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Production of dimethylsulphide during the seasonal anoxia off Goa

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Abstract:

Subsurface waters over the western Indian continental shelf experience seasonal anoxia towards the end of the southwest monsoon season. During a 3-day study carried out at the Candolim Time Series site (off the coast of Goa), dimethylsulphide (DMS) concentrations showed a 40-fold increase to a maximum of 442 nM at 25 m depth compared to the oxygenated surface waters. This extremely high DMS was found to be associated with relatively low chlorophyll *a*, low phytoplankton cell counts and a high concentration of hydrogen sulphide. However, total dimethylsulphoniopropionate, total dimethylsulphoxide and methanethiol concentrations were quite low and unlikely to account for the DMS build-up through presently known pathways of DMS production. While there are several possible mechanisms for the observed accumulation of DMS, we were unable to pinpoint the exact pathway of DMS production. Future work will involve investigation of the source of DMS through sediment slurry experiments, to explore this interesting link between the carbon and sulphur cycles under anoxic conditions.

Introduction:

The oxidation of dimethylsulphide (DMS) in the atmosphere results in the formation of sulphate aerosols which reflects solar radiation (Ayers and Gras 1991; Leck and Bigg 2005; Charlson et al. 1987). These aerosols also act as cloud condensation nuclei upon which water vapour can condense and form cloud droplets. Thus DMS may play an important role in controlling the amount of incident radiation reaching the Earth's surface. The two major sulphate precursors are sulphur dioxide from anthropogenic activities and DMS from marine plankton (Bates et al. 1992). In the more pristine southern hemisphere, DMS accounts for 43% of the non-sea salt (nss) sulphate while over the northern hemisphere, where anthropogenic loading is greater, it accounts for only 9% of the nss sulphate (Gondwe et al. 2003). Nevertheless the ocean leaving DMS contributes in a major way to aerosol formation, cloud chemistry and radiation balance (Watts et al. 2000).

Dimethylsulphoniopropionate (DMSP), an osmolyte produced by phytoplankton is considered the major precursor of DMS in seawater (Vairavamurthy et al. 1985). The production of DMSP varies in different species of phytoplankton and prymnesiophytes and dinoflagellates generally produce more DMSP than diatoms (Liss et al. 1993). Phytoplankton blooms have often been reported with high concentrations of DMS and DMSP (Holligan et al. 1987; Malin et al. 1993; Simo et al. 2000; Stefels et al. 2000). In addition, high DMS concentrations have also been reported during the senescence of phytoplankton blooms and due to zooplankton grazing and viral attacks (Wolfe et al. 1997; Malin et al. 1998).

Most reports on the variation of DMS and DMSP have come from oxygenated surface waters. There are very few reports on the variation of biogenic sulphur species from low oxygen zones and anoxic basins. One of the first reports was from a coastal salt pond in Cape Cod, Massachusetts, where high concentrations of DMS were associated with the oxygen-deficient metalimnion during summer when the pond was thermally stratified (Wakeham et al. 1987). Kiene and Capone (1988) observed DMS production in anoxic salt marsh sediments after addition of methylated sulphur compounds (DMSP, DMSO, methionine, S-methyl cysteine, dimethyldisulphide and methanethiol). Various bacterial strains have been reported to reduce dimethylsulphoxide (DMSO) to DMS. Vogt and Fischer (1998) observed that a marine purple 'non-sulphur' bacterium strain reduced DMSO to DMS under anoxic conditions. Similarly, Jonkers et al. (1996) found that marine sulphate-reducing bacteria converted DMSO to DMS in anoxic conditions. More recently in experiments conducted on anoxic lake sediments, Lin et al. (2010)

observed that addition of bicarbonate and hydrogen promoted formation of DMS via a reductive process analogous to methanogenesis and enhanced methylation of methanethiol (MT). Similarly other experiments and incubations have reported methylation of MT and hydrogen sulphide (H₂S) to DMS indicating that methanogens might play an important role in thiol methylation and DMS formation (Stets et al. 2004; Moran et al. 2008). These examples highlight the need to study the connections between the carbon and sulphur cycles under anoxic conditions in detail. This is especially important in the light of the increasing importance of anoxic zones due to the influence of anthropogenic activities (Naqvi et al. 2006).

The seasonal anoxia observed during the end of the southwest (SW) monsoon on the eastern continental shelf of the Arabian Sea was first reported by Naqvi et al. (2000). The study revealed the intensification of a naturally occurring low oxygen zone resulting in the accumulation of high concentrations of H₂S and nitrous oxide in open coastal waters. This shelf has revealed the occurrence of high DMS concentrations during the seasonal anoxia (Shenoy and Kumar 2007). The aim of this study was to obtain high resolution data to better understand the formation of anoxia and its influence on DMS production.

Materials and methods:

A 3-day observation was carried out at station G5 (Figure 1), which is part of the Candolim times series transect, known in short as CaTS. The quasi-time series transect (CaTS) was established in 1997 and is located off the coast of Candolim, a coastal village in North Goa. The CaTS-G5 station, which has a depth of approximately 28 m, was occupied from 1340 hours on 25th September'09 until 1824 hours on 28th September'09 with sampling at consecutive high and low tides. In all 13 time points were sampled during the study period. Samples were taken from 0, 6, 12, 18 and 25 m. Sub-sampling was done for H₂S, dissolved oxygen (DO), biogenic sulphur compounds (DMS, total dimethylsulphoniopropionate (DMSP_t), total dimethylsulphoxide (DMSO_t) and MT), chlorophyll *a*, phytoplankton speciation and enumeration.

H₂S was analysed by the spectrophotometric method as suggested in Cline (1969). DO was analyzed by the classical Winkler titration method. Chlorophyll *a* was determined by filtering 1L of seawater through GF/F filters. Extraction of pigments was carried out for 24 hours in 90% acetone at 4°C in the dark and the extracts were analyzed fluorometrically (UNESCO 1994). Sample aliquots of 250 ml were preserved

with Lugol's iodine (1% final concentration) for analyses of phytoplankton, which were examined by settling 10 – 50 ml of sample into Utermohl's chamber prior to counting under inverted microscope (Olympus IX 51; 400X). Phytoplankton taxa were identified following Tomas (1997), Subramanyan (1946, 1968), Lebour (1978). For carbon conversion, phytoplankton was broadly classified as diatoms and non-diatoms. Their bio-volumes were separately calculated, following Hillebrand et al. (1999) and converted to carbon biomass using equations given in Menden-Deuer and Lessard (2000). Only dominant phytoplankton taxa were considered for bio-volume calculations in the present study. The average bio-volume of dominant diatom and non-diatom taxa were then applied to other less dominant taxa (numerically contributing <5%) for carbon conversion. Since samples were analyzed immediately, effect of preservation and storage was not considered in this study. Wind speeds were measured below 10 m height from the sea surface using an automatic weather station (RM Young sensor) attached above the bridge of the coastal research vessel Sagar Shukti.

DMS, DMSP_t and DMSO_t measurements:

DMS samples were collected in 60 ml amber coloured ground glass stoppered bottles. Analysis commenced almost immediately upon collection and samples were sequentially analysed for DMS, DMSP_t and DMSO_t. Since each sample took approximately 80 minutes for analysis, the remaining samples were kept in dark at 4 °C. Storage time did not exceed 6 hours. DMS and MT were analysed by the purge and trap gas chromatography method as detailed in Shenoy and Kumar (2007). With this method MT eluted at 1.1 minute and DMS at 2.3 minutes. Following DMS analysis DMSP_t was analysed by converting it into DMS by adding 1 ml of 10 M NaOH and purging for 20 minutes (Turner et al. 1990). Later DMSO_t was analysed by reducing it to DMS by adding 1 ml of 50% HCl and 0.3 g of NaBH₄ and purging for 20 minutes (Simo et al. 1996). Tests revealed close to 100% conversion to DMS from both DMSP and DMSO. Calibration was performed using DMSP and DMSO standards. Using these methods the analytical precision was found to be between 6 and 10%.

Results:

General conditions:

In contrast to the intense upwelling observed off the Somali and Omani coast, upwelling off the eastern continental shelf of the Arabian Sea is weak and restricted to a narrow strip over the inner shelf. The

hydrographic climatology of the area is well established through measurements at the CaTS site since 1997 (Naqvi et al. 2006). During the SW monsoon (June to September) winds along the Indian coast favour upwelling. However, upwelling starts as early as May and continues well after the end of the SW monsoon indicating that the process cannot be driven by winds alone, but may be remotely forced to a large extent (Naqvi et al. 2006). The surface temperature at the start of the 3-day observation was 27.5 °C, and remained largely unchanged (within <0.5 °C higher) down to 15 m depth and then fell rapidly to around 24.2 °C at 26 m depth (data not shown). Tides in the study area are semi-diurnal in nature. During the study period the lowest tide (0.56 m) was observed around 2100 hours on 25th September 2009 while the highest tide (1.6 m) was observed around 0435 hours on 26th September 2009. The average amplitude of the tides was around 1 m.

DO, H₂S and wind speed:

During the study period the DO concentration varied from near saturation concentration in surface waters to below detection limits in bottom waters (Figure 2a). The top 10 m was well oxygenated with concentrations varying between 90 µM and 240 µM. From 0 to 40 hours the oxycline was between 10 m and 20 m where oxygen concentrations fell rapidly from around 160 µM to around 30 µM. Beyond 40 hours the thickness of the oxycline reduced from 20 m to 15 m. The bottom waters (20 m to 26 m) were mostly anoxic except between 20 and 45 hours where oxygen concentration increased up to 30 µM from the initial sub-oxic condition (Figure 2a). Towards the end of the 3-day study period the thickness of the anoxic bottom layer increased from 10 m to 15 m. H₂S was associated with the anoxic bottom layer and its concentrations varied between 2 µM to 12 µM (Figure 2b). Wind speeds during the study period varied between 0.04 m s⁻¹ to 8.7 m s⁻¹ (Figure 2c). The wind speeds were fairly low at the beginning and at the end of the study period except between 26 and 50 hours where it surged and remained fairly constant around 7 m s⁻¹.

Chlorophyll *a* and total phytoplankton biomass:

Figure 3a and 3b shows the variation of chlorophyll *a* and total phytoplankton biomass respectively during the study period. Chlorophyll *a* concentrations varied between 0.5 µg L⁻¹ and 6.44 µg L⁻¹ during the study period (Figure 3a). The surface oxic layer had relatively low chlorophyll *a*, while the bottom anoxic layer had chlorophyll *a* concentrations between 1.8 and 6.4 µg L⁻¹. High concentrations of chlorophyll *a* were observed in the surface and bottom waters at the beginning of the study period and in

surface waters towards the end of the 3-day study period. Microscopic observation of phytoplankton cell counts ($> 5 \mu\text{m}$) revealed that in general the diatom community dominated and accounted for 87.4 % of the phytoplankton biomass whereas the non-diatoms accounted for 12.6 % of phytoplankton biomass. The phytoplankton biomass varied between 3.8 and 659.1 $\mu\text{gC L}^{-1}$ with an average of 52.5 $\mu\text{gC L}^{-1}$ (Figure 3b). The high in phytoplankton biomass at 6 m at the beginning of the study period was attributed to dinoflagellates which made up for 96 % of the total phytoplankton biomass at that depth. Phytoplankton biomass was generally low in the anoxic bottom waters and varied between 16 and 37 $\mu\text{gC L}^{-1}$ with diatoms contributing 99 % of the phytoplankton biomass. The dominant diatom species comprised of *Thalassiosira sp.*, *Pleurosigma sp.*, *Nitzschia sp.*, *Navicula sp.* and *Guinardia sp.*, while the dominant dinoflagellates comprised of *Cochlodinium sp.*, *Gyrodinium sp.*, *Heterodinium sp.*, *Ceratium sp.* and *Protoperidinium sp.*

DMSP_t, DMS, DMSO_t and MT:

Figure 4 shows the variation in DMSP_t, DMS, DMSO_t and MT during the 3-day observation period. In general DMSP_t concentrations varied between 2.8 nM and 157.9 nM and followed a distribution pattern similar to that of chlorophyll *a*. High concentrations of DMSP_t ranging from 43 nM to 83 nM were observed throughout the water column in the beginning and in surface waters towards the end of the 3-day observation, where DMSP_t concentrations varied between 22 nM and 158 nM (Figure 4a). High DMSP_t pockets were also observed at 18 m depth at 7.3, 20.3 and 73 hours and at 25 m depth at 51.2 and 66.9 hours. On the other hand, relatively low DMSP_t was found to be associated with low chlorophyll in surface waters and in low oxygen waters at intermediate depths. In contrast DMS concentrations (Figure 4b) showed large variations with extremely high concentrations associated with the anoxic bottom waters containing H₂S (3.8 – 442 nM). The surface oxic waters had relatively low DMS concentrations varying between 3.6 nM and 16.5 nM. We also note that the high DMS concentrations observed were two orders of magnitude lower than the H₂S concentration. DMSO_t concentrations (Figure 4c) varied between 5.8 nM and 136.9 nM and in general followed a distribution pattern similar to DMSP_t. High DMSO_t pockets of varying concentrations were observed between 20 and 50 hours and matched with the wind speed increase and DO infusion (Figure 2) observed during that time. In contrast, a high DMSO_t of 64.5 nM was also found to be associated with the anoxic bottom waters at 60 hours. During the study period MT (Figure 4d) varied between 0.5 nM and 20.3 nM with a distribution pattern similar to that for DMS.

Discussion:

The Arabian Sea holds one of the world's largest oxygen minimum zones (OMZ). In addition to the open ocean pelagic system, there is also a seasonal low oxygen zone which forms along the eastern boundary (Naqvi et al. 2000; 2006; 2009). The open ocean system is perennial and two orders of magnitude larger in volume than the coastal system, which forms seasonally towards the end of the SW monsoon. The two systems differ in that the latter experiences complete anoxia with production of H_2S whereas pelagic conditions do not get beyond suboxia (Naqvi et al. 2006). Studies carried out at the CaTS since 1997 indicate intensification of the reducing conditions in comparison to data two decades ago and this has been attributed to the enhanced nutrient loading in the coastal zone (Naqvi et al. 2000; 2009). The present 3-day measurement series is the first where sampling was done at such close intervals to observe the water column conditions turn from sub-oxic to anoxic. In figure 2a the drop in wind speed around 20 hours corresponded with an intensification of reducing conditions, whereas the subsequent increase in wind speed resulted in infusion of DO from surface waters to sub-surface waters between 20 and 50 hours. Later, a similar decrease in wind speed between 50 and 70 hours was followed by further intensification of reducing conditions and complete anoxia. Naqvi et al. (2000) attributed the intense reducing conditions observed at CaTS to a variety of factors: upwelled waters having initial low oxygen concentrations, high primary productivity and increased bacterial oxygen demand to degrade the organic matter. In this study wind appeared to play an important role in controlling the intensity of the reducing conditions. We suggest that increase in the wind speed leads to induction of oxygen into the shallow system, and vice versa.

The circulation along the west coast of India changes with the seasons. Between April and September the West India coastal current (WICC) flows towards the equator in the opposite direction to the wind, while the West India under current (WIUC) flows pole ward. During October the flows switch direction (Schott and McCreary 2001). Current speeds during the last week of September are usually weak at 0.1 m s^{-1} (personal communication Y.K. Somayajulu). These weak currents and the high primary production support intensification of the low oxygen conditions (Naqvi et al. 2009). During the present 3-day study diatoms were found to dominate the phytoplankton population and were present all through the observation period especially in the intermediate and bottom waters.

In the central and eastern Arabian Sea, phytoplankton biomass varies spatially and has been found to be tightly coupled with hydrographic and chemical changes associated with the monsoonal cycle (Sawant and Madhupratap 1996; Parab et al. 2006). The range of chlorophyll *a* concentrations and diatom dominance observed during the present study was comparable to previous measurements reported from the eastern Arabian Sea (Parab et al. 2006). Results from an ongoing study (data not shown) clearly show a switch in both the autotrophic and heterotrophic communities of the region with the onset of SW monsoon, particularly when hypoxic conditions build-up during the late SW monsoon (Sunita et al. personal communication). Furthermore, this study has also shown that dinoflagellate diversity dwindles much more rapidly than diatom diversity during the sub-oxic conditions prevailing during the senescent phase of the SW monsoon in this region. Our study also showed a relatively higher abundance of dinoflagellates when an oxygenated water column prevailed at the beginning of the 3-day study (Figure 3b). This was then replaced by a diatom community dominated by species of *Guinardia*, *Navicula*, *Nitzschia* and *Thalassiosira*. Cultures of the latter two genera isolated from the Weddell Sea have been observed to release DMS at high light intensity and low temperatures (Baumann et al. 1994).

At the start of the 3-day observation dinoflagellates accounted for over 78% of the phytoplankton biomass in the water column and diatoms made up the remaining 22%. In particular at 6 m depth, *Cochlodinium sp.* accounted for nearly the entire phytoplankton biomass (96%). The high DMSP_t observed at the start of the 3-day study may be attributed to the high numbers of dinoflagellates (Liss et al. 1993; Shenoy and Patil 2003). Similarly the high DMSP_t observed at 6 m towards the end of the measurement series may again be attributed to dinoflagellates which accounted for 85% of the total phytoplankton population. In a time series study carried out in the Zuari estuary, Shenoy and Patil (2003) found high concentrations of DMSP_t (420 nM) in association with a mixed bloom of diatoms and dinoflagellates during the SW monsoon. Previous studies in the coastal Arabian Sea (off Goa) have reported high DMSP_t concentrations in association with anoxic waters (Shenoy and Kumar 2007). During the present study low DMSP_t in surface waters between 15 and 65 hours and in the anoxic zone may be attributed to diatoms which represent the majority of the phytoplankton and are generally considered to be low DMSP producers (Liss et al. 1993). On the other hand high DMSP_t concentrations (~30 to 50 nM) between 50 and 70 hours in the bottom waters may be attributed to DMSP production in the sediments (van Bergeijk et al. 2002).

In the present study the average surface DMS concentration (0 – 6 m) was 22 % of the average surface DMSP_t concentration. Most studies have shown that DMS is usually a minor product of DMSP degradation and generally accounts between 5 and 20 % of the total DMSP production (Kiene et al. 2000 and references therein). DMS began to build up in the bottom waters (20 – 26 m) 10 hours after the beginning of the sampling time series and peaked between 40 and 65 hours (Figure 4b). High DMSO concentrations (> 60 nM) around 15 hours in bottom waters and around 24 hours at 18 m depth decreased to less than 30 nM under sub-oxic conditions. This decrease coincided with an increase in DMS from 30 to 120 nM suggesting that a part of the DMS produced may be due to DMSO reduction under low oxygen conditions (Jonkers et al 1996). The extremely high DMS (442 nM) reported here is one of the highest concentrations observed in the water column to date. Conventionally DMS is thought to form from the breakdown of DMSP (Dacey and Blough 1987; Kiene et al. 1990), but there are reports of formation of DMS from DMSO and MT under anoxic conditions (Kiene and Capone 1988; Jonkers et al. 1996; Vogt and Fischer 1998; Stets et al. 2004). It is quite possible that in the present case the DMS may have arisen from a combination of all three processes mentioned above, but the sum of DMSP_t, DMSO_t and MT for this anoxic zone is less than the observed DMS concentration. This is suggestive of a different source of DMS production or low DMS turnover rates. In a study carried out in a stratified coastal salt pond Wakeham et al. (1984) found elevated concentrations of DMS to be associated with the oxygen-deficient metalimnion. In a later study (Wakeham et al. 1987) they observed similar profiles for DMSP and DMS and attributed conversion of DMSP to DMS under oxygen-deficient conditions to microorganisms. High concentrations of DMSP have also been reported from marine sediments (van Bergeijk et al. 2002; Visscher et al. 1994) where microorganisms are known to be involved in DMS production (Jonkers et al (1998a). Unfortunately DMSP in sediments was not measured in the present study. In a recent experiment Lin et al. (2010) found that methanogens were capable of reducing bicarbonate to DMS engaging methylation of MT via a reductive pathway analogous to methanogenesis under anoxic conditions. Incubation experiments conducted on the methanogen *Methanosarcina acetivorans* by Moran et al. (2008) suggested that DMS and MT were produced by the methylation of H₂S. Formation of DMS and MT from sulphur containing inorganic and organic substrates has been reported in both aerobic and anaerobic conditions (Kodata and Ishida 1972; Ferchichi et al. 1986; Kiene and Visscher 1987). The association of high DMS in the present study with high concentration of H₂S, which were 1-2 orders of magnitude higher than the DMS concentrations, indicates the possibility of a similar mechanism. Additionally, since the high DMS concentrations were close to the sediments their

role as the possible source for these substrates cannot be ruled out. Towards the end of the 3-day study DMSO build-up was observed around 60 hours DMS concentrations rapidly decreased to around 60 nM after 70 hours. In a study conducted using enrichment cultures Zeyer et al. (1987) demonstrated that phototrophic purple bacteria oxidised DMS to DMSO in anoxic conditions. On the other hand anaerobic phototrophic bacteria have been found to metabolise DMS in the presence of light (Wakeham et al. 1987), and other studies have shown anaerobic fermentation of DMS (Zinder and Brock 1978) and the use of DMS by methylotrophic bacteria as a carbon source.

Establishing substrates, their source and mechanisms of formation in such a complex system provides an interesting challenge for the future. Future work will involve measurements of biogenic sulphur compounds (DMSP, DMSO and MT) in the dissolved and particulate fraction in surface sediments. Sediment slurry experiments will be carried out to find the source and mechanism of the DMS production. This will involve setting up incubation experiments using sediment and seawater under different conditions (light/dark/oxic/anoxic) using different substrates (DMSP, DMSO, MT and sulphide). We hope that in addition to finding the source of high DMS observed during the seasonal anoxia, these experiments will also give an insight into the interactions between the carbon and sulphur cycles in anoxic environments.

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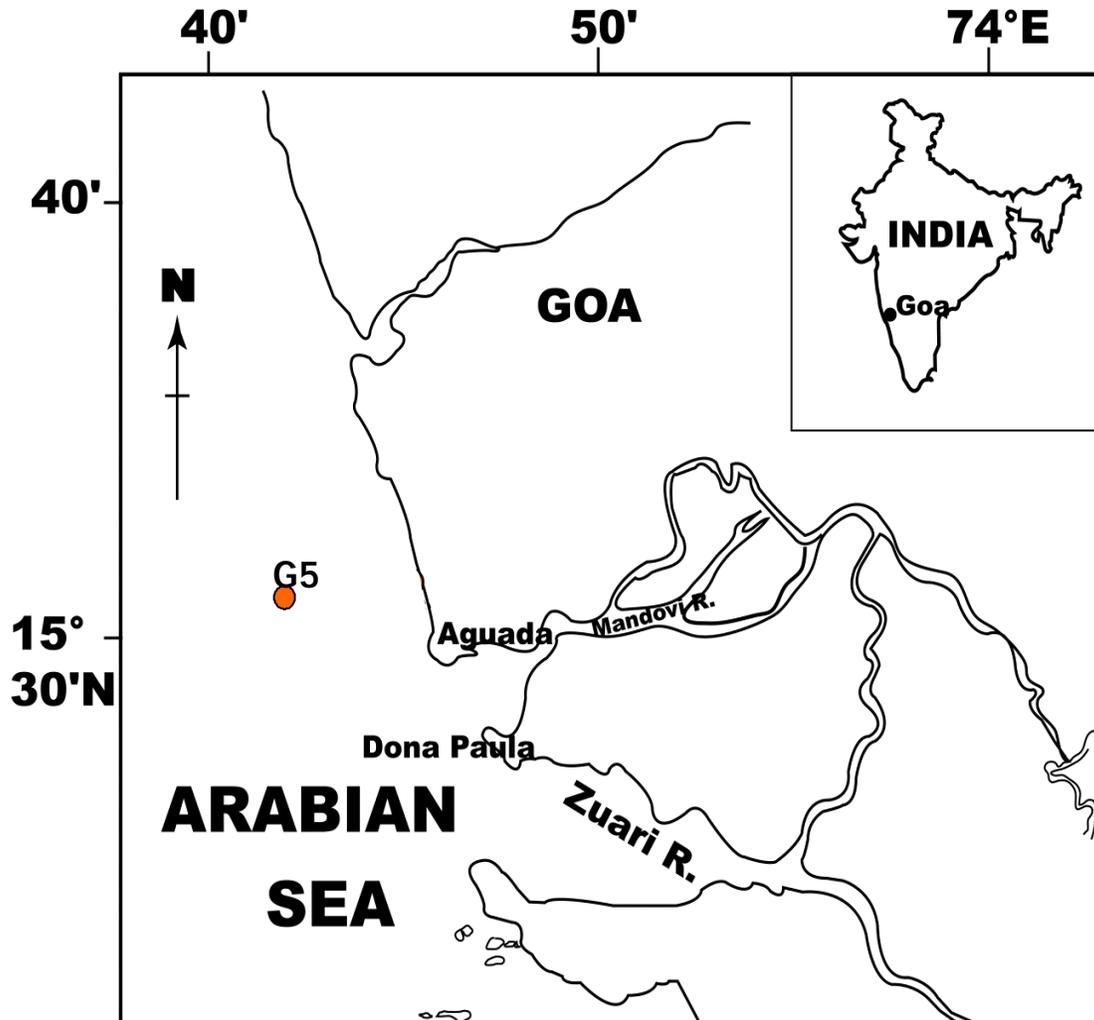


Figure 1: The area map showing the Candolim time series (CaTS) station located off Goa, (15.51° N, 73.65° E). The station was occupied from 1340 hours on 25th September'09 till 1824 hours on 28th September'09 with sampling at consecutive high and low tide.

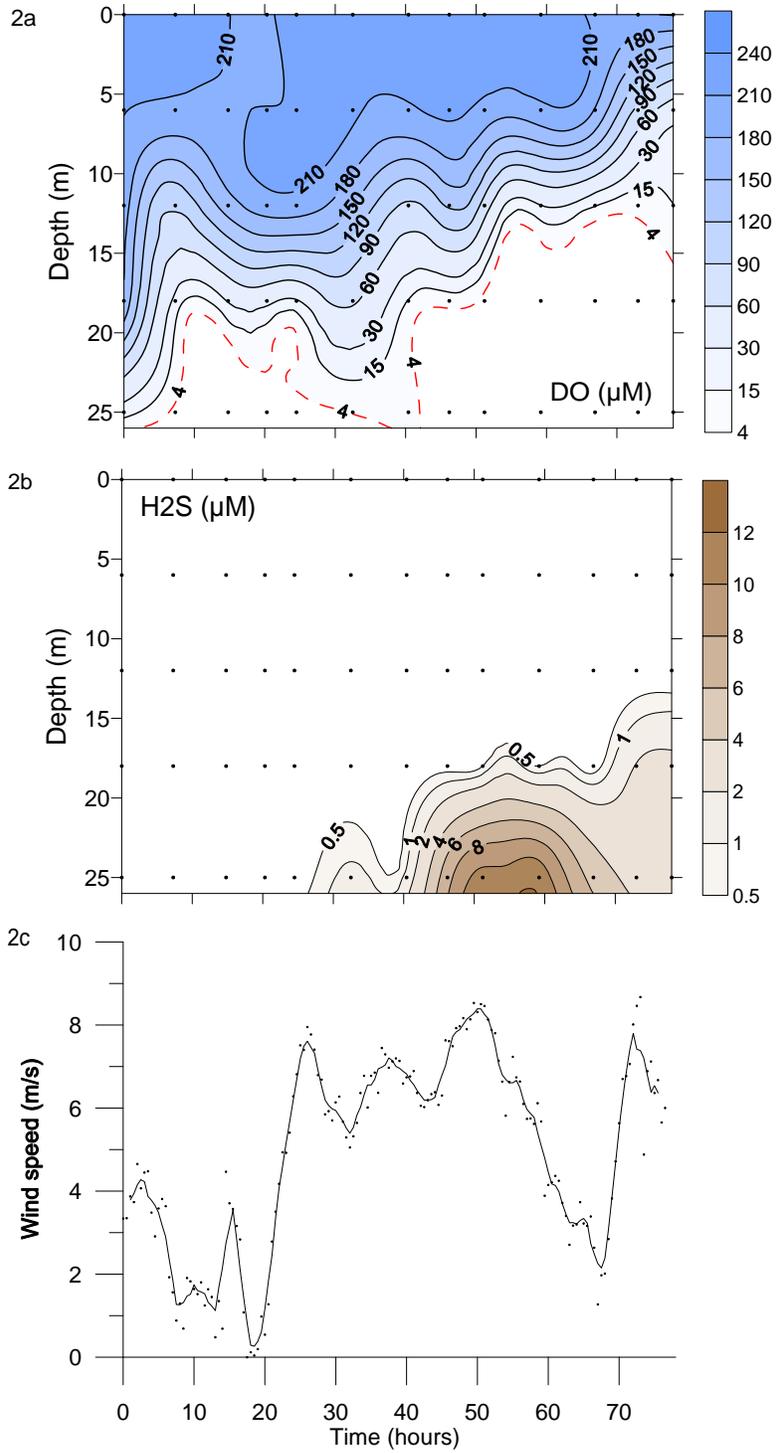


Figure 2: Variation of dissolved oxygen (DO), hydrogen sulphide (H_2S) and wind speed during the 3-day study period. The red dotted line in figure 2a is the 4 μM contour of dissolved oxygen which is considered the upper limit of suboxia (Naqvi et al 2000). The line in 2c represents the moving average for wind speeds.

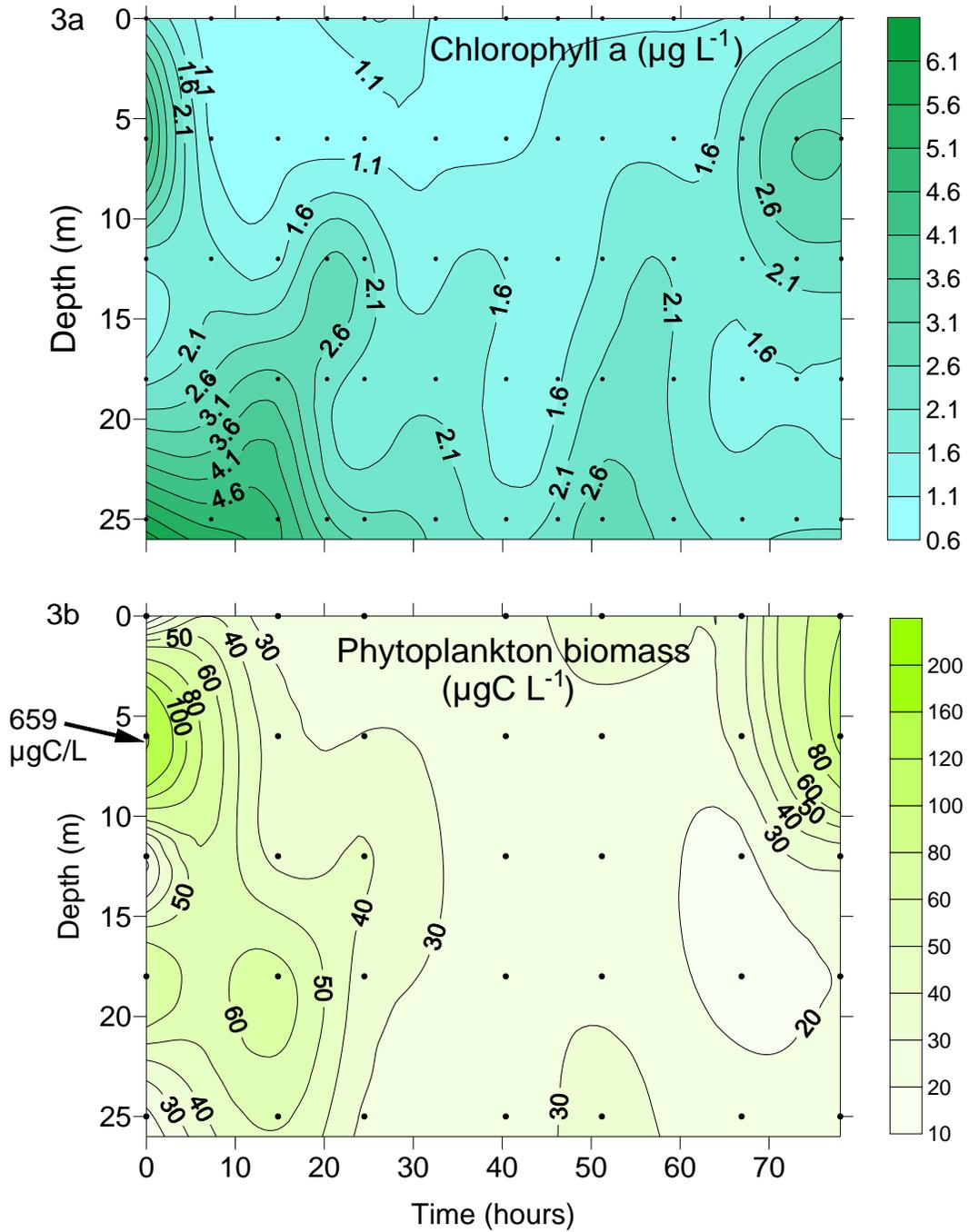


Figure 3: Contour plots showing vertical distribution of chlorophyll *a* and phytoplankton biomass during the 3-day study period. The high phytoplankton carbon biomass (659 $\mu\text{gC L}^{-1}$) at 6 m depth (0 hours) is arbitrarily assigned a value of 200 $\mu\text{gC L}^{-1}$ for ease of drawing the contours.

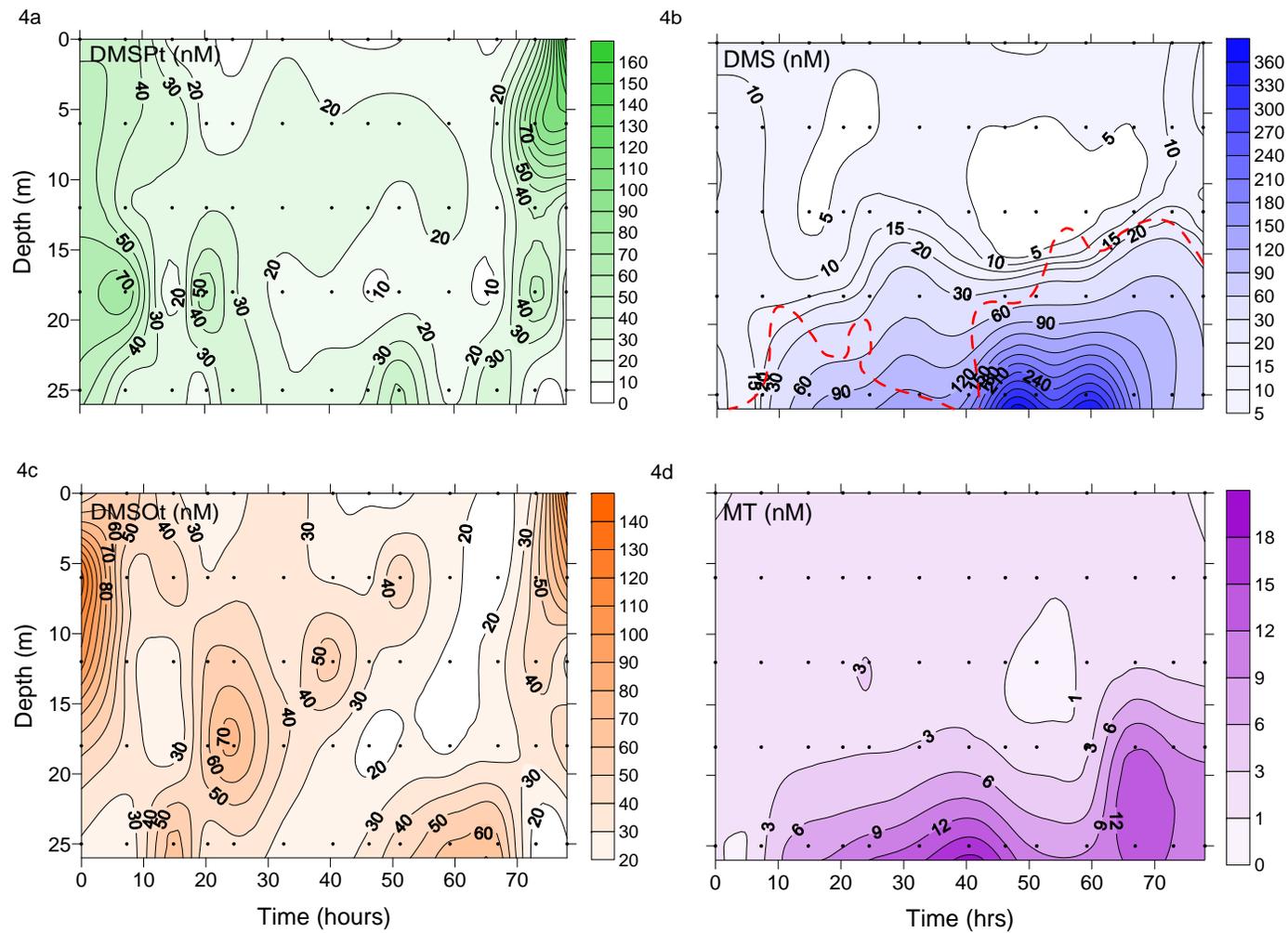


Figure 4: Contour plots showing vertical distribution of total dimethylsulphoniopropionate (DMSP_T), dimethylsulphide (DMS), dimethylsulphoxide (DMSO_T) and methanethiol (MT). The superimposed red dotted line in figure 4b is the 4 μM contour of dissolved oxygen which is considered the upper limit of suboxia (Naqvi et al 2000).