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


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 + 2NO3 + 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 [Wóodo et al., 2005; Jacob et al., 1996; Liu, 1977].

\[ \text{O}_x(\text{nocturnal}) = \text{O}_3 + \text{NO}_2 + 2\text{NO}_3 + 3\text{N}_2\text{O}_5 \] (1)

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].

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

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 Ox 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, speciated 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 O₃/ppbv HNO₃ due to the previous day’s NOₓ emissions. The positive correlation results from simultaneous photochemical O₃ production and photochemical oxidation of NO₂ to HNO₃, and the slopes are approximate upper limits to the amount of O₃ produced per unit NOₓ emitted [Ryerson et al., 2001; Trainer et al., 1993]. The negatively-correlated lobe results from nocturnal NOₓ emission and subsequent oxidation to HNO₃ with concurrent O₃ destruction. 

[5] Figures 2–4 show a series of plots of O₃ against three different stoichiometric sums of nitrogen oxide species measured in specific NOₓ plumes encountered on these two flights. The three sums are: NOₓ alone; NOₓ + 2NOₓ + 3NO₂O₃, or the sum of Oₓ contained in the nocturnal nitrogen oxide reservoir; and NOₓ + 2NOₓ + 3NO₂O₃ + 1.5HNO₃, which includes Oₓ loss to HNO₃ in the stoichiometric ratio that results from N₂O₅ hydrolysis. This analysis assumes negligible surface deposition of O₃ and HNO₃ in lofted plumes that are essentially decoupled from the shallow nocturnal boundary layer, and that NOₓ emission occurs exclusively as NO₂, which oxidizes rapidly to NO₂ in excess Oₓ. Nocturnal plumes that still contained NO exhibited a slope of −1 ± 0.1 in plots of O₃ vs. NO₂. The O₃ vs. NO₂ plots in Figures 2–4 show slopes steeper than m = −1, indicating that further reaction of NO₂ with O₃ had occurred.

[6] The slope, m, of a plot of O₃ vs. NO₂ for plumes emitted and sampled at night is an approximate measure of the plume age. Subsequent to the more rapid oxidation of NO to NO₂ in excess Oₓ, ozone and NO₂ 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 NOₓ is small...
Figure 4. Same as previous, but for an aged urban plume (9 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.

3. $O_3$ Budgets

Figure 2 illustrates the case of irreversible nocturnal $O_3$ loss due to HNO$_3$ formation after NO$_2$ 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 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 $O_3$ to NO$_2$ and N$_2$O$_5$ and a plume age of ~3 hours. Inclusion of NO$_3$ and N$_2$O$_5$ in $O_3$, i.e., $O_3$ vs. NO$_2$ + 2NO$_3$ + 3N$_2$O$_5$, increases this initial slope only slightly. Inclusion of $O_3$ loss to HNO$_3$, i.e., $O_3$ vs. NO$_2$ + 2NO$_3$ + 3N$_2$O$_5$ + 1.5HNO$_3$, yields $m = -1$, or a closed $O_3$ 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 $O_3$. Second, the $O_3$ budget closure occurs at a ratio of 1.5 HNO$_3$ formed per $O_3$ lost, indicating N$_2$O$_5$ hydrolysis as the mechanism. The determination of nearly exclusive loss of $O_3$ to HNO$_3$ is consistent with our recent analysis that showed rapid N$_2$O$_5$ loss rates over Pennsylvania and Ohio on 9 August due to a large sulfate aerosol loading and, consequently, efficient heterogeneous uptake coefficients for N$_2$O$_5$ (with subsequent release of HNO$_3$ to the gas phase) [Brown et al., 2006]. The time series of $O_3$ 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 $O_3$ to HNO$_3$ formation in the course of a 10-hour night.

Figure 3 shows the contrasting case of $O_3$ 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$_2$O$_5$ closes the $O_3$ budget (i.e., $m = -1$), with a minimal contribution of $O_3$ loss to HNO$_3$ despite the increased plume age. The time series of nocturnal $O_3$ 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 $O_3$ and N$_2$O$_5$. Conservation of $O_3$ downwind of New York City is again consistent with our previous analysis that showed immeasurably small heterogeneous uptake coefficients for N$_2$O$_5$ in this region in the early morning of 10 August [Brown et al., 2006].

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 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 $O_3$ emissions from urban sources in a shallow nocturnal boundary layer (~200 m) below the aircraft cruising altitude (500–2500 m) over the continent.
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{x} reactions with aldehydes or alkenes, 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{x}-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.

[11] 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{x} processing: photochemical oxidation of tens of ppb of NO\textsubscript{x} to HNO\textsubscript{3} in a VOC-rich urban plume could be expected 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{x} emission is therefore a crucial factor that substantially influences sources and sinks for O\textsubscript{3} in polluted environments.

4. Conclusions

[12] 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{x} [Winer et al., 1984]. The fourth is the seasonal dependence of the NO\textsubscript{x}-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].

[13] 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.

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