Impact of river discharge on distribution of dimethyl sulphide (DMS) and its fluxes in the coastal Bay of Bengal

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Abstract

A systematic study was conducted to examine the influence of river discharge on variations in DMS and DMSP_t during peak discharge period along the coastal Bay of Bengal.. The southern coastal Bay of Bengal (SCB) received a large quantity of suspended particulate matter (SPM) and nitrogen nutrients from the monsoonal estuaries and vice versa to the northern coastal Bay of Bengal (NCB) by glacial river (Ganges). The higher concentration of DMSP_t was observed in the NCB compared to SCB associated with low nitrate, and low salinity suggesting that their stress on phytoplankton increased DMSP_t production in the former region. The concentrations of DMS and DMSP_t in the surface waters displayed a linear relation with biovolume of Bacillariophyceae and Dinophyceae suggesting significant contributions by these two groups. In contrast, the weak spatial variability in DMS was attributed to removal of DMS to the atmosphere or bacterial consumption. The mean sea-to-air flux of DMS amounted to 5.5±4 µmol S m⁻² d⁻¹ suggesting that coastal Bay of Bengal is a significant source to atmospheric DMS during study period. This study revealed that river discharge brought significant modification in the chemical characteristics of the coastal Bay of Bengal leading to variable stress (salinity and nutrients) on phytoplankton resulting in significant flux of DMS to the atmosphere.

Key words: DMS; DMSP; Fluxes; River discharge; Nutrients inputs; Coastal Bay of Bengal; Southwest Monsoon

1. Introduction:

Climatically important gases, such as carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N_2O) , have direct impact on global radiation budget through absorption of energy in the thermal infrared region. On the other hand, reduced sulfur gases, such as dimethyl sulfide (DMS), have an indirect effect on climate through forming sulfate-based aerosols (Andreae, 1990), which have the potential to change the earth's albedo (Charlson et al., 1987; Andreae et al., 1995). Therefore sulfur gases are expected to reduce the atmospheric temperature rise (Charlson et al., 1987). The oceans contribute ~20% to the total sulfur gaseous emissions into the atmosphere in the form of DMS (Rodhe, 1999). Marine phytoplankton produce dimethylsulfoniopropionate (DMSP) to support osmoregulation process (Dickson and Krist, 1987; Krist 1990; Krist et al., 1991), defensive mechanism as anti-microbial, viral and grazing agent (Seiburth, 1960; Evans et al., 2006; Wolfe et al., 1997), secondary metabolite and metabolic overflow mechanism (Krist, 1996; Stefels, 2000) and antioxidant mechanism (Sunda et al., 2002). Photo-oxidation to dimethyl sulfoxide (Brimblecombe and Shooter, 1986; Brugger et al., 1998; Kieber et al., 1996) and bacterial assimilation (Kiene and Bates, 1990) are identified as two major sinks for DMS in the sea. DMS is produced when DMSP undergoes lysis by the action of DMSP lyase enzyme (Desouza and Yoch, 1996; Kiene and Bates, 1990; Malin and Kirst, 1997). The production of DMSP within the plankton's cell and subsequent release of DMS would depend on a variety of aspects, such as phytoplankton species composition (Liss et al., 1997), physico-chemical parameters (salinity and temperature), microbial community (Taylor and Gilchrist, 1991) and DMSP lyase activity (Stienke et al., 2002). Thus the production and flux of DMS in the marine environment, in general, are governed by a variety of biological and physicochemical factors.

Due to increasing human population and industrialization, significant amount of anthropogenic materials are discharged into the coastal oceans through rivers. River discharges are known to be a strong source of nutrients to the coastal ocean (e.g. Sarma et al., 2010a; 2012a). Discharges of such nutrient-rich waters into the coast lead to eutrophication in several regions in the world (Qian and Liang, 1999; Naqvi et al., 2000; Yan et al., 2001). Shifts in plankton speciation were also noticed in association with modifications in the concentrations and ratios of nutrients (Mee, 1992; Lancelot et al., 1987; VandenBerg et al., 1996). The production of DMS by phytoplankton is species dependent (Turner et al., 1988). For instance, the high DMS concentrations were associated with high abundance of DMSP producing phytoplankton groups (prymesiophytes and dinoflagellates) over diatoms as the latter have relatively low intracellular DMSP concentrations compared to the former. High DMS concentrations were found in association with diatoms-

dominated waters (Iverson et al., 1989), but several investigations suggested that microzooplankton grazing of particulate DMSP_t and bacterial conversion to DMS is also responsible for variations in concentrations of DMS and DMSP_t (Jones et al., 1998, Stefels et al., 2007). The Phytoplankton culture experiments suggested that low concentrations of nitrate and salinity enhance DMS production (Turner et al., 1996; Gage et al., 1997). Recently, Salgado et al (2014) studied influence of salinity on the routes of DMSP catabolism in Ruegeria pomeroyi DSS-3. They noticed that change of salinity from 10 to 20 resulted in a decrease in DMS accumulation by 47 to 87% while an increase in methanethiol accumulation by up to 90% was observed at change in salinity from 20 to 30. This suggests that salinity can modulate selection of the DMSP enzymatic degradation routes with a consequent potential impact on DMS and methanethiol release into the atmosphere. Therefore modifications in plankton composition, induced through changes in nutrient composition and physico-chemical factors, would have significant impact on DMS production in the coastal ocean.

The Bay of Bengal (northeastern Indian Ocean) receives large amount of fresh water runoff (1.6 \times 10¹² m³ a⁻¹; UNESCO, 1979) and sediment load (1.1 \times 10⁹ tones; Milliman and Syvitski, 1992; Milliman and Meade, 1983) during June to September from major rivers, such as the Ganges, Brahmaputra, Godavari, Mahanadi, Cauvery, and Krishna. The fluvial inputs are major sources of nutrients to the Bay of Bengal (for eg. Madhupratap et al., 1993; Sarma et al., 2012; 2013). The freshwater discharge leads to the formation of salinity fronts (Sarma et al., 2012a) and strong stratification (Shetye et al., 1993) impacting phytoplankton composition and therefore likely influencing the production of DMS (Sarma et al., 2013). The influence of river discharge on phytoplankton composition was previously studied with reference to DMS production (Shenoy and Patil, 2003; Chan and Hamilton, 2001). It was observed that the shift in the phytoplankton composition from diatoms to dinoflagellates occurred due to river discharge in the Zuari estuary and this shift was associated with increase in concentrations of DMS and DMSP_t (Shenoy and Patil, 2003; Pednekar et al., 2011). Shenoy et al. (2000) found that phytoplanktons alone did not seem to control the DMS concentration but changes in salinity effectively regulated the extent of DMSP_t production by phytoplankton in the Bay of Bengal. Several reports observed high concentrations of DMS in the estuarine plumes (Turner et al., 1996; Simo et al., 1997; Amouroux et al., 2002; Hu et al., 2005; Ma et al., 2005). A few studies in the American, European and Chinese estuaries suggested that DMS concentrations range widely (0 to 56.7 nM; Iverson et al., 1989; Cerqueira and Pio, 1999; Sciare et al., 2002; Hu et al., 2005), while reports from the Indian estuaries are rather scarce. Recent studies suggested that Indian estuaries are

strong source of nutrients and SPM to the coastal Bay of Bengal (Sarma et al., 2010a; 2012b) with possible impact on phytoplankton composition. It has been further observed that chemical characteristics of the Indian peninsular rivers that are draining to the coastal Bay of Bengal vary (Sarma et al., 2012a); hence its impact on DMS production may be different along the east coast of India. No observations have been carried out so far along the east coast of India during the peak discharge period to understand how discharges from different rivers influence DMS concentrations and its fluxes to the atmosphere in the coastal Bay of Bengal. The aim of this paper is to examine the influence of discharge from major Indian peninsular rivers and glacial river, Ganges, on concentrations of DMS and DMSP_t and sea-to-air fluxes of DMS from the coastal Bay of Bengal during peak discharge period.

2. Material and methods

2.1. Site description and sampling strategy

Water samples were collected on board ORV Sagar Nidhi (#SN 42) during 23 July to 10 August 2010 representing peak south west monsoon (SWM), along the east coast of India. The study area covered the mouths of the major rivers, Krishna (KS, KN transects), Godavari (GS, GN transects) and Mahanadi (MN, MS transects) and minor rivers, Vamsadara (VD Transect) and Hyadri (HD transect) (Fig. 1). Seventy one stations were occupied in 9 transects, covering both north and south of river mouths. Transect V (off Visakhapatnam) was chosen to represent a no discharge location. In addition, samples were also collected in the inner estuaries of the rivers Krishna, Godavari, Mahanadi and Ganges during the same time of coastal sampling to examine the properties of the discharged water into the coastal Bay of Bengal. Samples were collected in the estuary at 3 to 5 locations from the mouth to about 10 km upstream.

2.2 Physical, chemical and biological properties

Sea water samples were collected using 10 L Niskin samplers. Salinity and temperature were measured using CTD (Conductivity-Temperature-Depth, Seabird electronics, USA) system. Dissolved oxygen (DO) was measured following Winkler titration using automated end point potentiometric detection (Carritt and Carpenter, 1966) using Titrando 835 Metrohm autotitrator. Nutrients were measured following standard colorimetric procedures (Grashoff et al., 1983). About 2-3 liters of water samples were filtered on GF/F filter (0.7 µm pore size; Whatman) and Chlorophyll-a (henceforth, Chl-a) on the filter was extracted with N, N, Dimethyl Formamide (DMF) at 4^oC in dark for 24 h and was measured spectrofluorometrically (Cary Eclipse-Fluorescence Spectrophotometer, Varian Instruments, USA) following Suzuki and Ishimaru

(1990). The analytical precision for Chl-a analysis was ±4%. The weight of the suspended particulate matter (SPM) retained on 0.22 μm pore size polycarbonate filters (Millepore) after filtering about one liter of sample was measured. In order to determine the phytoplankton composition, 1 L of surface water samples was collected in a polyethylene bottle and fixed with lugols iodine solution. Before identification, water samples were allowed to settle for 24 h and the supernatant was decanted until the sample was concentrated to 10 ml. About 0.1 ml of concentrated sample were taken on a glass slide and observed under BX51 OLYMPUS microscope. Phytoplanktons were identified using standard works of Venkataraman (1939), Cupp (1943), Subrahmanyan (1946), Desikachary (1959, 1987), Hendey (1964), Steidinger and Williams (1970), Taylor (1976) and Anand et al. (1986). Total Bacterial Count (TBC) was measured using epifluoroscence microscopy (Olympus, Japan) following DAPI technique .

2.3. *Measurements of DMS and total DMSP (DMSP_t)*

DMS and DMSP_t samples were collected into 40 ml amber colored glass bottles to prevent their photochemical decomposition and were analyzed onboard using the Agilent 7890 Series Gas Chromatograph. The samples were stored in the dark at 4⁰ C until analysis. The storage time never exceed 4 hours. Calibration of the instrument has been carried out using standard DMSP (Research Plus, Netherlands) solutions. DMS and DMSP_t in the samples were analyzed using purge and trap method (Shenoy et al., 2002). A known volume (sample volume varied from 5 to 20 ml depending on the concentration of DMS) of a seawater sample was purged with ultra pure nitrogen gas (99.9995%) for 15 minutes. The released gases were trapped cryogenically in a Teflon column in line with 6 port valco valve. The trapped gases were injected by inserting the Teflon column into hot boiling water (temperature $> 80^{\circ}$ C) and switching the valco valve to inject position. The trapped and released gases were then separated over a Chromosil 330 column (Shenoy et al., 2002; Turner et al., 1990) and detected by Flame Photometric Detector (FPD). The DMS was measured first followed by DMSP_t. About 2ml of 10 M NaOH was added to the same samples after DMS has been analyzed and purged immediately for 20 min to hydrolyze DMSP_t to DMS. This results in cleavage of DMSP_t to DMS and acrylic acid (Turner et al., 1990). The DMS produced by cleavage was measured as detailed above.

2.4. Calculation of DMS flux

DMS flux was calculated using the equations given in Turner et al. (1996)

$$F_{DMS} = K_{w}.\Delta C \tag{1}$$

Where F_{DMS} = net flux of DMS; k=transfer (or piston) velocity; and ΔC =concentration difference, which drives the flux across at the air-sea interface. The concentration difference (ΔC) was obtained as follows,

$$\Delta C = C_{\rm w} - (C_{\rm a}/H) \tag{2}$$

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 air is very low relative to the concentration in water, C_a is generally taken to be zero, and thus ΔC is numerically equal to C_w

The transfer velocity of gases with reference to wind speed was derived by several investigators. The choice of transfer velocity introduces significant amount of uncertainties to the flux estimates (Sarma et al., 2010b). Hence, we used transfer velocity derived from Liss and Merlivat (1986), Wanninkhof (1992), Wanninkhof and McGills (1999), Nightingale et al., (2000) and Sarma et al., (2010b) for comparison of fluxes. In addition to this, fluxes were also estimated using both instantaneous and seasonal mean winds from Automated Weather Station (AWS) installed on board and along the Indian Coast (Indian Meteorological Department, IMD; www.imd.gov.in) respectively.

3. Results

3.1. Physico-chemical characteristics of the coastal Bay of Bengal

The southern coastal Bay of Bengal received discharge from monsoonal rivers, such as Godavari (1050 m³ s⁻¹) and Krishna (823 m³ s⁻¹) whereas Ganges (>14000 m³ s⁻¹) and monsoonal rivers (Mahanadi - 683 m³ s⁻¹; Vamsadhara and Hyadri - <100 m³ s⁻¹) poured in the northern Bay of Bengal (Sarma et al., 2012a). The surface water temperature during study period varied from 26.78 to 29.99 °C (Fig. 2a) whereas surface salinity ranged between 20.59 and 34.09 (Fig. 2b). Relatively cooler surface waters (26.8-28.8° C) associated with high salinity (~34) was observed in the southern transects compared to that of north (28.8-30° C and ~31) suggesting occurrence of mild upwelling in the former region. A sharp gradient in salinity and temperature was observed around 18° N resulting from the northward flowing East India Coastal Currents (EICC) and southward flowing discharge water from the Ganges (Shetye et al., 1993; Sarma et al., 2013). Based on the contrasting differences in the surface water temperature and salinity, the study area is divided into two regions, namely, southern coastal Bay of Bengal (SCB) comprising the transects of KS, KN, GS, and GN, which are influenced by monsoonal estuaries of Godavari and Krishna and northern coastal Bay of Bengal (NCB), including transects of VD, HD, MS and MN,

which are more influenced by discharge from river Ganges. The transect V is located in the region where no direct discharge occurs. The surface dissolved oxygen (DO) concentration was relatively higher in the NCB (194±9.5 µmol kg⁻¹) than in the SCB (166±14 µmol kg⁻¹; Fig. 2c). The suspended particulate matter (SPM) levels varied from 4.3 to 42.7 mg 1⁻¹ and decreased from SCB (23.7±9 mg l⁻¹) to NCB (10.4±3 mg l⁻¹; Fig. 2d) as sediments from the Ganges river do not reach to the shelf off the peninsular India (Rao et al., 1988; Sarma et al., 2012b). Nitrate and ammonium concentrations in the surface waters ranged from non-detectable to 13.6, and 0.1 to 3.8 µmol kg⁻¹ respectively, with the higher concentrations in the SCB (Fig. 2e and 2f). Relatively high phosphate and low silicate concentrations were found in the SCB and vice versa in the NCB (Fig. 2g, 2h). The N:P ratios were relatively higher than Redfield ratios in the SCB (6 to 61.4; mean 19.4±15) while they were significantly lower in the NCB (0.8 to 26.3; mean 6.3±6; Fig. 2i). The Si:N ratio was higher in the NCB (41.7±6) and they are close to Redfield ratios in the SCB (1.0±0.6) (Fig. 2j). The concentration of SPM has significant impact on the photic depth and therefore influences phytoplankton growth (Madhupratap et al., 2003). Higher Chl-a concentrations were observed in the NCB (3.0±2.1 mg m⁻³) where low SPM was observed than in the SCB (1.4±1.5 mg m⁻³; Fig. 2k). The physico-chemical characteristics of coastal Bay of Bengal suggest that fresher, warmer, stratified and nutrient poor waters were observed in the NCB and contrasting conditions were noticed in the SCB due to variations in discharged rivers properties.

3.2 Phytoplankton composition

Phytoplankton abundance in the surface waters varied between 0.15×10⁵ and 10.8×10⁵ cells 1⁻¹ whereas biovolume ranged between 0.08 x 10⁸ and 7.1 x 10⁸ μm³ 1⁻¹ (mean 1.7±2 x 10⁸ μm³ 1⁻¹) in the SCB and 0.2 x 10⁸ to 16.9 x 10⁸ μm³ 1⁻¹ (mean 6.1±4 x10⁸ μm³ 1⁻¹) in the NCB (Fig. 3a-3c). The phytoplankton community was composed mainly of Bacillariophyceae (mainly Diatoms), Dinophyceae (mainly Dinoflagellates) and Cyanophyceae (Cyanobacteria) with values ranging from 0.1×10⁵ to 9.0×10⁵, 0.02×10⁵ to 0.3×10⁵ and 0.02×10⁵ to 3.3×10⁵ cells 1⁻¹, respectively. Bacillariophyceae were the most abundant followed by Dinophyceae and Cyanophyceae. The contribution of Dinophyceae and Cyanophyceae was relatively higher along the transect V compared to other transects (Fig. 3).

3.3 Distribution of DMS and DMSP_t along the coastal Bay of Bengal

Surface DMS and DMSP_t concentrations ranged from 1.2 to 28.2 nM and 0.8 to 61.6 nM, respectively along the coastal Bay of Bengal (Fig. 4a and 4b). The significantly higher DMS

(18.5±8 nM) and DMSP_t (29.2±13 nM) concentrations were noticed along the transect V compared to other transects (8.7±5 and 15.7±12 nM respectively; t_{stat}=-3.28; p<0.001 for DMS and 2.63, p<0.01 for DMSP_t) (Fig. 4a, 4b). Both DMS and DMSP_t concentrations increased from near shore to offshore and a similar pattern was observed with the biovolume of Bacillariophyceae (t_{stat} =1.96; p<0.01) and Dinophyceae (t_{stat} =2.24; p<0.01) (Fig. 3 and 4). Unlike hydrographic properties, DMS concentrations did not show north-south variations (t_{stat} =0.67; p<0.6) whereas significantly higher DMSP_t was noticed in the NCB (21.6±13.9 nM) compared to that in SCB (10.1 \pm 7.7 nM; t_{stat} =4.01; p<0.001). DMS and DMSP_t did not display any relation with total phytoplankton biomass (Chl-a), however, a significant relationship was observed with biovolume of Bacillariophyceae ($r^2=0.41$; p<0.001) and Dinophyceae ($r^2=0.52$; p<0.001). Relatively higher DMS/Chl-a was observed in the SCB (8.8±6.6) than in the NCB (4.4±2.5; t_{Stat}=4.24; p<0.001; Figure 4c, 4d). The lowest DMS/Chl-a ratio was observed along MN and MS transects (2.3±1) where the highest phytoplankton biomass (4.5±1 mg m⁻³) was observed and was mainly contributed by Bacillariophyceae (>80%). No statistically significant north-south differences were noticed for DMSP_i:Chl-a ratios (10.3±6) in the study region, however, relatively lower values were noticed along KS, MN and MS transects. DMS and DMSP_t showed no relationship with either salinity or nutrients. The DMS:DMSP_t ratio was significantly higher in the SCB (1.2 \pm 0.5) than NCB (0.6 \pm 0.4) (t_{Stat} =2.3; p<0.01). The sea-to-air flux of DMS, calculated after Liss and Merlivat (1986) varied from 4.4 to 118.4 μ mol S m⁻² d⁻¹ and 0.7 to 16.4 µmol S m⁻² d⁻¹ using instantaneous and seasonal mean winds respectively.

4. Discussion

4.1. Influence of river discharge on physical and biogeochemical properties along coastal Bay of Bengal.

The prevailing winds during the study period were from the southwest direction (figure not shown) along the east coast of India, which favors coastal upwelling (Shetye et al., 1993). Low discharge of freshwater and weak stratification favoured coastal upwelling in the SCB.

Though upwelling brought nutrients to the surface in the SCB, higher phytoplankton biomass in the NCB was supported by higher light penetration due to clear waters leading to decrease in nutrients concentrations. Abundance and biovolume of Bacillariophyceae was three times higher in the NCB (310015 cells L⁻¹ and $4.4\pm3.8\times10^8$ µm³ Γ^1) than in the SCB (84746 cells L⁻¹; $1.3\pm1.3 \times10^8$ µm³ Γ^1) due to favorable conditions for their growth in the former region (Fig. 3). These conditions also brought slight variations in contribution of different groups of

phytoplankton to total biovolume. For instance, the contribution of diatoms to total phytoplankton biovolume was 86% in the NCB and decreased to 74% in the SCB whereas Cyanophyceae contributed 10 and 25% respectively and dinoflagellates contributed equally (~3-5%) in both the regions. The dominant genus of phytoplankton was also different in the NCB (Thallasirosira < Nitzchia < Chaetoceros) and SCB (Thallasirosira < Chaetoceros < Lauderia < Nitzchia < Guinardie). Since transect V falls between nutrients rich SCB and nutrient poor NCB with moderately higher SPM concentrations (16.8±3 mg l⁻¹; higher than NCB but lower than in the SCB), the contribution of various groups of phytoplankton were different. For instance, Dinophyceae contributed relatively more (11%) to total biomass along transect V compared to other transects (~4%).

4.2. Influence of river discharge on concentrations of DMS and DMSP_t in the coastal Bay of Bengal

Higher DMS and DMSP_t was observed along transect V and salinity frontal zone during study period. The transect V received nutrients from neither local rivers nor coastal upwelling; hence, low phytoplankton biomass was observed (1.3±0.3 mg m⁻³). The lower zooplankton biomass was observed along transect V compared to other study region suggesting that grazing pressure may not be significant reason for decrease in phytoplankton biomass (Our unpublished data). Among the phytoplankton groups, the contribution of dinophyceae (dinoflagellates) was the highest along transect V (10-60%) compared to other transects sampled in this study. Dinophyceae contain relatively higher intracellular DMSP than Bacillariophyceae, and Cyanophyceae (Liss et al., 1997). Hence the higher concentrations of DMS and DMSP_t along transect V could be due to higher abundance of Dinophyceae. In addition to this, low nutrients concentrations along the transect V further enhanced DMS production due to stress.

The East India Coastal Current (EICC) carries high saline water from south to north during study period. The salinity front develops in the coastal Bay of Bengal due to freshwater discharge from the rivers. Relatively higher DMS concentrations were observed in these salinity frontal zones between VD and HD transects (8.8 ± 6 nM) and also GN and GS transects (9.9 ± 6 nM) due to salinity shock to the phytoplankton leading to release of DMS (Fig. 2b and 4a, b). The work carried out with phytoplankton culture experiments suggest that DMS production increases at lower salinity and low nitrate concentrations (Turner et al., 1996; Gage et al., 1997; Shenoy and Patil, 2003; Salgado et al., 2014). Low nitrate concentrations were observed in the salinity frontal zone (non detectable to $2.2~\mu\text{M}$; mean $0.8\pm0.7~\mu\text{M}$) suggesting that higher DMS concentrations in the frontal zone might have resulted from nutrients and salinity stress. On the other hand

relatively lower concentrations of DMS and DMSP_t were observed along KS and KN transects (7.3±3nM and 6.0±4 nM respectively) associated with higher SPM and low Chl-a concentrations (Fig. 2d, k and Fig. 4) suggesting that decreased light availability resulting in decrease in phytoplankton biomass and low production of DMS and DMSP_t.

Despite higher concentrations of DMSP_t in the NCB than SCB, DMS did not show significant spatial variability. The variable spatial distribution pattern of DMS and DMSP_t was possibly due to several potential processes such as 1) stress due to nutrient limitation (Keller et al., 1999), 2) salinity stress (Shenoy and Patil, 2003; Salgado et al., 2014), 3) consumption of DMS through microbial processes (Wolfe and Kiene, 1993; Kiene and Linn, 2000), 4) increase in dissolved pool of DMSP due to grazing activity of zooplankton (Levasseur et al., 1996; Wolfe and Steinke, 1996; Dacey and Wakeham, 1986), 5) variable concentrations of DMS and DMSP_t in the discharged waters and 6) variations in instantaneous DMS flux to the atmosphere.

Though no experimental data are available in this study to identify the process responsible to spatial variations in DMS and DMSP_t along the coastal Bay of Bengal, we made an attempt using statistical analysis of our data. The mean N: P ratio in the NCB was lower (6.3±6) compared to SCB (19.4±14.9; t_{stat} =4.24; p<0.001; Fig. 2i) suggesting severe nitrogen limitation in the former and phosphate limitation in the latter regions. Hu et al. (2005) noticed high DMS in the shelf region of the South China Sea (SCS; 3.8-14.4 nM) due to severe phosphate limitation (Xu et al., 2008). On the other hand, Shenoy and Patil (2003) observed a sharp increase in DMS and DMSP_t in the Zuari estuary associated with a decrease in salinity due to river discharge from upstream river. The mean salinity in the NCB was significantly lower (24.8±3) compared to SCB (33.0±0.9; t_{stat} =8.83; p<0.001) due to an order of magnitude higher fresh water discharge by Ganges River (>14000 m³ s⁻¹) to the NCB than monsoonal rivers to the SCB (<2000 m³ s⁻¹). Lower concentration of DMSP_t in the SCB than in the NCB could possibly due to stress by both salinity and nutrients in the latter and only nutrient stress in the former region.

The spatial variations in DMS could also be driven by variable concentrations in the discharged waters from various rivers. The mean concentration of DMS in the monsoonal estuaries, Godavari and Krishna, was ~1 nM whereas it was almost double in the glacial river, Ganges (~1.9 nM; Table 2). The concentrations of DMS in the Indian estuaries were significantly lower than that of Pearl River Estuary (3.0-5.6 nM; Hu et al., 2005) whereas it is consistent with American estuaries (Iverson et al., 1989). Nevertheless the concentration of DMS in the Indian estuaries was significantly lower than in the coastal Bay of Bengal. The concentrations of DMS

in the rivers suggest that their contribution is insignificant to bring north-south variations in DMS in the coastal Bay of Bengal.

The lack of north-south variations in DMS in the study region could also be due to variable flux to the atmosphere. During study period, cyclonic conditions were observed mainly in the NCB region where wind speeds were significantly higher (21.5±3.7 m s⁻¹) compared to SCB (16.1±1.9 m s⁻¹). The mean flux of DMS at the SCB and NCB was 13.8 and 22.1 µmol S m⁻² d⁻¹ respectively using instantaneous winds in the respective region. Such enhanced flux in the NCB may result in weak north-south gradients in DMS in the coastal Bay of Bengal.

In addition to this, variable microbial activity can also cause north-south variations in DMSP_t as the production of DMS from DMSP can be modified and DMSP can be converted and accumulated in the pools of either volatile or nonvolatile degradation products by bacteria (Kiene and Linn, 2000). The mean total bacterial abundance were higher in the NCB (5.7±2 x 10⁵ cells L⁻¹) than in the SCB (2.9±1 x 10⁵ cells L⁻¹; t_{stat}=2.1; p<0.01), suggesting possible influence of bacteria on north-south gradients in DMS and DMSP_t in the coastal Bay of Bengal. However, experimental evidence is required to confirm this dominant process responsible for the spatial variations in DMS and DMSP_t could not be derived from our data, due to lack of information on accumulation of DMSP in various byproducts such as dissolved non-volatile sulfur (DNVS) and methanethiol (MeSH). However, this study suggest that discharge from different types of rivers into the Bay and local atmospheric processes invoked spatial variations in the DMS and DMSP_t in the coastal Bay of Bengal.

In order to examine the controlling factors on DMS and DMSP_t production in the study region, a statistical analysis was conducted with biological and physical variables. Both DMS and DMSP_t displayed no correlation with Chl-a (r^2 =0.06 for DMS and r^2 =0.05 for DMSP_t). Even though DMSP and in turn DMS are biogenic in origin, they do not always correlate with Chl-a as all phytoplankton groups do not produce DMSP at the same extent (Simo et al., 1997; Townsend and Keller, 1996; Uher et al., 2000; Shenoy and Patil, 2003). A significant linear relation was observed for DMS with biovolume of Bacillariophyceae (r^2 =0.41; p<0.001) and Dinophyceae (r^2 =0.52; p<0.001) suggesting that increased abundance of these groups of phytoplankton enhanced DMS concentrations. DMS showed inverse an correlation with salinity in the NCB (r^2 =0.63; p<0.001; Fig. 5a) and a linear relation was observed in the SCB (slope=43.4; r^2 =0.55; p<0.001; Fig. 5b). The former relation suggests selection of different pathway (such as formation of methanthiol; Salgado et al., 2014) while the latter suggests increased nutrients inputs through vertical mixing enhanced phytoplankton biomass and DMS production. Due to local river

discharge from the Godavari, the intercept of the relation between DMS and salinity was lower along GN transect (slope=27.3; r^2 =0.85; p<0.001; Fig. 5b) than SCB. Therefore this study suggests that both biomass of DMS producing phytoplankton and salinity are important factor governing distribution of DMS along the coastal Bay of Bengal.

The concentrations of DMS and DMSP observed in our study were different from that of earlier studies in this region. For instance, Shenoy and Kumar (2006) observed DMS and DMSP_t concentration of 3.3±3 nM (range: 1.2-7.2 nM) and 12.9±8 nM (range: 3.1-23.3 nM) respectively in the coastal Bay of Bengal during SW monsoon season which were lower than that in the present study (9.9±6 nM (1.2-28.2 nM) and 17.3±13 nM (0.8-61.6 nM) nM respectively). The observations carried out by Shenoy and Kumar (2006) and during present study were during the same time period (July-August), however, the coverage of geographical locations was different. For instance, unlike this study, Shenoy and Kumar (2006) made measurement at 6 stations along the coastal Bay of Bengal which were not close to the outfall of estuaries discharges. Hence the comparison of these two data sets may not be appropriate. Biogeochemistry in the coastal Bay of Bengal is very dynamic and can be influenced by the variable magnitude of river discharges (Acharyya et al., 2012) and difference in phytoplankton composition. These might be the potential reasons for the difference of present mean values of DMS and DMSP_t from that of Shenoy and Kumar (2006).

4.3. DMS/Chl-a and DMS/DMSP_t ratios in the coastal Bay of Bengal

In order to examine the spatial distribution of the DMS production ability per unit biomass, Chl-a normalized DMS (DMS/Chl-a) was used. The mean DMS/Chl-a values were several folds lower in the coastal Bay of Bengal (0.5-29.4) than South China Sea (38.6-60.5) (SCS) (Hu et al. (2005). Such high ratios in the SCS were attributed to severe phosphate limitation (Xu et al., 2008). Relatively higher DMS/Chl-a was observed in the SCB (8.8±6), where phosphate limitation was noticed, than in the NCB (4.4±3) where nitrogen limitation was observed. Despite similar composition of phytoplankton in the NCB and SCB, significant variations in the DMS/Chl-a suggest that phosphate limitation might have triggered more stress on phytoplankton leading to the production of high DMS than nitrogen limitation. This needs to be confirmed in future through laboratory experiments.

In order to examine the conversion of DMSP to DMS, we used the DMSP normalized DMS concentration (DMS:DMSP). The ratio of DMS/DMSP reflects the relationship between the intracellular pool of the precursor substance, DMSP, in the phytoplankton population, and its

cleavage product, DMS. In order to examine the impact of N:P ratios on formation/consumption of DMS, it was related to DMS/DMSP ratios in Figure. 6. The DMS:DMSP ratio showed a linear relation with N: P ratios (r²=0.35; p<0.01; Fig. 6) in the SCB suggesting that increased nitrogen inputs lead to the formation of nitrogen-containing osmolyte and decreased the synthesis of DMSP. Based on phytoplankton culture experiments using diatom strain (*Thalassiosira pseudonana*), Keller et al. (1999) found that DMSP production is favored over nitrogen containing osmolytes under low nitrogen conditions. More recently Zindler et al. (2012) observed that high DMSP and low DMS were associated with low N: P ratio (<7) and vice versa with high N:P ratio (>7) in the Mauritanian upwelling region. They further observed that switching in the production and/or consumption of DMSP and DMS is depending on the availability of dissolved inorganic nitrogenous nutrients. Our observations showed that DMS/DMSP increased with increase in N:P ratio and is in agreement with Zindler et al. (2012).

4.4. Flux of DMS to the atmosphere during SW monsoon

Due to occurrence of a low pressure system in the northern Bay, a sharp increase in the wind speeds was observed from SCB (13-16 m s⁻¹) to NCB (~25-27 m s⁻¹). Such high wind speed during the study period enhanced the transfer velocity of DMS and fluxes to the atmosphere. However, they may not represent the monthly/seasonal mean fluxes since such short-bursts may remain for just a couple of days. Hence fluxes were estimated using both instantaneous measured winds onboard and also seasonal mean winds (June to August; southwest monsoon). The winds during southwest monsoon (June to August) ranged between 6 and 16 m s⁻¹ with the seasonal mean of 6.7±3 m s⁻¹. The sea-to-air flux of DMS using Liss and Merlivat (1986) formulations varied from 4.4 to 118.4 µmol S m⁻² d⁻¹ and 0.7 to 16.3 µmol S m⁻² d⁻¹ using instantaneous and seasonal mean winds respectively. The daily mean wind speed data, obtained from Indian Meteorological Agency (IMD; www.imd.gov.in), during the monsoon period suggests that high winds of >10 m s⁻¹ were observed over 42 days due to frequent formation of local depressions. Such high variability in winds in the study region indicates that significantly short burst of DMS into the atmosphere and high time-resolution DMS data are required to account for their contribution. The flux calculated from different transfer velocity formulations ranged between 5 to 10.8 µmol S m⁻² d⁻¹ for the entire study region with relatively lower fluxes using the Wanninkhof and McGills (1999) formulation and higher fluxes using Sarma et al. (2010b) (Table 3). Nevertheless, the seasonal mean DMS flux from the coastal Bay of Bengal amounts to 5.5±4 μmol S m⁻² d⁻¹, and is higher than that of earlier estimates (0.18 to 9.03 μmol S m⁻² d⁻¹; mean of 3.3±3 µmol S m⁻² d⁻¹; Shenoy and Kumar, 2006) using Liss and Merlivat, (1986) formulations.

Such higher fluxes in the present study were contributed by higher DMS concentrations and wind speed compared to Shenoy and Kumar (2006). This study suggests that the coastal Bay of Bengal acts as a strong source for atmospheric DMS during the SW monsoon.

5. Summary and Conclusions

In order to examine the discharge from various rivers on phytoplankton biomass, distribution of DMS, DMSP_t and fluxes of DMS to atmosphere, a systematic study was carried out along the coastal Bay of Bengal during peak discharge period. The northern coastal Bay of Bengal (NCB) received discharge from Ganges with low SPM, low nitrate and phosphate but high silicate compared to southern coastal Bay of Bengal (SCB) from Godavari and Krishna rivers. Relatively higher phytoplankton biomass was observed in the NCB due to lower SPM than SCB. Bacillariophyceae were the dominant group of phytoplankton followed by Cyanophyceae and Dinophyceae in the study region. DMS and DMSPt showed strong linear relation with biovolume of bacillariophyceae and dinophyceae and insignificant relation with total phytoplankton biomass suggesting that phytoplankton groups are more important. The spatial variations in DMS along the coastal Bay of Bengal were contributed by nutrients stress (nitrate and phosphate) and salinity and also by variable magnitude of DMS fluxes to atmosphere due to extreme atmospheric conditions in the NCB. Relatively higher DMS/Chl-a were observed in the SCB (8.8±6), where phosphate limitation was noticed, than in the NCB (4.4±3) where nitrogen limitation was observed. The seasonal mean fluxes of DMS to atmosphere amounts to 5.5±4 μmol S m⁻² d⁻¹, which is higher than that of earlier estimations. This study revealed that river discharge modified the chemical composition of coastal Bay of Bengal and brought variable stress (salinity, nitrate, phosphate) on the phytoplankton that resulted in spatial variations in DMS and DMSP_t concentrations and flux of DMS to the atmosphere.

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Reference:

Acharyya. T., Sarma, V.V.S.S., Sridevi, B., Venkataramana, V., Bharathi, M.D., Naidu, S., Kumar, B.S.K., Prasad, V.R., Bandyopadhyay, D., Reddy, N.P.C., Kumar, M.D., 2012. Reduced river discharge intensifies phytoplankton bloom in Godavari estuary, India. Marine Chemistry. 132-133, 15-22.

Amouroux, D., Roberts, G., Rapsomanikis, S., Andreae, M.O., 2002. Biogenic gas (CH₄, N₂O, DMS) emission to the atmosphere from near-shore and shelf waters of the northwestern Black Sea. Estuary. Coast. Shelf Sci. 54, 575-587.

Anand, N., Mohan, E., Hopper, R.S.S., Subramanian, T.D., 1986. Taxonomic studies on blue green algae from certain marine environments Seaweed Research and Utilization Seaweed Research and Utilization Association, Marine Fishereies-623-520. Tamil Nadu. India 9(1-2) 49-56.

Andreae, M. O., 1990. Ocean- atmosphere interactions in the global biogeochemical sulfur cycle. Mar. Chem. 30, 1-29.

Andreae, M.O., Elbert, W., de Mora, S. J., 1995. Biogenic Sulfur emissions and aerosols over the tropical South Atlantic, 3. Atmospheric dimethylsulfide, aerosols and cloud condensation nuclei. J. Geophys. Res. 100, 11,335-11,356.

Brimblecombe, P., Shooter, D., 1986. Photooxidation of dimethyl sulphide in aqueous solution. Mar. Chem. 19, 343-353.

Brugger, A., Slezak, D., Obernosterer, I., Herndi, G. J., 1998. Photolysis of dimethylsulfide in the northern Adriatic Sea: Dependence on substrate concentration, irradiance and DOC concentration. Mar. Chem. 59, 321-331.

Charlson, R. J., Lovelock, J. E., Andreae, M. O., Warren, S. G., 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. Nature, 326, 655-661.

Chan, T. U., Hamilton, D.P., 2001. The effect of freshwater flow on biomass and succession of phytoplankton in a seasonal estuary. Marine and Freshwater Research 52, 869-884.

Carritt, D. E., Carpenter, J. H., 1966. Comparison and evaluation of currently employed modifications of the Winkler method for determining dissolved oxygen in seawater: a NASCO report. J. Mar. Res., 24, 286-318.

Cerqueira, M.A., Pio, C.A., 1999. Production and release of dimethylsulphide from an estuary in Portugal. Atmospheric Environment. 33, 3355-3366.

Cupp, E.E., 1943. Marine plankton diatoms of the west coast of North America. Bull. Scripps. Inst. Oceanogr. 5, 1-237.

Dacey J. W. H., Wakeham S. G., 1986. Oceanic dimethylsulfide: production during zooplankton grazing on phytoplankton. Science. 233, 1314-1316.

De Souza, M. P., Yoch, D. C., 1996. Differential metabolism of dimethyl-sulfonio-propionate and acrylate in saline and brackish intertidal sedments. Microb. Ecol. 31, 319-330.

- Desikachary, T.V., 1959. Cyanophyta, ICAR Monograph on algae, Indian Council of Agricultural Research (ICAR). New Delhi. India. 569 pp.
- Desikachary T.V., Prema, P., 1987. Diatoms from the Bay of Bengal. In: Atlas of Diatoms. Fasc. III. Madras Science Foundation. Madras. pp. 1-10.
- Dickson, D. M. J., Kirst. G. O., 1987. Osmotic adjustment in marine eukaryotic algae: the role of inorganic ions, quaternary ammonium, tertiary sulfonium and carbohydrate solutes. II. Prasinophytes and haptophytes. New Phytol. 106, 657-666.
- Evans, C., Malin, G., Wilson, W.H., Liss, P.S., 2006. Infectious titers of *Emiliania huxleyi* virus are reduced by exposure to millimolar dimethyl sulfide and acrylic acid. Limnol. Oceanogr. 51, 2468-2471
- Gage, D.A., Rhodes, D., Nolte, K.D., Hicks, W.A., Leustek, T., Cooper, A.J., et al., 1997. A new route for synthesis of dimethyl sulphoniopropionate in marine algae. Nature. 387, 891-894.
- Grasshoff, K., Ehrhardt, M., and Kremling, K. (Eds.)., 1983. Methods of Seawater Analysis. Verlag Chemie. Weinheim. pp. 89-224.
- Hendey, N.I., 1964. Bacillariophyceae (Diatoms), In: An introductory account of the smaller algae of British coastal waters. Fishery Inves. Ser. IV London. p. 317.
- Hu, M., Liu, L., Ma, Q., Zhu, T., Tian, X., Dai, M., 2005. Spatial–temporal distribution of dimethyl sulfide in the subtropical Pearl River Estuary and adjacent waters. Cont. Shelf Res. 25, 1996-2007.
- Iverson, R.L., Nearhoof, F.L., Andreae, M.O., 1989. Production of dimethylsulfonium propionate and dimethylsulphide by phytoplankton in estuarine and coastal water. Limnol. Oceanogr. 34, 53-67.
- Jones, G. B., Curran, M. A. J., Swan, H. B., Greene, R. M., Griffiths, F.B., Clementson, L. A., 1998. Influence of different water masses and biological activity on dimethylsulphide and dimethylsulphoniopropionate in the subantarctic zone of the Southern Ocean during ACE 1. J. Geophys. Res. 103, 16,691-16,701.
- Keller, M. D., Kiene, R. P., Matrai, P.A., Bellows, W.K., 1999. Production of glycine betaine and dimethylsulphoniopropionate in marine phytoplankton. I. Batch cultures. Mar. Biol. 135, 237-248.
- Kieber, D., Jianfujiao, J., Kiene, R. P., Bates, T.S., 1996. Impact of dimethylsulfide photochemistry on methyl sulfure cycling in the equatorial Pacific Ocean. J. Geophys. Res. 101, 3715-3722.
- Kiene, R.P., Bates, T.S., 1990. Biological removal of DMS from seawater. Nature. 345, 702-705.
- Kiene, R.P., Linn, L.J., 2000. The fate of dissolved dimethylsulfoniopropionate (DMSP) in seawater: Tracer studies using ³⁵S-DMSP. Geochemica et Cosmochemica Acta. 64, 2797-2810.
- Kirst, G.O., Thiel, C.H., Wolff, J., Nothnagel, M., Wanzek, R., Ulmke.,1991. Dimethyl-sulfoniopropionate (DMSP) in ice-algae and its possible biological role. Mar .Chem. 35, 381-388.

Kirst, G., 1996. Osmotic adjustment in phytoplankton and macroalgae. In: Kiene RP, Visscher PT, Keller MD, Kirst GO (eds) Biological and environmental chemistry of DMSP and related sulfonium compounds. Plenum Press. New York. pp. 121-129.

Lancelot, C., Billen, G., Sournia, A., Weisse, T., Colljn, F., Veldhuis, M.J.W., et al., 1987. Phaeocystis blooms and nutrient enrichment in the continental coastal zones of the North Sea. Ambio 16, 38-46.

Levasseur, M., Michaud, S., Egge, J., Cantin, G., Nejstgaard, J.C., Sanders, R., et al., 1996. Production of DMSP and DMS during a mesocosm study of an Emiliania huxleyi bloom: Influence of bacteria and Calanus finmarchicus grazing. Mar. Biol. 126, 609-618.

Liss, P. S., Merlivat, L., 1986. Air–sea gas exchange rates: introduction and synthesis. In The role of sea–air exchange in geochemical cycling (ed. P. Baut Menard). Dordrecht. Reidel. pp. 113-127.

Liss, P.S., Hatton, A.D., Malin, G., Nightingale, P.D., Turner, S.M., 1997. Marine sulphur emissions. Phil. Trans. R. Soc. B. 352, 159-168.

Ma, Q., Hu, M., Zhu, T., Lingli, L., Dai M., 2005. Seawater, atmospheric dimethylsulfide and aerosol ions in the Pearl River Estuary and the adjacent northern South China Sea. J. Sea Res. 53, 131-145.

Malin, G., Krist, G. O., 1997. Algal production of dimethyl sulfide and its atmospheric role. J. Phycol. 33, 889-896.

Madhupratap. M., Parulekar A.H., 1993. Biological Processes of Northern Indian Ocean., In. Monsoon Biogeochemistry, (eds). Ittekkot. V and Nair, R.R., SCOPE/UNEP Sonderband. 76, 51-83.

Madhupratap, M., Gauns, M., Ramaiah, N., Kumar, S. P., Muraleedharan, P. M., DeSousa, S.N., et al., 2003. Biogeochemistry of the Bay of Bengal: physical, chemical and primary productivity characteristics of the central and western Bay of Bengal during summer monsoon 2001. Deep Sea Res. Part II. 50, 881-896.

Magalhaes, C., Salgado, P., Kiene, R.P., Bordalo, A.A., 2012. Influence of salinity on dimethyl sulfide and methanethiol formation in estuarine sediments and its side effect on nitrous oxide emissions. Biogeochem. 110, 75-86.

Mee, L.D., 1992. The Black Sea in crisis: a need for concerted international action. Ambio-Journal of the Human Environment. 21, 278-286.

Milliman, J. D., Meade, R. H., 1983. World-wide delivery of river sediment to the oceans. J. Geol. 91, 1-21.

Milliman, J. D., Syvitski, J. P. M., 1992. Geomorphic/tectonic control of sediment discharge to the ocean: the importance of small mountainous rivers. J. Geol. 100, 525-544.

Naqvi, S.W.A., Jayakumar, R.A., Narvekar, P.V., Naik, H., Sarma ,V.V.S.S., D'souza, W., Joseph, S., George, M.D., 2000. Increased marine production of N2O due to intensifying anoxia on the Indian continental shelf. Nature. 408, 346-349

Nightingale, P. D., Malin, G., Law, C.S., Watson, A.J., Liss, P. S., Liddicoat, M. I., Boutin, J and Upstill-Goddard, R. C., 2000. In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers. Global Biogeochem. Cycles. 14, 373-387.

Niki, T., Shimizu, M., Fujishiro, A., Kinoshita, J., 2007. Effects of salinity Downshock on dimethylsulfide production. J. Oceanogr. 63, 873-877.

Pednekar, S. M, Matondkar, S.G.P., Gomes, H. D.R., Goes, J. I., Parab, S., Kerkar, V., 2011. Fine-scale responses of phytoplankton to freshwater influx in a tropical monsoonal estuary following the onset of southwest monsoon. J. Earth Syst. Sci. 120, 545-556.

Qian, H.L., Liang, S., 1999. Study on the red tide in the Pearl River Estuary and its near waters. Mar. Environ. Sci. 18, 70-74.

Rao, V. P., Reddy, N. P. C., Rao, Ch, M., 1988. Clay mineral distribution in the shelf sediments off the northern part of the eastcoast of India. Cont. Shelf Res. 8, 145-151.

Rodhe, H., 1999. Human Impact on the atmospheric sulphur balance. Tellus. 51, 110-122

Salgado, P., Kiene, R., Wiebe W., Magalhaes, C. 2014. Salinity as a regulator of DMSP degradation in Ruegeria pomeroyi DSS-3. J. Microbiol, 52, 948-954, doi: 10.1007/s12275-014-4409-1.

Sarma, V.V.S.S., Prasad, V.R., Kumar, B.S.K., Rajeev, K., Devi, B.M.M., Reddy, N.P.C., Sarma, V.V., Kumar, M.D., 2010a. Intra-annual variability in nutrients in the Godavari estuary, India. Cont. Shelf Res. 30, 2005-2014, doi:10.1016/j.csr.2010.10.001.

Sarma, V.V.S.S., Osamu Abe., Makio Honda., Toshiro Saino., 2010b. Estimating of Gas Transfer Velocity Using Triple Isotopes of Dissolved Oxygen. Journal of Oceanography. Vol. 66. pp. 505-512.

Sarma, V.V.S.S., Krishna, M.S., Rao, V.D., Viswanadham, R., Kumar, N.A., Kumari, T.R., Gawade, L., Ghatkar, S., Tari, A., 2012a. Sources and sinks of CO₂ in the west coast of Bay of Bengal. Tellus B. 64, 10961, doi: 10.3402/tellusb.v6i0.10961.

Sarma, V.V.S.S., Viswanadham, R., Rao, G.D., Prasad, V.R., Kumar, B.S.K., Naidu, S.A., Kumar, N.A., Rao, D.B., Sridevi, T., Krishna, M.S.R., Reddy, N.P.C., Sadhuram, Y., Murthy, T.V.R., 2012b. Carbon dioxide emissions from Indian monsoonal estuaries. Geophys. Res. Lettrs, Vol. 39, doi:10.1029/2011GL050709.

Sarma, V.V.S.S., Krishna, M.S., Viswanadham, R., Rao, G.D., Rao, V.D., Sridevi, B., Kumar, B.S.K., Prasad, V.R., Subbaiah, Ch.V., Acharyya, T., Bandyopadhyay, D., 2013. Intensified oxygen minimum zone on the western shelf of Bay of Bengal during summer monsoon: Influence of river discharge. J. Oceanogr. 69, 45-55.

Sciare, J., Mihalopoulos, N., Nguyen, B.C., 2002. Spatial and temporal variability of dissolved sulfur compounds in European estuaries. Biogeochem. 59, 121-141.

Shenoy, D.M., Kumar, M. D., Sarma, V.V.S.S., 2000. Control of dimethyl sulphide in the Bay of Bengal during BOBMEX Pilot Cruise 1998. Proc. Indian Acad. Sci. (Earth Planet. Sci.). 109, 279-283.

Shenoy, D. M., 2002. Biogeochemical cycling of Dimethyl sulfide in the northen Indian Ocean. Ph.D. thesis, Goa University, pp. 191.

Shenoy, D.M., Patil, J. S., 2003. Temporal variations in dimethylsulphoniopropionate and dimethyl sulphide in the Zuari estuary, Goa (India). Mar. Environ. Res. 56 (3), 387-402.

Shenoy, D.M., Jane T. Paul., Mangesh Gauns., Ramaiah, N., Dileep Kumar, M., 2006. Spatial variations of DMS, DMSP and phytoplankton in the Bay of Bengal during the summer monsoon 2001. Marine Environmental Research. 62, 83–97

Shetye, S. R., 1993. The movement and implications of the Ganges-Brahmaputra runoff on entering the Bay of Bengal. Curr. Sci. 64, 32-38.

Sieburth, J. M., 1960. Acrylic acid, an "Antibiotic" principle in Phaeocystis blooms in Antarctic Waters. Science. 132, 676-677.

Simo, R., Grimalt, J. O. and Albaiges, J., 1997. Dissolved dimethyl sulphide, dimethyl sulphoniopropionate and dimethyl sulphoxide in western Mediterranean waters. Deep Sea Res. Part II. 44, 929-950.

Stefels, J., 2000. Physiological aspects of the production and conversion of DMSP in marine algae and higher plants. J. Sea. Res. 43,183-197.

Stefels, J., Steinke, M., Turner, S., Malin, G., Belviso, S., 2007. Environmental constraints on the production and removal of the climatically active gas dimethylsulphide (DMS) and implications for ecosystem modeling. Biogeochemistry. 83, 245-275.

Steidinger, K.A., Willams, J., 1970. Dinoflagellates. Memories of the Hourglass Cruises. 2, 1-251.

Steinke, M., Malin, G., Gibb, S.W., Burkill, P.H., 2002. Vertical and temporal variability of DMSP lyase activity in a coccolithophoria bloom in the northern North Sea. Deep-Sea Res. II. 49, 3001-3016.

Subramanyan, R., 1946. A systematic account of the Marine plankton diatoms off the Madras Coast. Proceedings Indian Acad. Sci. 24, 85-197

Suzuki, R., Ishimaru, T., 1990. An improved method for the determination of phytoplankton chlorophyll using N,N-dimethylformamide. J. Oceanogr. 46, 190-194.

Sunda, W., Kieber, D.J., Kiene, R.P., Huntsman, S., 2002. An antioxidant function for DMSP and DMS in marine algae. Nature. 418, 317-320.

Taylor, F.J.R., 1976. Dinoflagellates from the International Indian Ocean Expedition. A report on material collected by the R.V. "Anton Bruun" 1963-1964. Bibiliotheca Botanica. 132, 1-226.

Taylor, B.F., Gilchrist, D.C., 1991. New routes for the aerobic biodegradation of dimethylsulfoniopropionate. Appl. Environ. Microbiol. 57, 3581-3584.

Townsend, D.W., Keller, M.D., 1996. Dimethylsulfide (DMS) and dimethylsulfonio-priopionate (DMSP) in relation to phytoplankton in the Gulf of Maine. Mar. Ecol. Prog. Ser. 137, 229-241.

Turner, S.M., Malin, G., Liss, P., Harbour, D.S., Holligan, P.M., 1988. The seasonal variation of dimethylsulfide and dimethylsulfoniopropionate concentrations in nearshore waters. Limnol. Oceanogra. 33, 364-375.

Turner, S.M., Malin, G., Bagander, L.E., Leck, C., 1990. Inter-laboratory calibration and sample analysis of dimethyl sulfide in water. Mar. Chem. 29, 47-62.

Turner, S. M., Malin, G., Nightingale, G. D., Liss, P. S., 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, R.G., Cummings, D.G., Mantoura, R.F.C., Rapsomanikis, S.R., et al., 2000. Distribution and air-sea gas exchange of dimethyl sulphide at the European western continental margin. Mar. Chem. 69, 277-300.

VandenBerg, A.J., Turner, S.M., VanDuyl, F.C., Ruardij, P., 1996. Model structure and analysis of dimethylsulphide (DMS) production in the southern North Sea, considering phytoplankton dimethylsulphoniopropionate- (DMSP) lyase and eutrophication effects. Mar. Ecol. Prog. Ser. 145, 233-244.

Venkataraman, K., 1939. A systematic account of some Indian diatoms. Proc. Indian Acad. Sci. 10, 293-368.

Wanninkhof, R., 1992. Relationship between gas exchange and wind speed over the ocean. J. Geophys. Res. 97, 7373-7381.

Wanninkhof, R., McGillis, W. R., 1999. A cubic relationship between air-sea CO2 exchange and wind speed. Geophys. Res. Lett. 26, 1889-1892.

Wolfe, G. V., Kiene, R. P., 1993. Radioisotope and chemical inhibitor measurements of dimethyl sulfide consumption rates and kinetics in estuarine water. Mar. Ecol. Prog. Ser. 99, 261-269.

Wolfe, G. V., Steinke, M., 1996. Grazing-activated production of dimethyl sulfide (DMS) by two clones of Emiliania huxleyi. Limnol. Oceanogr. 41, 1151-1160.

Wolfe, G.V., Steinke, M., Kirst, G.O., 1997. Grazing-activated chemical defence in a unicellular marine alga. Nature. 387, 894-897.

Xu, J., Yin, K., He, L., Yuan, X., Ho, A.Y.T., Harrison, P.J., 2008. Phosphorus limitation in the northern South China Sea during late summer: Influence of the Pearl River. Deep-Sea Res. 55, 1330-1342.

Yan, T., Zhou, M.J., Zhoum, J.Z., Qian, P.Y., 2001. Preliminary studies on red tide formation mechanism in Hong Kong and Pearl River Estuary. Acta Ecology Sinica. 21, 1634-1641.

Zindler, C., Peeken, I., Marandino, C. A., Bange, H. W., 2012. Environmental control on the variability of DMS and DMSP in the Mauritanian upwelling region. Biogeosciences. 9, 1041-1051, doi: 10.5194/bg-9-1041-2012.

Table 1: Mean (±SD) of Sea surface Temperature, Salinity, SPM, Chl a, DO, Ammonium, Nitrate, Phosphate, N:P Ratio, DMS, DMSPt, DMS:DMSP

Trans ects	Temp (°C)	Salinity	SPM (mg l ⁻¹)	Chl a (mg m-3)	DO (μM kg ⁻¹)	NH ₄ (μM kg ⁻¹)	NO_3 ($\mu M kg^{-1}$)	PO ₄ (μM kg ⁻¹)	N:P	DMS (nM)	$\begin{array}{c} DMSP_t \\ (nM) \end{array}$	DMS: DMSP	DMS:Chla
KS	28.3 ± 0.3	33.1 ± 1.1	33.7 ± 7.0	1.2 ± 0.4	172 ± 8.5	1.7 ± 0.7	3.3±0.5	0.5±0.2	10.9 ± 4.7	9.9 ± 6.5	6.4 ± 4.9	1.9 ±1.1	9.6±8
KN	27.7 ± 0.3	33.9 ± 0.1	20.5 ± 9	1.0 ± 0.3	153 ± 15	1.9 ± 1.5	7.7 ± 4.5	0.3 ± 0.2	39.5 ± 16	7.2 ± 5.3	6.8 ± 3.1	1.1 ± 0.6	6.6 ± 4
GS	28.2 ± 0.5	33.8 ± 0.1	19.9 ± 5.5	0.8 ± 0.5	171 ± 6	0.6 ± 0.2	2.5 ± 0.8	0.3 ± 0.1	8.8 ± 2	9.0 ± 4.2	13.6 ± 5.6	0.7 ± 0.2	13.7±7
GN	27.4 ± 0.6	32.2 ± 0.6	21.8 ± 7.6	2.7 ± 2	166 ± 20	0.6 ± 0.3	6.1 ± 2.6	0.4 ± 0.2	15.8 ± 4	10.9 ± 8.9	14.1 ± 12	1.0 ± 1.0	5.4±4
V	29.0 ± 0.4	33.3 ± 0.2	16.8 ± 2.9	1.3 ± 0.4	173 ± 12	0.2 ± 0.1	1.3 ± 1.1	0.3 ± 0.1	6.0 ± 6.8	18.5 ± 8.1	29.2 ± 13	0.7 ± 0.2	14.8 ± 6
VD	29.9 ± 0.1	29.2 ± 1.2	12.5 ± 3.2	1.0 ± 0.2	187 ± 7	0.8 ± 0.4	0.9 ± 0.9	0.2 ± 0.1	8.7 ± 3.7	5.3 ± 3.6	9.2 ± 8.7	1.4 ± 1.7	5.2±3
HD	29.1 ± 0.3	25.7 ± 1.6	9.2 ± 3.4	1.7 ± 1.0	191 ± 5	0.3 ± 0.3	0.7 ± 0.7	0.2 ± 0.2	4.8 ± 4.9	11.7 ± 7.4	30.9 ± 17	0.4 ± 0.2	8.3±5
MS	29.8 ± 0.1	21.7 ± 0.8	9.8 ± 2.6	3.6 ± 1.7	196 ± 6	0.6 ± 0.1	0.9 ± 0.6	0.2 ± 0.2	11.3 ± 9.2	9.5 ± 3.7	20.4 ± 7.5	0.5 ± 0.3	3.3 ± 2
MN	29.7 ± 0.1	23.5 ± 1.8	10.3 ± 2.7	5.3 ± 1.6	202 ± 13	0.3 ± 0.1	0.5 ± 0.6	0.4 ± 0.1	2.4±2	6.6 ± 1.7	25.4 ± 12	0.3 ± 0.2	1.3±0.5

Ratio and DMS:Chl a Ratio along the different cruise transects in the coastal Bay of Bengal.

Table 2: Mean±SD of hydrographic properties, DMS and DMS: Chla ratios in the surface waters in the inner estuaries.

Estuary	Discharge (m ³ s ⁻¹)	Salinity	SPM (mg l ⁻¹)	Chl-a (mg m ⁻³)	NO ₃ (μM)	NH ₄ (μM)	PO ₄ (μM)	SiO ₄ (μM)	N:P	DMS (nM)	DMS: Chla
Krishna (KS)	823#	5.27	309±55	8.2±4	27.1±10	4.9±2	2.2±1	7±3	17.1	1.06	0.2
Godavari (GN)	1050##	0.16	691±200	5.2±3	38.9±9	1.2±0.7	1.9±1	10±4	20.8	1.21	0.2
Mahanadi (MN)	683###	0.07	28.0±12	2.1±2	7.7±3	0.6 ± 0.2	2.3±1	15±6	4.1	0.59	0.3
Ganges Pearl ^{\$} River	15000 ^{####} 9500	0.71	109±42	3.5±1 7.1	15.5±2 40	1.0±0.5	4.9±2 0.5	46±8 50	3.6 80	1.94 4.5	0.5 1.6

[#] collected from Krishna Barrage, Vijayawada
##collected from Cotton Barrage, Dowleiswaram
###collected from Dam authorities, Cuttack
####collected from Indira Gandhi Dam authorities, Farakka.

\$ taken from Hu et al. (2007) during July 2000 in the Pearl River estuary

Table 3: Computation of Sea-to-air fluxes of DMS using different transfer velocity formulations and Seasonal mean winds.

Transfer Velocity Model	Flux of DMS in μmol S m ⁻² d ⁻¹				
	NCB	SCB	CBoB		
Liss and Merlivat (1986)	4.9±3	4.9±3	5.5±4		
Wanninkhof (1992)	7.7±4	6.9±5	8.2±5		
Wanninkhof and McGills (1999)	4.7±3	4.2±3	5.0±3		
Nightingale et al. (2000)	6.8±4	6.0±4	7.2±5		
Sarma et al. (2010b)	10.2±6	9.1±6	10.8±7		

Legend to Figures

- Figure 1. Map showing station locations.
- Figure 2. Spatial distribution of a) surface temperature, b) salinity, c) DO (μ M) d) SPM (mg l⁻¹) e) Nitrate (μ M), f) Ammonium (μ M), g) phosphate (μ M), h) SiO4 (μ M), i) N:P ratio, j) Si:N ratio and k) Chlorophyll-a (mg m⁻³).
- Figure 3. Spatial distribution of biovolume of phytoplanktons community a) Bacillariophycaea , b) Dinophyceae and c) Cyanophyceae (μm³).
- Figure 4. Spatial distribution of a) DMS (nM), b) DMSP $_t$ (nM), c) DMS/Chl and DMS:DMSP along the coastal Bay of Bengal
- Figure 5. Relationship between DMS and salinity at a) NCB and b) SCB (open circles at KS, KN, GS and closed circles at GN).
- Figure 6. Relationship of N:P with DMS:DMSP in the coastal Bay of Bengal (open circles in the SCB and closed circles in the NCB).

Figure. 1.

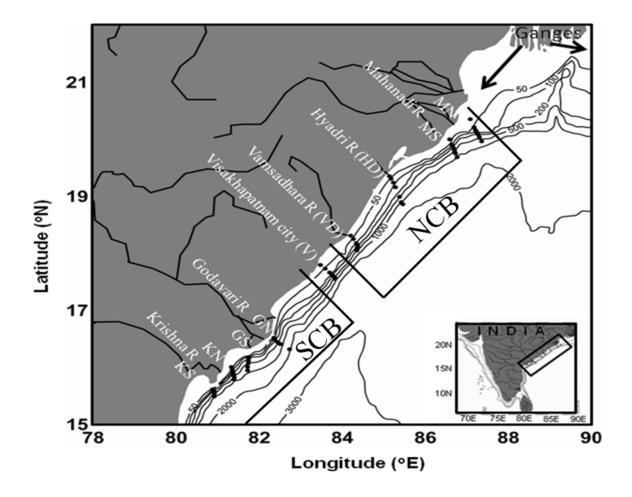


Figure. 2.

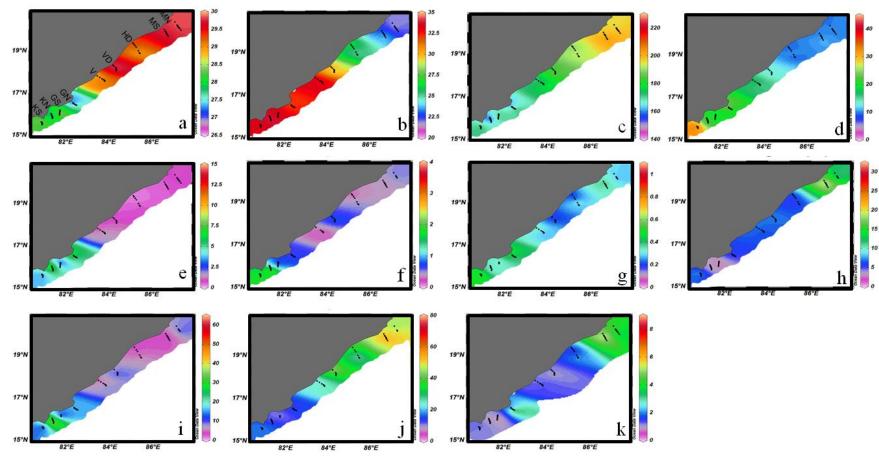


Figure. 3.

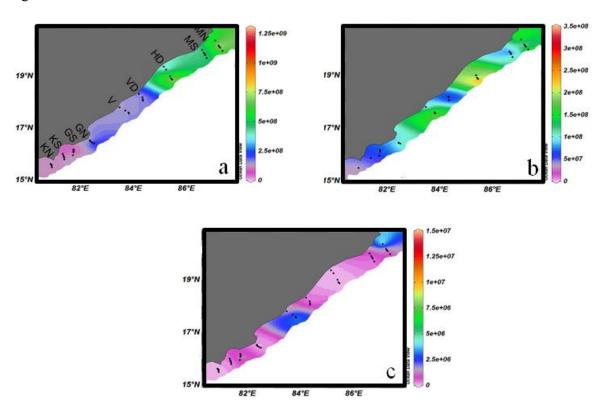


Figure 4:

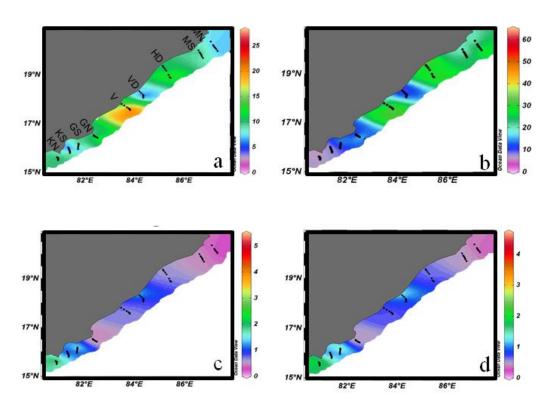


Figure 5

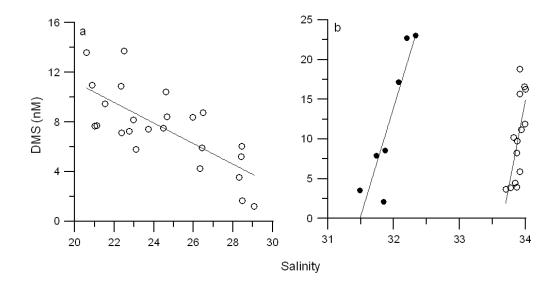


Figure 6:

