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On the relationship between ocean DMS and solar radiation

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[1] Biologically produced dimethylsulfide (DMS) is an important source of sulfur to the marine atmosphere that may affect cloud formation and properties. DMS is involved in a complex set of biochemical transformations and ecological exchanges so its global distribution is influenced by numerous factors, including oxidative stress from UV radiation. We re-examine correlations between global surface DMS concentrations and mixed layer solar radiation dose (SRD), and find that SRD accounts for only a very small fraction (14%) of total variance in DMS measurements when using minimal aggregation methods. Moreover this relationship arises in part from the fact that when mixed layers deepen, both SRD and DMS decrease. When we control for this confounding effect, the correlation between DMS and SRD is reduced even further. These results indicate that factors other than solar irradiance play a leading role in determining global DMS emissions. **Citation:** Derevianko, G. J., C. Deutsch, and A. Hall (2009), On the relationship between ocean DMS and solar radiation, *Geophys. Res. Lett.*, *36*, L17606, doi:10.1029/2009GL039412.

1. Introduction

[2] Clouds and cloud formation processes are poorly understood aspects of the climate system. Sulfur aerosols are of particular interest as they enhance cloud formation by acting as precursors to cloud condensation nuclei [*Andreae and Crutzen*, 1997]. The largest natural source of sulfur to the atmosphere is oceanic release of dimethylsulfide (DMS), a compound created by phytoplankton [*Charlson et al.*, 1987]. Under laboratory conditions, many phytoplankton species increase production of DMS and its precursor, dimethylsulfoniopropionate (DMSP) in response to higher oxidant levels due to UV exposure [*Sunda et al.*, 2002]. Once released from cells into the oceanic mixed layer, DMS is generally supersaturated and thus escapes to the atmosphere, where it can yield sulfate aerosols [*Dacey et al.*, 1998]. Areas of high oceanic DMS production may increase local atmospheric sulfur aerosol concentrations, affecting the local climate by increasing cloud formation and changing cloud albedo [*Charlson et al.*, 1987]. This link between sunlight and DMS production could constitute a feedback loop between phytoplankton productivity, DMS production, and solar radiation [*Charlson et al.*, 1987; *Kettle et al.*, 1999], but its strength is unknown.

[3] One crucial test for the existence of such a feedback is the correlation between DMS production and solar radiation intensity experienced by phytoplankton. Direct measurements of DMS production rates are too sparse to establish such a relationship. However, correlations have been reported between seasonal variations in DMS concentration and local solar irradiance at the sea surface [*Toole and Siegel*, 2004] as well as the average radiation in the surface mixed layer, which is the solar radiation dose (SRD) that plankton experience [*Vallina and Simó*, 2007]. A global relationship between solar irradiance and DMS concentration was also investigated by *Vallina and Simó* [2007] (hereinafter referred to as VS07) who found that, when averaged and binned over large spatial scales, the distribution of DMS concentrations was highly correlated to a single physical variable, the SRD.

[4] Here we test the robustness of the global DMS-SRD relationship to three potential complicating factors. First, DMS concentrations are not a direct measurement of its production, but reflect a combination of biological and physical processes. For instance, variations in mixed layer depth (MLD) will generate a correlation between SRD and DMS concentrations, even if the rate of DMS production is insensitive to solar intensity. Increasing MLD while keeping DMS formation rates constant dilutes the concentration of DMS since water with little to no DMS is entrained into the mixed layer, causing DMS to be inversely proportional to MLD (see auxiliary material).[2] At the same time, SRD is strongly anti-correlated with MLD simply because it is irradiance averaged over the layer's depth [*Vallina and Simó*, 2007]. This simultaneous "dilution" of both solar irradiance and DMS when mixed layers are deep will artificially strengthen the global correlation between SRD and DMS concentration.

[5] The second complication is that SRD varies greatly due to clouds, an effect that should be accounted for in a relationship between DMS and SRD. An increase in accuracy of SRD is possible using the International Satellite Cloud Climatology Project (ISCCP), which provides downwelling solar radiation flux data [*Zhang et al.*, 2004] on time and space scales better suited to the short residence time and spatial heterogeneity of DMS [*Nemcek et al.*, 2008]. Although ISCCP monthly climatology cannot resolve the full spatial and temporal variability in light intensity experienced by plankton, accounting for observed cloud cover at monthly resolution should improve the correlation between the two variables if SRD fluctuations are indeed key drivers of DMS variability.

[6] Finally, biological productivity varies by at least two orders of magnitude at the global scale, and should be included in a simple model for DMS concentration even though studies have shown the correlation between DMS concentration and chlorophyll to be weak [*Kettle et al.*, 1999]. While SRD is primarily a measure of variations in physical conditions that affect the surface ocean ecosystem,

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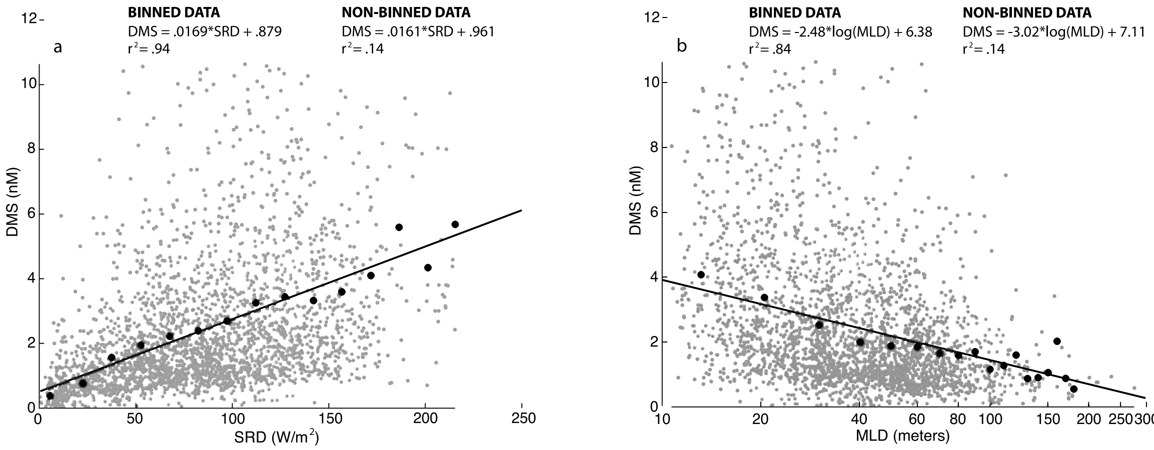

Figure 1. DMS concentration versus (a) solar radiation dose (SRD) and (b) the logarithm of mixed layer depth (MLD). Gray points are data averaged over areas of 2.5° width in latitude and longitude. Bold points are data averaged as per VS07 over 10° latitude by 20° longitude, then averaged in bins of 15 W/m^2 of SRD (Figure 1a) and 10 m of MLD (Figure 1b). The coefficients of determination (r^2) show a strong correlation between DMS and both SRD and MLD for data that is averaged over large regions and binned, but only poor correlations for non-binned data averaged over smaller areas (2.5°). The regression line is for binned data.

it incorporates no direct measure of biological productivity that is necessary for DMS production. Therefore, a strong correlation between DMS and SRD implies that these biological factors are less important than physical variations in determining the surface concentration of DMS. The result is that correlations between global DMS and physical parameters, such as SRD, have likely underestimated the importance of DMS production during algal blooms by removing the highest observed DMS concentrations.

2. Results

[7] To better understand the role of solar radiation in the ocean DMS cycle, we re-examine correlations between observed global DMS concentrations and the SRD estimated for the month and location in which each DMS measurement was made (see Methods). DMS concentrations show a very weak correlation to SRD (r^2 = .14) when averaged over 2.5° by 2.5° (Figure 1a, light points). Averaging the data across larger spatial regions (e.g., 10° by 20° [*Vallina and Simó*, 2007]) does not produce a significantly different result. However, when the data are binned according to SRD and averaged into a single value in each SRD range, the correlation between DMS and SRD increases dramatically (r^2 = .94) (Figure 1a, bold points). These artificially strong correlations result from the reduction in the total variance in the data due to binning. Correlations of similar strength but opposite in sign are obtained using MLD as a predictor variable, both for raw and averaged data (Figure 1b). This suggests that neither SRD nor MLD is the dominant source of variation in DMS concentration at spatial scales approaching that of DMS variability, and that the effect of solar radiation may be difficult to distinguish from the confounding effect of DMS dilution when mixed layers are deep.

[8] In order to control for the influence of MLD variations on both SRD and the concentration of DMS, correlations between DMS and SRD were computed for all data

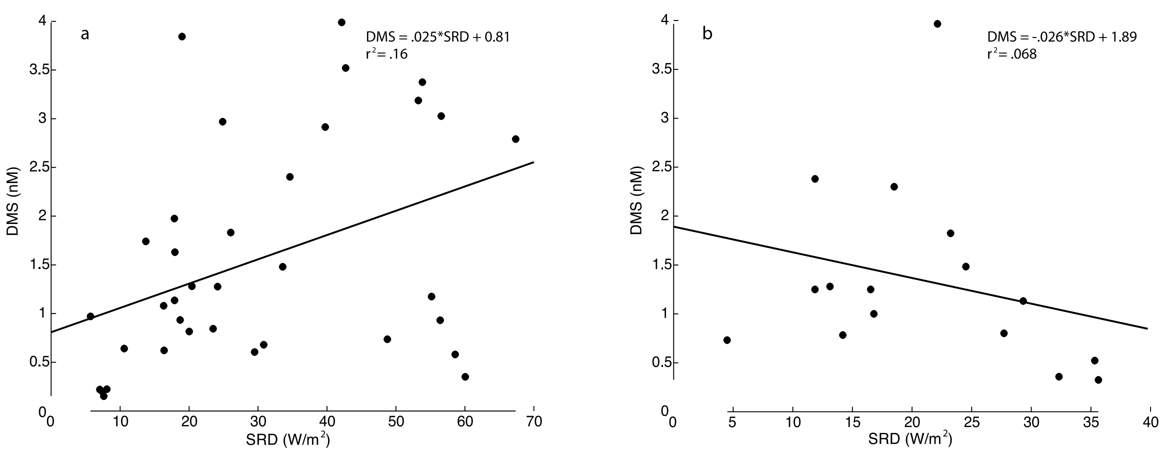

Figure 2. DMS concentration versus SRD for points with narrow ranges of mixed layer depth from (a) 75–85 meter and (b) 95–105 meter (see also Table 1). The points are the 10° latitude by 20° longitude non-binned data used for the bold points in Figure 1. The low correlations indicate that, after controlling for the dilution of DMS by variable mixed layer depths, SRD is a poor predictor of DMS concentration, even when data are averaged over large regions.

Table 1. Full Statistical Information for the DMS-SRD Relationship in Each MLD Bin[a]

Bin	Data Points	Slope	Intercept	R^2	Significance	Z-Test	DMS Spread	Min SRD	Max SRD
5–15	28	0.011	2.18	0.014	42.3%	0.00%	8.91	125.16	213.94
15–25	143	−0.003	3.76	0.001	40.4%	0.00%	10.10	46.72	183.08
25–35 *	174	0.014	1.05	0.070	>99.9%	12.70%	9.25	6.13	164.31
35–45 *	129	0.014	0.74	0.060	98.7%	1.42%	7.23	5.69	124.11
45–55 *	105	0.016	0.95	0.067	99.3%	16.45%	8.76	0.17	109.27
55–65 *	85	0.017	0.98	0.040	93.0%	5.12%	7.62	10.31	86.01
65–75 *	55	0.017	0.74	0.077	96.1%	0.06%	5.81	6.09	80.52
75–85	36	0.025	0.81	0.157	98.3%	1.20%	3.84	5.71	67.37
85–95	21	0.063	−0.34	0.424	99.9%	2.01%	4.41	10.33	49.67
95–105	16	−0.026	1.89	0.068	67.0%	2.96%	3.64	4.49	35.63
105–115	7	0.014	0.12	0.064	41.5%	0.44%	0.50	15.32	23.15
binned data	15	0.017	0.88	.94	>99.9%	>99.9%	3.99	0	215

[a]None of the bins with greater than 2 data points have a strong coefficient of correlation. Asterisks indicate the five bins with a regression line similar to the global regression. Four of these are significant at the 95% confidence level. Three of these bins are not significantly different from the data set from which they are drawn shown by a large z-test value. Only the 2 of the bins are significant at the 95% confidence level and sufficiently different from the source data to conclude that the correlation is not an artifact of the source data. Both of these bins show a correlation coefficient that is approximately half of that shown in Figure 1a. Bins of MLD greater than 115 meters are not shown because $n \leq 2$.

points within a narrow range of MLD. If the correlation between DMS and SRD is driven by light and not MLD, the correlation in each MLD bin should be very similar to the global correlation. The relationship between DMS concentration and SRD for two representative MLD bins shows the correlations are weak and inconsistent in sign (Figure 2). These two bins are not unique in their lack of correlation: Table 1 shows the statistical information for each 10 meter bin in MLD. Five bins have regression lines similar to the non-binned regression line between DMS concentration and SRD; however, these bins have r^2 values ranging between .04 and .08. This indicates that the dilution effect from MLD variability contributes about half of the variability in DMS concentration accounted for by SRD in the global dataset (Figure 1, r^2 = .14).

[9] To verify that dilution accounts for nearly half of the ability of SRD to explain DMS variations, a bivariate regression was performed using ISCCP enhanced SRD and the logarithm of MLD as the independent variables. This was done using the monthly mean, 2.5° by 2.5° grid data (Figure 1, light points). The total variance accounted by SRD and log(MLD) was 15.5%, with the covariance having the most explanatory power at 7%, followed by variance in log(MLD) at 4.5% and variance in SRD at 4%. These values are consistent with the individual bin analysis described by Table 1, further emphasizing the role of dilution in the connection between SRD and DMS concentration. The high covariance between SRD and log(MLD) in the bivariate regression also indicates that log(MLD) and SRD are highly anti-correlated with one another, and nearly half of their explanatory power cannot be unambiguously attributed to a single variable alone (Figure 3).

3. Discussion

[10] Since solar radiation accounts for about 5% of the variance in DMS concentrations, we conclude that other geophysical or biological variables must strongly affect DMS concentration. Indeed previous studies have attempted to show the connection between DMS and a unique geophysical parameter, but were unsuccessful [*Kettle et al.*, 1999]. Also, some method of incorporating biological productivity should be included in a global analysis because DMS is formed through biological processes in the ocean. While studies have found a very low correlation between DMS and chlorophyll climatology [*Kettle et al.*, 1999], other algorithms similar to VS07 incorporate chlorophyll in determining DMS concentration [*Simó and Dachs*, 2002]. A map of the DMS values used in this analysis (auxiliary material) shows a number of high DMS concentrations in areas of high biological productivity, supporting inclusion of a biological parameter in an algorithm determining the distribution of global DMS concentration.

[11] Despite the weak correlations found at the global scale, the SRD – DMS link may still hold at more regional scales [*Dacey et al.*, 1998; *Toole and Siegel*, 2004; *Vallina and Simó*, 2007]. It has been shown in regional studies of DMS, such as the Bermuda Atlantic Time-series Study, that there are significant correlations between SRD and DMS concentration [*Vallina and Simó*, 2007]. In fact, near

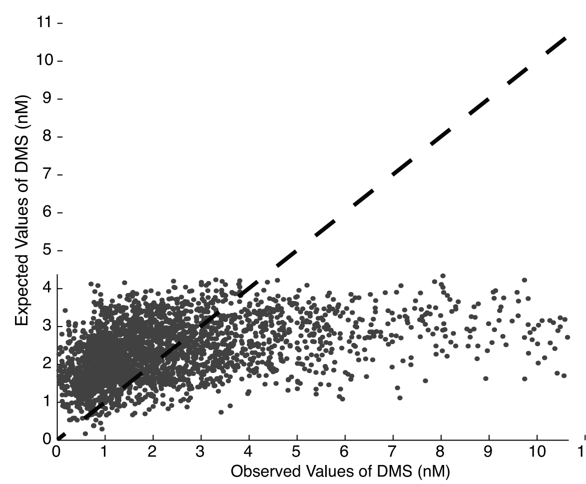

Figure 3. Expected DMS concentrations from the bivariate regression model versus measured DMS concentrations. DMS, SRD, and MLD data are averaged over 2.5° boxes and modeled by DMS = C_1*(SRD) + C_2*log(MLD) + C_3 with coefficients C_1 = .0087, C_2 = −1.71, and C_3 = 4.29. Only 4% of the variance in DMS concentration is accounted for by SRD, 4.5% by MLD, and 7% by the covariance between SRD and MLD.

Bermuda, variation in ultraviolet radiation accounts for 77% of the variability in DMS concentration for the mixed layer [*Toole and Siegel*, 2004]. At local scales, variation in biological factors may be small enough for the effect of SRD to be dominant. That is, the temporal variability in DMS concentration may be explained by SRD at some locations while the spatial variability is controlled by other factors. As noted by *Toole and Siegel* [2004], synoptic scale storms and associated cloud cover variation have a significant impact on DMS concentrations. The time scales of these phenomena are much shorter than a month, and therefore monthly mean data does not resolve them. This time-scale mismatch underscores the need for frequent and accurate measurement of other parameters taken in conjunction with the DMS measurements to provide further insight of global DMS emissions.

4. Methods

[12] To calculate SRD we use ISCCP surface solar irradiance averaged over a MLD climatology [*de Boyer Montégut et al.*, 2004] assuming an exponential decrease of solar radiation in seawater with a uniform extinction coefficient of 0.06 m^{-1} (see VS07 supplemental material). The use of ISCCP data limits our analysis to DMS data collected since 1984, removing only 4% of the data from the Global Surface Seawater DMS database (http://saga.pmel.noaa.gov/dms). From this subset, the top five percent DMS values are removed because they are considered indicative of bloom conditions: a short-lived, local complicating factor we neglect due to the spatial resolution of SRD (2.5° by 2.5°) and temporal resolution of MLD (monthly averages). As these are the least resolved parameters, all information is initially averaged to these resolutions to retain the full variance in the data before further manipulation is performed.

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