in December 1999 and November 2000 also coincide with the increase in phytoplankton. However the values during the December 1999 (11.6 for DMS and 216.1 nM for DMSP) were greater than the values observed during November 2000 (8.7 nM and 11.3 nM DMS and DMSP, respectively). Moret et al. [2000] reported surface DMS to be between 0.4 nM and 16.3 nM, with an average value of 3.7 nM, from surface waters of two time series stations in Venice Lagoon. They found maximal DMS levels to occur during phytoplankton and macro-algal blooms. Turner et al. [1996] have found a monthly mean of around 25 nM in May and coincidence of higher DMS with blooms of Phaeocystis. The present results confirm that DMS not only shows significant temporal variation but also exhibits species dependency.

4.3.4 Inter-annual variability

Fig. 4.4 shows the variations in DMS in subsequent years during the INDOEX (FFP- 1988 and IFP-1999). A clear increase (nearly five times) in
Fig. 4.8. Monthly Variability in phytoplankton abundance and chlorophyll in the Zuari estuary.
Fig. 4.9. Monthly Variability in diatoms, dinoflagellates and other algae in the Zuari estuary.
DMS concentrations was found in 1999 in comparison to that in 1998. During FFP the DMS concentrations in the upper 100 m varied between 0.4 and 2.6 nM with an average value of 0.6 nM whereas during IFP DMS concentrations varied between 0.1 nM and 13.9 nM with an average of 3.4 nM. This high degree of inter-annual variability is due to differential production during the two years. In spite of low chlorophyll contents in 1999 than in 1998 DMS abundance was higher in 1999 perhaps due to active biology supported by atmospheric disturbance and the consequent upward nutrient supply. On the other hand, higher chlorophyll found in 1998 might have been remnants of high production off Sumatra, following El Nino upwelling, as the nitrate supply from deep seem to not have been favoured (Fig. 3.11a,b). Thus DMS has shown significant inter-annual variability in response to oceanographic and atmospheric forcings.

**Salient features of DMS distribution in the Indian Ocean are:**

1. Maximal concentrations in DMS and DMSP occurred close to sea surface in the Arabian Sea and the Bay of Bengal whereas in the Central Indian Ocean these were found at deeper depths.

2. Zonal distribution indicated strong coastal to offshore gradients in DMS and DMSP in the Arabian Sea but not so in the Bay of Bengal.

3. Diurnal variability in DMS suggested peak abundance in the late afternoon.
4. Chlorophyll a is negatively related to incident UV radiation during stormy conditions in the Bay of Bengal but their influence on DMS was not clear since both the ocean and atmosphere were very turbulent.

5. The DMS in coastal waters of the western India exhibited very strong seasonality with the highest concentrations (~100 to 5000 times) occurring the late and post-southwest monsoon periods compared to that in pre-monsoon season.

6. Strong inter-annual variability in DMS was found in the Central Indian Ocean with five times higher abundance in 1999 than in 1998.