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

Steven S. Brown  
*National Oceanic and Atmospheric Administration*

J. A. Neuman  
*National Oceanic and Atmospheric Administration*

T. B. Ryerson  
*National Oceanic and Atmospheric Administration*

M. Trainer  
*National Oceanic and Atmospheric Administration*

W. P. Dubé  
*National Oceanic and Atmospheric Administration*

*See next page for additional authors*

Follow this and additional works at: [https://scholars.fhsu.edu/chemistry_facpubs](https://scholars.fhsu.edu/chemistry_facpubs)

Part of the *Chemistry Commons*

**Recommended Citation**


This Article is brought to you for free and open access by the Chemistry at FHSU Scholars Repository. It has been accepted for inclusion in Chemistry Faculty Publications by an authorized administrator of FHSU Scholars Repository. For more information, please contact ScholarsRepository@fhsu.edu.
Nocturnal odd-oxygen budget and its implications for ozone loss in the lower troposphere

S. S. Brown,1 J. A. Neuman,1,2 T. B. Ryerson,1 M. Trainer,1 W. P. Dubé,1,2 J. S. Holloway,1,2 C. Warneke,1,2 J. A. de Gouw,1,2 S. G. Donnelly,3 E. Atlas,4 B. Matthew,1,2 A. M. Middlebrook,1 R. Peltier,5 R. J. Weber,5 A. Stohl,6 J. F. Meagher,1 F. C. Fehsenfeld,1 and A. R. Ravishankara1,7

Received 30 January 2006; revised 27 February 2006; accepted 20 March 2006; published 18 April 2006.

[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 NOx (=NO + NO2) environments. Nocturnal tropospheric odd oxygen (Ox), defined as O3 + NO2 + 2NO + 3N2O5, is used to assess the impact of NOx emissions on nocturnal O3 loss. Recent aircraft measurements of the components of Ox and HNO3 yield a detailed accounting of the nocturnal Ox 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 NOx emissions, hydrocarbon and aerosol loading, seasonality and atmospheric mixing, govern the impact of NOx emissions on regional-scale air quality.


1. Introduction

[2] Tropospheric ozone (O3) is produced during the day from photochemical cycling of nitrogen oxides (NOx = 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 Ox [Wöed et al., 2005; Jacob et al., 1996; Liu, 1977].

\[ \text{O}_x(\text{nocturnal}) = \text{O}_3 + \text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5 \]  

The stoichiometric coefficients represent the number of Oₓ stored in each compound. Chemical Oₓ 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].

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O(het)} \rightarrow 2\text{HNO}_3 \]  

Each HNO3 thus produced is equivalent to the loss of 1.5 Oₓ [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 result in a net loss of 1–2 Oₓ per NO3 reacted, depending upon the reaction pathway [Atkinson and Arey, 2003; Geyer et al., 2003]. Conservation of nocturnal Oₓ 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, NOx [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, speculated VOC and aerosol composition. Based on nocturnal measurements of the compounds in equation (1) and HNO3, we present a budget for nocturnal Ox and examine its loss and/or transport overnight.

2. Nocturnal NOx 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
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 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 emitted [Ryerson et al., 2001; Trainer et al., 1993]. The negatively-correlated lobe results from nocturnal NO$_2$ emission and subsequent oxidation to HNO$_3$ with concurrent O$_3$ destruction.

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; NO$_2$ + 2NO$_3$ + 3N$_2$O$_5$, or the sum of O$_x$ contained in the nocturnal nitrogen oxide reservoir; and NO$_2$ + 2NO$_3$ + 3N$_2$O$_5$ + 1.5HNO$_3$, which includes O$_3$ loss to HNO$_3$ in the stoichiometric ratio that results from N$_2$O$_5$ 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 $-1 \pm 0.1$ 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.

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 (h3 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.

\[ t_{\text{plume}} \approx \frac{\ln(1 - S(m + 1))}{SkO_3} \]  

Here \( k \) is the rate coefficient for reaction of NO₂ with O₃, \( \overline{O_3} \) 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 \( 2 \times \text{NO}_2 \) from formation and hydrolysis of \( \text{N}_2\text{O}_5 \) [Brown et al., 2004].

3. O₃ Budgets

[7] Figure 2 illustrates the case of irreversible nocturnal O₃ loss due to HNO₃ formation after NO₂ emission from a power plant plume (indicated by large SO₂ and little to no CO enhancement). This plume resulted from a relatively concentrated NOₓ point source, and it shows the relationships between NO₂, O₃ and HNO₃ clearly. Analysis of multiple smaller NOₓ 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 O₃ to NO₃ and N₂O₅ and a plume age of \(~3\) hours. Inclusion of NO of \( +2\text{NO}_2 + 3\text{N}_2\text{O}_5 \), increases this initial slope only slightly. Inclusion of O₃ loss to HNO₃, i.e., O₃ vs. NO₂ + 2NO₂ + 3N₂O₅ + 1.5HNO₃, yields \( m = -1 \), or a closed O₃ 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 O₃. Second, the O₃ budget closure occurs at a ratio of 1.5 HNO₃ formed per O₃ lost, indicating N₂O₃ hydrolysis as the mechanism. The determination of nearly exclusive loss of O₃ 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 O₃ 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 O₃ to HNO₃ formation in the course of a 10-hour night.

[8] Figure 4 shows the contrasting case of O₃ 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 O₃ budget (i.e., \( m = -1 \)), with a minimal contribution of O₃ loss to HNO₃ despite the increased plume age. The time series of nocturnal O₃ 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 O₃ as NO₂ and N₂O₅. Conservation of O₃ 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 NOₓ-NOₓ 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 NOₓ 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 NOₓ 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 O₂ relative to the background at the end of the night. Nitric acid accounted for only about 2/3 of the lost O₃ as shown by the slope of \( m = -1.6 \) for O₃ vs. NO₂ + 2NO₂ + 3N₂O₅ + 1.5HNO₃ (again, measured aerosol nitrate was negligible). The lack of closure in the budget for the lost O₃ 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\textsubscript{x}, organic nitrates containing 2O\textsubscript{x} or HNO\textsubscript{3}, also containing 2O\textsubscript{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\textsubscript{3} production, resulting only from slower NO\textsubscript{3} reactions with aldehydes or alkanes, should be small by comparison. Loss of HNO\textsubscript{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\textsubscript{3} loss via heterogeneous reactions, which has been invoked previously to explain O\textsubscript{3} loss in lofted NO\textsubscript{3}-containing plumes [Berkowitz et al., 2001], appears the least likely explanation for the O\textsubscript{3} loss in Figure 4 based on the preceding discussion.

Regardless of the O\textsubscript{3} loss mechanism, the nocturnally aged New York plume shows that O\textsubscript{3} loss can be large within urban plumes in which N\textsubscript{2}O\textsubscript{5} hydrolysis and NO\textsubscript{3} reactions are rapid. This contrasts sharply with daytime NO\textsubscript{3} processing; photochemical oxidation of tens of ppb of NO\textsubscript{x} to HNO\textsubscript{3} in a VOC-rich urban plume could be expected to produce several times this much O\textsubscript{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\textsubscript{3} enhancements with a positive correlation to HNO\textsubscript{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\textsubscript{3} loss. The timing of NO\textsubscript{3} emission is therefore a crucial factor that substantially influences sources and sinks for O\textsubscript{3} in polluted environments.

4. Conclusions

The contrast between the behavior of NO\textsubscript{x} plumes emitted at night and during the day highlights several factors that influence net O\textsubscript{3} concentrations resulting from anthropogenic NO\textsubscript{x} emissions. The first, and most obvious, is emission timing: NO\textsubscript{x} emitted at night has a markedly different impact on O\textsubscript{3} pollution than does NO\textsubscript{x} emitted during the day. The second is aerosol particles, whose amount and composition influences nocturnal O\textsubscript{3} loss through the heterogeneous hydrolysis of N\textsubscript{2}O\textsubscript{5}. The third is the role of hydrocarbons. Reactive VOC are required to drive photochemical NO\textsubscript{x}-catalyzed O\textsubscript{3} production, but can also enhance nocturnal O\textsubscript{3} loss via reactions of NO\textsubscript{3} [Winer et al., 1984]. The fourth is the seasonal dependence of the NO\textsubscript{3}-O\textsubscript{3} interaction. In summer, O\textsubscript{3} exceedences in polluted regions are frequent. During winter, shorter day lengths and reduced actinic flux decrease photochemical O\textsubscript{3} production but increase nocturnal O\textsubscript{3} loss; reactive biogenic VOC emissions are reduced; and colder temperatures enhance the role of aerosol by shifting the NO\textsubscript{3}-N\textsubscript{2}O\textsubscript{5} equilibrium toward N\textsubscript{2}O\textsubscript{5} and the gas-particle equilibrium from HNO\textsubscript{3} to particulate nitrate [Calvert et al., 1985]. The final factor is the coupling between diurnal meteorology and NO\textsubscript{x}-O\textsubscript{3} chemistry. Nocturnal stratification of the lower atmosphere decouples NO\textsubscript{x} from sources that emit above the nocturnal boundary layer (e.g., power plant stacks) from the surface until the following day. Nocturnal NO\textsubscript{x} from urban sources is trapped within the boundary layer and affects surface O\textsubscript{3} throughout the night [Gusten et al., 1998; Stutz et al., 2004; Talbot et al., 2005].

As a consequence of these processes, total NO\textsubscript{x} emissions and/or NO\textsubscript{x} emissions per unit power generated from different sources are not the only indicators of the O\textsubscript{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\textsubscript{x} emissions) and nocturnal atmospheric stratification, influence the effectiveness of O\textsubscript{3} mitigation policies based on NO\textsubscript{x} control.

References

Berkowitz, C. M., et al. (2001), Aircraft observations of aerosols, O\textsubscript{3} and NO\textsubscript{x} in a nighttime urban plume, Atmos. Environ., 35, 2395–2404.
Dentener, F. J., and P. J. Crutzen (1993), Reaction of N\textsubscript{2}O\textsubscript{5} on tropospheric aerosols: Impact on the global distributions of NO\textsubscript{x}, O\textsubscript{3} and OH, J. Geophys. Res., 98, 7149–7163.
Dubé, W. P., et al. (2006), An aircraft instrument for simultaneous, in-situ measurements of NO\textsubscript{x} and N\textsubscript{2}O\textsubscript{5} via cavity ring-down spectroscopy, Rev. Sci. Instrum., in press.
Liu, S. C. (1977), Possible effects on tropospheric O\textsubscript{3} and OH due to NO\textsubscript{x} emissions, Geophys. Res. Lett., 4, 325–329.
Platt, U., et al. (1990), Peroxy radicals from night-time reactions of NO\textsubscript{x} with organic compounds, Nature, 348, 147–149.
Stutz, J., B. Aliche, R. Ackermann, A. Geyer, A. White, and E. Williams (2004), Vertical profiles of NO\textsubscript{x}, N\textsubscript{2}O\textsubscript{5}, O\textsubscript{3} and NO\textsubscript{x} in the nocturnal boundary layer: 1. Observations during the Texas Air Quality Study 2000, J. Geophys. Res., 109, D12306, doi:10.1029/2003JD004209.
Wood, E. C., et al. (2005), Measurements of NO₂, NO₂, and O₃ east of the

---

E. Atlas, Division of Marine and Atmospheric Chemistry, Rosenstiel
School of Marine and Atmospheric Science, University of Miami, 4600
Rickenbacker Causeway, Miami, FL 33149, USA.
S. S. Brown, J. A. de Gouw, W. P. Dubé, F. C. Fehsenfeld, J. S.
Holloway, B. Matthew, J. F. Meagher, A. M. Middlebrook, J. A. Neuman,
A. R. Ravishankara, T. B. Ryerson, M. Trainer, and C. Warneke, Chemical
Sciences Division, NOAA Earth System Research Laboratory, 325
Broadway, Boulder, CO 80305, USA. (steven.s.brown@noaa.gov)
S. G. Donnelly, Department of Chemistry, Fort Hays State University,
Hays, KS 67601, USA.
R. Peltier and R. J. Weber, School of Earth and Atmospheric Sciences,
Georgia Institute of Technology, Atlanta, GA 30332, USA.
A. Stohl, Norsk Institut for Luftforskning, P.O. Box 100, N-2027 Kjeller,
Norway.