



DIGITAL ACCESS TO
SCHOLARSHIP AT HARVARD
DASH.HARVARD.EDU



HARVARD LIBRARY
Office for Scholarly Communication

Hydrogen peroxide, organic hydroperoxide, and formaldehyde as primary pollutants from biomass burning

The Harvard community has made this
article openly available. [Please share](#) how
this access benefits you. Your story matters

Citation	Lee, Meehye, Brian G. Heikes, Daniel J. Jacob, Glen Sachse, and Bruce Anderson. 1997. "Hydrogen Peroxide, Organic Hydroperoxide, and Formaldehyde as Primary Pollutants from Biomass Burning." <i>Journal of Geophysical Research</i> 102 (D1): 1301. doi:10.1029/96jd01709.
Published Version	doi:10.1029/96JD01709
Citable link	http://nrs.harvard.edu/urn-3:HUL.InstRepos:14121819
Terms of Use	This article was downloaded from Harvard University's DASH repository, and is made available under the terms and conditions applicable to Other Posted Material, as set forth at http://nrs.harvard.edu/urn-3:HUL.InstRepos:dash.current.terms-of-use#LAA

Hydrogen peroxide, organic hydroperoxide, and formaldehyde as primary pollutants from biomass burning

Meehye Lee and Brian G. Heikes

Center for Atmospheric Chemistry Study, Graduate School of Oceanography, University of Rhode Island
Narragansett

Daniel J. Jacob

Harvard University, Cambridge, Massachusetts

Glen Sachse and Bruce Anderson

NASA Langley Research Center, Hampton, Virginia

Abstract. Hydrogen peroxide, organic hydroperoxide species, and formaldehyde were found to be enhanced within biomass burning plumes during the Transport and Atmospheric Chemistry near the Equator - Atlantic (TRACE A) experiment. This enhancement could have resulted from direct emission by the fires or by secondary photochemical production. In this study, direct production of hydroperoxide and formaldehyde from biomass burning is proposed and examined through comparisons of hydroperoxide and formaldehyde measurements, obtained from three fire flights in TRACE A, with model estimates, with other measurement data, and with results from fire experiments at the University of Rhode Island (URI). For highest concentrations of hydroperoxide and formaldehyde, model predictions fall short of those observed, and an additional source is required. H_2O_2 and CH_3OOH were noted to increase with CO and were significantly correlated with other measured species known to be produced from biomass burning. The enhancements of H_2O_2 and CH_3OOH relative to CO were different between flights in which the relative enhancements of CO to CO_2 were also different. The enhancement ratio of H_2O_2 and CH_3OOH relative to CO was 1.5×10^{-2} and 2.4×10^{-3} , respectively. CH_2O was correlated with CO. The enhancement ratios of CH_2O were determined in relation to both CO and CO_2 for three flights and were 7.19×10^{-3} and 3.5×10^{-4} , respectively. The correlations of CH_2O with other measured combustion species were more significant than those of H_2O_2 and CH_3OOH . To determine whether hydroperoxide and formaldehyde can be directly produced from biomass burning, simple biomass fire experiments were performed at URI. These species were observed to be clearly elevated in test biomass fires. These experiments present unequivocal evidence for the direct production of hydrogen peroxide and formaldehyde from biomass burning. The results from both TRACE A and our fire experiments also fit possible mechanisms of direct formation of hydroperoxide and formaldehyde in combustion processes. The atmospheric implication of the direct production of these species from biomass burning is their contribution to odd-hydrogen radical production, thereby affecting the oxidizing capacity of the atmosphere before O_3 would be photochemically developed. In TRACE A, odd-hydrogen radical production from the direct source of these species is estimated to be near 30% of the total radical production.

1. Introduction

Biomass burning is recognized as one of the most important biogeochemical processes with significant impacts on the atmosphere. During biomass burning, a wide range of trace gases including CO_2 , CO, CH_4 , NMHC, NO_x , and N_2O are released into the atmosphere [Crutzen and Andreae, 1990; Andreae, 1993]. CO_2 , N_2O , and CH_4 are known greenhouse gases contributing to climate change [Mitchell, 1989]. Halogen gases such as CH_3Cl and CH_3Br produced by biomass burning may have influence on stratospheric ozone chemistry [Manó and Andreae, 1994; Cicerone, 1994]. Photochemical reactions between emitted

hydrocarbons and NO_x lead to net ozone production. Ozone produces OH in humid air, and CO and CH_4 consume OH in the remote atmosphere; therefore biomass burning can affect OH concentrations, atmospheric oxidant concentrations, and the rate of oxidation of reduced compounds [Rodríguez *et al.*, 1991]. Hence biomass burning is believed to play an important role in global change [Levine, 1991; International Council of Scientific Unions (ICSU), 1994].

During the Transport and Atmospheric Chemistry near the Equator - Atlantic (TRACE A) experiment [e.g., Fishman *et al.*, 1994], hydrogen peroxide (H_2O_2), organic hydroperoxides (i.e., CH_3OOH , HOCH_2OOH , $\text{CH}_3\text{CH}(\text{OH})\text{OOH}$, and $\text{CH}_3\text{C}(\text{O})\text{OOH}$) and formaldehyde (CH_2O) concentrations were extremely high in and near biomass burning plumes [Lee *et al.*, 1996]. In the Pacific Exploratory Mission - West, Phase A (PEM-West A) experiment, the highest concentrations of H_2O_2 and CH_3OOH were observed over the Celbes Sea in air believed to be impacted

Copyright 1997 by the American Geophysical Union.

Paper number 96JD01709.
0148-0227/97/96JD-01709\$09.00

by fire emissions [Heikes *et al.*, 1996a]. Further, the highest H₂O₂ and CH₂O concentrations measured in the Mauna Loa Observatory Photochemistry Experiment (MLOPEX) were thought to be associated with fire emissions [Heikes, 1992]. These results led us to consider biomass burning as a direct source of H₂O₂, organic hydroperoxide, and CH₂O.

Hydrogen peroxide and methyl hydroperoxide are normally thought of as secondary photochemical products acting as reservoirs of odd-hydrogen radicals (e.g., OH, HO₂, and CH₃OO). Together with formaldehyde, which is a source of odd-hydrogen radicals, they are also precursors of odd-oxygen (e.g., O₃, O, and NO₂) [Logan *et al.*, 1981; Kleinman, 1986, 1991]. Both odd-hydrogen and odd-oxygen families are important oxidizing species that determine the distribution and abundance of reactive trace gases in the atmosphere and vice versa [National Academy of Sciences (NAS), 1984]. If H₂O₂, organic hydroperoxide, and CH₂O are directly produced from biomass burning, then their photolysis would enhance radical production near the fire and would affect the oxidizing capacity of the atmosphere [Thompson, 1992]. The TRACE A measurements indicate the potential for their direct production from biomass burning and the need to investigate the degree and extent to which biomass fires affect H₂O₂, organic hydroperoxide, and formaldehyde and consequently may affect atmospheric oxidants. In this paper we hypothesize the direct production of hydroperoxide and formaldehyde from biomass burning and test this hypothesis with data obtained from three fire flights during TRACE A (flights 6 and 7 over Brazil and flight 10 over Africa) and a limited number of test biomass burns performed at the University of Rhode Island (URI) Bay campus.

2. Observed Hydroperoxide and Formaldehyde in TRACE A

We measured H₂O₂ and organic hydroperoxide species with high-performance liquid chromatography (HPLC) system mounted in the NASA DC-8 aircraft during TRACE A. The details about the measurement scheme are supplied by Lee *et al.* [1995]. Formaldehyde was measured during TRACE A by using the method of Lazrus *et al.* [1988] as implemented by Heikes [1992] and Heikes *et al.* [1996b]. TRACE A was conducted in September-October 1992. Its primary objective was to investigate the cause of a seasonal tropospheric ozone maximum over the South Atlantic observed when biomass burning is the most prevalent in South America and Africa [Fishman, 1994; Fishman *et al.*, 1996]. A comprehensive set of chemical and meteorological data was obtained during 17 flights over the South Atlantic, Brazil, and southern Africa, including several flights within and downwind of fire plumes [Fishman *et al.*, 1996].

Three of 17 flights were made specifically to collect air samples over the biomass burning source regions. H₂O₂, CH₃OOH, and CH₂O concentrations were elevated in and near burning plumes and observed up to 10 ppbv, 2 ppbv, and 5 ppbv, respectively. These are extremely high values for H₂O₂ compared with those from undisturbed background conditions and from theoretical model values, although the CH₂O levels are comparable to those observed in urban environments. CH₃OOH was only slightly enhanced in the plumes, and other organic hydroperoxides such as hydroxymethyl hydroperoxide (HOCH₂OOH: HMHP) and 1-hydroxyethyl hydroperoxide (CH₃CH(OH)OOH: 1-HEHP) were sporadically detected during flights 6 and 10. Additional results related to H₂O₂, CH₃OOH, and CH₂O from this experiment can be found elsewhere [e.g., Jacob *et al.*, 1996; Heikes *et al.*, 1996c; Lee *et al.*, 1996].

3. Test of Hypothesis

3.1. Comparison of Observed Data With Photochemical Model Result

Figure 1 shows the observed concentrations of H₂O₂, CH₃OOH, and CH₂O versus their model values for the three flights near fires: flights 6, 7, and 10. A merged data set indexed

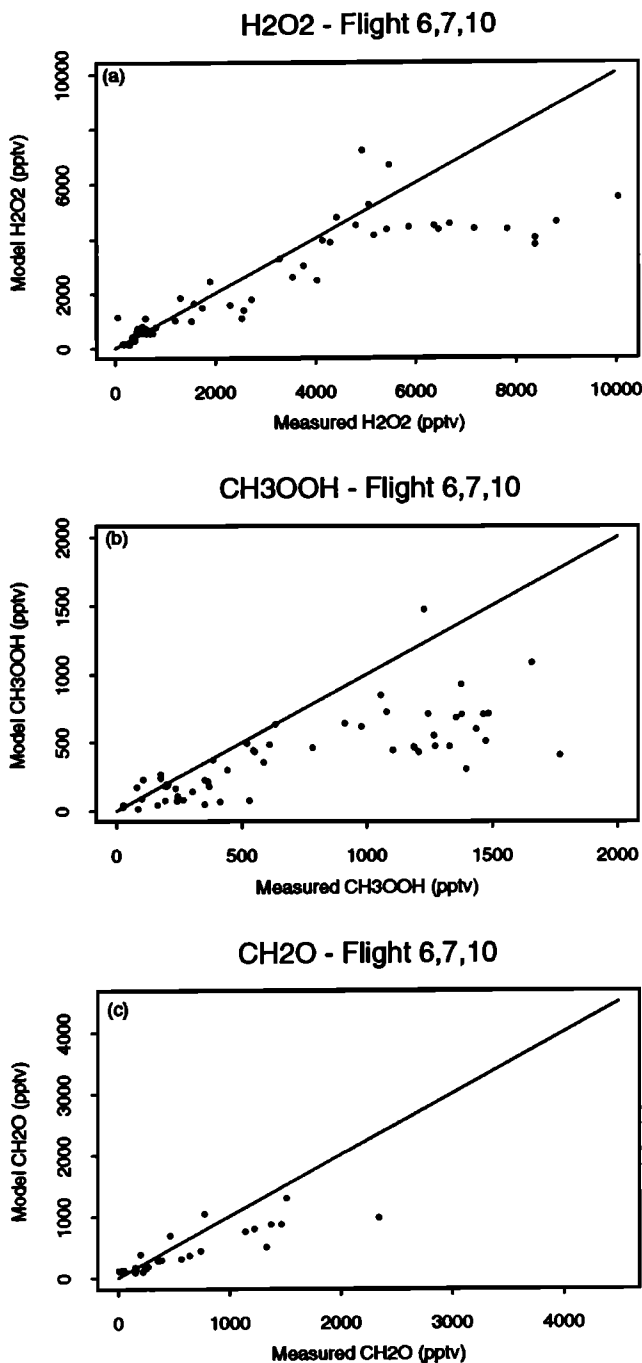


Figure 1. Observed concentrations of H₂O₂, CH₃OOH, and CH₂O compared with those predicted in the model for three flights (flights 6 and 7 over Brazil and flight 10 over Africa) in TRACE A. The x axis is the observed concentrations, and the y axis is those predicted from photochemical model: (a) H₂O₂, (b) CH₃OOH, and (c) CH₂O. Solid lines indicate a one-to-one ratio between observed concentrations and model values.

to hydroperoxide data [Jacob *et al.*, 1996] was used in this analysis. The lines indicate a one-to-one ratio between observed and predicted values. Below 5000 pptv of H₂O₂ and 1000 pptv of CH₃OOH these species appear to be near photochemical equilibrium. Above these observed concentrations, however, model values remain nearly constant, leading to greater differences between the two results at higher concentrations. This finding implies that photochemical production is insufficient to support the observed high concentrations of H₂O₂ and an additional source is needed. Although the case for CH₃OOH is visually weaker, Figure 1b suggests CH₃OOH may also require an additional source above 1000 pptv. The higher concentrations of CH₂O above 2000 pptv are not displayed in Figure 1c because of the lack of overlap between model and observed data due to the absence of other key chemical parameters needed by the model. However, there is a tendency for theoretical values to fall short of those observed, and an additional source would be necessary.

The observed hydroperoxide and formaldehyde data can be compared with those calculated from a photochemical point model. In general, agreement between observed and predicted results lies within the uncertainties of the measurement and the model calculation [Davis *et al.*, 1996; Jacob *et al.*, 1996]. However, a divergence between model and measurements was noted when high concentrations were observed immediately over biomass burning regions with observed values substantially higher than those predicted. Low model values suggest either missing sources or an overestimate of the sink for these species in fire plumes. An overestimate does not seem plausible, since the deposition of both hydroperoxide and formaldehyde, which is an important removal process for these species, was not included in the model. Further, reduction of OH and photolysis, the primary photochemical sinks for these species, also reduces their production with the resulting concentrations of H₂O₂, CH₃OOH, and CH₂O being little changed. Consequently, additional sources are needed to resolve the deviations between model and observed data over biomass fire source regions.

Direct production in biomass fires could cause the increased concentrations of these species in and near plumes. This possibility was not considered in the model. However, there may be short-lived hydrocarbons produced from biomass fires which were not measured during the experiment and which would have been oxidized prior to sampling of the plume by the aircraft. Peroxides might have been enhanced by photochemical reactions involving these hydrocarbons. This theory was also not taken into account in the model. Thus we could not exclusively rule out secondary photochemical production as an additional source for these species.

3.2. Correlation of Hydroperoxide and Formaldehyde With Other Measured Species

CO and CO₂ are often used to characterize biomass fires and to estimate the emissions of other species [Levine *et al.*, 1991; Lobert *et al.*, 1991]. If H₂O₂, CH₃OOH, and CH₂O are directly produced, then they should be significantly correlated with them. The emission of a species *X* can be related to the emission of CO₂ through an emission ratio, *ER*, defined by

$$ER(X) = \frac{\Delta X}{\Delta CO_2}$$

where ΔX is the excess concentration of species *X* produced by biomass burning over background and ΔCO_2 is the excess concentration of CO₂ produced by biomass burning over background. Since the emissions of gases are dependent on the stage of burning (flaming or smoldering), CO is also used as a reference

gas in calculating emission ratios, $ER' = \Delta X/\Delta CO$ [Lobert *et al.*, 1991]. There are no data for the direct emission of hydroperoxides from biomass burning. For CH₂O, Griffith *et al.* [1991] made measurements in several prescribed fires and calculated the emission ratio of CH₂O relative to CO₂. From ambient measurements of hydroperoxide, formaldehyde, CO, and CO₂ in TRACE A, emission ratio could not be determined, because measurements were not confined to fire plumes. In this study the enhancement ratio derived from the slope of the linear regression between the target species and either CO or CO₂ was

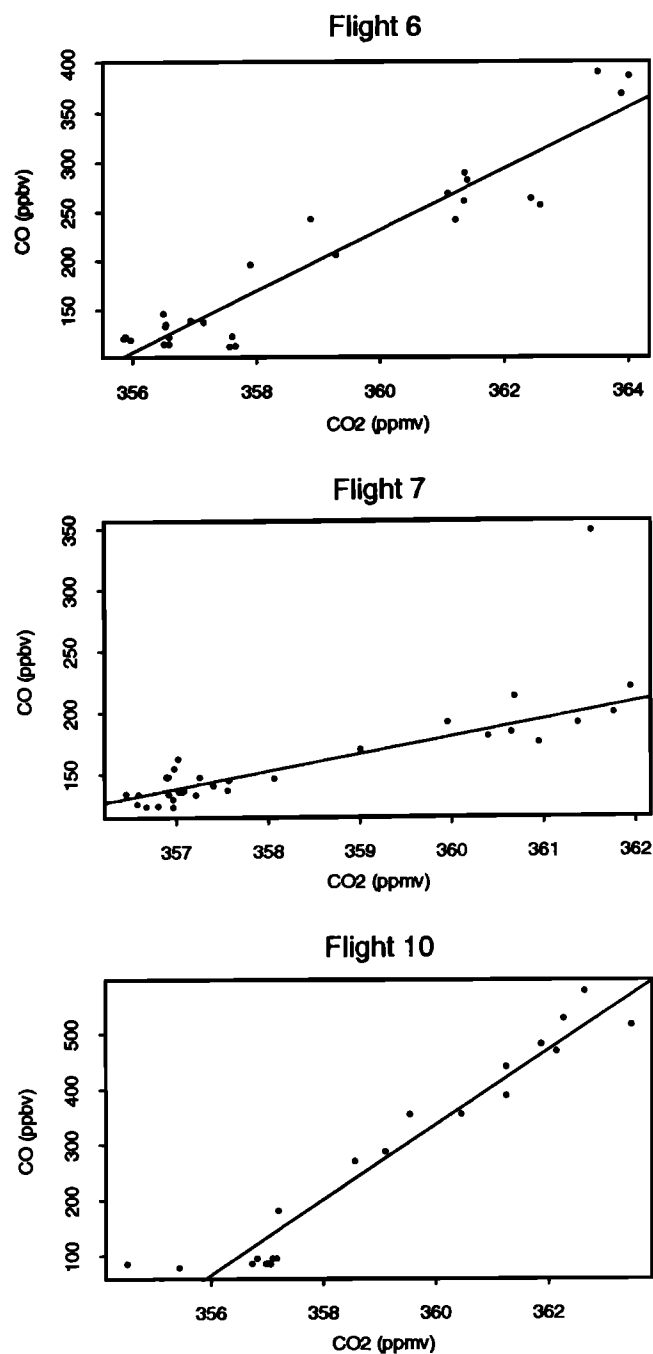


Figure 2. Plot of CO versus CO₂ for each flight. Solid lines are linear fitting between CO and CO₂, and the slope of the line corresponds to the enhancement ratio of CO relative to CO₂. Data below 5 km were included in this analysis through Figure 5.

Table 1. Summary of Linear Regression

Figure ^a	Species	r ² ^b	p ^c	N ^d	Slope ^e
<i>Flight 6</i>					
2	CO versus CO ₂	0.9056	3*10 ⁻¹⁴	27	3.1*10 ⁻²
3	H ₂ O ₂ versus CO	0.5004	4*10 ⁻⁵	27	1.4*10 ⁻²
3	CH ₃ OOH versus CO	0.3200	2*10 ⁻³	27	2.1*10 ⁻³
3	CH ₂ O versus CO	0.8808	6*10 ⁻⁵	10	8.8*10 ⁻³
5	CH ₂ O versus CO ₂	0.9031	3*10 ⁻⁵	10	3.1*10 ⁻⁴
4	H ₂ O ₂ versus CH ₃ OOH	0.4683	8*10 ⁻⁵	27	3.7
<i>Flight 7</i>					
2	CO versus CO ₂	0.8487	2*10 ⁻¹³	31	1.4*10 ⁻²
3	H ₂ O ₂ versus CO	0.2765	2*10 ⁻³	31	4.6*10 ⁻²
3	CH ₃ OOH versus CO	0.1665	2*10 ⁻²	31	4.0*10 ⁻³
3	CH ₂ O versus CO	0.8834	7*10 ⁻⁹	18	1.9*10 ⁻²
5	CH ₂ O versus CO ₂	0.5940	2*10 ⁻⁴	18	4.1*10 ⁻⁴
4	H ₂ O ₂ versus CH ₃ OOH	0.7499	2*10 ⁻¹⁰	32	7.6
<i>Flight 10</i>					
2	CO versus CO ₂	0.9314	4*10 ⁻¹³	22	6.7*10 ⁻²
3	H ₂ O ₂ versus CO	0.8094	2*10 ⁻⁹	24	1.1*10 ⁻²
3	CH ₃ OOH versus CO	0.6884	5*10 ⁻⁷	24	2.2*10 ⁻³
3	CH ₂ O versus CO	0.8541	2*10 ⁻⁵	12	7.0*10 ⁻³
5	CH ₂ O versus CO ₂	0.7038	3*10 ⁻⁴	13	4.7*10 ⁻⁴
4	H ₂ O ₂ versus CH ₃ OOH	0.9581	0	25	4.3

^a Corresponding figure.

^b Correlation coefficient of linear regression.

^c Linear correlation is significant at any confidence level greater than this *p* value.

^d Number of samples included.

^e Enhancement ratio of species relative to CO or CO₂.

used to estimate fire production of species *X* per unit CO or CO₂. Data below 5 km were included in this analysis.

CO is plotted versus CO₂ for each flight (Figure 2). There is a significant linear correlation between CO and CO₂ concentrations, and the slope of the linear regression corresponds to the enhancement ratio of CO relative to CO₂. Correlation coefficients, their significance, and enhancement ratios are listed in Table 1 for flights 6, 7, and 10. The enhancement ratio of CO is different for each flight. It is the lowest in flight 7 and the highest in flight 10. This finding implies that the quality of the fires sampled by each flight is different: a low ratio indicates high temperature and more oxygen availability, and a high ratio indicates low temperature and less oxygen availability [Hegg *et al.*, 1990; Lobert *et al.*, 1991]. Because of indicated fire variability, all correlations between measured species were made separately for each flight. CO was used as the combustion reference for the enhancement ratios of hydroperoxide and formaldehyde, because the enhancement signal of CO from biomass burning is stronger in relation to its background concentrations, whereas that of CO₂ is weaker in relation to its background level.

3.2.1. Hydroperoxide. H₂O₂ and CH₃OOH concentrations from the three flights are plotted versus CO in Figure 3. It can be seen that the concentrations of H₂O₂ and CH₃OOH increase with increasing CO concentration. Interpretation of H₂O₂ versus CO can be confounded by H₂O, because much of H₂O₂ variance has been explained in terms of H₂O [Luria *et al.*, 1989; Tremmel *et al.*, 1993]. These two hydroperoxides are also significantly correlated within the subset of fire data for each flight (Figure 4). Table 1 lists the H₂O₂ and CH₃OOH enhancement ratio for each flight. The H₂O₂ to CO enhancement ratio was 1.5*10⁻², and that for CH₃OOH was 2.4*10⁻³. Both H₂O₂ and CH₃OOH are highly enhanced relative to CO in flight 7 compared to the other

two flights, and the relative enhancement of H₂O₂ to CH₃OOH (Δ H₂O₂/ Δ CH₃OOH) is also the highest in flight 7, about twice that of flight 6 or 10 (Table 1). Also, it should be noted that organic hydroperoxides such as HMHP and 1-HEHP were detected in plumes from flights 6 and 10 but not in flight 7. From these observations the production of hydroperoxide appears to be subject to fire conditions.

The different enhancement ratios of CO to CO₂ could be a clue for different enhancements of hydroperoxides between flights. This ratio is a proxy for fire temperature with a low ratio indicating high temperature [Lobert *et al.*, 1991]. This ratio is lowest in flight 7, so the fire plumes in flight 7 should be hottest. Because the enhancement of CO is greatest in flight 10 and because the concentrations of aerosol and CH₃COOH, which are known to be produced from smoldering fires [Andreae, 1993], also increased with those of CO (not shown), flight 10 has the most consistent smoldering fire signature of the three flights. It is likely that the production of H₂O₂ is more favorable than that of organic hydroperoxide at high temperature, as discussed below.

H₂O₂ and CH₃OOH are correlated with CH₃Cl, aerosol, C₂H₂, HCOOH, CH₃COOH, and HNO₃. These species are all indicators of biomass burning [Crutzen and Andreae, 1990; Radke *et al.*, 1991; Helas *et al.*, 1992; Andreae, 1993].

3.2.2. CH₂O. Figure 3 and Table 1 show CH₂O to be correlated with CO. CH₂O concentrations linearly increase with CO concentrations, and the correlation coefficients approach the significance level of those found between CO and CO₂. The CH₂O to CO enhancement ratio ranged from 7*10⁻³ to 19*10⁻³ and is the greatest for flight 7.

Griffith *et al.* [1991] determined the emission ratio of CH₂O relative to CO₂ in four biomass fires. Their values were 1.9–2.3*10⁻³ and remained constant during the course of the fires.

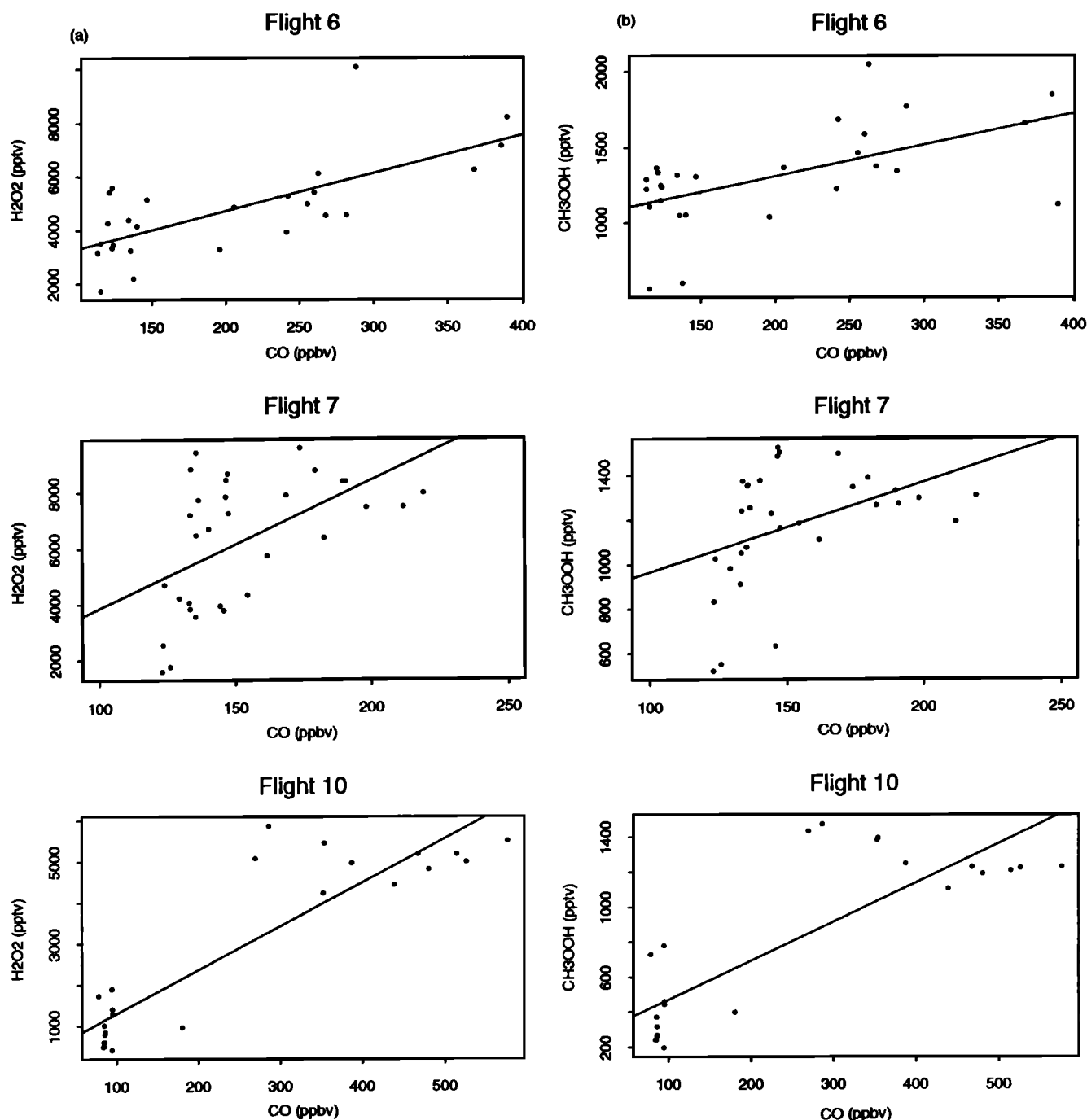


Figure 3. Plots of (a) H₂O₂, (b) CH₃OOH, and (c) CH₂O versus CO for each flight. The slope of the solid line is the enhancement ratio of these species relative to CO.

For comparison, $\Delta\text{CH}_2\text{O}/\Delta\text{CO}_2$ was also calculated for each flight. These values were $3.1\text{--}4.7 \times 10^{-4}$ (Table 1 and Figure 5), lower than those of Griffith *et al.* [1991]. Our CO enhancement ratios to CO₂ ($1.4\text{--}6.7 \times 10^{-2}$) were also lower than those of Griffith *et al.* [1991] (0.14–0.2). The correlation of CH₂O with other species such as CH₃Cl and aerosol were more significant than those for H₂O₂ and CH₃OOH.

This analysis provided convincing evidence for the direct production of CH₂O from fires. For hydroperoxide, however, secondary photochemical production through short-lived hydrocarbons seems to remain as a possible alternative to direct production.

3.3. Fire Experiment

To determine whether hydrogen peroxide, organic hydroperoxide species, and formaldehyde are directly produced from biomass burning, three sets of simple burning experiments were performed at the URI Bay campus in the summer of 1995. The emissions from 13 fires using charcoal, straw, or wood as fuel were sampled for H₂O₂, organic hydroperoxide, and CH₂O. The methods employed were the same as those used in TRACE A. The results are shown in Table 2. Direct CH₂O production by fire was always observed. H₂O₂ production observed during the fires was more variable than CH₂O production. CH₃OOH

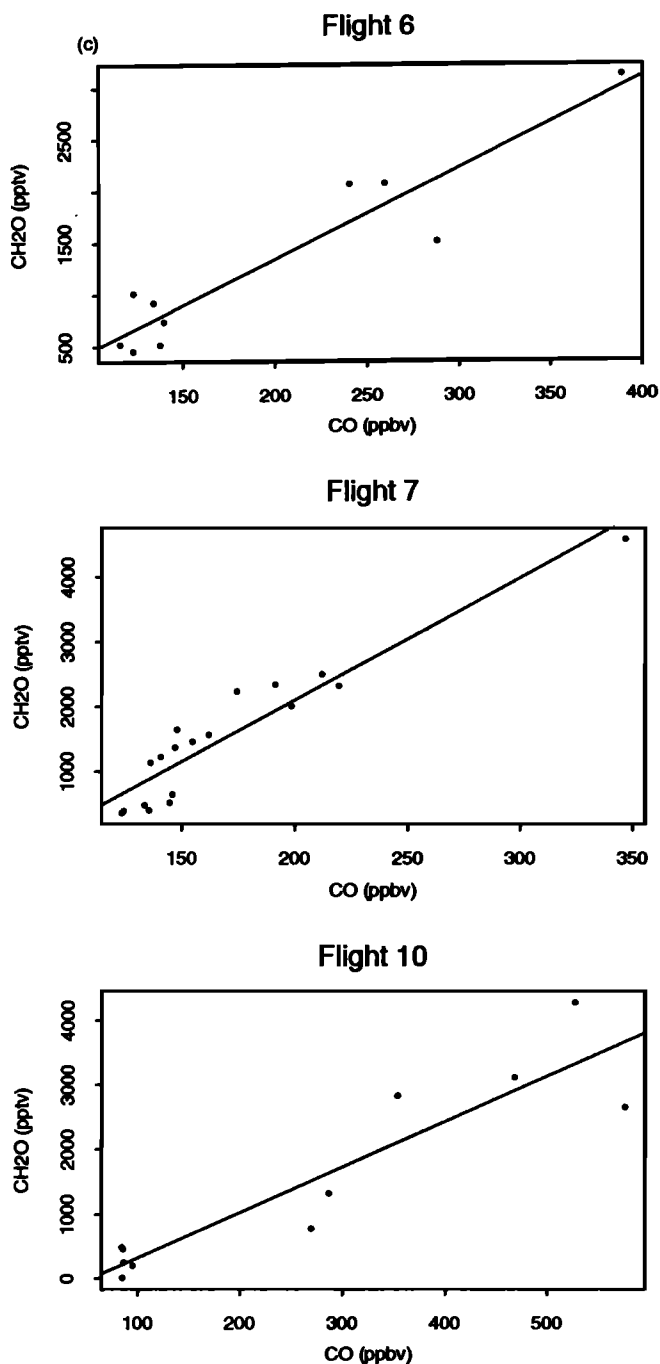


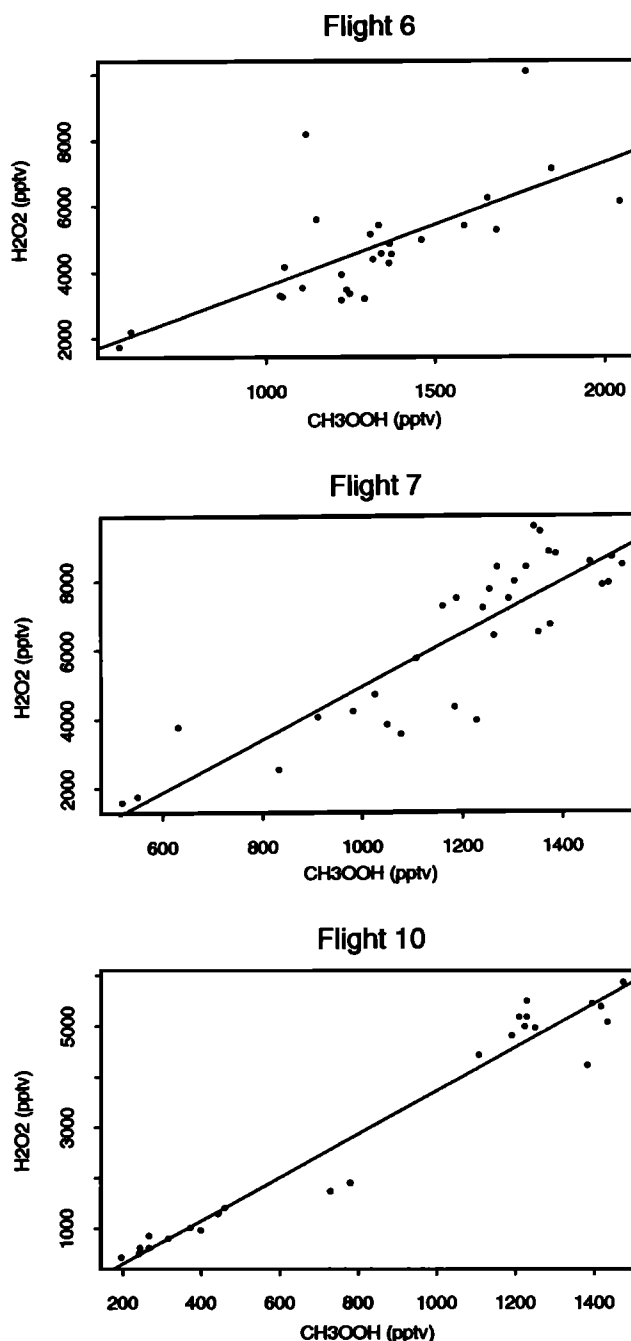
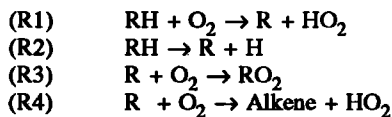
Figure 3. (continued)

showed the least and most various production by fires. High concentrations of organic hydroperoxides such as hydroxymethyl hydroperoxide, ethyl hydroperoxide, peroxyacetic acid, and 1-hydroxyethyl hydroperoxide were sporadically observed during burning. The maximum concentrations of CH₂O, H₂O₂, and organic hydroperoxide species were not observed simultaneously in time during the course of a fire. Qualitatively, the CH₂O maximum was >10 times that of H₂O₂ and >50 times that of CH₃OOH. H₂O₂ maximum was >5 times that of CH₃OOH. The results of the charcoal, straw, and wood fires clearly demonstrate the direct production of H₂O₂, organic hydroperoxides, and CH₂O from biomass burning. A CO instrument problem precluded our calculation of emission ratios, and these must be left for future experiments. Extreme care must be exercised in such experiments

to prevent condensation in the sample lines from the production of water by fire.

4. Mechanisms for the Direct Formation of Hydroperoxide and Formaldehyde From Biomass Burning

In combustion processes, hydroperoxides can be produced by the following reactions [Barnard and Bradley, 1984; Gardiner, 1984; Hucknall, 1985; Lewis and von Elbe, 1987]:

Figure 4. Linear regression between H₂O₂ and CH₃OOH for each flight.

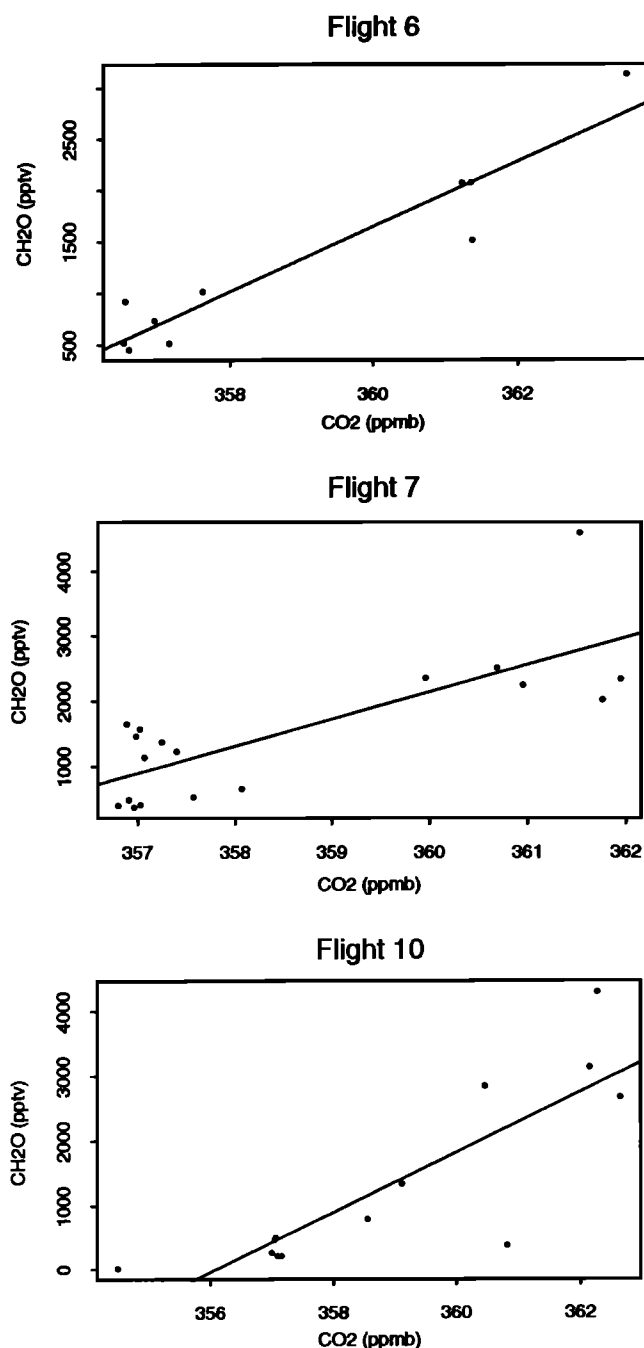
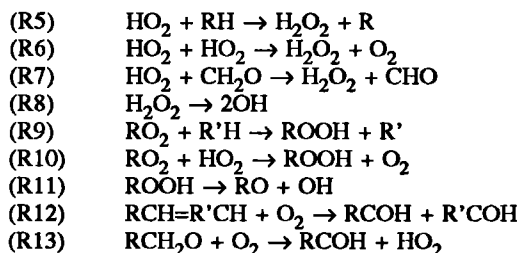


Figure 5. Plot of CH₂O versus CO₂ for each flight. The slope of the solid line is the enhancement ratio of CH₂O relative to CO₂.



where RH is alkane, R is alkyl radical, RO is alkoxy radical, and RO₂ is alkyl peroxy radical. These are examples which only include simple alkane chemistry. At high temperatures over

200°C, the backward reaction of (R3) is more favorable than the forward reaction. The organic hydroperoxide formed through (R9) and (R10) is also more prone to thermal decomposition through (R11) at high temperature. Therefore organic hydroperoxides can be an important intermediate only at lower temperature ($T < 200^\circ\text{C}$). As temperature increases, (R4) is more important than (R3), producing HO₂ radicals and leading to the formation of H₂O₂ by (R5) and (R6). The decomposition of H₂O₂ by (R8) occurs at temperatures above 400°C. At temperatures higher than 500°C, CH₂O can react with HO₂ and produce H₂O₂. Therefore H₂O₂ has a greater probability for formation and a lower probability for decomposition than organic hydroperoxides at higher temperatures. Consequently, more H₂O₂ than CH₃OOH would be expected in high-temperature fires. The observed trend of hydroperoxide enhancement in TRACE A and our fire experiments fits this expectation.

There are multiple paths leading to CH₂O formation during combustion processes (e.g., (R12) and (R13)), and CH₂O formation occurs over a wide range of fire temperature [Barnard and Bradley, 1984; Gardiner, 1984; Hucknall, 1985; Lewis and von Elbe, 1987]. Hence CH₂O is apt to be formed with less dependence on fire quality than hydroperoxides. This finding is consistent with observed data from both TRACE A and our fire experiments.

5. Atmospheric Implication

Hydroperoxides are reservoirs of odd-hydrogen radicals by their formation and subsequent photolysis. Their removal by wet and dry deposition and reaction with OH is a significant radical sink in the troposphere [Logan *et al.*, 1981; Kleinman, 1986]. If these species are produced directly through processes other than photochemical reactions, however, they can contribute as a direct source of radicals. This study presents evidence for a direct source of hydroperoxide and formaldehyde from biomass burning. The production of odd-hydrogen radicals from the direct source of these species can be estimated from the enhancement ratios relative to CO, CO enhancements, and photolysis rates of H₂O₂, CH₃OOH, and CH₂O. For three fire flights, approximately 30% of the total odd-hydrogen radical production in the lower troposphere near fires may be due to their direct emission.

Since odd-hydrogen radicals are indispensable to make new odd-oxygen radicals, the direct production of these species can affect ozone and the odd-oxygen cycle. The effect of enhanced hydroperoxide and formaldehyde due to biomass burning in TRACE A is to increase odd-hydrogen and odd-oxygen radicals and thus increase the oxidation capacity of the atmosphere [Lee *et al.*, 1996]. The extent and mechanism of their direct production need to be critically determined through additional laboratory experiments before the global consequence of biomass burning can be evaluated.

6. Conclusion

In TRACE A, hydroperoxide and formaldehyde were highly elevated in and near biomass fires. These high concentrations were not explained by photochemical production alone and suggested that an additional source was required. This tendency is clear for H₂O₂ and relatively less clear for both CH₃OOH and CH₂O. The correlations of CH₂O with CO are excellent, providing strong evidence for the direct production of CH₂O from biomass burning. H₂O₂ and CH₃OOH are moderately correlated with CO. The enhancement ratio relative to CO was 1.5×10^{-2} , 2.4×10^{-3} , and 7.17×10^{-3} for H₂O₂, CH₃OOH, and CH₂O, respectively. From simple fire experiments using charcoal, straw, and wood as fuel, these species were observed to be highly enhanced in comparison with ambient levels. These experiments support

Table 2. Fire Experiments at the University of Rhode Island Bay Campus

Fuel	Number of Experiments	CH ₂ O		H ₂ O ₂		CH ₃ OOH		Other ROOH ^a Observed Species During Fires
		Number of Fires ^b	Maximum Concentration ppbv ^c	Number of Fires	Maximum Concentration ppbv	Number of Fires	Maximum Concentration ppbv	
Charcoal	7	6	600	4	50	4	11	HMHP, EHP, U
Straw	2	2	700	2	32	2	6.3	PAA, 1-HEHP, U
Wood	4	4	650	2	55	3	2.4	PAA, EHP, 1-HEHP

Experiments were performed at the University of Rhode Island Bay Campus in July-August 1995.

^a HMHP, hydroxymethyl hydroperoxide; EHP, ethyl hydroperoxide; PAA, peroxyacetic acid; 1-HEHP, 1-hydroxyethyl hydroperoxide; and U, unidentified peroxide.

^b Number of fire experiments in which elevated concentrations (at least 3 times higher than ambient levels) of each species were observed.

^c Maximum concentrations observed during fires.

the hypothesis that hydroperoxide and formaldehyde are directly produced from biomass fires. The data obtained from TRACE A and fire experiments also comply with possible mechanisms for direct production of hydroperoxide and formaldehyde during combustion processes. In TRACE A the photolysis of these species produced from fires accounted for about 30% of the total radical production, which is to be a direct source of odd-hydrogen radicals in the troposphere. Thus further study needs to be carried out to determine the mechanism of production and emission factors of these species.

Acknowledgments. The TRACE A experiment was supported by the National Aeronautics and Space Administration through the Global Tropospheric Experiment program. The authors thank all participants in TRACE A for their support and help. M.L. and B.G.H. specially thank Kara Nakata for her work in fire experiments performed in the URI Bay campus through the Summer Undergraduate Research Fellowship in Oceanography sponsored by the National Science Foundation.

References

- Andreae, M. A., The influence of tropical biomass burning on climate and the atmospheric environment, in *Biogeochemistry of Global Change*, edited by R. S. Oremland, pp. 113-150, Chapman and Hall, New York, 1993.
- Barnard, J. A., and J. N. Bradley, *Flame and Combustion*, 2nd ed., 380 pp., Chapman and Hall, New York, 1984.
- Cicerone, R. J., Fire, atmospheric chemistry, and the ozone layer, *Science*, **263**, 1243-1245, 1994.
- Crutzen, P. J., and M. O. Andreae, Biomass burning in the tropics: Impact on atmospheric chemistry and biogeochemical cycles, *Science*, **250**, 1669-1678, 1990.
- Davis, D. D., et al., Assessment of ozone photochemistry in the western North Pacific as inferred from PEM-West A observations during the fall 1991, *J. Geophys. Res.*, **101**, 2111-2134, 1996.
- Fishman, J., Experiment probes elevated ozone levels over the tropical South Atlantic Ocean, *Eos Trans. AGU*, **33**, 380, 1994.
- Fishman, J., J. M. Hoell Jr., R. D. Bendura, V. W. J. H. Kirchhoff, and R. J. McNeal Jr., NASA GTE TRACE A experiment (September-October 1992): Overview, *J. Geophys. Res.*, in press, 1996.
- Gardiner, W. C., Jr., *Combustion Chemistry*, 509 pp., Springer-Verlag, New York, 1984.
- Griffith, D. W. T., W. G. Mankin, M. T. Coffey, D. E. Ward, and A. Riebau, FTIR remote sensing of biomass burning emissions of CO₂, CO, CH₄, CH₂O, NO, NO₂, NH₃, and N₂O, in *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implications*, edited by J. S. Levine, pp. 3-21, MIT Press, Cambridge, Mass., 1991.
- Hegg, D. A., L. A. Radke, P. V. Hobbs, R. A. Rasmussen, and P. J. Riggan, Emission of some trace gases from biomass burning, *J. Geophys. Res.*, **95**, 5669-5675, 1990.
- Heikes, B. G., Formaldehyde and hydroperoxides at Mauna Loa Observatory, *J. Geophys. Res.*, **97**, 18001-18013, 1992.
- Heikes, B. G., M. Lee, J. Bradshaw, S. Sandholm, D. D. Davis, W. Chameides, H. Rodriguez, S. Liu, and S. McKeen, Hydrogen peroxide and methyl hydroperoxide distributions related to ozone and odd hydrogen over the North Pacific in the fall of 1991, *J. Geophys. Res.*, **101**, 1891-1905, 1996a.
- Heikes, B. G., et al., Formaldehyde methods comparison in the remote lower troposphere during Mauna Loa Photochemistry Experiment 2, *J. Geophys. Res.*, **101**, 14741-14755, 1996b.
- Heikes, B. G., M. Lee, D. J. Jacob, R. Talbot, J. Bradshaw, H. Singh, D. Blake, B. Anderson, H. Fuelberg, and A. M. Thompson, Ozone, hydroperoxides, oxides of nitrogen, and hydrocarbon budgets in the marine boundary layer over the South Atlantic, *J. Geophys. Res.*, in press, 1996c.
- Helas, G., H. Bingemer, and M. O. Andreae, Organic acid over Africa: Results from DECAFE 88, *J. Geophys. Res.*, **97**, 6187-6193, 1992.
- Hucknall, D.J., *Chemistry of Hydrocarbon Combustion*, 415 pp., Chapman and Hall, New York, 1985.
- International Council of Scientific Unions (ICSU), *International Global Atmospheric Chemistry (IGAC) Project: The Operational Plan, International Geosphere-Biosphere Programme (IGBP) Rep. 32*, 134 pp., Stockholm, 1994.
- Jacob, D. J., et al., Origin of ozone and NO_x in the tropical troposphere: A photochemical analysis of aircraft observations over the South Atlantic basin, *J. Geophys. Res.*, in press, 1996.
- Kleinman, L. I., Photochemical formation of peroxides in the boundary layer, *J. Geophys. Res.*, **91**, 10889-10904, 1986.
- Kleinman, L. I., Seasonal dependence of boundary layer peroxide concentrations: The low and the high NO_x regimes, *J. Geophys. Res.*, **96**, 20721-20733, 1991.
- Lazrus, A. L., K. L. Fong, and J. A. Lind, Automated fluorometric determination of formaldehyde in air, *Anal. Chem.*, **60**, 1074-1078, 1988.
- Lee, M., B. C. Noone, D. O'Sullivan, and B. G. Heikes, Method for the collection and HPLC analysis of hydrogen peroxide and C₁ and C₂ hydroperoxides in the atmosphere, *J. Atmos. Oceanic Technol.*, **12**, 1060-1070, 1995.
- Lee, M., B. G. Heikes, and D. J. Jacob, Enhancements of hydroperoxides and formaldehyde in biomass burning impacted air and their effect on atmospheric oxidant cycles, *J. Geophys. Res.*, in press, 1996.
- Levine, J. S. (Ed.), *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implications*, 569 pp., MIT Press, Cambridge, Mass., 1991.
- Levine, J. S., W. R. Cofer III, E. L. Winstead, R. P. Rhinehart, D. R. Cahoon Jr., D. I. Seacher, S. Sebacher, and B. J. Stocks, Biomass burning: Combustion emissions, satellite imagery, and biogenic emissions, in *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implications*, edited by J. S. Levine, pp. 264-271, MIT Press, Cambridge, Mass., 1991.
- Lewis, B., and G. von Elbe, *Combustion, Flames and Explosion of Gases*, 3rd ed., Academic, San Diego, Calif., 1987.
- Robert, J. M., D. H. Scharffe, W. M. Hao, T. A. Kuhlbusch, R. Seuwen, P. Warneck, and P. J. Crutzen, Experimental evaluation of biomass burning emissions: Nitrogen and carbon containing compounds, in *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implications*, edited by J. S. Levine, pp. 289-304, MIT Press, Cambridge, Mass., 1991.
- Logan, J. A., M. J. Prather, S. C. Wofsy, and M. B. McElroy, Tropospheric chemistry: A global perspective, *J. Geophys. Res.*, **86**, 7210-7254, 1981.

- Luria, M., C. C. Van Valin, J. F. Boatman, and J. D. Ray, The relationship between ozone and hydrogen peroxide: Field observation and model evaluation, in *Ozone in the Atmosphere*, edited by R. D. Bojkov and P. Fabian, pp. 471-476, A. Deepak, Hampton, Va., 1989.
- Manó, S., and M. A. Andreae, Emission of methyl bromide from biomass burning, *Science*, 263, 1255-1256, 1994.
- Mitchell, J. F., The "greenhouse effect" and climate change, *Rev. Geophys.*, 27, 115-139, 1989.
- National Academy of Sciences (NAS), *Global Tropospheric Chemistry: A Plan for Action*, 194 pp., National Research Council, National Academy Press, Washington, D. C., 1984.
- Radke, L. F., D. A. Hegg, P. V. Hobbs, J. D. Nance, J. H. Lyons, K. K. Laursen, R. E. Weiss, P. J. Riggan, and D. E. Ward, Particulate and trace gas emissions from large biomass fires in North America, in *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implications*, edited by J. S. Levine, pp. 209-224, MIT Press, Cambridge, Mass., 1991.
- Rodriguez, J. M., M. K. W. Ko, N. D. Sze, and C. W. Heisey, Impact of biomass burning on tropospheric CO and OH: A two-dimensional study, in *Global Biomass Burning: Atmospheric, Climatic and Biospheric Implications*, edited by J. S. Levine, pp. 351-359, MIT Press, Cambridge, Mass., 1991.
- Thompson, A. M., The oxidizing capacity of the Earth's atmosphere: Probable past and future changes, *Science*, 256, 1157-1165, 1992.
- Tremmel, H. G., W. Junkermann, F. Slemr, and U. Platt, On the distribution of hydrogen peroxide in the lower troposphere over the northeastern United States during late summer 1988, *J. Geophys. Res.*, 98, 1083-1099, 1993.
-
- B. Anderson and G. Sachse, NASA Langley Research Center, Hampton, VA 23665. (e-mail: b.e.anderson@larc.nasa.gov; g.w.sachse@larc.nasa.gov)
- B. G. Heikes and M. Lee, Center for Atmospheric Chemistry Study, Graduate School of Oceanography, Narragansett, RI 02882. (e-mail: zagar@notos.gso.uri.edu; meehye@notos.gso.uri.edu)
- D. J. Jacob, Harvard University, Cambridge, MA 02138. (e-mail: djj@io.harvard.edu)

(Received January 3, 1996; revised May 18, 1996; accepted May 28, 1996.)