GEOPHYSICAL RESEARCH LETTERS, VOL. 29, NO. 2, 10.1029/2001GL013967, 2002

Export fluxes of dimethylsulfoniopropionate and its break down gases at the air-sea interface

M. Dileep Kumar, D. M. Shenoy, V. V. S. S. Sarma, M. D. George, and M. Dandekar

National Institute of Oceanography, Dona Paula, Goa, 403 004, India

Received 23 August 2001; accepted 19 September 2001; published 24 January 2002.

[1] Dimethylsulfide (DMS) results from the decomposition of dimethylsulfoniopropionate (DMSP), a biogenic product, in seawater. Diffusive transfer of DMS from sea-to-air is known to be the most important source of natural non- seasalt sulfur (NSS) in the atmosphere. Here, we report on the wider occurrence of DMSP in marine aerosols for the first time. We found DMSP (to about 4.7 pmol m^{-3}) and DMS (up to 5.8 pmol m^{-3}) in marine aerosols, over the Indian Ocean, wherein DMSP abundance appears to be a function of its concentration in surface seawater and wind speeds. An experiment on board revealed rapid loss (90%) of loaded DMSP from filters exposed to marine atmosphere. Hence, a photochemical or other mode of formation of NSS gases from DMSP in aerosols or in surface microlayer, not considered hitherto, can directly contribute to sulfur efflux. Although our computations suggest the DMSP fluxes from these sources to be much smaller (3.4×10^{10} g S y^{-1}) compared to DMS diffusive flux ($16-25 \times 10^{12}$ g S y^{-1}) the former could be significant in rough weather conditions similar to trends in water export. *INDEX TERMS:* 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504), 4820 Oceanography: Biological and Chemical: Gases, 4801 Oceanography: Biological and Chemical: aerosols (0305), 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions

1. Introduction

[2] Natural and anthropogenic emissions of sulfur are expected to promote indirect cooling of atmosphere. A significant fraction of natural sulfur emission occurs in the form of dimethylsulfide (DMS). The oceans account for about 20% of total sulfur gaseous emissions through DMS degassing. The atmospheric sulfur budget over the remote oceans is far from complete. For instance, the deposition flux of non-sea salt sulfur (NSS) back to the open ocean surface (12.4 μg S m^{-2} hr^{-1}) is found to be higher than the outgoing DMS flux (11 μg S m^{-2} hr^{-1}) in these regions [*Charlson et al.*, 1992]. The oceanic NSS gas flux, calculated based on DMS gradient between air and bulk seawater, has so far been considered to occur only through gaseous diffusion [*Andreae and Crutzen*, 1997]. However, material across the sea surface can also be transported along with aerosols, formed from bursting of bubbles, or by direct loss of NSS gases (formed from DMSP decomposition) from the microlayer. These pathways can be significant for NSS flux because the DMS precursor, dimethylsulfoniopropionate (DMSP), occurs also in dissolved form in seawater. DMSP is generally more abundant than DMS in seawater and is highly susceptible to photolysis and/or biological decomposition to produce the latter and other NSS compounds [*Andreae*, 1990; *Malin*, 1997] such as methanethiol. Gases produced from DMSP decomposition in microlayer can easily diffuse to gaseous envelope above and this process is not considered in sulfur emission calculations. Presence of DMSP in marine aerosols has been found over the Bay of Bengal [*Shenoy et al.*, 2000]. Here, we attempt to study wider occurrence and variability of DMSP in aerosols during five cruises in different seasons and regions over the Indian Ocean, and evaluate its export fluxes contribution to total NSS evasion from the ocean.

2. Methodology

[3] Aerosol samples were collected over the northern and central Indian Ocean during two cruises (SK 138C and SK 147) of Bay of Bengal Monsoon Experiment (BOBMEX), one cruise (SK 141) of Indian Ocean Experiment (INDOEX) and two cruises (SK 140 and SK 148) of Land-Ocean Interactions in the Coastal Zone (LOICZ) Programs. BOBMEX cruises were conducted in fall inter-monsoon (October–November) of 1998 (SK 138C) and summer monsoon (July–August) of 1999 (SK 147). SK 141 (central and northwest Indian Ocean, INDOEX) was in winter monsoon (January–March) of 1999 while SK 140 (coastal and open eastern central Arabian Sea, LOICZ) cruise was in winter monsoon (December) of 1998 and SK 148 (Southeastern Arabian Sea, LOICZ) was at the end of southwest monsoon (September–October) of 1999. Collections were made using GF/F Whatman filters (47 mm in diameter). Aerosol samples were collected under vacuum from a height of about 6 m above the sea surface. As both DMSP and DMS are natural in origin contamination of samples from ship's emissions does not occur. The aerosol samples, collected from known volumes (~ 2–80 m^3) of air, were immediately transferred to the stripping vessel and analyzed first for DMS and later for DMSP. To facilitate stripping the filter was wetted with Milli Q water. The DMS analyses were performed through cryogenic trapping in Teflon tube using liquid nitrogen. The DMS liberated under warm conditions (80°C) was separated on a Chromosil 330 column fitted to HP 5890 Series II GC and detected using a Flame Photometric Detector. Subsequently the same aerosol sample was hydrolyzed with alkali and analyzed for DMS again. The latter step yielded concentration of DMSP in terms of DMS. These methods are the same as those used for analyses of DMS and DMSP in seawater [*Turner et al.*, 1990; *Shenoy et al.*, 2000]. DMS and DMSP analyses were also performed in surface seawater samples collected, simultaneously, using Niskin samplers attached to a CTD rosette. The precision and accuracy of seawater DMS analyses were found to be 8–10% and 86%, respectively [*Shenoy et al.*, 2001]. We have also collected sea surface microlayer samples using the glass plate technique, for DMSP analyses, during SK 158 cruise in the eastern Equatorial Indian Ocean, January–February 2000. We represented DMS as a NSS gas, formed from DMSP, since the breakdown products of DMSP in atmosphere are not well known.

3. Results and Discussion

[4] The DMSP was found to occur in marine aerosols from below detection limits to 4.7 pmol m^{-3} (Figure 1) with an average of 0.92 pmol m^{-3}. Higher DMSP concentrations (1.5–4.7 pmol m^{-3}) were found in aerosols over the central Indian Ocean in 1999

0094-8276/02/2001GL013967$09.00

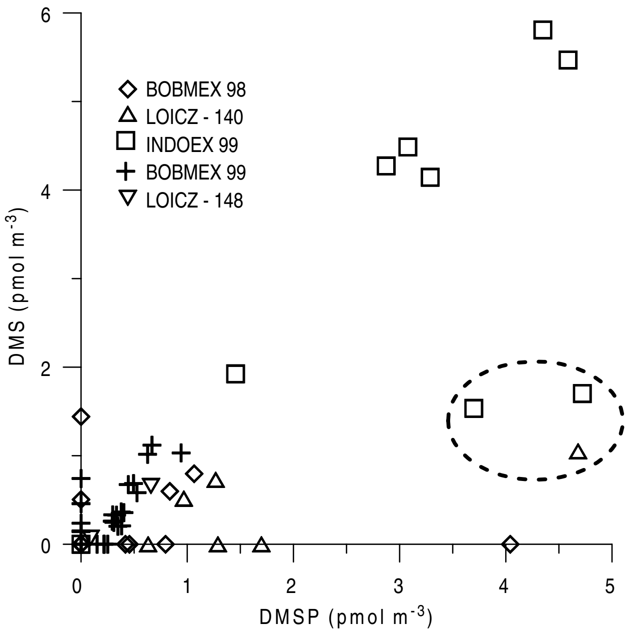

Figure 1. DMSP and DMS relationship in marine aerosols over the Indian Ocean.

(INDOEX) when its abundance was also higher in seawater (11.2–31.6 nM) than during other seasons and in other areas (Table 1). The fact that DMSP is unstable in surface seawater, through its susceptibility to photolysis and biological decomposition, makes its detection in marine aerosols significant. These decomposition processes can occur in troposphere (marine boundary layer) so also in surface microlayer and produce NSS substances. The relationship between DMSP and DMS in aerosols is positive and linear (Figure 1). However, DMS values (0–5.8 pmol m^{-3}) need to be treated with caution since the aerosol samples were collected under vacuum. These compounds are also susceptible to decomposition on filters during the sample collection; and hence the values reported in Figure 1 might be underestimates. Notwithstanding such artifacts there is a striking proportionality between DMSP and DMS (Figure 1), which is not a chance occurrence since these measurements were made in different regions and seasons. An important point in favor of this argument is the detection of higher DMS concentrations where DMSP levels were also higher not only in aerosols but also in surface seawater of the Central Indian Ocean (Table 1, Figure 1). On the other hand, DMS concentrations in aerosols do not seem to be a function of the extent of its concentrations in surface seawater or diffusive DMS fluxes across the interface. For instance, maximum diffusive flux occurred during the BOBMEX 1999 and maximal surface water DMS concentrations were found in LOICZ cruises in the Arabian Sea but higher DMS in aerosols occurred during INDOEX 1999 (Figure 1, Table 1).

[5] Relations of DMS and DMSP in aerosols with winds (Figure 2) suggest that variability and abundance of these compounds decreased with an increase in wind speed. Low levels of DMSP and DMS in aerosols at higher wind speeds might have been due to effective decomposition of DMSP and subsequent rapid evasion of NSS gases from aerosols. The escape will greatly be facilitated across the aerosol-air interface in turbulent winds. The observed ratio of about one for DMS/DMSP contrasts that (~ 0.2) in seawater (Table 1). As seawater is the source of aerosols in the remote marine atmosphere a ratio of 0.2 should have been maintained in these aerosols also, which is not the case. This suggests that a rapid DMS formation from DMSP is favored in aerosols than in seawater; if so DMSP loss during aerosol collection on filters could be significant also because of vacuum effect. We conducted an experiment on board to determine the rate of DMSP loss to atmosphere. Several filter papers loaded with DMSP of 0.34 nmol were exposed to marine air at a height of 6 m above sea level. These filters were periodically removed and analyzed for DMSP. Results showed a decreasing trend (Figure 3) in DMSP with time; drastic fall occurred in the first 5 minutes of exposure (the minimum time we could allow between loading and analysis). A loss of over 90% in 5 minutes suggests that significant portion of ejected aerosol DMSP could be rapidly lost to atmosphere. The loss rate might have been underestimated because the allowed 5 minutes may have been longer for 90% decomposition of DMSP.

[6] To understand the importance of DMSP export to global atmospheric NSS loading we evaluated its fluxes, to an approximation, as follows: Sea salt particle production rate at air-sea interface is estimated to be 100 cm^{-2} s^{-1} [*Hobbs*, 2000]. The total particle production at the sea surface, over an ocean area of 10^{14} m^2, would be 10^{20} s^{-1}. Assuming a droplet (from which a salt particle is produced) radius to be 10 μm each droplet volume works out to be 4.2×10^{-12} dm^3. Therefore, annually a total volume of 1.32×10^{16} dm^3 of seawater appears to be ejected as aerosols. Considering an average DMSP of 10 nmol dm^{-3} in seawater, from the ranges listed in Table 1, the total aerosol export flux of DMSP amounts to 0.42×10^{10} g S y^{-1}. Direct efflux of NSS gases produced from DMSP decomposition in the microlayer (similar to the mode of loss from DMSP loaded on filters, see Figure 3) should be added to the above aerosol flux to obtain total efflux. Our results in the eastern equatorial Indian Ocean revealed that DMSP varied from nondetectable levels to 78.8 nM (with an average of 18 nM) in a microlayer of 16 μm thick. On this basis if we consider the surface film thickness to be 10 μm and DMSP concentration in microlayer to be 10 nmol dm^{-3} (320 μg S m^{-3}) the DMSP inventory in the global oceanic microlayer amounts to 0.32×10^6 g S. Since the experiment discussed above (Figure 3) suggests 90% loss in 5 minutes of exposure the estimated DMSP loss from global oceanic surface will be ($288000 \times 12 \times 24 \times 365$ =) 3×10^{10} g S y^{-1}. Direct loss of DMSP products from the microlayer seems to contribute 7–8 times more than that by aerosol export to atmospheric NSS. The total DMSP loss (3.4×10^{10} g y^{-1}) to atmosphere is two to three orders of magnitude lower than that by DMS diffusive flux ($16–25 \times 10^{12}$ g y^{-1};

Table 1. Abundance of DMSP (nM) and DMS (nM) in surface seawater and sea-to-air diffusive fluxes of DMS (μmol m^{-2} d^{-1}). Columns 1–6 refer to Area of study, DMSP range, DMSP average, DMS range, DMS average and average DMS gas flux, respectively. A–E in column 1 respectively refer to areas Bay of Bengal (BOBMEX 1998), Central eastern Arabian Sea, Central Indian Ocean, Bay of Bengal (BOBMEX 1999) and Southeast Arabian Sea (see Methodology section)

1	2	3	4	5	6
A	5.2–17.6	14.3	1.4–4.7	2.9	1.6
B	—	—	0.9–31.7	7.0	4.78
C	11.2–31.6	20.6	1.6–11.9	4.4	7.26
D	6.9–21.8	13.4	1.5–5.5	3.0	16.3
E	—	—	0.6–220	19.3	5.13

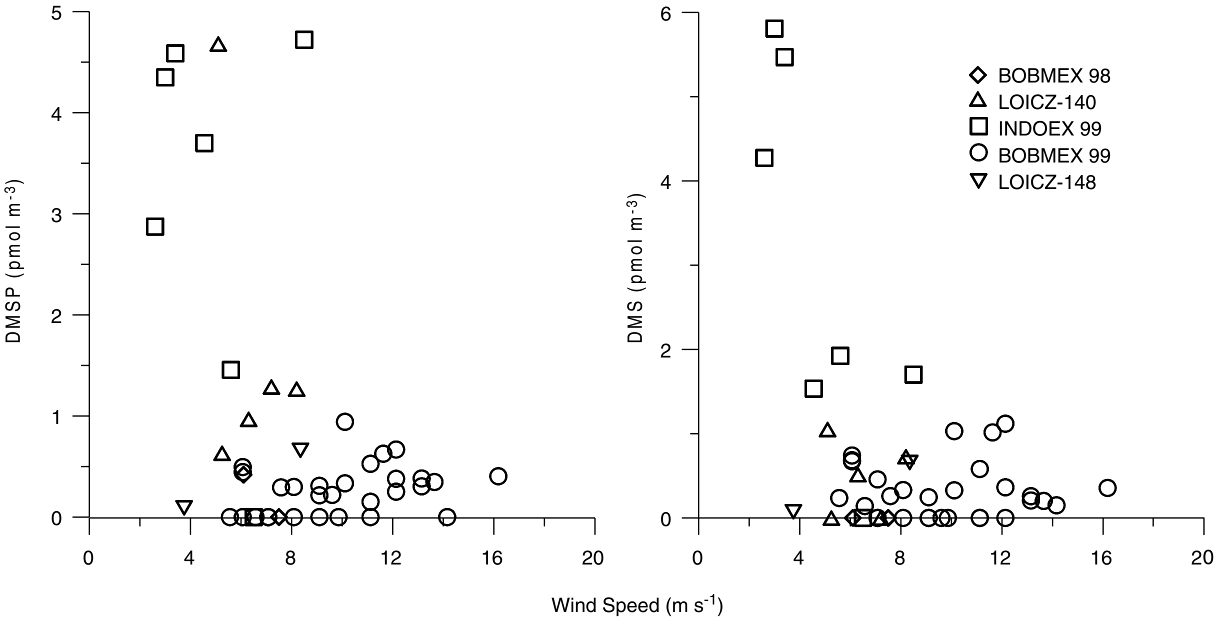

Figure 2. Dependence of DMS and DMSP concentrations in aerosols on wind speeds.

[*Bates et al.*, 1987; *Hobbs*, 2000]). However, the DMSP flux could potentially become an important one under stormy conditions since aerosol DMSP loss to air seems to be near quantitative at higher wind speeds (Figure 2). This situation is similar to the role of spray to mass transfer at the air-sea interface [*Pattison and Belcher*, 1999] that contributes little to the global mass transfer flux but recognized to significantly contribute under rough conditions. The above evaluations suggest a global lifetime of $((0.92 \times 32 \times 10^{-12} \times 10^{14} \times 10^{3})/(0.42 \times 10^{10}) =) 70 \times 10^{-5}$ y or 6 hrs for aerosol DMSP in the lower 1 km of the marine troposphere. Therefore, methanesulfonic acid or NSS with a residence time of 36 hrs [*Charlson et al.*, 1992] live at least six times longer than that by DMSP in air. Our present DMSP export calculations should be considered conservative since the measured DMSP in aerosols and its losses from loaded filters in marine air are likely underestimates.

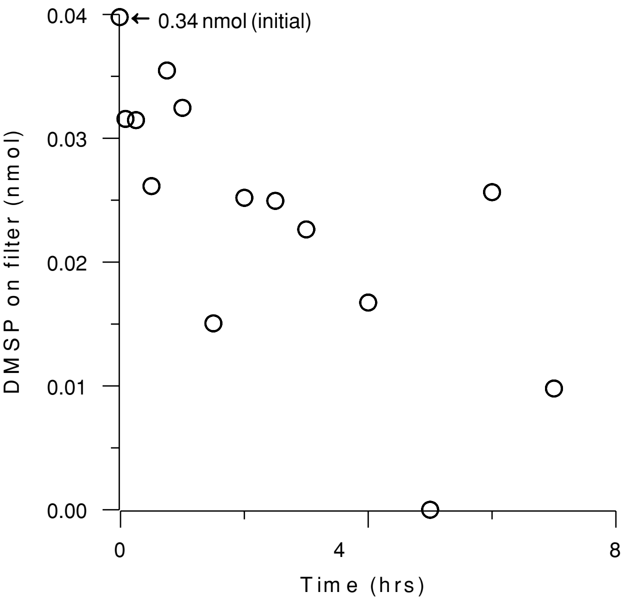

Figure 3. Loss of DMSP from membrane filters during its exposure to marine air.

[7] **Acknowledgments.** This study was supported by grants from the Departments of Ocean Development (DMS and LOICZ Projects and Ship time), Science and Technology (BOBMEX) and. Space (INDOEX), Government of India. D. M. Shenoy acknowledges support in the form of a Research Fellowship from CSIR whereas M. Dandekar for the financial support from DST, New Delhi. We thank Mr. A. Mahale for help in in preparation of final figures. This is NIO contribution 3704.

References

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

Andreae, M. O., and P. J. Crutzen, Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry, *Science*, *276*, 1052–1058, 1997.

Bates, T. S., J. D. Cline, R. H. Gammon, and S. R. Kelly-Hansen, Regional and Seasonal variations in the flux of oceanic dimehtylsulfide to the atmosphere, *J. Geophys. Res.*, *92*, 2930–2938, 1987.

Charlson, R. J., T. L. Anderson, and R. E. McDuff, The Sulfur Cycle. in *Global Biogeochemical Cycles*, edited by S. S. Butcher, et al., pp. 285–300, Academic Press, London, 1992.

Hobbs, P. V., *Introduction to Atmospheric Chemistry.* 262 pp., Cambridge University press, 2000.

Malin, G., Sulfur, climate and microbial maze, *Nature*, *387*, 857–859, 1997.

Pattison, M. J., and S. E. Belcher, Production rates of sea-spray droplets, *J. Geophys. Res.*, *104*, 18,397–18,407, 1999.

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

Shenoy, D. M., S. Joseph, M. Dileep Kumar, and M. D. George. Control and inter-annual variability of dimethyl sulfide in Indian Ocean., *J. Geophys. Res.*, in press, 2001.

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

Turner, S. M., G. Malin, G. D. Nightingale, and P. S. Liss, Seasonal variation of dimethyl sulfide in the North Sea and an assessment of fluxes to the atmosphere, *Mar. Chem.*, *54*, 243–262, 1996.

M. Dandekar, M. D. George, M. Dileep Kumar, V. V. S. S. Sarma, and D. M. Shenoy, National Institute of Oceanography, Dona Paula, Goa 403 004, India (Mukta@darya.nio.org; george@darya.nio.org; dileep@darya.nio.org; vvsarma@yahoo.com; dmshenoy@darya.nio.org)