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## Nocturnal odd-oxygen budget and its implications for ozone loss in the lower troposphere

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[1] Nitrogen oxides are important to the regulation of ozone throughout the Earth's atmosphere. Of particular interest for regional air quality is photochemical production and nocturnal destruction of O<sub>3</sub> in the lower troposphere in high NO<sub>x</sub>(=NO + NO<sub>2</sub>) environments. Nocturnal tropospheric odd oxygen (O<sub>x</sub>), defined as O<sub>3</sub> + NO<sub>2</sub> + 2NO<sub>3</sub> + 3N<sub>2</sub>O<sub>5</sub>, is used to assess the impact of NO<sub>x</sub> emissions on nocturnal O<sub>3</sub> loss. Recent aircraft measurements of the components of O<sub>x</sub> and HNO<sub>3</sub> yield a detailed accounting of the nocturnal O<sub>x</sub> budget in a regionally polluted environment. The analysis demonstrates the role of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> reactions in nocturnal O<sub>3</sub> destruction and shows that multiple factors, including timing of NO<sub>x</sub> emissions, hydrocarbon and aerosol loading, seasonality and atmospheric mixing, govern the impact of NO<sub>x</sub> emissions on regional-scale air quality.

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### 1. Introduction

[2] Tropospheric ozone (O<sub>3</sub>) is produced during the day from photochemical cycling of nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) in the presence of VOC (= volatile organic compounds, or hydrocarbons). At night, O<sub>3</sub> reacts irreversibly with emitted NO to form NO<sub>2</sub>, which further reacts with O<sub>3</sub> to yield NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> (the latter from association of NO<sub>3</sub> with NO<sub>2</sub>) [Wayne *et al.*, 1991]. Because NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> reconvert at sunrise to NO<sub>2</sub> and O<sub>3</sub>, which in turn rapidly interconvert during the day, these compounds may

be grouped as a single chemical family, odd oxygen or O<sub>x</sub> [Wood *et al.*, 2005; Jacob *et al.*, 1996; Liu, 1977].

$$O_x(\text{nocturnal}) = O_3 + NO_2 + 2NO_3 + 3N_2O_5 \quad (1)$$

The stoichiometric coefficients represent the number of O<sub>x</sub> stored in each compound. Chemical O<sub>x</sub> loss at night occurs only upon reaction of NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> to form products not listed in equation (1). Perhaps the most important loss mechanism is heterogeneous (i.e., on the surface of aerosol particles) hydrolysis of N<sub>2</sub>O<sub>5</sub> [Dentener and Crutzen, 1993].



Each HNO<sub>3</sub> thus produced is equivalent to the loss of 1.5 O<sub>x</sub> [see, e.g., Parrish *et al.*, 1998]. This reaction is regionally important on anthropogenic aerosol and globally important on both aerosol and in clouds, particularly in winter [Lelieveld and Crutzen, 1990]. Reactions of NO<sub>3</sub> with VOC, or peroxy radicals derived from VOC oxidation, also results in a net loss of 1–2 O<sub>x</sub> per NO<sub>3</sub> reacted, depending upon the reaction pathway [Atkinson and Arey, 2003; Geyer *et al.*, 2003]. Conservation of nocturnal O<sub>x</sub> occurs if NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> are sufficiently unreactive to serve as reservoir species overnight. The balance between these nocturnal processes *k* is a determining factor in the amount of O<sub>3</sub> available within an air mass at sunrise.

[3] The New England Air Quality Study – Intercontinental Transport and Transformation 2004 (NEAQS-ITCT 04, <http://www.al.noaa.gov/2004/>) included a deployment of the NOAA WP-3D (P-3) aircraft. The P-3 carried an array of instruments, including rapid time resolution (1 s) measurements of O<sub>3</sub>, NO<sub>x</sub> [Ryerson *et al.*, 2000], NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub> [Dubé *et al.*, 2006] and HNO<sub>3</sub> [Neuman *et al.*, 2002]. Additional instruments relevant to the current analysis included CO, SO<sub>2</sub>, speciated VOC and aerosol composition. Based on nocturnal measurements of the compounds in equation (1) and HNO<sub>3</sub>, we present a budget for nocturnal O<sub>x</sub> and examine its loss and/or transport overnight.

### 2. Nocturnal NO<sub>x</sub> Plumes

[4] Anthropogenic plumes that have undergone mainly nighttime reactions can be identified, and their ages determined, from the correlation between O<sub>3</sub> and various nitrogen-containing compounds. Figure 1 shows tracks for two nighttime flights over the northeast U.S. in August, 2004 and a scatter plot of O<sub>3</sub> against HNO<sub>3</sub> for the 11 August

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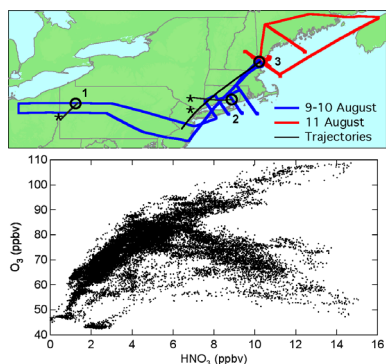
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<sup>4</sup>Division of Marine and Atmospheric Chemistry, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida, USA.

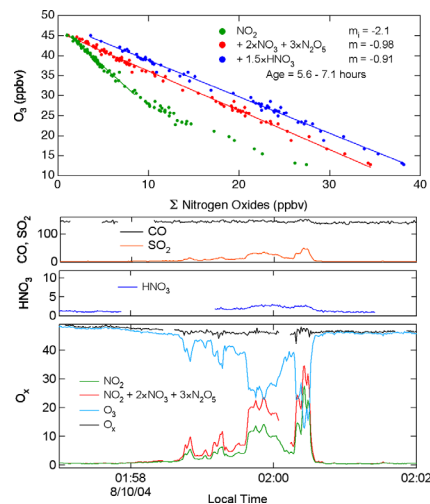
<sup>5</sup>School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia, USA.

<sup>6</sup>Norsk Institutt for Luftforskning, Kjeller, Norway.

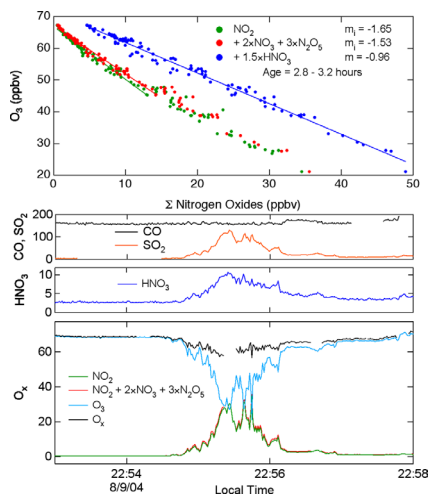
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**Figure 1.** (top) Map of the northeast United States showing tracks for two nighttime flights during NEAQS-ITCT and the locations at which the three  $\text{NO}_x$  plumes in Figures 2–4 were sampled. The solid black lines are calculated backward air mass trajectories over the age of each plume. Asterisks indicate the most likely source regions for each; plumes 1 and 2 are power plants, and plume 3 is most likely the New York urban plume. (bottom) Scatter plot of  $\text{O}_3$  vs.  $\text{HNO}_3$  for the flight of 11 August, 2004, showing clusters of data with either a positive and a negative correlation, indicative of daytime and nighttime  $\text{NO}_x$  processing, respectively.



**Figure 3.** Plume #2 (800 m ASL, 760 m AGL) is plotted in the same format as Figure 2. Like the plume in Figure 2, the plume age has been determined from the initial slope of  $\text{O}_3$  vs.  $\text{NO}_2$ . Unlike Figure 2, the stoichiometric relationship between  $\text{O}_3$  and  $\text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5$  here is linear due to the conservation of  $\text{O}_x$ , as seen in the bottom panel.

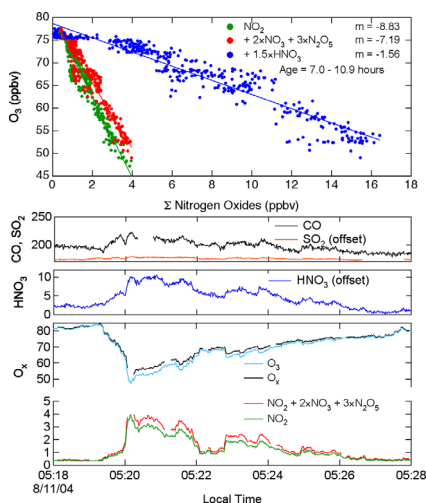


**Figure 2.** (top) Plot of  $\text{O}_3$  vs. three different nitrogen oxide sums,  $\text{NO}_2$  alone (green),  $\text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5$  (red) and  $\text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5 + 1.5\text{HNO}_3$  (blue), for plume #1 (altitude 1100 m above sea level (ASL), 640 m above ground level (AGL)) in Figure 1. The plume age is determined from the  $\text{O}_3$  vs.  $\text{NO}_2$  plot using equation (3) and the initial slope at small  $\text{NO}_2$  concentrations (i.e., plume edges). The  $\text{O}_3$  to  $\text{NO}_2$  relationship is not linear over the entire range in  $\text{NO}_2$  because the kinetics of the  $\text{NO}_2 + \text{O}_3$  reaction are second order at larger  $\text{NO}_2$ . The slope of  $\text{O}_3$  vs. the sum of  $\text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5 + 1.5\text{HNO}_3$  depends on stoichiometry rather than kinetics and so is linear even for large  $\text{O}_3$  depletions. (middle) Time series of CO and  $\text{SO}_2$  identifying this as a power plant plume, and  $\text{HNO}_3$ . All concentrations in ppbv. (bottom) Time series of  $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5$ , and  $\text{O}_x$  (all in ppbv) from equation (1).

flight, which sampled 1–2 days (transport time) downwind of the northeast U. S. urban corridor [Stohl *et al.*, 1998]. One lobe of the data shows a positive correlation with linearly fitted slopes varying between 3–7 ppbv  $\text{O}_3$ /ppbv  $\text{HNO}_3$  due to the previous day's  $\text{NO}_x$  emissions. The positive correlation results from simultaneous photochemical  $\text{O}_3$  production and photochemical oxidation of  $\text{NO}_2$  to  $\text{HNO}_3$ , and the slopes are approximate upper limits to the amount of  $\text{O}_3$  produced per unit  $\text{NO}_x$  emitted [Ryerson *et al.*, 2001; Trainer *et al.*, 1993]. The negatively-correlated lobe results from nocturnal  $\text{NO}_x$  emission and subsequent oxidation to  $\text{HNO}_3$  with concurrent  $\text{O}_3$  destruction.

[5] Figures 2–4 show a series of plots of  $\text{O}_3$  against three different stoichiometric sums of nitrogen oxide species measured in specific  $\text{NO}_x$  plumes encountered on these two flights. The three sums are:  $\text{NO}_2$  alone;  $\text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5$ , or the sum of  $\text{O}_x$  contained in the nocturnal nitrogen oxide reservoir; and  $\text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5 + 1.5\text{HNO}_3$ , which includes  $\text{O}_x$  loss to  $\text{HNO}_3$  in the stoichiometric ratio that results from  $\text{N}_2\text{O}_5$  hydrolysis. This analysis assumes negligible surface deposition of  $\text{O}_3$  and  $\text{HNO}_3$  in lofted plumes that are essentially decoupled from the shallow nocturnal boundary layer, and that  $\text{NO}_x$  emission occurs exclusively as  $\text{NO}$ , which oxidizes rapidly to  $\text{NO}_2$  in excess  $\text{O}_3$ . Nocturnal plumes that still contained  $\text{NO}$  exhibited a slope of  $-1 \pm 0.1$  in plots of  $\text{O}_3$  vs.  $\text{NO}_2$ . The  $\text{O}_3$  vs.  $\text{NO}_2$  plots in Figures 2–4 show slopes steeper than  $m = -1$ , indicating that further reaction of  $\text{NO}_2$  with  $\text{O}_3$  had occurred.

[6] The slope,  $m$ , of a plot of  $\text{O}_3$  vs.  $\text{NO}_2$  for plumes emitted and sampled at night is an approximate measure of the plume age. Subsequent to the more rapid oxidation of  $\text{NO}$  to  $\text{NO}_2$  in excess  $\text{O}_3$ , ozone and  $\text{NO}_2$  evolve in time according to second-order kinetics; however the determination of plume age is simplified under the assumption of pseudo first-order kinetics, valid if the input of  $\text{NO}_x$  is small



**Figure 4.** Same as previous, but for an aged urban plume (#3 in Figure 1, 500 m ASL, 470 m AGL). The entire range of the  $O_3$  vs.  $NO_2$  plot has been used for the plume age determination. The background mixing ratio of 4.5 ppbv, due to photochemical production prior to the emission of the urban plume near sunset, has been subtracted from the  $HNO_3$  data for clarity of presentation. The  $SO_2$  data in the center graph has been offset by +170 ppbv to show it on the same scale as CO. Note the change in scale between the two halves of the lower graph.

in comparison to the excess  $O_3$ . The resulting expression for the plume age is as follows.

$$t_{plume} \approx \frac{\ln[1 - S(m + 1)]}{Sk\bar{O}_3} \quad (3)$$

Here  $k$  is the rate coefficient for reaction of  $NO_2$  with  $O_3$ ,  $\bar{O}_3$  is the average  $O_3$  concentration during the evolution of the plume (i.e., the average of the  $O_3$  present in the plume and that in the background outside of the plume), and  $S$  is a stoichiometric factor that varies between 1 for dominant  $NO_3$  loss and 2 for dominant  $N_2O_5$  loss (or during the approach to steady state) to account for the consumption of  $2 \times NO_2$  from formation and hydrolysis of  $N_2O_5$  [Brown et al., 2004].

### 3. $O_x$ Budgets

[7] Figure 2 illustrates the case of irreversible nocturnal  $O_x$  loss due to  $HNO_3$  formation after  $NO_x$  emission from a power plant plume (indicated by large  $SO_2$  and little to no CO enhancement). This plume resulted from a relatively concentrated  $NO_x$  point source, and it shows the relationships between  $NO_2$ ,  $O_3$  and  $HNO_3$  clearly. Analysis of multiple smaller  $NO_x$  plumes show similar results. The initial (i.e., at the plume edges, where  $NO_2$  is relatively dilute) slope of  $O_3$  vs.  $NO_2$  ( $m = -1.65$ ) indicates conversion of  $O_x$  to  $NO_3$  and  $N_2O_5$  and a plume age of  $\sim 3$  hours. Inclusion of  $NO_3$  and  $N_2O_5$  in  $O_x$ , i.e.,  $O_3$  vs.  $NO_2 + 2NO_3 + 3N_2O_5$ , increases this initial slope only slightly. Inclusion of  $O_x$  loss to  $HNO_3$ , i.e.,  $O_3$  vs.  $NO_2 + 2NO_3 + 3N_2O_5 +$

$1.5HNO_3$ , yields  $m = -1$ , or a closed  $O_x$  budget (there was negligible nitrate present in the aerosol). There are two important conclusions. First, the measured concentrations of  $O_3$ ,  $NO_2$  and  $HNO_3$  account for all of the  $O_x$ . Second, the  $O_x$  budget closure occurs at a ratio of 1.5  $HNO_3$  formed per  $O_x$  lost, indicating  $N_2O_5$  hydrolysis as the mechanism. The determination of nearly exclusive loss of  $O_x$  to  $HNO_3$  is consistent with our recent analysis that showed rapid  $N_2O_5$  loss rates over Pennsylvania and Ohio on 9 August due to a large sulfate aerosol loading and, consequently, efficient heterogeneous uptake coefficients for  $N_2O_5$  (with subsequent release of  $HNO_3$  to the gas phase) [Brown et al., 2006]. The time series of  $O_x$  in the lower plot also illustrates this point, showing a deviation at plume center of 10–15% from the baseline outside of the plume. This 3-hour old plume, which was emitted near sunset, would have lost 50% of its  $O_x$  to  $HNO_3$  formation in the course of a 10-hour night.

[8] Figure 3 shows the contrasting case of  $O_x$  conservation in a power plant plume east of New York City. The steeper initial slope of the  $O_3$  vs.  $NO_2$  plot ( $m = -2.1$ ) yields a plume age of approximately 6 hours. In this case, the contribution of  $NO_3$  and  $N_2O_5$  closes the  $O_x$  budget (i.e.,  $m = -1$ ), with a minimal contribution of  $O_x$  loss to  $HNO_3$  despite the increased plume age. The time series of nocturnal  $O_x$  and its components in the lower graph corroborate the analysis, showing no measurable deviation at plume center and storage of up to 20% of total  $O_x$  as  $NO_3$  and  $N_2O_5$ . Conservation of  $O_x$  downwind of New York City is again consistent with our previous analysis that showed immeasurably small heterogeneous uptake coefficients for  $N_2O_5$  in this region in the early morning of 10 August [Brown et al., 2006].

[9] Figure 4 shows the case of an urban  $NO_x$ - $O_3$  plume (modest CO and smaller  $SO_2$  enhancements) from the 11 August flight, sampled 25 minutes prior to local sunrise over southern New Hampshire. The steep  $O_3$  vs.  $NO_2$  slope ( $m = -8.8$ ) corresponds to a plume age between 7–11 hours, or the duration of the entire night. Indeed, backward air mass trajectory calculations [Draxler and Rolph, 2003; Stohl et al., 1998] place the air mass in the vicinity of New York City near sunset. Such urban  $NO_x$  plumes observed at night consistently had times of emission either well before sunset (i.e., positive  $O_3$ - $HNO_3$  correlations, as in Figure 1, indicating photochemical production that preceded the nocturnal reactions) or close to sunset, consistent with the trapping of nocturnal  $NO_x$  emissions from urban sources in a shallow nocturnal boundary layer (<200 m) below the aircraft cruising altitude (500–2500 m) over the continent.

[10] The most striking feature of the lower graph in Figure 4 is the 40% deficit in both  $O_3$  and  $O_x$  relative to the background at the end of the night. Nitric acid accounted for only about 2/3 of the lost  $O_x$ , as shown by the slope of  $m = -1.6$  for  $O_3$  vs.  $NO_2 + 2NO_3 + 3N_2O_5 + 1.5HNO_3$  (again, measured aerosol nitrate was negligible). The lack of closure in the budget for the lost  $O_x$  may have resulted from any of a number of factors. Reactions of  $NO_3$  with VOC were likely more important in this plume, which exhibited substantially larger concentrations of reactive anthropogenic VOC (alkenes, aldehydes) than were present in the plumes on 9–10 August. These reactions lead to production of reactive peroxy radicals [Platt et al., 1990] and to either



oxygenated VOC containing one  $O_x$ , organic nitrates containing  $2O_x$  or  $HNO_3$ , also containing  $2O_x$  [Atkinson and Arey, 2003]. The specific oxygenated VOC and organic nitrates produced from these reactions were not measured in this study, and the  $HNO_3$  production, resulting only from slower  $NO_3$  reactions with aldehydes or alkanes, should be small by comparison. Loss of  $HNO_3$  to surface deposition or to exchange with the nocturnal boundary layer may also have been more important in this larger, more diffuse urban plume. Finally, nocturnal  $O_3$  loss via heterogeneous reactions, which has been invoked previously to explain  $O_3$  loss in lofted  $NO_x$ -containing plumes [Berkowitz et al., 2001], appears the least likely explanation for the  $O_x$  loss in Figure 4 based on the preceding discussion.

[11] Regardless of the  $O_x$  loss mechanism, the nocturnally aged New York plume shows that  $O_x$  loss can be large within urban plumes in which  $N_2O_5$  hydrolysis and  $NO_3$  reactions are rapid. This contrasts sharply with daytime  $NO_x$  processing; photochemical oxidation of tens of ppbv of  $NO_x$  to  $HNO_3$  in a VOC-rich urban plume could be expected produce several times this much  $O_3$  depending on the VOC mixture. Indeed, plumes emitted during the day, such as those in the upper lobe of Figure 1 (which were also influenced by emission from the New York City area), showed large  $O_3$  enhancements with a positive correlation to  $HNO_3$ . Emitted in late day or early evening, an urban plume such as the one in Figure 4 gives rise instead to a large, irreversible  $O_x$  loss. The timing of  $NO_x$  emission is therefore a crucial factor that substantially influences sources and sinks for  $O_3$  in polluted environments.

#### 4. Conclusions

[12] The contrast between the behavior of  $NO_x$  plumes emitted at night and during the day highlights several factors that influence net  $O_3$  concentrations resulting from anthropogenic  $NO_x$  emissions. The first, and most obvious, is emission timing:  $NO_x$  emitted at night has a markedly different impact on  $O_3$  pollution than does  $NO_x$  emitted during the day. The second is aerosol particles, whose amount and composition influences nocturnal  $O_3$  loss through the heterogeneous hydrolysis of  $N_2O_5$ . The third is the role of hydrocarbons. Reactive VOC are required to drive photochemical  $NO_x$ -catalyzed  $O_3$  production, but can also enhance nocturnal  $O_3$  loss via reactions of  $NO_3$  [Winer et al., 1984]. The fourth is the seasonal dependence of the  $NO_x$ - $O_x$  interaction. In summer,  $O_3$  exceedences in polluted regions are frequent. During winter, shorter day lengths and reduced actinic flux decrease photochemical  $O_3$  production but increase nocturnal  $O_3$  loss; reactive biogenic VOC emissions are reduced; and colder temperatures enhance the role of aerosol by shifting the  $NO_3$ - $N_2O_5$  equilibrium toward  $N_2O_5$  and the gas-particle equilibrium from  $HNO_3$  to particulate nitrate [Calvert et al., 1985]. The final factor is the coupling between diurnal meteorology and  $NO_x$ - $O_x$  chemistry. Nocturnal stratification of the lower atmosphere decouples  $NO_x$  from sources that emit above the nocturnal boundary layer (e.g., power plant stacks) from the surface until the following day. Nocturnal  $NO_x$  from urban sources is trapped within the boundary layer and affects surface  $O_3$  throughout the night [Gusten et al., 1998; Stutz et al., 2004; Talbot et al., 2005].

[13] As a consequence of these processes, total  $NO_x$  emissions and/or  $NO_x$  emissions per unit power generated from different sources are not the only indicators of the  $O_3$  forming potential of those emissions, even though these are the quantities normally subject to regulation. These results show that additional factors, such as emission timing, aerosols, nocturnal hydrocarbon reactions (related to the location of  $NO_x$  emissions) and nocturnal atmospheric stratification, influence the effectiveness of  $O_3$  mitigation policies based on  $NO_x$  control.

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