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Variation of biogenic sulphur compounds in the estuarine and coastal waters of Goa, West coast of India

S G Borker[a,b], D M Shenoy*[,a], K F Bepari[a], S Kurian[a] & H Uskaikar[a]

[a]CSIR - National Institute of Oceanography, Chemical Oceanography Division, Dona Paula, Goa – 403 004, India
[b]School of Earth, Ocean and Atmospheric Sciences, Goa University, Taleigao Plateau, Goa – 403 206, India

*[E-mail: dmshenoy@nio.org]

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Dimethylsulphide (DMS) originates predominantly from dimethylsulphoniopropionate (DMSP), a metabolite produced by phytoplankton. Through its contribution to the production of new aerosols and cloud condensation nuclei, a high concentration of DMS has the potential to influence the radiation budget of the earth. Estuaries and coastal regions being dynamic may produce significantly high concentrations of DMS and DMSP. The present study aimed to investigate the spatial variation of DMS, its precursor total dimethylsulphoniopropionate ($DMSP_t$), and its sink total dimethylsulphoxide ($DMSO_t$) at 7 estuarine locations in 4 rivers and a coastal station in Goa during the North East Monsoon (NEM). Generally, higher concentrations of DMS and $DMSP_t$ were observed at the near mouth stations and the coastal station compared to upstream stations. Though a positive correlation was observed between salinity and $DMSP_t$, it was not significant, indicating the involvement of other factors influencing DMSP and DMS concentrations. Diatoms were the most abundant group accounting for > 90 % of the phytoplankton. However, higher fractions of dinoflagellates, nano- and picoplankton probably contributed to the $DMSP_t$, DMS and $DMSO_t$ production at the coastal and near mouth stations. As the wind speeds were low, DMS flux was governed by surface DMS concentrations and varied between 0.07 and 2.11 µmoles S m^{-2} D^{-1} with an average of 0.92±0.80 µmoles S m^{-2} D^{-1}. In comparison to $DMSP_t$ and DMS, a relatively higher concentration of $DMSO_t$ was observed in the study area. While the high $DMSO_t$ concentration at the estuarine mouths may be attributed to the photo- or biological oxidation of DMS, those in the upper reaches point to an unknown source and warrants further investigation.

[**Keywords**: Coast, DMS, $DMSP_t$, $DMSO_t$, Estuary, Phytoplankton, Salinity]

Introduction

The ocean is the primary source of DMS, a volatile natural sulphur gas emanating into the atmosphere during air-sea interactions. Its oxidation in the atmosphere contributes significantly to the formation of non-sea-salt (nss) sulphate aerosols and secondary particulate matter over the oceans[1]. Aerosols cool the earth by reflecting the incoming solar radiation and increase the earth's albedo through cloud formation[2]. Through this participation, DMS plays an essential role in the radiation balance of the earth. DMS is produced as a result of biological processes involving marine phytoplankton[3,4] and is estimated to account for approximately 60 % of the total marine sulphur gas released to the atmosphere[5]. Its synthesis in phytoplankton is species-specific, with coccolithophores producing more DMSP than dinoflagellates and diatoms[6,7].

Oceanic DMS emission is estimated to be about 24 − 27 Tg(S)/yr[8]. Some of the highest concentrations of DMSP and DMS were observed in temperate and polar zones during spring and summer in association with blooms of *Phaeocystis* and dinoflagellates[9,10]. On the other hand, diatoms which bloom during spring in the temperate regions do not produce large amounts of DMSP and DMS[4]. Similar is the case in the tropics during high productivity conditions, where diatoms dominate[11,12] but lack DMS production. DMS production is also governed by other factors such as zooplankton grazing[13], viral lysis of phytoplankton cells[14] and stage of phytoplankton cell[7]. Only a small fraction of DMS is transferred to the atmosphere, while a significant portion of DMS is converted to DMSO by photochemical and bacterial oxidation[15,16]. Estuaries are dynamic zones connecting the land and the ocean, facilitating the exchange of materials between the river and the shelf systems. Both natural and anthropogenic conditions influence these zones. Prime among the natural conditions is the influence of salinity, which vary over tides and with seasons. This often induces blooms of phytoplankton and, in turn, the production of DMSP and DMS. A positive

correlation of DMSP with salinity has been observed in the tropical and temperate estuaries highlighting the role of DMSP in osmoregulation in algal cells[17,18]. A high concentration of DMSP, DMS and DMSO has been reported from tropical and temperate estuaries during spring and summer[11,19]. Also, diel variations in DMSP and DMS have been observed in estuaries depending on light availability and plankton migration[20]. While studies on biogenic sulphur compounds are available from estuaries, these are limited considering these systems' dynamic nature. The present study was carried out during the NEM from 7 different estuarine locations in Goa and at a coastal station (off Goa) with an aim to assess the spatial variation of $DMSP_t$, DMS and $DMSO_t$ in the estuarine and coastal waters of Goa during the NEM.

Materials and Methods

Study area

The sampling was carried out from December 2015 – February 2016 (NEM) at eight stations comprising four distinct zones; coastal (CaTS-G5), near mouth (Z1, M1, Cutbona Jetty and Chapora Jetty), mid estuary (Chorao Island) and upstream (Z7 and M6) stations as detailed in Table 1 (Fig. 1). CaTS-G5, which is located ~12 km off Goa, is influenced by fishing activity. Near the mouth, stations are affected by the tidal change and marine and fishing movement with human settlement around its banks. The mid-estuary station is located on a mangrove island. In contrast, the upstream stations are situated in the Zuari and the Mandovi estuaries' upper reaches, having strong freshwater influence sourced from the Western Ghats.

Sampling and analysis

Temperature and salinity were logged using a portable CTD unit (SeaBird Scientific SBE25 plus V2). Water samples were collected using a 5 L Niskin

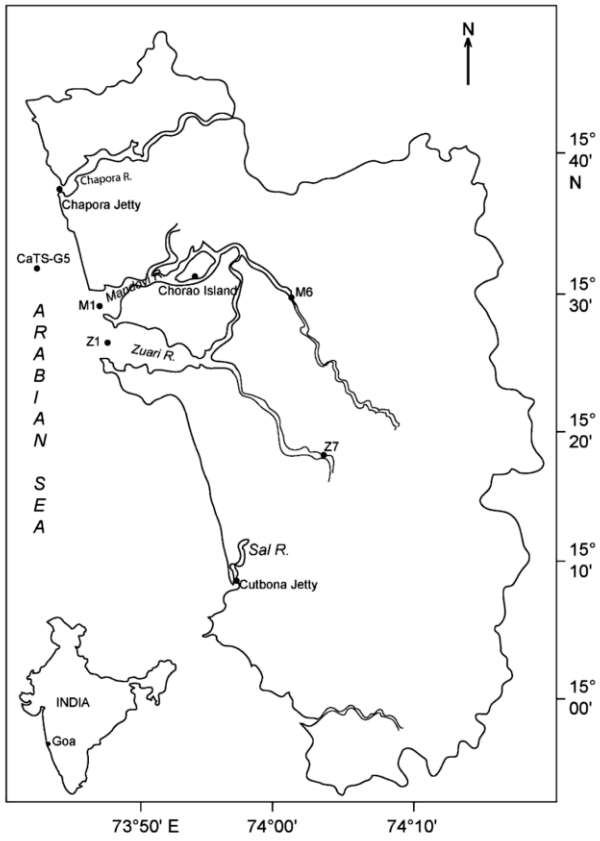

Fig. 1 — Station locations in the study area: Candolim Time Series station (CaTS G5), Z1 - mouth of Zuari Estuary, M1 - mouth of Mandovi Estuary, Cutbona Jetty, Chapora Jetty, Chorao Island, Z7 - upstream station of Zuari River, and M6 - upstream station of Mandovi River

Table 1 — Details of estuarine and coastal stations sampled during the study

Zones	Stations	Date	Time	Sampling depths	Latitude	Longitude	Tide
Coastal station	CaTS-G5	17/12/15	11:30 AM	1 m (Surface)	15°30.109' N	73°38.681' E	High
		17/12/15	11:30 AM	27 m (Bottom)	15°30.109' N	73°38.681' E	High
Near-mouth stations	Z1	15/12/15	07:05 AM	1 m (Surface)	15°26.338' N	73°47.847' E	Low
		15/12/15	07:05 AM	3.5 m (Bottom)	15°26.338' N	73°47.847' E	Low
	M1	16/12/15	07:10 AM	1 m (Surface)	15°28.449' N	73°47.083' E	Low
		16/12/15	07:10 AM	8 m (Bottom)	15°28.449' N	73°47.083' E	Low
	Cutbona Jetty	15/01/16	12:40 PM	1 m (Surface)	15°09.242' N	73°57.176' E	High
		15/01/16	12:40 PM	4 m (Bottom)	15°09.242' N	73°57.176' E	High
	Chapora Jetty	22/01/16	11:20 AM	1 m (Surface)	15°36.531' N	73°44.328' E	High
		22/01/16	11:20 AM	4 m (Bottom)	15°36.531' N	73°44.328' E	High
Mid-estuary station	Chorao Island	12/02/16	01:30 PM	1 m (Surface)	15°30.493' N	73°51.498' E	High
		12/02/16	01:30 PM	3.5 m (Bottom)	15°30.493' N	73°51.498' E	High
Upstream stations	Z7	15/12/15	12:30 PM	1 m (Surface)	15°16.151' N	73°16.253' E	High
		15/12/15	12:30 PM	4 m (Bottom)	15°16.151' N	73°16.253' E	High
	M6	16/12/15	12:00 PM	1 m (Surface)	15°30.119' N	73°59.985' E	High
		16/12/15	12:00 PM	10 m (Bottom)	15°30.119' N	73°59.985' E	High

sampler (Ocean Test Equipment) from the surface and bottom (Table 1). Sub-samples were collected for dissolved oxygen (DO), DMS, $DMSP_t$, $DMSO_t$, nutrients, Chlorophyll (Chl) *a*, phytoplankton pigments, phytoplankton taxonomy and abundance. Extreme care was taken while collecting dissolved gases to avoid any atmospheric exchange, and these samples were analyzed within 4 h of collection. DO was fixed immediately upon collection and analyzed later in the laboratory following the Winkler titration method as detailed in Grasshoff[21]. Nutrient (nitrate, phosphate and silicate) samples were frozen at -20 °C and later analyzed using a Skalar autoanalyzer, with a precision of 0.8, 1.8 and 1.5 %, respectively. 1 L of water sample was filtered through Whatman GF/F (0.7 µm) filter under low light conditions for Chl-*a*, and analyzed using 10-AU TURNER Fluorometer[22].

For pigment analysis, 500 mL of water sample was filtered using GF/F (0.7 µm) filter paper under low light conditions and stored at -80 °C until analysis. Samples were later run for pigments on an HPLC (Agilent Technologies) following the modified method of Van Heukelem[23], as detailed in Kurian[24]. Phytoplankton samples were collected in 250 mL amber-coloured plastic bottles and preserved using 2 mL of Lugol's Iodine Solution. 1 mL of sample was taken on a Sedgewick rafter counting chamber and counted using an inverted microscope (Olympus IX51) at 200X magnification. Phytoplankton was identified to the generic/species level following established identification keys.

Biogenic sulphur compounds (DMS, $DMSP_t$ and $DMSO_t$)

Biogenic sulphur compounds were analyzed using the purge and trap method as detailed in Shenoy[25]. A Shimadzu Gas Chromatograph (GC-2010) fitted with a Flame Photometric Detector (FPD) was used for the analysis. A known volume of sample (generally 10 mL) was purged using dry nitrogen for 15 min at the rate of 60 mL min^{-1}. Further, the stripped sulphur gases were passed through a series of moisture traps (ice bath, Nafion tubing and calcium chloride) to render the gas stream moisture-free. The stripped gases were then trapped on a Teflon loop suspended in liquid nitrogen kept at a controlled temperature of -145 °C. After 15 min of purging, the stripped gases were released by submerging the loop in near-boiling water and injected into the GC using a 6-port gas sampling valve. The gaseous mixture was separated using a Chromosil-330 column (kept at 45 °C) under a carrier gas flow rate of 35 mL min^{-1} and detected using the FPD. Under these conditions, the retention time of DMS was 1.9 min. Following DMS analysis, 1 mL of 10 M NaOH was added to the same sample and purged for 20 min to convert the $DMSP_t$ to DMS and analyzed as above. Following $DMSP_t$, $DMSO_t$ was analyzed by reducing it to DMS by adding 0.3 – 0.5 g of $NaBH_4$ to the same sample and purging for 20 min. The GC was calibrated using DMSP standards (Santa Cruz Biotechnology, Asia), which gave a precision ranging from 1 to 1.5 % for the DMSP standards. For natural samples, a precision of 2.8, 13.8 and 17.5 % were obtained for DMS, $DMSP_t$ and $DMSO_t$, respectively (n =10).

DMS flux

DMS flux was calculated following the Turner method[26] using correction factors given by Saltzman[27] as per the following equation:

$$F_{DMS} = k.\ \Delta C$$

Where, F_{DMS} = net flux of DMS; k = transfer (or piston) velocity; and ΔC = concentration gradient across the air-sea interface.

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

Where, C_w = concentration of DMS in seawater; C_a = concentration of DMS in air; and h = Henry's Law constant expressed as the ratio of air to water concentrations at equilibrium.

As the concentration of DMS in the air is very low, C_a is considered to be zero[26], and thus, C_w equals ΔC.

Results and Discussion

Hydrographic, chemical and biological variability

As the sampling was done during the NEM, a temperature inversion was generally observed in the morning hours due to surface cooling. During the present study, the temperature ranged between 26.0 and 30.2 °C (Fig. 2a), with an average temperature of 28.5±1.3 °C. Temperature inversions were observed in the Mandovi and the Zuari estuaries at the near mouth stations, as these stations were sampled during the early morning hours and low tide. In contrast, high temperatures (max. 30.2 °C) were recorded at the upstream stations, which were sampled during the latter half of the day. On the contrary, the lowest temperature (26 °C) detected in Chapora Jetty may be attributed to sampling before noon. Intriguingly, salinity did not show much variation at most of the stations, except at the upstream stations (Z7 and M6),

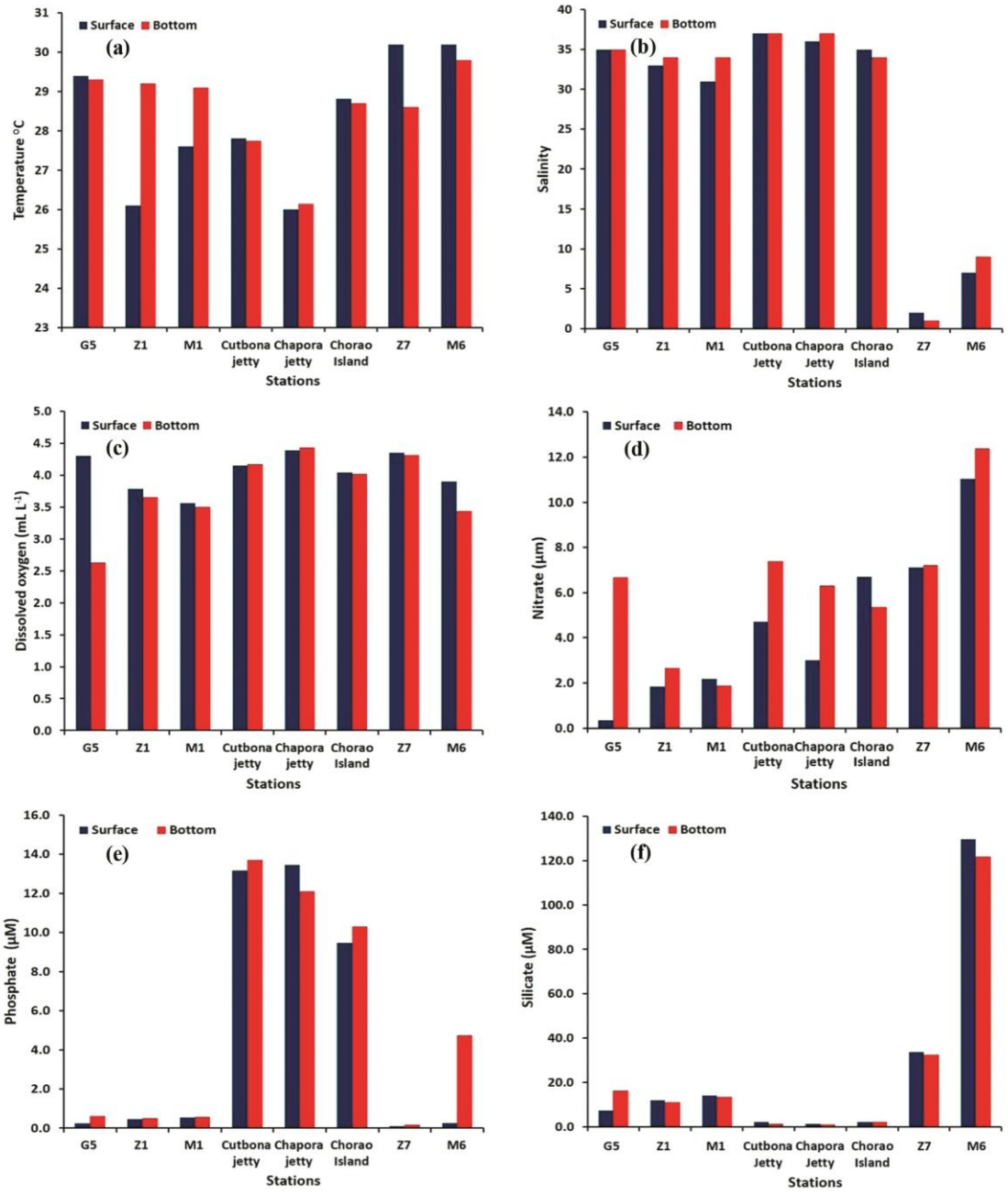

Fig. 2 — Variation of a) temperature, b) salinity, c) dissolved oxygen, d) nitrate, e) phosphate, and f) silicate in the study region

where low salinities (< 10) were observed due to the freshwater runoff from the Western Ghats and also as these stations were beyond the influence of the high tides (Fig. 2b).

All eight stations remained well oxygenated during the study period, with DO concentrations ranging between 2.6 and 4.4 mL L^{-1} (Avg 3.9±0.5 mL L^{-1}) (Fig. 2c). The low concentration in the bottom waters at the coastal station was possibly due to the remineralisation of organic matter[28]. This station had the maximum depth in the study. The relatively lower DO near the river mouth stations Z1 (Avg. 3.7 mL L^{-1}) and M1 (Avg. 3.5 mL L^{-1}) compared to the other two (Cutbona and Chapora Jetty) may be ascribed to high overnight biological respiration[29] and the availability of organic matter in these estuaries[28], as these waters were sampled during the early morning period, whereas the rest of the stations were collected in the afternoon. Nitrate concentrations in the study area varied between 0.4 and 12.4 µM (Avg. 4.9±3.5 µM).

While higher concentrations (7 – 12 µM) were observed in the upstream stations, moderate concentrations (2 – 5 µM) were seen at the rest of the stations (Fig. 2d). The phosphate concentrations (Fig. 2e) in the study area varied between 0.1 and 13.7 µM (Avg. 4.2±5.8 µM). Unusually high phosphate concentrations (9.5 – 13.7 µM; Fig. 2e) were detected at the two coastal jetties and the mangrove Island station, pointing to high biological activity at these stations. These stations also marked the lowest silicate concentrations (1 – 2.2 µM; Fig. 2f). The increased oxygen concentration at these stations was probably due to the shallow nature of these stations. On the other hand, the riverine runoff resulted in very high silicate concentrations (up to 130 µM) at the upstream stations (Fig. 2f).

Chl-*a* concentration in the study region varied between 0.3 and 5.6 µg L^{-1} (Avg 1.6±1.5 µg L^{-1}). Maximum Chl-*a* concentration was recorded at the mid estuarine station, whereas the minimum was seen at the near mouth station (M1; Fig. 3a). The high nutrient concentrations at the mid estuarine and the upstream stations probably supported the phytoplankton biomass there. On the other hand, the moderate nutrient concentrations at the rest of the stations supported the moderate Chl-*a* level (1 – 2 µg L^{-1}). Overall, the general distribution of Chl-*a* reflects the moderately productive nature of the study area during the NEM. The phytoplankton abundance ranged from 0.015 – 1.69×10^5 cells L^{-1} (Avg. $0.36\pm0.46\times10^5$ cells L^{-1}).

The phytoplankton population was dominated by diatoms accounting for ~ 90 % of the biomass. Maximum phytoplankton abundance was recorded at Chorao Island (Fig. 3b, Table S1), followed by Z7 and Chapora Jetty. The rest of the stations observed diatoms as a substantial contributor to the phytoplankton population, but the cell counts were low. A few stations (M1 and M6 surface and the CaTS-G5 station) showed dinoflagellates contributing up to 15 %, with *Ceratium* spp. as the most abundant dinoflagellate species.

$DMSP_t$ variability

Studies are available on the distribution of biogenic sulphur compounds from the coastal and open ocean environments[30]; however, reports on their variability from the estuarine environments are sparse, more so from the tropics. The present study was carried out during the NEM when the productivity was moderate. $DMSP_t$ exhibited significant spatial variability in the study region. The concentration of $DMSP_t$ varied between 1 and 37.8 nM (Avg. 14.1±10.7 nM, Fig. 4a). High concentrations of $DMSP_t$ were observed at the near mouth stations (Z1, M1, Chapora and Cutbona Jetty), followed by the coastal station (CaTS-G5), and the lowest observed in the upstream stations (Z7 and M6). The upstream stations (M6 and Z7) recorded low $DMSP_t$ concentrations of 1 nM and 1.5 nM, respectively, compared to the coastal and near mouth stations, where $DMSP_t$ concentrations ranged from 8.6 to 37.8 nM, respectively.

In temperate estuaries, production of DMSP mainly occurs during spring and summer coupled with the temperature rise and increase in algal biomass[19]. Although $DMSP_t$ is thought to be directly proportional to primary production, it usually does not correlate well with the concentration of Chl-*a*[31]. In the present study, $DMSP_t$ concentrations did not correlate with the concentration of Chl-*a* (Fig. 5, R^2 = 0.024, n = 30), emphasizing species-specific DMSP

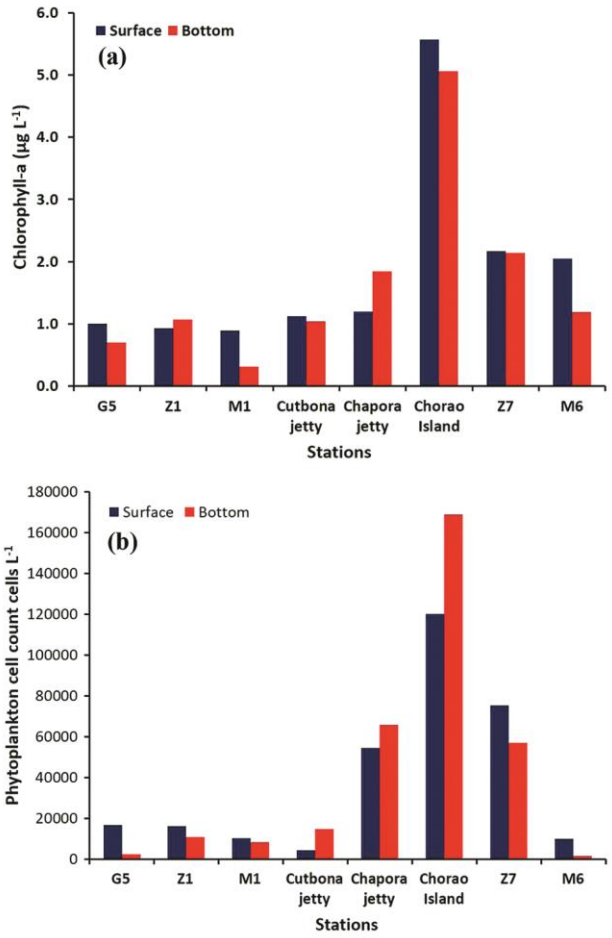

Fig. 3 — Variation of a) Chlorophyll-*a*, and b) phytoplankton cell count in the study area

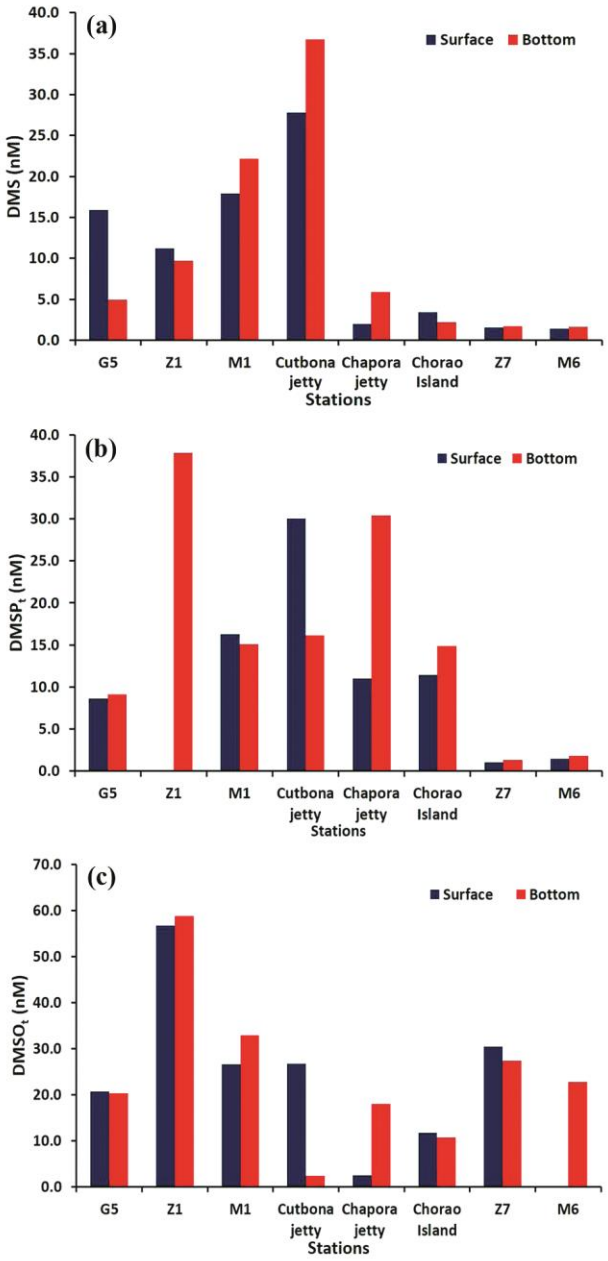

Fig. 4 — Variation of a) $DMSP_t$, b) DMS, and c) $DMSO_t$ in the study region. $DMSP_t$ at Z1 (surface) and $DMSO_t$ M6 (surface) are unavailable

production[6]. The mid estuarine station recorded the maximum Chl-*a* concentration with the presence of diatom bloom of genera *Chaetoceros* and *Asterionellopsis*. Despite this, the $DMSP_t$ concentration was relatively lower. Diatoms are known to produce low $DMSP_t$ compared to dinoflagellates and coccolithophores[6,7], and thus the low $DMSP_t$ concentration despite high phytoplankton abundance at this station may be attributed to the

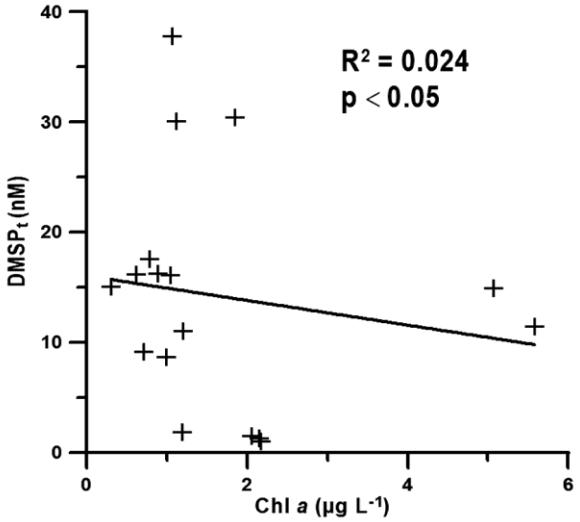

Fig. 5 — Correlation between $DMSP_t$ and Chl-*a* in the study region

dominance of diatoms in the phytoplankton population.

Conversely, the low $DMSP_t$ (Fig. 4a) at the upstream station (M6) may be due to the low phytoplankton numbers (Fig. 3b). It may, however, be noted that the $DMSP_t$ concentrations were generally higher at those stations where the salinity (Fig. 2b) was high (> 31), wherein the phytoplankton cells may be producing/ releasing DMSP to counter the impact of salinity via osmoregulation[32]. In comparison, in the marine environment, DMSP concentration varies spatially (shelf to the open ocean) and temporally (with seasonal blooms of phytoplankton), highlighting the importance of phytoplankton speciation in DMSP production. Thariath[33] conducted growth experiments on *Prymnesium simplex* (Prymnesiophyceae) to ascertain DMSP production under varying salinity conditions and reported higher production of DMSP at higher salinities. Though a positive correlation was observed between salinity and $DMSP_t$ in the present study indicating higher DMSP production with salinity increase (Fig. 6, R^2 = 0.47, n = 30), the correlation was not significant ($p > 0.05$), pointing to phytoplankton assemblage as the dominant controller of DMSP production.

In a study in the estuarine and coastal waters of Delaware Bay, Chesapeake Bay and Ochlockonee Bay, Iverson[34] described a general increase in the concentration of DMSP from the inner estuary towards the river mouth. Chl-*a* normalized DMSP revealed a positive correlation between salinity and DMSP, where DMSP concentrations increased

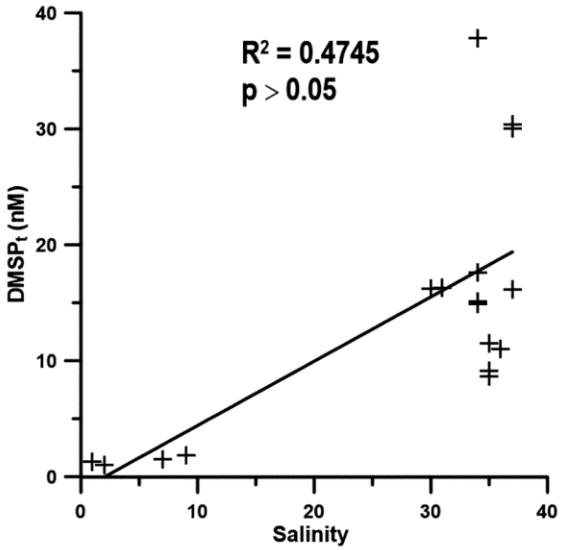

Fig. 6 — Correlation between $DMSP_t$ and salinity in the study region

nonlinearly from the inner estuary to coastal and shelf environments. However, the DMSP concentrations were also observed to fall from the shelf to the open ocean[34]. A similar correlation has also been reported in other estuaries[17,18]. The increase in DMSP was mostly seen from the low salinity part (upstream) toward the high salinity part of the estuary (mouth of the estuary). Thus, the positive correlation with salinity highlights the osmoregulatory role of DMSP in algal cells. Tides have also been reported to influence DMSP and DMS concentrations in estuaries[17]. A diel study conducted in the Elbe estuary, France, revealed higher concentrations of dissolved DMSP and DMS during the high tide in conjunction with higher salinity values[17].

Contrastingly, Kumar[20] detailed high concentrations of DMSP during the day compared to the night with no apparent connection to the tides. They attributed the variation of DMSP to biological variables rather than tides. In the present study, near-mouth stations were sampled early in the morning during the low tide, whereas the rest of the stations were sampled during the high tide, mostly in the afternoon (Table 1). Assessment of tides on the variation of $DMSP_t$ was however not possible in the present study due to sampling points' paucity.

Chemotaxonomy relations

Recent years have seen extended use of chemotaxonomy as a tool to understand phytoplankton taxonomy in natural waters. As all species of phytoplankton do not majorly produce Chl-*a*, and microscopy has a limitation with organisms (< 10 µm), marker pigments provide a unique insight into other species contributing to the phytoplankton population. In the present study, the concentrations of diadinoxanthin and fucoxanthin were high (Fig. 7a and b) at the mid estuarine and the upstream station (Z7), indicating an abundance of diatoms, which was also supported by the high concentration of silicate and nitrate (Fig. 2d and f). The pigment 19-hexanoyloxyfucoxanthin, indicative of nanoplankton, showed higher concentrations just as $DMSP_t$ at the rest of the stations compared to the upstream stations (Fig. 7d). Nanoplankton is known to grow well under high/moderate phosphate concentrations[35] and produce high concentrations of DMSP[4,7]. The high/moderate phosphate concentrations (Fig. 2e) observed in the bottom waters at the coastal station, near mouth stations, and the mid-estuarine station probably supported the nanoplankton population. The picoplankton (cyanobacteria) population, as seen from the zeaxanthin distribution, was observed to be higher in the coastal surface waters, the two jetties and the mid estuarine station (Fig. 7e). Except for the coastal, mid estuarine and upstream (Z7) stations, the rest of the stations had higher concentrations of peridinin (Fig. 7c), which is generally indicative of dinoflagellates and one of the high DMSP producers[6]. Thus, the high $DMSP_t$ concentrations observed at the coastal, near mouth and mid-estuarine stations may be attributed to the smaller forms (nanoplankton and picoplankton) and the dinoflagellate population at these stations contributing to higher DMSP production.

DMS variability

The DMS distribution exhibited a similar trend to that of $DMSP_t$ at all the stations and varied from 1.4 to 36.7 nM (Avg. 11.7±10.9 nM), except at the Chapora Jetty and Chorao Island (Fig. 4b), where DMS concentrations were lower as compared to the $DMSP_t$ concentration. Higher concentrations of DMS were recorded at the near mouth and coastal stations Z1 (10.5 nM), M1 (20.1 nM), Cutbona Jetty (32.3 nM) G5 (16.4 nM); (Fig. 4b). The high DMS concentrations may be assigned to the higher $DMSP_t$ observed at these stations. In contrast, the upstream stations M6 and Z7 recorded minimum DMS concentrations, 1.6 nM and 1.5 nM, respectively, matching the low $DMSP_t$. The lower DMS concentrations at Chorao Island and Chapora Jetty,

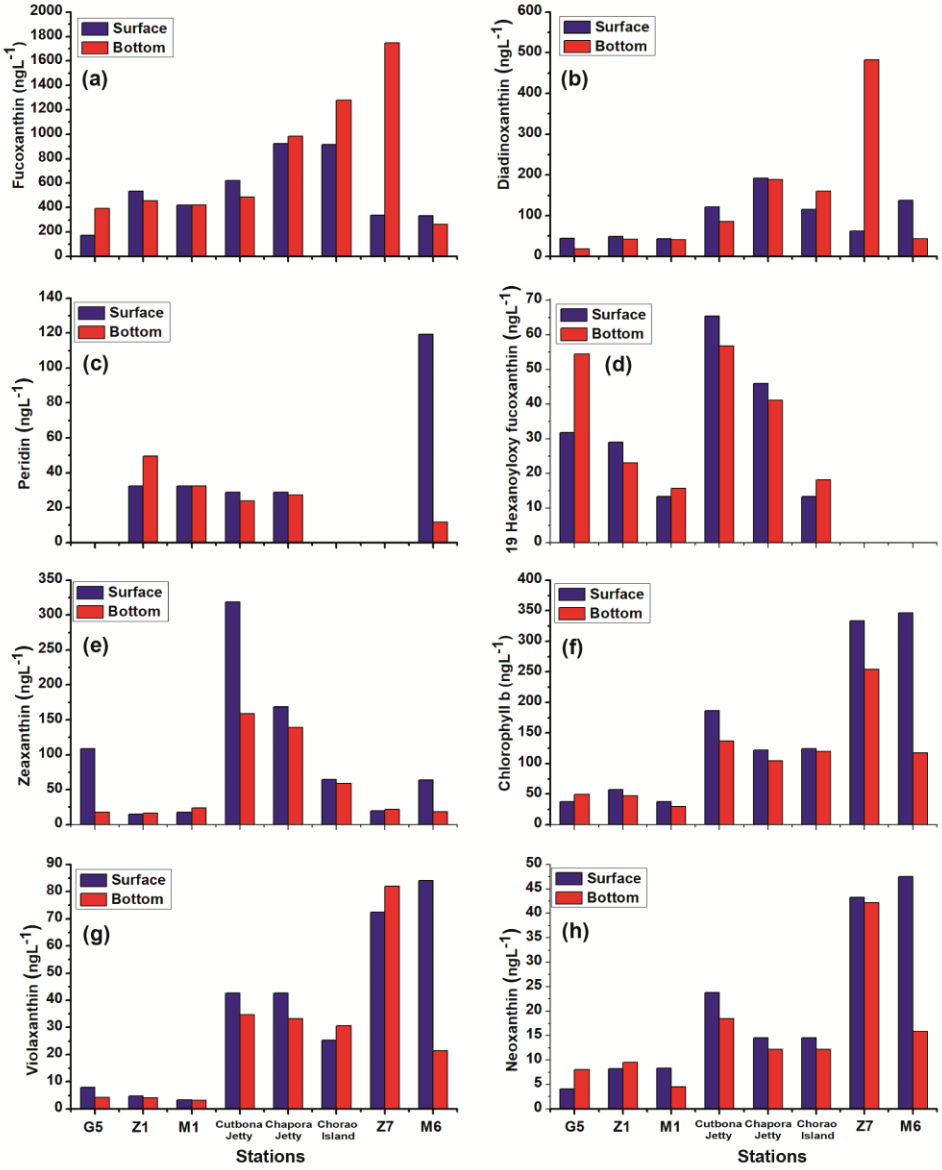

Fig. 7 — Variation of phytoplankton marker pigments: a) fucoxanthin, b) diadinoxanthin, c) peridinin, d) 19'-hexanoyloxyfucoxanthin, e) zeaxanthin, f) Chlorophyll-*b*, g) violaxanthin, and h) neoxanthin in the study region. Wherever values are not plotted the concentrations are below the detection limit

despite having modest concentrations of $DMSP_t$, may be ascribed to high biological activity resulting in the assimilation of DMSP[36]. While we have not measured the bacterial productivity at these stations, the higher phytoplankton cell counts (Fig. 3b) and the high nutrient concentrations (Fig. 3d, e and f) indicate the high biological activity at these stations[37]. Recent studies have shown that DMS can be estimated using a satellite-derived concentration of Chl-*a* and light penetration regimes, including PAR[38]. While Chl-*a* did not show any correlation with the concentration of DMS (data not shown), the dependency of DMS production on PAR could not be assessed as PAR data was not available.

DMSO variability

In general, $DMSO_t$ varied between 2.3 and 58.8 nM (Avg 24.3±15.3 nM), showing high variability with relatively higher concentrations at all the stations (Fig. 4c). Maximum $DMSO_t$ concentration was seen at the near mouth station Z1, whereas the minimum was found in the bottom waters of the Cutbona Jetty. While the highs and lows in $DMSP_t$ and DMS concentration in the study area can be explained in the light of phytoplankton speciation,

pigment distribution, and DMSP assimilation, the variation of $DMSO_t$ is complicated. The high concentration of $DMSO_t$ recorded at all the stations except the upstream stations may be due to the biological or photo-oxidation of DMS[15,39], coupled with a longer residence time of DMSO[40]. It may be noted that the $DMSO_t$ concentration at the near-mouth station (Z1) is more than five times the DMS concentration, which suggests rapid oxidation of DMS to DMSO.

Some phytoplankton species are known to produce DMSO within their cells, which can slowly diffuse out of the cell membrane into the surroundings[41]. This could also explain the high $DMSO_t$ seen at the coastal station, near-mouth station (Z1) and the two Jetty stations. The low $DMSO_t$ concentration at Chapora Jetty (surface) may be attributed to the low DMS concentration at this station. However, it was interesting to detect the high $DMSO_t$ concentration at the upstream stations without high $DMSP_t$ and DMS. A diatom bloom of *Thalassiosira* spp. was observed at Z7; there is only one report of high DMSO produced by this species, and that too under iron deplete conditions[42]. Though we did not measure dissolved iron, the study area is surrounded by laterite mountains, and the depletion of iron in the study area would hardly be the case. At the same time, the marker pigments such as violaxanthin, neoxanthin, and Chl-*b* indicate the presence of green algae at the upstream stations (Fig. 7). So far, no reports are available for DMSO production in green algae. Thus, the high $DMSO_t$ concentrations at the upstream stations point to an unknown source and warrant further investigation.

DMS Flux

The flux of DMS estimates the transfer of the gas from the sea surface to the atmosphere. The flux depends primarily on the gas concentration on the sea surface and the prevailing wind speed. Figure 8 depicts the surface DMS, wind speed and DMS flux in the study region. While the surface DMS varied between 1.4 and 27.8 nM, the wind speed varied between 1.1 and 3.1 m s^{-1}. The DMS flux in the study area during the NEM ranged from 0.07 to 2.11 µmoles S m^{-2} D^{-1} with an average of 0.92±0.80 µmoles S m^{-2} D^{-1}. The maximum flux was observed at the Cutbona Jetty followed by M1, G5 and Z1. Low DMS flux was observed at the rest of the stations. Figure 8 showed that during the NEM, the DMS flux primarily depended on the DMS concentration as the

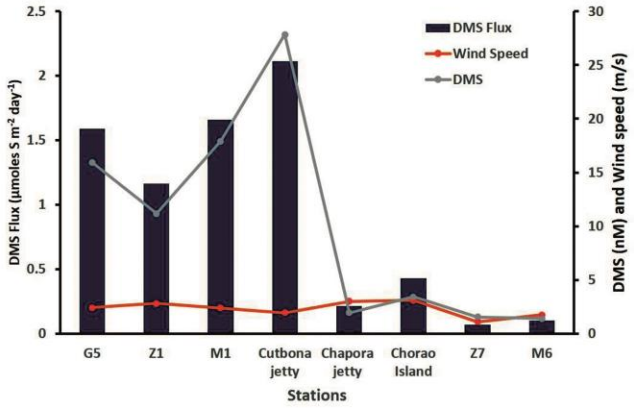

Fig. 8 — Variation of DMS Flux, DMS and Wind Speed in the study region

observed wind speeds were low. The average flux in the present study was comparable to the survey carried out by Shenoy[11] in the Zuari Estuary towards the end of the last century. It was comparable to the flux from some of the temperate estuaries[17,43], but much lower than the Pearl River in China[18]. The average flux was also much lower than the flux (4.7 µmoles S m^{-2} D^{-1}) reported by Shenoy[12] for the west coast of India and by Viswanadham[44] for the estuaries along the west coast of India (3.1±2.8 µmoles S m^{-2} D^{-1}) during the dry period.

Comparison with other studies

The average $DMSP_t$ and DMS in the study area were 14.1 nM and 11.7 nM, respectively. While the $DMSP_t$ in the present study was nearly five times lower than the surface $DMSP_t$, the DMS was more than double the surface DMS reported by Shenoy[11] for the Zuari Estuary. The high $DMSP_t$ observed by Shenoy[11] was attributed to the mixed bloom of diatoms and dinoflagellates during the wet season. In comparison, the present study was carried out during the moderately productive dry period wherein smaller forms (nanoplankton and picoplankton) probably contributed to the moderate DMSP. $DMSP_t$ from our study, however, was comparable with that of Kumar[20] in Dona Paula Bay (DMSP, 15.8 nM) during December, coinciding with a higher percentage of dinoflagellate.

On the other hand, Vishwanadham[44] reported an average DMS of 19.5 nM for the Mandovi and the Zuari estuaries during the dry period (January), which is higher than the concentration observed in our study. The above studies showcase the high spatial and temporal behaviour of $DMSP_t$ and DMS in tropical environments. Other reviews from the tropics with comparable results include the Pearl River estuary and

adjacent waters, which reported an average DMS concentration of 6.8 nM[18].

In comparison, $DMSP_t$ and DMS concentrations reported for the European estuaries were lower than in the present study. Sciare[17] reported an average DMS of 0.6 nM for 6 European estuaries. While they reported *Phaeocysis* and dinoflagellates in various estuaries at higher salinities, their average DMS concentration was low compared to our study. A recent study in the Changjiang Estuary, China[19] observed relatively higher concentrations of $DMSP_t$, DMS and $DMSO_t$ during summer, reporting an average of 14.4 nM, 2.2 nM and 31 nM, respectively. While the $DMSP_t$ and $DMSO_t$ are comparable to our study, our average DMS is nearly five times higher than the reported average DMS. Though limited, all studies, including the present one, showed an increase in DMSP and DMS concentration with salinity towards the mouth. While the temperate estuaries display high levels of DMSP, DMS and DMSO during spring and summer, the tropical estuaries depict high concentrations during the wet period. However, in both cases, phytoplankton speciation and bloom formation are essential contributors to the DMSP, DMS and DMSO pool. While the DMSO near the estuarine mouths/coastal region is probably due to biological or photo-oxidation of DMS, the high concentrations upstream may have a different source. There's also the possibility of an immediate release from phytoplankton or an alternate terrestrial source; however, this requires further investigation.

Conclusion

$DMSP_t$, DMS and $DMSO_t$ were measured in the estuarine and coastal waters of Goa to study their spatial variation during the NEM. Compared to the upstream stations, higher concentrations of $DMSP_t$ and DMS were observed in the coastal and near-mouth stations. While diatoms were the dominant phytoplankton species, a higher fraction of dinoflagellates and smaller phytoplankton probably contributed to the DMSP/DMS. DMS flux was mainly driven by its surface concentrations. While the high DMSO at the near-mouth stations may be attributed to biological or photo-oxidation of DMS, that in the upstream stations point to an unknown source warranting further investigation.

Data Availability Statement

The datasets generated during and/or analysed during the current study are available from the corresponding author upon reasonable request.

Supplementary Data

Supplementary data associated with this article is available in the electronic form at http://nopr.niscpr.res.in/jinfo/ijms/IJMS_51(06)517-528_SupplData.pdf

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Conflict of Interest

The authors declare that they have no conflict of interest.

Author Contributions

SB carried out sampling, analysis and wrote the manuscript, DMS helped in sample collection, analysis, and manuscript writing, KFB assisted in sample analysis, and SK provided pigment data and assisted in manuscript writing. HU provided nutrient data.

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