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Interaction between nitrogen and sulfur cycles in the polluted marine boundary layer

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Abstract. Simultaneous measurements are reported of the nitrate radical (NO_3), nitrogen dioxide (NO_2), ozone (O_3), and dimethylsulfide (DMS) in the nighttime marine boundary layer over Biscayne Bay in South Florida. These field observations are analyzed and used to initialize a boundary layer box model which examines the relative importance of the various sinks for NO_x in the marine boundary layer. The results show that the observed lifetime of NO_3 (≤ 6 min.) is probably controlled both by the loss of nitrogen pentoxide (N_2O_5) to reaction with water vapor and aerosols and by the reaction between NO_3 and DMS. The model is then extended to investigate the loss of nitrogen oxides from an air parcel that remains in the boundary layer with a constant sea-to-air DMS flux for several days. The principal conclusions are (1) that DMS is a much more important sink for NO_3 at lower NO_2 levels and (2) that the reaction between NO_3 and DMS is an important sink for DMS in the marine boundary layer and could exceed that of the daytime removal by OH.

Introduction

Dimethylsulfide (DMS) is the most important source of biogenic sulfur in the atmosphere [Saltzman and Cooper, 1989; Andreae, 1990; Bates *et al.*, 1992]. It is produced in the upper ocean by phytoplankton and evades into the marine boundary layer (MBL), where its mixing ratio ranges between about 40 and 300 parts per trillion by volume (pptv) [Saltzman and Cooper, 1989; Andreae, 1990; Bates *et al.*, 1992]. It is oxidized by the hydroxyl radical (OH) during the daytime and by the nitrate radical (NO_3) at night. In both cases the eventual reaction products containing sulfur are believed to be non-sea-salt sulfate and methanesulfonic acid [Plane, 1989; Jensen *et al.*, 1991], which are probably sources of cloud condensation nuclei [Charlson *et al.*, 1987]. The reaction between NO_3 and DMS has been shown also to produce HNO_3 , which is rapidly lost from the gas phase by dry deposition or adsorption onto aerosols or droplets [Jensen *et al.*, 1991]. Thus this reaction effectively removes gas-phase nitrogen oxides (N_xO_y). In fact, the reaction is rapid enough for the chemistry of the sulfur and nitrogen oxide cycles to be very closely coupled [Winer *et al.*, 1984; Plane and Nien, 1991; Barnes *et al.*, 1991].

The chemistry of NO_3 has been reviewed recently [Wayne *et al.*, 1991]. NO_3 is produced by the oxidation of NO_2 by O_3 , and it then exists in an equilibrium with NO_2 and N_2O_5 . During the daytime, however, NO_3 is rapidly photolyzed at wavelengths below 600 nm [Orlando *et al.*, 1993], and so its

concentration only becomes significant (i.e., greater than 0.1 pptv) during the night [Wayne *et al.*, 1991]. It has been shown that N_2O_5 adsorbs readily onto wet aerosol particles to form aqueous HNO_3 , with an accommodation coefficient of up to 0.05 [DeMore *et al.*, 1990; Dentener and Crutzen, 1993]. N_2O_5 may also react very slowly with gas-phase H_2O to form HNO_3 . Since N_2O_5 is coupled to NO_3 through the equilibrium with NO_2 , these loss pathways for N_2O_5 cause the indirect loss of NO_3 . It should be noted that although NO_3 reacts very rapidly with a variety of unsaturated hydrocarbons [Atkinson, 1991; Wayne *et al.*, 1991], the concentrations of these species in the MBL are unlikely to be large enough for their reaction with NO_3 to compete with the other loss processes for NO_3 discussed above [Russell *et al.*, 1986]. Last, the unimolecular thermal decomposition of NO_3 to NO and O_2 has been suggested as a significant loss pathway in the atmosphere [Davidson *et al.*, 1990]. However, a recent photodissociation study of NO_3 [Davis *et al.*, 1993] has shown that the potential energy barrier for this process is $(198 \pm 3) \text{ kJ mol}^{-1}$, so the rate of this process will be negligible at tropospheric temperatures. This is in accord with the hour-long lifetime of the radical that has been observed in the boundary layer at low relative humidities [Platt *et al.*, 1984].

Here we report the results of a field and modeling study of the relative importance of these loss pathways of N_xO_y in the nighttime MBL. The results are then generalized to investigate the relative importance of these nighttime losses of N_xO_y compared to the daytime loss, which occurs principally through the recombination of OH and NO_2 to form HNO_3 [Finlayson-Pitts and Pitts, 1986].

A related problem is then to examine the diel variation in the rate of oxidation of DMS. The major sink for DMS in the MBL is thought to be through its reaction with OH. Given a constant sea-to-air flux of DMS and this sink, the expected diel cycle for atmospheric DMS should show a predawn maximum due to nighttime accumulation and a late afternoon minimum due to daytime oxidation by OH. This cycle has been seen in data collected in the remote MBL [Yvon *et al.*, 1996] where NO_x is low. The reaction between DMS and

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NO₃ may be a significant nighttime sink for DMS in relatively polluted environments [Andreae *et al.*, 1985; Plane and Nien, 1991]. This nighttime sink could affect the amplitude and, if it is large enough, the sense of the DMS diel cycle.

Field Observations

The field study was carried out at the Rosenstiel School of Marine and Atmospheric Science (RSMAS) during 1989. NO₃, NO₂, and O₃ were measured by a differential optical absorption spectrometer (DOAS) [Plane and Nien, 1992], placed in a rooftop laboratory at RSMAS. The light path was folded once by a retro-reflector which was placed on the roof of a building 2.4 km away on Key Biscayne, thus providing a total path length of 4.8 km. Only 200 m of this path was over land, the remainder passing at a height of 20 m over Biscayne Bay (Figure 1). NO₃, NO₂, and O₃ were measured at about 30-min intervals throughout each night. The technique for measuring NO₃ by taking a daylight reference spectrum against which the nighttime spectra are then compared was first described by Platt and Perner [1983]. The DOAS used in the present study has been shown to have detection limits of 1 pptv for NO₃ and 600 pptv for NO₂ over a 5-km path length [Plane and Nien, 1992]. The uncertainty in the NO₃ concentration is about ±20% when [NO₃] < 20 pptv; the uncertainty in NO₂ is ±15% when [NO₂] < 25 parts per billion by volume (ppbv).

Dimethylsulfide was measured by using a technique described, in detail, by Cooper and Saltzman [1993]. The inlet was located on the RSMAS roof. The sample airstream is drawn through a cold potassium iodide bubbler to remove oxidants. The oxidant free sample air is drawn through a tube containing Tenax at -20°C, and the DMS is trapped on the Tenax. This preconcentration step takes approximately 10 min depending upon the concentrations being measured. The

Tenax is then heated to 80°C to release the DMS, which is then injected onto a Chromosil 330 packed column. The DMS is separated isothermally at 50°C. DMS elutes at approximately 6 min and is detected by using a flame photometric detector. This method has a detection limit of 3 pptv.

Wind speed and direction, and ancillary measurements of O₃ and NO_x, were made by Dade County Environmental Resources Management (DERM), which has an air quality monitoring station in the rooftop laboratory at RSMAS.

Results and Discussion

Field Measurements

Most data were recorded during the months May-July and October-November 1989. It became apparent that the nighttime NO₃ levels were generally less than 2 pptv in clean marine air from the prevailing southeasterly wind. However, this situation altered when urban emissions were mixed into the marine air. Figure 2a illustrates the wind pattern during the night of July 18, 1989. For the first 6 hours after 1800 EST the wind was from the city or else stagnant, and then it swung round to the SSE and blew steadily from the ocean for the rest of the night. Figure 2b shows the NO₃ and DMS concentrations during the night. Figure 2c is a comparison of NO₂, O₃, and NO₃. NO₃ appeared at about 2030 EST, which was just after local sunset. It then tracked the changing concentrations of NO₂ and O₃, peaking when both NO₂ and O₃ were high at midnight. This finding is expected, since the rate of production of NO₃ is proportional to the product of NO₂ and O₃. NO₃ then dropped away rapidly as the wind switched to the SSE, and finally it disappeared at dawn. Inspection of Figure 2b indicates a striking anticorrelation between NO₃ and DMS. Although one might be tempted to conclude that this was due to the rapid reaction between NO₃ and DMS, it should also be noted that high DMS levels are a reliable indicator of air of marine origin, which may have lower NO_x levels than continental air. Either of these last two factors will also tend to decrease the NO₃ concentration.

Figure 3 shows a study over the nights of November 20 and 21, 1989, during which a weather front passed through South Florida. On the night of November 20 (Figure 3a), frontal precipitation occurred after 2000 EST, and both NO₂ and NO₃ were substantially washed out in the following 2 hours. During the following night (Figure 3b) the wind blew steadily from the north to NNE, conditions typical immediately after the passage of a cold front. The DMS concentration was highly variable, indicating significant mixing of urban and marine air, which is to be expected, since the wind was blowing parallel to the coast. Under these conditions the NO₂ remained high most of the night. We began recording nighttime spectra about 30 min after sunset, when the NO₃ was already up to 14 pptv. Thereafter it tracked the variations in NO₂ and O₃ and disappeared at dawn. The NO₃ concentrations recorded on this night were the highest during 45 nights of measurements between May and December 1989.

The NO₃ lifetime can be estimated from the steady state relationship shown below:

$$\tau(\text{NO}_3) = \frac{[\text{NO}_3]}{k[\text{NO}_3][\text{O}_3]}$$

Figure 1. A map of the location of the field study of NO₃ and DMS in the marine boundary layer off Miami.

Figure 2. Boundary layer chemistry over Biscayne Bay during the night of July 18, 1989: (a) wind speed and direction, (b) concentrations of NO_3 and DMS, and (c) concentrations of NO_3 , O_3 , and NO_2 .

where k is the rate constant for the reaction between NO_2 and O_3 [Platt *et al.*, 1984]. In urban air (for example, the first part of the night in Figure 2 and in Figure 3b), $\tau(\text{NO}_3)$ was about 1 min or less. NO_3 reacts rapidly with a number of organic species such as aldehydes, unsaturated hydrocarbons, and aromatics [Atkinson, 1991; Wayne *et al.*, 1991]. The most likely reactive nonmethane hydrocarbon of anthropogenic origin to affect $\tau(\text{NO}_3)$ in this study was *i*-butene. The rate constant for the reaction between *i*-butene and NO_3 is $3.9 \times$

$10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K [Benter *et al.*, 1992], so that an *i*-butene concentration of 2 ppbv would produce a $\tau(\text{NO}_3)$ value less than 1 min. This level of *i*-butene is typical of air that has experienced fresh vehicle emissions [Finlayson-Pitts and Pitts, 1986]. Furthermore, NO reacts with NO_3 with a rate constant of $2.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [Hammer *et al.*, 1986], so that an NO concentration of only 25 pptv would reduce $\tau(\text{NO}_3)$ to 1 min. However, during the night, NO is itself very rapidly oxidized to NO_2 by O_3 . Under the conditions shown in Figure 2 an initial concentration of 1 ppbv of NO would be reduced to below 1 pptv in about 20 min. Thus only very fresh NO emissions would have affected the NO_3 lifetime. As shown in Figure 1, the Rickenbacker Causeway ran within about 200 m of the optical path of the DOAS. It is therefore quite probable that $\tau(\text{NO}_3)$ was reduced to 1 min by fresh vehicle emissions of NO and perhaps *i*-butene during the evening.

By contrast, during the second part of the night the combination of very little traffic on the causeway and the relatively strong onshore wind would have made the contributions of these two species to the removal of NO_3 insignificant. Indeed, the longest $\tau(\text{NO}_3)$, of about 6 min, is observed during this period. However, if the reaction between NO_3 and DMS were the only mechanism for NO_3 removal during this period, then the average DMS concentration of about 50 pptv would have resulted in a lifetime of over 12 min. Under these conditions it seems likely that the

Figure 3. Boundary layer chemistry over Biscayne Bay: (a) concentrations of NO_3 , NO_2 , and DMS during the night of November 20, 1989, and (b) concentrations of NO_3 , NO_2 , O_3 , and DMS during the night of November 21, 1989.

heterogeneous removal of N_2O_5 provided an additional loss process. If the accommodation coefficient of N_2O_5 on aqueous aerosol surfaces is taken to be 0.05 [DeMore *et al.*, 1990], then an aerosol surface area concentration of $500 \mu\text{m}^2 \text{cm}^{-3}$ (expressed as the available surface area per unit volume of air) reduces the overall $\tau(\text{NO}_3)$ to 6 min [Plane and Nien, 1991]. In fact, this aerosol concentration is the average of typical urban and remote marine aerosol loadings [Whitby *et al.*, 1972].

Modeling

We use a zero-dimensional time-dependent photochemical box model of an air mass in the MBL [Yvon and Saltzman, 1993] to examine the coupling of the nitrogen and sulfur species NO_3 and DMS. This is an extension of the nighttime-only model of Plane and Nien [1991], based on the original scheme of Russell *et al.* [1986].

The chemistry of this model is similar to that described by Thompson and Lenschow [1984] with the addition of some reactions involving $\text{O}(^3\text{P})$ and some reactions affecting the concentrations of peroxyacetyl nitrate (PAN). A complete list of the daytime and nighttime NO_x reactions used in the model is shown in Table 1. This set of reactions emphasizes the importance of NO_3 as a nighttime oxidant of many reduced species, as well as its role in coupling NO_x to HNO_3 and PAN. The model employs fourth-order Runge-Kutta integration [Press *et al.*, 1986] to solve the coupled ordinary differential equations describing the time-resolved variation of the minor species.

Table 1. Nitrogen Chemistry Used in the Model

Reaction	Rate Coefficient
$\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}$	$k = 3.7 \times 10^{-12} \text{Exp}(240/T)$
$\text{OH} + \text{NO}_2 (+\text{M}) \rightarrow \text{HNO}_3 (+\text{M})$	$k_0 = 2.6 \times 10^{-30} (T/300)^{-3.2}$ $k_\infty = 2.4 \times 10^{-11} (T/300)^{-1.3}$
$\text{NO} + \text{OH} (+\text{M}) \rightarrow \text{HNO}_2 (+\text{M})$	$k_0 = 7.0 \times 10^{-31} (T/300)^{-2.6}$ $k_\infty = 1.5 \times 10^{-11} (T/300)^{-0.5}$
$\text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3$	$k_0 = 7.2 \times 10^{-15} \text{Exp}(785/T)$ $k_2 = 4.1 \times 10^{-16} \text{Exp}(1440/T)$ $k_3 = 1.9 \times 10^{-33} \text{Exp}(725/T)$
$\text{OH} + \text{HNO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_2$	$k = 6.6 \times 10^{-12}$
$\text{HO}_2\text{NO}_2 (+\text{M}) \rightarrow \text{HO}_2 + \text{NO}_2 (+\text{M})$	$k = k_p / (2.1 \times 10^{-27} \text{Exp}(10,900/T))$
$\text{NO}_3 + \text{CO} \rightarrow \text{products}$	$k < 4.0 \times 10^{-19}$
$\text{N}_2\text{O}_5 (+\text{M}) \rightarrow \text{NO}_2 + \text{NO}_3$	$k = k_p / (4.0 \times 10^{-27} \text{Exp}(10,930/T))$
$\text{O} + \text{HNO}_3 \rightarrow \text{OH} + \text{NO}_3$	$k = 3.0 \times 10^{-17}$
$\text{CH}_3\text{OO} + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$	$k = 4.2 \times 10^{-12} \text{Exp}(180/T)$
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$k = 2.0 \times 10^{-12} \text{Exp}(-1400/T)$
$\text{NO}_3 + \text{NO} \rightarrow 2 \text{NO}_2$	$k = 1.7 \times 10^{-11} \text{Exp}(150/T)$
$\text{NO}_3 + \text{NO}_2 (+\text{M}) \rightarrow \text{N}_2\text{O}_5 (+\text{M})$	$k_0 = 2.2 \times 10^{-30} (T/300)^{-4.3}$ $k_\infty = 1.5 \times 10^{-12} (T/300)^{-0.5}$
$\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$	$k = 1.0 \times 10^{-11}$
$\text{Alkanes} + \text{NO}_3 \rightarrow \text{HNO}_3 + \text{products}$	$k = 3.6 \times 10^{-17b}$
$\text{NO}_2 + \text{NO}_3 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$	$k = 8.2 \times 10^{-14} \text{Exp}(-1480/T)$
$\text{NO}_3 + \text{DMS} \rightarrow \text{HNO}_3 + \text{products}$	$k = 1.1 \times 10^{-12}$
$\text{NO}_3 + \text{CH}_3\text{CHO} \rightarrow \text{HNO}_3 + \text{CH}_3\text{CO}_3$	$k = 1.4 \times 10^{-12} \text{Exp}(-1900/T)$
$\text{H}_2\text{S} + \text{NO}_3 \rightarrow \text{products}$	$k < 8.0 \times 10^{-16}$
$\text{HNO}_3 + h\nu \rightarrow \text{OH} + \text{NO}_2$	$j = j \text{HNO}_3^c$
$\text{PAN} + h\nu \rightarrow \text{NO}_2 + \text{CH}_3\text{CO}_3$	$j = j \text{PAN}^c$

Table 1. Continued

Reaction	Rate Coefficient
$\text{HNO}_2 + h\nu \rightarrow \text{OH} + \text{NO}$	$j = j \text{HNO}_2^c$
$\text{N}_2\text{O}_5 + h\nu \rightarrow \text{NO}_2 + \text{NO}_3$	$j = j \text{N}_2\text{O}_5^c$
$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$	$k = 1.3 \times 10^{-21}$
$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	$k = 1.2 \times 10^{-13} \text{Exp}(-2450/T)$
$\text{O} + \text{NO} (+\text{M}) \rightarrow \text{NO}_2 (+\text{M})$	$k_0 = 9.0 \times 10^{-32} (T/300)^{-1.5}$ $k_\infty = 3.0 \times 10^{-11} (T/300)^0$
$\text{HO}_2 + \text{NO}_2 (+\text{M}) \rightarrow \text{HO}_2\text{NO}_2 (+\text{M})$	$k_0 = 1.8 \times 10^{-31} (T/300)^{-3.2}$ $k_\infty = 4.7 \times 10^{-12} (T/300)^{-1.4}$
$\text{O} + \text{HO}_2\text{NO}_2 \rightarrow \text{products}$	$k = 7.8 \times 10^{-11} \text{Exp}(-3400/T)$
$\text{OH} + \text{HO}_2\text{NO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{NO}_2$	$k = 1.3 \times 10^{-12} \text{Exp}(380/T)$
$\text{N}_2\text{O}_5 + \text{aerosols} \rightarrow \text{HNO}_3(\text{aq})$	$k = 304^a$
$\text{NO}_3 + \text{OH} \rightarrow \text{products}$	$k = 7.1 \times 10^{-11b}$
$\text{O}_3 + \text{HNO}_2 \rightarrow \text{O}_2 + \text{HNO}_3$	$k < 5.0 \times 10^{-19}$
$\text{HO}_2 + \text{NO}_3 \rightarrow \text{OH} + \text{NO}_2 + \text{O}_2$	$k = 4.1 \times 10^{-12}$
$\text{CH}_3\text{CO}_3 + \text{NO}_2 \rightarrow \text{PAN}$	$k = 4.7 \times 10^{-12b}$
$\text{PAN} \rightarrow \text{NO}_2 + \text{CH}_3\text{CO}_3$	$k = 1.9 \times 10^{-16} \text{Exp}(-13,543/T)^b$
$\text{C}_2\text{H}_5\text{O}_2 + \text{NO} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{NO}_2$	$k = 8.9 \times 10^{-12}$
$\text{SO}_2 + \text{NO}_2 \rightarrow \text{products}$	$k < 2.0 \times 10^{-26}$
$\text{SO}_2 + \text{NO}_3 \rightarrow \text{products}$	$k < 7.0 \times 10^{-21}$
$\text{CH}_3\text{O} + \text{NO}_3 \rightarrow \text{CHO} + \text{HNO}_3$	$k = 5.8 \times 10^{-16}$
$\text{O} + \text{NO}_3 \rightarrow \text{O}_2 + \text{NO}_2$	$k = 1 \times 10^{-11}$
$\text{CH}_3\text{CO}_3 + \text{NO} \rightarrow \text{CH}_3 + \text{CO}_2 + \text{NO}_2$	$k = 2.38 \times 10^{-12}$
$\text{Alkenes} + \text{NO}_3 \rightarrow \text{products}$	$k = 7.6 \times 10^{-15b}$
$\text{NO}_3 + h\nu \rightarrow \text{NO}_2 + \text{O}(^3\text{P})$	$j = j \text{NO}_3 (\text{a})^c$
$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}(^3\text{P})$	$j = j \text{NO}_2^c$
$\text{NO}_3 + h\nu \rightarrow \text{NO} + \text{O}_2$	$j = j \text{NO}_3 (\text{b})^c$
$\text{HO}_2\text{NO}_2 + h\nu \rightarrow \text{OH} + \text{NO}_3$	$j = j \text{HO}_2\text{NO}_2^c$

Units for rate constants are as follows: unimolecular, s^{-1} ; bimolecular and pseudobimolecular, $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$. M, third body; PAN, peroxy acetyl nitrate; DMS, dimethylsulfide. A single rate coefficient ($2.3 \times 10^{-6} \text{s}^{-1}$) encompassing both rainout and dry deposition is used for PAN, HNO_3 , and HO_2NO_2 [Thompson and Lenschow, 1984]. Rate constants are from DeMore *et al.* [1990].

^aRate constant from Russell *et al.* [1986].

^bPhotolysis rates calculated [Yvon and Saltzman, 1993].

^cAssuming an accommodation coefficient of 0.05.

The input parameters for the model runs discussed later are shown in Table 2. We have adopted a value of 0.05 for the accommodation coefficient of N_2O_5 on aqueous aerosol surfaces [DeMore *et al.*, 1990] and have assumed that the accommodation of NO_3 onto such surfaces is much less probable [Wayne *et al.*, 1991]. There is, in fact, some uncertainty regarding the accommodation coefficient of NO_3 .

Table 2. Model starting conditions for Case 1, Case 2, and Case 3

Parameter	Case 1	Case 2	Case 3
Nighttime NO_2 , ppbv	2	25	2
DMS flux, $\mu\text{mole m}^{-2} \text{d}^{-1}$	11	11	6
Aerosol surface area, $\mu\text{m}^2 \text{cm}^{-3}$	500	500	500
Dry deposition of NO_3 and N_2O_5 , cm s^{-1}	0.8	0.8	0.8
HCHO, ppbv	0.5	0.5	0.5
CH_3CHO , ppbv	0.5	0.5	0.5
Alkanes, ppbv	10	10	10
Alkenes, ppbv	2	2	2
Entrainment velocity, cm s^{-1}	0.3	0.3	0.3
O_3 , ppbv	20	25	20

on aerosol-type surfaces, with some evidence for much larger values [Thomas *et al.*, 1993; Shao-Meng *et al.*, 1993; Dentener and Crutzen, 1993]. However, because the accommodation coefficient for N_2O_5 is large, and since NO_3 and N_2O_5 are in equilibrium and their concentrations are similar (Figure 4), the direct heterogeneous loss of NO_3 probably makes only a small contribution to the total loss of N_xO_y . This assumption will hold unless the accommodation coefficient of NO_3 is very close to unity. The aerosol concentration of $500 \mu m^2 cm^{-3}$ is taken as the average of estimated urban and remote marine aerosol loadings [Whitby *et al.*, 1972]. This aerosol loading results in a $\tau(NO_3)$ of ~ 6 min for NO_3 which is consistent with the field results from the second half of the night shown in Figure 2. The rate constants that are listed as upper limits in Table 1 are assumed to be at their respective upper limits for the model calculations. A dry deposition velocity of $0.8 cm s^{-1}$ is assumed for both NO_3 and N_2O_5 [Dentener and Crutzen, 1993]. A fixed boundary layer height of 1 km is used for all model runs. An entrainment velocity of $0.3 cm s^{-1}$ is taken from Lenschow *et al.* [1988], and the free tropospheric concentration of O_3 , DMS, NO , and NO_2 are assumed to be 30 ppbv [Routhier *et al.*, 1980; Carroll *et al.*, 1990], 0 pptv [Andreae *et al.*, 1988; Berresheim *et al.*, 1990], 13 pptv, and 36 pptv [Carroll *et al.*, 1990], respectively. The concentrations of organics that are used in the model simulations are typical of a polluted coastal polluted boundary layer [Russell *et al.*, 1986] with $[HCHO] = 0.5$ ppbv, $[CH_3CHO] = 0.5$ ppbv, [alkanes] = 10 ppbv, and [alkenes] = 2 ppbv.

We have looked in detail at three scenarios. Case 1 is typical of a coastal urban air mass with relatively low pollution with the average $[NO_2] = 2$ ppbv and $[O_3] = 20$ ppbv (the second half of the night illustrated in Figure 2). A constant DMS flux of $11 \mu mol m^{-2} d^{-1}$ is used in this case to maintain a mean nighttime DMS concentration of ~ 50 pptv. This flux is the upper limit given by Andreae [1990] for coastal and shelf waters. Case 2 is typical of more highly polluted conditions with the average $[NO_2] = 25$ ppbv and $[O_3] = 25$ ppbv (Figure 3b). In this case the DMS flux is the same as that used in case 1 and maintains a mean nighttime DMS concentration of ~ 50 pptv in this case as well. Case 3 is designed to examine the effect that DMS has on NO_3 concentrations. This case uses the same conditions as case 1 with the exception of the DMS flux, which was set to zero.

All simulations begin at sunrise. A constant source of NO is specified for the first 6 days (until the diel variations stabilize) in order to sustain an average nighttime NO_2 concentration of 2 ppbv or 25 ppbv, depending on which starting conditions are required. The O_3 and hydrocarbon concentrations are held constant during this time as well. After 150 hours the source of NO is turned off, and the O_3 and hydrocarbons are allowed to vary. The remainder of the 12-day simulation illustrates the effect that DMS emissions can have on NO_x levels as the air mass moves off shore.

Table 3 shows the relative importance of the various sinks for N_xO_y for both case 1 and case 2, where the DMS sea-to-air flux was held constant at $11 \mu mol m^{-2} d^{-1}$. During the first half of the model runs when the source of NO is turned on and a constant average NO_x concentration is maintained (days 2-6 in Table 3), $NO_2 + OH$ is the most important sink for N_xO_y in case 1, while in the higher NO_x case (case 2) entrainment of NO and NO_2 and the reaction of N_2O_5 with water and aerosols also become important. The importance of the N_2O_5 reactions

Table 3. Relative Importance of the Different Losses of N_xO_y Given as Percent Total Loss for Both Case 1 and Case 2

Day	NO ₂ + OH, %		NO ₃ + DMS, %		NO ₃ + Ald, %		NO ₃ + NMHC, %		N ₂ O ₅ + H ₂ O, %		N ₂ O ₅ + Aer, %		Deposition N ₂ O ₅ and NO ₃ , %		Entrainment NO ₂ and NO, %	
	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2
2	45	30	7	1	<1	<1	3	<1	9	14	17	25	<1	<1	18	29
3	45	30	7	1	<1	<1	3	<1	9	14	17	26	<1	<1	19	29
4	44	30	7	1	<1	<1	3	<1	9	14	17	26	<1	<1	19	29
5	45	31	7	1	<1	<1	3	<1	9	14	17	25	<1	<1	18	29
6	44	30	7	1	<1	<1	3	<1	10	14	17	26	<1	<1	19	29
7	46	33	25	1	<1	<1	1	<1	5	15	8	26	<1	<1	15	24
8	47	45	38	15	<1	<1	<1	<1	1	9	2	16	<1	<1	12	13
9	47	47	45	33	<1	<1	<1	<1	<1	<1	1	5	<1	<1	7	11
10	51	47	49	39	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0	10
11	49	47	50	44	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0	8
12	49	49	50	47	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0	2
13	48	50	51	50	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0	0
14	49	49	51	50	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0	0
15	48	49	52	51	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0	0

Each day covers a 24-hour period beginning at sunrise and continuing until the following sunrise. DMS, dimethylsulfide; Ald, aldehydes; NMHC, normethane hydrocarbons; and Aer, aerosols.

in the higher NO_x case (case 2) is due to the shift in the equilibrium between NO_3 and N_2O_5 toward N_2O_5 at higher NO_2 concentrations. This shift also significantly reduces the importance of the $\text{NO}_3 + \text{DMS}$ reaction during the first half of the case 2 model run. It should be mentioned here that the rate constant for the reaction of N_2O_5 with water vapor is an upper limit, and this reaction may be very much slower. However, the shift in the equilibrium between NO_3 and N_2O_5 toward N_2O_5 at higher NO_2 concentrations would still occur, and the reaction between N_2O_5 and aerosols would remain an important sink for N_xO_y in this case. After the NO source is turned off and NO_x concentrations begin to decrease, the reaction between NO_3 and DMS becomes increasingly significant as a sink, until it becomes as important as the reaction between NO_2 and OH in removing N_xO_y . The two reactions $\text{NO}_2 + \text{OH}$ and $\text{NO}_3 + \text{DMS}$ provide the only real sinks for N_xO_y as the air mass moves away from pollution sources. This is because the equilibrium between NO_3 and N_2O_5 moves increasingly to the NO_3 side as the NO_2 concentration falls, and we have assumed in this model that NO_3 does not undergo heterogeneous loss directly.

It should be noted that the loss of NO_x due to entrainment becomes zero near the end of the model runs because the NO and NO_2 concentrations in the boundary layer are lower than those prescribed for the free troposphere. Entrainment then becomes a source of NO_x to the boundary layer. The model used here does not model the chemistry of the free troposphere; therefore the free tropospheric concentrations of O_3 , DMS, NO, and NO_2 remain fixed throughout the model runs. Horizontal mixing will also reduce the NO_x concentrations as the air mass is advected out over the ocean and away from pollution sources, although this dilution process is not included in the present model.

Figure 4 shows the detailed results from case 1, which was designed to represent the latter half of the night shown in

Figure 2. It can be seen from the top panels in this figure that the nighttime NO_2 was sustained at approximately 2 ppbv until 150 hours into the run, when the NO source was turned off. After the NO source was turned off, the NO and NO_2 concentrations fall off rapidly. NO_x concentrations fall below 40 pptv within 3 days of moving offshore. The middle panels in this figure show how the NO_3 and N_2O_5 concentrations vary with time during this model run. The N_2O_5 concentration becomes insignificant once the NO_2 concentration falls below 100 pptv. The nighttime NO_3 concentrations shown here are in good agreement with those measured during the latter half of the night shown in Figure 2, and they too fall off rapidly after the air mass is advected off shore.

The results from case 2 are shown in Figure 5. This case was designed to represent the more polluted night shown in Figure 3b. The starting NO_x concentrations in this case are an order of magnitude higher than they were in case 1, and within 6 days the NO_x concentrations fall below 40 pptv. This is only twice as long as in case 1. As shown in the middle panels of Figure 5, both the NO_3 and N_2O_5 concentrations are much higher in this case than in case 1. The shift in the $\text{NO}_3/\text{N}_2\text{O}_5$ equilibrium mentioned earlier is apparent during the first part of the model run with the N_2O_5 concentrations being 5 times higher than the NO_3 concentrations, while in case 1, NO_3 is approximately 1.5 times greater than N_2O_5 . The NO_3 concentrations predicted for the first part of the case 2 model run are in good agreement with the concentrations measured during the first half of the night shown in Figure 3b. The agreement becomes worse for the second half of that night, because the drop in the measured O_3 concentrations during this period is not accounted for in the model run.

We also examined the effect that NO_3 can have on the oxidation rate of DMS. Because the flux of DMS into the boundary layer and the entrainment velocity into the free troposphere are constant, changes in the diel cycle of DMS are

Figure 4. Model results from case 1, in which the nighttime mean NO_2 concentration is ~ 2 ppbv and the sea-to-air flux of DMS is $11 \mu\text{mol m}^{-2} \text{d}^{-1}$. For all model runs, temperature is 300 K, and RH = 80%.

Figure 5. Model results from case 2, in which the nighttime mean NO_2 concentration is ~ 25 ppbv and the sea-to-air flux of DMS is $11 \mu\text{mol m}^{-2} \text{d}^{-1}$. For all model runs, temperature is 300 K, and RH = 80%.

due to changes in its oxidation rate. The bottom panels in Figures 4 and 5 show how the rate of oxidation of DMS changes over time in case 1 and case 2, respectively. When the NO source is turned on, the nighttime oxidation is the dominant DMS sink, resulting in a rapid decrease in DMS during the night with a predawn minimum and a late afternoon maximum. As the NO_x levels drop after the source is removed, OH becomes increasingly important as the sink, and the diel cycle becomes increasingly representative of that found in clean marine air masses where there is a predawn maximum and a late afternoon minimum [Yvon *et al.*, 1996]. A comparison of the top and middle panels to the bottom panel in Figures 4 and 5 indicates that in or near regions where NO_x levels are equal to or greater than approximately 30 pptv the DMS diel cycle should have a smaller amplitude or appear reversed from that predicted by models using oxidation by OH radicals as the only sink. These results also illustrate that using the rate of nighttime accumulation of DMS is not an acceptable method for estimating the sea-to-air flux of DMS, except in extremely clean environments.

The results from case 3 are shown in Figure 6. Because there is no DMS flux, only the first 150 hours are shown. This case is used to illustrate the effect that DMS can have on N_xO_y concentrations. Removing DMS does not appear to have a significant effect on the total NO_x concentrations. However, there is some effect on the NO_3 and N_2O_5 concentrations. NO_3 is $\sim 17\%$ higher in this case than in case 1, and N_2O_5 is $\sim 13\%$ higher. The presence of ~ 50 pptv DMS can reduce this N_xO_y reservoir ($\text{NO}_3 + \text{N}_2\text{O}_5$) by $\sim 13\%$. For the same DMS concentration and a lower NO_2 concentration the effect should be greater, and conversely, for higher NO_2 concentrations the effect should be less. This is due to the shift in equilibrium between NO_3 and N_2O_5 relative to the NO_2 concentration, as mentioned earlier.

The results from this model indicate that NO_3 responds with timescales of under an hour to changing concentrations

of NO_2 , O_3 , and DMS. This is important, because the "snapshots" of NO_3 in different air masses can be analyzed without having to consider the complication of NO_3 undergoing significant transport and mixing. The major conclusions are (1) that DMS is a much more important sink for NO_3 in the presence of lower NO_2 concentrations and (2) that the reaction between NO_3 and DMS is an important sink for DMS in the MBL and could exceed that of the daytime removal by OH.

Figure 6. Model results from case 3, in which the nighttime mean NO_2 concentration is ~ 2 ppbv and the sea-to-air flux of DMS is $0 \mu\text{mol m}^{-2} \text{d}^{-1}$. For all model runs, temperature is 300 K, and RH = 80%.

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