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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 O₃ in the lower troposphere in high NO_x(=NO + NO₂) environments. Nocturnal tropospheric odd oxygen (O_x), defined as O₃ + NO₂ + 2NO₃ + 3N₂O₅, is used to assess the impact of NO_x emissions on nocturnal O₃ loss. Recent aircraft measurements of the components of O_x and HNO₃ yield a detailed accounting of the nocturnal O_x budget in a regionally polluted environment. The analysis demonstrates the role of NO₃ and N₂O₅ reactions in nocturnal O₃ destruction and shows that multiple factors, including timing of NO_x emissions, hydrocarbon and aerosol loading, seasonality and atmospheric mixing, govern the impact of NO_x emissions on regional-scale air quality. **Citation:** Brown, S. S., et al. (2006), Nocturnal odd-oxygen budget and its implications for ozone loss in the lower troposphere, *Geophys. Res. Lett.*, 33, L08801, doi:10.1029/2006GL025900.

1. Introduction

[2] Tropospheric ozone (O₃) is produced during the day from photochemical cycling of nitrogen oxides (NO_x = NO + NO₂) in the presence of VOC (= volatile organic compounds, or hydrocarbons). At night, O₃ reacts irreversibly with emitted NO to form NO₂, which further reacts with O₃ to yield NO₃ and N₂O₅ (the latter from association of NO₃ with NO₂) [Wayne et al., 1991]. Because NO₃ and N₂O₅ reconvert at sunrise to NO₂ and O₃, which in turn rapidly interconvert during the day, these compounds may

be grouped as a single chemical family, odd oxygen or O_x [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_x stored in each compound. Chemical O_x loss at night occurs only upon reaction of NO₃ and N₂O₅ 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 N₂O₅ [Dentener and Crutzen, 1993].



Each HNO₃ thus produced is equivalent to the loss of 1.5 O_x [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 NO₃ with VOC, or peroxy radicals derived from VOC oxidation, also results in a net loss of 1–2 O_x per NO₃ reacted, depending upon the reaction pathway [Atkinson and Arey, 2003; Geyer et al., 2003]. Conservation of nocturnal O_x occurs if NO₃ and N₂O₅ are sufficiently unreactive to serve as reservoir species overnight. The balance between these nocturnal processes *k* is a determining factor in the amount of O₃ 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 O₃, NO_x [Ryerson et al., 2000], NO₃, N₂O₅ [Dubé et al., 2006] and HNO₃ [Neuman et al., 2002]. Additional instruments relevant to the current analysis included CO, SO₂, speciated VOC and aerosol composition. Based on nocturnal measurements of the compounds in equation (1) and HNO₃, we present a budget for nocturnal O_x and examine its loss and/or transport overnight.

2. Nocturnal NO_x Plumes

[4] Anthropogenic plumes that have undergone mainly nighttime reactions can be identified, and their ages determined, from the correlation between O₃ 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 O₃ against HNO₃ for the 11 August

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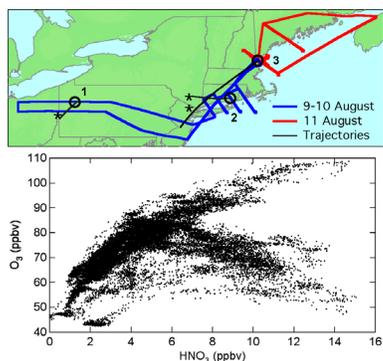


Figure 1. (top) Map of the northeast United States showing tracks for two nighttime flights during NEAQS-ITCT and the locations at which the three NO_x plumes in Figures 2–4 were sampled. The solid black lines are calculated backward air mass trajectories over the age of each plume. Asterisks indicate 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 O_3 vs. 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 NO_x processing, respectively.

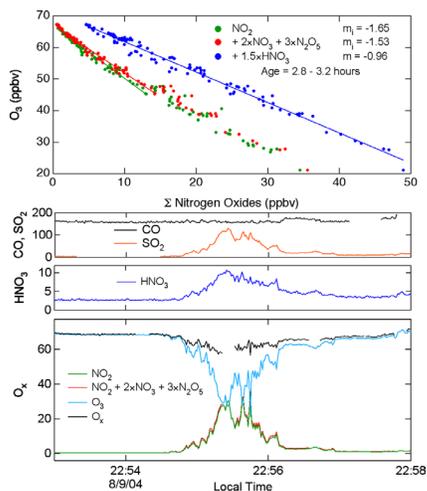


Figure 2. (top) Plot of O_3 vs. three different nitrogen oxide sums, NO_2 alone (green), $\text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5$ (red) and $\text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5 + 1.5\text{HNO}_3$ (blue), for plume #1 (altitude 1100 m above sea level (ASL), 640 m above ground level (AGL)) in Figure 1. The plume age is determined from the O_3 vs. NO_2 plot using equation (3) and the initial slope at small NO_2 concentrations (i.e., plume edges). The O_3 to NO_2 relationship is not linear over the entire range in NO_2 because the kinetics of the $\text{NO}_2 + \text{O}_3$ reaction are second order at larger NO_2 . The slope of 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 O_3 depletions. (middle) Time series of CO and SO_2 identifying this as a power plant plume, and HNO_3 . All concentrations in ppbv. (bottom) Time series of O_3 , NO_2 , $\text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5$, and O_x (all in ppbv) from equation (1).

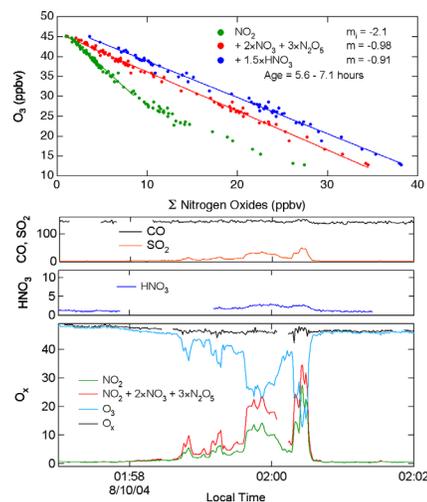


Figure 3. Plume #2 (800 m ASL, 760 m AGL) is plotted in the same format as Figure 2. Like the plume in Figure 2, the plume age has been determined from the initial slope of O_3 vs. NO_2 . Unlike Figure 2, the stoichiometric relationship between O_3 and $\text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5$ here is linear due to the conservation of O_x , as seen in the bottom panel.

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 O_3 /ppbv HNO_3 due to the previous day's NO_x emissions. The positive correlation results from simultaneous photochemical O_3 production and photochemical oxidation of NO_2 to HNO_3 , and the slopes are approximate upper limits to the amount of O_3 produced per unit NO_x emitted [Ryerson *et al.*, 2001; Trainer *et al.*, 1993]. The negatively-correlated lobe results from nocturnal NO_x emission and subsequent oxidation to HNO_3 with concurrent O_3 destruction.

[5] Figures 2–4 show a series of plots of O_3 against three different stoichiometric sums of nitrogen oxide species measured in specific NO_x plumes encountered on these two flights. The three sums are: NO_2 alone; $\text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5$, or the sum of 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 O_x loss to HNO_3 in the stoichiometric ratio that results from N_2O_5 hydrolysis. This analysis assumes negligible surface deposition of O_3 and HNO_3 in lofted plumes that are essentially decoupled from the shallow nocturnal boundary layer, and that NO_x emission occurs exclusively as NO , which oxidizes rapidly to NO_2 in excess O_3 . Nocturnal plumes that still contained NO exhibited a slope of -1 ± 0.1 in plots of O_3 vs. NO_2 . The O_3 vs. NO_2 plots in Figures 2–4 show slopes steeper than $m = -1$, indicating that further reaction of NO_2 with O_3 had occurred.

[6] The slope, m , of a plot of O_3 vs. NO_2 for plumes emitted and sampled at night is an approximate measure of the plume age. Subsequent to the more rapid oxidation of NO to NO_2 in excess O_3 , ozone and 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 NO_x is small

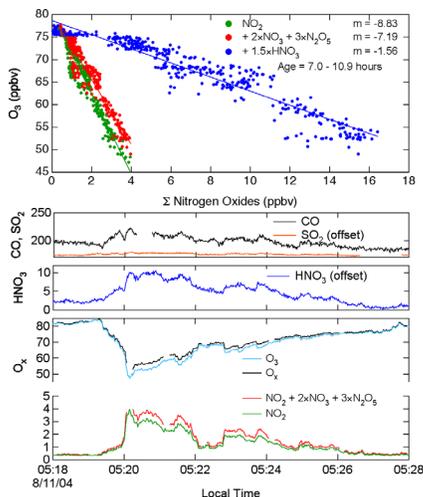


Figure 4. Same as previous, but for an aged urban plume (#3 in Figure 1, 500 m ASL, 470 m AGL). The entire range of the O₃ vs. NO₂ plot has been used for the plume age determination. The background mixing ratio of 4.5 ppbv, due to photochemical production prior to the emission of the urban plume near sunset, has been subtracted from the HNO₃ data for clarity of presentation. The SO₂ 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 O₃. The resulting expression for the plume age is as follows.

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

Here k is the rate coefficient for reaction of NO₂ with O₃, \bar{O}_3 is the average O₃ concentration during the evolution of the plume (i.e., the average of the O₃ 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 NO₃ loss and 2 for dominant N₂O₅ loss (or during the approach to steady state) to account for the consumption of 2xNO₂ from formation and hydrolysis of N₂O₅ [Brown *et al.*, 2004].

3. O_x Budgets

[7] Figure 2 illustrates the case of irreversible nocturnal O_x loss due to HNO₃ formation after NO_x emission from a power plant plume (indicated by large SO₂ and little to no CO enhancement). This plume resulted from a relatively concentrated NO_x point source, and it shows the relationships between NO₂, O₃ and HNO₃ clearly. Analysis of multiple smaller NO_x plumes show similar results. The initial (i.e., at the plume edges, where NO₂ is relatively dilute) slope of O₃ vs. NO₂ ($m = -1.65$) indicates conversion of O_x to NO₃ and N₂O₅ and a plume age of ~3 hours. Inclusion of NO₃ and N₂O₅ in O_x, i.e., O₃ vs. NO₂ + 2NO₃ + 3N₂O₅, increases this initial slope only slightly. Inclusion of O_x loss to HNO₃, i.e., O₃ vs. NO₂ + 2NO₃ + 3N₂O₅ +

1.5HNO₃, 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 O₃, NO₂ and HNO₃ account for all of the O_x. Second, the O_x budget closure occurs at a ratio of 1.5 HNO₃ formed per O_x lost, indicating N₂O₅ hydrolysis as the mechanism. The determination of nearly exclusive loss of O_x to HNO₃ is consistent with our recent analysis that showed rapid N₂O₅ loss rates over Pennsylvania and Ohio on 9 August due to a large sulfate aerosol loading and, consequently, efficient heterogeneous uptake coefficients for N₂O₅ (with subsequent release of HNO₃ 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 HNO₃ 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 O₃ vs. NO₂ plot ($m = -2.1$) yields a plume age of approximately 6 hours. In this case, the contribution of NO₃ and N₂O₅ closes the O_x budget (i.e., $m = -1$), with a minimal contribution of O_x loss to HNO₃ 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 NO₃ and N₂O₅. Conservation of O_x downwind of New York City is again consistent with our previous analysis that showed immeasurably small heterogeneous uptake coefficients for N₂O₅ 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-O₃ plume (modest CO and smaller SO₂ enhancements) from the 11 August flight, sampled 25 minutes prior to local sunrise over southern New Hampshire. The steep O₃ vs. NO₂ 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 O₃-HNO₃ 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 O₃ 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 O₃ vs. NO₂ + 2NO₃ + 3N₂O₅ + 1.5HNO₃ (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 NO₃ 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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