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OH, HO₂, and NO in two biomass burning plumes: Sources of HO_x and implications for ozone production

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Abstract. The ER-2 made two descents through upper tropospheric biomass burning plumes during ASHOE/MAESA. HO_x (= OH + HO₂) concentrations are largely self-limited outside the plumes, but become progressively more limited by reactions with NO_x (= NO + NO₂) at the higher NO_x concentrations inside the plumes. Sources of HO_x in addition to H₂O and CH₄ oxidation are required to balance the known HO_x sinks both in the plumes and in the background upper troposphere. HO_x concentrations were consistently underestimated by a model constrained by observed NO_x concentrations. The size of the model underestimate is reduced when acetone photolysis is included. Models which do not include the additional HO_x sources required to balance the HO_x budget are likely to underestimate ozone production rates.

1. Introduction

Ozone is produced in the troposphere by the oxidation of hydrocarbons in the presence of NO_x and HO_x. Tropical deep convection can inject ozone precursors such as NO, CO, and other hydrocarbons from biomass burning into the upper troposphere [Thompson *et al.*, 1996, Pickering *et al.*, 1996, Folkins *et al.*, 1997]. However the way in which the short lived HO_x radicals respond to these elevated NO_x and hydrocarbon concentrations has not yet been characterized. This is due to the lack, until recently, of upper tropospheric HO_x measurements. This letter discusses OH and HO₂ measurements within and outside two plumes encountered during the 1994 ASHOE/MAESA campaign.

The sources and sinks of HO_x, in standard CH₄ - HO_x - NO_x chemistry, can be grouped as follows,

$$L_{HO_x}(HO_2 + OH) = -2k_1[OH][HO_2]$$

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$$L_{HO_x}(H_2O_2) = -2k_2[HO_2][HO_2] + 2J_{H_2O_2}[H_2O_2]$$

$$L_{HO_x}(HNO_3) = -k_3[OH][NO_2] - k_4[OH][HNO_3] \\ + J_{HNO_3}[HNO_3]$$

$$L_{HO_x}(HNO_4) = -k_5[HO_2][NO_2] + J_{HNO_4}[HNO_4] \\ - k_6[OH][HNO_4]$$

$$P_{HO_x}(O^1D + H_2O) = 2k_7[O^1D][H_2O]$$

$$P_{HO_x}(CH_4) = -k_8[OH][CH_4] + k_9[O^1D][CH_4] \\ + k_{10}[CH_3O_2][NO] + 2J_{CH_2O}[CH_2O] - k_{11}[HO_2][CH_2O] \\ - k_{12}[HO_2][CH_3O_2] + 2J_{CH_3OOH}[CH_3OOH] \\ - 0.7k_{13}[OH][CH_3OOH]$$

It is assumed that the reaction of OH with HNO₄ does not produce a HO_x species. J_{CH_2O} refers to the photolysis of CH₂O into H and HCO. The reaction of OH with CH₃OOH is assumed to produce CH₃O₂ with a yield of 70 percent [DeMore *et al.*, 1994].

2. October 23 Descent into Fiji

Figure 1 shows OH, HO₂ [Wennberg *et al.*, 1997], and NO [Fahey *et al.* 1989] during a portion of the October 23 ER-2 descent into Fiji. Temperature and N₂O variations during the descent indicate that the tropopause occurred near 17 km. The NO enhancement of up to 350 pptv between 14 and 16 km coincided with enhancements in NO_y, CO, and O₃. We have previously argued that this layer probably originated from biomass burning in Southeast Asia [Folkins *et al.*, 1997].

The above sources and sinks of HO_x are plotted in the top panel of Figure 2. They were calculated only if, in addition to the OH, HO₂, and NO measurements shown in Figure 1, there also existed simultaneous measurements of NO_y, H₂O, and O₃. H₂O₂, HNO₄, O¹D, NO₂, CH₃O₂, CH₃OOH, and CH₂O were estimated using instantaneous steady state (ISS) approximations. The nitric acid concentration was set equal to $[HNO_3] = [NO_y] - [NO] - [NO_2] - [HNO_4]$. (This expression probably overestimates [HNO₃], since other

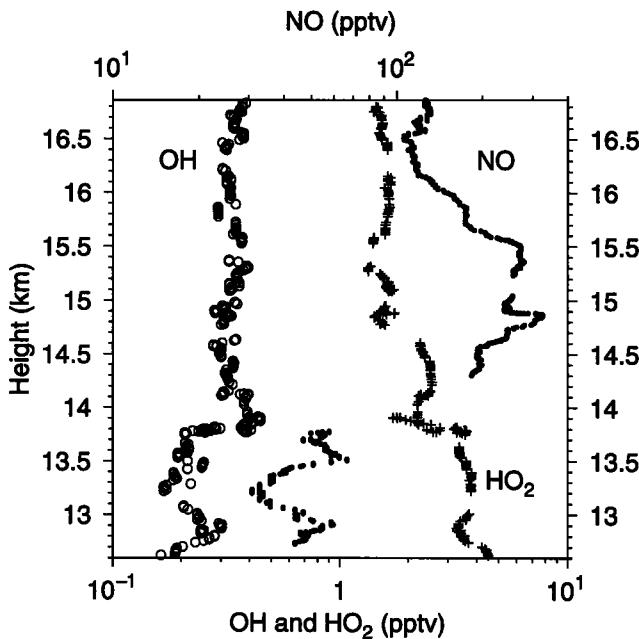


Figure 1. OH (open circles), HO₂ (crosses) and NO (closed circles) during part of the October 23 ER-2 descent into Fiji. The data have been smoothed with a 12 second median filter. The afternoon solar zenith angle was 64°. The pressure height was obtained from pressure using a scale height of 7 km.

reactive nitrogen compounds such as Peroxy Acetyl Nitrate (PAN) are likely to be present. However setting the concentration of HNO₃ equal to zero results in only a modest decrease in $L_{HO_x}(HNO_3)$, since the dominant term in this expression arises from the OH + NO₂ reaction. This is a characteristic of fresh plumes in which the NO_x/NO_y ratio is much higher than the steady state value.) CH₄ was fixed at 1.7 ppmv.

The top panel of Figure 2 shows that $P_{HO_x}(O^1D + H_2O)$, the dominant HO_x source in the lower troposphere, was always very small. This is partly because of the very low H₂O mixing ratios of the upper troposphere (≤ 10 ppmv in this portion of the descent). $L_{HO_x}(HO_2 + OH)$ is the largest HO_x sink in the background upper troposphere (NO ≤ 100 pptv). However $L_{HO_x}(HNO_3)$ increases rapidly with NO and becomes comparable with $L_{HO_x}(HO_2 + OH)$ at the largest NO mixing ratios. The growth of this term is due to increases in both NO₂ (as inferred from the ISS approximation) and OH (see Figure 1). In the process, HO_x concentrations undergo a transition from being self to NO_x limited.

It is clear from Figure 2 that the sum of the four HO_x sinks exceeds the sum of the two HO_x sources for all NO mixing ratios. This suggests that models based on CH₄ - HO_x - NO_x chemistry alone will underestimate HO_x concentrations in biomass burning plumes and in the background atmosphere. We confirm this through the use of a fixed NO_x diurnal steady state (DSS) model. In this approach, the concentration of

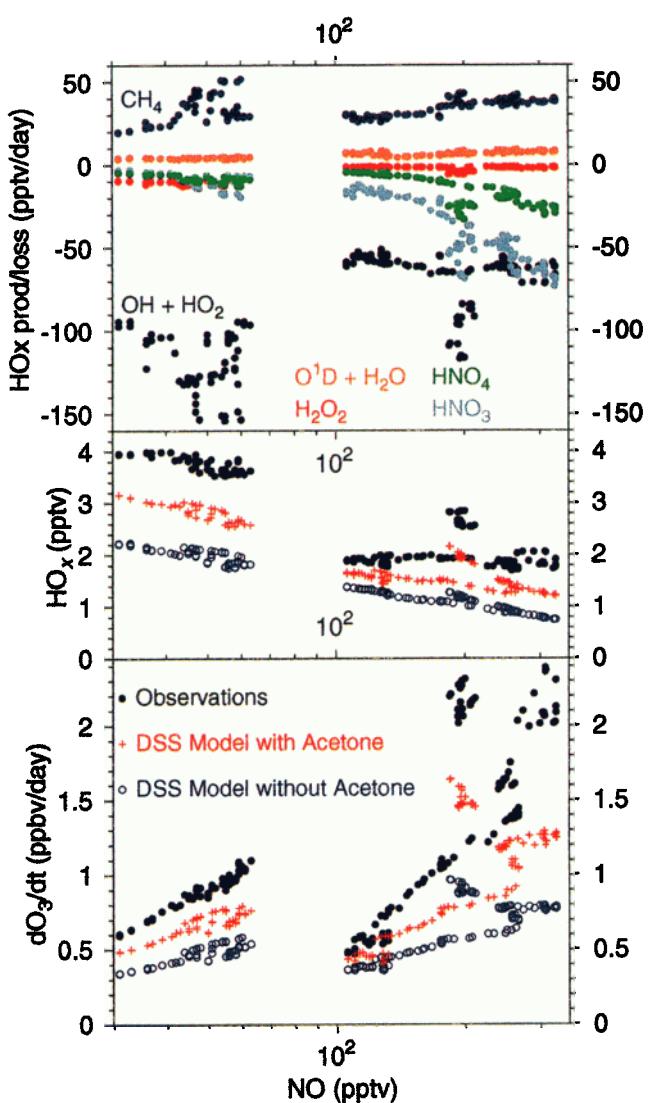


Figure 2. (top) HO_x sources and sinks, as defined in the text, from the altitude interval shown in Figure 1, plotted against NO. (middle) Observed HO_x (solid circles), HO_x from the DSS model with (red crosses), and without (open blue circles) acetone, plotted against NO. (bottom) dO_3/dt using observed HO_x (solid circles), and dO_3/dt from the DSS model with (red circles) and without (open blue circles) acetone, calculated using Equation (1).

NO_x is kept fixed over a diurnal cycle, and set equal to the sum of the observed NO concentration at the time of the measurement, plus the NO₂ concentration inferred from the standard ISS expression. The model is run until a steady state partitioning of the balance of NO_y is achieved, in this case 30 days. Photolysis rates during each diurnal cycle were calculated using the same method as used to get the rates on the ASHOE/MAESA CD. O₃, CO, NO_y, and H₂O were kept fixed at their observed mixing ratios. In one of the model runs, a fixed amount of acetone, based on a climatological correlation with CO [McKeen et al., 1997], was added. The photolysis of each acetone molecule was assumed to generate

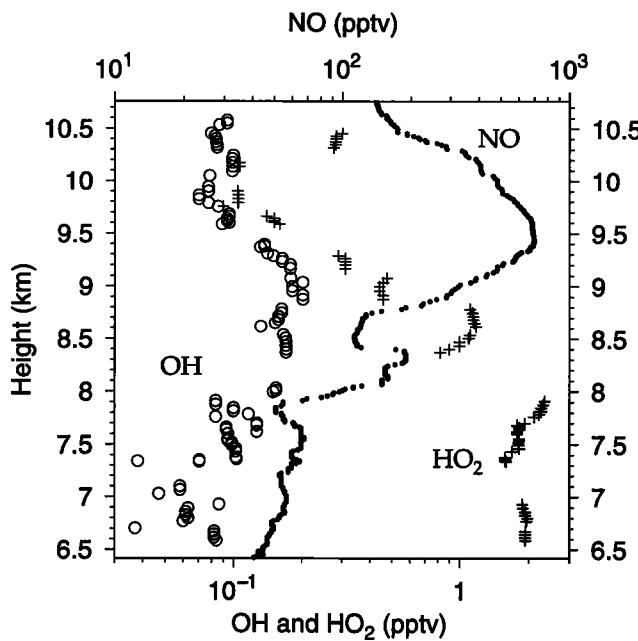


Figure 3. OH (open circles), HO₂ (crosses) and NO (closed circles) during part of the May 28 ER-2 descent into Christchurch. The solar zenith angle was 77°.

3.2 HO_x radicals [Singh *et al.*, 1995]. Acetone was not included in the other run, so that the dominant HO_x sources and sinks were those discussed above.

Observed HO_x mixing ratios are compared with those calculated by the DSS model in the middle panel of Figure 2. The DSS runs without acetone (shown in blue) underestimate observed HO_x mixing ratios by about 50 percent. The addition of acetone (shown in red) significantly reduces, but does not eliminate, this discrepancy.

The net rate of ozone production in the troposphere, provided the effects of non-methane hydrocarbons can be neglected, is usually written,

$$\begin{aligned} dO_3/dt = & k_{14}[NO][HO_2] + k_{10}[NO][CH_3O_2] \\ & -k_{15}[O_3][OH] - k_{16}[O_3][HO_2] \\ & -k_7[O(^1D)][H_2O]. \end{aligned} \quad (1)$$

Since the first term is usually dominant, models which underestimate HO_x are also likely to underestimate dO_3/dt . This is shown in the bottom panel of Figure 2. The solid circles denote dO_3/dt calculated using the observed mixing ratios of OH, HO₂, NO, H₂O, and O₃. The open blue circles and the red crosses denote dO_3/dt using the HO_x concentrations of the DSS model without and with acetone. Both versions of the DSS model significantly underestimate “observed” dO_3/dt .

The full impact of the needed HO_x sources on the ozone budget cannot be fully assessed until these sources are identified. For example, acetone oxidation produces ozone via reactions not represented in Equation (1). In addition, acetone oxidation in the presence of NO_x produces PAN, which will sequester NO_x and tend to suppress ozone production. Any HO_x source will reduce

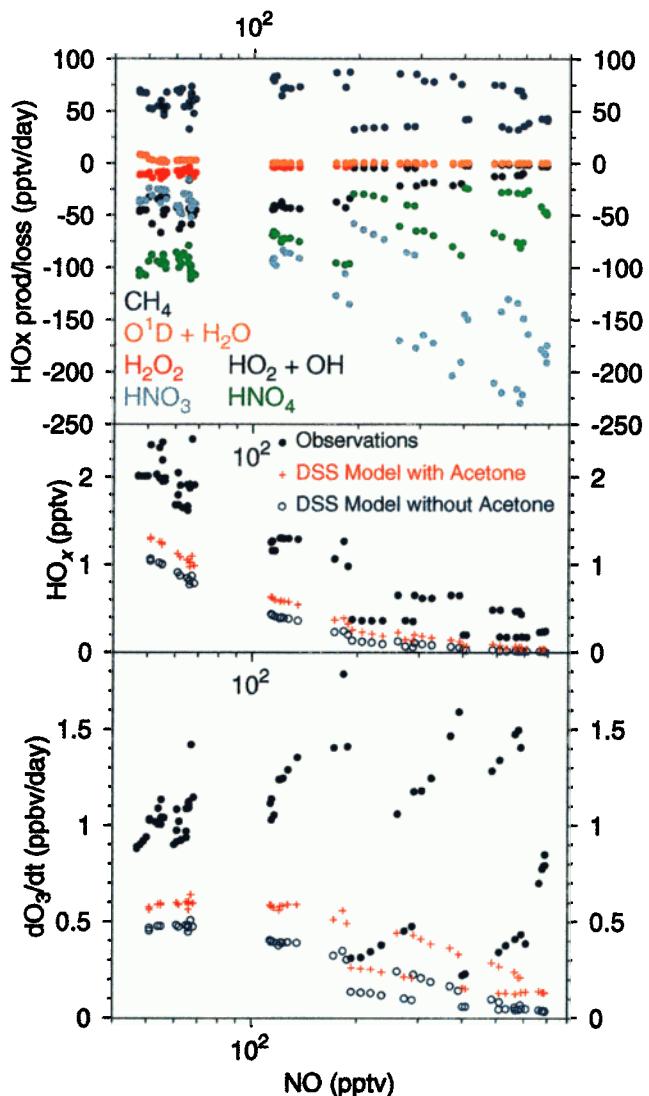


Figure 4. (top) HO_x sources and sinks, as defined in the text, from the altitude interval shown in Figure 3, plotted against NO. (middle) Observed HO_x (solid circles), and HO_x from the DSS model with (red crosses), and without (open blue circles) acetone plotted against NO. (bottom) dO_3/dt using observed HO_x (solid circles), and dO_3/dt from the DSS model with (red circles) and without (open blue circles) acetone, calculated using Equation (1).

NO_x by increasing the rate at which NO_x is converted to HNO₃ via the reaction of NO₂ with OH. The ozone production comparisons shown in Figure 2 refer only to the restricted reaction set given in Equation (1), and do not take into account time dependent effects of HO_x sources on NO_x concentrations.

3. May 28 Descent into Christchurch

The ER-2 encountered another upper tropospheric NO plume as it descended into Christchurch on May 28, 1994. Figure 3 shows the variation of OH, HO₂, and NO during a portion of this descent. The most likely origin

of the NO enhancement centered at 9.5 km is again biomass burning. An examination of isentropic back trajectories from this plume indicates that it originated twelve days earlier over southern Australia. This region was characterized by near drought conditions in May 1994 [Kousky, 1994]. (These trajectories were derived from National Meteorological Center temperatures and pressures using geostrophic balance).

The six terms in the HO_x budget were calculated using the same procedure discussed above, and plotted versus NO in the top panel of Figure 4. Since NO_y was not measured below 9.3 km, it was assumed to be 1000 pptv between 9.3 km and 8.0 km, and 500 pptv below 8.0 km. $L_{HO_x}(HNO_3)$ does not depend strongly on the NO_y mixing ratio within a realistic range of values. In contrast to Figure 2, $L_{HO_x}(HNO_4)$ is the largest HO_x sink in the background atmosphere. $L_{HO_x}(HNO_3)$ is the dominant HO_x sink in the plume, and as shown in the middle panel of Figure 4, increasingly suppresses HO_x at the larger NO mixing ratios. Both of the DSS models again underestimate observed HO_x. (Since CO was not measured it was assumed to have a constant mixing ratio of 80 ppbv. HO_x estimates were not sensitive to a realistic range about this value). "Observed" and model calculated ozone production rates are shown in the bottom panel of Figure 4. Both versions of the DSS model suggest that NO mixing ratios were sufficiently large near the center of the plume to suppress dO_3/dt . The fact that this did not occur again implies the existence of additional HO_x sources within the plume counterbalancing $L_{HO_x}(HNO_3)$.

4. Conclusions

Acetone is likely to be a significant HO_x source to the upper troposphere [Singh et al., 1995, McKeen et al., 1997, Wennberg et al., 1997]. HO_x concentrations may also be enhanced by the convective injection of peroxides into the upper troposphere [Chatfield et al., 1984, Jaeglé et al., 1997, Prather and Jacob, 1997]. This letter demonstrates that additional HO_x sources are also needed inside upper tropospheric biomass burning plumes. These HO_x sources may be associated with emissions from fires, or they may be introduced into the plume as it mixes with the background troposphere. Although definitive estimates of ozone production in biomass burning plumes cannot be made until these HO_x sources are accounted for, it is likely that they significantly increase ozone production rates.

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