

# **Hydroperoxide Measurements during the 1995 Nashville / Middle Tennessee Study**

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# ***ABSTRACT***

Peroxide measurements in the Nashville region were conducted on 23 flights of the U.S. Department of Energy's G-1 aircraft during the SOS/Middle Tennessee program in the summer of 1995. Brookhaven National Laboratory's three-channel continuous flow peroxide analyzer was deployed for the first time from the aircraft during this study, yielding measurements of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), methyl hydroperoxide ( $\text{CH}_3\text{OOH}$  or MHP) and hydroxymethyl hydroperoxide ( $\text{HOCH}_2\text{OOH}$  or HMHP). The median concentration of total peroxide in the boundary layer (BL) between 11:00 and 14:00 CDT was approximately 5 ppbv, with over 50% contributed by organic hydroperoxide. Inhibition of peroxide production by high  $\text{NO}_x$  concentrations in the region was evidenced by markedly lower peroxide concentrations within urban and power plant plumes.

# ***INTRODUCTION***

Hydroperoxides are the principal sink for peroxy radicals that participate in tropospheric ozone formation. As such, peroxide concentrations and ratios of peroxide to  $\text{NO}_z$  can be used to indicate whether ozone formation is limited by the availability of  $\text{NO}_x$  or hydrocarbons. Hydroperoxides are largely responsible for the aqueous-phase oxidation of atmospheric  $\text{SO}_2$ , resulting in the formation of acid precipitation and visibility-reducing sulfate aerosol.

Formation of hydrogen peroxide by the self-reaction of  $\text{HO}_2$  radicals, and of organic peroxide by the analogous reaction between  $\text{HO}_2$  and  $\text{RO}_2$ , terminate the free-radical chain sequence initiated by ozone photolysis in the atmosphere. Laboratory experiments have shown that the reaction of ozone with alkenes in moist air may be a significant non-radical source of  $\text{H}_2\text{O}_2$  and hydroxyalkyl hydroperoxides. Recent ground and aircraft-based peroxide measurements, some using HPLC to quantitate individual peroxides, have demonstrated that organic peroxides can constitute a significant fraction of the total (Hewitt and Kok, 1991; Heikes et al, 1992; Tremmel et al., 1994). Although the formation of higher molecular weight peroxides is expected to occur,  $\text{H}_2\text{O}_2$ , MHP, and HMHP are the major peroxides so far identified in significant concentrations in the atmosphere. Reliable measurements of individual peroxides are necessary to validate our understanding of the mechanism of atmospheric photochemistry and the relative importance of competing oxidative pathways.

# **INSTRUMENTATION**

The BNL 3-channel analyzer uses three stripping coils for collection of gas-phase peroxides. Peroxide mixtures in the three channels are converted to fluorescent products for detection. A solution of p-hydroxyphenylacetic acid (pOHPAA) and horseradish peroxidase (HRP) is used in channel 1 to produce a fluorescent pOHPAA dimer whose signal is a measure of the concentration of total peroxide. In channels 2 and 3, the Fenton reaction produces hydroxybenzoic acid by the reaction of Fe(II) with H<sub>2</sub>O<sub>2</sub> in the presence of benzoic acid (BA). Sensitivity is enhanced in channel 1 by pH adjustment and in channels 2 and 3 by pH adjustment and complexation with Al(III).

Scrubbing solution is maintained at pH 5.5 for one channel; the other two are kept at pH 9 to convert HMHP to H<sub>2</sub>O<sub>2</sub> prior to derivatization. The signals from the high pH pOHPAA/HRP, high pH FeBA and low pH FeBA channels are respectively:

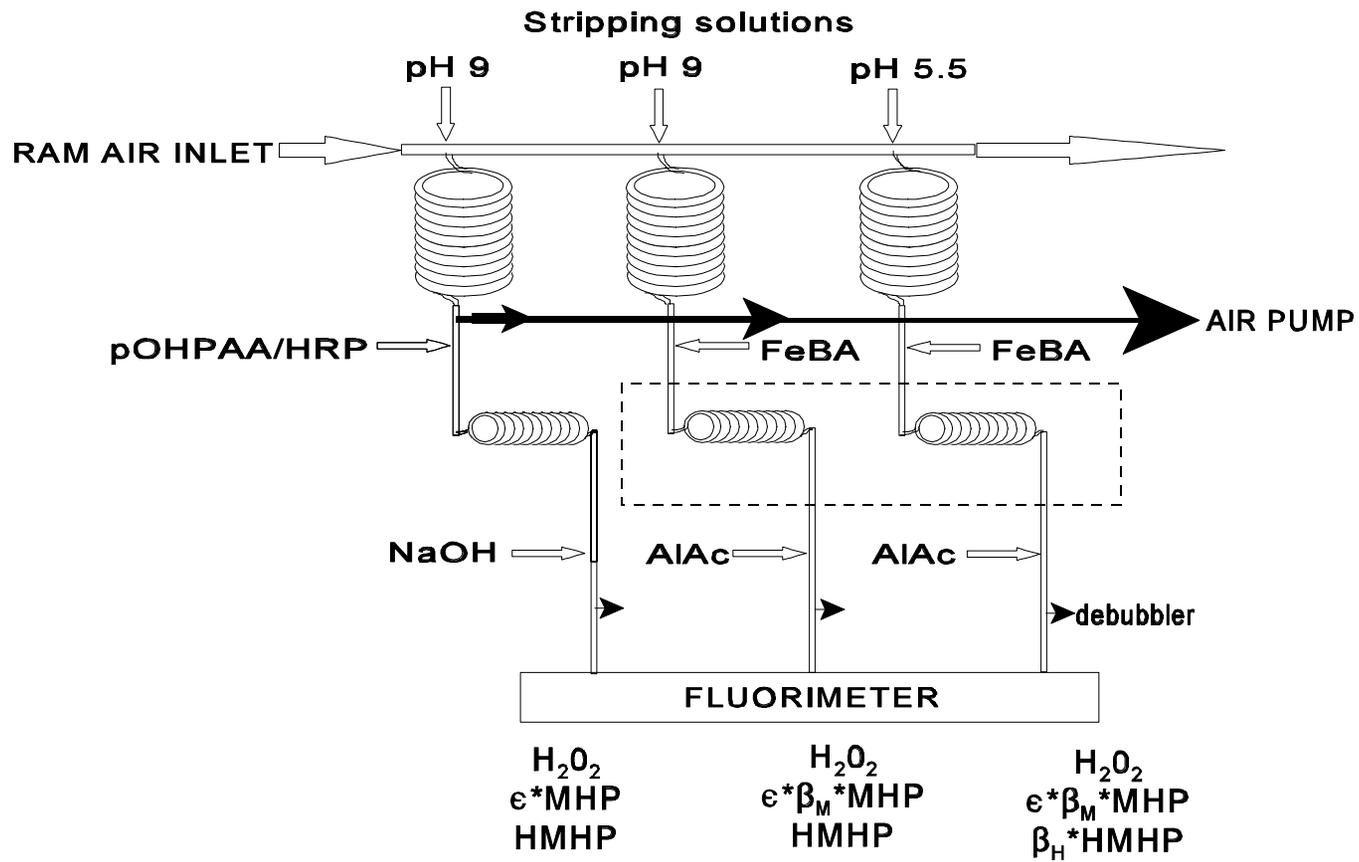
$$S_1 = [H_2O_2] + [HMHP] + \epsilon[MHP]$$

$$S_2 = [H_2O_2] + [HMHP] + \epsilon\beta_M[MHP]$$

$$S_3 = [H_2O_2] + \beta_H[HMHP] + \epsilon\beta_M[MHP]$$

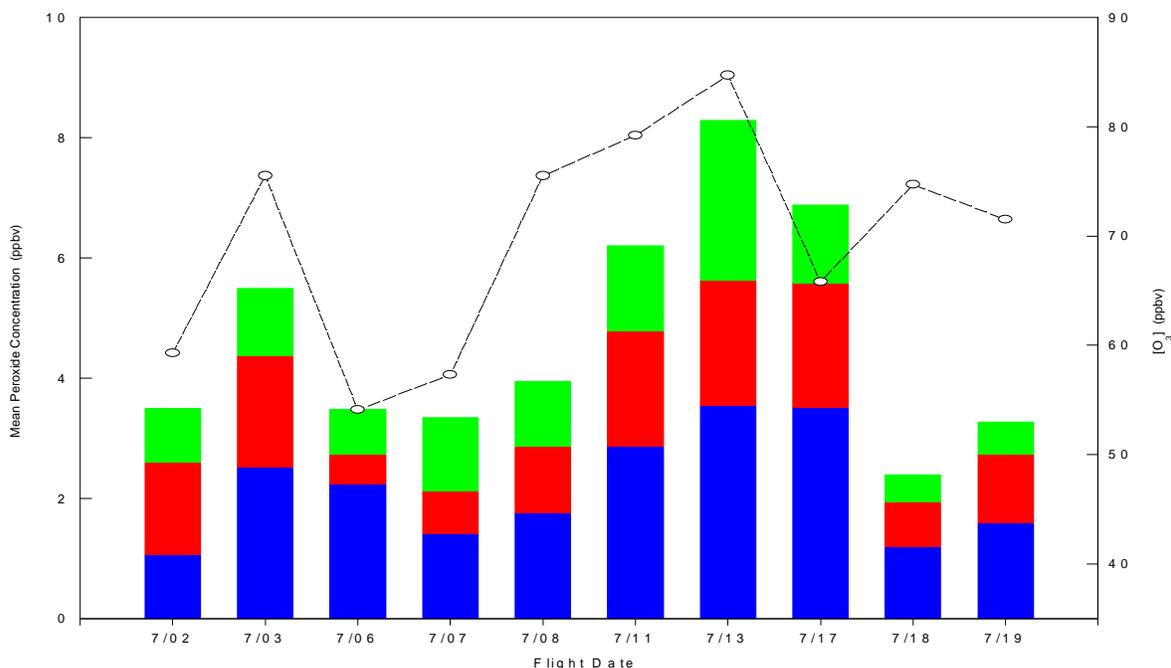
where  $\epsilon$  is the collection efficiency for MHP and the  $\beta$ 's represent the relative response of the Fenton channels to organic peroxides. For the Nashville program, these parameters were:  $\epsilon = 0.68$ ,  $\beta_M = 0.20$  and  $\beta_H = 0.40$ .

# 3-CHANNEL PEROXIDE ANALYZER BROOKHAVEN NATIONAL LAB



# ***PRINCIPAL FINDINGS***

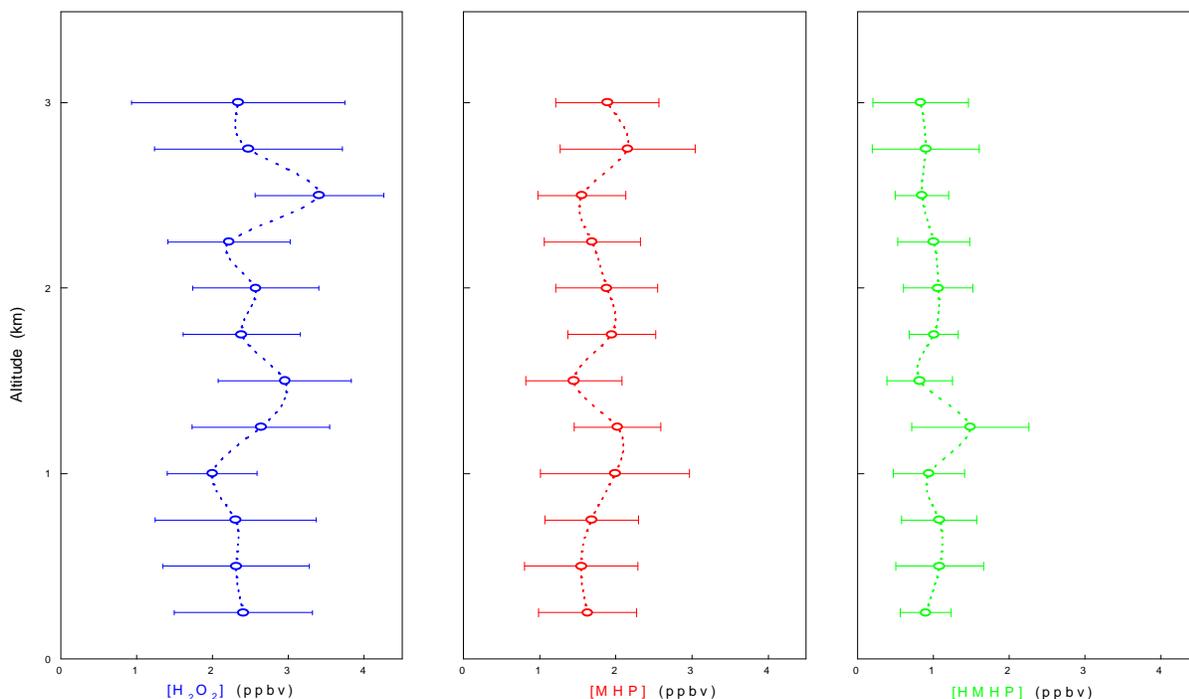
◆ **Organic hydroperoxides make up over half of the total peroxides measured in Nashville.**



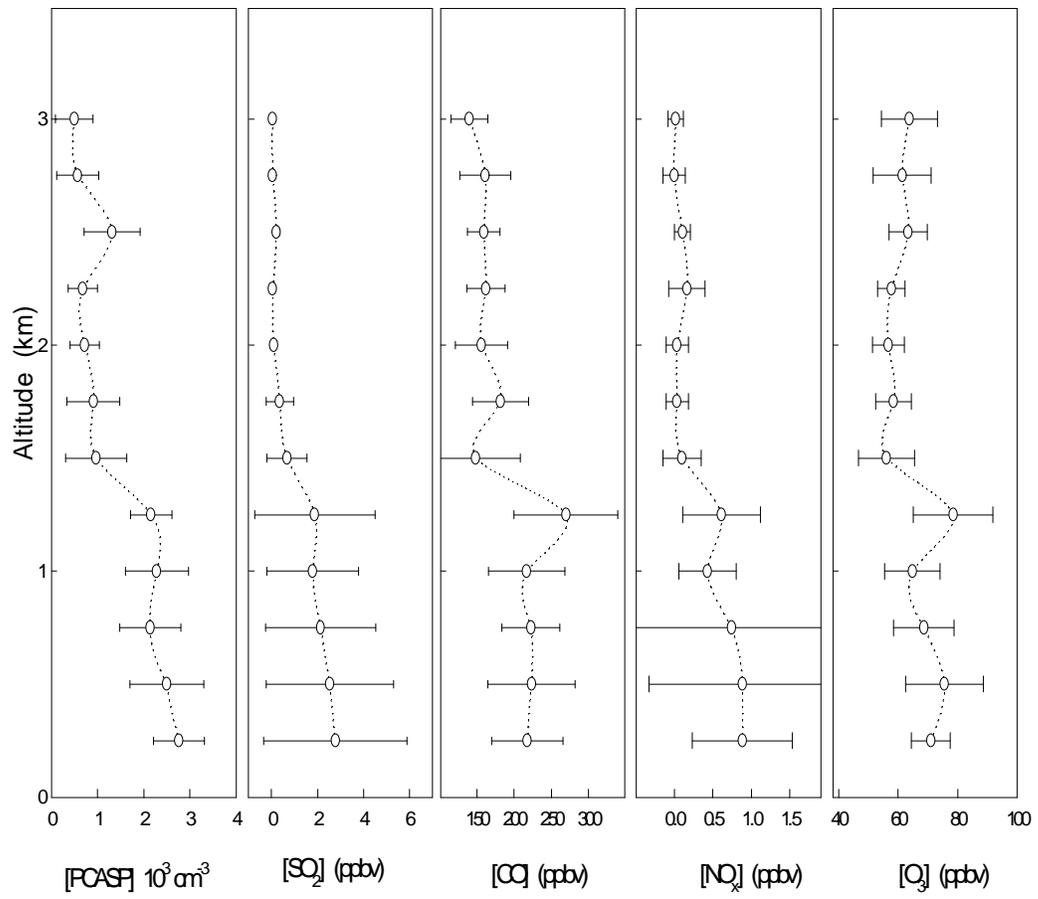
■ H<sub>2</sub>O<sub>2</sub>
■ MHP
 ■ HMHP
 ○ O<sub>3</sub>

Median concentrations of individual peroxides for each flight are shown above. These results are for a subset of the data representing boundary layer air sampled during the period of peak photochemical activity, i.e., 11:30 to 13:30 CDT, and includes approximately 40% of the data collected. In general, the highest concentrations were observed between July 11<sup>th</sup> and July 17<sup>th</sup>, a period also characterized by elevated temperature, humidity and ozone concentration. Approximately 54% of total peroxide is contributed by MHP and HMHP in this subset of data. The fraction of organic peroxide observed is large compared to previous summer aircraft measurements in Canada and winter measurements on the U.S. east coast, but is similar to recent summer measurements over the eastern U.S. and south Atlantic ocean. This is a significant finding, because there are doubts about the reliability of peroxide measurements obtained using the dual-channel catalase instrument when organic peroxide comprises a significant fraction of the total.

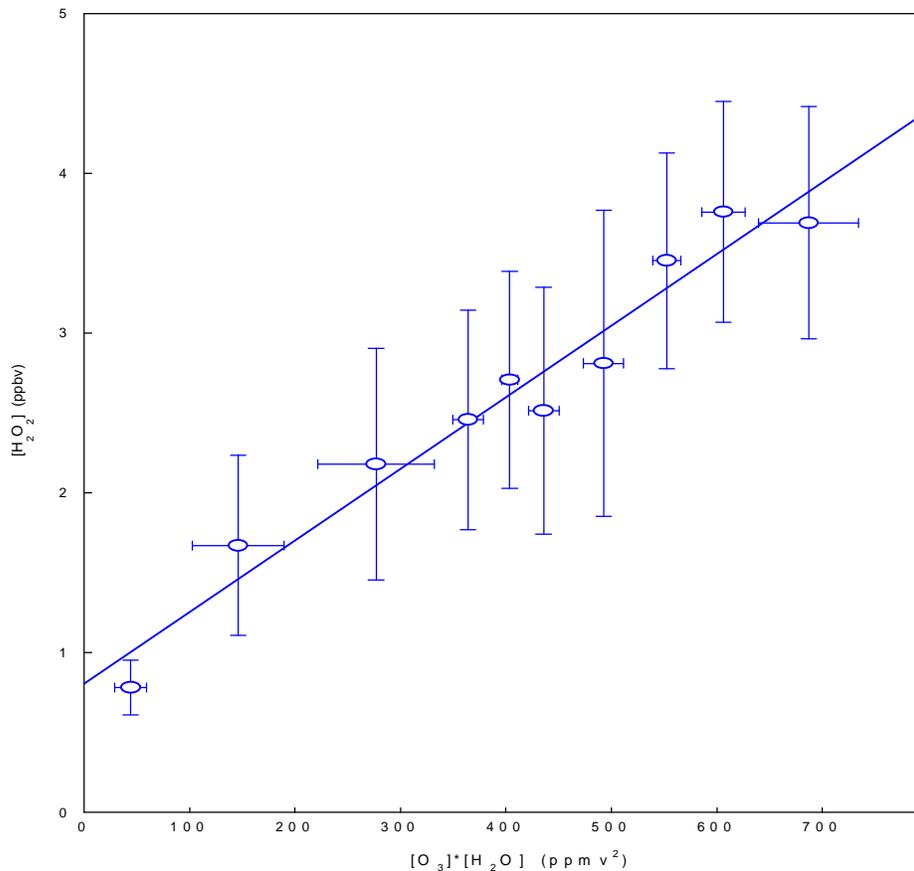
## ◆ Peroxide profiles show no significant vertical gradients



Composite vertical profiles for  $H_2O_2$ , MHP and HMHP for all flights of the G-1, comprising approximately 13,500 data points, are shown above. Symbols indicate the median and bars show interquartile range for each 250 m altitude bin. Peroxide distributions are fairly uniform, demonstrating that the peroxide abundance is representative of background air rather than local production. In contrast, profiles of ozone and primary pollutants such as  $NO_x$ ,  $SO_2$  and accumulation mode aerosol particles, shown below, exhibit noticeably higher concentrations below 1500 m, consistent with sources in the boundary layer.

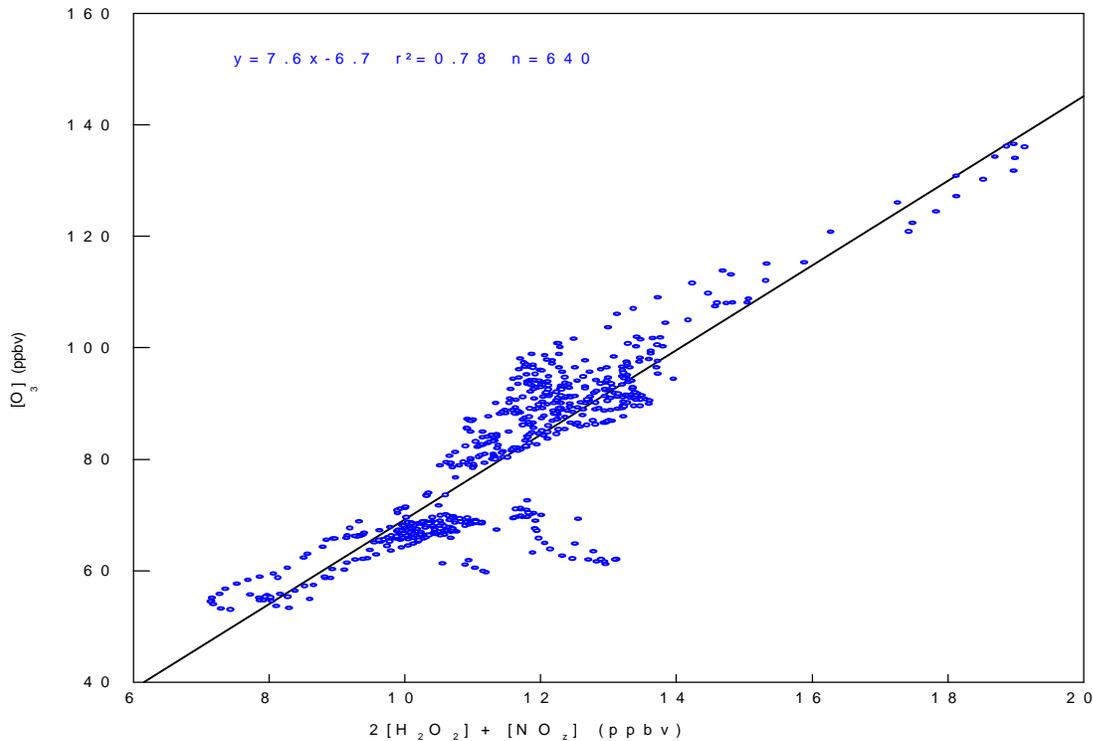


◆ **Hydrogen peroxide concentration in the free troposphere is governed largely by the concentrations of precursors,  $O_3$  and  $H_2O$**



Free radical formation in the atmosphere is initiated by the photolysis of ozone. Termination involves two competing processes: reaction of OH with  $NO_2$  to form nitric acid and self-reaction of  $HO_2$  radicals to form peroxides. In the free troposphere, where  $NO_x$  concentrations are low and peroxides the principal radical sink, peroxide formation is expected to depend on the ozone photolysis rate, and the concentrations of ozone and water vapor. The figure above shows the relationship between these species for all data obtained at altitudes greater than 1500 m, corresponding to  $NO_x < 1$  ppbv. Each symbol represents the mean of a 10% bin of the data (ordered by abscissa value) and the bars give the standard deviation of each bin. The linear relationship observed indicates that this model accounts for most of the variance in the low- $NO_x$  data set.

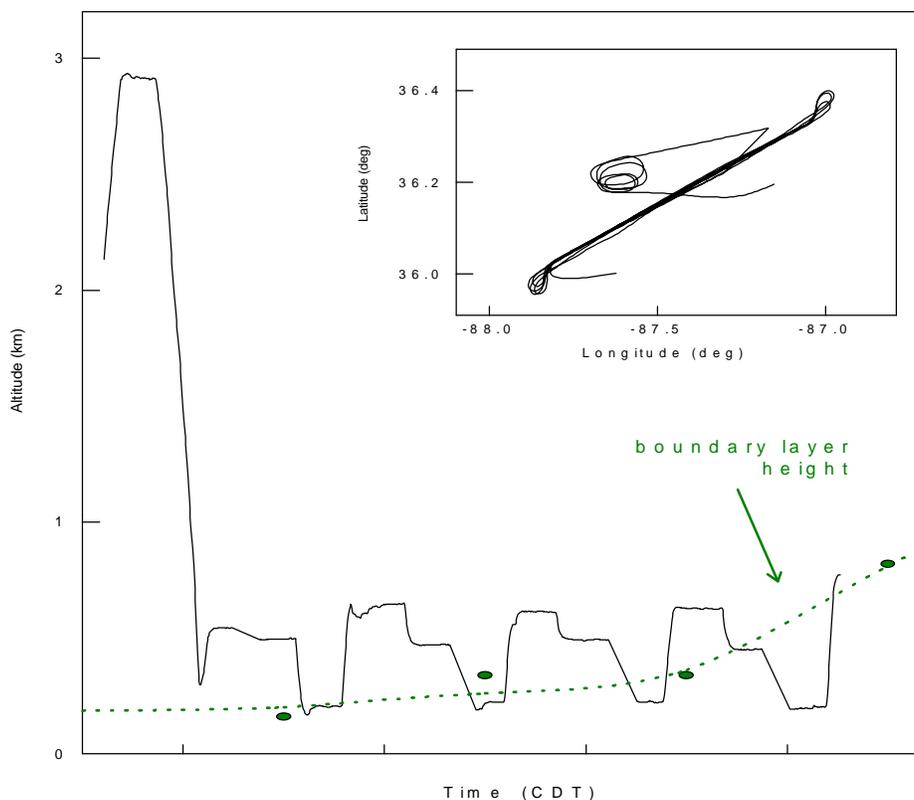
- ◆ ***A linear correlation between  $[O_3]$  and the quantity  $2[H_2O_2]+[NO_x]$  shows the balance between sources and sinks of  $HO_x$  radicals ( $OH + HO_2$ ).***



A good linear correlation is observed between  $[O_3]$  and the sum  $2[H_2O_2]+[NO_x]$  for flights on July 11<sup>th</sup>, 12<sup>th</sup> and 13<sup>th</sup>, as illustrated in the figure above for the 13<sup>th</sup>. Sillman (1995, 1998) explained this relationship, which he also observed in results of model calculations, as arising from the balance between sources and sinks of  $HO_x$  radicals. Ozone concentration limits the availability of radicals and radicals must terminate in the production of either  $H_2O_2$  or  $NO_x$  oxidation products such as  $HNO_3$  or PAN.

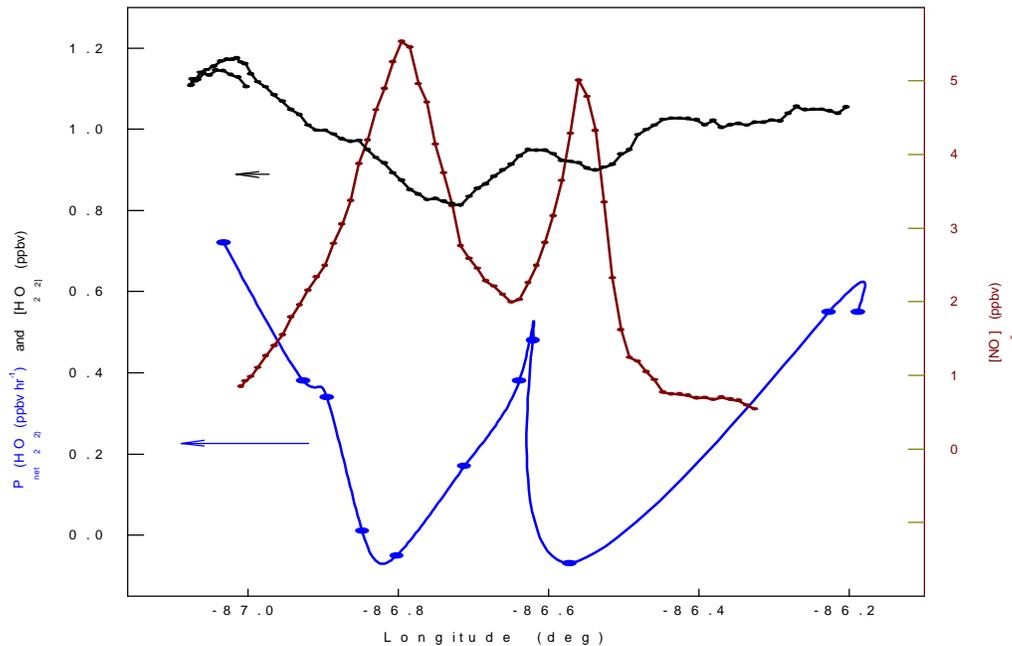
A linear relationship between these quantities was not observed for the entire data set; we attribute the strong correlations seen during this period to stagnant conditions which minimized deposition and mixing of different air masses.

◆ **Hydrogen peroxide is depleted by deposition within the nocturnal boundary layer**



On July 20<sup>th</sup>, the G-1 repeatedly traversed a SW/NE path upwind of Nashville at three altitudes. The increase in BL height between 7:30 and 11:30 CDT is illustrated along with the flight profile in the figure above. The median  $\text{H}_2\text{O}_2$  concentration was significantly higher above the mixed layer than below (2.7 VS 2.0 ppbv), while concentrations of MHP (2.2 VS 2.1 ppbv) and HMHP (0.9 ppbv both) were not significantly different. We attribute the decrease in  $\text{H}_2\text{O}_2$  concentration to overnight deposition on wet surfaces, in accord with its high solubility. The smaller Henry's Law coefficient for MHP may explain its lack of variability. HMHP is highly soluble, and should deposit overnight, but may also continue to form via the  $\text{O}_3$  - alkene pathway. Although we did not measure ground-level peroxides, these measurements confirm that nighttime losses are limited to a region very near the surface, and clearly illustrate the existence of the peroxide reservoir that contributes the background for the next day's photochemistry.

◆ ***Attenuated peroxide concentrations in plumes compared to background air are predicted by model calculations.***

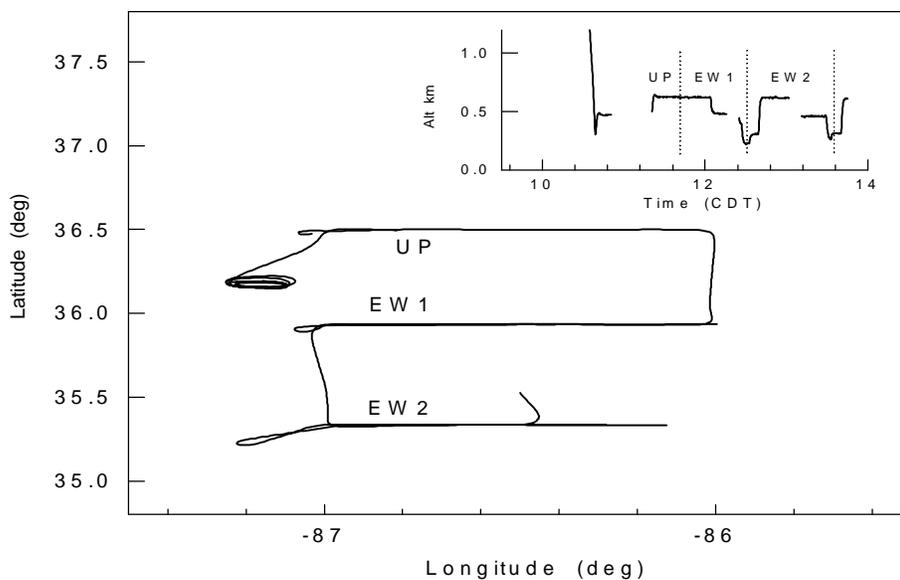


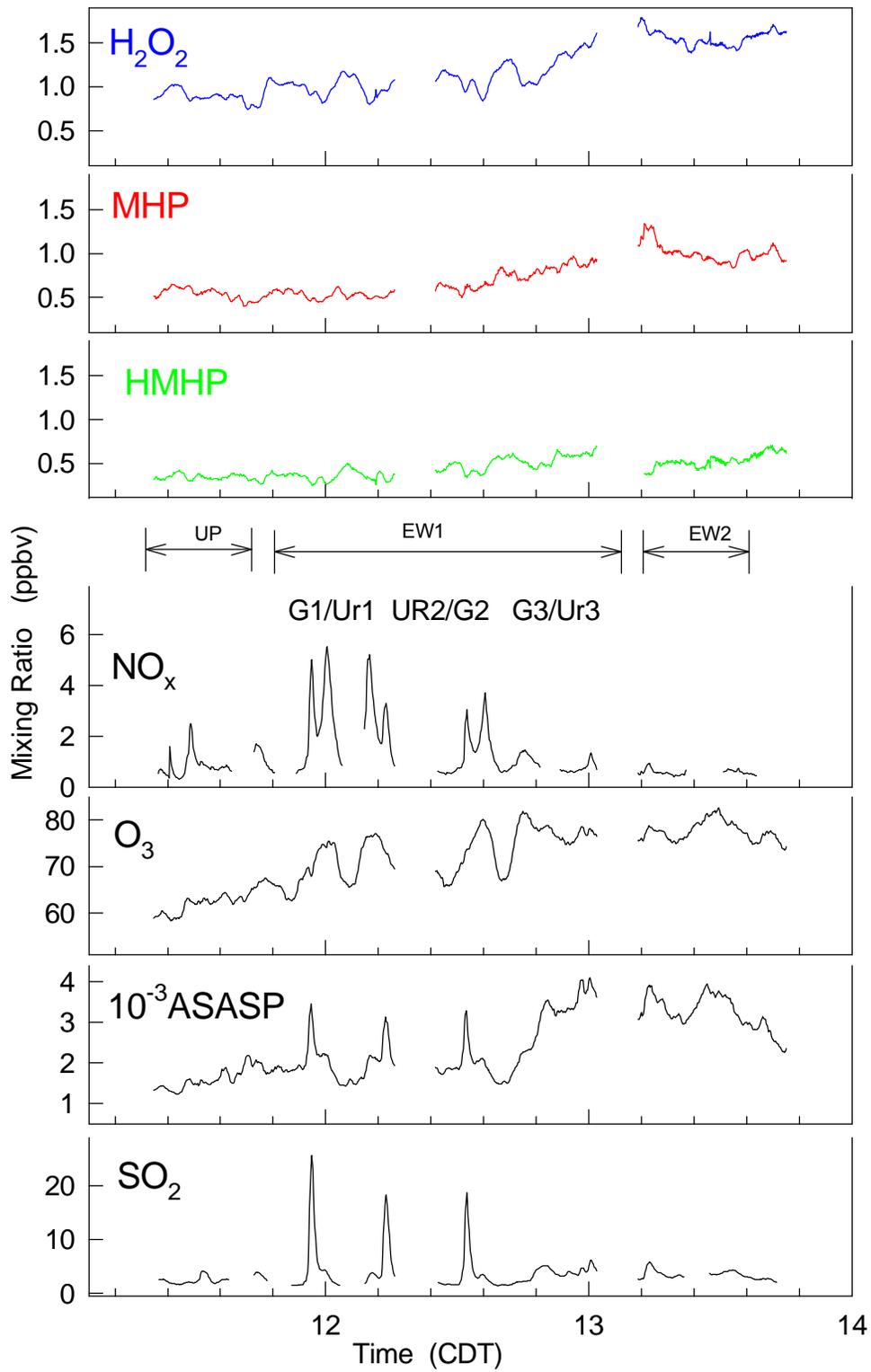
Within urban and power plant plumes, high  $\text{NO}_x$  and low VOC concentrations are expected to inhibit the production of  $\text{H}_2\text{O}_2$  from  $\text{HO}_2$  radicals. We used a constrained steady state box model, described by Kleinman et al. (1997), to predict the instantaneous production and loss rates for  $\text{H}_2\text{O}_2$  using measured concentrations of  $\text{O}_3$ ,  $\text{NO}$ ,  $\text{CO}$ ,  $\text{HCHO}$  and hydroperoxides, and measured or interpolated VOC concentrations for the flight of July 18<sup>th</sup>. The calculated net rate of change due to production (P) and loss (L) by photolysis and reaction with OH is given by  $P_{\text{net}}(\text{H}_2\text{O}_2) = P(\text{H}_2\text{O}_2) - L(\text{H}_2\text{O}_2)$ . The figure above shows  $P_{\text{net}}(\text{H}_2\text{O}_2)$  for a traverse that sampled the urban and Gallatin plumes at an altitude of 620 m, calculated at 11 points for which VOC concentrations were available. The absence of  $\text{H}_2\text{O}_2$  production in plume centers is evident. Also shown are measurements of  $\text{H}_2\text{O}_2$  and  $\text{NO}_x$  for this traverse.  $\text{H}_2\text{O}_2$  concentration in plume is lower than non-plume air by approximately 30% (0.4 ppbv). The sampled air mass was approximately 2 hrs downwind of the sources. We estimate that  $\text{H}_2\text{O}_2$  concentration in background air, obtained from upwind measurements conducted earlier in the day, will increase by 0.7 ppbv during this 2 hrs, while  $\text{H}_2\text{O}_2$  in plume air will decrease by 0.1 ppbv. The combination of the background rising and plume center falling gives a predicted  $\text{H}_2\text{O}_2$  dip of 0.8 ppbv, twice that observed.

# Flight Descriptions

**July 18, 1995**

The G-1 flew three crosswind transects within the boundary layer between 11:00 and 14:00 CDT, one upwind and two downwind of the urban center (UP, EW1 and EW2 in the figures). Each downwind transect sampled air at 310, 470 and 620 m. Particle and SO<sub>2</sub> emissions from the Gallatin power plant are observed at each altitude on EW1 (G1, G2 and G3 in the figures). The urban plume, distinguishable by high NO<sub>x</sub> and particle concentrations without coincident SO<sub>2</sub>, is indicated in the figure as Ur1, Ur2 and Ur3. Hydroperoxide concentrations show a gradual increase throughout the day, with superimposed negative excursions associated with plumes.





**July 13, 1995**

This flight occurred during an extended stagnation period characterized by high temperature, humidity and elevated concentrations of  $\text{NO}_y$  and ozone. Median concentrations of MHP and HMHP were 2.3 and 2.6 ppbv respectively; together these species comprised 58% of total peroxide. The unusually high HMHP concentration is supported by an intercomparison with NOAA's P-3 aircraft, which showed good agreement for concentrations of total organic peroxide. HMHP may be produced from the reaction between ozone and isoprene in the presence of water vapor. Since isoprene emissions increase exponentially with temperature, this day's high HMHP concentration may result from elevated temperature and precursor concentrations. However, there is no simple relationship between HMHP concentration, temperature and ozone for the composite data set.

A vertical profile at 12:30 CDT shows a layer of dry air sandwiched between two more humid layers. Panel c shows a region near 1 km where  $\text{O}_3$  has been titrated within the Johnsonville plume. Again we see evidence of decreased net peroxide production in the plume. Above 1.5 km, profiles of all three peroxides parallel those of water vapor and ozone, in keeping with their formation from free-radical precursors. At the highest altitude, MHP concentration is nearly twice its value at 500 m; lower concentrations of NMHC in the free troposphere may facilitate reaction of OH with  $\text{CH}_4$ , leading to MHP production. While  $\text{H}_2\text{O}_2$  and MHP are fairly well mixed below 1 km, HMHP concentration increases sharply near the surface. These profiles suggest that HMHP has its origin in both ozone-alkene and free radical pathways.



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