Convective injection and photochemical decay of peroxides in the tropical upper troposphere: methyl iodide as a tracer of marine convection

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Abstract

The convective injection and subsequent fate of the peroxides H_2O_2 and CH_3OOH in the upper troposphere is investigated using aircraft observations from the NASA Pacific Exploratory Mission - Tropics (A) (PEM-Tropics (A)) over the South Pacific up to 12-km altitude. Fresh convective outflow is identified by high CH_3I concentrations; CH_3I is an excellent tracer of marine convection because of its relatively uniform marine boundary layer concentration, relatively well-defined atmospheric lifetime against photolysis, and high sensitivity of measurement. We find that mixing ratios of CH_3OOH in convective outflow at 8-12 km altitude are enhanced on average by a factor of 6 relative to background, while concentrations of H_2O_2 are enhanced by less than a factor of 2. The scavenging efficiency of H_2O_2 in the precipitation associated with deep convection is estimated to be 55-70%. Scavenging of CH_3OOH is negligible. Photolysis of convected peroxides is major sources of the HO_x radical family (OH + peroxy radicals) in convective outflow. The time scale for decay of the convective enhancement of peroxides in the upper troposphere is determined using CH_3I as a chemical clock and is interpreted using photochemical model calculations. Decline of CH_3OOH takes place on a time scale of 1-2 days but the resulting HOx converts to H_2O_2, so that H_2O_2 concentrations show no decline for ~5 days following the convective event. The perturbation to HOx at 8-12 km altitude from deep convective injection of peroxides decays on a time scale of 2-3 days for the PEM-Tropics (A) conditions.

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