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Measurements of Hydrogen Peroxide and Formaldehyde in Glendora, California

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by

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ABSTRACT

Gas-phase hydrogen peroxide (H_2O_2) and formaldehyde (HCHO) were measured in Glendora, California from August 14-21, 1986. These measurements were part of the Carbonaceous Species Methods Comparison Study sponsored by the California Air Resources Board. Both of these species were measured using enzymatic techniques, H_2O_2 by the peroxidase catalyzed dimerization of p-hydroxyphenylacetic acid and formaldehyde by the formaldehyde dehydrogenase catalyzed reduction of NAD+ to NADH. Both H_2O_2 and HCHO showed a strong diurnal variation with the highest concentrations measured during the period of maximum photochemical activity. H_2O_2 concentrations ranged from less than 0.1 ppbv at night to a maximum of 3 ppbv for the hourly average on one day. The HCHO concentrations ranged from a low of 5 ppbv a night to a maximum of 20 ppbv during the day.

The first identification of hydrogen peroxide (H_2O_2) in the Los Angeles air was made by Haagen-Smit (1951). He used peroxidase enzyme coupled with colorimetric reaction to monitor the peroxide concentration. Other measurements of H_2O_2 have been made by Bufalini, Gay and Brubaker (1972), and Kok *et al.* (1978). The accuracy of these measurements are in question due to the formation of H_2O_2 from the reaction of ozone (O_3) with the collecting solution for H_2O_2 and due to the possible aqueous reaction of H_2O_2 with other gases (Zika and Salzman, 1982; Heikes *et al.* 1984). Since that time a number of techniques have been developed for the measurement of H_2O_2 in ambient air (Lazrus *et al.*, 1986; Tanner *et al.*, 1986; Sakugawa and Kaplan, 1987; Dasgupta *et al.*, 1988; Slemr *et al.*, 1986; Jacob, Tavares and Klockow, 1986). The first four techniques utilize the enzyme catalyzed dimerization of p-hydroxyphenylacetic acid (POPHA) as the analytical procedure with different methods for the collection of the H_2O_2. The last two techniques employ tunable diode laser absorption spectroscopy and chemiluminescence of a peroxylate ester as the analytical procedures, respectively. With the exception of the last analytical technique all of these measurement techniques were brought together during the summer of 1986 as part of the Carbonaceous Species Methods Comparison Study (CSMCS). The sampling site was located on the Citrus College campus in Glendora, California, approximately fifteen miles east of Pasadena, California. Details on the measurements of H_2O_2 made by the other analytical techniques are presented elsewhere in this volume (Dasgupta, Dong and Hwang, 1988; Tanner and Shen, 1988; Sakugawa and Kaplan, 1988; Schiff, Mayne and Mackay, 1988).

The presence of formaldehyde (HCHO) in Los Angeles air has been recognized since 1960 and has been associated with the intense eye irritation often observed (Renzetti and

Bryan, 1961). Since that time a number of measurements of HCHO have been made in the Los Angeles area, and a review of these is contained in Carlier, Hannachi and Mouvier (1986). As part of the CSMCS, three spectroscopic techniques for HCHO measurement (Atkinson *et al.*, 1988; Schiff, Mayne and Mackay, 1988), one DNPH (Fung and Wright, 1988), one continuous colorimetric technique (Dasgupta, Dong and Hwang, 1988), and an enzyme based method (Lazrus, Fong and Lind, 1988), were brought together for ambient HCHO sampling. This paper presents the results obtained with the enzyme technique. A comparison of the data from the HCHO measurements during this study is presented by Lawson *et al.*, (1988a).

Analytical Techniques

Measurements of H_2O_2 were made using the peroxidase enzyme technique of Lazrus *et al.*, (1986). In this technique, H_2O_2 and some of the organic peroxides (ROOH) are scrubbed from the air into aqueous solution using continuous flow concurrent extraction. 0.4 ml/min of scrubbing solution is drawn with the air sample into a glass coil; the velocity of the air spins the scrubbing solution to the walls and the peroxides are dissolved into solution. The collection efficiency for H_2O_2 is 100% and about 60% for methylhydroperoxide and peroxyacetic acid. The collection efficiency is lower for the higher molecular weight organic hydroperoxides. The analytical chemistry for H_2O_2 is based on the reaction of peroxides with p-hydroxyphenylacetic acid (POPHA) in the presence of the enzyme peroxidase (Lazrus *et al.*, 1985). This reaction forms the dimer of the POPHA which fluoresces with an emission wavelength of 420 nm when excited at 326 nm. Both H_2O_2 and short-chain organic hydroperoxides drive the analytical reaction. To separate the response from each of these species a dual channel approach is employed. The sample collection is performed

in duplicate, and in one channel a measure of the total soluble (100% of H_2O_2 and some fraction of the ROOH) is made. In the other channel, catalase enzyme is added to the aqueous solution of peroxides prior to the addition of the peroxide analytical reagent. The catalase removes the H_2O_2 with a majority of the ROOH remaining. With the addition of the analytical reagent a measure of the ROOH concentration is obtained. The H_2O_2 concentration is computed from the difference between the total peroxide measurement and the ROOH concentration after corrections have been applied for the discrimination of the catalase reaction.

Details on the discrimination of catalase reaction at low concentrations of methylhydroperoxide have been given in Lazrus *et al.*, (1985, 1986). Some reaction of catalase with methylhydroperoxide does occur. If the concentration of methylhydroperoxide is less than about 30% of the H_2O_2 concentration, this reaction is minimal and the correction to the H_2O_2 is small. The measurements presented here from Glendora are significantly more complex in that the concentration of ROOH is frequently larger than that of H_2O_2. At equal concentrations of methylhydroperoxide and H_2O_2 the reaction of catalase with the methylhydroperoxide will lead to an overcalculation the H_2O_2 concentration by about 20%. The data analysis for Glendora study is complicated in that the identity of the ROOH species are not known. In the present data analysis two conditions were treated, one where the ROOH did not react with catalase and the second where the reactivity was treated as methylhydroperoxide. For the measurement of H_2O_2 as applied to the conditions encountered in Glendora where a high concentration of organic hydroperoxides were encountered, this analytical technique should be used with caution.

The H_2O_2 analytical instrumentation was calibrated using standards. These are pre-

pared by serial dilution of a stock standard which was certified by titration with standard permanganate. The calibration accuracy (aqueous standards and sample flow rate) in the analytical technique was approximately 10% at the 95% confidence level. The accuracy of the H_2O_2 concentration is calculated from the propagation of errors on the experimental parameters. The percent error on the H_2O_2 data is 19% and 51% for conditions corresponding to mid-afternoon and midnight respectively. Under the high ozone conditions encountered during daylight hours in this study, the O_3 derived H_2O_2 artifact may occur at levels up to 0.10 ppbv H_2O_2. At night the O_3 concentrations dropped to near zero due to emissions of nitric oxide (NO) so that this artifact should be negligible. The accuracy for ROOH can also be estimated, and is 12% and 17% for ROOH equal to 0.8 ppbv and 0.2 ppbv respectively corresponding to midday and midnight conditions. The accuracy calculation applies to the concentration of ROOH as a lower limit. The H_2O_2 and ROOH detection limits were estimated as two times the standard deviation of the blanks and were 0.040 ppbv. In addition, all H_2O_2 data where the concentration of ROOH was more than twice the H_2O_2 concentration was rejected. Both the H_2O_2 and ROOH values below 0.15 ppbv should be interpreted with caution owing to the above discussion on accuracy.

HCHO was determined following the technique outlined by Lazrus, Fong and Lind (1988). Gas-phase HCHO was collected into aqueous solution using a technique similar to that for H_2O_2. Under these conditions the collection efficiency for HCHO is better than 98%. The aqueous solution of HCHO reacts with β-nicotinamide adenine dinucleotide (NAD+) in the presence of the enzyme, formaldehyde dehydrogenase. The NAD+ is reduced to NADH, which is quantitated by fluorescence measurement. HCHO calibrations were conducted using aqueous standards prepared by serial dilution of a stock standard

which was prepared gravimetrically. The concentration of this standard was verified by dimedone precipitation. The calibration accuracy of the analytical technique was approximately 15%. The estimated accuracy for the HCHO measurement is 17% and 21% for midday and midnight conditions respectively. Operational difficulties with the enzyme chemistry and the zero trap system degraded the precision to 25% for this study. Since this study refinements have eliminated these difficulties.

The data from the analytical instruments were recorded on an IBM PC based data system. Approximately 60 data points were collected over a 20 second time period. These instantaneous data were averaged and stored on disc. Hourly averages were assembled from this data. The computer controlled the hourly zero checks and checked the span every four hours. A full multipoint calibration was performed every other day.

Sampling was conducted through a PFA Teflon manifold. The inlet was approximately 4 m above the ground. The measurements of Texas Tech University (Dasgupta, Dong and Hwang, 1988), Brookhaven National Laboratory (Tanner and Shen, 1988), and the data reported here utilized a common manifold. The entire manifold was shielded from sunlight and the residence time was 10 seconds or less. No provisions were made for separating aerosols from the sampled air.

H_2O_2 Results and Discussion

The data for the H_2O_2 and ROOH measurements are given in Figure 1. The identity of the ROOH is not known, and these data can be assumed to be a lower limit of concentration, because the collection efficiency is approximately 60% for methylhydroperoxide and peroxyacetic acid and less for larger ROOH species. For the H_2O_2 data the upper

limit represents the case where the ROOH contains no methylhydroperoxide and the lower limit is where the collected ROOH is all methylhydroperoxide.

These are the first measurements with the enzymatic technique in a region such as Los Angeles where there is strong photochemical activity and heavy pollution. The data show a strong diurnal variation, and the measured concentration of ROOH is always greater than one-half the H_2O_2 concentration. In addition, there is considerable variation in the maximum concentration of H_2O_2 measured. Table 1 gives the values for O_3, temperature and relative humidity at the time the maximum hourly values for H_2O_2 were measured. The H_2O_2 and temperature data appear to be stratified into two periods, with the lowest H_2O_2 values measured on 8/14 and 15 and the higher concentrations measured on 8/17-8/19. The days of 8/16 and 8/20 are transition days. The temperatures corresponding to the time of maximum H_2O_2 fall into two strata: from 8/14-8/17 the temperature is 30° C, while from 8/17-8/20 the afternoon temperatures are around 37 °C. No stratification is seen in the O_3 data. The present data set is too limited to draw any conclusions on the factors influencing the maximum H_2O_2 levels.

The nighttime concentrations of H_2O_2 and ROOH at the sampling site are governed by the horizontal transport of the previous day's pollutants out of the basin, the vertical transport/mixing of the air aloft to the surface layer, and deposition to surfaces which may be dew covered. The early morning hours of August 15 and 16 were characterized by relative humidity (RH) levels of better than 95% and heavy dew formation. The H_2O_2 concentrations fall below the detection limit and the ROOH levels are between 50-100 pptv. The early morning hours of August 19 were characterized by virtually no dew formation and the mixing of aged pollution at the sampling site. Several hundred pptv of both H_2O_2

and ROOH remain throughout the night. On the following morning, August 20, stagnant conditions were present with light dew formation. The preferential deposition of H_2O_2 over ROOH to a dew covered surface is inferred as the concentration of ROOH rises to several times that of H_2O_2. This behavior follows the higher solubility of H_2O_2 than ROOH species in water. (Lind and Kok, 1986). As part of this study dew samples were collected and analyzed for a number of species including total hydroperoxide content (H_2O_2 and ROOH) (Pierson and Brachaczek, 1988). Of the 13 samples analyzed for hydroperoxides the highest measured concentration was 0.62 micromolar and ten of the samples were below the detection limit of 0.13 micromolar.

The measurements of H_2O_2 made using the enzyme technique are generally higher during the photochemically active period than those made by the other four participants in this study. A complete comparison for the H_2O_2 data will be made at a later date (Lawson *et al.*, 1988b). In June of 1986 an intercomparison study was conducted between the tunable diode laser technique (Slemr *et al.*, 1986), enzyme analytical technique with diffusion scrubbing collection, (Dasgupta *et al.*, 1987) and the enzyme analytical technique with continuous collection (Lazrus *et al.*, 1986) showing agreement within 20 % over a wide range of standard samples (Kleindienst *et al.*, 1988). The larger differences observed in this study will need additional detailed field studies to reconcile the differences. The measurements made in this study are factors of 100 and 10 lower than those made previously in the Los Angeles Basin (Bufalini, Gay and Brubaker, 1972; Kok, *et al.*, 1978) respectively. This reduction in the measured concentrations of H_2O_2 is presumably the result of improved measurement techniques.

An interesting aspect of this data set are the significant concentrations of ROOH mea-

sured. Measurements of H_2O_2 and ROOH in the Eastern United States showed that the ROOH concentration, measured in the boundary layer, was 10-20% of the H_2O_2 concentration (Heikes *et al.*, 1987). In these Los Angeles measurements, the ROOH concentration was about one-half of the H_2O_2 concentration during the daytime and increased to a factor of two or more at night. These higher levels of ROOH are presumably the result of the relatively high non-methane hydrocarbon (HC) to NO_x ratio characteristic of the air in the Los Angeles Basin. Measurements of this ratio in 1986 in central Los Angeles over a period of 25 days gave a value of 10 (Dolislager, 1987). Comparison of these measurements with computer simulations of a moderately polluted atmosphere (10 ppbv NO_x, HC/NO_x =6) gave a production ratio of ROOH to H_2O_2 of about 1:1 at the maximum (Calvert *et al.*, 1985). Since the formation of one ROOH results in a sink for one HO_2 and one RO_2, it is important to include measurements of ROOH in studies of the Los Angeles area to obtain an accurate accounting of the sinks of the peroxyl radicals for comparison with the model results.

HCHO Results and Discussion

HCHO measurements for the period August 14-19, 1986 are given in Figure 2. The data points are hourly averages compiled from the real-time data. The data set shows the influence of the three sources of HCHO in the Los Angeles Basin. From midnight until the early morning HCHO concentrations are at their lowest values ranging from 5-8 ppbv. A majority of this HCHO arises from stationary sources and this is presumably the range of the background concentration of HCHO in the Los Angeles basin. A sharp rise in the HCHO concentration is seen around 8 AM representing the added input from mobile sources, photochemistry and mixing from aloft. The maximum HCHO concentrations

were typically observed around 11 AM indicating the magnitude of the HCHO emissions from mobile sources and the downwash of pollutants from above with the breakage of the nocturnal boundary layer. A secondary maximum was seen in the mid-afternoon presumably from photochemically produced HCHO.

The HCHO data measured using the enzyme analytical technique are in good agreement with those determined by the other methods (Lawson *et al.*, 1988a). Within the accuracy limits of the analytical technique no systematic differences can be seen. These HCHO measurements are also consistent with those made previously in the Los Angeles basin (Tuazon, Winer and Pitts, 1981; Grosjean, 1982; Grosjean, D., Swanson, R. D., and Ellis, C., 1983). The maximum concentrations measured at Citrus College appear to be slightly lower than those measured previously. Since the maximum concentration of HCHO is strongly dependent on the proximity to sources and the amount of photochemistry, these variations in the maximum concentration are not significant.

Conclusions

In this study two enzyme analytical techniques were used to provide measurements of H_2O_2 and ROOH and HCHO. One hour average concentrations of H_2O_2 ranged from less than 100 pptv to 3.1 ppbv. At night the H_2O_2 concentrations were frequently less than the detection limit of 40 pptv. The ROOH concentrations ranged from a low of 70 pptv at night to a maximum of 1.4 ppbv during the day. HCHO concentrations were typically 5-8 ppbv at night and ranged up to 20 ppbv at mid-day. The hydroperoxides showed a strong diurnal variation where it was much less pronounced for HCHO.

Acknowledgments

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Table 1

Hourly Average Values[a]

Date	Maximum H_2O_2 (ppbv)	Maximum O_3[b] (ppbv)	Temperature °C	RH %
8/14/86	0.95-1.1	210	30.5	33
8/15/86	0.92-1.1	210	30.0	37[d]
8/16/86	1.2-1.4	220	30.6	37
8/17/86	2.5-3.0	240[c]	36.0[c]	24
8/18/86	1.8-2.2	220	38.0[c]	17
8/19/86	1.8-2.1	230[c]	36.6	25
8/20/86	1.1-1.5	220[c]	37.0[c]	28

[a]) One-hour integrated average.

[b]) Data provided by the Haagen-Smit Laboratory Division of the ARB.

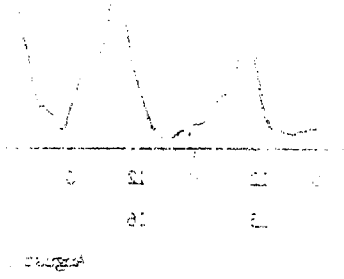
[c]) Daily maximum.

[d]) Minimum in RH.

Figure Captions

Figure 1 Measurements of H_2O_2 (top) and ROOH (bottom), August 14-21, 1986, at Glendora, California. The thickness of the line indicates upper and lower limits on the H_2O_2 concentrations. The data for ROOH is a lower limit as the collection efficiencies are unknown.

Figure 2 Measurements of HCHO, August 14-19, 1986 at Glendora, California.



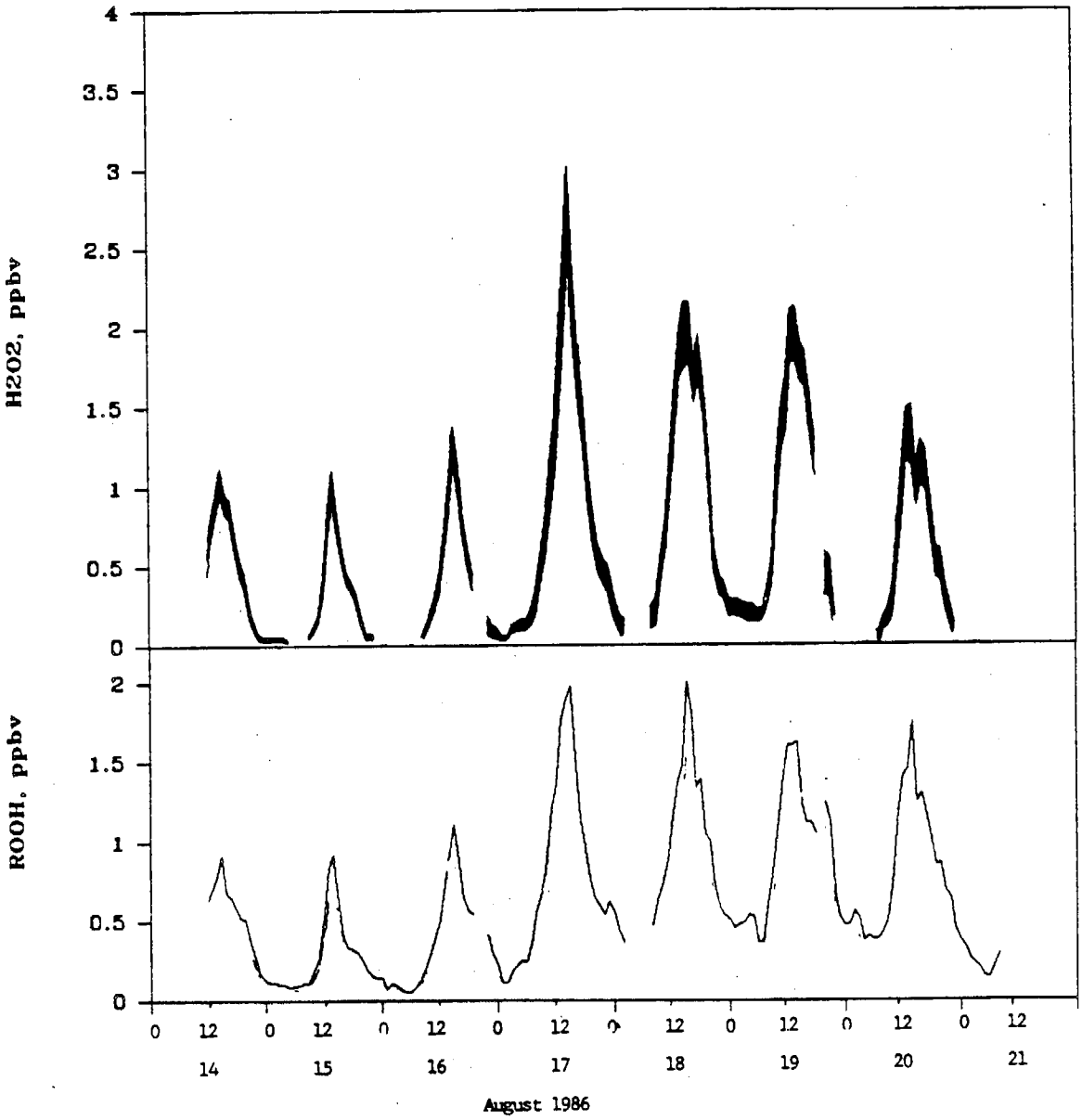

H2O2, ppbv
4
3.5
3
2.5
2
1.5
1
0.5
0
ROOH, ppbv
2
1.5
1
0.5
0
0 12 0 12 0 12 0 12 0 12 0 12 0 12 0 12
14 15 16 17 18 19 20 21
August 1986

Figure 1

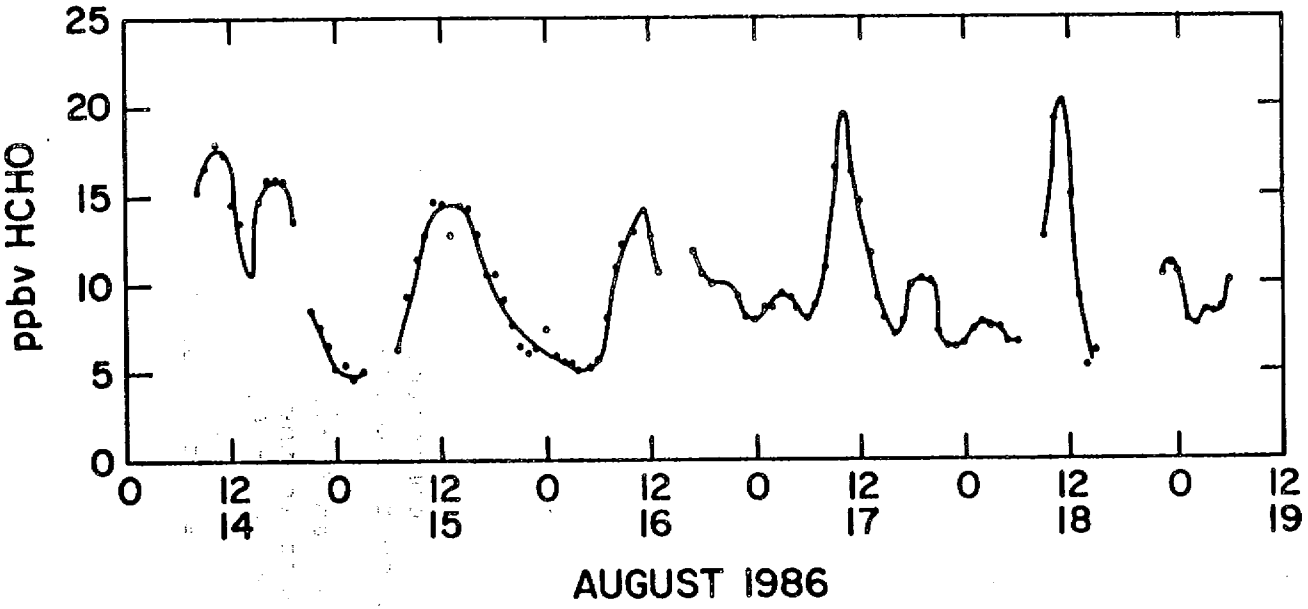

25
20
15
10
5
0
ppbv HCHO
0
12
14
0
12
15
0
12
16
0
12
17
0
12
18
0
12
19
AUGUST 1986

Figure 2

DATA TABLE

The attached table provides the listing for the data on hydroperoxides and formaldehyde (HCHO) measured at Glendora, California by the National Center for Atmospheric Research during August of 1986. The following details the column identifiers:

j-day Julian day for the year 1986.

hour, PDT Starting time for the hour over which the data are integrated, referenced to Pacific Daylight Time.

dec-day decimal representation of the day and hour.

H202 (ppbv) Lower Limit
Lower limit of H202 concentration computed assuming all of the organic hydroperoxide present reacted with catalase at the same rate constant as methylhydroperoxide.

H202 (ppbv) Upper Limit
Upper limit on the computed concentration of H202 assuming that none of the organic hydroperoxide present reacted with the catalase. The units are in parts per billion by volume.

ROOH (ppbv) Lower Limit
The measured concentration of organic hydroperoxides, given as the lower limit since the collection efficiency and the identity of these species is not known.

HCHO (ppbv)
Measured concentration of formaldehyde in parts per billion by volume.

Details on the analytical techniques and data reduction procedures can be found in the paper, "Measurements of Hydrogen Peroxide and Formaldehyde in Glendora, California" G.L. Kok, J.G. Walega, E.G. Heikes, J. Lind and A.L. Lazrus, Aerosol Science and Technology, submitted for publication, 1986.

j-day	hour,PDT	dec-day	H2O2(ppbv) Lower Limit	H2O2(ppbv) Upper Limit	ROOH(ppbv) Lower Limit	HCHO(ppbv)
226.00	12.00	226.50	0.44	0.56	0.64	14.6
226.00	13.00	226.54	0.67	0.80	0.70	13.4
226.00	14.00	226.58	0.81	0.95	0.78	10.5
226.00	15.00	226.63	0.95	1.12	0.91	14.8
226.00	16.00	226.67	0.83	0.96	0.68	15.8
226.00	17.00	226.71	0.79	0.92	0.65	15.8
226.00	18.00	226.75	0.60	0.70	0.58	15.9
226.00	19.00	226.79	0.45	0.55	0.53	13.4
226.00	20.00	226.83	0.36	0.46	0.51	
226.00	21.00	226.88	0.18	0.25	0.38	8.5
226.00	22.00	226.92	0.08	0.13	0.26	7.4
226.00	23.00	226.96	0.04	0.07	0.17	6.2
227.00	0.00	227.00	0.03	0.06	0.12	5.0
227.00	1.00	227.04	0.03	0.06	0.12	5.2
227.00	2.00	227.08	0.04	0.06	0.11	4.6
227.00	3.00	227.13	0.04	0.06	0.10	5.0
227.00	4.00	227.17	0.03	0.05	0.10	
227.00	5.00	227.21			0.09	
227.00	6.00	227.25			0.09	
227.00	7.00	227.29			0.10	6.2
227.00	8.00	227.33			0.11	9.1
227.00	9.00	227.38	0.04	0.06	0.11	11.3
227.00	10.00	227.42	0.07	0.11	0.19	12.9
227.00	11.00	227.46	0.14	0.20	0.28	14.5
227.00	12.00	227.50	0.33	0.43	0.51	14.5
227.00	13.00	227.54	0.67	0.84	0.83	12.7
227.00	14.00	227.58	0.92	1.10	0.92	14.4
227.00	15.00	227.63	0.69	0.82	0.62	14.3
227.00	16.00	227.67	0.51	0.59	0.40	12.8
227.00	17.00	227.71	0.39	0.46	0.34	10.5
227.00	18.00	227.75	0.34	0.40	0.33	10.0
227.00	19.00	227.79	0.26	0.32	0.31	9.0
227.00	20.00	227.83	0.13	0.18	0.26	7.6
227.00	21.00	227.88	0.04	0.08	0.20	6.3
227.00	22.00	227.92	0.05	0.08	0.16	6.0
227.00	23.00	227.96			0.13	5.4
228.00	0.00	228.00			0.13	7.2
228.00	1.00	228.04			0.07	5.8
228.00	2.00	228.08			0.11	5.0
228.00	3.00	228.13			0.10	5.4
228.00	4.00	228.17			0.07	5.1
228.00	5.00	228.21			0.06	5.1
228.00	6.00	228.25			0.05	5.1
228.00	7.00	228.29			0.07	8.0
228.00	8.00	228.33			0.12	10.6
228.00	9.00	228.38	0.06	0.10	0.20	12.3
228.00	10.00	228.42	0.14	0.20	0.29	12.7
228.00	11.00	228.46	0.23	0.31	0.41	14.1
228.00	12.00	228.50	0.37	0.47	0.50	12.8
228.00	13.00	228.54	0.58	0.73	0.73	10.5
228.00	14.00	228.58	0.84	1.03	0.92	
228.00	15.00	228.63	1.15	1.38	1.11	
228.00	16.00	228.67	0.95	1.13	0.89	
228.00	17.00	228.71	0.66	0.80	0.65	11.9
228.00	18.00	228.75	0.50	0.62	0.57	10.7
228.00	19.00	228.79	0.35	0.46	0.55	10.0
228.00	20.00	228.83				
228.00	21.00	228.88				

228.00	22.00	228.92	0.07	0.19	0.42	9.3
228.00	23.00	228.96			0.30	7.9
229.00	0.00	229.00			0.23	8.0
229.00	1.00	229.04			0.12	8.6
229.00	2.00	229.08			0.11	8.7
229.00	3.00	229.13	0.08	0.13	0.19	9.4
229.00	4.00	229.17	0.09	0.15	0.23	9.2
229.00	5.00	229.21	0.10	0.17	0.25	8.7
229.00	6.00	229.25	0.10	0.17	0.25	8.2
229.00	7.00	229.29	0.13	0.23	0.36	9.0
229.00	8.00	229.33	0.20	0.35	0.56	11.1
229.00	9.00	229.38	0.39	0.58	0.66	16.4
229.00	10.00	229.42	0.55	0.79	0.84	19.4
229.00	11.00	229.46	0.86	1.20	1.21	16.2
229.00	12.00	229.50	1.06	1.45	1.37	14.0
229.00	13.00	229.54	1.48	1.98	1.77	11.5
229.00	14.00	229.58	1.91	2.44	1.90	9.1
229.00	15.00	229.63	2.46	3.01	1.98	7.8
229.00	16.00	229.67	1.90	2.33	1.54	7.1
229.00	17.00	229.71	1.52	1.85	1.16	7.8
229.00	18.00	229.75	1.26	1.54	0.98	10.0
229.00	19.00	229.79	0.87	1.09	0.78	10.3
229.00	20.00	229.83	0.63	0.82	0.65	10.2
229.00	21.00	229.88	0.46	0.63	0.61	7.2
229.00	22.00	229.92	0.39	0.54	0.54	6.4
229.00	23.00	229.96	0.34	0.51	0.63	6.4
230.00	0.00	230.00	0.19	0.34	0.56	6.8
230.00	1.00	230.04	0.10	0.22	0.44	7.5
230.00	2.00	230.08			0.37	7.6
230.00	3.00	230.13				7.5
230.00	4.00	230.17				7.3
230.00	5.00	230.21				6.8
230.00	6.00	230.25				6.6
230.00	7.00	230.29				
230.00	8.00	230.33	0.11	0.25	0.48	
230.00	9.00	230.38	0.13	0.31	0.64	12.7
230.00	10.00	230.42	0.39	0.55	0.73	18.9
230.00	11.00	230.46	0.62	0.81	0.89	20.2
230.00	12.00	230.50	0.99	1.23	1.16	14.9
230.00	13.00	230.54	1.36	1.64	1.37	6.8
230.00	14.00	230.58	1.68	1.99	1.49	5.1
230.00	15.00	230.63	1.74	2.15	2.01	6.0
230.00	16.00	230.67	1.78	2.15	1.82	
230.00	17.00	230.71	1.53	1.80	1.34	
230.00	18.00	230.75	1.67	1.96	1.40	
230.00	19.00	230.79	1.45	1.67	1.05	
230.00	20.00	230.83	1.01	1.22	1.01	
230.00	21.00	230.88	0.48	0.63	0.73	
230.00	22.00	230.92	0.31	0.43	0.58	10.3
230.00	23.00	230.96	0.29	0.41	0.54	11.1
231.00	0.00	231.00	0.18	0.29	0.51	10.7
231.00	1.00	231.04	0.19	0.29	0.46	7.8
231.00	2.00	231.08	0.18	0.28	0.48	7.5
231.00	3.00	231.13	0.17	0.27	0.49	8.5
231.00	4.00	231.17	0.15	0.26	0.54	8.8
231.00	5.00	231.21	0.15	0.26	0.54	8.7
231.00	6.00	231.25	0.15	0.22	0.37	10.3
231.00	7.00	231.29	0.16	0.24	0.37	
231.00	8.00	231.33	0.24	0.37	0.61	
231.00	9.00	231.38	0.39	0.56	0.82	

231.00	10.00	231.42	0.88	1.10	1.09
231.00	11.00	231.46	1.22	1.51	1.41
231.00	12.00	231.50	1.35	1.69	1.61
231.00	13.00	231.54	1.78	2.11	1.61
231.00	14.00	231.58	1.78	2.12	1.63
231.00	15.00	231.63	1.65	1.91	1.24
231.00	16.00	231.67	1.62	1.85	1.12
231.00	17.00	231.71	1.35	1.58	1.12
231.00	18.00	231.75	1.06	1.28	1.06
231.00	19.00	231.79			
231.00	20.00	231.83			1.25
231.00	21.00	231.88			1.13
231.00	22.00	231.92			0.65
231.00	23.00	231.96			0.53
232.00	0.00	232.00			0.48
232.00	1.00	232.04			0.48
232.00	2.00	232.08			0.57
232.00	3.00	232.13			0.52
232.00	4.00	232.17			0.38
232.00	5.00	232.21			0.41
232.00	6.00	232.25			0.39
232.00	7.00	232.29			0.39
232.00	8.00	232.33	0.09	0.18	0.43
232.00	9.00	232.38	0.12	0.23	0.51
232.00	10.00	232.42	0.19	0.35	0.74
232.00	11.00	232.46	0.53	0.78	1.19
232.00	12.00	232.50	0.84	1.14	1.42
232.00	13.00	232.54	1.17	1.48	1.46
232.00	14.00	232.58	1.12	1.51	1.75
232.00	15.00	232.63	0.87	1.15	1.25
232.00	16.00	232.67	1.01	1.29	1.31
232.00	17.00	232.71	0.98	1.23	1.17
232.00	18.00	232.75	0.68	0.91	1.02
232.00	19.00	232.79	0.43	0.61	0.86
232.00	20.00	232.83	0.41	0.60	0.87
232.00	21.00	232.88	0.22	0.37	0.70
232.00	22.00	232.92	0.09	0.23	0.64
232.00	23.00	232.96			0.46
233.00	0.00	233.00			0.38
233.00	1.00	233.04			0.34
233.00	2.00	233.08			0.27
233.00	3.00	233.13			0.24
233.00	4.00	233.17			0.21
233.00	5.00	233.21			0.16
233.00	6.00	233.25			0.15
233.00	7.00	233.29			0.22
233.00	8.00	233.33			0.30

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