

Light-driven cycling of dimethylsulfide (DMS) in the Sargasso Sea: Closing the loop

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[1] The factors driving dimethylsulfide (DMS) cycling in oligotrophic environments are isolated using a time-series of DMS sampled in the Sargasso Sea. The observed distribution of DMS is inconsistent with bottom-up processes related to phytoplankton production, biomass, or community structure changes. DMS concentrations and estimates of net biological community production are most highly correlated with physical and optical properties, with the dose of ultraviolet radiation (UVR) accounting for 77% of the variability in mixed layer DMS concentrations. Physiological stresses associated with shallow mixed layers and high UVR are the first order determinant of biological production of DMS, indicating that DMS cycling in open-ocean regions is fundamentally different than in eutrophic regions where phytoplankton blooms provide the conditions for elevated DMS concentrations. The stress regime presented here effectively closes the DMS-climate feedback loop for open-ocean environments. This response may also provide a climatic role for phytoplanktonic processes in response to anthropogenic forcing. **INDEX TERMS:** 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 1635 Global Change: Oceans (4203); 1615 Global Change: Biogeochemical processes (4805); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 4842 Oceanography: Biological and Chemical: Modeling; **KEYWORDS:** Dimethylsulfide, DMS Sulfur cycling, Ultraviolet radiation, Climate feedbacks. **Citation:** Toole, D. A., and D. A. Siegel (2004), Light-driven cycling of dimethylsulfide (DMS) in the Sargasso Sea: Closing the loop, *Geophys. Res. Lett.*, 31, L09308, doi:10.1029/2004GL019581.

1. Introduction

[2] The oceanic ventilation of the volatile organic sulfur compound dimethylsulfide (DMS) affects the radiative properties of the atmosphere through the formation of cloud condensation nuclei, suggesting a negative climate feedback where phytoplankton respond to elevated temperature and solar radiation levels by increasing their DMS production [e.g., Charlson *et al.*, 1987]. Increased in situ DMS concentrations will result in larger DMS emissions to the atmosphere, thus theoretically maintaining optimal conditions by decreasing incident solar radiation. Central to closing this feedback loop is a measure of the processes that modulate net DMS production. The Dacey *et al.* [1998]

1992–1994 organic sulfur time-series is the only dataset that allows the assessment of open-ocean organic sulfur cycling on annual timescales. This time-series was sampled in concert with the U.S. JGOFS Bermuda Atlantic Time-series Study (BATS) [Steinberg *et al.*, 2001], and includes determinations of DMS and particulate and dissolved dimethylsulfoniopropionate (pDMSP and dDMSP respectively) concentrations sampled twice monthly in the upper 140 meters in the Sargasso Sea near Bermuda (Hydrostation S, 32°10'N, 64°30'W, ~20 km SE of Bermuda). This study region is the site of numerous ongoing research programs providing a concurrently sampled dataset to isolate the relevant mechanisms of sulfur cycling. Here we assess the time-series in relationship to measured properties drawn from these studies to explore the processes and mechanisms that drive DMS cycling in the upper water column of the Sargasso Sea.

2. Organic Sulfur Time-Series

[3] Mixed layer (ML) averaged DMS (DMS_{ML}) concentrations exhibit a clear annual cycle ranging from less than 0.5 $\mu\text{mol m}^{-3}$ in the winter to greater than 5.0 $\mu\text{mol m}^{-3}$ in the summer associated with high stratification and the shoaling of the mixed layer (Figure 1a). DMS stocks peak in July and August, coincident with annual minima in phytoplankton pigment biomass and primary production (Figure 1b), more than two months later than the maxima for its biological precursors, pDMSP and dDMSP (Figure 1c) [see Dacey *et al.*, 1998]. The observed decoupling of DMS concentration from any measure of its precursors ($r^2 = 0.14$, 0.11, and 0.26 for DMS versus pDMSP, dDMSP, and chlorophyll respectively) embodies the 'DMS summer paradox' [Simó and Pedrós-Alió, 1999].

[4] Past observations have suggested a positive or insignificant relationship between water column DMS concentrations and phytoplankton abundance [e.g., Kettle *et al.*, 1999, and references therein]. Contrary to this, DMS stocks and chlorophyll a concentrations are inversely correlated ($r = -0.51$; Table 1). This (and other poor observed correlations; Table 1) may be due to the fact that significant DMSP production is limited to a few classes of phytoplankton [Keller *et al.*, 1989] and that shallow summertime mixing may promote phytoplankton succession to pDMSP producing species [Simó and Pedrós-Alió, 1999]. Correlations between organic sulfur stocks and DMSP-relevant pigment markers (as well as their ratios to chlorophyll a) show negative relationships (on sample-to-sample and mixed layer averaged bases) indicating that neither phytoplankton abundance nor community structure are useful predictors of DMS or DMSP stocks. A single exception is

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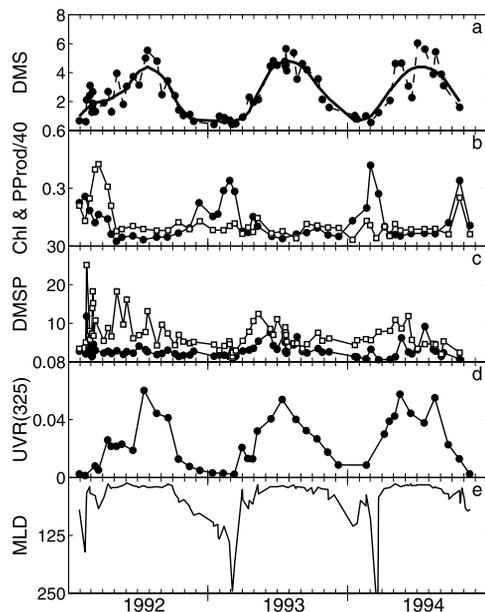


Figure 1. Upper mixed layer averaged time-series observations. (a) DMS concentrations (dashed, ●; $\mu\text{mol m}^{-3}$) and LOESS curve fit used to smooth the ML averaged DMS concentrations (solid), (b) chlorophyll a concentration (●; mg m^{-3}) and primary production scaled by a factor of 40 (PProd, □; $\text{mg C m}^{-3} \text{d}^{-1}$), (c) dDMSP (●; $\mu\text{mol m}^{-3}$) and pDMSP (□; $\mu\text{mol m}^{-3}$) concentrations, (d) daily estimates of downwelling UVR dose at 325 nm (●; $\text{W m}^{-2} \text{nm}^{-1}$), and (e) ML depth (MLD; m) calculated based on a potential density difference of 0.02 kg m^{-3} from the surface.

the correlation between DMS_{ML} and the 19'-Hex. to chlorophyll a ratio ($r = 0.21$); however, this statistically insignificant correlation is simply driven by large annual changes in chlorophyll a. While Prymnesiophytes constitute

a slightly larger percentage of the eukaryotic community in the summer, in absolute terms they are more abundant during the spring bloom [DuRand *et al.*, 2001]. Summer phytoplankton communities in the Sargasso Sea are dominated by *Prochlorococcus* and *Synechococcus* both of which have been shown to produce negligible amounts of DMS and DMSP [Corn *et al.*, 1996]. Thus, the DMS summer paradox cannot be explained by changes in phytoplankton biomass or community structure.

[5] DMS concentrations are most highly correlated with physical, seasonally varying factors such as sea surface temperature (SST), solar fluxes in the visible (400–700 nm) and the ultraviolet (280–400 nm), and diffuse spectral light attenuation coefficients ($K_d(\lambda)$; Table 1). Correlations between DMS_{ML} and $K_d(\lambda)$ decrease with increasing wavelength suggesting that the shorter, more energetic wavelengths of light are more important in regulating DMS stocks and that the vertical attenuation of solar radiation is a factor. Mixed layer depth and $K_d(\lambda)$ are the major determinants of daily mean light levels for a mixed layer. In fact, daily estimates of mean mixed layer downwelling ultraviolet radiation dose at 325 nm, UVR(325) [see Toole *et al.*, 2003], account for 77% (r^2) of the variability in DMS_{ML} (Table 1). This, in conjunction with the regular seasonal progression in DMS_{ML} without a corresponding biological source, indicates that upper-ocean DMS concentrations are regulated by the availability and spectral quality of the underwater light flux.

3. Net Biological Production

[6] Net DMS_{ML} stocks result from production and destruction within a complex web of processes including phytoplankton production, bacterial consumption and production, zooplankton grazing, viral activity, sea-to-air ventilation, photolysis, and vertical mixing [Simó, 2001, and references therein]. Although we cannot partition the time

Table 1. Correlation Coefficients for DMS Concentration, ML Average DMS, pDMSP, and dDMSP Concentrations, and ML Average Net Biological DMS Production Versus Relevant Water Column Properties^a

In-water property	DMS(z, t)	DMS_{ML}^b	$\text{pDMSP}_{\text{ML}}^b$	$\text{dDMSP}_{\text{ML}}^b$	Net biological production ^b
SST	0.71	0.72	-0.11	0.16	0.73
Bacterial Count	-0.32	-0.43	0.08	-0.11	-0.36
Bacterial Production	0.22	0.26	0.27	0.45	0.22
PProd	-0.27	-0.24	0.11	-0.11	-0.18
Chlorophyll a	-0.51	-0.61	-0.36	-0.31	-0.61
Peridinin ^c	-0.43	-0.47	-0.13	-0.16	-0.33
19'-Hex. ^c	-0.52	-0.60	-0.27	-0.27	-0.58
Peridinin/Chl a	-0.34	-0.24	0.07	-0.02	-0.17
19'-Hex./Chl a	0.22	0.21	-0.04	0.26	0.36
$K_d(410,z)$	-0.66	-0.73	-0.01	-0.21	-0.69
$K_d(443,z)$	-0.61	-0.70	-0.08	-0.22	-0.67
PAR(z)	0.43	0.64	0.25	0.10	0.69
UVR(325,z)	0.21	0.88	0.01	0.21	0.91
MLD	-	-0.63	-0.40	-0.29	-0.57

^aDue to large synoptic variability only samples collected within ± 2 days (or, due to sampling frequency, ± 4 days for optical data) from the sulfur samples were used in the analysis. None of the correlations were performed on smoothed datasets. Significant correlations at the 95% level are in bold. Physical, biological, and chemical water column properties are drawn from the BATS datasets [Steinberg *et al.*, 2001], optical determinations are drawn from the Bermuda Bio-Optics Project datasets [Siegel *et al.*, 2001], and estimates of UVR(325,z) were calculated following Toole *et al.* [2003].

^bCorrelation coefficients are calculated between ML averaged DMS, pDMSP, and dDMSP concentration and net biological DMS production rate versus ML averaged in-water properties.

^cPeridinin is the marker pigment commonly used for dinoflagellate abundance and 19'-Hexanoxyloxyfucoxanthin (19'-Hex.) corresponds to Prymnesiophyte abundance.

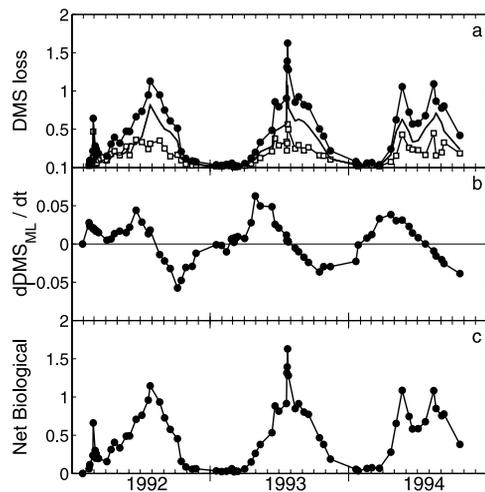


Figure 2. Upper mixed layer averaged DMS turnover rates. (a) DMS loss rates for photolysis (solid), sea-to-air flux (solid, \square), and total physical loss (solid, \bullet ; all $\mu\text{mol m}^{-3} \text{d}^{-1}$), (b) the time rate of change for DMS concentration ($d\text{DMS}_{\text{ML}}/dt$; \bullet ; $\mu\text{mol m}^{-3} \text{d}^{-1}$), and (c) net biological DMS production (\bullet ; $\mu\text{mol m}^{-3} \text{d}^{-1}$). In 2a the rate data is presented as the daily rate over the time period between successive DMS samplings. The photolysis result is from *Toole et al.* [2003] and sea-to-air exchange is calculated based on sampled windspeed from the Bermuda airport tower. Calculations of $d\text{DMS}_{\text{ML}}/dt$ are made using the LOESS curve fit shown in Figure 1a.

dependent fluxes among all of these processes using the present dataset, the net biological production can be diagnosed by examining the budget for DMS_{ML} , or

$$d\text{DMS}_{\text{ML}}/dt = \text{net biological production} - \text{photolysis} - \text{sea-to-air exchange} + \text{entrainment} \quad (1)$$

where “net biological production” represents the net sum of all biological processes, “photolysis” refers to photochemical loss, “sea-to-air exchange” is its outgassing to the atmosphere distributed over the mixed layer, and “entrainment” refers to the vertical turbulent flux. Mean mixed layer DMS photolysis rates range from $0.5\text{--}0.8 \mu\text{mol m}^{-3} \text{d}^{-1}$ in the summer to less than $0.05 \mu\text{mol m}^{-3} \text{d}^{-1}$ in the winter (Figure 2a) [see *Toole et al.*, 2003]. Similarly, estimated sea-to-air DMS fluxes peak in the summer, ranging from $0.3\text{--}0.5 \mu\text{mol m}^{-3} \text{d}^{-1}$, as a result of higher DMS concentrations and temperatures. Sea-to-air exchange rate constants were estimated from a moderate windspeed/gas exchange parameterization [*Nightingale et al.*, 2000] and different choices do not significantly impact the final results [data not shown]. Combined, these loss processes correspond to summertime net physical/chemical loss rates of $0.8\text{--}1.6 \mu\text{mol m}^{-3} \text{d}^{-1}$ (Figure 2a) and a specific mixed layer DMS turnover time of ~ 3 days (over these timescales, entrainment fluxes are negligibly small). Net biological production rates must be just slightly faster than the aggregate loss fluxes and vary in concert in order for mixed layer DMS stocks to accumulate and produce the summer paradox.

[7] The rapid physical/chemical turnover rates suggest that DMS_{ML} stocks will respond quickly to synoptic

weather disturbances including storms and periods of cloudiness. Hence, an every two-week sampling regimen will collect observations that are statistically independent from one another making the point-to-point determination of temporal gradients noisy at best. To best calculate temporal gradients, values of DMS_{ML} were smoothed using locally weighted linear regression (Figure 1a) [LOESS, *Cleveland and Devlin*, 1988] enabling the estimation of $d\text{DMS}_{\text{ML}}/dt$ (Figure 2b) and net biological production rates (Figure 2c). Estimated rates of net biological DMS production peak in the summer ranging from $0.8\text{--}1.8 \mu\text{mol m}^{-3} \text{d}^{-1}$. $d\text{DMS}_{\text{ML}}/dt$ rates are an order of magnitude smaller than both the DMS production and loss rates indicating that the summer paradox is the result of a slight decoupling of rapid rate processes. Estimated DMS biological production rates are negatively or insignificantly correlated with phytoplankton and bacterial indices for abundance and productivity while more than 82% of the variability is explained by UVR(325) (Table 1). These results provide further evidence that light is the dominant driving force regulating DMS production in the Sargasso Sea.

4. Discussion

[8] So, how does light regulate net DMS production? One way is through the interactions of UVR with the processing of organic sulfur by bacteria. Microbial DMS and $d\text{DMSP}$ consumption can be inhibited at surface levels of irradiance [*Slezak et al.*, 2001]. High levels of variability have been observed in these rate processes and *Ledyard and Dacey* [1996] found that in the Sargasso Sea, dark microbial mediated DMS concentration changes ranged from net consumption to net production without a clear seasonal pattern. Because of the scarcity of data with respect to the impact of UVR on these rates though, bacterial processes cannot be strictly ruled out. As both DMS and $d\text{DMSP}$ consumption are inhibited however, it appears unlikely that light mediated changes in the DMS yield from microbial $d\text{DMSP}$ consumption can account for the >10 -fold increase in net biological DMS production in the summer.

[9] It seems unlikely that zooplankton grazing will modify DMS production in a way that is well correlated with UVR flux. Although zooplankton data at BATS are not available for the time period in question, peaks in mesozooplankton biomass and grazing tend to follow peaks in primary production [e.g., *Madin et al.*, 2001]. Microzooplankton abundances are greater in the summer but their grazing rates suggest they consume a smaller percentage of the primary production and filter a smaller percentage of the photic zone during this time [*Roman et al.*, 1993]. This, combined with the reduced phytoplankton biomass, suggests that grazing is not responsible for the elevated rates of biological DMS production in the summer.

[10] The patterns observed here are consistent with recent laboratory results [e.g., *Sunda et al.*, 2002] and indicate that phytoplanktonic DMSP and DMS photo-production resulting from UVR stress is likely a dominant mechanism. Using several archetypical phytoplankton species, *Sunda et al.* [2002] demonstrated that intracellular DMSP and DMS concentrations dramatically increase under conditions of acute oxidative stress such as exposure to high levels of UVR. Further, it seems unlikely that nutrient limitation

stresses exert a dominant role as, with the exception of brief deep mixing periods in the winter/spring, nitrate levels at the sampling site remain below detectability within the upper 80 m of the water column [Steinberg *et al.*, 2001]. Although the present analysis is correlative, these results are consistent with DMS production by UVR stressors.

[11] The present analyses show no significant positive relationship between DMS stocks and all available indices of phytoplankton and bacterial abundance or productivity. This fundamentally alters how one looks at the controls on DMS stocks. We postulate that there are two distinct regimes for DMS cycling: a stress-forced regime, as we have described for the Sargasso Sea, and a bloom-forced regime, where phytoplankton blooms dictate DMS stocks and distributions. The bloom-forced regime occurs in regions characterized by mono-species blooms of pDMSP-producing phytoplankton such as Coccolithophores and *Phaeocystis* often found in the North Sea, the subpolar North Atlantic Ocean, and the Southern Ocean. For the stress-forced regime, changes in DMS stocks are driven by stressors created by the physical environment.

[12] Hints of the two DMS cycling regimes can be found in a recent global modelling study which successfully predicts surface DMS concentrations [Simó and Dachs, 2002]. For 15% of the ocean consisting primarily of high latitude, continental shelf, and equatorial upwelling regions, DMS is accurately predicted as a function of the ratio of surface chlorophyll derived from satellite to climatological mixed layer. This corresponds to the bloom-forced regime. For the remaining 85% of the ocean, modelled surface DMS concentrations are independent of chlorophyll and are a function of mixed layer depth. UVR dose will be strongly controlled by the mixed layer depth and we interpret this as the stress-forced regime. Thus, open-ocean sulfur cycling is not driven by the blooming of high pDMSP producing phytoplankton which is critical as >50% of the DMS ventilated from the ocean to the atmosphere originates from the subtropical oceans [Kettle and Andreae, 2000].

5. Conclusions

[13] Our results have important implications for potential climate feedbacks associated with the marine sulfur cycle. DMS-climate feedbacks are created by the atmospheric oxidation products of DMS reducing incident solar fluxes and SST values which in turn reduce phytoplankton primary production rates and biogenic DMS production. For the stress-forced regime, biological populations produce DMSP and DMS in response to physiological stresses associated with high UVR doses enabling the DMS-climate feedback loop to be effectively closed. These results also suggest the potential of a global change-DMS-climate feedback. UVR doses will increase as a result of observed decreases in stratospheric ozone and the shoaling of ocean mixed layers as a result of global warming [e.g., Boyd and Doney, 2002]. In response, open-ocean phytoplankton communities should increase their DMS production and ventilation to the atmosphere, increasing cloud condensing nuclei, and potentially playing out a coupled global change-DMS-climate feedback.

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