Ozone production in the upper troposphere and the influence of aircraft during SONEX: approach of NO x -saturated conditions

The Harvard community has made this article openly available. Please share how this access benefits you. Your story matters

Citation

Published Version
doi:10.1029/1999GL900451

Citable link
http://nrs.harvard.edu/urn-3:HUL.InstRepos:14117808

Terms of Use
This article was downloaded from Harvard University’s DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA
Ozone production in the upper troposphere and the influence of aircraft during SONEX: Approach of NOx-saturated conditions

L. Jaeglé,1 D.J. Jacob,1 W.H. Brune,2 I.C. Faloona,2 D. Tan,2 Y. Kondo,3 G.W. Sachse,4 B. Anderson,4 G.L. Gregory,4 S. Vay,1 H.B. Singh,5 D.R. Blake,6 R. Shetter7

Abstract. During October/November 1997, simultaneous observations of NO, HO2, and other species were obtained as part of the SONEX campaign in the upper troposphere. We use these observations, over the North Atlantic (40-60°N), to derive ozone production rates, P(O3), and to examine the relationship between P(O3) and the concentrations of NOx (= NO + NO2) and HOx (= OH + peroxy) radicals. A positive correlation is found between P(O3) and NOx over the entire data set, which reflects the association of elevated HO2 with elevated NOx injected by deep convection and lightning. By filtering out this association we find that for NOx<70 pptv, P(O3) is nearly independent of NOx, showing the approach of NOx-saturated conditions. Predicted doubling of aircraft emissions in the future will result in less than doubling of the aircraft contribution to ozone over the North Atlantic in the fall. Greater sensitivity to aircraft emissions would be expected in the summer.

Introduction

In recent years, considerable attention has been given to the potential role of aircraft emissions of nitrogen oxides (NOx = NO + NO2) on the concentration of upper tropospheric ozone, an effective greenhouse gas [NASA, 1997]. Ozone is produced in the troposphere by the photochemical oxidation of CO and hydrocarbons which is catalyzed by NOx radicals and hydrogen oxide radicals (HOx = OH + peroxy). Oxidation of CO dominates in the upper troposphere, and the rate-limiting step for ozone production is the reaction of HO2 with NO (R2):

\[
\text{CO} + \text{OH} (\text{+} \text{O}_3) \rightarrow \text{CO}_2 + \text{H}_2 \text{O} \quad \text{(R1)}
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad \text{(R2)}
\]

\[
\text{NO}_2 + \text{hv} (\text{+} \text{O}_3) \rightarrow \text{NO} + \text{O}_3 \quad \text{(R3)}
\]

The sensitivity of the ozone production rate, P(O3), to increasing NOx is critical to the assessment of aircraft effects. Photochemical models [e.g., Brasseur et al., 1996] predict that P(O3) should increase with increasing NOx (NOx-limited regime) up to a turnover point of a few hundred pptv NOx, beyond which further increases in NOx cause P(O3) to decrease (NOx-saturated regime). These two regimes result from the dual role of NOx in regulating the chemistry of HOx radicals. On the one hand, NOx drives the ozone production cycle (R1)-(R3). On the other hand, NOx promotes the removal of HO2 through reactions of OH with HO2, HNO4, and NO2 [Wennberg et al., 1998]. The chemical regime for ozone production is largely determined by the relative magnitudes of the sources of HO2 and NOx [Jaeglé et al., 1998].

Ozone production rates in the upper troposphere have been previously determined from simultaneous measurements of HO2 and NO during three recent aircraft campaigns: ASHOE/MAESA, STRAT and SUCCESS [Folkins et al., 1997; Wennberg et al., 1998; Brune et al., 1998; Jaeglé et al., 1998]. Examination of the P(O3) versus NOx relationships indicated a much greater prevalence for NOx-limited conditions than expected from models [Folkins et al., 1997; Jaeglé et al., 1998]. However, as we will see, interpretation of this relationship in terms of the chemical regime for ozone production can be biased by a commonality of sources for NOx and HO2.

We present here the first direct evidence of NOx-saturated conditions for ozone production in the upper troposphere and show that a simple interpretation of the observed P(O3) versus NOx relationship as a partial derivative \( \partial P(O_3)/\partial NO_x \) overestimates the actual sensitivity of ozone concentrations to emissions from aircraft. We use concurrent observations of HO2 and NO obtained during the Subsonic assessment: Ozone and NOx Experiment (SONEX) DC-8 aircraft campaign. SONEX took place in October and November 1997 in the North Atlantic flight corridor, a region of dense aircraft traffic in the upper troposphere [Singh et al., this issue]. Companion papers use the SONEX data to improve our understanding of the chemistry and sources of NOx [Kondo et al., this issue; Thompson et al., this issue], and HO2 [Brune et al., this issue].

Calculation of ozone production

Singh et al. [this issue] describe the flight tracks and the instruments aboard the DC-8 aircraft during SONEX. We focus here on observations made in the upper troposphere (8-12 km) between 40 and 60°N latitude, the main theater of operations. We exclude observations made in clouds (diagnosed by an abundance of particles larger than 3 µm), in fresh aircraft exhaust plumes (short duration peaks of elevated NOx and condensation nuclei), at high solar zenith angles (>80°), and in air masses with stratospheric influence (O3>90 ppbv and CH4<1760 ppbv).

We define the budget of ozone as that of the odd-oxygen family, O3 (O3=O3 + O + O(1D) + NO2 + HNO3 + HNO2 + 2NO2 + 3N2O5), to account for rapid chemical cycling within this family. Ozone typically accounts for over 99% of O3, so the budgets of ozone and O3 can be viewed as equivalent. In addition to reaction (R2), ozone can be produced by the reaction of organic peroxy radicals, RO2, with NO:

\[
\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 . \quad \text{(R4)}
\]

Ozone chemical loss is almost exclusively due to:

\[
\text{O}_3 + \text{HO}_2 \rightarrow \text{OH} + 2 \text{O}_2 \quad \text{(R5)}
\]

\[
\text{O}_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2 \quad \text{(R6)}
\]

\[
\text{O} + (\text{D}) + \text{H}_2 \text{O} \rightarrow 2 \text{OH} \quad \text{(R7)}
\]

\[
\text{N}_2 \text{O}_5 + \text{aerosols} \rightarrow 2 \text{HNO}_3 . \quad \text{(R8)}
\]

The ozone production and loss rates, P(O3) and L(O3), can thus be expressed as:

\[
P(O_3) = k_o [\text{HO}_2][\text{NO}] + k_o [\text{RO}_2][\text{NO}] \quad \text{(1)}
\]
\[ L(O_3) = k_3[O_3][HO_2] + k_4[O_3][OH] + k_5[O(1D)][H_2O] + k_6[N_2O_5]. \]

where \( k_i \) is the rate constant for reaction \( (R_i) \), and \( k_4 \) is weighted over the different RO_2 radicals contributing to ozone production. In the above expressions, we neglect the role of HNO_3+OH, which is a minor source of ozone (as per our definition of the O_x chemical family).

We use equations (1) and (2) with 1-minute averages of concurrent observations of NO, HO_2, OH, H_2O, O_3, UV actinic flux, aerosol surface area, temperature and pressure, to calculate instantaneous values of \( P(O_3) \) and \( L(O_3) \) along the flight tracks of the DC-8. For species which are not observed (RO_2, O(1D), N_2O_5) we use calculations from a diel steady state model [Jaeglé et al., 1998] constrained with local observations of O_3, H_2O, NO, HNO_3, PAN, acetone, CO, CH_4, C_2H_6, C_3H_8, C_4 alkanes, UV actinic flux, aerosol surface area, temperature and pressure. The resulting instantaneous \( P(O_3) \) and \( L(O_3) \) rates are then scaled to 24-hour average values by using local results from the diel steady state model:

\[ \langle \text{Rate}_{\text{obs}} \rangle_{24h} = \text{Rate}_{\text{obs}}(t) \times \frac{\langle \text{Rate}_{\text{model}} \rangle_{24h}}{\text{Rate}_{\text{model}}(t)}. \]

\[ \frac{\partial P(O_3)}{\partial NO_x} = 0. \]

A more detailed description of the model as applied to SONEX observations can be found in Jaeglé et al. [Photochemistry of HO_x in the upper troposphere at northern midlatitudes, submitted to J. Geophys. Res., 1999, hereafter referred to as J99].

### Relationships between NO_x, HO_x, and ozone production

Figure 1a shows the relationship between the 24-hour average values of \( P(O_3) \) derived from observed HO_2 and NO, and the local NO_x concentrations in the upper troposphere (8-12 km) between 40\(^\circ\)N and 60\(^\circ\)N latitude. The calculated median \( P(O_3) \) for SONEX was 0.57 ppbv/day. The median \( L(O_3) \) was 0.13 ppbv/day (not shown here), resulting in a net ozone production of 0.44 ppbv/day. Reaction of NO with HO_2 dominates ozone production; reaction (R4) contributes on average less than 15% of the total \( P(O_3) \). Reactions of O_3 with HO_2 and OH contribute more than 80% of \( L(O_3) \), while reactions (R7) and (R8) contribute 10% and 5% respectively.

The line in Figure 1a shows the expected dependence of ozone production on NO_x for diel steady state model calculations where model input variables are specified from median background conditions observed during SONEX at 10 km [J99]: 55 ppbv O_3, 120 ppbv H_2O, 120 pptv HNO_3, 64 pptv PAN, 510 pptv acetone, 90 ppbv CO, 1761 ppbv CH_4, 670 pptv C_2H_6, 79 pptv C_3H_8, 55...
pptv C<sub>3</sub> alkanes, 50°N latitude, 285 DU ozone column, 8 μm<sup>2</sup>cm<sup>-3</sup> aerosol surface area, 227 K temperature, on November 1. In the model, P(O<sub>3</sub>) becomes relatively independent of NO<sub>x</sub> above 70 pptv; and the turnover to the NO<sub>x</sub>-saturated regime (∂P(O<sub>3</sub>)/∂NO<sub>x</sub>=0) takes place at 300 pptv. The bulk of the observations (NO<sub>x</sub>&lt;300 pptv) shows indeed a leveling off of the dependence of P(O<sub>3</sub>) on NO<sub>x</sub> as NO<sub>x</sub> increases above 70 pptv, in accordance with the expected behavior. However, for the highest NO<sub>x</sub> concentrations, the values of P(O<sub>3</sub>) computed from observed HO<sub>2</sub> and NO continue to increase with increasing NO<sub>x</sub>, suggesting a consistently NO<sub>x</sub>-limited regime which is at odds with model results.

The largest NO<sub>x</sub> concentrations (&gt;300 pptv) shown in Figure 1 correspond to relatively fresh convective outflows sampled close to the U.S. East coast [Thompson et al., this issue]. Elevated NO<sub>x</sub>/NO<sub>y</sub> ratios (&gt;0.5 mol/mol), backtrajectory calculations and satellite lightning imagery all support a strong source of NO<sub>x</sub> from lightning associated with this convection [Pickering et al., 1999]. These air masses were also characterized by an enhanced HO<sub>x</sub> source resulting from convective transport of surface air with elevated concentrations of HO<sub>x</sub> precursors such as peroxides and CH<sub>2</sub>O [Jaeglé et al., 1999]. Based on (1), comparison between observed and modeled P(O<sub>3</sub>) for a given NO<sub>x</sub> concentration is roughly equivalent to comparison of observed and modeled HO<sub>2</sub> concentrations. We see from Figure 1b that the model constrained with background conditions for SONEX underestimates HO<sub>2</sub> by a factor of two or more when NO<sub>x</sub>&gt;300 pptv. Using the locally observed concentrations of HO<sub>x</sub> precursors (H<sub>2</sub>O, acetone, peroxides and CH<sub>2</sub>O) for these high-NO<sub>x</sub> points improves the agreement but still comes short of the observed levels. The discrepancy suggests the presence of other unmeasured sources, such as higher aldehydes, possibly also resulting from convection [Müller and Brasseur, 1999]. It could also reflect flaws in our understanding of HO<sub>x</sub> chemistry in the high-NO<sub>x</sub> regime [Falloon et al., 1999], or other unknown HO<sub>x</sub> sources [Chatfield et al., 1999]. For the remaining observations (NO<sub>x</sub>&lt;300 pptv), the dependence of HO<sub>2</sub> and OH on NO<sub>x</sub> is generally well reproduced (Fig. 1b and 1c). The scatter around the model lines in Figure 1 can be explained by variations in the magnitude of the local HO<sub>x</sub> sources [Jaeglé et al., 1998].

In models of the upper troposphere, P(O<sub>3</sub>) is largely determined by two variables: NO<sub>x</sub> mixing ratios and the strength of the primary HO<sub>x</sub> source, P(HO<sub>x</sub>) [Jaeglé et al., 1998]. Figure 2 shows the variations of P(O<sub>3</sub>) as a function of NO<sub>x</sub> and P(HO<sub>x</sub>). We separate primary sources (i.e. sources independent of HO<sub>x</sub>) from secondary sources (i.e. sources dependent on a preexisting pool of HO<sub>x</sub>), and define the primary HO<sub>x</sub> source as:

\[ P(HO_x) = 2k_1[H(O)] + J_{acet}n_{acet}[Acetone] + \sum_{i} J_{x_i} n_{x_i}[X_i] \]  

where \(J_{acet}\) and \(n_{acet}\) are the photolysis rate constant and HO<sub>x</sub> yield for acetone, and \(J_{x_i}\) and \(n_{x_i}\) are the photolysis rate constants and HO<sub>x</sub> yields for other convected HO<sub>x</sub> precursors such as peroxides and aldehydes (see Müller and Brasseur [1999] for this definition of the primary HO<sub>x</sub> source). The value of \(n_{acet}\) is about three [Singh et al., 1995]. Methane oxidation by OH, and the subsequent photolysis of CH<sub>2</sub>O was an important HO<sub>x</sub> source during SONEX [Jaeglé et al., 1999]. We do not include this source in our definition of P(HO<sub>x</sub>) because it is a secondary HO<sub>x</sub> source.

In Figure 2a, we calculate P(HO<sub>x</sub>) based on the observed H<sub>2</sub>O and acetone. P(HO<sub>x</sub>) is averaged over 24 hours using (3). In Figure 2b, in addition to H<sub>2</sub>O and acetone, we include an additional HO<sub>x</sub> source (\(\sum n_{x_i}[X_i]\)) as required to match the observed HO<sub>x</sub> concentrations. This source might include contributions from convected peroxides and aldehydes, which we cannot easily quantify from our model. Its impact on P(HO<sub>x</sub>) is small (less than 50%) except for observations in continental convective outflows with elevated NO<sub>x</sub> (15% of the points in Figure 2b). As seen in Figure 2, model calculations of P(O<sub>3</sub>) for median background SONEX conditions with varying NO<sub>x</sub> and P(HO<sub>x</sub>) (contour lines) generally reproduce the observations (square symbols).

**Chemical regime for ozone production**

To diagnose the actual dependence of P(O<sub>3</sub>) on NO<sub>x</sub> in the SONEX observations, the additional sensitivity to P(HO<sub>x</sub>) must be resolved. We therefore examined the dependence of P(O<sub>3</sub>) on NO<sub>x</sub> for similar primary HO<sub>x</sub> production rates. Figure 3 illustrates this
dependence for three ranges of P(HO$_3$). The P(HO$_3$) values used to segregate the observations are those required in order to match the observed HO$_2$ (Fig. 2b). Choosing instead the P(HO$_3$) values computed from H$_2$O and acetone only (Fig. 2a) results in some small differences in Figure 3c.

Figure 3 shows that P(O$_3$) derived from observations increases nearly linearly with NO$_x$ for NO$_x$<70 pptv. In Figures 3a and 3b, P(O$_3$) shows very little dependence on NO$_x$ between 70 pptv and 300 pptv, approaching the NO$_x$-saturated regime. The bin with the highest levels of P(HO$_3$) (Fig. 3c), shows a positive dependence of P(O$_3$) on NO$_x$ extending to a higher NO$_x$ concentration (200 pptv) but there is still clear evidence of NO$_x$-saturated conditions beyond this. The median NO$_x$ mixing ratio was 93 pptv in the upper troposphere (8-12 km) during SONEX, and the median P(HO$_3$) was 50 pptv/day. These conditions correspond to a regime where ozone production is less sensitive to changes in NO$_x$.

Because of the slow photochemistry in October-November and the elevated levels of NO$_x$, the conditions during SONEX allowed extensive sampling of the transition region between the NO$_x$-limited and NO$_x$-saturated regimes as illustrated in Figure 3. Previous aircraft campaigns (ASHOE/MAESA, STRAT, SUCCESS), where ozone production was consistently NO$_x$-limited, featured lower NO$_x$ concentrations and more active photochemistry. In the tropical upper troposphere during STRAT, NO$_x$ mixing ratios were generally less than 100 pptv [Wennberg et al., 1998]. Over the central United States during SUCCESS, springtime conditions resulted in more rapid photochemistry compared to SONEX and thus a higher transition from NO$_x$-limited to NO$_x$-saturated regimes (NO$_x$<500 pptv) [Jaeglé et al., 1998].

Delineation of the regimes for ozone production is critical when assessing the effect of aircraft emissions. Aircraft, unlike deep convection and lightning, inject NO$_x$ into the upper troposphere without injecting HO$_x$ precursors (the aircraft sources of H$_2$O and HONO are negligibly small [NASA, 1997]). As summarized in Singh et al. [this issue], aircraft emissions might have contributed 20-70% of the observed NO$_x$ in the upper troposphere during SONEX. A 40% aircraft effect corresponds to a 37 pptv contribution to the median observed NO$_x$ concentration of 93 pptv. Based on the dependence shown in Figure 3b, and assuming a SONEX median value for P(HO$_3$) of 50 pptv/day, such a NO$_x$ increase results in an increase of P(O$_3$) from 0.45 to 0.6 ppbv/day. For a 2-week residence time of air in the upper troposphere at midlatitudes, these conditions correspond to a regime where ozone production is less sensitive to changes in NO$_x$.

A further doubling of NO$_x$ concentrations due to future aircraft emissions (NO$_x$>93 pptv) would only result in an additional 0.1 ppbv/day ozone production under SONEX conditions (northern midlatitudes in the fall) because of the NO$_x$-saturated regime. However, if the primary source of HO$_x$ were to rise in the future, P(O$_3$) would become more sensitive to increases in NO$_x$ from aircraft emissions. As noted above, during summer the transition to NO$_x$-saturated regime occurs at higher levels of NO$_x$, and thus increases in aircraft emissions should continue to result in O$_3$ increases in the foreseeable future [NASA, 1997].

Conclusions

We computed ozone production rates P(O$_3$) in the upper troposphere at northern midlatitudes, using simultaneous observations of HO$_3$ and NO during SONEX (October-November 1997). High levels of NO$_x$ due to lightning and convection were associated with high concentrations of HO$_x$ precursors also supplied by convection. The observed correlation between elevated NO$_x$ and HO$_x$ sources resulted in a positive relationship between P(O$_3$) and NO$_x$ extending over the full range of NO$_x$ concentrations observed (up to 1 ppbv). By segregating the data according to the primary HO$_x$ production rate, P(HO$_3$), we find that ozone production in fact approached NO$_x$-saturated conditions for NO$_x$ concentrations larger than 70 pptv. This result implies little sensitivity of P(O$_3$) to future increases in NO$_x$ emissions from aircraft (which unlike convective injection are not associated with a large source of HO$_x$) during the fall at northern midlatitudes. A greater sensitivity of P(O$_3$) to NO$_x$ would be expected under summer conditions.

Acknowledgments. This work was supported by the Subsonic Assessment Program (SASS) of the National Aeronautics and Space Administration (NASA).

References


D. Blake, Department of Chemistry, University of California, Irvine, CA 92717.

W. Brune, I. Faloona, D. Tan, Pennsylvania State University, Department of Meteorology, University Park, PA 16802.

D. Jacob, L. Jaeglé (corresponding author), Division of Engineering and Applied Sciences, and Department of Earth and Planetary Sciences, Harvard University, 29 Oxford Street, Pierce Hall, Cambridge, MA 02138. (e-mail: lj@io.harvard.edu)

Y. Kondo, Solar Terrestrial Environment Laboratory, Nagoya University, Japan.


R. Shetter, National Center for Atmospheric Research, Boulder, CO 80307.

H. Singh, NASA Ames Research Center, Moffett Field, CA 94035. (Received March 8, 1999; revised May 13, 1999; accepted May 14, 1999)