

Variability in abundance and fluxes of dimethyl sulphide in the Indian Ocean

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Abstract Dimethyl sulphide (DMS) is a biogenic gas of climatic significance on which limited information is available from the Indian Ocean. To fill this gap, we collected data on DMS and total dimethylsulphoniopropionate (DMSP_t) by participating in a dozen cruises. Here, we discuss the variability in DMS and DMSP_t in the north and central Indian Ocean in terms of their spatial and temporal variation. DMS and DMSP_t exhibited significant spatial and temporal variability. Apart from the concentration gradients in DMS within the Arabian Sea, Bay of Bengal and Central Indian Ocean basins, differences in average abundances were conspicuous between these basins. The Arabian Sea contained more DMS (mixed layer average was 7.8 nM) followed by the Bay of Bengal (2.8 nM) and the Central Indian Ocean (2.7 nM). The highest concentrations of DMS and DMSP_t (525 nM and 916 nM, respectively) were found in upwelling regimes along the west coast of India during the Southwest monsoon and fall intermonsoon seasons. Average

surface DMS was the highest in the Arabian Sea. On the other hand observed sea-to-air fluxes of DMS were higher in the Bay of Bengal due to the prevalence of turbulent conditions. In the Arabian Sea wind speeds were low and hence the sea-to-air fluxes. The total diffusive flux of DMS from the study area to atmosphere is estimated to be about 1.02×10^{12} g S y⁻¹, which contributes to 4.1–6.3% of the global DMS emission

Keywords DMS · DMSP_t · Fluxes · Indian Ocean · Monsoon

Introduction

Dimethyl sulphide is the most dominant of the reduced sulphur gas found in surface layers of the ocean (Lovelock et al. 1972). The emission of dimethyl sulphide from seawater is expected to balance the excess sulphur deposition over the remote oceans (Charlson et al. 1992). Charlson et al. (1987) proposed a hypothesis, known as the CLAW (after the authors Charlson, Lovelock, Andreae and Warren) hypothesis connecting biogenic DMS emissions to changes in albedo, in which increased production of DMS due to global warming is expected to lead to more sulphate aerosols and subsequently to more cloud condensation nuclei (CCN) that in turn enhances back radiation.

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In seawater, DMS is produced from dimethylsulphoniopropionate (DMSP), which in turn is produced by phytoplankton. Specific species of phytoplankton are found to be responsible for most of the DMSP production in seawater. According to Liss et al. (1993) the potential for production of DMS in various taxonomic groups follows the order:

Coccolithophores > *Phaeocystis*
> Dinoflagellates > Diatoms

DMSP in phytoplankton was initially proposed to function as an osmolyte (Vairavamurthy et al. 1985). Over the years we now have evidence for its role in other processes such as for cryopreservation (Kirst et al. 1991), as a deterrent against grazing (Dacey and Wakeham 1986; Wolfe and Steinke 1996) and against bacteria (Wolfe et al. 1997). In the recent past the anti-oxidant role of DMSP is becoming more popular (Sunda et al. 2002). Factors controlling DMSP production, its conversion to DMS, fate of DMSP and DMS sulphur in the marine environment are well documented in the review by Stefels et al. (2000) and in the present issue.

Extensive measurements on DMS and DMSP have been done in different parts of the oceans (Kettle et al. 1999 and references therein) including estuarine and lagoon waters (Iverson et al. 1989; Moret et al. 2000). A few studies have been made in the Indian Ocean, which include Hatton et al. (1999), Shenoy et al. (2000, 2002), Kumar et al. (2002) and Shenoy and Patil (2003) and some unpublished data in eastern Indian Ocean (of T.S. Bates, as mentioned by Kettle et al. 1999) and for Amsterdam station (Nguyen et al. 1990, 1992).

Hatton et al. (1999) found elevated concentrations of DMS, DMSP and dimethyl sulphoxide (DMSO) in the eutrophic zone (Arabian Sea) immediately after the SW monsoon. In addition DMSO concentrations were found to correlate with near surface DMS and DMSP. Shenoy et al. (2000) reported the first ever measurements of DMS from the Bay of Bengal where salinity appeared to play an important role in the DMSP production. Shenoy et al. (2002) documented five times higher concentrations of DMS and DMSP in

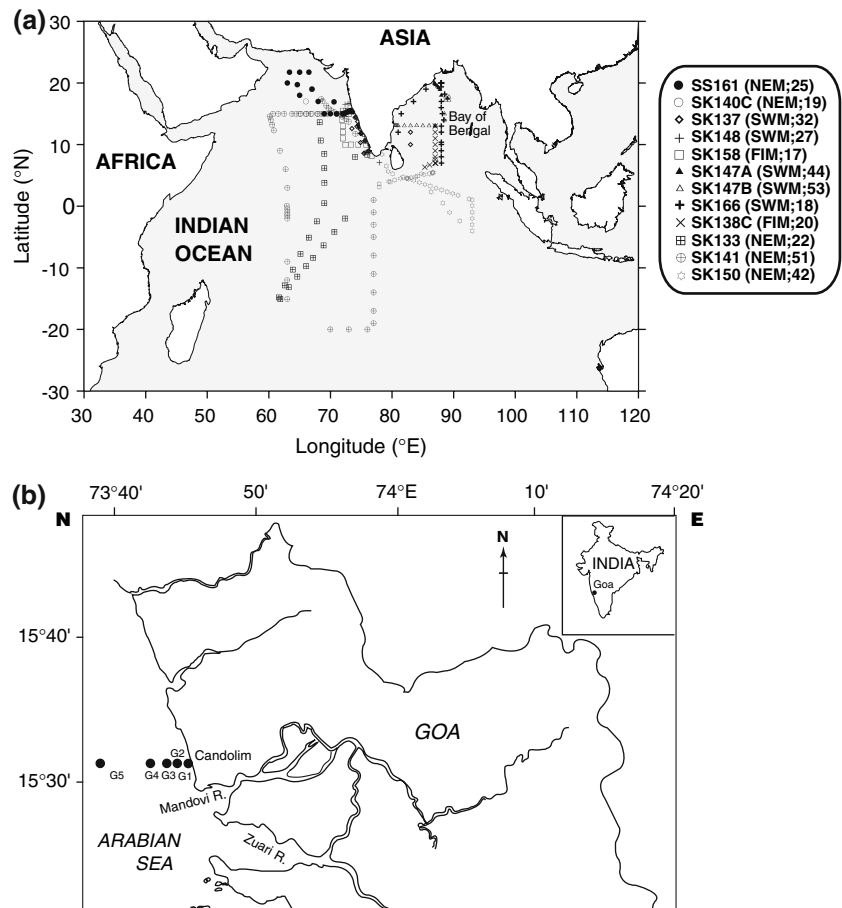
winter season of 1999 than that in 1998, which has been attributed to differences in physical forcing and associated biological processes. In a time series experiment carried out in estuarine waters of Goa, on the west coast of India, Shenoy and Patil (2003) recorded elevated concentrations of DMS and DMSP during the monsoon season (maximum DMS 15.4 nM and DMSP_t 419.5 nM) due to the possible prevalence of mixed population of diatoms and dinoflagellates. Covariations among oceanic and atmospheric DMS and atmospheric SO₂, wet deposition of methane sulphonic acid (MSA), non-sea salt (NSS) SO₄²⁻, and rain acidity have been shown by Nguyen et al. (1990, 1992) near Amsterdam island (southern Indian Ocean).

While the biogeochemistry of carbon dioxide and nitrogen species are reasonably well known, particularly in the northern Indian Ocean, our knowledge of sulphur species is limited. DMS and associated sulphur compounds are climatically important, particularly in the monsoon-dominated tropical Northern Indian Ocean, in regard to air-sea interactions and feedbacks. Significant diversity in physical and associated biological regimes in the Indian Ocean together with dynamic climate offers a potentially interesting region to understand the DMS cycling and its controlling factors. Therefore, this study has been undertaken to study spatial (especially inshore-offshore gradients off the coast of India and surface variation) and temporal variations of DMS and DMSP_t in the Indian Ocean and to evaluate its atmospheric emissions in regional and global context.

Material and methods

Sampling for this study was attempted keeping in view the large spatial and temporal variability of the biogeochemical processes in the Indian Ocean. Data were collected for temperature, salinity, dissolved oxygen, nitrate, chlorophyll *a*, DMS and DMSP_t in seawater. Besides, data were collected for wind speed and atmospheric temperature. Figure 1a depicts the study area in the Indian Ocean, where a dozen oceanic expeditions were undertaken on board ORV Sagar Kanya (SK) and FORV Sagar Sampada (SS) covering a total of 320 stations. Data were mainly collected

Fig. 1 (a) Station locations occupied for dimethyl sulphide studies in the central and north Indian Ocean. Symbol index indicates cruise number, season and number of stations. (b) Station locations off Candolim, Goa



from the upper 200 m of the water column as the initial study revealed DMS and DMSP_t to be below detectable levels at depths greater than 200 m. Surface waters were sampled at many locations besides regular stations. Figure 1b depicts the stations locations along a section off Candolim, Goa used for collection of DMS data particularly during and after the southwest monsoon. The data presented in this paper were collected under different projects in the Indian Ocean: land-ocean interaction in the coastal zone (LOICZ), the Bay of Bengal monsoon experiment (BOBMEX), the Bay of Bengal process studies (BOBPS), ocean observing systems (OOS) and the Indian Ocean experiment (INDOEX).

Hydrographic and biological properties

Seawater samples were collected using a rosette attached to the conductivity–temperature–depth

(CTD) system, fitted with 12 Niskin bottles. Subsampling of water was made in the order: dissolved oxygen (DO), DMS, DMSP_t , nutrients, salinity and chlorophyll *a*. Care was taken while sampling dissolved gases to avoid trapping of bubbles. Temperature and conductivity were measured using the sensors fitted to the Sea-bird CTD system. Temperature sensed by the probe was periodically checked against the values obtained from reversing thermometers. Conductivity measurements of CTD, and hence salinity were calibrated against data obtained using an Autosol salinometer (model 8400). Dissolved oxygen was measured by the classical Winkler titration method. Nutrients (nitrate) were measured using a Skalar autoanalyser (SA 4000).

For chlorophyll *a* analysis, a known volume of seawater sample (0.5–1 l for coastal and estuarine samples or 2–3 l for open ocean waters) was filtered through Whatman GF/F filters under low

vacuum. Chlorophyll pigments on the filter paper were then extracted into 10 ml of 90% acetone under dark and refrigerated conditions for 24 h. Fluorescence was measured using a Hitachi spectrofluorometer (UNESCO, 1994).

DMS and DMSP measurements

Water samples for DMS and DMSP_t analyses were collected in two separate 60 ml dark ground-glass bottles. Water samples were not filtered because even with extreme care DMS losses cannot be prevented during the filtrations and this process can alter the contents of DMSP_t. Thus the concentrations reported here refer to total dissolved DMS and DMSP. Following the collection DMS samples were immediately kept in the dark at 4°C. DMS was measured using a Hewlett Packard 5890 series II plus gas chromatograph fitted with a flame photometric detector (FPD). The details of the analysis are described in Shenoy et al. (2002). The detection limit for DMS measurements, found as twice the standard deviation from regression analysis for values <0.1 nmol, was 0.012 nmol. Precision in DMS measurements was found to be 6% for standards. Reproducibility of DMS and DMSP_t in seawater samples was periodically checked in all the cruises for paucity of time and availability of a dedicated gas chromatograph.

Immediate repeat analysis of a sample showed no detectable DMS indicating its negligible production from DMSP_t, if any, during the stripping process. DMSP_t was measured after hydrolyzing the unfiltered water sample for 6 h using 10 M NaOH (1 ml), which was added immediately after sample collection (Turner et al. 1990; Shenoy et al. 2002). Alkali hydrolysis resulted in the cleavage of DMSP_t into DMS and acrylic acid. DMSP_t concentrations were read from the DMS calibration curve. Tests revealed about 95% conversion of DMSP_t to DMS during the alkali hydrolysis for 6 h. The precision of seawater DMS analysis is found to be 8–10%.

Wind Speed

Wind speed data used in DMS flux calculations were collected using an automatic weather station

(AWS) on board the research vessels or on top of the institute building. Wind speed was measured using Young's wind monitor (model 05103). The wind speeds were normalized for 10 m height and corrected for direction.

DMS Flux

DMS fluxes were calculated using the formulations proposed by Turner et al. (1996) and the correction factors given by Saltzman et al. (1993). The flux of DMS gas between sea and air is proportional to the concentration gradient across the air-sea interface and is calculated according to the following equation.

$$F_{\text{DMS}} = k \cdot \Delta C$$

where F_{DMS} = net flux of DMS

k = transfer (or piston) velocity and

ΔC = concentration gradient across the air-sea interface.

$$\Delta C = C_w - C_a \cdot h^{-1}$$

where C_w = concentration of DMS in seawater

C_a = concentration of DMS in air

h = Henry's law constant, expressed as the ratio of air to water concentrations at equilibrium.

As the concentration of DMS in air is very low (nearly three orders of magnitude less than that in water) C_a is generally considered to be zero and thus C_w equals ΔC .

Mixed layer depth (MLD)

Mixed layer depths (MLD) were calculated based on density criteria where MLD was defined as the depth at which density increased by 0.125 kg dm³ with reference to that at the sea surface. MLDMS is the DMS averaged in the water column above the MLD.

Results

Hydrography in brief

The southwest and northeast monsoons of the Indian Ocean region play a major role in controlling

the biogeochemical processes. Between November and February, the intertropical convergence zone (ITCZ) lies in the southern hemisphere ($\sim 10^{\circ}\text{S}$) and the region experiences the northeast monsoon (NEM). During this period cold dry winds from the north (north-easterlies) blow over the northern Indian Ocean. These cool dry winds facilitate enhanced evaporation in the northern Arabian Sea and thus set in winter convection (Fig. 2). The occurrence of convection pumps in nutrients into the surface layers. During the present study the average nitrate concentration in surface waters of the Arabian Sea where convection occurred was found to be $\sim 4.9 \mu\text{M}$. Such high nitrate levels promote primary production. During NEM the surface circulation in the Arabian Sea is quite similar to the circulation in the North Pacific and Atlantic Oceans.

The extensive heating of the Indo-Gangetic plain and Himalayan terrain from March to May (spring intermonsoon) leads to the development of low pressure which makes the ITCZ move northward. This transition changes the direction of the winds, which now move in the south-westerly direction during the southwest monsoon (June to September, SWM). The surface circulation in the Arabian Sea in SWM is totally opposite to that of the NEM. The circulation along the coasts of Oman and Somali is towards the pole and away from the coast. This causes intense upwelling in these regions. Similarly upwelling also occurs along the south west coast of India, where the flow of water is towards the equator.

One of the major characteristics of the northern Indian Ocean is the differential riverine discharges in to the Arabian Sea and the Bay of Bengal. The Bay of Bengal receives $1.6 \times 10^{12} \text{ m}^3 \text{ y}^{-1}$, which is five times more than the run off received by the Arabian Sea ($0.3 \times 10^{12} \text{ m}^3 \text{ y}^{-1}$). This reduces the surface salinity in the Bay and the lowest salinities are mostly confined to areas of river mouths. The salinity increases from north to south in the Bay. The low salinity lens results in a strong surface stratification and prevents surfacing of subsurface nutrients through vertical mixing.

The month of October is referred to as the fall intermonsoon (FIM) period. During the FIM the temperature contours show a stratified structure

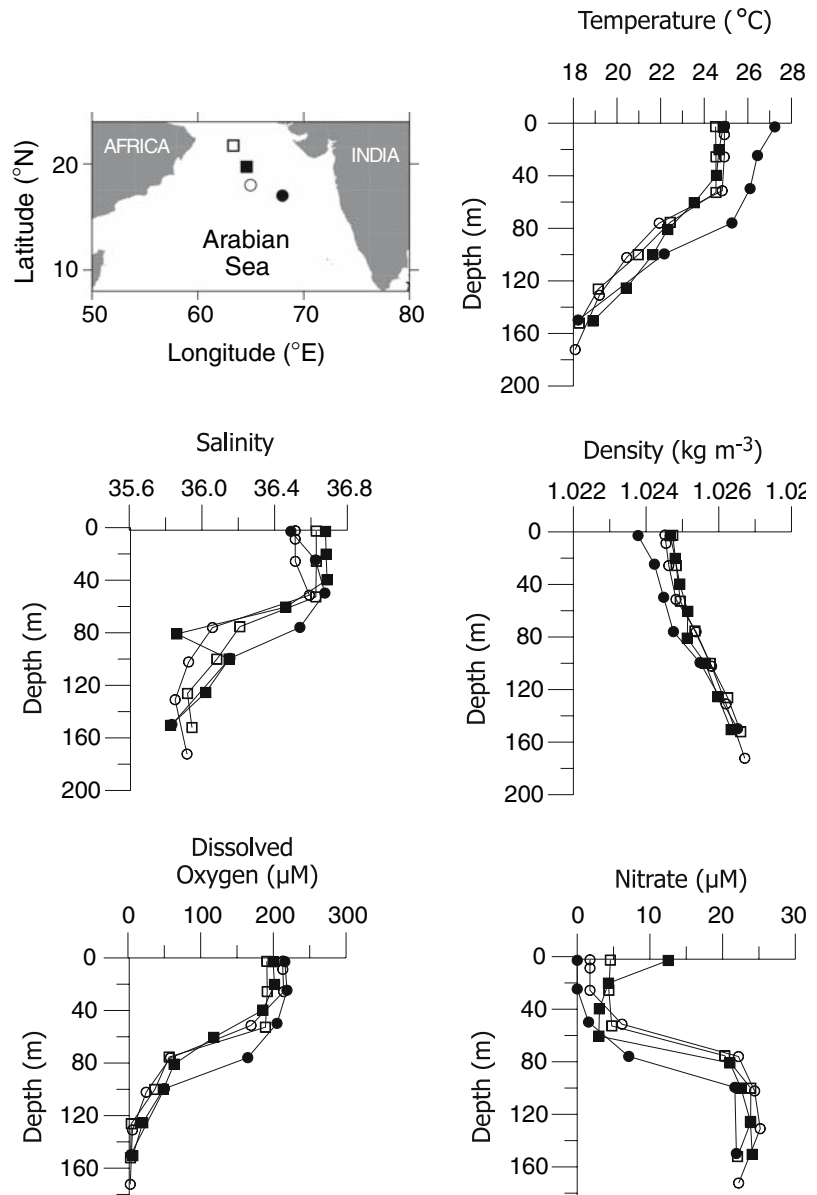
unlike in the SWM. Low wind speeds during this period lead to shallow MLD's. There are no detectable nutrients in the surface layers. One of the prominent features of the fall-intermonsoon is the occurrence of high nitrate levels near the base of MLD, which occurs within the euphotic zone. This leads to basin wide subsurface chlorophyll maximum (SCM, Bhattathiri et al. 1996) as shown in Fig. 3. All these make the Northern Indian Ocean one of the most productive basins in comparison to the rest of the world in general (Behrenfeld and Falkowski 1997).

Central Indian Ocean characteristics have been discussed in detail in Shenoy et al. (2002). In order to get an overview on the variation of DMS and DMSP in the Indian Ocean, their variability is discussed in the following sections.

Vertical distributions

Vertical distributions of DMS and DMSP_t in the coastal and open ocean waters of the Arabian Sea (AS), Bay of Bengal (BoB) and in the Central Indian Ocean (CIO) are shown in Fig. 4. Both DMS and DMSP_t showed very distinct trends in their vertical distributions. Concentrations of DMS and DMSP_t were very low (less than or around the detection limits) in waters deeper than 200 m in the Indian Ocean. Therefore, DMS sampling was restricted to the top 200 m of water column in most cruises. In coastal waters of the Arabian Sea (76°E , 10.19°N) maximal concentrations of DMS and DMSP_t were found at shallow depths. In the present study the highest values of 525 nM of DMS and 916 nM of DMSP_t 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_t maximum of 15.5 nM occurred at 10 m whereas the peak DMS of 1.7 nM was found at the sea surface. Therefore, depths of occurrence of maximal levels of DMS and DMSP_t did not necessarily coincide at all stations but the higher abundances mostly occurred closer to the surface. The DMS and DMSP_t concentrations rapidly decreased to undetectable levels below 120 m. Similar behaviours were observed in their vertical distributions in the coastal and open ocean waters of the Bay of Bengal. In the central Indian Ocean,

Fig. 2 Vertical profiles of temperature, salinity, density, dissolved oxygen and nitrate in the northern Arabian Sea during the northeast monsoon (SS161)



however, peaks in DMS (9.7 nM of DMS at 41 m) and DMSP_t (DMSP_t maximum of 31.3 nM) were found around a depth of 40 m (Fig. 4). Further, DMS and DMSP_t 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.

Table 1 lists DMS and DMSP_t variations as averages in the surface mixed layer. In the coastal

(southwest coast of India) Arabian Sea the highest values occurred during the SWM and the least were during the intermonsoons. In the Bay of Bengal the concentrations of DMS and DMSP_t near the coast are almost same as the open ocean. The DMS and DMSP_t concentrations in the Central Indian Ocean are nearly similar to those in the Bay of Bengal. On the whole, the Arabian Sea (coastal + open ocean) surface mixed layer contained more than double DMS and DMSP_t (7.8 nM and 43.6 nM,

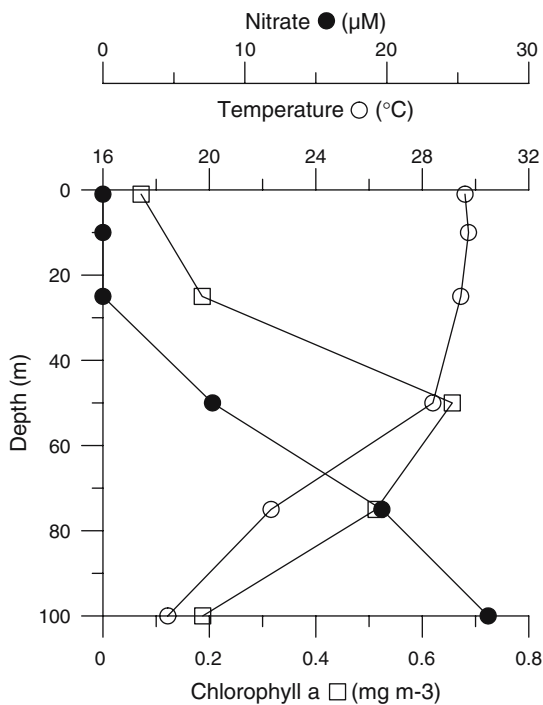
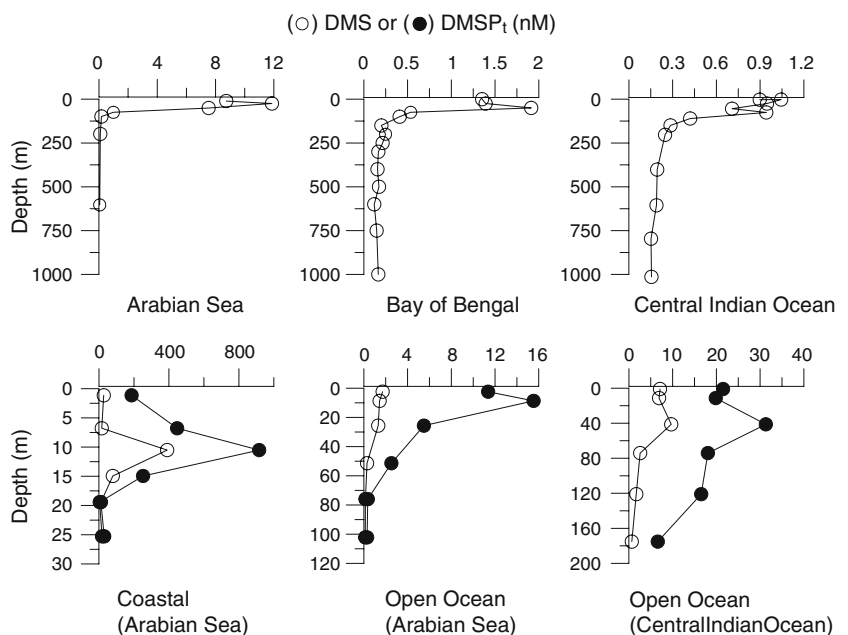


Fig. 3 Profiles of temperature, nitrate and chlorophyll (at 9.94°N, 72.44°E, SK158) showing subsurface chlorophyll maximum

respectively) than the Bay of Bengal (2.8 nM and 12.6 nM, respectively) and central Indian ocean (2.7 nM and 10.1 nM, respectively) and followed

Fig. 4 Typical vertical profiles of DMS and DMSP_t in different regions of the Indian Ocean



the same trend as that of the primary production (Behrenfeld and Falkowski, 1997).

Spatial variations

Figure 5 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 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 summer (July 1998), DMS values were higher near the bottom in coastal waters (29 nM), and decreased towards the open ocean. Features similar to those in summer were seen in 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.

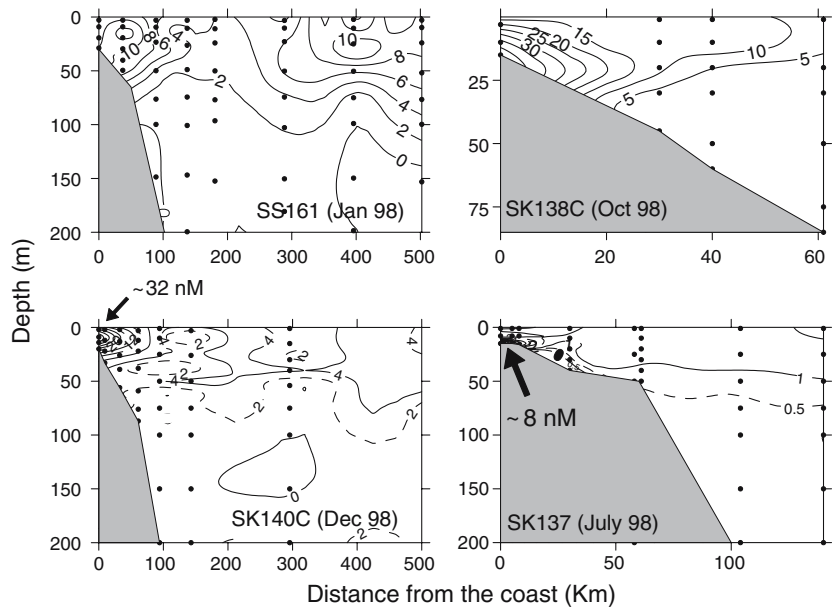
Data obtained through periodic sampling along a small transect (~13 km, Fig 1b) off the Candolim

Table 1 Averages and ranges (in parenthesis) of DMS and DMSP_t in the surface mixed layer (defined by 0.125 kg m⁻³ density difference) in different seasons and in different regions of the Indian Ocean

Area	Season	Coastal		Open ocean	
		DMS (nM)	DMSP (nM)	DMS (nM)	DMSP (nM)
Arabian Sea	SWM	32.9 (0.3–525.6)	81.1 (2.0–915.9)	1.6 (0.5–3.7)	NM
	NEM	9.0 (1.8–51.0)	NM	2.3 (0.2–11.9)	9.8 (3.6–16.7)
	FIM	5.8 (0.2–64.4)	26.1 (0.5–160.1)	1.4 (0.9–2.2)	9.4 (4.9–16.1)
Bay of Bengal	SWM	3.3 (1.2–7.2)	12.9 (3.1–23.3)	2.8 (0.2–11.1)	13.3 (1.5–30.9)
	FIM	NM	NM	2.8 (0.8–5.5)	10.9 (4.1–19.5)
Central Indian Ocean	NEM	–	–	2.7 (0.2–13.9)	10.1 (1.3–35.9)

NM: Not measured

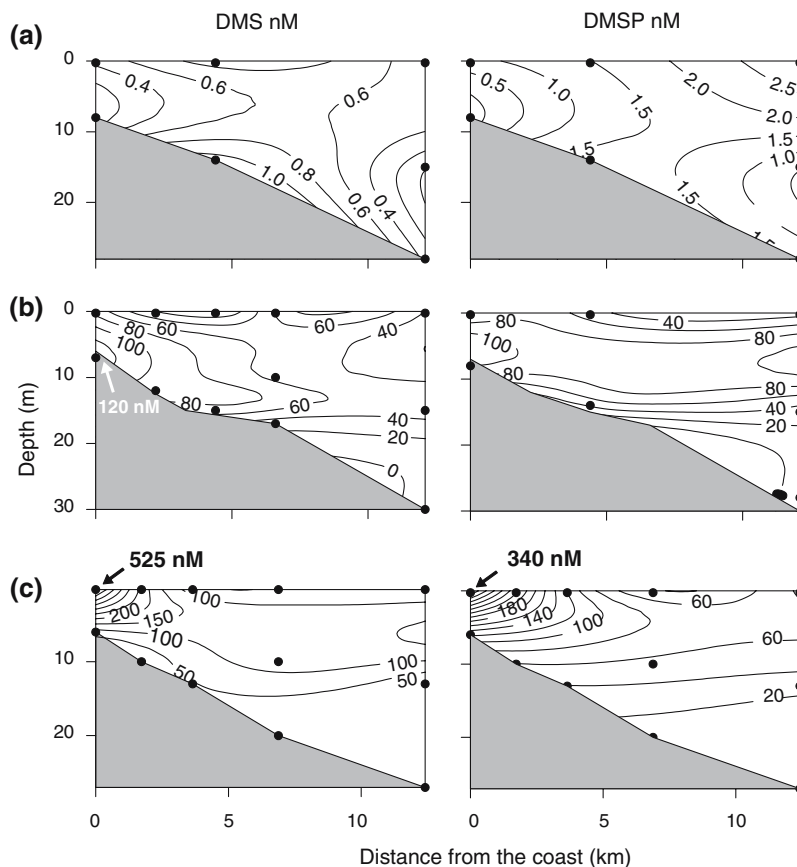
SWM, NEM and FIM refer to southwest, northwest and fall intermonsoon seasons, respectively

Fig. 5 Longitudinal variations in DMS off Goa in different seasons

coast (Goa) enabled us to examine the extent of seasonal variability in DMS and DMSP_t in close proximity to the coast. During the pre-monsoon (March) of 2001 (Fig. 6a) concentrations of DMS and DMSP_t varied, respectively, from 0.2 to 0.9 nM with an average value of 0.6 nM and between 0.5 and 2.9 nM with a mean of 1.4 nM. These concentrations changed in SW monsoon as upwelled water with low oxygen and high nitrate dominate the coastal regions (Naqvi et al. 2000). DMS and DMSP_t are, in general, higher at the surface because of intense biological activities at surface. Very high photosynthetic fixation and the presence of traces of nitrate seem to have aided higher production of DMSP_t (9–113 nM) and DMS (13–132 nM). The DMS levels found in these

coastal waters on 29 September 2000 (Fig. 6b) are about 100 times more than that occurred in March 2001. On the other hand, the highest value for DMS of 525 nM was found very close to the coast in November 1999, where DMS levels varied from 6 nM to 525 nM and DMSP_t varied between 8 nM and 339 nM (Fig. 6c). Coinciding with this trend, extremely high DMSP_t values were found in the same season in the neighbouring Zuari estuary (~419 nM) and in western continental marginal waters off Mangalore (~916 nM). Thus, DMS varied from 0.2 nM in the pre-monsoon season to 525 nM in the fall intermonsoon (or post-SW monsoon) season exhibiting a variability by 2500 times in coastal waters of Goa. Such behaviour could be occurring in at least a few other places

Fig. 6 Time series observations of DMS (left panels) and DMSP_i (right panels) off Candolim in Goa on (a) 28/3/2001, (b) 29/9/2000 and (c) 11/11/1999



along the west coast of India since the oceanographic conditions are similar.

Zonal variations of DMS in the Bay of Bengal are shown in Fig. 7. Near Paradip (86.87°E, 19.98°N), DMS concentrations varied between 0.5 and 3.3 nM in coastal waters but 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 was found. Figure 8 depicts the variation of DMS in the central Indian Ocean observed during the INDOEX cruises of 1998 and 1999. High DMS concentrations (0.1–13.9 nM) were observed between 5°S and 15°S in 1999. These were observed as pockets between surface and 75 m with detectable concentrations down to 100–150 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.

Thus DMS in the Indian Ocean exhibits very high spatial variability in which higher concentrations were observed near to the coast and lower concentrations in the open Ocean. Further, DMS concentrations (MLD average) showed a gradual increase from the central Indian Ocean (2.7 nM) and the Bay of Bengal (2.8 nM) to the Arabian Sea (7.8 nM).

Discussion

DMS at sea surface and its emission

Variations in surface DMS

The envisaged indirect global cooling by DMS products depends on its emission from the ocean.

Fig. 7 Variations in DMS and DMSP_i off Paradip (a) and (b) during SK147A and (c) during SK147B and off Chennai (d) during SK147B

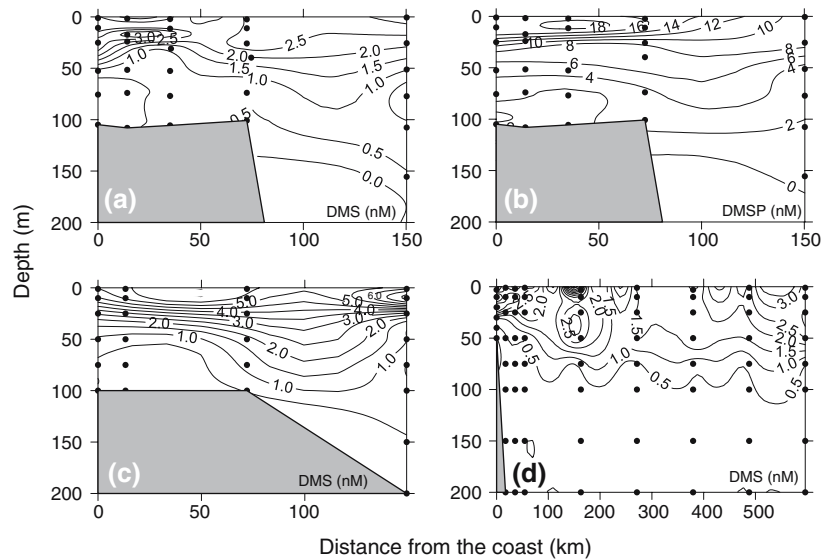
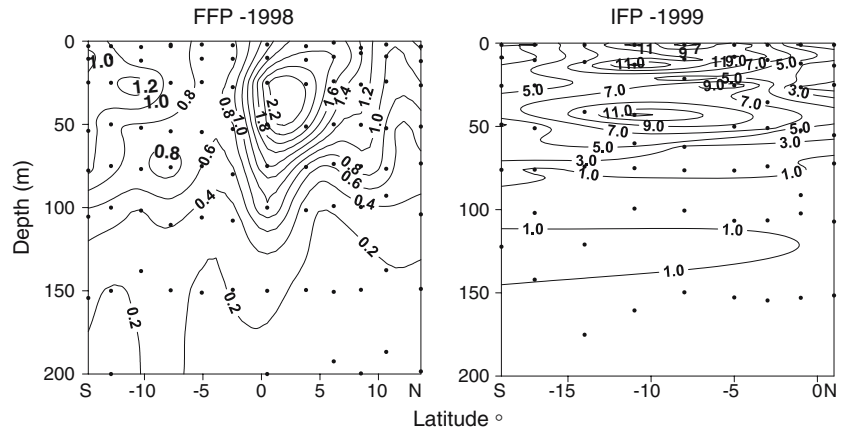


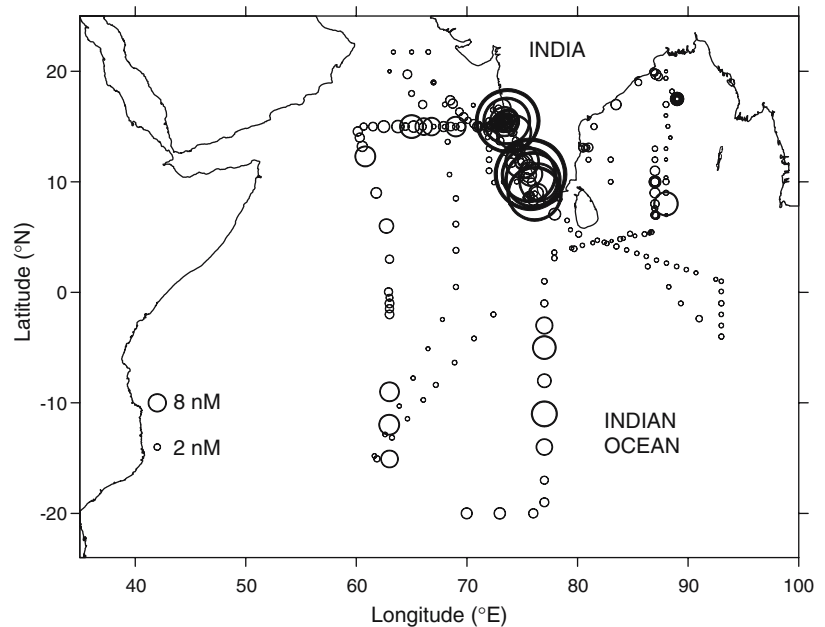
Fig. 8 Variations in DMS (nM) in the central Indian Ocean in the winter season of 1998 (FFP; SK133) and 1999 (IFP; SK141) of the INDOEX project



Variations in surface DMS in the Indian Ocean are shown in Fig. 9. During the northeast monsoon the surface DMS in coastal waters of the Arabian Sea (central and southern regions of the west coast of India) varied between 0.7 nM and 31.7 nM with an average of 6.3 nM, while in the open ocean it was between 0.3 nM and 10.9 nM with a mean of 3.3 nM. The average DMS concentrations in the coastal region were nearly twice that of the open ocean. During the SW monsoon the surface DMS in coastal waters varied between 0.5 nM and 525 nM (the highest value is not shown in Fig. 9) with an average value of 10.3 nM. The highest value was found in near-shore waters of Goa due to very high

primary production driven by coastal upwelling and the associated biological processes including hypoxia. In contrast, the intermonsoon, which is a slack period with respect to primary production but rich in bacterial production, experienced low concentrations of DMS. The coastal surface DMS varied between 0.9 nM and 10.7 nM with an average concentration of 2.6 nM while the open ocean surface DMS varied between 0.9 nM and 1.7 nM (average of 1.3 nM) in this season. The mean DMS concentrations at surface were greater in the SW monsoon (10.3 nM) followed by winter (4.3 nM) and intermonsoon (2.1 nM). The annual surface DMS average, in general, for the coastal Arabian Sea was 8.2 nM whereas it was

Fig. 9 Variations in surface DMS concentration in the Indian Ocean. The maximum concentration of 525 nM found in the coastal waters of Goa is not shown here



3 nM for the open Arabian Sea. Thus the surface DMS in the Arabian Sea shows very high spatial and temporal variability. The overall surface DMS average for the Arabian Sea was 6.3 nM.

On the other hand, surface DMS concentration in the coastal waters (off the Paradip in the north and Chennai in the south) in the western Bay of Bengal varied from 1.2 to 3.9 nM with an average of 2.6 nM during the SW monsoon, when the central Bay waters contained the surface DMS concentrations of 0.2–11.1 nM having a mean of 2.7 nM. Thus the surface DMS concentrations during the SW monsoon are almost the same in the coastal and open waters of the Bay of Bengal. During intermonsoon, the southern and central Bay of Bengal exhibited surface DMS concentrations between 1.4 and 4.7 nM with a mean of 2.9 nM. The overall average surface DMS concentration in the Bay of Bengal was 2.7 nM. In the central Indian Ocean surface DMS ranged from 0.2 to 11.9 nM during the northeast monsoon with an average concentration of 2.2 nM. All the observations made in the central Indian Ocean were in winter as part of the INDOEX project. The surface DMS in the Arabian Sea was more than double to that in the Bay of Bengal and nearly thrice than that in the Central Indian Ocean. In general the surface DMS

concentrations in coastal waters were higher than in the open ocean. The overall average surface DMS for the entire Indian Ocean covered in the present study was 4.2 nM.

Barnard et al. (1982) reported a surface DMS mean of 2.8 nM for the Atlantic Ocean. Wong et al. (2005) in a time series study in the subarctic northeast Pacific Ocean (an HNLC region) found that the mean surface DMS was low in winter (2 nM) in comparison to summer (10 nM). High variability in surface DMS concentrations is found in the southern North Sea with minimal concentrations of 0.13 nM in winter to a maximum of 25 nM in May, which coincided with large blooms of *Phaeocystis pouchetti* (Turner et al. 1996). In the Arctic Ocean surface DMS was found to vary between 0.04 and 12 nM with maximal values occurring along the ice edge (Leck and Persson 1996). Surface DMS concentrations have been found to range between 0.002 and 4.63 nM with a mean of 2.6 nM in the South China Sea, and from 1.8 to 5.7 nM (a mean of 3.4 nM) for the East China Sea, where the highest concentrations occurred in shelf waters and DMS showed strong correlation with chlorophyll (Yang, 2000). Uher et al. (2000) found highly variable surface DMS concentrations in the European western continental margin. In

September 1994 it ranged between 0.6 and 33.4 nM (mean of 2.8 nM) while in July 1995 it varied from 2.9 to 38.5 nM (mean of 7.2 nM). It is apparent from the above comparisons that the Indian Ocean surface DMS average is nearly double that of the Atlantic, the Pacific and the other seas in the Northern hemisphere and is also more than the surface DMS concentrations reported for the China Sea. Our values are, however, comparable to the July 1995 average for the European western continental margin. In addition we also compared our data with the data set for the Indian Ocean from the Pacific Marine Environmental Laboratory (PMEL) database. The database server is the first of its kind to hold 31,059 surface seawater DMS measurements with contributions from more than 50 researchers for different parts of the world's Ocean. From this server (<http://saga.pmel.noaa/dms/>) data were downloaded for the Indian Ocean region, which basically covered central and western Arabian Sea and Central Indian Ocean over different seasons. The surface DMS over this coverage varied between 0.76 nM and 12.05 nM with an average of 3.7 nM. Our surface DMS average for the entire Indian Ocean is comparable with that of the PMEL database. A bit higher average surface DMS for the present study might have resulted from the fact that this study covers a lot of the Indian coastline, which is influenced by intense biological activity driven by monsoons (Naqvi et al. 2000).

Wind

Wind is an important driving force in air–sea interaction processes that largely determines the extents of exchanges of heat and materials. The Indian Ocean covered in the present study experienced seasonally variable winds. During the northeast monsoon wind speeds along the eastern coastal Arabian Sea were between 0.7 and 10.4 m s⁻¹ with an average speed of 4.2 m s⁻¹ while in the open ocean they varied from 1.4 to 9 m s⁻¹ with a mean of 4.9 m s⁻¹. During the SW monsoon the winds along the coastal Arabian Sea of India were weaker and varied between 0.5 and 8 m s⁻¹ with an average of 3.1 m s⁻¹. During the intermonsoon periods, they ranged between 1.8

and 12.5 m s⁻¹ and 3.7 and 6.3 m s⁻¹ with average wind speeds of 5.8 and 5.2 m s⁻¹ for the coastal and the open ocean regions, respectively. Thus maximal wind speeds in the Arabian Sea were encountered during the intermonsoons along the west coast of India. Along the east coast of India, winds varied between 2.2 and 8.9 m s⁻¹ with an average speed of 5.5 m s⁻¹ during the SW monsoon while in the open bay winds varied from 4 m s⁻¹ to 18.2 m s⁻¹ (in association with a low-pressure system), with an average speed of 9.3 m s⁻¹. During the intermonsoons, however, winds in the open bay varied between 1.6 and 8.6 m s⁻¹ (an average of 3.8 m s⁻¹). In the central Indian Ocean the winds showed a variation from 1.1 to 12.7 m s⁻¹ (with a mean of 5.7 m s⁻¹) in winter. These wind speeds were higher in 1999, than in 1998, because of the development of stormy conditions associated with the Inter Tropical Convergence Zone. The measured wind speeds were in general agreement with the climatological winds recorded in Hastenrath and Lamb (1979). The observed wind speeds in the eastern Arabian Sea, however, are much weaker than those reported for the western parts (~18 m s⁻¹) in the southwest monsoon.

Sea-to-air flux of DMS

In DMS flux calculations it is assumed that DMS in air is negligible compared to that in seawater and therefore the concentration difference used in the flux calculation is essentially equal to DMS concentration in seawater. Figure 10 depicts variations in surface DMS flux in the coastal and open ocean areas of the Indian Ocean. The DMS fluxes from the coastal waters of India are lower than that from the open Ocean. Higher DMS fluxes in the central Indian Ocean are associated with higher DMS abundance and high wind speeds in winter of 1999. In the coastal areas the DMS flux varied between 0.04 μmol m⁻² d⁻¹ and 34.4 μmol m⁻² d⁻¹ with an average value of 3.4 μmol m⁻² d⁻¹ while in the open ocean it varied from 0.03 μmol m⁻² d⁻¹ to 41.1 μmol m⁻² d⁻¹ having a mean DMS flux of 6.3 μmol m⁻² d⁻¹. Table 2 lists the DMS fluxes from the Indian Ocean both on a seasonal and regional basis. Average DMS fluxes were higher in the northeast

monsoon than in other seasons both in coastal and open Arabian Sea regions. During the intermonsoon period, open Arabian Sea fluxes were nearly half of that in winter. Comparatively low winds were found when the measurements were made in coastal waters of the Arabian Sea in summer monsoon. The annual coastal mean DMS flux was $3.4 \mu\text{mol m}^{-2} \text{d}^{-1}$ while the open ocean mean flux was $3.8 \mu\text{mol m}^{-2} \text{d}^{-1}$ resulting in an average flux from the Arabian Sea of $3.5 \mu\text{mol m}^{-2} \text{d}^{-1}$. The fluxes estimated here for the Arabian Sea have to be considered to be low since our coverage is limited to central and eastern parts and excluded regions of strong winds during the southwest monsoon. Fluxes in the Bay of Bengal were higher in the SW monsoon than in intermonsoon. Higher fluxes (average of $11.1 \mu\text{mol m}^{-2} \text{d}^{-1}$) during the BOB-MEX time series experiment resulted from the enhanced production of surface DMS due to increased biological activity triggered by turbulent conditions and strong winds associated with the low-pressure system. A large variability in flux at this time-series location is seen in Fig. 10. In the central Indian Ocean the DMS flux varied between 0.06 and $29.1 \mu\text{mol m}^{-2} \text{d}^{-1}$ with an average value of $3.5 \mu\text{mol m}^{-2} \text{d}^{-1}$. Thus the Bay of Bengal exhibited the maximal DMS fluxes

during the present study (due to the prevailing low pressure systems) with nearly three times to that in the Arabian Sea and in the central Indian Ocean. The overall DMS flux for the entire Indian Ocean is estimated to be $5.42 \mu\text{mol m}^{-2} \text{d}^{-1}$. Table 3 shows a comparison between the DMS flux from the Indian Ocean (this study) with those estimated for other regions. It is evident that flux from the Indian Ocean is higher than in many regions of the world Oceans, e.g., the north Pacific, the Atlantic, the North Sea and the Arctic Polar Ocean, but is lower than that reported for the northeast Pacific Ocean. The only DMS estimate for the Indian Ocean, available from the earlier studies, is that of Nguyen et al. (1990) near Amsterdam Island situated near 38°S , which is nearly one-half of that in the present work. However, our flux estimate agrees well with that made by Yang (2000) for the South China Sea. In the present study an area of around $16.1 \times 10^6 \text{ km}^2$ was covered for DMS and DMSP_t study, which is about 21.5% of the total Indian Ocean area or around 4.5% of the global oceanic area. The total flux of DMS from the study area was estimated to be $1.02 \times 10^{12} \text{ g S y}^{-1}$. This works out to contribute 4.1–6.3% to the global DMS emission, which has a range of $16\text{--}25 \times 10^{12} \text{ g S y}^{-1}$. One of the

Fig. 10 Variations in DMS flux in the Indian Ocean. Time series station (SK147A & B) in the Bay of Bengal depicts wide variations in the DMS flux

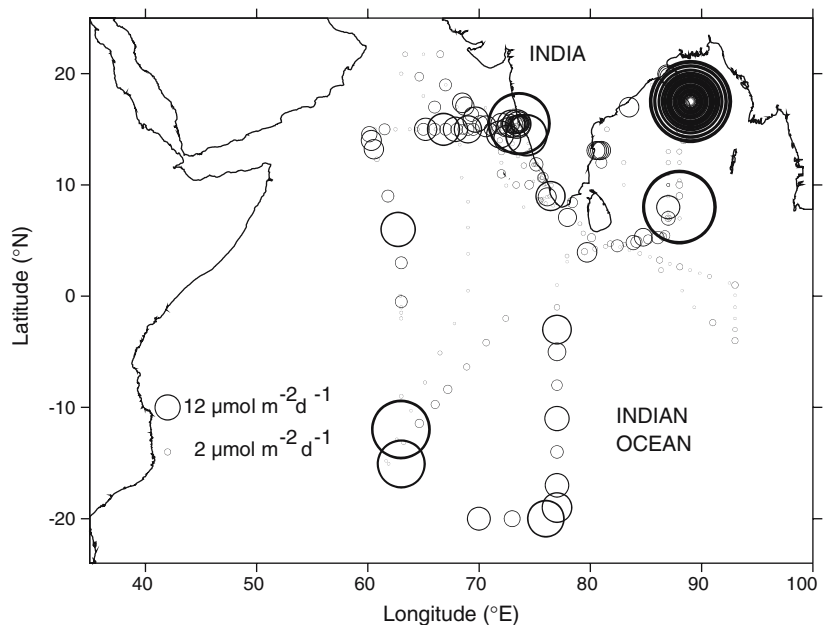


Table 2 Sea-to-air fluxes of DMS ($\mu\text{mol S m}^{-2} \text{d}^{-1}$) in the Indian Ocean*

Area/season	Coastal ocean			Open ocean			Total		
	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
<i>Arabian Sea</i>									
NE monsoon	0.05	34.4	4.7	0.03	16.8	4.2	0.03	34.4	4.3
SW monsoon	0.04	31	2.6	–	–	–	0.04	31	2.6
Intermonsoon	0.1	13.1	3.9	0.4	3.1	1.6	0.1	13.1	3.13
Average	0.04	34.4	3.4	0.03	16.8	3.8	0.03	34.4	3.5
<i>Bay of Bengal</i>									
SW monsoon	0.18	9.03	3.7	0.4	41.1	11.5	0.18	41.1	11.1
Intermonsoon	–	–	–	0.16	10.9	1.63	0.16	10.9	1.63
Average				0.16	41.1	11.02	0.16	41.1	9.63
<i>Central Indian Ocean</i>									
NE monsoon				0.06	29.1	3.5	0.06	29.1	3.5
Average				0.06	29.1	3.5	0.06	29.1	3.5
Indian Ocean	0.04	34.4	3.4	0.03	41.1	6.3	0.03	41.1	5.42

*Wherever data are not available for coastal/open ocean regions or seasons the available values were assumed to represent the same in other regions/seasons in deriving average fluxes

Table 3 Comparison of DMS fluxes from the Indian Ocean (this study) with that from other oceanic regions

Source	Area	Average flux, $\mu\text{mol S m}^{-2} \text{d}^{-1}$
Wong et al. (2005)	Northeast Pacific Ocean	16
Sharma et al. (1999)	North Pacific Ocean	2.3
Berresheim et al. (1991)	Western North Atlantic Ocean	3.4
Turner et al. (1996)	North Sea	3.84
Leck and Persson (1996)	Arctic Polar Ocean (summer)	2.0
Nguyen et al. (1990)	Amsterdam Island (Indian Ocean, 38°S)	2.1
Yang (2000)	South China Sea	5.5
Yang et al. (2000)	East China Sea	3.4
Present study	Arabian Sea	3.5
	Bay of Bengal	9.63
	Central Indian Ocean	3.5
	Indian Ocean (total)	5.42

limitations of the study is the lack of coverage of certain important areas in the Indian Ocean such as the intense upwelling zones off the coast of Somali and Oman, the east coast of Africa, the west coast of the Indonesian Islands and the south Indian Ocean. Considering the fact that this study covered only 21.5% of the total Indian Ocean, the Indian Ocean could be an important source for DMS sulphur to the atmosphere. It should, however, be cautioned that the flux trends observed among various basins in the Indian Ocean studied here may be different from that expected since we occupied the Bay of Bengal (BOBMEX) and Central Indian Ocean (INDO-EX) under turbulent conditions but could not

cover high-wind regimes in the Arabian Sea during the southwest monsoon.

Conclusions

Significant spatial and temporal variability in DMS was found in the north and central Indian Ocean. Very high DMS and DMSP of 526 nM and 916 nM, respectively, were found in coastal waters of the Arabian Sea. These are among the highest values found in the world oceans. In the Arabian Sea the lowest DMS and DMSP_t concentrations were observed during the intermonsoons. Lower DMS and DMSP_t concentrations

were found to occur in the Bay of Bengal compared to that in the Arabian Sea which might have been due to relatively less biological production and trophic diversity in the bay, as also can be seen from generally lower DMSP_t levels in the bay. Average surface DMS is the highest in the Arabian Sea whereas the average flux is the highest from the Bay of Bengal. DMS from the study area was found to contribute 4–6% to the total global emission, which is comparable to other regions of the world. Export fluxes of sulphur compounds from the Indian Ocean are important since this is one of the most turbulent regions, with regular occurrence of monsoons.

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References

- Barnard WR, Andreae MO, Watkins WE, Bingemer H, Georgii HW (1982) The flux of dimethylsulfide from the oceans to the atmosphere. *J Geophys Res* 87C:8787–8793
- Behrenfeld MJ, Falkowski PG (1997) Photosynthetic rates derived from satellite-based chlorophyll concentration. *Limnol Oceanogr* 42(1):1–20
- Berresheim H, Andreae MO, Iverson RL, Li SM (1991) Seasonal variations of dimethylsulfide emissions and atmospheric sulfur and nitrogen species over the western north Atlantic Ocean. *Tellus* 43:353–372
- Bhattachiri PMA, Pant A, Sawant S, Gauns M, Matondkar SGP, Mohanraju R (1996) Phytoplankton production and chlorophyll distribution in the eastern and central Arabian Sea in 1994–95. *Curr Sci* 71:857–862
- Charlson RJ, Lovelock JE, Andreae MO, Warren SC (1987) Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* 326:655–661
- Charlson RJ, Anderson TL, McDuff RE (1992) The sulfur cycle. In: Butcher SS, Charlson RJ, Orians GH, Wolfe GV (eds) *Global biogeochemical cycles*. Academic Press, London, pp 285–300
- Dacey JWH, Wakeham SG (1986) Oceanic dimethyl sulfide: production during zooplankton grazing on phytoplankton. *Science* 233:1314–1316
- Hastenrath S, Lamb PJ (1979) *Climatic atlas of the Indian Ocean*. University of Wisconsin Press, Wisconsin 19 + 97 charts
- Hatton AD, Malin G, Liss PS (1999) Distribution of biogenic sulphur compounds during and just after the southwest monsoon in the Arabian Sea. *Deep Sea Res II* 46:617–632
- Iverson RL, Nearhoof FL, Andreae MO (1989) Production of dimethyl-sulfonium propionate and dimethyl-sulfide by phytoplankton in estuarine and coastal waters. *Limnol Oceanogr* 34:53–67
- Kettle AJ et al (1999) A global database of sea surface dimethyl sulphide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude and month. *Global Biogeochem Cycles* 13:399–444
- Kirst GO, Thiel CH, Wolff J, Nothnagel M, Wanzek R, Ulmke (1991) Dimethyl-sulfoniopropionate (DMSP) in ice-algae and its possible biological role. *Mar Chem* 35:381–388
- Kumar MD, Shenoy DM, Sarma VVSS, George MD, Dandekar M (2002) Export fluxes of dimethylsulfoniopropionate and its break down gases at the air-sea interface. *Geophys Res Lett* 29(2):10.1029/2001GL013967. 8-1 to 8-3
- Leck C, Persson C (1996) Seasonal and short-term variability in dimethyl sulfide, sulfur dioxide and biogenic sulfur and sea salt aerosol particles in the arctic marine boundary layer during summer and autumn. *Tellus* 48B:272–299
- Liss PS, Malin G, Turner SM (1993) Production of DMS by marine phytoplankton. In: Restelli G, Angeletti G (eds) *Dimethyl sulphide: Oceans, atmosphere and climate*. Kluwer Academic, Dordrecht, pp 1–14
- Lovelock JE, Maggs RJ, Rasmussen RA (1972) Atmospheric dimethyl sulphide and the natural sulphur cycle. *Nature* 237:452–453
- Moret I, Gambaro A, Piazza R, Barbante C, Andreoli C, Corami F, Scarponi G (2000) The seasonal variations of dimethyl sulphide and carbon disulphide in surface waters of the Venice lagoon. *Mar Chem* 71:283–295
- Naqvi SWA, Jayakumar RA, Narvekar PV, Naik H, Sarma VVSS, D'souza W, Joseph S, George MD (2000) Increased marine production of N₂O due to intensifying anoxia on the Indian continental shelf. *Nature* 408:346–349
- Nguyen BC, Mihalopoulos N, Belviso S (1990) Seasonal variation of atmospheric dimethylsulphide at Amsterdam Island in the southern Indian Ocean. *J Atmos Chem* 11:123–141
- Nguyen BC, Mihalopoulos N, Putaud JP, Gaudry A, Gallet L, Keene WC, Galloway JN (1992) Covariations in oceanic dimethyl sulfide, its oxidation products and rain acidity at Amsterdam Island in the Southern Indian Ocean. *J Atmos Chem* 15:39–53

- Saltzman ES, King DB, Holmen K, Leck C (1993) Experimental determination of the diffusion coefficient of dimethylsulfide in water. *J Geophys Res* 98C:16481–16486
- Sharma S, Barrie LA, Plummer D, McConnell JC, Brickell PC, Levasseur M, Gosselin M, Bates TS (1999) Flux estimation of oceanic dimethyl sulfide around North America. *J Geophys Res* 104D:21327–21342
- Shenoy DM, Kumar MD, Sarma VVSS (2000) Controls of dimethyl sulphide in the Bay of Bengal during BOBMEX Pilot Cruise 1998. *Proc Indian Acad Sci (Earth Planet Sci)* 109:279–283
- Shenoy DM, Joseph S, Dileep Kumar M, George MD (2002) Control and inter-annual variability of dimethyl sulfide in Indian Ocean. *J Geophys Res* 107: 10.1029/2001JD000371
- Shenoy DM, Patil JS (2003) Temporal variations in dimethylsulphonio-propionate and dimethyl sulphide in the Zuari estuary, Goa (India). *Mar Environ Res* 56/3:387–402
- Stefels J (2000) Physiological aspects of the production and conversion of DMSP in marine algae and higher plants. *J Sea Res* 43:183–197
- Sunda W, Kieber DJ, Kiene RP, Huntsman S (2002) An antioxidant function for DMSP and DMS in marine algae. *Nature* 418:317–320
- Turner SM, Malin G, Bagander LE, Leck C (1990) Inter-laboratory calibration and sample analysis of dimethyl sulfide in water. *Mar Chem* 29:47–62
- Turner SM, Malin G, Nightingale GD, Liss PS (1996) Seasonal variation of dimethyl sulphide in the North Sea and an assessment of fluxes to the atmosphere. *Mar Chem* 54:243–262
- Uher G, Schebeske G, Barlow RG, Cummings DG, Mantoura RFC, Rapsomanikis SR, Andreae MO (2000) Distribution and air-sea gas exchange of dimethyl sulphide at the European western continental margin. *Mar Chem* 69:277–300
- UNESCO (1994) Protocols for the Joint Global Ocean Flux Study (JGOFS). Core Measurements, Scientific committee on Oceanic Research Manual and Guides 29:170
- Vairavamurthy A, Andreae MO, Iverson RL (1985) Biosynthesis of dimethylsulfide and dimethylpropiothetin by *Hymenomonas carterae* in relation to sulfur source and salinity variations. *Limnol Oceanogr* 30:59–70
- Wolfe GV, Steinke M (1996) Grazing-activated production of dimethyl sulfide (DMS) by two clones of *Emiliania huxleyi*. *Limnol Oceanogr* 41:1151–1160
- Wolfe GV, Steinke M, Kirst GO (1997) Grazing-activated chemical defence in a unicellular marine alga. *Nature* 387:894–897
- Wong CS, Wong SE, Richardson WA, Smith GE, Arychuk MD, Page JS (2005) Temporal and spatial distribution of dimethylsulfide in the subarctic northeast Pacific Ocean: a high-nutrient-low-chlorophyll region. *Tellus* 57B:317–331
- Yang GP (2000) Spatial distributions of dimethylsulfide in the South China Sea. *Deep Sea Res I* 47:177–192
- Yang GP, Cong XD, Zhang ZB, Zhao W (2000) Dimethylsulfide in the South China Sea. *Chin J Oceanol Limnol* 18:162–168