

Variations in concentrations and fluxes of dimethylsulphide (DMS) from the Indian estuaries

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Abstract

In order to examine the variations in concentrations of dimethylsulphide (DMS) and its fluxes to the atmosphere, 25 major and medium estuaries from Indian subcontinent were sampled during wet and dry periods. River discharge brought substantial amount of nutrients and suspended particulate matter (SPM) to the Indian estuaries, however, the concentration of phytoplankton biomass was severely limited by latter due to shallowing of photic depth. Bacillariophyceae was the dominant phytoplankton group in the Indian estuaries followed by green algae, cyanophyceae and dinophyceae. Relatively higher concentrations of DMS were observed in the estuaries located along the east (3.6 ± 5.7 nM) than west coast of India (0.8 ± 0.3 nM) during wet period whereas no significant differences were observed during dry period. The concentrations of DMS were significantly lower during wet than dry period and it was consistent with the phytoplankton biomass. The slope of the relation between DMS and phytoplankton biomass displayed significant spatial variation due to contribution of different groups of phytoplankton in the Indian estuaries. The concentrations of DMS in the Indian estuaries were higher than other estuaries in the world except some Chinese estuaries. The annual mean flux (1.95 ± 2.5 $\mu\text{mol m}^{-2} \text{d}^{-1}$) from the Indian estuaries is lower than that of other estuaries in the world, except Pearl River Estuary due to inhibition of phytoplankton growth by suspended load and low flushing rates.

Key words: DMS; Fluxes; River discharge; Nutrients inputs; Indian Monsoonal estuaries

1. Introduction

Dimethyl sulfide (DMS) is an important biogenic sulfur gas, produced mainly by marine phytoplankton (Iverson et al. 1989; Belviso et al. 1990) and dimethylsulfoniopropionate (DMSP) is a major precursor of DMS. DMS is produced from a complex interplay of biological and non-biological pathways, such as phytoplankton production and microbial cleavage of DMSP to DMS (Schafer et al. 2010; Simo 2004; Stefels et al. 2007). DMSP acts as an osmoregulator in marine algae. The emission of DMS from seawater is expected to balance the excess sulfur deposition over the remote oceans (Charlson et al. 1992) and proposed a CLAW hypothesis (after the authors Charlson, Lovelock, Andreae and Warren). DMS is oxidized to form aerosol particles and Cloud Condensation Nuclei (CCN) in the atmosphere that in turn enhances back scattering of radiation. According to Liss et al. (1993), the major DMS producing groups are Coccolithophores followed by Phaeocystis, Dinoflagellates and Diatoms. In addition, nutrients (nitrate and phosphate) limitation (Turner et al. 1988; Stefels and van Boekel, 1993; Hu et al. 2005) and decrease in salinity (Shenoy and Patil, 2003) enhances the biological production of DMS. Moreover, enhanced liberation of DMSP as well as DMS occurs resulting from cell lysis during zooplankton grazing on DMSP-producing phytoplankton (Dacey and Wakeham, 1986; Yang et al. 2000). Once released from phytoplankton into the water column, DMSP is subjected to rapid turnover into DMS at the rate of 1 to 129 nM d⁻¹ (Ledyard and Dacey 1996; Kiene and Linn 2000). Only minor part of DMSP undergoes enzymatic cleavage resulting in formation of DMS (Kiene and Linn 2000). DMS is the major reduced product of DMSO during the photodegradation and/or microbial processes. Production and fate of DMSO in seawater is an important issue as DMSO can in turn act as a source of DMS from bacterial reduction. Continental shelf regions have been identified as a significant source of DMS to the atmosphere (Andreae 1986; Leak and Rhode 1991; Turner et al. 1996) and several studies revealed that estuaries (Iverson et al. 1989) and corresponding plumes to the open ocean (Turner et al. 1996; Simo et al. 1997) could represent an important source of atmospheric DMS.

Though several studies have been carried out on distribution of DMS in the marine ecosystems, however, the studies in the estuaries are rather limited (for ex. Cerqueira and Pio 1999; Moret et al. 2000; Hu et al. 2005). These studies suggested that the concentrations of DMS varied widely between 0.05 and 52.7 nM in the world estuaries due to variable phytoplankton composition, nutrients stress and zooplankton grazing etc (Iverson et al. 1989; Cerqueiro and Pio 1999; Sciare and Mihalopoulos 2002; Hu et al. 2005). However, studies on the distribution of DMS in the tropical estuaries are rather sparse (Shenoy and Patil 2003). Several recent studies on biogeochemical

properties of Indian estuaries revealed that they are significantly different from other estuaries in the world with reference to pattern and magnitude of discharge (Sarma et al. 2009, 2010, 2012). Indian estuaries receive substantial amount of freshwater only during southwest monsoon period (June - September) when entire estuary turns in to a freshwater lake. Moderate discharge occurs during October to December resulting in formation of strong salinity stratification with increased stability of water column that promotes phytoplankton blooms (Acharyya et al. 2012). Negligible discharge occurs between January and May, when seawater dominates in the estuary through tides. Recently the distribution and fluxes of carbon dioxide and nitrous oxide from the Indian estuaries were observed to be significantly lower than that of European and American estuaries (Sarma et al. 2012; Rao and Sarma 2013). They noticed significant differences in concentrations and fluxes of trace gases between wet and dry period in the Indian estuaries. Hence, we conducted experiments in the Indian estuaries during wet and dry periods to examine the spatial and temporal variations in concentrations of DMS to evaluate potential controlling factors on its distribution and quantify the contribution to atmospheric DMS.

2. Materials and methods

2.1. Study Area

In order to cover spatial and temporal variations in DMS concentrations and fluxes, 25 major and medium estuaries have been selected from both east and west coast of India (Fig. 1). Sampling was conducted during peak discharge (wet) period (28th July to 18th August 2011) and dry period (2nd to 15th January 2012). Since average depth of the Indian estuaries is <5 m, surface samples were collected at 3 to 5 stations covering variable salinity from mouth of the estuary to 30-40 kms upstream where near freshwater is encountered. The water temperature and salinity were measured using a CTD system (SBE 19 plus, Sea Bird Electronics, USA). About one liter of water sample was filtered through GF/F (0.7 μm ; Whatman) filter at low vacuum and Chlorophyll-*a* (Chl-*a*) retained on the filter was extracted with N, N, Dimethyl formamide at 4⁰C in dark for 24 h. The fluorescence in the extract was measured using spectrofluorophotometer (Varian Instruments, USA) following Suzuki and Ishimaru (1990). The analytical precision for Chl-*a* analysis was $\pm 4\%$. The concentrations of Chl-*a* was represented as phytoplankton biomass. Nutrients (Dissolved Inorganic Nitrogen (DIN)=nitrate+nitrite+ammonium); Dissolved Inorganic Phosphate (DIP); and Dissolved Silicate (DSi)) were measured using Spectrophotometric method following Grashoff et al. (1983). The suspended particulate matter (SPM) was measured based on the weight of the matter retained on 0.22 μm pore size polycarbonate filter after passing 500-1000 ml of water. In order to determine phytoplankton composition, one liter of surface water sample was collected in a polythene bottle and

fixed with lugol iodine solution. Before identification, water samples were allowed to settle for 24 h and the supernatant was decanted until sample was concentrated to 10 ml. About 0.1 ml of the concentrated sample was taken on glass slides and observed under *BX51 OLYMPUS* microscope.

DMS samples must be measured at the earliest possible time due to photochemical degradation. Since the estuaries are several hundred kilometers away from the laboratory and it is difficult to carry Gas Chromatography in the vehicle at all the estuaries. Hence, we adapted a new method to collect these samples. DMS in the samples was extracted using the purge-and-trap technique (Andreae and Barnard 1983; Bates et al. 1987; Burgermeister et al. 1990; Hu et al. 1997; Shenoy et al. 2002) with some modification. In brief, DMS samples were collected into 40 ml amber colored glass bottles to prevent their photochemical decomposition. About 15 ml of sub-sample was purged with ultra pure nitrogen at a flow rate of 30-40 ml min⁻¹ for 15 min and then evolved gases were trapped by passing through a glass ‘U’ tube kept at liquid nitrogen temperature in the gas line to freeze the evolved gas. Once the extraction was completed, the ‘U’ tube was sealed with gas burner and these tubes were kept at dark until analysis in the laboratory after a week time. In order to examine the possible changes in concentrations of DMS during this process, several experiments were conducted in the laboratory before field trip by measuring DMS samples immediately following Shenoy et al. (2002) method and extracting the gas into ‘U’ tubes and measuring them after two weeks. The difference between these two sets yielded 0.05 nM over 20 numbers of aliquots. This additional error is added to the DMS samples apart from the error involved in the measurements. DMS was analyzed using Gas Chromatography system (Agilent 7890A) equipped with Chromosil 330 packed column and Flame Photometric Detection (FPD) (Shenoy et al. 2002; Turner et al. 1990). Isothermal (at 55°C) operation gave a retention time for DMS of around 2.5 min. Calibration of the instrument has been carried out using standard DMSP (Research Plus, Netherlands) and the precision of this method was within 8%.

2.2. Calculation of DMS flux from estuaries

The flux of DMS from water to air (F) is calculated following Turner et al. (1996)

$$F=k(C_w-(C_a h^{-1})) \quad 1$$

Where F = net flux of DMS; k is the DMS transfer velocity (m d⁻¹), h is Henry’s law constant; C_w and C_a are DMS concentrations in the water and air phase respectively. C_a is taken as zero, and thus

$$F=k.C_w \quad 2$$

Transfer velocity (k) is parameterized in terms of wind speed and water temperature according to formulations given by Liss and Merlivat (1986). Schmidt number of DMS is calculated from

Saltzman et al. (2007). Wind speed data at different estuaries were obtained from automated weather stations installed along the coast by Indian Meteorological Department (IMD) (www.imd.gov).

3. Results and Discussion

The estuaries in the Indian subcontinent are called monsoonal estuaries as the river discharge is mainly controlled by monsoonal precipitation (Sarma et al. 2009; Vijith et al. 2009). Hence, these estuaries are significantly different from other estuaries with reference to the discharge pattern. Indian estuaries receive discharge during monsoon period (3-4 months) when significant amount of precipitation occurs. The magnitude of freshwater discharge from various rivers on Indian subcontinent depends on the spatial variations in monsoonal precipitation. India receives annual monsoon rainfall in the order of 3000 km^3 (Soman and Kumar 1990) and the distribution over Indian subcontinent depends on the south-west and north-east monsoons, shallow cyclonic depressions, disturbances and local storms. Most of it takes place under the influence of south-west monsoon between June and September with strong spatial variations. For instance southwestern India receives the maximum rainfall ($\sim 3000 \text{ mm}$) followed by northeastern ($1000\text{-}2500 \text{ mm}$) and the least over the southeastern ($300\text{-}500 \text{ mm}$) and northwestern India ($200\text{-}500 \text{ mm}$) (Soman and Kumar 1990). Hence, the spatial variations in river discharge by various rivers are governed by the rainfall received in the watershed of the river.

3.1. Seasonal variations in hydrographic conditions in the Indian estuaries

The annual mean river discharge into the Indian estuaries varied from ~ 28 to $3505 \text{ m}^3 \text{ s}^{-1}$ (Table 1) with relatively high discharges in the estuaries located along the east coast ($1168 \pm 1159 \text{ m}^3 \text{ s}^{-1}$) than west coast ($399 \pm 486 \text{ m}^3 \text{ s}^{-1}$; t-test=2.86; $p < 0.01$; Table 3) during wet period. Even though precipitation is more on the western India, most of the western originated rivers flow eastward and open to the Bay of Bengal. Salinity ranged between 0.1 and 28.8 in the Indian estuaries during wet period with significant spatial variability. Relatively higher salinities (>20) were observed in the minor estuaries such as Rushikulya, Nagavali and Vaigai, due to low freshwater discharge than major estuaries such as Godavari, Mahanadi, Krishna (Table 1). The magnitude of river discharge determines the amount of organic matter as well as nutrients inflow into the estuaries and the stability of water column governs their interaction with the microbial processes (Sarma et al., 2011, 2012, 2014). Biogeochemical properties in the monsoonal estuaries are also significantly variable and are depend on the composition of material received along the flow path. For instance, higher concentrations of SPM ($0.4\text{-}918 \text{ mg l}^{-1}$) were observed in the Indian estuaries during wet period and were relatively higher in the estuaries located along the west coast ($150 \pm 285 \text{ mg l}^{-1}$) than in the east

coast of India ($70 \pm 69 \text{ mg l}^{-1}$; $t\text{-test}=2.73$; $p < 0.01$; Table 3). The magnitude of SPM modified the light penetration depth (photic) that influences phytoplankton biomass and production (Caffrey et al. 1998; Sarma et al. 2009). As a result, phytoplankton biomass (represented as chlorophyll-a) was lower by ten times in the west coast ($1.0 \pm 1.6 \text{ mg m}^{-3}$) compared to the east coast estuaries ($9.5 \pm 7.5 \text{ mg m}^{-3}$; $t\text{-test}=2.86$; $p < 0.01$). In contrast, higher nutrients concentrations, except silicate, were observed in the west coast (DIN= $38.3 \pm 26.0 \text{ }\mu\text{M}$, and DIP= $11.5 \pm 9.6 \text{ }\mu\text{M}$) than in the east coast estuaries (DIN= $11.3 \pm 11.6 \text{ }\mu\text{M}$; $t\text{-test}=2.86$; $p < 0.01$, and DIP= $4.6 \pm 4.2 \text{ }\mu\text{M}$; $t\text{-test}=1.70$; $p < 0.1$ respectively). On the other hand, higher dissolved silicate concentrations were observed in the east coast ($85 \pm 82 \text{ }\mu\text{M}$) than in the west coast ($34.6 \pm 8.6 \text{ }\mu\text{M}$; $t\text{-test}=2.45$; $p < 0.01$) estuaries during wet period.

The contrasting conditions were observed during dry period with relatively higher salinities in the Indian estuaries (1.8 to 29.5) due to less precipitation and drying of upstream river and closing of dam gates for storage of water to meet domestic and industrial needs. Low salinity values were observed at Kali (1.8), Ponnayyar (5.8) and Cauvery (8.3) as this region receives significant rainfall during winter (north east) monsoon (Soman and Kumar 1990). In contrast to wet period, the concentrations of nutrients were relatively higher in the east coast (DIN= 16.4 ± 18.4 , DIP= 6.0 ± 6.2 ; DSi= $133.2.6 \pm 77.6 \text{ }\mu\text{M}$) than in the west coast estuaries (DIN= 11.3 ± 10.5 ; DIP= 5.7 ± 4.3 ; DSi= $65.4 \pm 34.5 \text{ }\mu\text{M}$) during dry period (Table 3). The concentrations of SPM were ranged between 20.6 and 83.2 mg l^{-1} (except Ponnayyar) and these concentrations are significantly lower than those of wet period. The phytoplankton biomass was also relatively high during dry period (1.6 to 31.5 mg m^{-3}) compared to that of wet period (0.8 to 27.7 mg m^{-3} ; $t\text{-test}=1.71$; $p < 0.1$) due to low SPM during former period.

3.2. Seasonal variations in phytoplankton abundance and composition in the Indian estuaries

Phytoplankton abundance in the Indian estuaries varied from 0.4 to $14.9 \times 10^5 \text{ Cells l}^{-1}$ (except Ponnayyar; $78.1 \times 10^5 \text{ Cells l}^{-1}$ and Ambalayaar ; $26.8 \times 10^5 \text{ Cells l}^{-1}$) during wet period and 0.5 to $26.9 \times 10^5 \text{ Cells l}^{-1}$ during dry period with significant spatial variations. Relatively higher phytoplankton abundance was noticed in the estuaries located along the east coast ($11.3 \pm 20.6 \times 10^5 \text{ Cells l}^{-1}$) than in the west coast ($3.0 \pm 1.4 \times 10^5 \text{ Cells l}^{-1}$; $t\text{-test}=2.26$; $p < 0.01$) during wet period (Table 3). The cell abundance was not significantly different in the east coast ($7.2 \pm 9.1 \times 10^5 \text{ Cells l}^{-1}$) and west coast estuaries ($6.2 \pm 7.3 \times 10^5 \text{ Cells l}^{-1}$; $t\text{-test}=0.37$; $p < 0.5$) during dry period (Table 3). The phytoplankton abundance decreased (increased) during dry period from that of wet period in the east (west) coast estuaries. It could be due to availability of nutrients and SPM concentration that controlled the growth of phytoplankton. Within the phytoplankton, cyanobacteria dominated in the east coast

estuaries ($6.8 \pm 18 \times 10^5$ cells L^{-1}) whereas diatoms were abundant in the west coast estuaries ($2.4 \pm 1.0 \times 10^5$ cells L^{-1}) compared to other groups of phytoplankton during wet period (Table 3). The relative contribution of diatoms, cyanobacteria, green algae and dinoflagellates to total phytoplankton abundance was 59, 27, 12, 2% and 84, 3, 6, 7% respectively in the estuaries located along the east and west coasts during wet period. Similarly the most dominant phytoplankton group was diatoms (56%) followed by cyanobacteria (27%), green algae (15%) and dinoflagellates (2%) in the east coast estuaries whereas 43, 18, 24, and 16% respectively in the west coast estuaries during dry period. Over all, bacillariophyceae (diatoms) was the most dominant/abundant group in the Indian estuaries during both wet and dry periods except during wet period in the estuaries located in the southeast coast, where cyanophyceae was dominated. Cyanophyceae abundance was 68 times higher in the east coast estuaries ($6.8 \pm 18.0 \times 10^5$ cells L^{-1}) than in the west coast estuaries ($0.1 \pm 0.1 \times 10^5$ cells L^{-1}) during wet period (Table 3). On the other hand, the abundance of Green algae was about 12 times higher in the east ($1.2 \pm 2.1 \times 10^5$ cells L^{-1}) than west coast estuaries ($0.1 \pm 0.1 \times 10^5$ cells L^{-1}) whereas higher abundance of dinoflagellates was noticed in the latter ($0.3 \pm 0.8 \times 10^5$ cells L^{-1}) than former estuaries ($0.1 \pm 0.1 \times 10^5$ cells L^{-1}) during wet period (Table 3). This pattern is consistent with nutrients distribution as higher silicate concentrations were observed in the east coast estuaries whereas higher nitrate and phosphate concentrations were noticed in the west coast estuaries. Such spatial variations in groups of phytoplankton in the Indian estuaries have resulted from variable river discharge patterns, flushing time, mixing regime and concentrations of nutrients received through variable sources. Therefore, it may have significant impact on the DMS concentrations in the Indian estuaries as the salinity and nutrients stress on phytoplankton are expected to be different and variable composition of phytoplankton also govern the DMS production. In order to examine this, spatial variations in DMS and their controlling factors were measured.

3.3. Spatial variations in concentration of DMS in the Indian estuaries and their controlling factors

The DMS concentrations ranged from 0.1 to 38.3 nM during wet period (Table 1) and 1.4 to 56.4 nM during dry period in the Indian estuaries (Table 2). Relatively higher mean DMS concentrations were noticed in Vamsadhara (12.1 nM) and Nagavali (20.5 nM), compared to other estuaries (<3 nM) during wet period whereas >12 nM were observed all estuaries sampled during dry period except Godavari, Ponnayaar and Kochi back waters (Table 2). The mean DMS concentrations were relatively higher in the estuaries located along the east coast (3.6 ± 5.7 nM) than in the west coast estuaries (0.8 ± 0.4 nM; $t\text{-test}=2.27$; $p<0.01$) during wet period and it was consistent with the phytoplankton biomass, which was higher in the former (9.5 ± 7.5 mg m^{-3}) than latter estuaries (1.0 ± 1.6 mg m^{-3} ; $t\text{-test}=2.86$; $p<0.01$; Table 3). On the other hand, no significant differences in DMS

concentrations were noticed between estuaries located in the east (15.3 ± 10.1 nM) and west coast (15.0 ± 15.4 nM) during dry period with relatively comparable phytoplankton biomass was observed in the former (12.5 ± 13.9 mg m⁻³) and latter estuaries (9.5 ± 17.3 mg m⁻³) suggesting that phytoplankton biomass has significant impact on their production. The observed DMS concentrations in the Indian monsoonal estuaries (0.1 to 56.4 nM) close to Pearl River estuary (0.05 to 52.7 nM) compared to those in other estuaries in the temperate regions (range 0-25 nM; Table 4).

3.4. Influence of salinity on DMS concentrations in the Indian estuaries

Higher DMS concentrations in the Indian estuaries were broadly associated with high salinity during both wet and dry periods (Fig. 2; Table 1, 2). However, no significant relation was observed between salinity and DMS suggesting that salinity does not alone control the concentrations of DMS in the Indian estuaries. Walker et al. (2000) noticed a sharp increase in DMS concentrations coinciding with a surface lens of freshwater in the shelf region of north-eastern New Zealand. Shenoy and Patil (2003) also observed that sharp increase in DMS concentrations in Zuari estuary is associated with decrease in salinity. In contrast, our results in the Indian estuaries suggest that low DMS concentrations were observed at low salinity suggesting that alternative processes may be controlling the DMS production. There are two potential reasons for such differences. The enhanced DMS concentrations expected with sharp decrease in salinity due to initiation of freshwater discharge in to the estuary. As a result phytoplankton cells experience salinity shock leading to release of DMS (Shenoy and Patil 2003). On the other hand, Indian estuaries were filled with low saline water during peak discharge period, when sampling was conducted; hence, such salinity shock is possible to occur only during initial phase of discharge and not during peak discharge period. Since our observations were carried out during peak discharge period, low DMS concentrations were observed. On the other hand, increased SPM concentration was associated with decrease in salinity resulting in shallow photic depth and decrease in phytoplankton biomass as well DMS production in the Indian estuaries. This could be potential reason for low DMS concentrations in the estuaries that received higher magnitude of river discharge.

3.5. Influence of phytoplankton and zooplankton biomass on concentrations of DMS in the Indian estuaries

DMS showed significant correlation with phytoplankton biomass (Fig.2) in the Indian estuaries during both wet and dry periods, however, the slopes were found to be region specific east coast estuaries (slope=0.12; $r^2=0.36$; $p<0.001$) and west coast estuaries (slope=0.35; $r^2=0.82$; $p<0.001$) during wet period and dry period (slope=1.07; $r^2=0.28$; $p<0.01$ and slope=1.14; $r^2=0.63$; $p<0.001$) respectively. Such variable slopes in the relation could be due to differences in the phytoplankton

community (Kettle et al. 1999). In addition to this, variations in the grazing pressure on phytoplankton biomass could also contribute to the seasonal and spatial variations in the DMS concentrations. The zooplankton abundance was relatively higher during dry period (514.3 Nos/m³) compared to that of wet period (254.1 Nos/m³) in the Indian estuaries (Mr. V. Venkata Ramana, personal communication, 2014). The higher DMS concentrations during dry period could possibly be due to higher grazing pressure leading to enhanced DMS production. Zooplankton grazing accelerates the production of DMSP_P from the phytoplankton cells increasing the production of DMS (Dacey and Wakeham 1986; Cantin et al. 1996). Though DMSP production is a species-specific, it is mainly controlled by extra-cellular processes involving the entire planktonic community (Simo et al. 1997), such as zooplankton grazing (Leck et al. 1990; Christaki et al. 1996; Wolfe et al. 1997; Jones et al. 1998), microbial activity (Kiene and Bates 1990; Kiene 1992; Wolfe et al. 1994; Zimmer-Faust et al. 1996; Jones et al. 1998) and the release of algal lysis upon senescence or cell breakage (Wolfe et al. 1994). Shenoy and Patil (2003) noticed that higher concentrations of DMS coincide with the low in phytoplankton abundance in the Zuari estuary during summer period along with higher abundance of zooplankton. As a result of this stress, the relation between phytoplankton biomass and DMS may be weaker during dry period (Fig. 2).

3.6. Influence of nutrients stress on concentrations of DMS in the Indian estuaries

Nutrients stress on the phytoplankton cell enhances DMS production to the water column. For instance, Hu et al. (2005) noticed increase in concentrations of DMS with salinity from Peal River estuary to shelf region of the South China Sea (3.8-14.4 nM) and attributed to phosphate limitation (Xu et al. 2008). Niki et al. (2007) also noticed that phosphate limitation is identified as an important controlling factor for the production of DMS in the in Bay of Japan. The possible explanation for the increase of DMS in these estuaries could be resulted from cell lysis under phosphate limitation that lead to release of intracellular DMSP (and perhaps DMSP lyase) into the estuarine water. Eva and William (2003) reported that a significant increase of intra cellular DMSP concentration occurred for each type of nutrient (N, P and Si) limitation. In addition to this, the nutrient limitation influences population growth of small cells (picophytoplankton), which could promote anti-grazing adaptive strategies such as DMSP lysis to DMS and acrylate that are rapidly grazed by microzooplankton (Calbet and Landry 2004) that further enhances DMSP cleavage to DMS through grazing mediated mechanism (Dacey et al. 1998; Archer et al. 2001a). The higher DMS concentrations were observed in Nagavali (20.5 nM) and Vamsadhara (12.1 nM) estuaries during wet period and were associated with low phosphate concentrations (Table 1). In addition to this, higher DMS levels were observed in most of the east coast estuaries associating with lower nitrate

concentrations compared to that of west coast estuaries. Therefore, estuaries along the east coast might have experienced nitrate limitation that lead to increase in DMS production. The impact of nutrients limitation on DMS production in the Indian estuaries must be evaluated in the future studies.

3.7. *DMS:Chl-a ratios in the Indian estuaries*

The DMS:Chl-a ratio ranged from 0.1 to 7.5 (0.7 ± 1.5) mmole/mg, and 0.3 to 16.3 (4.5 ± 5.1) mmole/mg during wet and dry period respectively in the Indian estuaries (Table 1 and 2). Hu et al. (2005) noticed that though phytoplankton biomass was higher in the Pearl River estuary compared to South China Sea (SCS), the average DMS concentrations were about equal or higher in the latter than in the former regions. The mean DMS:Chl-a values were higher in the shelf region of the SCS (32.0 ± 18.8 , 28.6 ± 30.9 and 60.5 ± 79.1 mmole/mg) during July 2000, May 2001 and November 2002 respectively) compared to that of the Pearl River estuary (1.6 to 6.2 mmole/mg) (Hu et al. 2005) and this was attributed to severe phosphate limitation in the former region (Xu et al. 2008). On the other hand, the mean DMS:Chl-a values during wet and dry period in the Indian estuaries were relatively higher than that of Pearl River estuary. Higher DMS:Chl-a ratios were observed in Vamsadhara and Nagavali (>1 mmole/mg) during wet period where low SPM and high salinity were noticed. On the other hand, DMS:Chl-a ratio was <1 mmole/mg in all other estuaries and such low ratios were associated with high SPM concentrations resulting in light limitation and low phytoplankton biomass during wet period. On the other hand, DMS:Chl-a ratios were >2 mmole/mg in all estuaries except Ponnayyar, Cauvery and Kochi Back Waters during dry period associating with low SPM suggesting that increased light penetration depth resulting in phytoplankton growth that promoted DMS production in these estuaries. This study suggests that river discharge modified physical processes (salinity, flushing rates and stratification) that brought significant modifications in the chemical (variable concentrations and ratios of nutrients), geological (suspended particulate matter) that impacted composition of phytoplankton resulting in variable rates of DMS production in the Indian estuaries.

3.8. *DMS Flux from the Indian estuaries*

The DMS flux from the Indian estuaries at water-air interface ranged from 0.02 to 2.71 $\mu\text{mol m}^{-2} \text{d}^{-1}$ ($0.3 \pm 0.6 \mu\text{mol m}^{-2} \text{d}^{-1}$) and 0.51 to 6.01 $\mu\text{mol m}^{-2} \text{d}^{-1}$ ($2.9 \pm 1.8 \mu\text{mol m}^{-2} \text{d}^{-1}$) during wet and dry period respectively. The mean fluxes of DMS to the atmosphere were ~ 10 times higher during dry than wet period. Such higher fluxes were also contributed by higher wind speeds in the former than latter region. The flux values are in good agreement with those reported in the coastal and open Arabian Sea regions (Shenoy 2002). The DMS fluxes were relatively higher in the estuaries located along the

east coast ($0.49 \pm 0.8 \mu\text{mol}^{-1} \text{m}^{-2} \text{d}^{-1}$) than west coast estuaries ($0.15 \pm 0.08 \mu\text{mol} \text{m}^{-2} \text{d}^{-1}$) during wet period whereas no significant variations were noticed between east coast ($2.7 \pm 2.8 \mu\text{mol}^{-1} \text{m}^{-2} \text{d}^{-1}$) and west coast estuaries ($3.1 \pm 2.8 \mu\text{mol}^{-1} \text{m}^{-2} \text{d}^{-1}$) during dry period. Higher DMS fluxes were found in the east coast estuaries during wet period namely Nagavali, Vamsadara, Baitarani, Godavari, Vaigai and Penna (2.71, 1.57, 0.55, 0.30, 6.0, and $5.0 \mu\text{mol} \text{m}^{-2} \text{d}^{-1}$ respectively) than other estuaries in India. Even though wind speeds were low over these estuaries, high DMS concentration in the surface water led to higher DMS flux during dry period (Table 1). The observed mean DMS flux in the west coast estuaries is ~ 2 times lower than that of previously reported for the Zuari estuary (Shenoy and Patil 2003) during wet period. But our mean DMS flux for Indian estuaries ($1.92 \pm 2.5 \mu\text{mol} \text{m}^{-2} \text{d}^{-1}$) is higher than that of elsewhere in the world except in Pearl river estuary (Table 4). The mean DMS flux from the Indian estuaries is nearly less than half of coastal Bay of Bengal ($5.5 \pm 4 \mu\text{mol} \text{m}^{-2} \text{d}^{-1}$; Rao et al. 2015) and an orders of magnitude less than that of reported for the European coastal and shelf waters ($32 \mu\text{mol} \text{m}^{-2} \text{d}^{-1}$; Turner et al. 1998) and also global coastal and shelf zones ($7.76 \mu\text{mol} \text{m}^{-2} \text{d}^{-1}$; Andreae, 1986). Such low DMS fluxes from the Indian estuaries were attributed to significant control of SPM, brought by the river discharge, resulting in decreased light penetration depth and growth of phytoplankton.

4. Conclusions

First-ever report on comprehensive DMS measurements from 25 major and medium estuaries from Indian sub-continent have been presented. Freshwater discharge into Indian estuaries was controlled by the precipitation pattern over Indian sub-continent. The concentrations of nutrients were different in various Indian estuaries that brought significant modifications in the phytoplankton community structure. Bacillariophyceae (Diatoms) were mostly dominant in the Indian estuaries followed by green algae, cyanophyceae and dinophyceae. The surface DMS concentrations were relatively lower during wet than dry period in the Indian estuaries due to higher SPM concentration during former resulting in low plankton biomass. The concentrations of DMS were higher in the estuaries located along the east coast ($3.6 \pm 5.7 \text{ nM}$) than in the west coast ($0.8 \pm 0.4 \text{ nM}$) of India during wet period whereas such spatial variations were not observed during dry period. DMS concentrations showed linear relation with phytoplankton biomass, however, the slope of the relation showed significant spatial variation and were attributed to contribution of different groups of phytoplankton in the Indian estuaries. . The DMS fluxes from Indian estuaries ranged from 0.02 to $2.71 \mu\text{mol} \text{m}^{-2} \text{d}^{-1}$ ($0.3 \pm 0.6 \mu\text{mol} \text{m}^{-2} \text{d}^{-1}$) during wet and 0.51 to $6.01 \mu\text{mol} \text{m}^{-2} \text{d}^{-1}$ ($2.9 \pm 1.8 \mu\text{mol} \text{m}^{-2} \text{d}^{-1}$) during dry period. The mean DMS flux from the Indian estuaries ($1.95 \pm 2.5 \mu\text{mol} \text{m}^{-2} \text{d}^{-1}$) is significantly higher than other estuaries in the world, except Pearl River estuary whereas nearly two orders of magnitude

lower than that of reported for the European coastal and shelf waters ($32 \mu\text{mol m}^{-2} \text{d}^{-1}$). This study suggested that discharge has significant impact on the production of DMS through shallowing of light penetration depth (turbidity) and decrease in plankton biomass.

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Table 1: Variations in Annual Mean Discharge, Salinity, SPM, PB, DIN, DIP, DSi, N:P, DMS, DMS/Chla, Diatoms and DMS flux in Indian estuaries during wet period (Mean Values; Calculated from 3-7 points from each station).

Estuary	Area (km ²)	Annual mean discharge (m ³ s ⁻¹)	Salinity	SPM (mg l ⁻¹)	PB (mg m ⁻³)	DIN (μM)	DIP (μM)	DSi (μM)	N:P	DMS (nM) Mean(Range)	DMS /Chla	Diatoms(x10 ⁵ cells)	Phytoplankton Abundance	Flux (μM m ⁻² d ⁻¹)
Rivers Flowing towards Bay of Bengal														
Haldia	18.15	1600	0.7	229.7	2.9	20.1	13.4	26.2	4.4	1.9(1.1-2.4)	0.7	1.29	1.7	0.22
Subarnalekha	23.15	392 [#]	4.0	50.8	18.0	7.2	0.8	28.2	9.0	1.6(1.5-1.8)	0.1	14.52	14.9	0.04
Baitarani	22.69	903 [#]	0.1	149.7	2.0	11.9	2.7	36.1	4.4	2.5(1.4-3.6)	1.2	0.36	0.5	0.55
Rushikulya	12.57	*	20.7	18.4	9.8	5.5	1.1	16.0	6.3	1.0(0.8-1.3)	0.1	10.05	10.2	0.07
Mahanadi	13.56	2121 [#]	0.1		4.1	8.3	3.4	57.9	2.7	0.6(0.3-0.9)	0.1	1.02	1.4	0.04
Vamsadhara	15.05	*	13.3	31.8	6.3	6.8	1.4	23.9	5.0	12.1(3.6-21)	1.9	2.28	3.4	1.57
Nagavali	13.94	*	28.8	23.9	13.9	4.9	1.3	14.0	5.0	20.5(16.5-24.5)	1.5	1.62	1.7	2.71
Godavari	241.1	3505 [#]	0.2	175.0	4.3	49.1	1.7	67.0	28.1	3.0(0.1-2.97)	0.9	0.22	0.4	0.30
Krishna	36.49	2213 [#]	5.3	15.8	7.5	9.5	9.8	185.7	1.8	1.6(0.2-1.6)	0.2	3.49	8.5	0.15
Penna	27.97	200 [#]	9.3	26.0	6.3	4.5	5.8	204.9	2.3	0.7(0.6-0.8)	0.1	0.46	1.7	0.29
Ponnayyar	9.89	*	0.3	32.0	12.7	6.8	3.3	270.0	2.0	0.5(0.1-0.3)	0.1	4.66	78.1	0.05
Cauvery	20.63	677 [#]	12.0	28.7	27.7	10.8	12.1	125.0	1.5	1.7(4.6-19.9)	0.1	2.55	7.4	0.29
Ambalayaar	4.57	28	4.2	67.5	16.8	8.6	5.7	103.8	2.0	1.6	0.1	1.96	26.8	0.49
Vaigai	0.22	36	27.9	39.3	1.9	4.3	2.0	31.3	2.4	0.6(5.4-38.3)	0.3	1.18	1.4	0.12
Rivers Flowing towards Arabian Sea														
Kochi back waters	231.1	391	3.5	33.7	4.1	33.8	8.6	34.6	4.9	1.1(0.1-1.2)	0.3	3.38	3.7	0.28
Chalakudi	9.69	*	0.1	17.0	2.5	22.0	6.5	45.7	3.5	0.9(0.5-1.3)	0.4	3.23	3.7	0.13
Bharathapuzha	19.12	*	0.1	31.0	3.4	8.3	6.6	41.9	1.3	0.4(0.3-0.4)	0.1	2.88	3.7	0.06
Sharavathi	16.44	*	0.2	18.0	3.5	28.6	8.2	28.4	3.5	0.6	0.2	2.28	2.3	0.06
Kali	17.59	152	5.9	6.5	3.8	17.2	10.0	30.9	1.7	1.1(0.9-1.2)	0.3	3.09	3.2	0.11
Zuari	14.62	103	7.3	28.3	2.6	29.7	13.6	23.7	2.2	1.0(0.1-1.5)	0.3	2.28	2.9	0.24
Mandovi	27.68	105	0.4	13.3	1.7	19.5	38.6	31.7	0.5	0.9(0.2-0.9)	0.3	3.00	5.8	0.21
Narmada	115.5	1447 [#]	0.2	918.0	0.8	75.7	3.0	37.6	25.5	0.4	0.4	0.68	0.9	0.02
Tapti	41.04	472 [#]	0.1	441.0	1.0	71.8	13.4	37.3	11.7	0.4	0.4	1.02	1.5	0.16
Sabarmathi	66.29	120 [#]	0.1	0.4	1.2	31.2	5.1	47.8	10.0	0.6	0.5	1.77	1.9	0.03
Mahisagar	14.28	*	0.1	138.0	1.5	83.3	13.4	20.6	13.6	1.6	7.5	0.01		0.08

* Data not available and # represents data take from kumar et al., 2005 and other taken from dam authorities of respective rivers; *-PB=Phytoplankton biomass

Table 2: Variations in Salinity, SPM, Phytoplankton biomass, DIN, DIP, DSi, N:P, DMS, DMS/Chla, Diatoms , Phytoplankton Abundance and DMS flux in Indian estuaries during dry period (Mean Values; Calculated from 3-7 points from each station).

Estuary	Salinity	SPM (mg l ⁻¹)	PB* (mg m ⁻³)	DIN (μM)	DIP (μM)	DSi (μM)	N:P	DMS (nM) Mean (Range)	DMS/ Chla	Diatoms (x10 ⁵ Cells l ⁻¹)	Phytoplankton Abundance	Flux (μM m ⁻² d ⁻¹)
Rivers Flowing towards Bay of Bengal												
Godavari	15.4	20.6	3.6	7.7	3.1	98.6	2.1	9.3(1.4-26.9)	2.6	3.6	6.2	0.51
Krishna	19.4	41.3	5.7	7.5	2.7	43.8	5.7	25.1(12.3-31.6)	4.4	0.3	1.9	2.07
Penna	12.4	58.1	4.8	13.6	4.5	64.6	3.3	12.7(5.4-16.9)	2.6	10.6	17.7	5.01
Ponnayaar	5.8	308.6	12.8	26.4	13.8	188.2	1.8	9.3(4.6-15.1)	0.7	21.4	26.9	0.94
Cauvery	8.3	62.7	14.2	1.1	5.4	172.6	1.4	12.7(4.6-19.9)	0.9	0.2	0.5	1.28
Vaigai	29.5	74.0	31.5	3.7	6.2	137.9	2.6	21.3(5.4-38.3)	2.4	1.1	1.2	6.01
Rivers Flowing towards Arabian Sea												
Kochi back waters	18.1	83.2	24.4	6.1	2.7	60.0	3.0	7.4(3-15.9)	0.3	1.9	4.3	1.99
Bharattapuzha	12.0	41.7	2.4	0.9	4.2	81.8	0.5	29.3(2.3-56.4)	16.3	0.8	8.4	3.23
Kali	1.8	63.8	1.6	19.2	6.5	91.5	3.9	20.5(7.7-50.9)	12.4	0.4	0.9	1.98
Zuari	19.2	47.5	5.5	7.8	4.9	45.6	2.2	19.6(10-32.2)	3.6	2.2	5.9	4.58
Mandovi	18.9	44.7	6.2	8.3	10.4	39.5	1.0	19.5(2.5-44.6)	3.1	4.7	11.3	4.39

*-PB=Phytoplankton biomass

Table 3: Concentrations of different physical and biogeochemical properties of estuaries located along the east and west coast of India.

Parameter	Wet Period		Dry Period	
	East Coast	West Coast	East Coast	West Coast
Discharge (m^3s^{-1})	1168±1159	399±486	-	-
Temperature ($^{\circ}\text{C}$)	30.9±1.3	27.4±1.3	28.0±1.3	28.1±1.9
Salinity	10.4±10.2	1.9±2.7	11.4±10.4	14.5±12.1
DIN (μM)	11.3±11.6	38.3±26.0	16.4±18.4	11.3±10.5
DIP (μM)	4.6±4.2	11.5±9.6	6.0±6.2	5.7±4.3
DSi (μM)	85.0±82	34.6±8.6	133.2±77.6	65.4±34.5
SPM (mg l^{-1})	70±69	150±285.0	65.7±45.0	51.3±25.4
Phytoplankton biomass (mg m^{-3})	9.5±7.5	1.0±1.6		
TVC (cfu ml^{-1})	$(88.2\pm264.6)\times10^5$	$(10.7\pm33.8)\times10^5$	-	-
Phytoplankton abundance (cell L^{-1})				
¹⁾	$(11.3\pm20.6)\times10^5$	$(3.0\pm1.4)\times10^5$	$(7.2\pm9.1)\times10^5$	$(6.2\pm7.3)\times10^5$
Diatoms abundance (cell L^{-1})				
¹⁾	$(3.3\pm4.1)\times10^5$	$(2.4\pm1.0)\times10^5$	$(5.7\pm7.4)\times10^5$	$(4.9\pm7.6)\times10^5$
Dinoflagellates abundance (cell L^{-1})				
	$(0.1\pm0.1)\times10^5$	$(0.3\pm0.8)\times10^5$	$(0.2\pm0.3)\times10^5$	$(0.8\pm0.6)\times10^5$
Green algae abundance (cell L^{-1})				
	$(1.2\pm2.1)\times10^5$	$(0.1\pm0.1)\times10^5$	$(1.9\pm2.7)\times10^5$	$(1.6\pm2.5)\times10^5$
Cyanobacteria abundance (cell L^{-1})				
	$(6.8\pm18.0)\times10^5$	$(0.1\pm0.1)\times10^5$	$(0.2\pm0.3)\times10^5$	$(1.8\pm3.4)\times10^5$
DMS (nM)	3.6±5.7	0.8±0.4	15.3±10.1	15.0±15.4
DMS/Chla	0.5±0.6	1.8±2.4	3.8±6.5	7.8±8.1
DMS flux	0.49±0.8	0.15±0.08	2.7±2.8	3.1±2.8

Table 4: Concentrations and flux of DMS in various estuaries in the world

Estuary	DMS range (nM)	Average	Average DMS flux ($\mu\text{mol m}^{-2}\text{d}^{-1}$)	Reference
Pearl River, China	0.05-52.7	3.0-8.6	27.0	Hu and Liu (2005)
Zuari, India	0.3-12.8	5.8	0.6	Shenoy and Patil (2003)
Potomac, USA	1-18	-		Iverson et al. (1989)
Scheldt, Belgium	0.4-1.2	0.6		Sciare, and Mihalopoulos (2002)
Rhine, Netherlands	0.4-10	4.2		Sciare, and Mihalopoulos (2002)
Ems, Netherlands	0-2.5	0.2		Sciare, and Mihalopoulos (2002)
Loire, Netherlands	0.5-3.6	1.3		Sciare, and Mihalopoulos (2002)
Gironde, France	0.05-1.7	0.7		Sciare and Nguyen (2001)
Scheldt, Belgium	0-2.5	0.4-0.6	1.3	Sciare et al., (2002)
Elbe, Belgium	0-25	0.9	1.3	Sciare et al., (2002)
Ria de Aveiro, Portugal	2-9-5.3	8.25	0.7	Cerqueira and Pio (1999)
Indian	0.39-20.5 (Wet)	3.26	0.34	
	2.30-56.4 (Dry)	15.2	2.7	Present Study

Legend to Figures

Figure 1: Station locations map where major rivers are shown with larger font letters. The main course of the river is shown as dark line while tributaries were shown in grey color.

Figure 2: Relationship between DMS and Salinity during a) wet and b) dry period. The relation of DMS with Phytoplankton biomass during c) wet and d) during dry period. The roman numbers I and II represent the data from west and east coast estuaries respectively.

Figure 1.

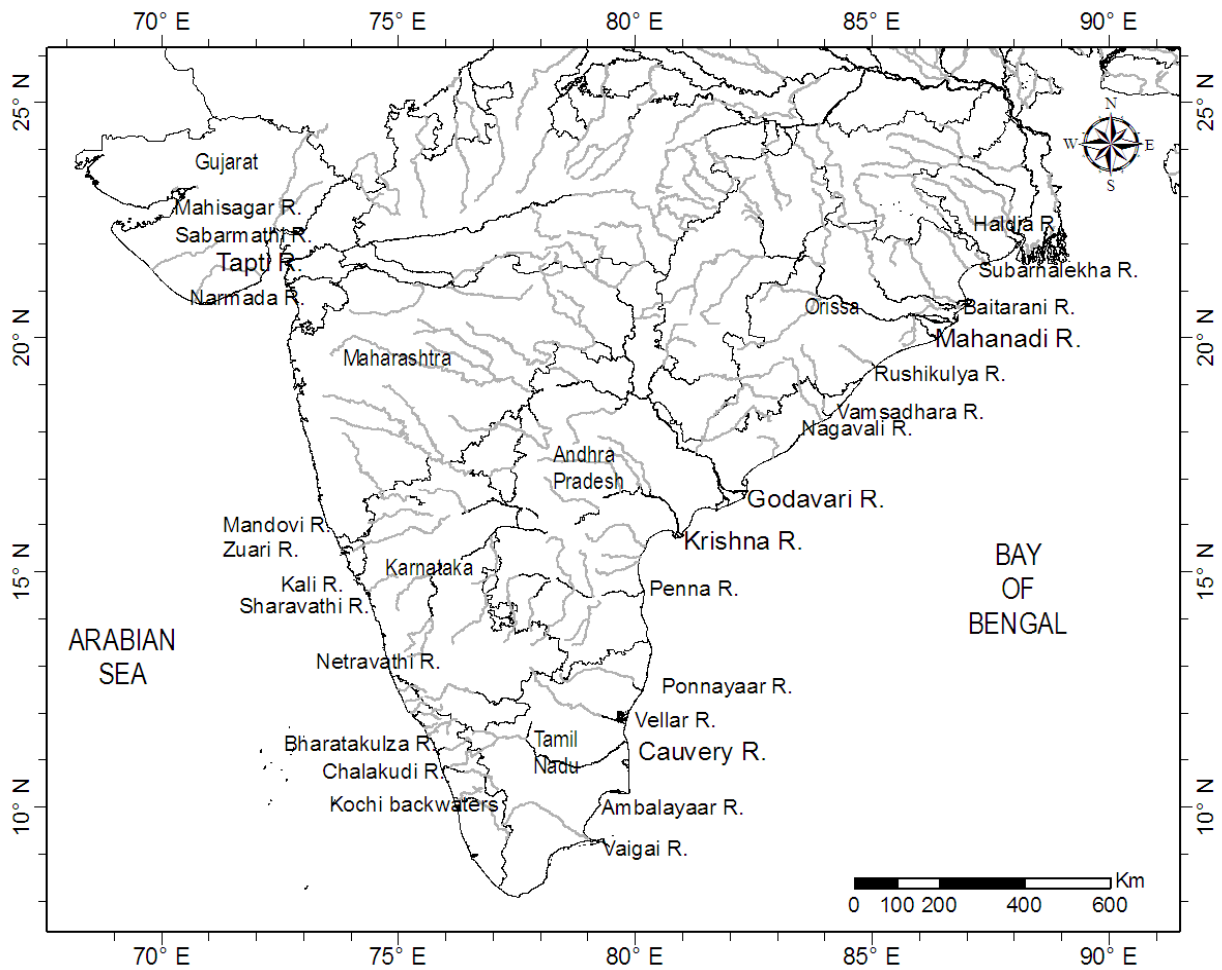


Figure 2.

