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


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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 $\approx$30 pptv at night compared to the daytime minimum of $\approx$40 pptv, indicating a stronger oxidation by NO$_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$_3^-$/NO$_x$ 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.


1. Introduction

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$_3$SCH$_3$) 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$_2$SO$_4$). 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].

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$_2$O$_5$). 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$_2$O$_5$ via mostly heterogeneous reactions. Aside from its reaction with DMS, NO$_3^-$ reacts rapidly with a variety of other atmospheric trace gases.
of biogenic and anthropogenic origin, e.g., NO from recent NO\textsubscript{x} emissions (i.e., from nearby NO\textsubscript{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\textsubscript{3} is highly variable and is driven by the availability of anthropogenic NO\textsubscript{3} in marine environments.

[4] There have been numerous laboratory and theoretical investigations of the mechanism for gas phase DMS oxidation, establishing OH and NO\textsubscript{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 Pinn, 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\textsubscript{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\textsubscript{2}SO\textsubscript{4} and, subsequently, aerosol yields from reaction of DMS with OH and NO\textsubscript{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\textsubscript{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\textsubscript{3} and N\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{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\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} were measured at 0.2 Hz and DMS was measured at 5 minute averages every 30 min. The detection limits for NO\textsubscript{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\textsubscript{3} loss and O\textsubscript{18}D production [Stark et al., 2007]; speciated VOC measurements by gas chromatography – mass spectrometry (GC-MS) [Goldan et al., 2004], and chemiluminescence determination of O\textsubscript{3} and NO\textsubscript{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 mmol/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, 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, 2000; 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\textsubscript{3} [Barnes et al., 1991; Allan et al., 2000; Vrekoussis et al., 2004, 2006].

[11] Simultaneous measurements of DMS and NO\textsubscript{3} have been reported previously in campaigns that have taken place in coastal areas, where land-based measurements of NO\textsubscript{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\textsubscript{3} measurements, recorded during OCEANO-NO\textsubscript{3} in Brittany, France in 1988 and 1989 and

Table 1. Ancillary Measurements Used for Data Interpretation

<table>
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<tr>
<th>Data Type</th>
<th>Technique</th>
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<tr>
<td>Photolysis rates</td>
<td>spectro radiometer</td>
<td>Stark et al. [2007]</td>
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<td>VOC</td>
<td>GC-MS</td>
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<td>NO\textsubscript{3}</td>
<td>chemiluminescence</td>
<td>Thornton et al. [2003]</td>
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concluded that NO₃ 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 NOₓ 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 NOₓ and DMS oxidation by NOₓ was more important than by OH. Vrekoussis et al. [Vrekoussis et al., 2004] have recently reported NOₓ and DMS measurements from the MINOS campaign in Crete in 2001 that show an anticorrelation. They also suggested NOₓ as the primary oxidant for DMS. A more recent study by Vrekoussis et al. [Vrekoussis et al., 2006] described long-term measurements of NOₓ and DMS and concluded that, depending on season, NOₓ 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 NOₓ and DMS: [13] First, the point of sampling was removed by at least 1 hour of transport time from most direct NOₓ 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, NOₓ and DMS were both sampled from the same air mass using in situ instruments. This is important because both NOₓ 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 NOₓ, which tends to occur in relatively discrete plumes. Long-path measurements of NOₓ 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 NOₓ 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 NOₓ and DMS measurements were available, there was a clear anticorrelation between the mixing ratios of the two. On the remaining 4 nights, either NOₓ 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 NOₓ along with the sun angle, and Figure 2b shows the cruise track during this time period and large land-based NOₓ sources such as power plants. During this time, Ronald H. Brown was off the coast of New Hampshire, 2–22 hours downwind of NOₓ sources (estimated from back trajectories). During the course of both nights, DMS mixing ratios dropped sharply whenever there was an observed rise in NOₓ, consistent with the oxidation of DMS in NOₓ containing plumes. At dawn, the DMS mixing ratios rose rapidly as the NOₓ oxidant was lost to other reaction pathways such as photolysis and reaction with NO from fresh emissions and from the onset of NO₂ 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 NOₓ concentrations had not yet risen above detection limit. Even though the diurnal behavior of NOₓ and DMS was quite similar for both 24-hour periods, the conditions under which
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$_3$ 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, $\alpha$- and $\beta$-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 $\alpha$- and $\beta$-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$_3$ 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$_3$-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 $\mu$mol m$^{-2}$ day$^{-1}$
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

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.

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.

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. Exited 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$_3$ 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$_3$ 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.

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.

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 transport 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.
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 $\mu$mol 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].

\[
\text{Cl + DMS} \rightarrow \text{Products} \quad k \approx 4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

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 $8 \times 10^4$ 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 $3.4 \times 10^{-13}$ 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

\[
\text{loss rate} = k_{DMS-Oxidant} \times [\text{DMS}] \times [\text{Oxidant}].
\]

[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$_3$ levels were encountered during NEAQS

<table>
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<tr>
<td>NO$_3$ + DMS</td>
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<td>no temperature dependence$^a$</td>
</tr>
<tr>
<td>OH + DMS</td>
<td>$6.5 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
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</tr>
<tr>
<td>Halogen + DMS</td>
<td>$4 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</td>
<td>only in expanded model</td>
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<td>DMS flux</td>
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<tr>
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<td>Boundary layer height</td>
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$^a$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.

Table 2. Processes Used in Chemical Box Model
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 $4 \times 10^{-10}$ 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$_2$O$_5$ in polluted versus remote regions. In a coastal environment, DMS is not the only sink compound for NO$_3$. Hydrocarbons of marine origin can contribute significantly to NO$_3$ loss [Warneke et al., 2004; Aldener et al., 2006]. Heterogeneous hydrolysis of N$_2$O$_5$ 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$_2$O$_5$ in favor of NO$_3$, thereby reducing the importance of N$_2$O$_5$ 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:

(R1) NO$_3$ production: NO$_2$ + O$_3$ → NO$_3$ + O$_2$

NO$_3$ loss (also DMS loss): DMS + NO$_3$ → CH$_3$SCH$_2$ + HNO$_3$

(R2)

(R3a) DMS loss by OH: DMS + OH → CH$_3$SCH$_2$ + H$_2$O

(R3b) → CH$_3$S(OH)CH$_3$

[33] During daytime, photolysis is the main NO$_3$ loss process, which leads to negligible daytime NO$_3$ concentrations:

(R4) NO$_3$ + h$\nu$ → 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:

$$[NO_3]_{24} = \frac{1}{2} \frac{k_2 \cdot [NO_2] \cdot [O_3]}{k_3 \cdot [DMS]}$$

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$_3$:

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

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 $8 \times 10^5$ 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$_3$ 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...
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$_2$SO$_4$, 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$_2$SO$_4$ 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$_2$SO$_4$ 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$_3$SCH$_2$ [Jensen et al., 1992; Butkovskaya and Lebras, 1994]. A key step in the further oxidation of DMS is subsequent processing of the CH$_3$SCH$_2$O peroxy radical, formed from reaction of CH$_3$SCH$_2$ with O$_2$. During daytime, this radical reacts with NO to form CH$_3$SCH$_2$O, which then decomposes to form CH$_3$S and CH$_2$O. 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$_3$S and CH$_2$O [Barnes et al., 1991; Le Bras et al., 1993; Allan et al., 2000], the same products formed during daytime:

\[(R5) \quad \text{CH}_3\text{SCH}_2\text{O} + \text{NO}_3 \rightarrow \text{CH}_3\text{S} + \text{CH}_2\text{O} + \text{NO}_2 + \text{O}_2\]

Other possible reactions are self-reaction of two peroxy radicals, which would lead to two CH$_3$S radicals (and formaldehyde) or reaction with HO$_2$ or RO$_2$ to form the relatively stable hydroperoxide CH$_3$SCH$_2$OOH or other organoperoxides CH$_3$SCH$_2$OOR, 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$_3$SCH$_2$, 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
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 NO₃ (see above) describes all possible outcomes for DMS oxidation.

The picture is further complicated by the inclusion of DMS oxidation by halogens, which has been investigated in several 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 CH₂SCH₂ and HCl formation, and we assume again a 100% H₂SO₄ 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; Arsené et al., 2005]. Oxidation of DMS by BrO is believed to exclusively form DMSO, which would not lead to nss production [Bédjian 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

\[
\text{relative nss yield} = \frac{\text{nss yield}(\text{NO}_x, \text{OH(Cl)})}{\text{nss yield}(\text{OH(Cl)})}. \tag{4}
\]

Table 3 shows the results for several cases. Non-sea-salt sulfate aerosol production with NO₃ 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 NO₃ is assumed, nss production can be reduced to 21% of the case without NO₃ oxidation. More laboratory work is needed to quantitatively assess the importance of DMS oxidation by NO₃ for nss production. However, under NO₄-rich conditions, oxidation of DMS by NO₃ will typically be the dominant loss process. This result, combined with the result from the previous section, shows that DMS oxidation by NO₃ 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

Simultaneous, in situ measurements of NO₃ 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 NOₓ-DMS reaction. Comparison with calculated OH and estimated halogen levels showed that DMS oxidation by NO₃ 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 NO₃. Also, anthropogenic NOₓ sources may influence marine chemistry up to 5 days or 3000 km downwind from NOₓ source regions.

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