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Discovery

Environmental drivers of temporal variability in DMS (P) in the surfwater of a tropical intertidal beach

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ABSTRACT

Tropical estuaries are potential contributors of dimethylsulfide (DMS), a climatically relevant volatile sulfur compound and its precursor dimethylsulphoniopropionate (DMSP). In order to understand the distribution of DMS and its consequent fluxes from the intertidal beach of a tropical estuary, we monitored the DMS concentrations and estimated the flux from the surfwater of Dona Paula Bay for a period of one year. The probable drivers of variability of this compound were also measured. Our results show that the average DMS concentration was highest during the monsoon season (7.64nM) followed by post-monsoon (6.71nM) and pre-monsoon (1.58nM). Consequently, the estimated sea-air flux of DMS is monsoon > post-monsoon > pre-monsoon at 24.75> 18.93> 2.29 uM $m^{-2}d^{-1}$ respectively. Besides light, temperature affected DMS concentrations irrespective of the season. Influence of salinity was restricted to monsoon and was responsible for 26% variation in DMS. Our study highlights the significant contribution of the

anti-greenhouse gas, DMS from intertidal beaches especially during monsoon when it exceeds some of the coastal and open ocean measurements reported earlier.

Key words: DMS, flux, seasonal variability, intertidal sediment, tropical estuary.

1. INTRODUCTION

Diemthylsulfide (DMS) is a trace gas emitted from the oceans and probably the only link between marine and atmospheric sulphur cycle. It is produced after degradation of its precursor dimethylsulfoniopropionate (DMSP), a tertiary sulphur compound serving multiple purposes in marine phytoplankton (Stefels et al., 2007). Some marine algae and plant halophytes produce DMSP in high concentration for regulation of their internal osmotic environment, cryoprotection, or as an antioxidant (Yoch, 2002). Research on DMSP and its product DMS, has attracted a lot of attention since decades due to the proposed link between biological production of DMS, atmospheric aerosols and cloud albedo (Charlson et al., 1987). DMS released from the marine environment is oxidized in the atmosphere to various compounds like dimethyl sulfoxide, dimethyl sulfone, methane sulfonic acid and sulphuric acid. The sulphate aerosols in the atmosphere act as cloud condensation nuclei and help in the formation of clouds. The massive production of DMS over the oceans may have a potential impact on the Earth's climate.

The variability and flux of DMS from open oceans has been covered widely, but studies from tropical estuaries and intertidal sediments are few. However, researchers have highlighted the role of estuaries and their plumes in the open sea as important sources of atmospheric DMS (Iverson et al., 1989; Turner et al., 1996; Simo et al., 1997). The Intertidal zone of an estuary is much more dynamic and complex due to tidal fluctuations. The continuous wave actions also help in mixing of saline water and fresh water in estuaries, which supports a variety of life in this system (Alongi, 1998). Such changes in biota could contribute directly and indirectly to the variation in DMS. These variations are also affected by the seasonal changes.

The tropical climate is characterised by prominent dry and wet seasons. The Indian sub-continent is punctuated by the monsoons from (June – September), the dry season includes pre - monsoon (February – May) and post monsoon (October–January) in a year. Hence we monitored DMS concentrations and related environmental variables in the intertidal zone of a tropical estuary over a period of one year. Due to its volatile nature and high turnover rate, DMS was monitored at six hour intervals. Intertidal sediments could be an ideal site for measurement of DMS flux due to the prevalence of various stressors/triggers which release DMS from DMSP. Baring a few studies by Bergeijk et al. (2002), Belviso et al. (2006), intertidal ecosystems have been overlooked by most of the researchers. Hence in this paper the seasonal trend observed in DMS variability and flux from the surf waters of the intertidal zone of Dona Paula Bay are presented. The probable drivers of the observed variability in DMS are also discussed.

2. MATERIALS AND METHODS

2.1. Study area

The study area chosen is a sand flat at Dias Beach (15^0 27′ N; 73^0 48′ E), near Dona Paula Bay, surrounded by the Zuari estuary (Figure 1). Surfwater samples were collected during flood tide and ebb tide covering successive high tides and low tides every month from March 2010 to March 2011.

2.2. Sample collection and methods

Surfwater samples were collected in acid washed PVC bottles and carried to the laboratory for further analysis in icebox within an hour of collection. Temperatures of the surfwater were recorded at the study site using a mercury bulb thermometer, and salinity was measured with the help of a hand held refractometer. Light intensity was measured using TES digital Lux Meter. Samples for dissolved oxygen estimation were fixed on site with Winkler A and B reagents and further analyzed in the laboratory. pH of the samples was measured using a Elico, LI614 pH meter within few minutes of sample collection. Estimation of nutrients such as ammonium (NH_4-N), nitrate (NO_3-N), nitrite (NO_2-N), phosphate (PO_4-P) and silicate (SiO_3) were carried out by standard procedures (Parsons et al., 1984).

DMSP was measured by cold alkaline hydrolysis method after its conversion to DMS (Turner et. al., 1990, Kumar et.al., 2009) by gas chromatography. Calibration standards were analyzed following the same protocol using DMSP salt procured from Research Plus, USA (Visscher et al., 1992). Phytoplankton abundance was estimated by Utermohl's sedimentation method. Phytoplankton diversity was assessed by microscopy using identification keys by Tomas (1997). Sea-to-air fluxes of DMS were calculated based upon DMS concentration and temperature of surfwater and wind speed over sea. The equation is given by Liss and Merlivat (1986) which is as follows:

Flux $_{(DMS)}$ = K_w. Δ DMS;

Where K_w= piston velocity / gas exchange coefficient (cmh^{-1}); Δ DMS = DMS concentration difference across the air – sea interface.
K_w= $0.222u^2 + 0.333u\ (Sc/600)^{-0.5}$ (Nightingale *et al.,* 2000); where u = daily averaged wind speed at 10m height ($m\ s^{-1}$), (http://inet.nio.org)
Sc = 2674.0 – 147.12 (T) + 3.726 $(T)^2$ – 0.038 $(T)^3$ (Schmidt number as calculated by Saltzman et al., 1993)
Statistical analysis of the data was performed using *Statistica* 6.0 and Data Analysis Tool pack of Microsoft Office 2010.

3. RESULTS

3.1. Environmental variables

Light intensity was the highest during the post-monsoon season at an average of 24194 lux units and least during the monsoon at 11134 lux units. Average temperature was highest during pre-monsoon at 30.75° C, followed by post-monsoon (26.33°C) and 25.33°C during pre monsoon. Significant fluctuations in salinity ranging from 13 – 33 were observed only during monsoon. During pre-monsoon salinity varied from 28-30, and from 20-29 during post monsoon season. All nutrients were generally higher in the monsoon season with silicate being the most abundant nutrient. The molar concentration of nutrients was in the order Silicate >Nitrate> Phosphate> Nitrite (Table 1).

3.2. DMSP, DMS

DMSPt (DMSP total) concentrations were highest during the monsoon season (June – September) at an average of ~21nM followed by post and pre-monsoon (table 1). DMSP related with phytoplankton abundance in all the three seasons however the strength of the correlations varied. This could be attributed to the fact that DMSP is species-specific. A very clear shift in the salinity, temperature and concentration of nutrients was discernible during the monsoon which affected the phytoplankton species composition and consequently the DMSP levels in the surfwater. During the post-monsoon, the intermittent peaks of DMS coincided with the abundance of dinoflagellates in the surfwater. It is known that dinoflagellates are affected by the nitrate and nitrite concentration. Alkawri and Ramaiah (2010) in their study of dinoflagellates from the west coast of India have established that nutrients have the great influence on dinoflagellates abundance in our study area. Keller et al., (1988, 1989) have established that dinoflagellates are significant sources of DMSP. Most recently Caruana and Malin (2014) in their extensive study confirmed the role of dinoflagellates as significant DMSP producers. In the present study too there was a predominance of *Alexandrium minutum* at 0 - 6.12 x 10^2 cells/L during monsoon and 0 – 58 cells/L during post-monsoon,The other dinoflagellate encountered during these seasons was *Prorocentrum* sp. in the range 0 – 3.83x 10^2 cells/L during monsoon and 0 – 19 cells/L during post – monsoon. Both these genera are known to produce high amount of DMSP (Caruana and Malin, 2014). Other DMSP producing genera in the samples were *Dinophysis* sp. and *Scripsiella* sp. DMS levels varied from non- detectable limits to 1.98nM during pre-monsoon. During the monsoon, average DMS concentrations ranged from 4.63nM in June to a maximum of 19.38nM in August (Figure 2). During post-monsoon, the variability was similar and averaged at 6.7 nM. Our results are in agreement with Shenoy and Patil (2003) from their study in the Zuari Estuary where they reported high temporal variations in DMS and DMSP with maximal concentrations during the southwest monsoon coinciding with a dinoflagellate bloom.

Ecosystems are complex and dynamic hence it is difficult to ascertain the specific drivers of DMS variability in natural samples. To investigate potential environmental drivers of DMS dynamics, linear relationships between a suite of physical, chemical and biological factors were tested. Various researchers have stressed on the role of physical forces such as UV radiation dose and depth of mixing layer as important drivers of DMS variability in oceanic surface waters (Simo´ and Pedros-Allio 1999; Toole and Siegel 2004; Vallina and Simo´ 2007). In our study, among the variables examined, light intensity, temperature and salinity were the major constraints for DMS variability (Table 2; Figure 3). Irrespective of the season, light intensity was responsible for ~25% of the variation in DMS concentrations. This is in agreement with Vallina and Simo 2007 where incident solar irradiance correlated with surface water DMS concentrations. Cerquira and Pio (1999) in their study from intertidal mudflats of Canal de Mira in Portugal reported strong seasonal variations in the DMS emission rates and attributed the summer peaks in DMS emissions to ambient temperature. More recently, Arnold et al., (2013) in their laboratory mesocosm study on *Emiliania huxleyi* cultures reported that slight increase in temperature decreases the solubility of DMS in the water and leads to higher flux to the air. Salinity correlated negatively with the DMS concentrations only during the monsoon season ($r = -0.513$, $p<0.05$) which explained about 26% of the variation (Table 2). The fluctuation in salinity was highest during the monsoon, due to influx of rainwater and riverine fresh water. High values of salinity were encountered during high tide due to the intrusion of water from the Arabian Sea. The negative correlation of salinity with DMS suggests higher DMS content in low saline waters which was formed due to the mixing of freshwater and seawater from the Arabian Sea. The temperature of surfwater related to the DMS concentrations positively in all the three seasons, but the strength of correlation was marginally higher in the pre-monsoon season as compared to the other two (spearman's rank r = 0.461during pre-monsoon > 0.456 during post-monsoon > 0.433 during monsoon). Intriguingly, the high values of DMS during monsoon coincided with the low Chl a concentration which is possibly due to the higher abundance of dinoflagellates during this season. Our resultsconfirm the significant temporal variation in DMS and species dependency in the study area.

Table 1

Characteristics of intertidal surfwater of Dona Paula Bay from March 2010 – March 2011

Variable	Pre-monsoon	Monsoon	Post-monsoon
Light (lux)	18194.44 ± 0.0	11134.167 ± 0.06	24194.44 ± 0.0
Temperature(°C)	30.75 ± 1.75	25.33 ± 0.15	26.33 ± 0.12
Salinity	30.67 ± 1.97	20.67 ± 3.21	28.33 ± 2.15
pH	7.86 ± 0.24	7.25 ± 0.14	7.54 ± 0.32
DO (ml L^{-1})	4.40 ± 0.51	2.54 ± 0.68	2.86 ± 1.01
Nitrate (μM)	1.15 ± 0.11	8.8 ± 0.23	2.71 ± 0.88
Nitrite (μM)	0.41 ± 0.18	1.13 ± 0.18	0.84 ± 0.21
Phosphate (μM)	0.10 ± 0.04	3.57 ± 0.4	2.60 ± 0.08
Silicate (μM)	3.89 ± 1.31	11.13±2.31	12.32 ± 2.54
Ammonium(μM)	0.02 ± 0.009	1.25 ± 0.09	1.01 ± 0.02
DMSP (nM)	9.46 ± 1.33	20.98 ± 2.13	12.73 ± 1.53
DMS (nM)	1.58 ± 0.02	7.64 ± 0.13	6.71 ± 0.53
DMS sea-air flux (uMm^{-2}d^{-1})	2.29 ± 0.001	24.75 ± 0.03	18.93 ± 0.01
Chl a (μg/L)	1.40± 0.12	1.31± 0.09	2.19± 0.1
Phytoplankton abundance (cells/L)	3.15E+05	3.45E+05	4.67E+05

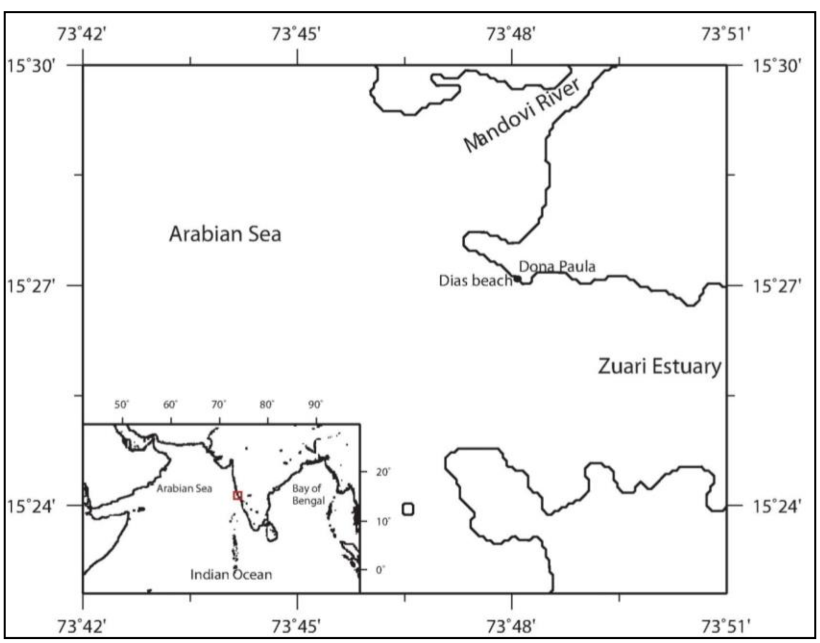

Figure 1

Study area

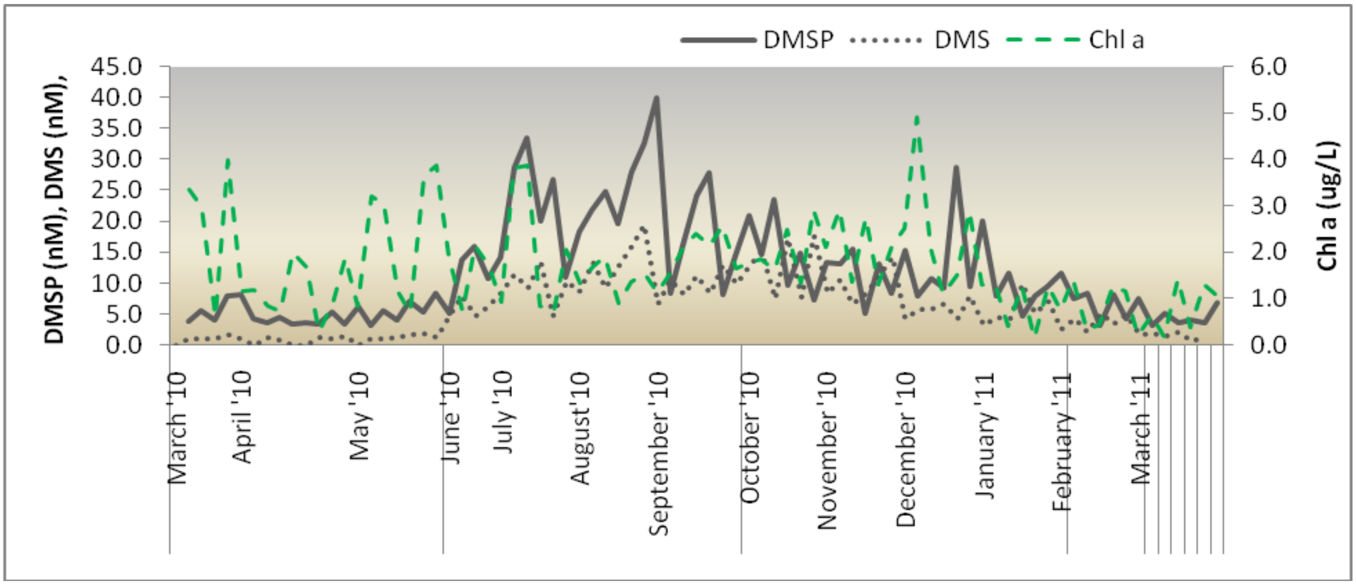

Figure 2

DMS (P) and Chl *a* variability in Dona Paula Bay surfwater from March 2010 – March 2011

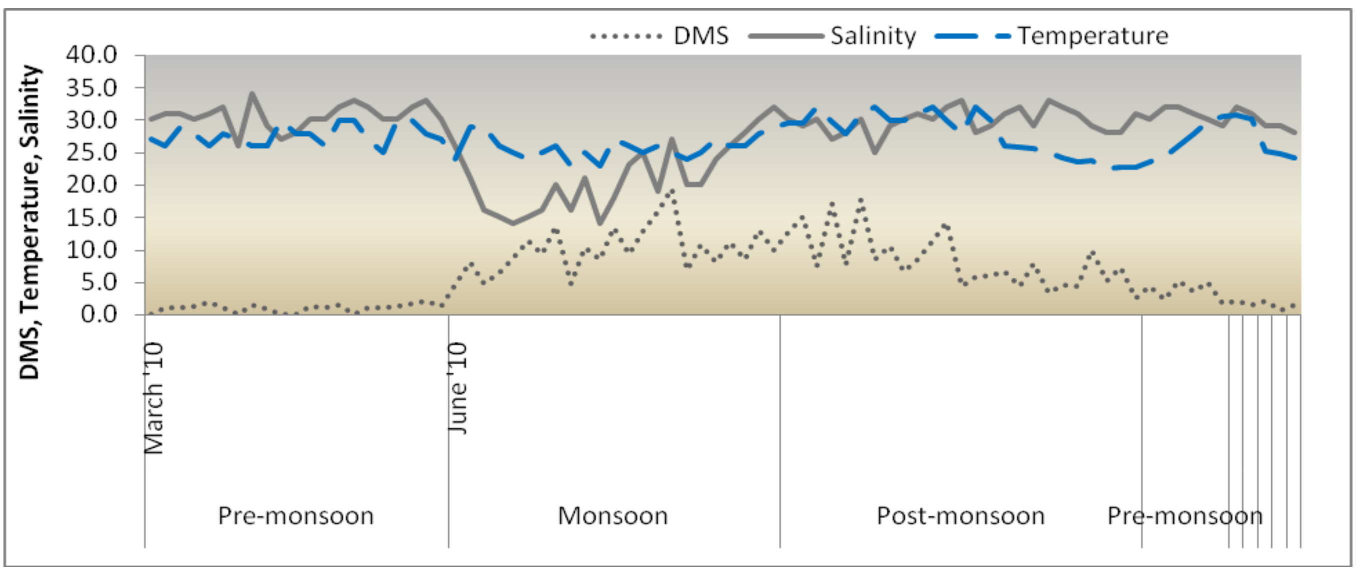

Figure 3

Variability in DMS, salinity and temperature of Dona Paula Bay surfwater from March 2010 – March 2011

Table 2

Significant correlations tested by Spearman's rank r correlation

Correlating variables		Pre-monsoon	Monsoon	Post-monsoon
DMS	Light	0.569	-0.501	-0.541
	Temperature	0.461	0.456	0.433
	Salinity	ns	-0.513	ns
	Chlorophyll a	0.415	0.384	-0.429
DMSP	Phytoplankton	0.634	0.513	0.498
	Light	-0.569	-0.584	0.321
	Temperature	0.513	-0.461	0.484
	Salinity	ns	0.615	0.463
Phytoplankton	Nitrate	0.657	0.584	0.629
	Phosphate	-0.402	0.389	0.481
	TVC	0.639	0.574	-0.388

3.3. Sea – air DMS flux

The calculated sea-air flux of DMS was highest during the monsoon season where it ranged from 0.3 to 60.91uMm^{-2}d^{-1} (Figure 4). The average flux during this season was almost 10 times higher (24.75 uMm^{-2}d^{-1}) than the pre-monsoon (2.29 uMm^{-2}d^{-1}) (table 1). In the post-monsoon season, the DMS flux was comparable to the value during monsoon (18.93 uMm^{-2}d^{-1}), (Table 1). The peaks in DMS flux were due to higher DMS concentrations and wind speed which varied from 0.2 m s^{-1} to 3.4 ms^{-1}. During the pre-monsoon season, as DMS concentrations in many samples were below detection limit, the flux varied from 0 to 2.31 uMm^{-2}d^{-1}. The annual mean flux of DMS from the surfwater of tropical intertidal beach of Dona Paula was 15.32 uM m^{-2} d$^{-1.}$ During the southwest monsoon, the DMS flux was as high as 60.91 uM m^{-2} d^{-1}. These values exceeded the earlier reports on intertidal sediment of Westerschelde Estuary, The Netherlands where the flux varied from 0 .96 – 1.92 uM m^{-2} d^{-1} (Berjeigket al., 2002). The present values are also higher than the annual averages e recorded for the coastal Arabian Sea (3.4 uMm^{-2} d$^{-1)}$ and the open ocean 3.8 uM m^{-2} d^{-1} (Shenoy et al., 2007).

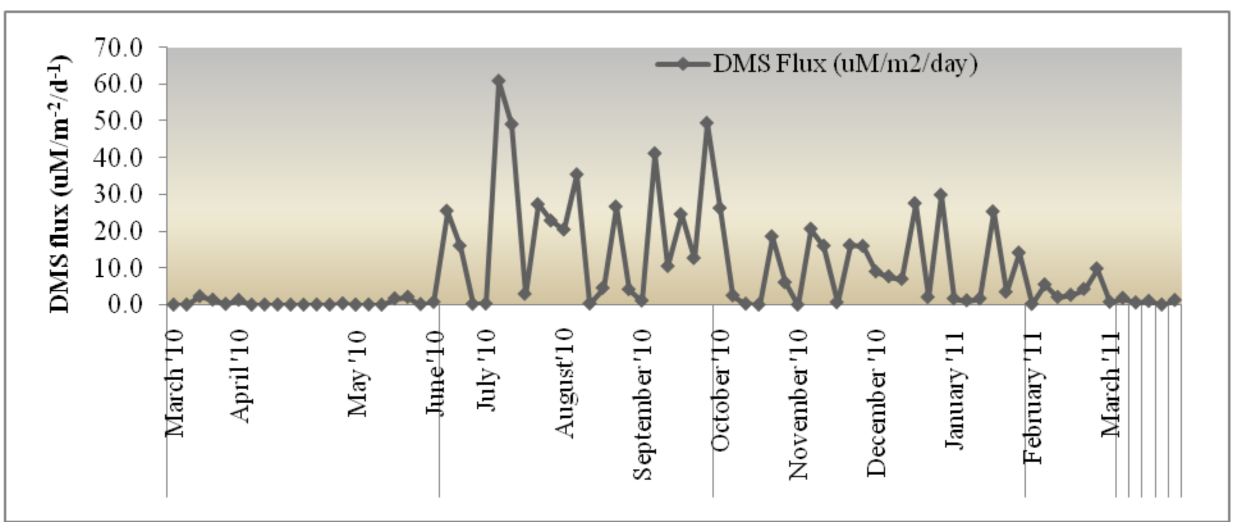

Figure 4

Sea-air flux of DMS from Dona Paula Bay surfwater from March 2010 – March 2011

4. CONCLUSION

The present findings thus indicate that intertidal ecosystems could be as important a source of DMS as the Open Ocean and coastal waters contributing higher flux particularly during the monsoon. The intra-seasonal variation in DMS flux from surfwater especially during monsoon was greater than inter-seasonal variations. Though intertidal system could be complex under the influence of system wide variables, we could observe the influence of light and temperature through the three seasons and the effect of salinity during monsoon. Laboratory mesocosm studies would be helpful in confirming the specific drivers of DMS dynamics.

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