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$_2$O$_2$ and CH$_3$OOH 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$_3$I concentrations; CH$_3$I 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$_3$OOH in convective outflow at 8-12 km altitude are enhanced on average by a factor of 6 relative to background, while concentrations of H$_2$O$_2$ are enhanced by less than a factor of 2. The scavenging efficiency of H$_2$O$_2$ in the precipitation associated with deep convection is estimated to be 55-70%. Scavenging of CH$_3$OOH 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$_3$I as a chemical clock and is interpreted using photochemical model calculations. Decline of CH$_3$OOH takes place on a time scale of 1-2 days but the resulting HOx converts to H$_2$O$_2$, so that H$_2$O$_2$ 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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