

## P1.22 MEASUREMENT OF HYDROPEROXIDES DURING THE TEXAS 2000 AIR QUALITY STUDY

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### 1. INTRODUCTION

Hydroperoxides are important atmospheric oxidants. They are responsible for most of the oxidation of aqueous-phase  $\text{SO}_2$  to sulfate in the northeastern United States, resulting in the formation of acid precipitation and visibility-reducing sulfate aerosol (Penkett et al., 1979; Lind et al., 1987; Madronich and Calvert, 1990; Tanner and Schorran, 1995). Atmospheric hydrogen peroxide ( $\text{H}_2\text{O}_2$  or HP) is produced by the self-reaction of hydroperoxyl radicals ( $\text{HO}_2$ ); higher organic peroxides are produced by reaction of  $\text{HO}_2$  with alkylperoxyl radicals ( $\text{RO}_2$ ). Peroxyl radicals, along with OH, are chain carriers in the complex photochemical process that produces tropospheric ozone. Thus, concentrations of peroxides and their free radical precursors depend on solar intensity and ambient concentrations of water vapor, ozone,  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ), and VOCs (volatile organic compounds). Several investigators have demonstrated that HP and hydroxymethyl hydroperoxide ( $\text{HOCH}_2\text{OOH}$  or HMHP) also may be formed when ozone reacts with alkenes in moist air (Becker et al., 1990; Hewitt and Kok, 1991; Gäb et al., 1995).

Peroxides are the expected sink for peroxy radicals when concentrations of NO are low. Otherwise, these radicals react with NO to form  $\text{NO}_2$ . Under high  $\text{NO}_x$  conditions,  $\text{NO}_2$  (oxidation products of NO and  $\text{NO}_2$ ) becomes the principal radical sink. Therefore, formation rates of peroxides relative to  $\text{NO}_2$  provide information about the history of an air mass and the expected sensitivity of ozone production to reduced emissions (Kleinman et al., 1997; Sillman, 1995; 1997). Through photolysis and reaction with OH, peroxides also act as a radical source; thus, reliable peroxide measurements are necessary for calculating ozone

production rates.

In this paper, we will summarize peroxide observations at the Williams Tower, and aboard the U.S. Department of Energy G-1 research aircraft in Houston, TX, during August and September 2000. Temporal and geographical distribution of individual peroxides will be discussed, as well as correlations between peroxides and other trace gas measurements.

### 2. EXPERIMENTAL

Hydroperoxides were measured using Brookhaven National Laboratory's 3-channel fluorescence analyzer, a modification of the widely used Kok and Lazrus instrument (Kok et al., 1986; Lazrus et al., 1986). The instrument employs a Fenton reagent, which is specific for HP, along with p-hydroxyphenylacetic acid, which reacts with all hydroperoxides, to yield measurements of HP, HMHP and methyl hydroperoxide ( $\text{CH}_3\text{OOH}$  or MHP). Details of the peroxide analytical technique and instrument design can be found in the papers by Lee et al. (1990, 1994).

Two-point calibrations were conducted before each flight, using aqueous standards prepared from commercial 3% hydrogen peroxide stock. The latter was titrated against standardized  $\text{KMnO}_4$  before and after the study; a change of < 1% was observed over the one-month period. The instrument had a  $1.8 \text{ L min}^{-1}$  air flow rate and  $0.62 \text{ mL min}^{-1}$  liquid flow rate, resulting in a 120 s response time and a 0.2 ppbv detection limit. Baselines were established at least twice during each flight by passing air through a hopcalite (copper oxide and manganese dioxide) column. Details of the analytical techniques for other trace gases and particle composition have been published (L.J. Nunnermacker et al. 1998; R.J. Weber et al., 2001). Originally acquired at 1s intervals, the G-1 data set was averaged to 10s for the analysis described here, except for particle composition data, which are integrated over 2 minutes. Peroxide concentrations reported here have been corrected for  $\text{SO}_2$  interference.

A similar peroxide analyzer was deployed on the 62<sup>nd</sup> floor of the Williams Tower site in downtown Houston from August 21 to September

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12. The ground instrument had its sampler mounted outdoors to minimize surface losses, and analysis was conducted on the aqueous stream brought into the building through 30 ft of Teflon spaghetti tubing. The response time of this instrument was 6 min, and data are reported as 15 min averages. Additional information about the Tower site can be found in Berkowitz et al. (2001) and Spicer et al (2001).

### 3. RESULTS

#### 3.1 Williams Tower

A time series for total peroxides observed at Williams Tower between September 2 and September 8 is given in Figure 1. The diurnal profile is consistent with photochemical production during the day and nighttime deposition. An exception occurred on September 5, when peroxide concentrations during the night remained elevated. Daily maxima occurred near 17:30 CST, approximately 2 hours later than the ozone maximum.

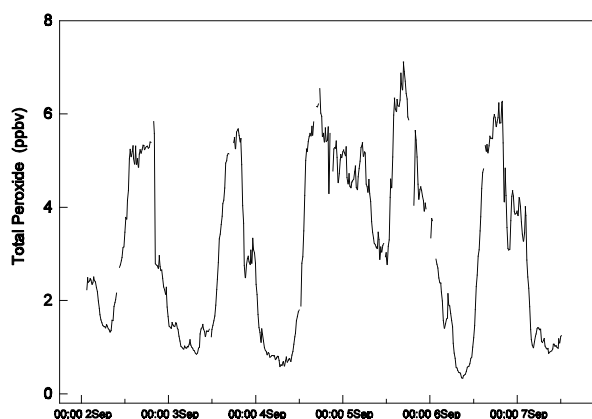


Figure 1. Time series for total peroxide measurements at Williams Tower.

#### 3.2 Flight Description

Peroxide concentrations were recorded during 15 flights on 11 days between August 19 and September 1. Flights generally included one or more vertical profiles, but 71% of the data points were collected between 400 and 600 m MSL (mean sea level). Most flights were conducted within 100 km of downtown Houston. On several occasions, we conducted two flights on the same day to

observe changes in trace gas abundances.

#### 3.3 General flight observations

Figure 2 illustrates median peroxide abundances for morning and afternoon flight legs conducted within the mixed layer. Median total peroxide concentration in the afternoon was 6.8

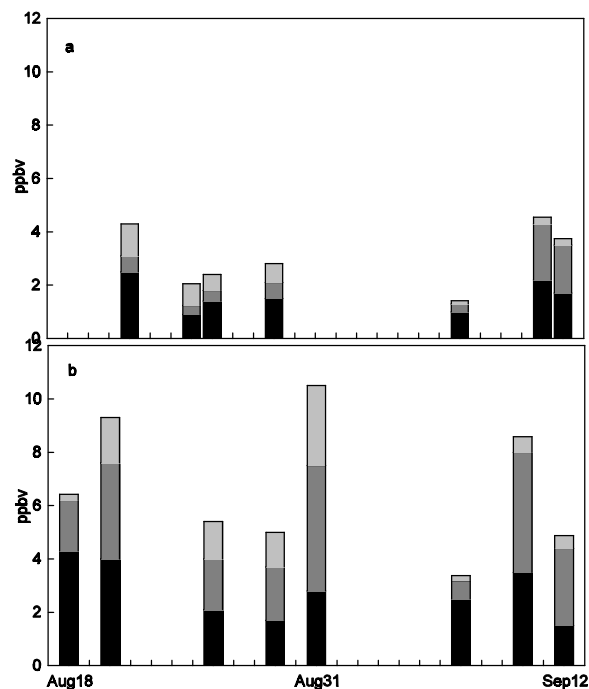


Figure 2. Median peroxide concentrations in the BL for G-1 flights (a, morning flights; b, afternoon flights; black, HP; grey, MHP, light grey, HMHP).

ppbv, with organic peroxide (MHP plus HMHP), representing 59% of the total. Days that included two flights showed a median increase of 91% in total peroxide between the two flights. The highest total peroxide (16 ppbv at 1500 m) was recorded over Galveston Bay under easterly wind conditions during the August 31 afternoon flight. Vertical profiles during morning flights showed significantly higher concentrations of HP and MHP just above the top of the boundary layer.

#### 3.4 Individual Flights

In this section, we describe observations of peroxides and other trace gases on three days: August 29, a day featuring a flow reversal from off-to on-shore winds; September 7, characterized by

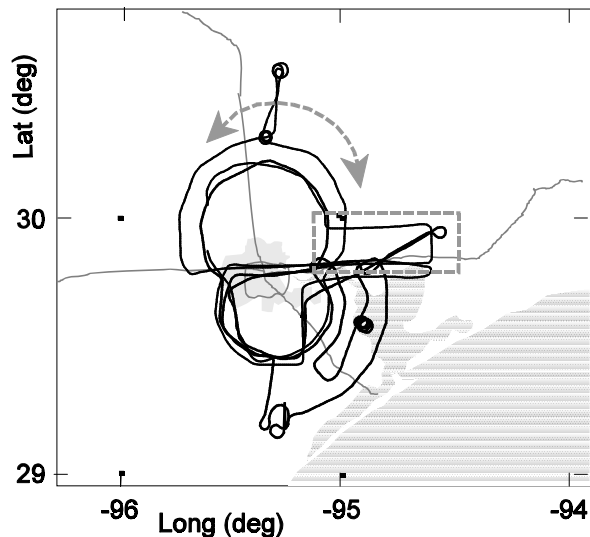


Figure 3. August 29 flight tracks. Dashed box encloses measurements in shaded regions in Figure 4; curved arrow corresponds to elevated peroxides observed between 14.9 and 15.4 CST in Figure 4.

northeasterly winds all day, and September 10, when the flight traced the evolution of a power plant plume northwest of Houston.

### 3.4.1 August 29

Winds on August 29 exhibited a wind flow reversal characteristic of several flight days during the measurement period. There were two G-1 flights, one between 8:30 and 11:00, and later between 13:30 and 15:50 CST. Profiler measurements show that winds above 2 km were from the SE for the entire period. Surface winds averaged  $3 \text{ m s}^{-1}$  from the WSW in the morning,  $3 \text{ m s}^{-1}$  from the SSE in the afternoon, and were calm during the 2½ hour interval between flights ([www.al.noaa.gov/TexAQS2k/ProfilerData](http://www.al.noaa.gov/TexAQS2k/ProfilerData)).

August 29 flight paths, illustrated in Figure 3, passed over Galveston Bay as well as the I10 corridor that includes Houston's downtown area and industrialized ship channel. In the morning, we observed numerous sharp plumes in the corridor, characterized by elevated  $\text{NO}_y$ ,  $\text{SO}_2$ , and accumulation mode aerosol particles (PCASP). These were recent emissions, with median ratio of  $\text{NO}_x/\text{NO}_y = 0.95$ . Ozone and peroxide mixing ratios were low and fairly constant throughout the flight (median values of  $\text{O}_3$ , HP, MHP, and HMHP were 30, 1.5, 0.4 and 0.6 ppbv respectively) except for the southeastern portion of the flight, over Galveston

Bay. This air mass, which appeared to be more photochemically aged, had a median  $\text{NO}_x/\text{NO}_y$  ratio of 0.3,  $\text{O}_3$  in excess of 120 ppbv and slightly elevated  $\text{H}_2\text{O}_2$  and MHP. On a vertical profile over the bay, we observed increasing concentrations of HP and MHP above the mixed layer, with HP reaching 2.6, MHP 1.4, and  $\text{O}_3$  50 ppbv at 2.2 km.

Trace gas concentrations for the afternoon flight are illustrated in Figure 4. Peroxide concentrations were broadly elevated (median HP = 2, MHP = 3 and HMHP = 1.6 ppbv) for a distance of 50 km downwind of the source region (curved arrow in Figure 3). We again observed fresh industrial emissions over the I10 corridor and on the southwest arcs. As in the morning, neither  $\text{O}_3$  nor peroxides were elevated in fresh plumes. However,  $\text{O}_3$  and all three peroxides were elevated upwind of Galveston Bay, indicated by the shaded areas in Figure 4 and the box in Figure 3. These aged plumes, ( $\text{NO}_x/\text{NO}_y = 0.25$ ) still retained signif-

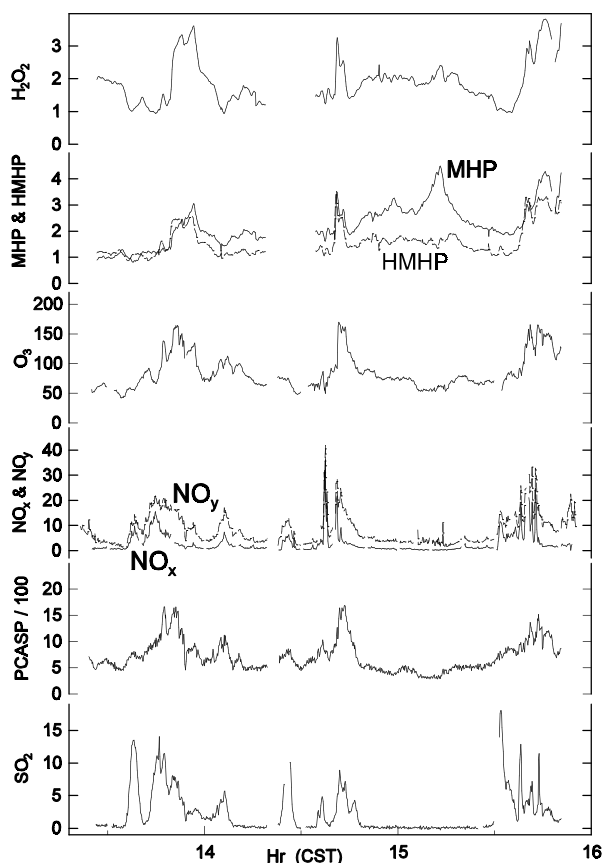


Figure 4. Trace gas measurements for the August 29 flight. Shaded areas correspond to the dashed box in Figure 3.

-icant concentrations of  $\text{NO}_y$ . The wind flow reversal on this day suggests a plausible explanation: ozone formation occurred during the morning, as WSW morning winds advected emissions offshore. Once depleted of  $\text{NO}_x$ , this plume containing elevated  $\text{O}_3$ ,  $\text{NO}_z$ , and VOCs produced peroxides during the early afternoon stagnation period, and was transported back to land during the subsequent flow reversal.

As in the morning, vertical profiles revealed concentrations of HP and MHP that increased with altitude. Although this may be attributed to deposition of peroxides near the surface, it also may reflect a difference in air mass origin. Above 2 km, southeasterly winds prevailed throughout the day. Thus, higher MHP and HP observed at high altitude during both morning and afternoon flights may have been produced in a low- $\text{NO}_x$  environment and advected onshore. In contrast, HMHP concentration decreased with altitude during this and other profiles, suggesting that its source differs from that of the other peroxides. We observed a good correlation between concentrations of  $\text{O}_3$  and HMHP on this day (Figure 5), consistent with production of the latter via ozonolysis of alkenes.

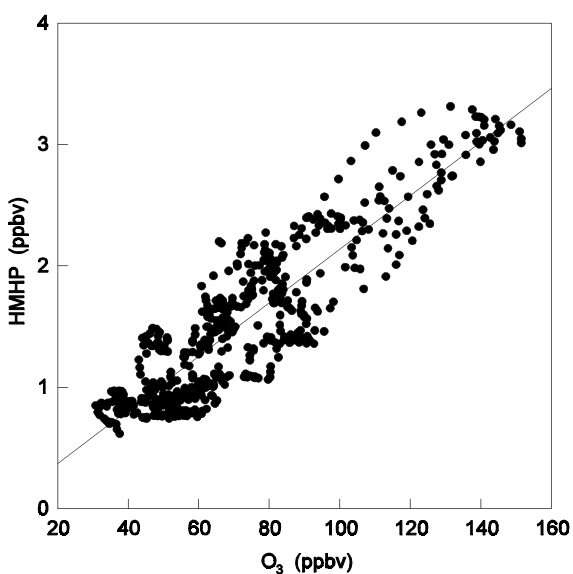


Figure 5. Correlation between  $\text{O}_3$  and HMHP on the August 26 morning flight.

### 3.4.2 September 7

On September 7, we conducted two flights in

the same region as August 29, during similar time periods. This day was unusual in that it featured strong winds from the northeast all day. In contrast to August 29, peroxides were quite low on this day in both morning (median HP = 0.8, MHP = 0.4 and HMHP = 0.2 ppbv) and afternoon (median HP = 2.5, MHP = 0.7 and HMHP = 0.2 ppbv), and there was a smaller contribution from organic peroxides. A broad plume of HP, reaching 3 ppbv, was observed for almost 50 km along the northern arc of the morning flight path. The origin of this plume, with high concentrations of CO and PCASP, but no organic peroxide,  $\text{O}_3$ , or  $\text{NO}_y$ , is unknown. In the afternoon, only one peroxide plume was encountered, again composed entirely of HP, along the southernmost flight leg directly downwind of the HP plume observed in the morning. The lower fraction of organic peroxide observed on September 7<sup>th</sup> did not reflect low VOC emissions, which were similar on these two days. While lower temperature and dilution from higher winds on the 7<sup>th</sup> may be contributing factors, it is likely that the higher organic peroxide observed on August 29<sup>th</sup> originated in the extra processing time afforded by the wind flow reversal.

### 3.4.3 September 10

On September 10, we tracked the plume from the Sandow Alcoa power plant near Rockdale, TX. Winds blew steadily from the SSE at  $4.5 \text{ m s}^{-1}$  during the flight. Figure 6a, a contour image of  $\text{SO}_2$  created from the plume traverses, shows the plume origin and its gradually decreasing concentration downwind for a distance of  $\sim 60 \text{ km}$ . The final plume traverse sampled air that had traveled for 3.6 h, assuming constant wind speed. HP concentration was 4.5 ppbv in background air and was clearly depleted within the plume, reaching a minimum of 2.3 ppbv approximately 20 km downwind of the point of maximum  $\text{SO}_2$  (Figure 6b). By the end of the flight, HP had recovered to background levels. Median sulfate was  $1.3 \mu\text{g m}^{-3}$  in background air, and appeared to be produced as the plume aged, reaching a maximum of  $4.3 \mu\text{g m}^{-3}$  at roughly the same location as the maximum HP loss (Figure 6c). Gas phase oxidation is an unlikely source of this sulfate, as a plume containing  $10^6 \text{ OH radicals cm}^{-3}$  and 60 ppbv  $\text{SO}_2$  would produce less than  $1 \mu\text{g m}^{-3}$  sulfate during the one hour interval between plume origin and the observed sulfate maximum. The apparent agreement between the rates of HP loss and sulfate production suggests that sulfate is produced in aerosol particles within the plume. Although this aqueous phase process is

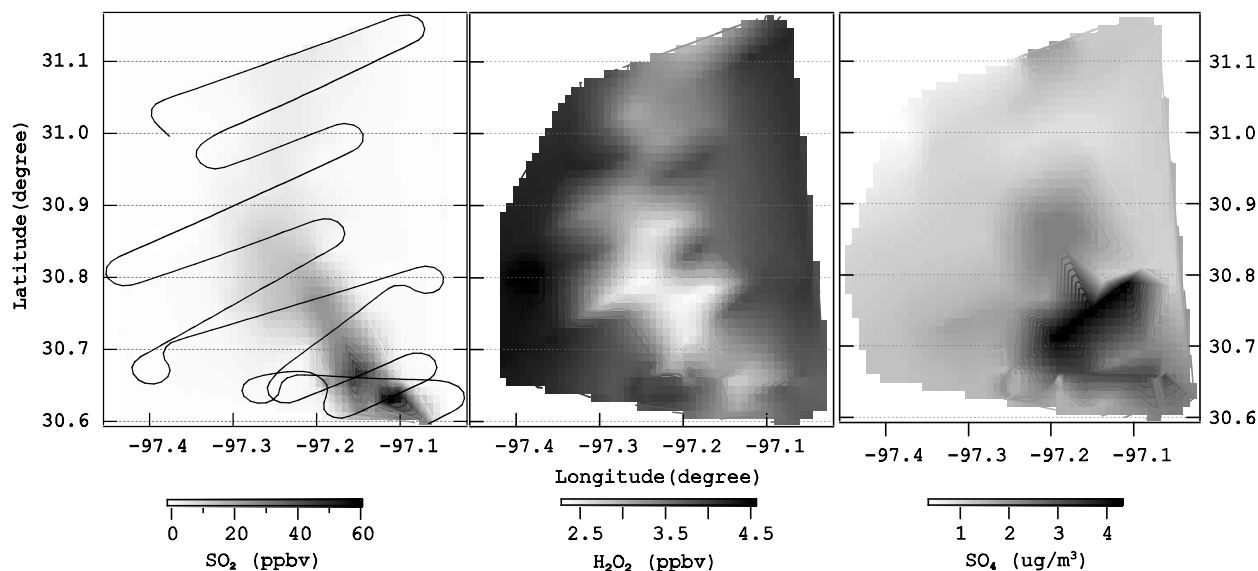


Figure 6. Contour plots of  $\text{SO}_2$  (a),  $\text{H}_2\text{O}_2$  (b) and  $\text{SO}_4^{2-}$  (c) for the September 10 flight. Flight track shown in a.

difficult to quantitate, the 0.74 ppbv HP decrease during this hour would produce the observed  $3 \mu\text{g m}^{-3}$  sulfate if loss were due to reaction with an equivalent amount of  $\text{SO}_2$ . Further details of the chemistry in the Sandoz plume may be found in Springston et al. (2001).

#### 4. DISCUSSION

High peroxide concentrations with a large proportion of organic peroxides were distinctive features of peroxide measurements in the boundary layer during the Texas 2000 Air Quality Study. During morning flights, elevated peroxides were observed in the residual layer aloft. We observed widespread increases in HP and MHP in afternoon compared to morning flights, in part due to mixing down of air aloft. Plumes of elevated peroxides were observed in air masses that experienced long processing times as a result of photochemistry and off- to on-shore flow reversals. Observed correlation between  $\text{O}_3$  and HMHP is evidence of HMHP formation via ozonolysis of alkenes. A simple calculation shows that HP may be responsible for the formation of sulfate in a power plant plume.

The analysis described here assumes that HP, MHP and HMHP are the only peroxides sampled by our instrument. High solar intensity and humidity, together with the large variety and high

concentrations of anthropogenic hydrocarbons in Houston, may have produced measurable quantities of higher organic peroxides. If present, these species would be collected with different efficiencies and may exhibit variable reactivity toward the derivatizing reagents in our instrument. This cannot be verified without HPLC separation of peroxides prior to analysis. The identity and distribution of individual peroxides in this region merits further study.

#### 5. ACKNOWLEDGMENTS

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