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# High dimethylsulfide photolysis rates in nitrate-rich Antarctic waters

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[1] The photochemistry of dimethylsulfide (DMS) was examined in the Southern Ocean to assess its impact on the biogeochemical dynamics of DMS in Antarctic waters. Very high DMS photolysis rate constants (0.16–0.23 $h^{-1}$) were observed in surface waters exposed to full sunlight. DMS photolysis rates increased linearly with added nitrate concentrations, and 35% of the DMS loss in unamended samples was attributed to the photochemistry of ambient nitrate (29 μM). Experiments with optical filters showed that the UV-A band of sunlight (320–400 nm) accounted for ~65% of DMS photolysis suggesting that dissolved organic matter was the main photosensitizer for DMS photolysis. During the austral spring, DMS photolysis was the dominant loss mechanism under non-bloom and non-ice cover conditions owing to the high doses and deep penetration of UV radiation in the water column, low observed microbial consumption rates, and high in situ nitrate concentrations. *INDEX TERMS:* 4852 Oceanography: Biological and Chemical: Photochemistry; 4207 Oceanography: General: Arctic and Antarctic oceanography; 4820 Oceanography: Biological and Chemical: Gases; 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615). **Citation:** Toole, D. A., D. J. Kieber, R. P. Kiene, E. M. White, J. Bisgrove, D. A. del Valle, and D. Slezak (2004), High dimethylsulfide photolysis rates in nitrate-rich Antarctic waters, *Geophys. Res. Lett.*, *31*, L11307, doi:10.1029/2004GL019863.

## 1. Introduction

[2] Oceanic dimethylsulfide (DMS) comprises over 90% of the marine sulfur flux and over 50% of the global biogenic flux of sulfur to the troposphere [*Andreae*, 1986]. The climatically relevant trace gas, DMS, and its precursor, dimethylsulfoniopropionate (DMSP), are produced and consumed in a complex network of food web interactions across a variety of trophic levels. DMS photolysis makes an important contribution to the time/space variability of DMS concentrations in a variety of oceanic environments [e.g., *Kieber et al.*, 1996]. DMS readily photolyzes in seawater when exposed to ultraviolet radiation (UVR, 280–400 nm), with variable contributions from the UV-B (280–320 nm) and UV-A (320–400 nm) spectral regions [*Kieber et al.*, 1996; *Toole et al.*, 2003]. Since DMS does not absorb radiation above 260 nm, its photolysis must occur through photosensitized pathways [*Brimblecombe and Shooter*, 1986]. To date no determinations of DMS photolysis rate constants have been carried out in the Southern Ocean. This fundamental gap limits our ability to assess how changes in radiative forcing will alter DMS cycling on a global scale. Therefore, we studied the photolysis of DMS in the Southern Ocean as part of a larger study that examined factors controlling the biogeochemistry of DMS and DMSP in these waters. Salient findings of our study are that (1) photolysis rate constants are unusually high, with photolysis dominating DMS cycling in the austral spring, (2) dissolved organic matter (DOM) was the predominant factor contributing to the photolysis of DMS, and (3) high nitrate concentrations in Southern Ocean waters also played an important role.

## 2. Experimental

[3] Seawater samples were collected aboard the RV *Nathaniel B. Palmer* at several hydrographic stations in the Southern Ocean north of the Ross Sea (between 65.3 S, 177.0 E and 67.5 S, 176.0 E) during non-ozone hole conditions from November 8 to 13, 2003. Seawater was filtered directly from Niskin sampling bottles into 500 mL pre-cleaned Qorpak bottles using silicone tubing and 0.2 μm POLYCAP filter capsules [see *Toole et al.*, 2003 for details regarding sample filtration and glassware preparation]. Samples were placed in either quartz tubes with Teflon stoppers or quartz tubes with Teflon-faced butyl rubber stoppers and crimp caps. DMS and dimethylsulfoxide (DMSO) concentrations were determined using a modified purge and trap gas chromatography (GC) procedure [*Kiene and Service*, 1991; *Kiene and Gerard*, 1994]. Photolysis experiments were conducted with either amendments of $^{35}$S-DMS tracer [*Kiene and Linn*, 2000], which has the advantage of not significantly perturbing the natural concentration of DMS, or by the addition of dissolved DMS (produced from high purity DMSP, Research Plus, Inc.) to final concentrations of 12–16 nM. The $^{35}$S-DMS was added as a gas to seawater giving ~1000–3000 dpm $mL^{-1}$ (specific activity 984,000 dpm $pmol^{-1}$). Photolysis of the volatile $^{35}$S-DMS tracer was quantified by measuring production of non-volatile $^{35}$S ($^{35}$S which remained in solution after sparging samples (100 ml $min^{-1}$) for 10 min with nitrogen). Nitrate and nitrite stock solutions were prepared by dissolving either sodium nitrate (99.995+%, Aldrich) or sodium nitrite (99.99+%, Fluka) in Milli-Q water. Nitrate and nitrite concentrations were determined by HPLC [*Kieber and Seaton*, 1995].

[4] Quartz tubes were incubated in a shallow, UVR transparent water bath with a black base and circulating

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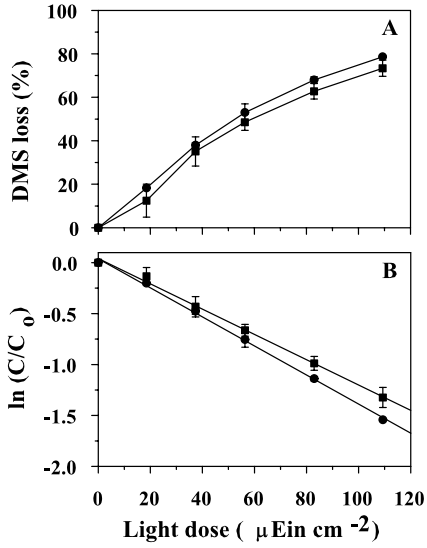


**Figure 1.** A) Percent DMS photolyzed (±sd) as a function of UV-A 330–380 nm light dose for 0.23 nM DMS with $^{35}$S-DMS addition (●) or 15.4 ± 0.3 nM unlabeled DMS (■), and B) Natural log final concentration (C) divided by initial concentration ($C_o$) vs. light dose ($r^2$ = 0.993 and 0.996 for the $^{35}$S-DMS (●) and GC (■) techniques, respectively). In panel B, solid lines represent the best fit of the data from linear regression analysis. Samples were collected from 4 m on Nov. 8, 2003 (67.5 S, 176.0 E). Sunlight-incubated samples were analyzed every 60–75 minutes from 0835 to 1415 local time.

surface seawater (ca. −1.8°C). Tubes were attached to a black, plastic-coated, metal grill suspended ∼5 cm from the incubator bottom. The incident irradiance at 330–380 nm was monitored by chemical actinometry in parallel tubes containing the nitrite actinometer in 0.7 M NaCl to prevent freezing [*Jankowski*, 1999].

## 3. Results

[5] The surface mixed layer (ca. 0–100 m) at the main hydrographic stations (65 S, 177 E and 67 S, 176 E) was characterized by a temperature of −1.8°C, chromophoric DOM absorption at 300 nm of 0.240–0.309 $m^{-1}$, and 1% light depths ranging from 26–28 m for 320 nm and >75 m for 395 nm. Ice coverage was moderate with patches of open water constituting ∼50% of the sea surface area. DMS concentrations ranged from 0.23–1.5 nM at the surface to 0.10–0.89 nM at the base of the mixed layer. Concentrations of DMSO, a DMS photolysis product, decreased from 1.3 nM at the surface to 0.34 nM at 70 m. Nitrate and nitrite concentrations in these waters were 29 μM and 150–199 nM respectively.

[6] The photolysis of DMS in 0.2 μm-filtered seawater samples from these stations was extremely fast in full sunlight, with nearly 75% of the in situ DMS (0.23 nM) photolyzed during a 5.67-hour incubation (Figure 1A). The rate constant derived from $^{35}$S-DMS loss (Figure 1B) was 0.23 ± 0.04 $h^{-1}$ (±sd) corresponding to a DMS loss rate of 0.053 nM $h^{-1}$ at the ambient DMS concentration of 0.23 nM. Parallel irradiations of seawater amended to 15.4 nM DMS and monitored by GC yielded the same rate constant (0.22 ± 0.01 $h^{-1}$) within experimental error (Figure 1B). Using day length derived from latitude and Julian Day (∼17.5 hours) and the $^{35}$S-DMS derived rate constant, the daily photolysis rate was 0.93 nM $day^{-1}$ at the ambient DMS concentration, indicating that (at surface levels of irradiance) DMS turnover times due to photolysis were significantly less than 1 day (i.e., 6 hours). The DMSO yield from DMS (±sd) was 33 ± 5.6% for this sample and did not vary significantly with irradiation time or DMS concentration [data not shown]. These results were typical of several such experiments conducted in this region where rate constants varied from 0.16 to 0.23 $h^{-1}$ and DMSO yields ranged from 33 to 45%. The DMS photolysis rate constants reported here are high compared to those previously measured in temperate and subtropical waters [vide infra]. In addition, the DMSO yields from DMS photolysis in Antarctic waters are somewhat higher than those observed in temperate and subtropical samples (ca. 14–32%) [*Kieber et al.*, 1996; *Kieber*, unpublished results].

[7] We evaluated potential artifacts associated with the incubation vessel (Teflon bottle, quartz tubes), stopper type (Teflon, Teflon faced butyl rubber, Viton), filtration method (POLYCAP, GF/F gravity filtered, large all-polycarbonate filter rig), quartz tube cleaning protocol (10% HCl and Milli Q-water rinsed with or without muffling at 450°C for 6 hours), and sample collection (CTD, polypropylene bucket), but these approaches all gave the same high rate constants within experimental error (ca. <5%) [data not shown].

[8] To assess the basis for the unusually high rate constants, we conducted experiments to determine the impact of nitrate and nitrite on DMS photolysis rates. These species were examined because they are present at high concentrations in Antarctic waters and are known to be photochemically reactive, producing hydroxyl (OH) radicals and other reactive species [see *Mack and Bolton*, 1999, for review]. Nitrate and nitrite concentrations were varied in 0.2 μm-filtered seawater from 28.6 μM (ambient) to 430 μM (∼15 times ambient) for nitrate and from 0.15 μM (ambient) to 4.12 μM (∼27.5 times ambient) for nitrite. Lower concentrations of nitrite were added because nitrite is much more photoreactive compared to nitrate in Antarctic water. For example, under typical Antarctic non-ozone hole conditions, nitrate accounted for only ∼4 times as much OH radical production as nitrite even though ambient nitrate concentrations (24 μM) were approximately 300 times greater than nitrite (80 nM) [*Qian et al.*, 2001].

[9] Nitrate additions up to 430 μM substantially increased the percentage of DMS photolyzed in a 70-minute incubation under midday sun (Figure 2A). The calculated photolysis rate constant (±sd) increased linearly with added nitrate from 0.16 ± 0.02 $h^{-1}$ to 1.46 ± 0.04 $h^{-1}$ (∼9 times the unamended rate constant; slope = 0.0032 $h^{-1}$ $\mu M^{-1}$, $r^2$ = 0.997, Figure 2B). Nitrite additions had no effect on the percent DMS photolyzed, yielding photolysis rate constants that were not different from those in the unamended sample (0.16 ± 0.02 $h^{-1}$, Figure 2A). Parallel unamended and nitrate-amended dark controls resulted in no loss of DMS, verifying that the stimulatory effect of nitrate was a light mediated process. The photolysis rate constant plotted as a function of nitrate concentration yielded a statistically significant non-zero y-intercept of 0.107 $h^{-1}$ (Figure 2B)

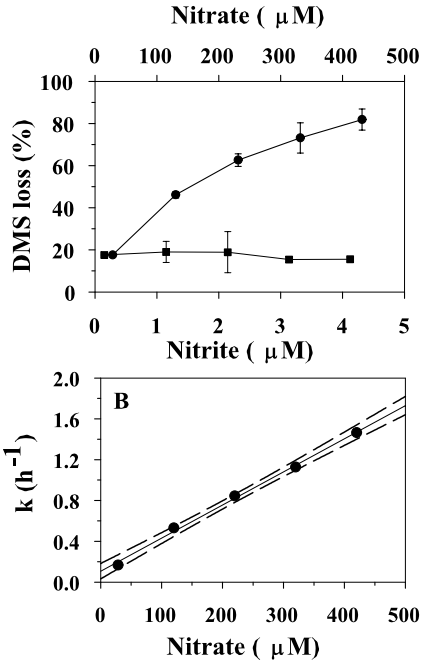


**Figure 2.** A) Percent DMS photolyzed (±sd) as a function of [nitrate] (●) and [nitrite] (■). 0.2 μm-filtered samples were collected Nov. 10, 2003 (65.3 S, 176.8 E) from 10 m and incubated from 1328 to 1438 local time with a 330–380 nm photon exposure of 17.4 μEin $cm^{-2}$. Concentrations were monitored by the $^{35}$S-DMS technique with an initial DMS concentration of 1.14 nM. The lowest concentrations in each series represent ambient nitrate (28.6 μM) and nitrite (0.15 μM). B) Pseudo first order rate constant for photolysis. The solid line denotes the best-fit employing linear regression analysis ($r^2$ = 0.997, slope = 0.0032 $h^{-1}$ $\mu M^{-1}$, y-intercept = 0.107 $h^{-1}$). Dashed lines denote the 95% CI.

indicating rapid photolysis even at zero nitrate. In fact, the rate constant corresponding to the y-intercept was 65% of the rate constant measured at the ambient nitrate concentration (0.16 $h^{-1}$ at 28.6 μM nitrate) suggesting that other factors, such as DOM, were mainly responsible for DMS photolysis in Antarctic waters.

[10] The wavelength region primarily responsible for DMS photolysis in Antarctic waters was determined by incubating 0.2 μm-filtered seawater, collected from 10 and 150 m, for 4.33 hours under a range of long-pass optical filters. Similar to past results [see *Toole et al.*, 2003], photolysis rates were greatest in the full sunlight treatment and decreased to almost undetectable levels under the 395 nm cutoff filter (Figure 3). Based on differences between light treatments, maximum photolysis rates were observed in the UV-A accounting for 64.3% and 67.6% of the total photolysis in the 10 and 150 m samples respectively. The dominance by UV-A in the photolysis of DMS was observed in numerous samples collected from a variety of depths, with deeper samples consistently yielding higher photolysis rates and a slightly larger contribution by UV-A wavelengths [data not shown]. Since nitrate absorption at wavelengths longer than 320 nm is low [*Jankowski et al.*, 2000], this further supports the supposition that DOM contributes to the observed high rate constants of DMS photolysis in Antarctic waters.

## 4. Discussion

[11] Photolysis rate constants observed in the Southern Ocean (0.16–0.23 $h^{-1}$) are significantly greater than surface photolysis rate constants from the equatorial Pacific (0.01–0.04 $h^{-1}$, [*Kieber et al.*, 1996]) and the North Sea (0.03–0.07 $h^{-1}$, [*Hatton*, 2002]), and are larger than those from the Adriatic Sea (0.12 $h^{-1}$, [*Brugger et al.*, 1998]). Turnover times were always less than 1 day at surface levels of irradiance suggesting rapid photochemical cycling of DMS in the upper water column. Because of the water clarity in the early spring in this region, UV radiation penetrates deeply into the water column (1% light levels were 27 and >75 m for UV-B and UV-A respectively). This, coupled with a long photoperiod and a DMS photolysis action spectrum dominated by UV-A, results in significant DMS photolysis occurring over a large depth horizon. Assuming that photolysis rate constants attenuated in proportion to integrated UVR attenuation (305–395 nm, $K_d$ = 0.085 $m^{-1}$ on Nov. 10, 2003), the turnover times for DMS in the 100 m mixed layer due to photolysis ranged from 1.4–2.0 days. By comparison, concurrently measured dark microbial DMS consumption rate constants were quite low, ranging from 0.0035 to 0.0085 $h^{-1}$, yielding turnover times in the mixed layer ranging from 4.9–12 days. Further, based on a standard gas exchange parameterization [*Nightingale et al.*, 2000], the sea-to-air ventilation turnover time was 42.7 days. Thus, photolysis was the dominant loss process mediating mixed layer DMS concentrations at this station.

[12] While our experiments do not conclusively demonstrate reaction mechanisms, they do provide evidence against a role for the OH radical in DMS photolysis in Antarctic waters. Nitrate and nitrite photolysis generates the OH radical and daughter radicals (e.g., the bromide radical) [for a recent review see *Kieber et al.*, 2003]. However, the lack of an effect of added nitrite on DMS photolysis rates

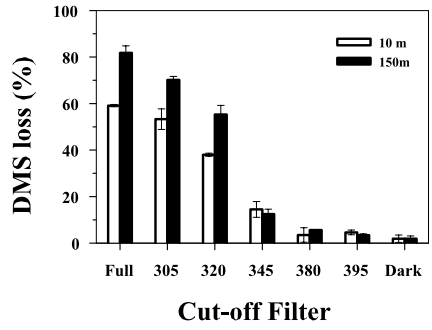


**Figure 3.** Percentage of initial DMS photolyzed (±sd) under a variety of long-pass filters during a 4.33-hour incubation (1020–1440 local time) for 0.2 μm-filtered, 10 m (white bars), and 150 m (black bars) water samples collected on Nov. 11, 2003 (65.3 S, 177.0 E). Loss was monitored using $^{35}$S-DMS with in situ concentrations of 1.02 and 0.17 nM for the 10 and 150 m samples respectively. Full indicates no cut-off filter and dark indicates samples wrapped in aluminum foil. The 330–380 nm light dose was 81.3 μEin $cm^{-2}$ in the full light treatment.

(Figure 2) suggests that these radicals are not important reactants in the photolysis of DMS in Antarctic waters. Further evidence against the involvement of the OH radical in DMS photolysis comes from the fact that DMSO did not photolyze in 0.2 μm-filtered Antarctic seawater during an 8-hour incubation in full sunlight (initial concentration 10.3 ± 0.4 nM; final concentration 10.4 ± 0.7 nM). DMSO is ~3 times less reactive towards the OH radical than DMS [*Sunda et al.*, 2002 and references therein], but if the OH radical was directly involved in DMS photolysis, measurable losses of DMSO would have been detected during our day-long irradiation. These results suggest that light driven OH radical production was not responsible for the high DMS photolysis rate constants observed in Antarctic waters. We do not know the mechanism(s) involved, but the high reactivity of nitrate and corresponding lack of reactivity with nitrite suggests that specific DMS-reactive species are produced from nitrate photolysis, which are not produced during nitrite photolysis at low μM levels. Some nitrate-derived radical species that have been detected [*Mack and Bolton*, 1999] and warrant further investigation include the nitrite radical or peroxynitrite.

[13] Another fascinating aspect of this study is that DOM, or some component of the Antarctic seawater other than nitrate or nitrite, largely accounted for the very high rate constants. We conducted an experiment (with stored, 0.2 μm-filtered seawater) at the Dauphin Island Sea Lab to compare the DMS photolysis rate in Antarctic seawater with that in 30 μM nitrate-amended Sargasso Sea seawater. Both waters had nearly identical DOM absorption coefficients ($a_{DOM}(300)$ = 0.279 $m^{-1}$ vs. 0.290 $m^{-1}$) and nearly the same nitrate concentration (28.6 vs. 30 μM). Despite these similarities, the Sargasso Sea seawater yielded a DMS rate constant (0.097 $h^{-1}$) that was ~13 fold lower than that obtained with stored Antarctic seawater (1.22 $h^{-1}$); note the rate constant for the Antarctic water in this experiment was higher than those measured shipboard (e.g., Figure 1) because of a higher incubation temperature of 10–12°C and higher UV-A photon exposure during this experiment. Since both samples had nearly identical DOM absorption coefficients and nitrate concentrations, the very different rate constants that were observed must reflect differences in unmeasured quantities such as OH scavengers or variations in DOM quality or composition. Several authors (see *Toole et al.*, 2003 and Figure 3 of this manuscript) have demonstrated that UV-A drives a large percentage of DMS photolysis and therefore, although we don't know the mechanism(s), it is likely that DOM is involved in the photochemical loss of DMS.

[14] The fact that DMS photolysis rates are influenced by nitrate has far reaching consequences for sulfur cycling in upwelling, coastal, or seasonally oligotrophic regions. A pulse of nitrate associated with coastal runoff, upwelling, or deep winter convective mixing will increase DMS photolysis rates until the nitrate is drawn down by biological productivity. In high nutrient, low chlorophyll regions such as the Southern Ocean, DMS photolysis rates should remain proportionally large compared to oligotrophic gyres characterized by similar chlorophyll concentrations and DOM absorption, but undetectable nutrients in the seasonal mixed layer. While DOM absorption may be a passive tracer for mixing and thus nitrate concentrations, DOM is produced and consumed through different processes than nitrate suggesting that, for modeling purposes, nitrate concentrations should be explicitly included to parameterize DMS photolysis rates. Overall, observed photolysis rate constants are extremely high in nitrate-rich Antarctic waters and thus photolysis dominates the biogeochemical cycling of DMS in the austral spring.

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