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Ozone production in the upper troposphere and the influence of aircraft during SONEX: Approach of NOx-saturated conditions


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 (40-60ºN), 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 HOx 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 hydroxyl (OH) radicals. Oxidation of CO dominates in the upper troposphere, and the rate-limiting step for ozone production is the reaction of HOx with NO (R2):

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

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

\[ \text{NO}_2 + \text{hv} (+ \text{O}_3) \rightarrow \text{NO} + \text{O}_3 \] (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, O3 promotes the removal of HOx 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 HOx and NOx [Jaeglé et al., 1998].

Ozone production rates in the upper troposphere have been previously determined from simultaneous measurements of HO2 and NO obtained during three recent aircraft campaigns: ASHOLE/MASEA, STRAT and SUCCESS [Folkins et al., 1997; Wennberg et al., 1998; Brune 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 HOx.

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 \( \partial P(O_3)/\partial NOx \) overestimates the actual sensitivity of ozone concentrations to emissions from aircraft. We use concurrent observations of HO2 and NOx 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 HOx [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 60ºN 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 (>80º), and in air masses with stratospheric influence (O3>90 ppbv and CH4<760 ppbv).

We define the budget of ozone as that of the odd-oxygen family, \( O_3-O+O+O(D)+NO_2+HNO_4+HNO_3+2NO_2+3N_2O_5 \), to account for rapid chemical cycling within this family. Ozone typically accounts for over 99% of \( O_3 \), so the budgets of ozone and \( O_3 \) can be viewed as equivalent. In addition to reaction (R2), ozone can be produced by the reaction of organic peroxy radicals, RO2, with NO:

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

Ozone chemical loss is almost exclusively due to:

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

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

\[ \text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2 \text{OH} \] (R7)

\[ \text{N}_2\text{O}_5 + \text{aerosols} \rightarrow 2 \text{HNO}_3 \] (R8)
The ozone production and loss rates, \( P(O_3) \) and \( L(O_3) \), can thus be expressed as:

\[
P(O_3) = k_2[HO_2][NO] + k_4[RO_2][NO] \tag{1}
\]

\[
L(O_3) = k_3[O_3][HO_2] + k_4[RO_2][OH] + k_6[O(1D)][H_2O] + k_7[N_2O_5] \tag{2}
\]

where \( k_i \) is the rate constant for reaction \( (R_i) \), and \( k_4 \) is weighted over the different RO2 radicals contributing to ozone production. In the above expressions, we neglect the role of HNO3+OH, which is a minor source of ozone (as per our definition of the OX chemical family).

We use equations (1) and (2) with 1-minute averages of concurrent observations of NO, HO2, OH, H2O, O3, 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 (RO2, O(1D), N2O5) we use calculations from a diel steady state model [Jaeglé et al., 1998] constrained with local observations of O3, H2O, NO, HNO3, PAN, acetone, CO, CH4, C2H6, C3H8, C4 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:

\[
<\text{Rate}_{\text{obs}}\rangle_{24h} = \text{Rate}_{\text{obs}}(t) \times \frac{<\text{Rate}_{\text{model}}\rangle_{24h}}{\text{Rate}_{\text{model}}(t)} \tag{3}
\]

Figure 1. Observed ozone production rates \( P(O_3) \), and concentrations of HO2 and OH in SONEX (8-12 km altitude, 40-60°N latitude) plotted as a function of the NOx concentration (NOx = observed NO + modeled NO2). The observed rates and concentrations are averaged over 24 hours, using diel factors obtained from a locally constrained photochemical model. The lines on the three panels correspond to model-calculated values for median upper tropospheric background conditions during SONEX (see text).

Figure 2. Ozone production rate \( P(O_3) \) (ppbv/day) in SONEX as a function of NOx mixing ratio and the primary HOx source, \( P(HOx) \), in the upper troposphere (8-12 km). The contour lines correspond to model calculations of 24-hour average \( P(O_3) \) for background conditions during SONEX. Values of \( P(O_3) \) computed from observed NO and HO2 and scaled to 24-hour averages (see Figure 1) are shown as. In panel a, the values of \( P(HOx) \) corresponding to the observed \( P(O_3) \) are calculated using the observed concentrations of H2O and acetone. In panel b, \( P(HOx) \) was increased in order to match the observations of HO2 where required (see text). The dashed line corresponds to \( \partial P(O_3)/\partial NOx=0 \).

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

 Relationships between NOx, HOx, and ozone production

Figure 1a shows the relationship between the 24-hour average values of \( P(O_3) \) derived from observed HO2 and NO, and the local NOx concentrations in the upper troposphere (8-12 km) between 40°N and 60°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 HO2 dominates ozone production; reaction \( (R4) \) contributes on average less than 15% of the total \( P(O_3) \). Reactions of O3 with HO2 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 NOx, 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 O3, 120 pptv H2O, 120 pptv HNO3, 64 pptv PAN, 510 pptv acetone, 90 pptv CO, 1761 ppmv CH4, 670 pptv C2H6, 79 pptv C3H8, 55 pptv C5 alkanes, 50‰ latitude, 285 DU ozone column, 8 µm3 aerosol surface area, 227 K temperature, on November 1. In the model, PO3 becomes relatively independent of NOx above 70 pptv; and the turnover to the NO2-saturated regime (∂PO3/∂NOx=0) takes place at 300 pptv. The bulk of the observations (NOx<300 pptv) shows indeed a leveling off of the dependence of PO3 on NOX as NOX increases above 70 pptv, in accordance with the expected behavior. However, for the highest NOX concentrations, the values of PO3 computed from observed HO2 and NO continue to increase with increasing NOX, suggesting a consistently NOX-limited regime which is at odds with model results.

The largest NOX concentrations (>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 NOX/NOy ratios (>0.5 mol/mol), backtrajectory calculations and satellite lightning imagery all support a strong source of NOX from lightning associated with this convection [Pickering et al., 1999]. These air masses were also characterized by an enhanced HO2 source resulting from convective transport of surface air with elevated concentrations of HO2 precursors such as peroxides and CH3O [J99]. Based on (1), comparison between observed and modeled PO3 for a given NOX concentration is roughly equivalent to comparison of observed and modeled HO2 concentrations. We see from Figure 1b that the model constrained with background conditions for SONEX underestimates HO2 by a factor of two or more when NOX>300 pptv. Using the locally observed concentrations of HOX precursors (H2O, acetone, peroxides and CH3O) for these high-NOX 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 HOX chemistry in the high-NOX regime [Chatfield et al., 1999]. For the remaining observations (NOX<300 pptv), the dependence of HO2 and OH on NOX 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 HOX sources [J99].

In models of the upper troposphere, PO3 is largely determined by two variables: NOX mixing ratios and the strength of the primary HOX source, PO3 [Jaegle et al., 1998]. Figure 2 shows the variations of PO3 as a function of NOX and PO3. We separate primary sources (i.e. sources independent of HOX) from secondary sources (i.e. sources dependent on a preexisting pool of HOX) and define the primary HOX source as:

\[
P(\text{HOX}) = 2k_i[\text{O(1D)}][\text{H}_2\text{O}] + \sum_j y_{\text{acce}}[\text{Acetone}] + \sum_j y_{\text{alde}}[\text{Aldehydes}],
\]

where J_{\text{acce}} and y_{\text{acce}} are the photolysis rate constant and HOX yield for acetone, and J_{\text{alde}} and y_{\text{alde}} are the photolysis rate constants and HOX yields for other convected HOX precursors such as peroxides and aldehydes (see Müller and Brasseur [1999] for this definition of the primary HOX source). The value of y_{\text{acce}} is about three [Singh et al., 1995]. Methane oxidation by OH, and the subsequent photolysis of CH3O was an important HOX source during SONEX [J99]. We do not include this source in our definition of P(\text{HOX}) because it is a secondary HOX source.

In Figure 2a, we calculate P(\text{HOX}) based on the observed H2O and acetone. P(\text{HOX}) is averaged over 24 hours using (3). In Figure 2b, in addition to H2O and acetone, we include an additional HOX source (\sum_j y_{\text{alde}}[\text{Aldehydes}]) as required to match the observed HOX concentrations. This source might include contributions from convected peroxides and aldehydes, which we cannot easily quantify from our model. Its impact on P(\text{HOX}) is small (less than 50%) except for observations in continental convective outflows with elevated NOX (15% of the points in Figure 2b). As seen in Figure 2, model calculations of P(\text{HOX}) for median background SONEX conditions with varying NOX and P(\text{HOX}) (contour lines) generally reproduce the observations (square symbols).

The primary HOX source in the SONEX data displays large variations, with 24-hour average values ranging from 10 pptv/day to 700 pptv/day (Fig. 2). Elevated P(\text{HOX}) values (200-700 pptv/day) are sometimes associated with low NOX concentrations (<30-40 pptv). These air masses were influenced by recent marine convection and high concentrations of water vapor; despite the enhanced source of HOX, the low levels of NOX result in relatively low P(\text{HOX}) (0.1-0.5 ppbv/day). Elevated P(\text{HOX}) is also found in association with high NOX concentrations (>300 pptv). As noted above, the elevated NOX was the result of recent lightning and convection, and concurrent enhancement of P(\text{HOX}) would be expected from the convective injection of HOX precursors. The positive correlation between high NOX and P(\text{HOX}) in the observations is particularly apparent in Figure 2b, but can also be seen in Figure 2a. This correlation results in the highest levels of P(\text{HOX}) observed. By supplying HOX precursors together with NOX, deep convection extends the NOX-limited regime to higher concentrations of NOX.

**Chemical regime for ozone production**

To diagnose the actual dependence of PO3 on NOX in the SONEX observations, the additional sensitivity to P(\text{HOX}) must be resolved. We therefore examined the dependence of PO3 on NOX for similar primary HOX production rates. Figure 3 illustrates this dependence for three ranges of P(\text{HOX}). The P(\text{HOX}) values used to segregate the observations are those required in order to match the observed HO2 (Fig. 2b). Choosing
instead the P(HOx) values computed from H2O and acetone only (Fig. 2a) results in some small differences in Figure 3c.

Figure 3 shows that P(O3) derived from observations increases nearly linearly with NOx for NOx<70 pptv. In Figures 3a and 3b, P(O3) shows very little dependence on NOx between 70 pptv and 300 pptv, approaching the NOx-saturated regime. The bin with the highest levels of P(HOx) (Fig. 3c), shows a positive dependence of P(O3) on NOx extending to a higher NOx concentration (200 pptv) but there is still clear evidence of NOx-saturated conditions beyond this. The median NOx mixing ratio was 93 pptv in the upper troposphere (8-12 km) during SONEX, and the median P(HOx) was 50 pptv/day. These conditions correspond to a regime where ozone production is less sensitive to changes in NOx.

Because of the slow photochemistry in October-November and the elevated levels of NOx, the conditions during SONEX allowed extensive sampling of the transition region between the NOx-limited and NOx-saturated regimes as illustrated in Figure 3. Previous aircraft campaigns (ASHOE/MAESA, STRAT, SUCCESS), where ozone production was consistently NOx-limited, featured lower NOx concentrations and more active photochemistry. In the tropical upper troposphere during STRAT, NOx 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 NOx-limited to NOx-saturated regimes (NOx~500 pptv) [Jaegle 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 NOx into the upper troposphere without injecting HOx precursors (the aircraft sources of H2O 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 NOx in the upper troposphere during SONEX. A 40% aircraft effect corresponds to a 37 pptv contribution to the median observed NOx concentration of 93 pptv. Based on the dependence shown in Figure 3b, and assuming a SONEX median value for P(HOx) of 50 pptv/day, such a NOx increase results in an increase of P(O3) from 0.45 to 0.6 ppbv/day. For a 2-week residence time of air in the upper troposphere at midlatitudes, this increase of 0.15 ppbv/day adds about 2.1 ppbv of ozone, resulting in a 4% increase in upper tropospheric ozone in the north Atlantic flight corridor in the fall. For a larger range of P(HOx) values (20-100 pptv/day), the increase in ozone is 2-6%.

A further doubling of NOx concentrations due to future aircraft emissions (NOx=93+37 pptv) would only result in an additional 0.1 ppbv/day ozone production under SONEX conditions (northern midlatitudes in the fall) because of the NOx-saturated regime. However, if the primary source of HOx were to rise in the future, P(O3) would become more sensitive to increases in NOx from aircraft emissions. As noted above, during summer the transition to NOx-saturated regime occurs at higher levels of NOx, and thus increases in aircraft emissions should continue to result in O3 increases in the foreseeable future [NASA, 1997].

Conclusions

We computed ozone production rates P(O3) in the upper troposphere at northern midlatitudes, using simultaneous observations of HOx and NO during SONEX (October-November 1997). High levels of NOx due to lightning and convection were associated with high concentrations of HOx precursors also supplied by convection. The observed correlation between elevated NOx and HOx sources resulted in a positive relationship between P(O3) and NOx extending over the full range of NOx concentrations observed (up to 1 ppbv). By segregating the data according to the primary HOx production rate, P(HOx), we find that ozone production in fact approached NOx-saturated conditions for NOx concentrations larger than 70 pptv. This result implies little sensitivity of P(O3) to future increases in NOx emissions from aircraft (which unlike convective injection are not associated with a large source of HOx) during the fall at northern midlatitudes. A greater sensitivity of P(O3) to NOx would be expected under summer conditions.

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References


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