Peroxide Measurements from the 1998 Phoenix Ozone Study

J. B. Weinstein-Lloyd and I. Amin
Chemistry/Physics Department
State University of New York / Old Westbury

ABSTRACT

Gaseous hydroperoxides were determined for the Phoenix, AZ Ozone Study during May and June 1998. Measurements were conducted on the U.S. Department of Energy's G-1 aircraft and at a ground site at Usery Pass, 25 km east of the city. On the G-1, hydrogen peroxide (H_2O_2), methyl hydroperoxide (CH_3OOH or MHP) and hydroxymethyl hydroperoxide ($HOCH_2OOH$ or HMHP) were determined with Brookhaven National Laboratory's three-channel continuous flow peroxide analyzer. Ground-based measurements were limited to total peroxide.

We present here a preliminary analysis of the data. The median concentration of total peroxide in the boundary layer (BL), 1.7 ppbv, was similar for morning and afternoon flights. Organic peroxides made up between 15 and 85% of the total hydroperoxide observed, and very little HMHP was seen. Near the ground, total peroxide concentration generally remained below 0.5 ppbv and showed no diurnal pattern. Concentration gradients suggest that local photochemistry produces little peroxide in this vicinity, and that observed values represent regional background concentrations.

INTRODUCTION

Hydroperoxides are the principal sink for peroxy radicals that participate in tropospheric ozone formation. As such, peroxide concentrations and ratios of peroxide to NO_z can be used to indicate whether ozone formation is limited by the availability of NO_x or hydrocarbons. Hydroperoxides are largely responsible for the aqueous-phase oxidation of atmospheric SO_2, resulting in the formation of acid precipitation and sulfate aerosol.

Photolysis of ozone in the presence of water vapor, CO and VOCs results in the formation of HO_2 and RO_2 free radicals. When NO_x concentrations are low, HO_2 radicals self-react to produce hydrogen peroxide, and HO_2 and RO_2 react to produce organic hydroperoxides, ROOH. In addition, hydroxyalkyl hydroperoxides are produced via molecular ozonolysis reactions under ambient conditions. A number of recent ground and aircraft-based peroxide measurements have demonstrated that organic peroxides can constitute a significant fraction of the total. Although the formation of higher molecular weight peroxides probably occurs in the atmosphere, H_2O_2, methyl hydroperoxide (MHP), and hydroxymethyl hydroperoxide (HMHP) are the major peroxides so far identified in significant concentrations. 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.

INSTRUMENT

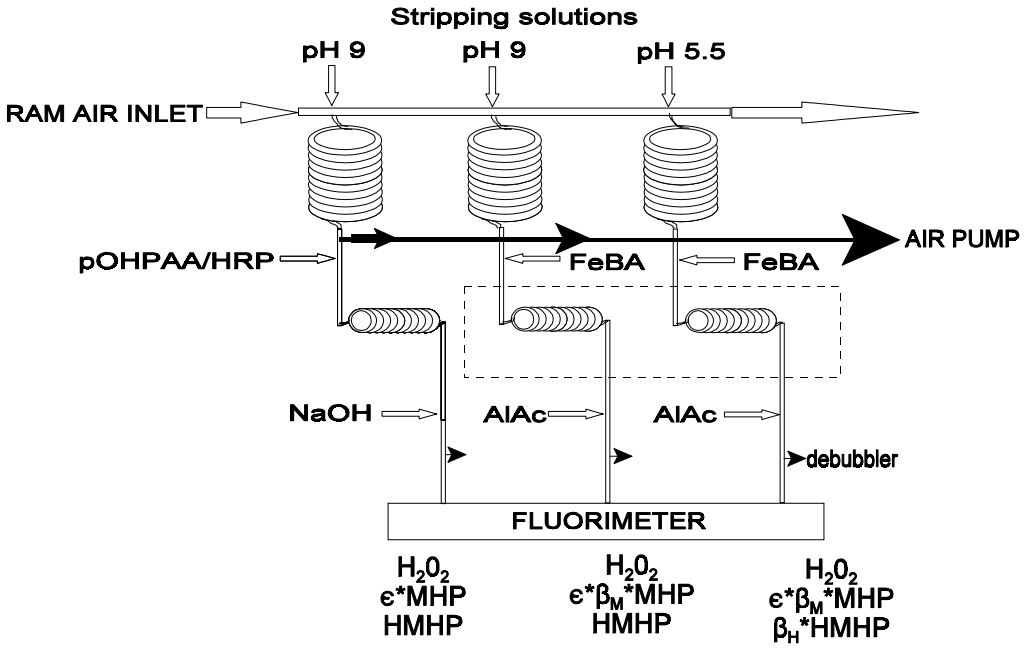
The BNL 3-channel analyzer uses three stripping coils for collection of gas-phase peroxides (see Figure 1 below). Peroxide mixtures in the three channels are converted to fluorescent products for detection. A solution of p-hydroxyphenylacetic acid (pOHPAA) and horseradish peroxidase (HRP) is used in 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_2O_2 in the presence of benzoic acid (BA). Sensitivity is enhanced in channel 1 by raising the pH 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_2O_2 prior to derivatization. The signals from the high pH pOHPAA/HRP, high pH FeBA and low pH FeBA channels are respectively:

$$S_{pOH} = [H_2O_2] + [HMHP] + \epsilon[MHP]$$
$$S_{FeHi} = [H_2O_2] + [HMHP]$$
$$S_{FeLo} = [H_2O_2] + \beta_H[HMHP]$$

where ϵ is a temperature-dependent collection efficiency for MHP and β_H represents the relative response of the low-pH Fenton channel to HMHP. For the Phoenix program, these parameters were: $\epsilon \approx 0.7$ and $\beta_H = 0.3$.

Figure 1: 3-CHANNEL PEROXIDE ANALYZER BROOKHAVEN NATIONAL LAB



A description of the flights and observed peroxide mixing ratios follows. These are *preliminary results*, principal findings are summarized after the figures.

Figure 2: Flight Summaries

AM Flights

Flight #	Count	Time hrs*	Date
1	658	15.2	May 18
3	610	16.7	May 21
5	727	16.6	May 22
7	471	16.2	May 23
9	848	16.7	May 27†
10	858	16.6	May 28
12	904	16.8	May 29
14	678	17.7	Jun 1
16	788	17.6	Jun 2
19	787	17.7	Jun 5
21	761	17.7	Jun 6

PM Flights

Flight	Count	Time hrs*	Date
2	612	21.8	May 18
4	667	23.0	May 21
6	598	22.9	May 22
11	607	23.0	May 28
15	580	24.0	Jun 1
17	536	24.0	Jun 2
18	606	23.9	Jun 4
20	647	23.9	Jun 5
22	340	23.5	Jun 6‡

*Times are Median UTC Hrs = Local Hrs + 7

†Regional flight, all upwind of city

‡Regional flight, all downwind of city

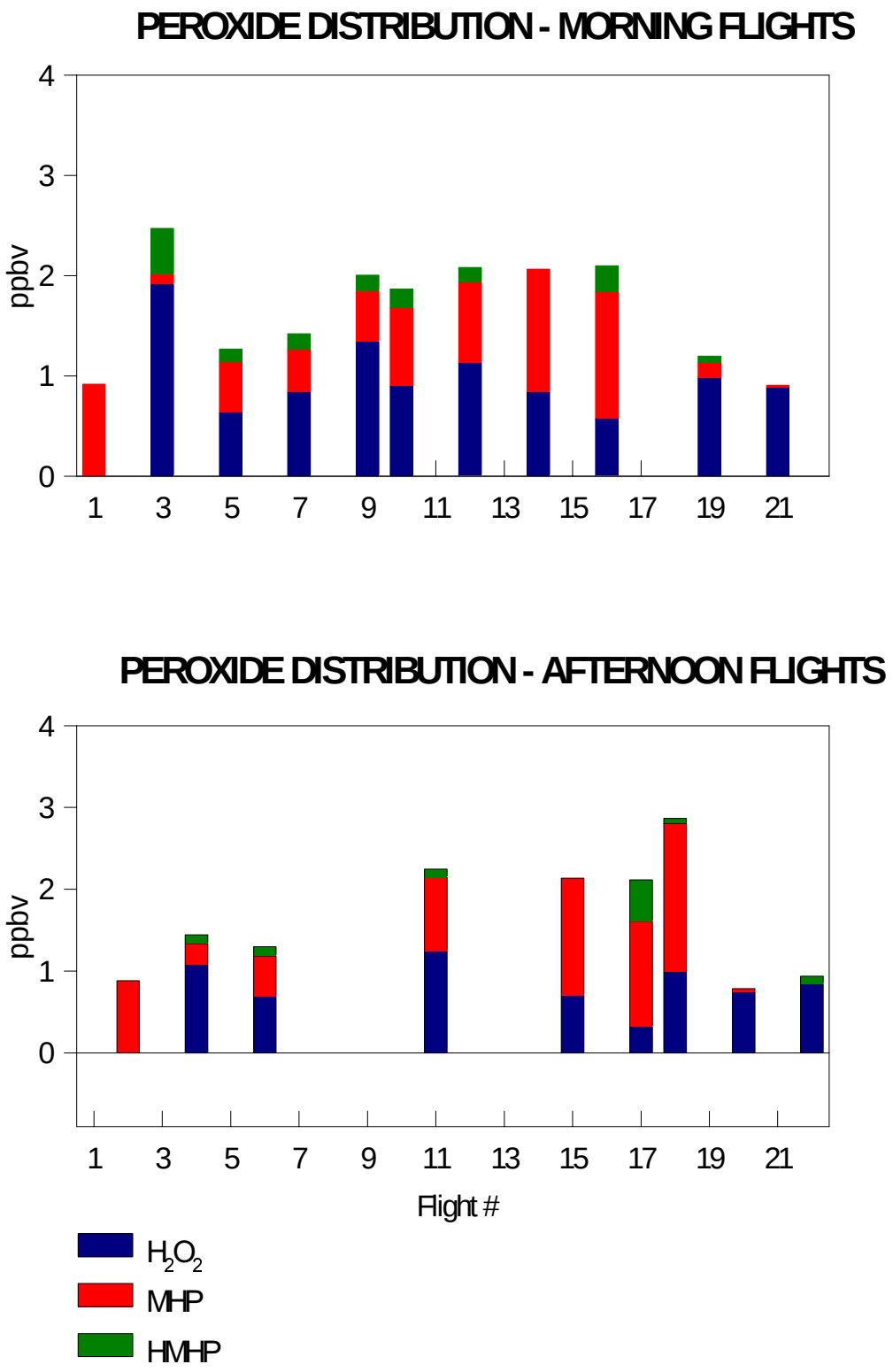


Figure 3: Observed hydroperoxide mixing ratios.

Morning Flights Phoenix '98

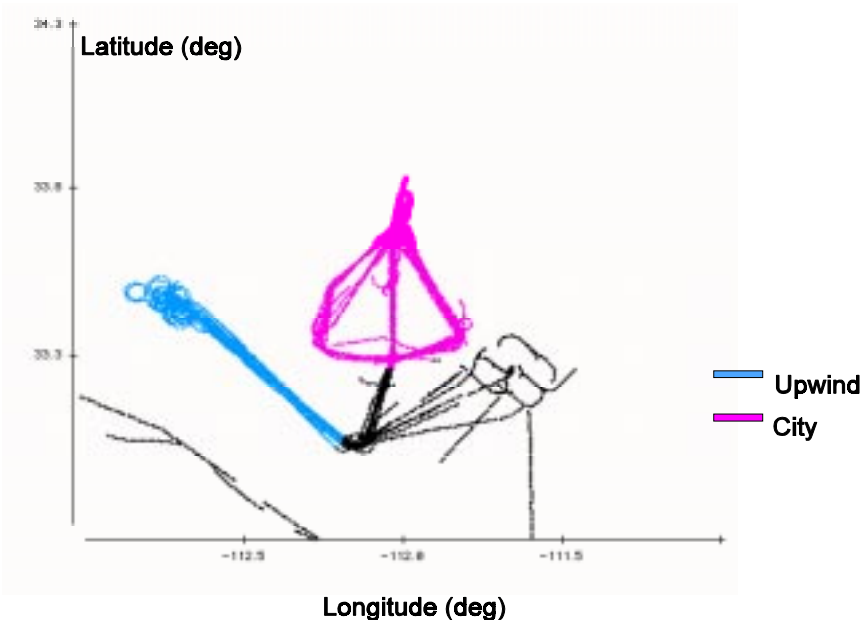


Figure 4: Overlaid paths for all morning flights.

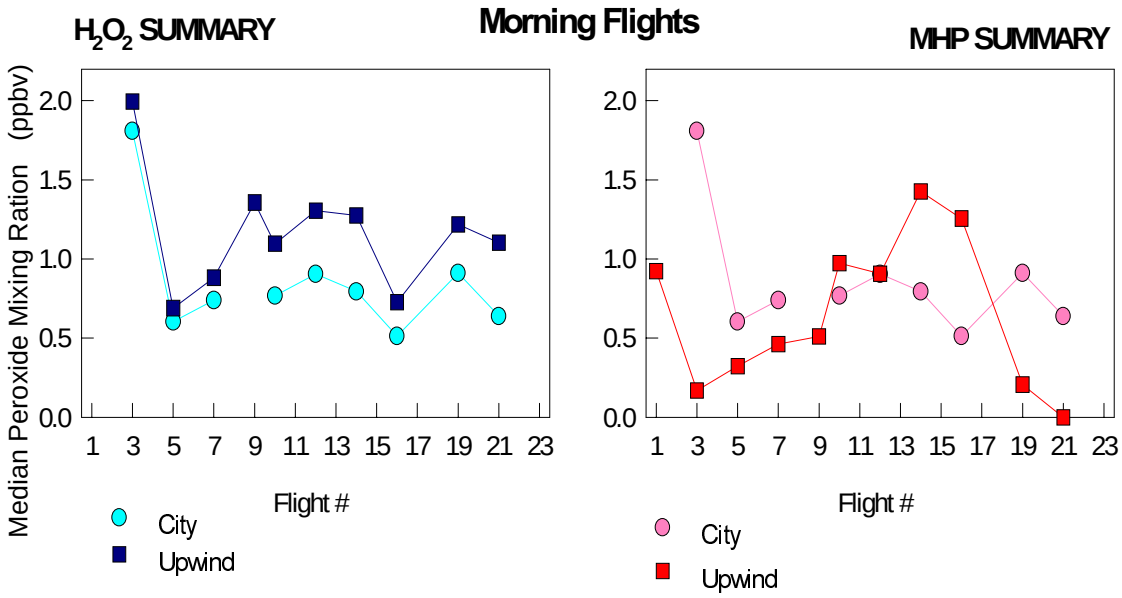


Figure 5: Comparison of H_2O_2 and MHP mixing ratios (upwind *vs* city, morning flights).

Afternoon Flights Phoenix '98

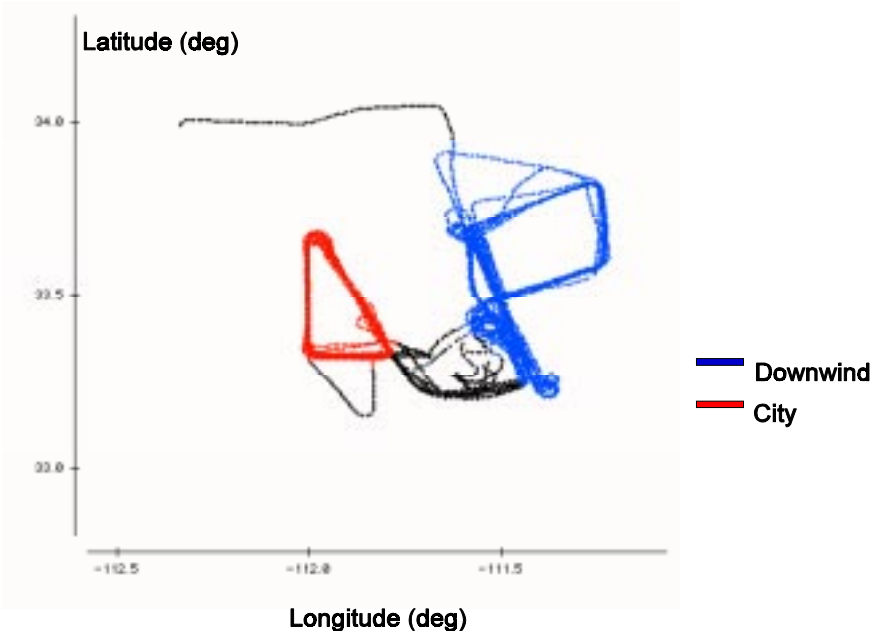


Figure 6: Overlaid paths for all afternoon flights.

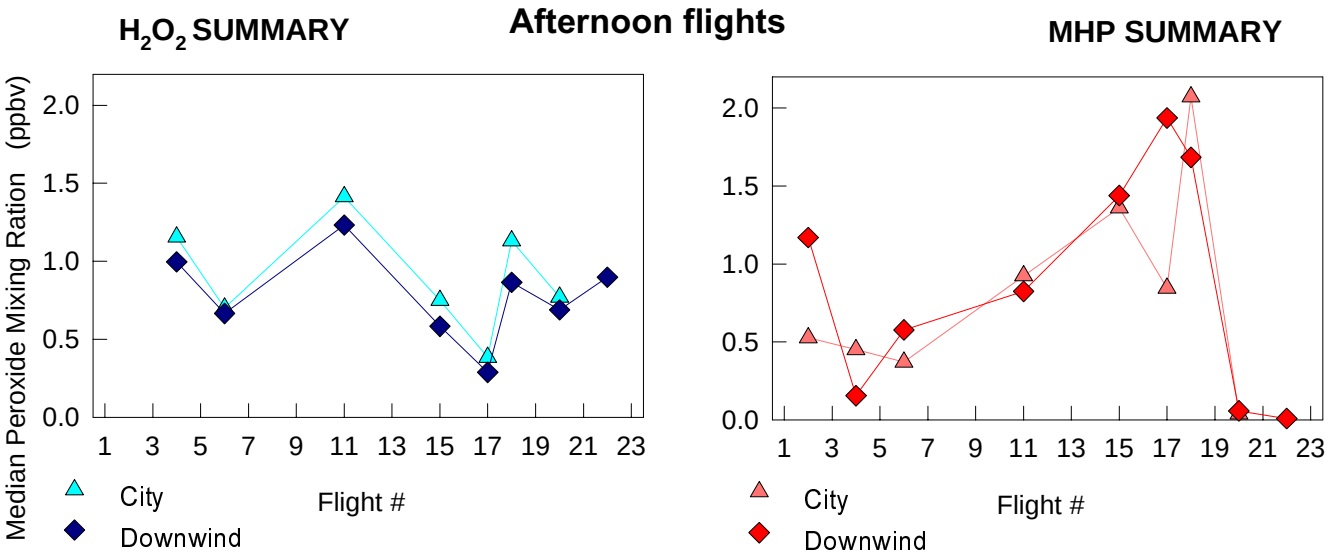


Figure 7: Comparison of H_2O_2 and MHP mixing ratios (city *vs* downwind, afternoon flights).

PRINCIPAL FINDINGS

Ground

- Total peroxide concentration remained below 0.5 ppbv.
- Typical diurnal profiles (maximum afternoon concentrations) were not observed.

Aircraft

- Although total peroxide was similar for morning and afternoon flights, the proportion of MHP frequently was higher in the afternoon.
- Median H_2O_2 concentrations as high as 1.8 ppbv were observed.
- MHP concentrations as high as 1.9 ppbv were observed; MHP constituted between 15 and 85% of the total.
- HMHP concentrations as high as 0.4 ppbv were observed; HMHP constituted between 0 and 19% of the total.
- In general, concentrations of H_2O_2 over the city were lower than upwind values in the morning, higher than downwind values in the afternoon, and *lower* in the afternoon than in the morning. MHP concentrations show no such obvious trend.

Concentration gradients we observed suggest that hydrogen peroxide is not produced, but rather is destroyed as air passes through the downtown area. This is likely due to low water vapor concentration, high NO_x concentrations that divert radicals to NO_y pathways, and

peroxide losses due to photolysis and dry deposition.

Upwind concentrations observed in the morning represent regional background values. The poor correlation with precursor concentrations, and relatively high proportion of ROOH we observe are consistent with peroxide losses in transit. Peroxide losses also explain the lack of correlation between O_3 as a radical source and the sink $2*H_2O_2+NO_z$.

ACKNOWLEDGMENTS

This study was supported by the U.S. Department of Energy Atmospheric Chemistry Program (98ER62586) and the National Science Foundation (ATM9843248). The authors are grateful for assistance from members of the BNL Environmental Chemistry group (Peter Daum, Leonard Newman, Larry Kleinman, Stephen Springston, Yin-Nan Lee, Linda Nunnermacker, Paul Klotz), Pacific Northwest National Laboratory, the G-1 crew, and the Arizona Department of Environmental Quality.