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Influence of nitrate radical on the oxidation of dimethyl sulfide in a polluted marine environment

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[1] Simultaneous in situ measurements of dimethyl sulfide (DMS) and nitrate radical (NO_3) from the NOAA research vessel *Ronald H. Brown* off the New England Coast during the summer of 2002 show a clear anticorrelation between these compounds. The anticorrelation indicates a strong interaction between anthropogenic NO_x emissions and natural sulfur emissions from the ocean surface. The anticorrelation was invariant with the distance from the continent over the range sampled during this study. Diurnal averages showed maxima in DMS concentrations during dawn and dusk and a lower minimum of ≈30 pptv at night compared to the daytime minimum of ≈40 pptv, indicating a stronger oxidation by NO_3 at night than by OH at daytime under polluted conditions. This conclusion is also supported by agreement between a box model calculation and the measurements. Including DMS oxidation by halogens (Cl and BrO) into the model improved the agreement significantly. Calculation of the relative DMS loss due to either NO_3 or OH oxidation indicated that between 65 and 90% of the DMS oxidation was due to NO_3, depending on NO_3 mixing ratios. The area over which DMS oxidation by NO_3 is at least as strong as by OH can extend as far as 3000 km from coastal anthropogenic NO_x sources. These increased DMS oxidation rates by NO_3 may have an impact on global non-sea-salt sulfate aerosol production, depending on the DMS chemical oxidation mechanism.

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1. Introduction

[2] Aerosol particles produced from marine sulfur emissions may have a significant influence on the Earth's climate [*Shaw*, 1983; *Bates et al.*, 1987; *Charlson et al.*, 1987; *Clarke et al.*, 1998]. Dimethylsulfide (DMS, CH_3SCH_3) is produced in the ocean by plankton activity. Its release rate to the atmosphere depends on surface wind speed and concentration of DMS in surface water of the ocean [*Liss and Merlivat*, 1986; *Wanninkhof*, 1992; *Nightingale et al.*, 2000]. It is the largest natural source of non-sea-salt sulfate (nss) aerosol via its oxidation to sulfuric acid (H_2SO_4). The most important oxidants for DMS are hydroxyl (OH) and nitrate (NO_3) radicals. Halogen compounds, especially Cl atoms and BrO radicals, have also recently been suggested as oxidants for DMS in the marine environment [*Toyota et al.*, 2004; *Wingenter et al.*, 2005; *Barnes et al.*, 2006]. By contrast, DMS oxidation by O_3 in the gas phase is thought to be unimportant, although this conclusion is based on only a small number of laboratory studies [*Martinez and Herron*, 1978]. It has been suggested recently that heterogeneous DMS oxidation by O_3 on cloud droplets could be important to total DMS oxidation in the atmosphere [*Gershenzon et al.*, 2001].

[3] Nitrate radical (NO_3) is an important nocturnal oxidant. Figure 1 shows the most important reaction pathways for NO_3 in the troposphere. Nitrate radical is produced by the reaction of ozone (O_3) with nitrogen dioxide (NO_2). Nitrate radical rapidly equilibrates with NO_2 and exists in equilibrium with dinitrogen pentoxide (N_2O_5). It is present at significant concentrations almost exclusively during night because of two efficient loss processes during daytime; photolysis ($J(NO_3) \approx 0.2\ s^{-1}$ at midday [*Wayne et al.*, 1991]) and reaction with NO. Nitric oxide is present mainly during daytime because it is produced from NO_2 photolysis and rapidly lost via its reaction with O_3. NO_2 itself is mainly produced by oxidation of NO emissions by O_3. At night, NO_3 is lost via direct gas phase reactions as well as the often rapid loss of N_2O_5 via mostly heterogeneous reactions. Aside from its reaction with DMS, NO_3 reacts rapidly with a variety of other atmospheric trace gases

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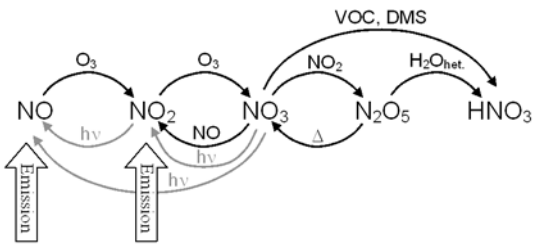

Figure 1. Tropospheric NO_y processes related to NO_3. Solid indicates daytime and nighttime processes, and shaded indicates daytime only processes.

of biogenic and anthropogenic origin, e.g., NO from recent NO_x emissions (i.e., from nearby NO_x sources, such as marine vessels, at night), monoterpenes, and isoprene and, to a lesser extent, volatile organic compounds (VOC) of anthropogenic origin (e.g., alkenes). Therefore the oxidation of DMS by NO_3 is highly variable and is driven by the availability of anthropogenic NO_x in marine environments.

[4] There have been numerous laboratory and theoretical investigations of the mechanism for gas phase DMS oxidation, establishing OH and NO_3 as the main oxidants and leading to various products, which will be discussed later [*Hynes et al.*, 1986; *Yin et al.*, 1990; *Jensen et al.*, 1992; *Le Bras et al.*, 1993; *Turnipseed et al.*, 1996; *Capaldo and Pandis*, 1997; *Ravishankara et al.*, 1997; *Davis et al.*, 1999; *Arsene et al.*, 2001; *Williams et al.*, 2001; *Lucas and Prinn*, 2002, 2005]. Several recent studies have pointed out that Cl atoms and BrO radicals could play an important role as DMS oxidants [*Keene et al.*, 1996; *Knipping et al.*, 2000; *Sciare et al.*, 2000; *Toyota et al.*, 2004; *Dyke et al.*, 2005; *Wingenter et al.*, 2005; *Barnes et al.*, 2006]. The subsequent reactions, yields, and end products arising from each of the possible oxidants OH, NO_3, and halogens, are important to the impact of DMS on the global source for nss aerosols. For example, if there are significantly different H_2SO_4 and, subsequently, aerosol yields from reaction of DMS with OH and NO_3, then any change in the relative amount of DMS oxidized by either radical will have an influence on nss aerosol production.

[5] This study exploits in situ measurements of both NO_3 and DMS to estimate the relative amount of DMS oxidized by the nocturnal pathway. The results will be discussed in terms of their potential regional and global impacts for nss aerosol.

2. Observations

[6] The 2002 New England Air Quality Study (NEAQS) was a campaign that included a combination of ground-, ship-, and aircraft-based measurements with meteorological and chemical forecasting as well as modeling studies. One of the goals of NEAQS 2002 was to investigate the linkage between local air quality and climate. Especially important was the study of both nighttime and daytime chemical transformation within polluted air masses. The study also offered the opportunity to investigate the impact of air pollution on marine atmospheric chemistry.

[7] As part of this campaign, the NOAA research vessel *Ronald H. Brown* (*RHB*) cruised along the coastal area of the eastern United States from 12 July to 10 August 2002. The primary target study areas were downwind from large anthropogenic emission sources, e.g., Boston and New York City, at distances between 10 and 700 km. *RHB* carried an array of instruments to characterize the chemical composition of these air masses. Of particular interest for this study were the measurements of NO_3 and N_2O_5 by cavity ring-down spectroscopy [*Brown et al.*, 2002] and DMS by gas chromatography – mass spectrometry (GC-MS) [*Goldan et al.*, 2004]. Nitrate radical/N_2O_5 and DMS were measured using separate inlets located less than 5 m apart, 15 m forward of the ship's superstructure and about 18 m above sea level. NO_3 and N_2O_5 were measured at 0.2 Hz and DMS was measured at 5 minute averages every 30 min. The detection limits for NO_3 and DMS were 0.5 pptv and 0.6 pptv, respectively.

[8] Three sets of ancillary measurements supplied information for the interpretation of the primary measurements: photolysis rates of NO_2 loss and $O(^1D)$ production [*Stark et al.*, 2007]; speciated VOC measurements by gas chromatography–mass spectrometry (GC-MS) [*Goldan et al.*, 2004], and chemiluminescence determination of O_3 and NO_2 [*Thornton et al.*, 2003]. Table 1 lists these techniques.

[9] Several previous campaigns have included measurements of atmospheric and seawater DMS concentrations, and some of them have been in the North Atlantic region. The seawater DMS concentrations reported from the studies varied between 0.8 and 8.8 nmol/l [*Bürgermeister et al.*, 1990; *Cantin et al.*, 1996; *Bates et al.*, 2000; *Andreae et al.*, 2003] without an apparent diurnal cycle. Atmospheric DMS concentrations measured on different campaigns varied between 0 and 400 pptv [*Andreae et al.*, 1985; *Cooper and Saltzman*, 1991; *Spicer et al.*, 1996; *Sharma et al.*, 1999].

[10] In clean marine conditions, atmospheric DMS concentrations typically exhibit minima in the afternoon and maxima at night resulting from daytime DMS oxidation by OH [*Cooper and Saltzman*, 1991; *Yvon et al.*, 1996b; *Davis et al.*, 1999; *Sharma et al.*, 1999; *de Bruyn et al.*, 2002]. Under polluted conditions, the diurnal cycle can be significantly altered because of oxidation of DMS at night by NO_3 [*Barnes et al.*, 1991; *Allan et al.*, 2000; *Vrekoussis et al.*, 2004, 2006].

[11] Simultaneous measurements of DMS and NO_3 have been reported previously in campaigns that have taken place in coastal areas, where land-based measurements of NO_3 by differential optical absorption spectroscopy (DOAS) can be combined with in–situ measurements of DMS by a variety of techniques. *Barnes et al.* [1991] presented the first simultaneous DMS-NO_3 measurements, recorded during OCEANO-NO_x in Brittany, France in 1988 and 1989 and

Table 1. Ancillary Measurements Used for Data Interpretation

Data Type	Technique	Reference
Photolysis rates	spectroradiometer	*Stark et al.* [2007]
VOC	GC-MS	*Goldan et al.* [2004]
NO_2	chemiluminescence	*Thornton et al.* [2003]

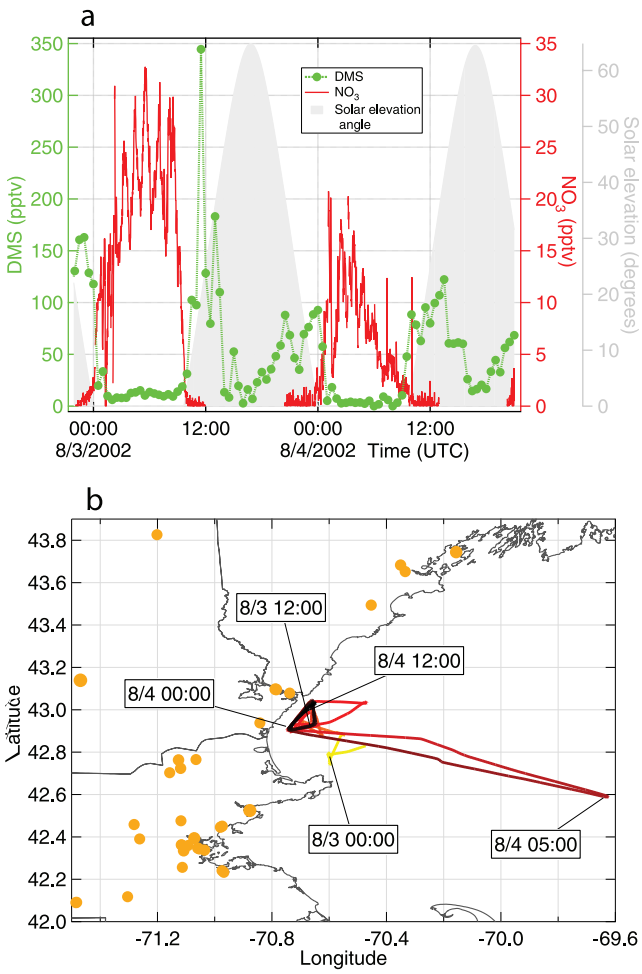

Figure 2. (a) Time series of NO_3 (solid lines), 1 min data, and DMS (dotted lines and circles), 30 min data, from 2 August 2002, 2100 UTC, to 4 August 2002, 2100 UTC. Daytime is indicated by sun angle above horizon (light gray areas). (b) Ship track for same time period (solid lines with time markers, darker shading equals later time), outline of eastern United States (thin gray lines), and NO_x ground point sources (circles).

concluded that NO_3 reaction can be the most important loss pathway for DMS. *Yvon et al.* [1996a] observed these compounds together on a single night in Florida in 1989; they observed an anticorrelation, but concluded that it was due to transport rather than chemistry. *Allan et al.* [1999, 2000] reported simultaneous NO_3 and DMS measurements from three field campaigns (EASE'96 and EASE'97, Mace Head, Ireland, 1996 and 1997 and ACE2, Tenerife, 1997) and concluded that under certain conditions DMS was the main reaction partner for NO_3 and DMS oxidation by NO_3 was more important than by OH. Vrekoussis et al. [*Vrekoussis et al.*, 2004] have recently reported NO_3 and DMS measurements from the MINOS campaign in Crete in 2001 that show an anticorrelation. They also suggested NO_3 as the primary oxidant for DMS. A more recent study by Vrekoussis et al. [*Vrekoussis et al.*, 2006] described long-term measurements of NO_3 and DMS and concluded that, depending on season, NO_3 can be up to 8.5 times more effective in the winter time and 2.7 times more during the summer than OH as an oxidant for DMS.

[12] The ship-based study reported here had two advantages for studying the interaction between NO_3 and DMS:

[13] First, the point of sampling was removed by at least 1 hour of transport time from most direct NO_x emissions (other than marine vessels, whose discrete emission plumes can be easily filtered from the data set if necessary), such that there is better mixing of the many individual sources on land. Therefore the study avoids the effect of inhomogeneous mixing of air masses, as was observed, for example, in the study of *Yvon et al.* [1996a].

[14] Second, NO_3 and DMS were both sampled from the same air mass using in situ instruments. This is important because both NO_3 and DMS can exhibit considerable spatial variability as a result of their mutual reactivity, the spatial variability in the DMS emission, and the inhomogeneity in the emission of NO_x, which tends to occur in relatively discrete plumes. Long-path measurements of NO_3 may not capture the full range of this variability and may, in some cases, sample different air masses from those in which the in situ DMS measurement is made.

3. Results

[15] We reported NO_3 data for 17 out of 26 nights during the campaign. Mixing ratios ranged from below the detection limit of 0.6 pptv to peak values of about 140 pptv. DMS was present throughout the campaign with mixing ratios ranging from below the detection limit of 0.5 pptv to peak values of 790 pptv. On 13 of the 17 nights on which simultaneous NO_3 and DMS measurements were available, there was a clear anticorrelation between the mixing ratios of the two. On the remaining 4 nights, either NO_3 or DMS was at or near its instrumental detection limit for a large fraction of the night, making it difficult to assess the correlation.

[16] As an example of the anticorrelation, Figure 2 shows a 48-hour period from 2 August, 2100 UTC, to 4 August 2100 UTC. Figure 2a shows mixing ratios of DMS and NO_3 along with the sun angle, and Figure 2b shows the cruise track during this time period and large land-based NO_x sources such as power plants. During this time, *Ronald H. Brown* was off the coast of New Hampshire, 2–22 hours downwind of NO_x sources (estimated from back trajectories). During the course of both nights, DMS mixing ratios dropped sharply whenever there was an observed rise in NO_3, consistent with the oxidation of DMS in NO_3 containing plumes. At dawn, the DMS mixing ratios rose rapidly as the NO_3 oxidant was lost to other reaction pathways such as photolysis and reaction with NO from fresh emissions and from the onset of NO_2 photolysis. At midday (local noon is around 1700 UTC) on both the 3rd and 4th, there was another apparent minimum in the DMS mixing ratio that is consistent with loss due to OH oxidation (see next section for calculation of the OH concentrations). Finally, there was a late afternoon maximum in DMS on both days during the period when the calculated OH concentrations began to fall but the measured NO_3 concentrations had not yet risen above detection limit. Even though the diurnal behavior of NO_3 and DMS was quite similar for both 24-hour periods, the conditions under which

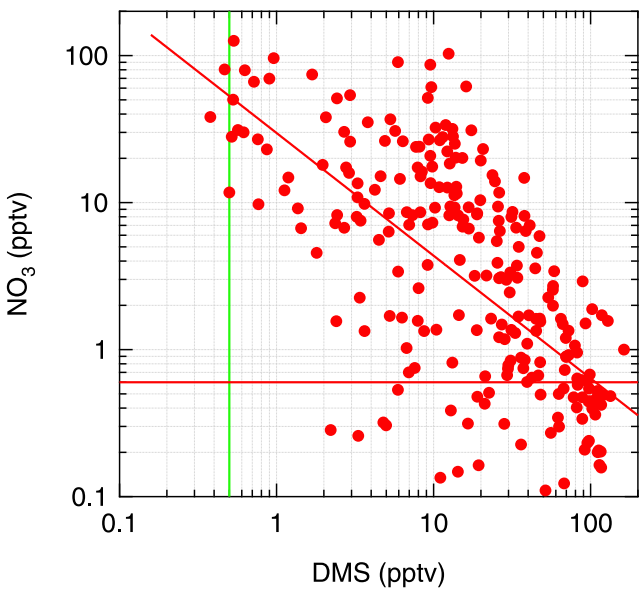

Figure 3. Correlation plot of NO_3 versus DMS measured from 29 July 2002 to 5 August 2002. Only nighttime data are included. Correlation is fit on double logarithmic scale. Slope = −0.83, R^2 = 0.4, horizontal line indicates NO_3 detection limit, and vertical line indicates DMS detection limit.

they were sampled were different. In the first 24 hours, *RHB* stayed close to the coast, at maximum distances about 20 km or 2 hours downwind from the shore (calculated from back trajectories). In the second 24 hours, *RHB* was further away from the shore (up to 165 km or 22 hours downwind, calculated from back trajectories); the similarity of the NO_3-DMS interaction here showed that oxidation of DMS by NO_3 was dominant, even well downwind of the NO_x source regions over land.

[17] If a constant source strength for DMS and a constant boundary layer height are assumed (see also below), the DMS loss at night is stronger than during the day for the two diurnal cycles shown in Figure 2, seen by the lower night than day DMS mixing ratios. Concentrations of isoprene, α- and β-pinene were low during both 24-hour periods, and therefore not likely to cause additional interferences.

[18] Figure 3 shows a correlation plot of NO_3 versus DMS for the first 7 days of the second part of the cruise (29 July to 5 August 2002), measured in locations around 43°N, 70°W. Although the anticorrelation is evident, there is considerable scatter in the data. The variability superimposed on the NO_3-DMS anticorrelation is the result of a number of factors, including varying source strengths for NO_3 (i.e., variation in the concentrations of NO_2 and O_3), varying emission rates for DMS, varying air mass age and therefore hydrocarbon, aerosol and NO_x content (all of which affect NO_3 sources and sinks), and variation in the amount of terrestrial biogenic hydrocarbons emitted into different air masses. The latter is important, because compounds such as isoprene and α- and β-pinene react rapidly with NO_3 and were occasionally present in large enough mixing ratios to consume a considerable fraction of NO_3. This allowed for larger steady state concentrations of DMS even in air masses with strong NO_3 sources. In addition, the DMS source strength likely varied with the measurement location because of different phytoplankton populations. Since the ship moved essential at random over a long period of time (4 weeks) and the biological sources for DMS production are often not radiation-dependent [*Nguyen et al.*, 1988], no diurnal variation in DMS source strength over this time period could be expected.

[19] The anticorrelation shown in Figures 2 and 3 can most easily be explained by reaction of NO_3 with DMS rather than by transport or mixing. As noted in the introduction, the measurements were always taken over the ocean at least 1 hour downwind of NO_x sources. Therefore a significant amount of DMS was always added from the ocean surface to the air mass measured at the ship.

[20] Further evidence for the importance of NO_3 as an oxidant for DMS, and an indication of the magnitude of DMS flux from the ocean surface, can be seen in the behavior of DMS under clean marine conditions in which the source for NO_3 is expected to be much smaller than in the NO_x-rich, polluted continental outflow. Figure 4 shows data from 1 August. The data were characterized by marine conditions with easterly winds. Back trajectories originated from the marine boundary layer to the east to southeast and had not crossed over land within the preceding 24 hours. Anthropogenic pollution tracers, e.g., toluene and benzene (not shown), were also 5–10 times lower than during any of the other nights. NO_3 was not detectable during most of the night, and DMS was nearly constant at approximately 100 pptv during nighttime and decreased to minimum values around 50 pptv during the day. The temporary decrease of DMS between 0300 and 0530 UTC was associated with a wind shift to the north and, therefore a different air mass. The relatively large and constant nocturnal DMS concentration compared to all of the other nights from the NEAQS 2002 data set is consistent with DMS loss from the marine boundary layer (MBL) primarily via entrainment into the free troposphere in the absence of a nocturnal oxidant. An atmospheric turnover lifetime of 11 hours and a boundary layer height of 100 m leads to an entrainment velocity of 2.5 mm/s (W. Angevine, personal communication, 2006). A DMS ocean-to-atmosphere flux of 1.6 μmol m^{-2} day^{-1}

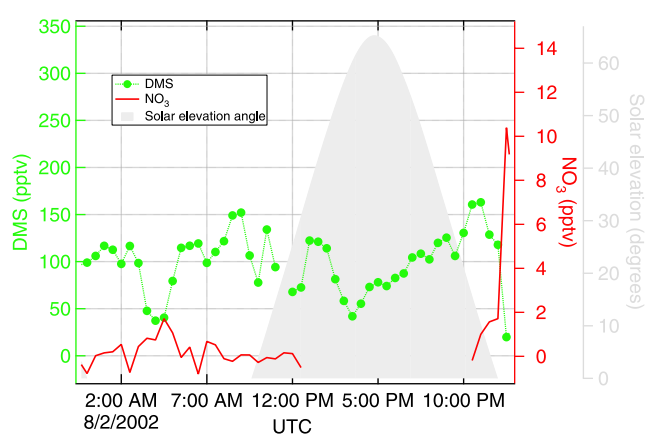

Figure 4. Time series under clean marine conditions: NO_3 (solid lines), 1 min data, and DMS (dotted lines and circles), 30 min data, sun elevation angle (light gray area).

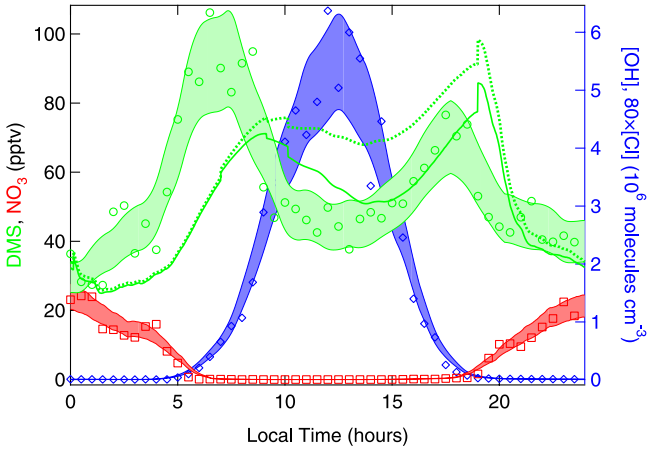

Figure 5. Diurnal averages of measured DMS (circles) and NO_3 (squares), mixing ratios, and calculated OH concentrations (diamonds). Bands are 2 hour running averages with uncertainties. Dotted line indicates numerical box model simulation of DMS, with OH and NO_3 as oxidants only. Solid line indicates Cl, scaled to OH with factor 1/80 as additional oxidant.

yields atmospheric DMS mixing ratios as encountered during this clean night. This flux value is in the low range of flux values measured in previous campaigns in the North Atlantic region [*Bates et al.*, 1987; *Tarrason et al.*, 1995; *Sharma et al.*, 1999]. Without the availability of DMS seawater measurements during NEAQS 2002, we decided to use this DMS flux value for the further analysis in this study.

3.1. Diurnal Averages

[21] The diurnal variation of the DMS concentration provides the clearest evidence for DMS oxidation by NO_3 at night and by OH, and possibly halogens, during the day. It also allows for a mean quantitative assessment of the relative contribution of each pathway to the total DMS loss.

[22] In order to quantitatively assess the diurnal correlation between NO_3 and DMS concentrations, certain prerequisites have to be met. First, the flux of DMS from the ocean to the atmosphere must be invariant with the time of day. Previous DMS flux measurements have not shown a diurnal variation. The constant DMS concentrations during the night of the unpolluted episode also support a constant DMS flux (see previous section) when assuming a constant transport velocity as a balancing sink. Furthermore, there was no diurnal trend in the wind speed, which is known to be a determining factor for DMS flux [*Liss and Merlivat*, 1986; *Wanninkhof*, 1992; *Nightingale et al.*, 2000]. The second condition is a diurnally invariant boundary layer height. *Angevine et al.* [2004] determined boundary layer heights of 100 ± 50 m from radiosonde data during NEAQS 2002 on board RHB that were well decoupled from the troposphere above.

[23] Figure 5 shows diurnal averages of measured NO_3 and DMS mixing ratios and calculated OH according to Ehhalt and Rohrer [*Ehhalt and Rohrer*, 2000] for time periods when NO_3 data were available. Also included in Figure 5 are results of two different model calculations. Two maxima in the DMS concentration at 0600 and 1800 local time (LT) are apparent in Figure 5, the one in the morning being larger (around 90 pptv) than the one in the afternoon (around 50 pptv). These two time periods are marked by the lowest radical concentrations, making them interesting for tropospheric chemistry. Nitrate radical concentrations are small because of rapid loss due to photolysis and reaction with NO, while OH concentrations are small because of low production rates for $O(^1D)$ from O_3 photolysis. The difference between the magnitudes of these processes lies in different diurnal behavior for $O(^1D)$ production and NO_3 loss. Excited oxygen, $O(^1D)$, is produced by O_3 photolysis between 290 and 330 nm, whereas NO is produced by NO_2 photolysis between 300 and 400 nm, and NO_3 is photolyzed between 420 and 630 nm. Photolysis rates for NO_2 loss and $O(^1D)$ production were calculated for NEAQS 2002 using measured actinic fluxes from a spectroradiometer together with literature spectra and quantum yields for O_3 and NO_2, for experimental details see *Stark et al.* [2007]. These photolysis rates show different diurnal time behavior, with NO_2 photolysis onsetting before $O(^1D)$ production in the morning and decreasing later than $O(^1D)$ in the afternoon. The source for this behavior is much stronger attenuation of radiation at shorter wavelengths in the early morning and late afternoon because of more efficient scattering and absorption of UV light by O_3 over the longer atmospheric path lengths at higher solar zenith angles. NO_3 photolysis rates can be expected to increase even earlier during the day and decrease later than NO_2 photolysis. During this time of low radical concentrations, DMS is emitted but not oxidized, which enables it to build up to the highest concentrations during the day.

[24] The average nocturnal (2100–0300 LT) concentration of DMS was 29 pptv with a variation of ±27 pptv (1σ), while during the day (0900–1500 LT) it was 39 ± 60 pptv. Because of the invariance of the depth of the marine boundary layer and the presumed invariance of the flux of DMS from the ocean surface, the smaller average nighttime concentrations of DMS indicate that it is more strongly oxidized by NO_3 during this period than by OH during the daytime. The model calculation in the next section supports this conclusion.

[25] Overlaid on Figure 5 is a numerical box model calculation of the DMS concentration (dotted green line) assuming a constant source for DMS, homogeneous and instantaneous mixing into a constant marine boundary layer, loss by reaction with NO_3 and OH, and vertical transportation out of the boundary layer with a constant velocity of 2.5 mm/s. The model was run for all individual days when NO_3 was measured and then diurnally averaged. The box model would not give reasonable results for a single 24 hour period if run using the diurnally averaged concentrations, because the two compounds, NO_3 and DMS, are almost mutually exclusive: each one frequently reaches a zero mixing ratio in the presence of an excess of the other. However, when diurnally averaged, they both show positive concentrations. Therefore the diurnal average cannot be seen as a typical diurnal concentration profile for these compounds and therefore cannot be used as input to a model. Input parameters included individual mixing ratios

Table 2. Processes Used in Chemical Box Model

Process	Value	Comment
NO_3 + DMS	1.0×10^{-12} cm^3 molecule^{-1} s^{-1}	no temperature dependence[a]
OH + DMS	6.5×10^{-12} cm^3 molecule^{-1} s^{-1}	no temperature dependence[a]
Halogen + DMS	4×10^{-10} cm^3 molecule^{-1} s^{-1}	only in expanded model
DMS flux	1.6 μmol m^{-2} day^{-1}	
Entrainment loss	2.5 mm/s	
Boundary layer height	100 m	

[a]The combination of a weak temperature dependence of these reaction rate coefficients with a narrow temperature range encountered on *RHB* during NEAQS 2002 suggested the use of temperature-independent rate coefficients for these reactions.

for NO_3 measured during NEAQS 2002 and calculated mixing ratios of OH using the parameterization by *Ehhalt and Rohrer* [2000]. The OH parameterization is based on measured photolysis rates for NO_2 and O_3 (to produce $O(^1D)$), and NO_2 mixing ratios. The calculated OH concentrations compare well (within 20%) to OH concentrations calculated using a different parameterization that included speciated VOC [*Warneke et al.*, 2004]. The parameterization of *Ehhalt and Rohrer* [2000] was preferable for this analysis because of the greater coverage of available input data from the NEAQS 2002 data set. A constant DMS flux of 1.6 μmol m^{-2} day^{-1} and a transport velocity of 2.5 mm/s combined with a constant well mixed boundary layer of 100 m height were used as fixed parameters. We used evaluated rate coefficients k_{NO3} and k_{OH} from *Sander et al.* [2003]. Table 2 summarizes the model conditions. The simulation (dotted green line) agrees well with the measurements only at night and reproduces the overall shape of the DMS concentration during the day, but overestimates the measured daytime DMS concentrations by about a factor of 1.5. Also, the relation of the morning versus the afternoon peaks is reversed. The overall discrepancy between modeled and measured DMS concentration during the day implies that daytime DMS losses are not fully accounted for. A higher OH concentration or an additional loss process with a diurnal profile similar to OH could explain this discrepancy. Several previous studies [*Chin et al.*, 1996; *Yvon et al.*, 1996b; *Sciare et al.*, 2000; *Gershenzon et al.*, 2001] also found the need to assume an oxidation rate of DMS increased from that by OH by a factor of two to three to explain their results.

[26] One candidate for the additional loss for DMS during daytime is reaction with halogen radicals, e.g., Cl or BrO. These halogen compounds can be produced by a photochemical mechanism involving release from sea salt and subsequent photolysis or reaction with OH to produce halogen radicals [see, e.g., *Oum et al.*, 1998; *Knipping et al.*, 2000]. For example, Cl atoms can be produced by reaction of HCl released from sea salt with OH. The diurnal profile of these halogen compounds can be expected to be similar to each other and proportional to the OH diurnal profile because of the photolytic production pathway and, in the case of HCl, the reaction with OH. For simplicity, we have chosen Cl atoms as a proxy for all halogen compounds. The rate coefficient for reaction of Cl with DMS is about 60 times faster than reaction with OH [*Sander et al.*, 2003]:

$$\mathrm{Cl + DMS \rightarrow Products} \qquad k \approx 4 \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

We included the above reaction with Cl mixing ratios, scaled to OH by a factor of 1/80, with a maximum noon mixing ratio of 8×10^4 molecules cm^{-3} to the box model (solid green trace). These Cl levels are in agreement with levels measured in the equatorial Pacific Ocean [*Wingenter et al.*, 2005] and the North Atlantic (P. D. Goldan, personal communication, 2006). The mixing ratio of BrO needed to yield the same oxidation rates would be approximately 4 pptv, using a rate coefficient for the reaction of BrO with DMS of 3.4×10^{-13} cm^3 molecule^{-1} s^{-1} [*Sander et al.*, 2006]. These BrO mixing ratios are in agreement with a study investigating DMS oxidation in the Atlantic by Sciare et al. [*Sciare et al.*, 2000].

[27] The agreement between modeled and measured DMS was significantly improved over the model in which OH was the only daytime oxidant for DMS.

[28] The only observation that is not represented correctly by the model with the oxidation by NO_3, OH and Cl are the relative magnitudes and timing of the morning and afternoon DMS peaks. The period in the early morning, where the discrepancy between measurements and model is the largest, is also the period where the DMS variation was the greatest, with a standard deviation of 100 pptv. Therefore it is possible that magnitude of the maximum during this time might not be statistically significant for quantitative comparison with the model.

3.2. DMS Loss

[29] To estimate the relative contribution of DMS oxidation by NO_3 compared to OH and halogens, absolute DMS loss rates can be calculated from measured NO_3 and DMS and calculated OH and halogen concentrations, using

$$loss\ rate = k_{DMS+Oxidant} \times [DMS] \times [Oxidant]. \qquad (1)$$

[30] We have calculated loss rates for all days when NO_3 was measured and OH could be calculated. We used the same rate coefficients for OH + DMS and for NO_3 + DMS as in the model (see Table 2). Integrating the loss rates yielded total losses. Under the assumption that DMS is oxidized only by NO_3 and OH, between 65 and 90% of the DMS was lost to NO_3 oxidation on individual days. When integrated over the entire campaign, 79% of the DMS was oxidized by NO_3. These relative DMS losses due to NO_3 oxidation are considerably larger than those predicted in two previous studies [*Allan et al.*, 2000; *Vrekoussis et al.*, 2004] and agree with spring-time values determined in the eastern Mediterranean sea by *Vrekoussis et al.* [2006]. Higher NO_x levels were encountered during NEAQS

2002. Nitrogen dioxide (NO_2) had a median concentration of 2 ppbv and a mean concentration of around 4 ppbv during NEAQS 2002, while *Allan et al.* [2000] encountered NO_2 levels around 1 ppbv under continentally influenced air and *Vrekoussis et al.* [2004, 2006] observed 0.3–0.6 ppbv in the Mediterranean.

[31] When including DMS loss by Cl oxidation with a rate coefficient of 4×10^{-10} cm^3 molecule^{-1} s^{-1} [*Sander et al.*, 2003] and a OH/Cl ratio of 80, the overall importance of NO_3 oxidation would be reduced to 68%. Oxidation by Cl would contribute to 14% to the total DMS oxidation, while oxidation by OH would be reduced to 18%.

4. Discussion

4.1. Spatial Extent of NO_3 Oxidation

[32] The importance of DMS oxidation by NO_3 may not be limited to areas in close proximity to large, coastal NO_x sources. A modeling study assuming NO_3 and OH as the only DMS oxidants predicted a global influence on the order of 30% by NO_3 of the total DMS oxidation [*Chin et al.*, 1996]. This is because of the balance of sinks for NO_3 and N_2O_5 in polluted versus remote regions. In a coastal environment, DMS is not the only sink compound for NO_3. Hydrocarbons of continental origin can contribute significantly to NO_3 loss [*Warneke et al.*, 2004; *Aldener et al.*, 2006]. Heterogeneous hydrolysis of N_2O_5 in high NO_x regions with large loading of continental aerosol is also an important NO_3 loss channel [*Brown et al.*, 2004]. However, the further NO_x pollution is transported away from the coast, the more important DMS should become as a sink for NO_3. This is because of the loss of terrestrially emitted VOC and the decrease in NO_2 during transport, which shifts the equilibrium between NO_3 and N_2O_5 in favor of NO_3, thereby reducing the importance of N_2O_5 hydrolysis. Under the assumption that DMS is the only nighttime sink for NO_3, the reaction mechanism for DMS and NO_3 nocturnal loss in remote marine air can be simplified to three reactions:

$$\text{(R1)} \qquad NO_3 \text{ production} : NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$\text{(R2)} \qquad NO_3 \text{ loss (also DMS loss)} : DMS + NO_3 \rightarrow CH_3SCH_2 + HNO_3$$

$$\text{(R3a)} \qquad \text{DMS loss by OH} : DMS + OH \rightarrow CH_3SCH_2 + H_2O$$

$$\text{(R3b)} \qquad \rightarrow CH_3S(OH)CH_3$$

[33] During daytime, photolysis is the main NO_3 loss process, which leads to negligible daytime NO_3 concentrations:

$$\text{(R4)} \qquad NO_3 + h\nu \rightarrow \text{Products}$$

We can further assume a simplified steady state for NO_3 during nighttime that is a balance between reactions (R1) and (R2). Defining daytime to last for 12 hours, the 24-hour average NO_3 concentration can be calculated by:

$$[NO_3]_{Avg} = \frac{1}{2} \cdot \frac{k_2 \cdot [NO_2] \cdot [O_3]}{k_3 \cdot [DMS]} \tag{2}$$

Inserting the 24-hour average NO_3 steady state concentration into the rate equation for DMS gives a simple expression based on 24-hour averaged mixing ratios of OH, DMS, NO_2, and O_3:

$$\frac{d[DMS]}{dt} = P - k_4 \cdot [OH] \cdot [DMS] - \frac{k_2}{2} \cdot [NO_2] \cdot [O_3], \tag{3}$$

with P: DMS production rate. Interestingly, the DMS loss due to NO_3 in this simplified picture depends only on the NO_3 source strength rather than on the steady state concentration itself. Assuming a temperature of 298 K and typical remote OH, DMS, and O_3 24-hour average mixing ratios of 8×10^5 molecules cm^{-3} [*Prinn et al.*, 1992; *Allan et al.*, 1999], 150 pptv [*Andreae et al.*, 1985], and 16 ppbv [*Monks et al.*, 1998; *Dickerson et al.*, 1999], respectively, only 120 pptv of NO_2 would be required to give equal removal rates for DMS by OH and NO_3. As noted in the introduction, the reaction of O_3 with DMS is negligibly slow [*Martinez and Herron*, 1978]. If this reaction were more rapid, the range of the NO_2 concentration over which NO_3 oxidation of DMS is important would be different.

[34] To get an estimate of the spatial extent of NO_3 as a DMS oxidant, the average lifetime of NO_2, or the average extent of anthropogenic NO_2 into the marine boundary layer must be estimated. A satellite study yielded an average 1/e length of 670 km for anthropogenic NO_2 over the North Atlantic and of larger values over other continental east coasts in the Northern Hemisphere [*Leue et al.*, 2001; *Kunhikrishnan et al.*, 2004]. Applying this distance scale, a plume containing 10 ppbv of NO_2 transported from a coastal source would be reduced to 120 pptv after traveling some 3000 km.

[35] Therefore the impact of the nocturnal, NO_x-driven oxidation of DMS on the production of non-sea-salt sulfate aerosol may have a widespread impact globally, depending on the extent of transport of NO_x containing plumes. Not only would this effect be important in areas well out into the North Atlantic because of North American NO_x emissions, but it could be significant in large areas of the Pacific and Indian oceans that are downwind of the large NO_x emission regions in Asia. Furthermore, NO_x emissions from global shipping in remote regions may also affect DMS oxidation and therefore nss production.

4.2. Non-Sea-Salt Sulfate Aerosol Production

[36] As shown in the previous section, DMS oxidation by NO_3 may be important globally. This section assesses the enhancement of non-sea-salt sulfate aerosol (nss) production from this oxidation pathway from an evaluation of existing laboratory studies on the various DMS oxidation mechanisms combined with our measurements of the relative DMS oxidation rates. Certain aspects of this oxidation

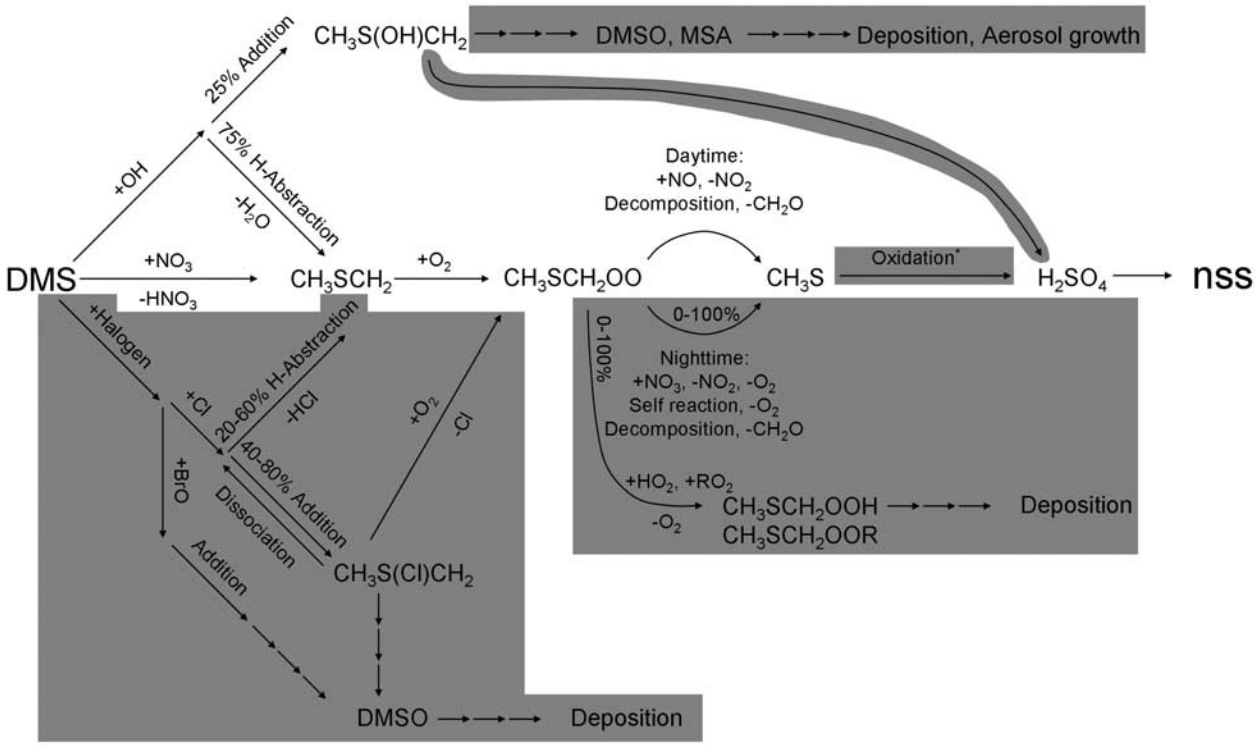

Figure 6. Proposed production scheme of nss from DMS oxidation by OH, NO_3, and halogens. Shaded areas indicate uncertainties in the literature. Asterisk indicates that the oxidation mechanism of CH_3S is complex. For a more complete description, see, e.g., *Lucas and Prinn* [2002]. For simplicity, we assume unit production of nss from CH_3S oxidation. See text for more details.

mechanism are still uncertain. We estimate the range of possibilities and include them in the results on total nss enhancement or reduction due to DMS oxidation by NO_3.

[37] End products from DMS oxidation by NO_3, OH, and Cl include sulfuric acid, H_2SO_4, which is a known precursor for nss, dimethylsulfoxide (DMSO), which is readily deposited on the ocean surface, and methane sulfonic acid (MSA), which contributes to aerosol growth. The different yields of H_2SO_4 production from the different oxidants will determine the yield of nss produced per unit DMS oxidized. We discuss our results by first excluding the influence of halogens on DMS oxidation. Then we include DMS oxidation by halogens and compare the differences. Figure 6 gives an overview of the DMS oxidation mechanism including assumptions made in this section.

[38] The amount of H_2SO_4 produced from DMS oxidation by NO_3 is uncertain. It is established that the first reaction step is H-atom abstraction from DMS by NO_3 with a unit yield to form CH_3SCH_2 [*Jensen et al.*, 1992; *Butkovskaya and Lebras*, 1994]. A key step in the further oxidation of DMS is subsequent processing of the $CH_3SCH_2O_2$ peroxy radical, formed from reaction of CH_3SCH_2 with O_2. During daytime, this radical reacts with NO to form CH_3SCH_2O, which then decomposes to form CH_3S and CH_2O. Since NO is usually not present during nighttime, other processes will dominate. Several studies suggested that the peroxy radical can react with nitrate radical to form CH_3S and CH_2O [*Barnes et al.*, 1991; *Le Bras et al.*, 1993; *Allan et al.*, 2000], the same products formed during daytime:

$$\text{(R5)} \quad CH_3SCH_2O_2 + NO_3 \rightarrow CH_3S + CH_2O + NO_2 + O_2$$

Other possible reactions are self-reaction of two peroxy radicals, which would lead to two CH_3S radicals (and formaldehyde) or reaction with HO_2 or RO_2 to form the relatively stable hydroperoxide CH_3SCH_3OOH or other organoperoxides CH_3SCH_3OOR, which may be predominantly deposited to the ocean surface during nighttime and will therefore not lead to nss production [*Berresheim et al.*, 1995]. We will consider the impact of three possible cases of this oxidation mechanism (see Table 3) depending on the amount of HO_2 present relative to NO_3. Under low HO_2 conditions, the reactions with NO_3 and self reaction would be dominant for the peroxy radical, therefore leading to an nss production of 100%. In the case where HO_2 and NO_3 show comparable mixing ratios, about 50% nss production can be expected. Finally, when HO_2 is present in much higher concentrations than NO_3, nss production can be completely suppressed.

[39] During daytime, the OH radical is the dominant reaction partner of DMS. 75% of the OH radicals will abstract an H-atom from DMS to form CH_3SCH_2, while 25% will add to DMS forming the DMS(OH) adduct [*Hynes et al.*, 1986]. For simplicity, we will assume that the abstraction channel will lead exclusively to nss, and the

Table 3. Predicted Relative Non-Sea-Salt Sulfate Aerosol Production Yields During NEAQS 2002 Due to the Oxidation of DMS by NO_3 Radicals at Night Compared to the Case in Which This Oxidation Is Absent[a]

	Relative nss Yield to DMS + OH (and Cl) Only, %		
Oxidants Used	100% nss From DMS+NO_3	0% nss From DMS+NO_3	50% nss From DMS+NO_3
OH, NO_3 only	126	21	74
OH, NO_3, Cl			
20% nss from Cl	165	32	99
50% nss from Cl	138	32	85
100% nss from Cl	111	32	72

[a]Different cases of nss production from DMS oxidation by halogens are included. The first column includes the assumption that 100% nss are produced from DMS + NO_3. The second columns shows results from the case where DMS + NO_3 does not lead to any nss formation at all. The third column shows results from the intermediate case where DMS+NO_3 leads to 50% nss production. See text for further explanation on the choice of these cases.

addition channel will not produce any nss. Although this assumption may not be completely accurate because the abstraction channel may have an nss yield below 100% and the addition channel may lead to some nss production, inclusion of broad ranges for the nss production from DMS oxidation by NO_3 (see above) describes all possible outcomes for DMS oxidation.

[40] The picture is further complicated by the inclusion of DMS oxidation by halogens, which has been investigated in a few laboratory studies and evaluated in a recent review [*Barnes et al.*, 2006]. For DMS oxidation by Cl, the initial step of this reaction proceeds via two channels, H-atom abstraction and Cl addition. The H-atom abstraction leads to CH_3SCH_2 and HCl formation, and we assume again a 100% H_2SO_4 yield from this channel. The addition channel initially leads to a Cl-DMS adduct. The branching ratio for the addition channel at ambient temperature and pressure was determined to be between 40 and 80% [*Stickel et al.*, 1992; *Diaz-de-Mera et al.*, 2002; *Barnes et al.*, 2006]. The further fate of the Cl-DMS adduct is uncertain and may lead either to a null cycle in which the adduct redissociates to DMS and Cl or to the formation of DMSO [*Enami et al.*, 2004; *Arsene et al.*, 2005]. Oxidation of DMS by BrO is believed to exclusively form DMSO, which would not lead to nss production [*Bedjanian et al.*, 1996; *Ingham et al.*, 1999; *Sciare et al.*, 2000; *Ballesteros et al.*, 2002]. We will discuss our results using a range of 100% to 20% nss production from DMS + halogen.We calculated relative nss yields using

$$relative\ nss\ yield = \frac{nss\ yield(NO_3, OH(Cl) as\ oxidants)}{nss\ yield\ (OH(Cl) as\ oxidant)}. \quad (4)$$

[41] Table 3 shows the results of several cases. Non-sea-salt sulfate aerosol production with NO_3 included as a DMS oxidant can be between 111 and 165% of the nss production from oxidation of DMS by OH alone, depending on the assumed mechanism. As noted earlier, these enhancement ratios can only be seen as upper limits, or even lead to overall aerosol reduction, since the assumptions made for nss production may not be fully correct. For instance, when no nss production from DMS oxidation by NO_3 is assumed, nss production can be reduced to 21% of the case without NO_3 oxidation. More laboratory work is needed to quantitatively assess the importance of DMS oxidation by NO_3 for nss production. However, under NO_x-rich conditions, oxidation of DMS by NO_3 will typically be the dominant loss process. This result, combined with the result from the previous section, shows that DMS oxidation by NO_3 may be important in large areas of the world's oceans and may influence the production rate of nss, and therefore radiative forcing of nss from DMS emission and oxidation.

5. Summary

[42] Simultaneous, in situ measurements of NO_3 and DMS during the summer of 2002 off the coast of New England from the NOAA research vessel *Ronald H. Brown* showed a strong anticorrelation between these compounds. This anticorrelation was almost certainly due to the NO_3-DMS reaction. Comparison with calculated OH and estimated halogen levels showed that DMS oxidation by NO_3 was much larger than by OH and halogen. This result may have an impact on non-sea-salt sulfate aerosol production that should be further investigated through laboratory studies and in global atmospheric sulfur models. Our analysis shows that nss aerosol production may be enhanced by up to 65% because of NO_3. Also, anthropogenic NO_2 sources may influence marine chemistry up to 5 days or 3000 km downwind from NO_x source regions.

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