

# OH, HO<sub>2</sub>, and NO in two biomass burning plumes: Sources of HO<sub>x</sub> 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<sub>x</sub> (= OH + HO<sub>2</sub>) concentrations are largely self-limited outside the plumes, but become progressively more limited by reactions with NO<sub>x</sub> (= NO + NO<sub>2</sub>) at the higher NO<sub>x</sub> concentrations inside the plumes. Sources of HO<sub>x</sub> in addition to H<sub>2</sub>O and CH<sub>4</sub> oxidation are required to balance the known HO<sub>x</sub> sinks both in the plumes and in the background upper troposphere. HO<sub>x</sub> concentrations were consistently underestimated by a model constrained by observed NO<sub>x</sub> concentrations. The size of the model underestimate is reduced when acetone photolysis is included. Models which do not include the additional HO<sub>x</sub> sources required to balance the HO<sub>x</sub> 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<sub>x</sub> and HO<sub>x</sub>. 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<sub>x</sub> radicals respond to these elevated NO<sub>x</sub> and hydrocarbon concentrations has not yet been characterized. This is due to the lack, until recently, of upper tropospheric HO<sub>x</sub> measurements. This letter discusses OH and HO<sub>2</sub> measurements within and outside two plumes encountered during the 1994 ASHOE/MAESA campaign.

The sources and sinks of HO<sub>x</sub>, in standard CH<sub>4</sub> - HO<sub>x</sub> - NO<sub>x</sub> chemistry, can be grouped as follows,

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

$$\begin{aligned} L_{HO_x}(H_2O_2) &= -2k_2[HO_2][HO_2] + 2J_{H_2O_2}[H_2O_2] \\ L_{HO_x}(HNO_3) &= -k_3[OH][NO_2] - k_4[OH][HNO_3] \\ &\quad + J_{HNO_3}[HNO_3] \\ L_{HO_x}(HNO_4) &= -k_5[HO_2][NO_2] + J_{HNO_4}[HNO_4] \\ &\quad - k_6[OH][HNO_4] \\ P_{HO_x}(O^1D + H_2O) &= 2k_7[O^1D][H_2O] \\ P_{HO_x}(CH_4) &= -k_8[OH][CH_4] + k_9[O^1D][CH_4] \\ &\quad + k_{10}[CH_3O_2][NO] + 2J_{CH_2O}[CH_2O] - k_{11}[HO_2][CH_2O] \\ &\quad - k_{12}[HO_2][CH_3O_2] + 2J_{CH_3OOH}[CH_3OOH] \\ &\quad - 0.7k_{13}[OH][CH_3OOH] \end{aligned}$$

It is assumed that the reaction of OH with HNO<sub>4</sub> does not produce a HO<sub>x</sub> species.  $J_{CH_2O}$  refers to the photolysis of CH<sub>2</sub>O into H and HCO. The reaction of OH with CH<sub>3</sub>OOH is assumed to produce CH<sub>3</sub>O<sub>2</sub> with a yield of 70 percent [DeMore *et al.*, 1994].

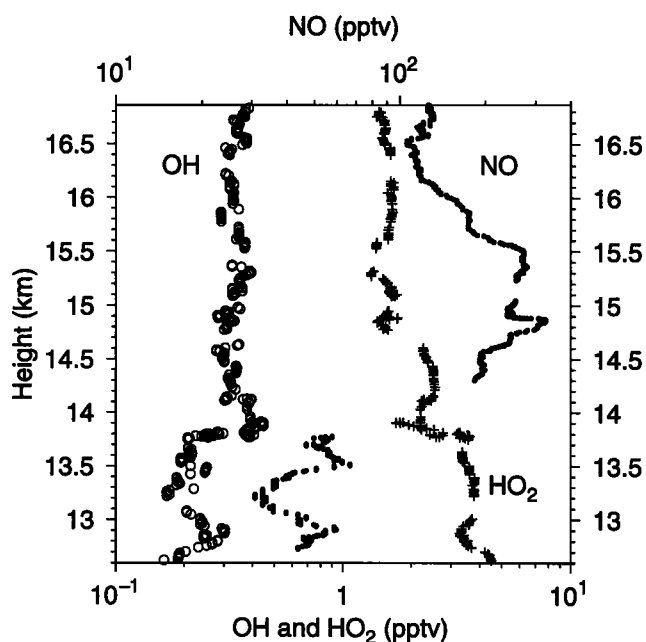
## 2. October 23 Descent into Fiji

Figure 1 shows OH, HO<sub>2</sub> [Wennberg *et al.*, 1997], and NO [Fahey *et al.* 1989] during a portion of the October 23 ER-2 descent into Fiji. Temperature and N<sub>2</sub>O 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<sub>y</sub>, CO, and O<sub>3</sub>. 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<sub>x</sub> are plotted in the top panel of Figure 2. They were calculated only if, in addition to the OH, HO<sub>2</sub>, and NO measurements shown in Figure 1, there also existed simultaneous measurements of NO<sub>y</sub>, H<sub>2</sub>O, and O<sub>3</sub>. H<sub>2</sub>O<sub>2</sub>, HNO<sub>4</sub>, O<sup>1</sup>D, NO<sub>2</sub>, CH<sub>3</sub>O<sub>2</sub>, CH<sub>3</sub>OOH, and CH<sub>2</sub>O 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 [HNO<sub>3</sub>], since other

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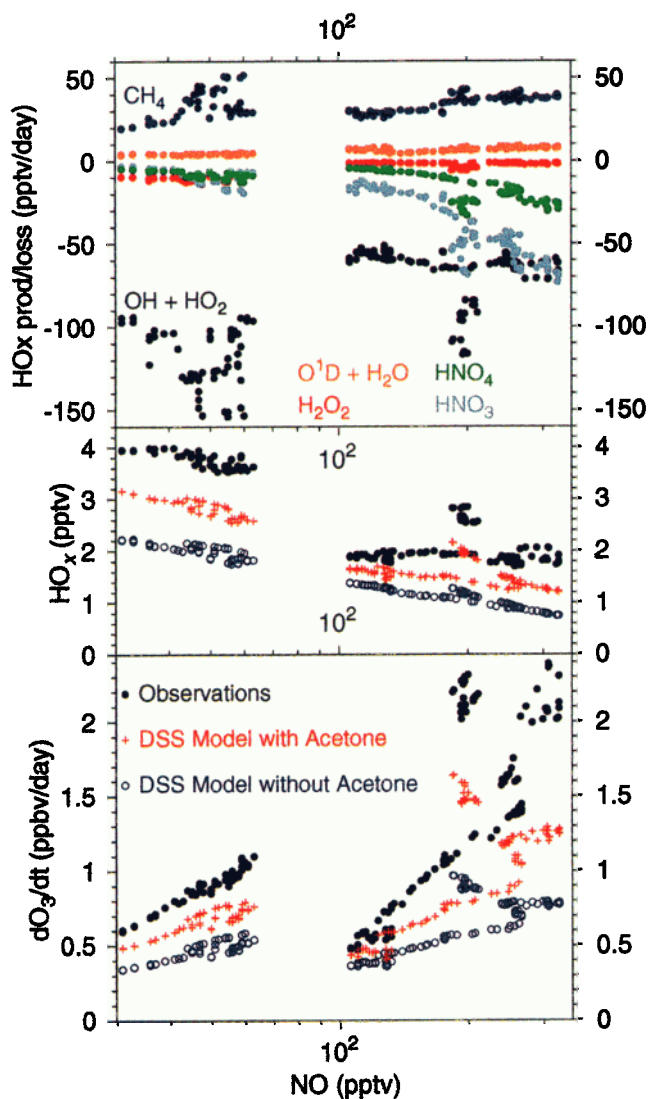


**Figure 1.** OH (open circles), HO<sub>2</sub> (crosses) and NO (closed circles) during part of the October 23 ER-2 descent into Fiji. The data have been smoothed with a 12 second median filter. The afternoon solar zenith angle was 64°. The pressure height was obtained from pressure using a scale height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

reactive nitrogen compounds such as Peroxy Acetyl Nitrate (PAN) are likely to be present. However setting the concentration of HNO<sub>3</sub> 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 + NO<sub>2</sub> reaction. This is a characteristic of fresh plumes in which the NO<sub>x</sub>/NO<sub>y</sub> ratio is much higher than the steady state value.) CH<sub>4</sub> was fixed at 1.7 ppmv.

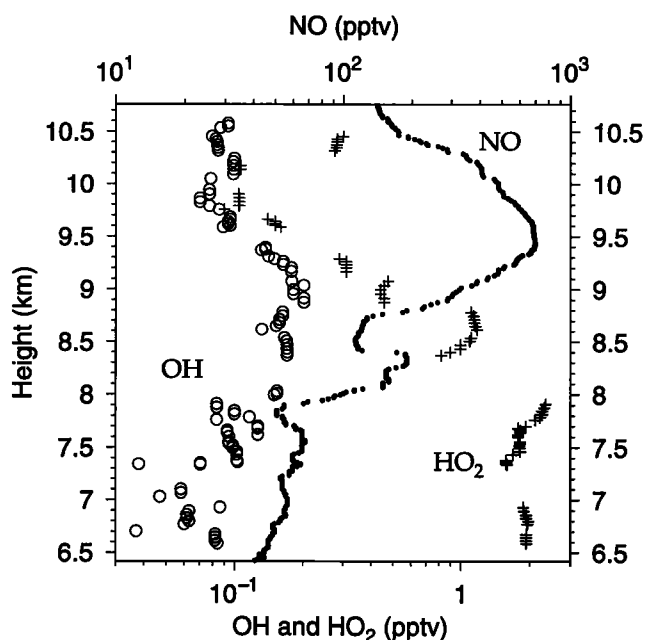
The top panel of Figure 2 shows that  $P_{HO_x}(O^1D + H_2O)$ , the dominant HO<sub>x</sub> source in the lower troposphere, was always very small. This is partly because of the very low H<sub>2</sub>O mixing ratios of the upper troposphere ( $\leq 10$  ppmv in this portion of the descent).  $L_{HO_x}(HO_2 + OH)$  is the largest HO<sub>x</sub> sink in the background upper troposphere (NO  $\leq 100$  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 NO<sub>2</sub> (as inferred from the ISS approximation) and OH (see Figure 1). In the process, HO<sub>x</sub> concentrations undergo a transition from being self to NO<sub>x</sub> limited.

It is clear from Figure 2 that the sum of the four HO<sub>x</sub> sinks exceeds the sum of the two HO<sub>x</sub> sources for all NO mixing ratios. This suggests that models based on CH<sub>4</sub> - HO<sub>x</sub> - NO<sub>x</sub> chemistry alone will underestimate HO<sub>x</sub> concentrations in biomass burning plumes and in the background atmosphere. We confirm this through the use of a fixed NO<sub>x</sub> diurnal steady state (DSS) model. In this approach, the concentration of



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

NO<sub>x</sub> 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 NO<sub>2</sub> concentration inferred from the standard ISS expression. The model is run until a steady state partitioning of the balance of NO<sub>y</sub> 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. O<sub>3</sub>, CO, NO<sub>y</sub>, and H<sub>2</sub>O 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), HO<sub>2</sub> (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<sub>x</sub> radicals [Singh *et al.*, 1995]. Acetone was not included in the other run, so that the dominant HO<sub>x</sub> sources and sinks were those discussed above.

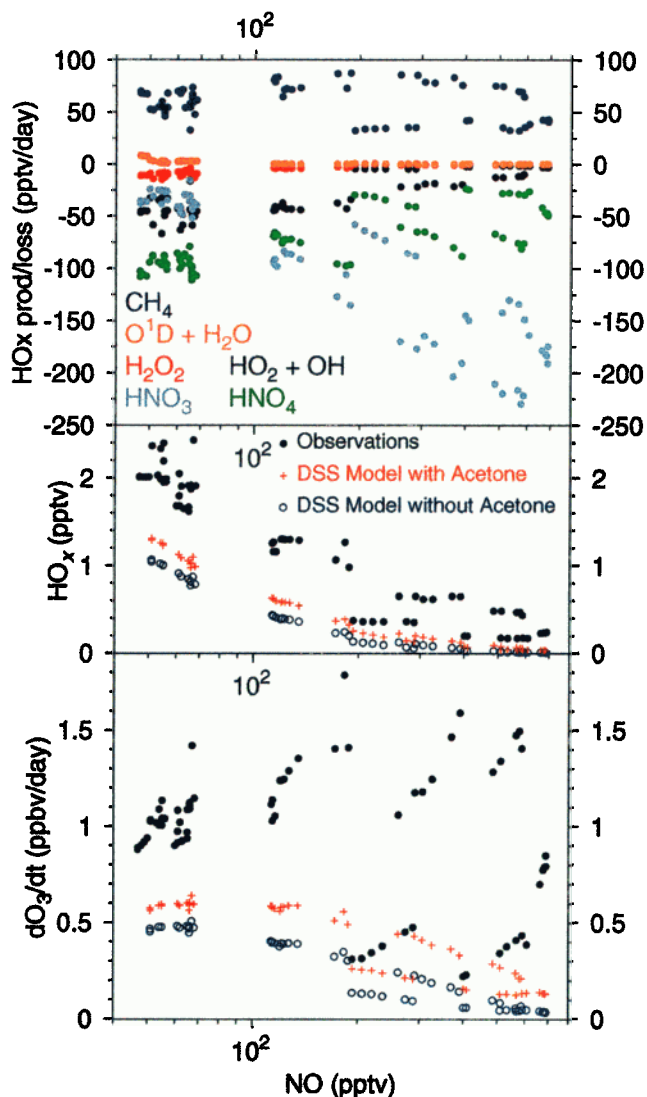
Observed HO<sub>x</sub> mixing ratios are compared with those calculated by the DSS model in the middle panel of Figure 2. The DSS runs without acetone (shown in blue) underestimate observed HO<sub>x</sub> mixing ratios by about 50 percent. The addition of acetone (shown in red) significantly reduces, 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<sub>x</sub> 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, HO<sub>2</sub>, NO, H<sub>2</sub>O, and O<sub>3</sub>. The open blue circles and the red crosses denote  $dO_3/dt$  using the HO<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> produces PAN, which will sequester NO<sub>x</sub> and tend to suppress ozone production. Any HO<sub>x</sub> source will reduce



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

NO<sub>x</sub> by increasing the rate at which NO<sub>x</sub> is converted to HNO<sub>3</sub> via the reaction of NO<sub>2</sub> 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<sub>x</sub> sources on NO<sub>x</sub> 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, HO<sub>2</sub>, 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<sub>x</sub> budget were calculated using the same procedure discussed above, and plotted versus NO in the top panel of Figure 4. Since NO<sub>y</sub> 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<sub>y</sub> mixing ratio within a realistic range of values. In contrast to Figure 2,  $L_{HO_x}(HNO_4)$  is the largest HO<sub>x</sub> sink in the background atmosphere.  $L_{HO_x}(HNO_3)$  is the dominant HO<sub>x</sub> sink in the plume, and as shown in the middle panel of Figure 4, increasingly suppresses HO<sub>x</sub> at the larger NO mixing ratios. Both of the DSS models again underestimate observed HO<sub>x</sub>. (Since CO was not measured it was assumed to have a constant mixing ratio of 80 ppbv. HO<sub>x</sub> 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<sub>x</sub> sources within the plume counterbalancing  $L_{HO_x}(HNO_3)$ .

#### 4. Conclusions

Acetone is likely to be a significant HO<sub>x</sub> source to the upper troposphere [Singh *et al.*, 1995, McKeen *et al.*, 1997, Wennberg *et al.*, 1997]. HO<sub>x</sub> 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<sub>x</sub> sources are also needed inside upper tropospheric biomass burning plumes. These HO<sub>x</sub> 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<sub>x</sub> sources are accounted for, it is likely that they significantly increase ozone production rates.

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