

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

Lee, M., B.G. Heikes, D.J. Jacob, G. Sachse, and B. Anderson

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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 measurement, 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 $1\text{-}5 \times 10^{-2}$ and $2\text{-}4 \times 10^{-3}$, 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 $7\text{-}19 \times 10^3$ and $3\text{-}5 \times 10^{-4}$, 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.
