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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 mixing ratios 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 a major source of the HO radical family (OH + peroxy radicals) in convective outflow. The timescale 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 timescale of 1-2 days, but the resulting HO$_x$ converts to H$_2$O$_2$, so H$_2$O$_2$ mixing ratios show no decline for ~5 days following a convective event. The perturbation to HO$_x$ at 8-12 km altitude from deep convective injection of peroxides decays on a timescale of 2-3 days for the PEM-Tropics A conditions.

1. Introduction

Updrafts in deep convective clouds can raise boundary layer air into the upper troposphere in a matter of minutes; outflow occurs primarily from the cloud top and anvil [Chatfield and Crutzen, 1984]. Model studies have suggested that convective injection of the peroxides H$_2$O$_2$ and CH$_3$OOH could provide an important source of hydrogen oxide radicals (HO$_x$ = OH + peroxy radicals) to the upper troposphere, resulting in enhanced production of O$_3$ and gas-phase H$_2$SO$_4$ [Chatfield and Crutzen, 1984; Prather and Jacob, 1997]. Jaegle et al. [1997, 1998] found that recent observations of OH and HO$_2$ in the upper troposphere [Brune et al., 1998; Wennberg et al., 1998] are consistent with a major source of HO$_x$ from convective injection of peroxides and formaldehyde. In the present study we use aircraft observations of CH$_3$I, H$_2$O$_2$, and CH$_3$OOH taken up to 12 km altitude over the tropical South Pacific to investigate the convective injection and subsequent chemical decay of peroxides in the upper troposphere. As previously shown by Davis et al. [1996] and further demonstrated here, CH$_3$I provides a sensitive tracer of deep marine convection.

The peroxides H$_2$O$_2$ and CH$_3$OOH are produced in the atmosphere by combination reactions of the HO radicals, HO$_2$ + HO$_2$ and CH$_3$O$_2$ + HO$_2$, respectively. They photolyze on a timescale of the order of 1 day to regenerate HO$_x$ radicals and thus serve as reservoirs for HO$_x$. Water vapor is the main source of HO$_x$ in most of the troposphere, so the abundance of peroxides is correlated in general with humidity. Mixing ratios of H$_2$O$_2$ and CH$_3$OOH are of the order of 1000 parts per trillion by volume (pptv) in the marine boundary layer and 100 pptv in the upper troposphere [Heikes et al., 1996]. The large concentration gradient between the boundary layer and the upper troposphere, combined with the 10-day characteristic time for overturning of the upper troposphere with boundary layer air in the tropics [Prather and Jacob, 1997], implies that deep marine convection could provide a major source of peroxides to the upper troposphere. On the basis of the respective Henry's Law constants for H$_2$O$_2$ and CH$_3$OOH, 8 × 10$^4$ M atm$^{-1}$ and 3 × 10$^5$ M atm$^{-1}$ at room temperature [O'Sullivan et al., 1996], one would expect H$_2$O$_2$ but not
CH$_2$OOH to be scavenged in the precipitation associated
with the convective updraft [Chatfield and Crutzen, 1984].
In the upper troposphere the peroxides photolyze to release HO$_x$
and subsequent cycling takes place within the HO$_x$ family
(sum of HO$_x$ and peroxides). Eventual conversion of HO$_x$ back
to water vapor terminates the process. A schematic of the re-
resulting life cycle for HO$_x$ is shown in Figure 1.

The observations analyzed in this paper are from the Pacific
Exploratory Mission-Tropics A (PEM-Tropics A) flown in
September-October 1996 [Hoell et al., this issue]. PEM-
Tropics A used two aircraft, a DC-8 and a P-3B, to survey at-
mospheric composition over a broad expanse of the Pacific
from 45°N to 72°S. Most of the data were collected between
0°S and 30°S and extended zonally across the South Pacific.
We limit our attention to data from the DC-8, which had a
higher ceiling (12 km) than the P-3B (7 km). Measurements
aboard the DC-8 included H$_2$O$_2$, CH$_3$OOH, CH$_3$I, and a num-
ber of other species. We use CH$_3$I together with high relative
humidity as a tracer of fresh outflow of marine convection in
the upper troposphere (section 2). From there we examine the
enhancement of peroxides and other species in the convective
outflow and estimate scavenging efficiencies in the precipita-
tion associated with deep convection (section 3). We then use
CH$_3$I as a chemical clock to determine the timescale for decay
of HO$_x$ in the upper troposphere following convection and in-
terpret the results with a photochemical model calculation
(section 4). Conclusions are in section 5.

2. Methyl Iodide as a Tracer of Marine
Convection

Methyl iodide (CH$_3$I) is emitted ubiquitously by the
oceans. Though biological production of CH$_3$I may be impor-
tant in coastal and upwelling regions, photochemical
reactions of methyl radicals and iodine atoms in seawater are
thought to be the dominant marine source [Moore and
Zafiriou, 1994; Happell and Wallace, 1996; Manley and de
la Cuesta, 1997]. Indeed, in the marine boundary layer during
PEM-Tropics A, concentrations of methyl iodide were not
correlated with concentrations of biologically produced ma-
rine tracers such as DMS. Biomass burning is thought to be a
much smaller source of CH$_3$I emissions globally [Andreae et
al., 1996], but as discussed below, its impacts are non-
negligible even over the remote Pacific.

Methyl iodide is removed from the atmosphere mainly by
photolysis, with a mean lifetime of 4 days in the tropical tro-
posphere (Figure 2). Oxidation by OH accounts for only ~1%
of the loss from photolysis. The Henry's Law constant of CH$_3$I
is sufficiently low ($K_H = 0.14 \text{ M atm}^{-1}$ at room temperature
[Moore et al., 1995]) that rain-out is negligible.

Observations in PEM-Tropics A indicate relatively uni-
form concentrations of CH$_3$I in the marine boundary layer
(MBL) over the tropical South Pacific, with an interquartile
range of 0.21-0.44 pptv at 0-2 km altitude (Figure 3). This is a
much narrower range than that observed for other marine trac-
ners, such as DMS, which have highly variable biological
sources [Andreae et al., 1985]. Atmospheric measurements of
CH$_3$I concentrations can be made with high sensitivity (detec-
tion limit of 0.01 pptv) [D. Blake et al., 1996]. The
combination of relatively uniform boundary layer concentra-

![Figure 2. Vertical profiles of the 24-hour average photolysis
frequency of CH$_3$I for three different latitudes. Calculations
were done for a solar declination angle of 0° (equinox), an
ozone column of 280 DU, and cloud-free conditions. Absorp-
tion cross sections for CH$_3$I are taken from Roehl et al. [1997],
a nd a quantum yield of unity for photolysis is assumed.](image-url)
tion, relatively well defined lifetime, and low limit of
detection makes CH₃I an attractive tracer for deep marine con-
vection and the age of air in the upper troposphere. A parallel
can be drawn to the radioisotope ²²²Rn, which is emitted by
soils and provides a sensitive tracer of continental convection
[Jacob et al., 1997].

Figure 4a shows the latitudinal distribution of CH₃I mixing
ratios measured in PEM-Tropics A. Values are higher in the
tropics than at high southern latitudes, as might be expected
from the trend in UV radiation and hence in the photochemical
source. We focus our analysis on the southern tropics (0°-
30°S), where mixing ratios are high and relatively uniform and
where the aircraft data are most extensive. Mixing ratios of
CH₃I in the tropics decline by a factor of 5, on average, from
the surface to 4 km altitude and are then relatively uniform up
to 12 km altitude (Figure 5a). The lack of vertical gradient

![Figure 3](image)

**Figure 3.** Probability distribution of CH₃I concentrations over the tropical South Pacific at 0-2 km altitude (circles) and at 8-12 km altitude (triangles). The abscissa is a normal probability scale that a normal distribution would plot as a straight line with standard deviations indicated as the quantiles of standard normal.

![Figure 4](image)

**Figure 4.** Latitudinal distributions of median mixing ratios of (a) CH₃I, (b) CH₃OOH, and (c) H₂O₂ at 0-2 km altitude in PEM-Tropics A. Each symbol contains at least 10 samples.
above 4 km suggests a major contribution from deep convection to vertical transport. Vertical gradients are least at the western edge of the flight domain near the highly convective Pacific Warm Pool (west of 170°E). Mixing ratios of CH$_3$I over this region decline by only a factor of 2 in the lower 4 km, in contrast to a factor of 5 over the rest of the Pacific.

Previous aircraft observations of CH$_3$I during the same season (September-October) were made in the Pacific Exploratory Mission-West A (PEM-West A) campaign over the western equatorial Pacific [Hoell et al., 1996] and the Transport and Atmospheric Chemistry Near the Equatorial Atlantic (TRACE A) campaign over biomass burning regions of Brazil and southern Africa [Fishman et al., 1996]. The CH$_3$I mixing ratios measured over the Pacific in PEM-West A [Davis et al., 1996] and in a shipboard mission [Yokouchi et al., 1997] were about a factor of 2 higher than in PEM-Tropics A although the vertical distributions in PEM-West A were similar. Even higher CH$_3$I mixing ratios, averaging 0.7-0.9 pptv in the boundary layer and 0.2-0.4 pptv at 8-12 km, were measured over Brazil and South Africa during TRACE A [N. Blake et al., 1996]. These high mixing ratios point to a large biomass burning source of CH$_3$I in addition to the oceanic source.

Biomass burning pollution layers were sampled throughout the South Pacific troposphere during the PEM-Tropics A [Schultz et al., this issue]. Interference from biomass burning must be considered when using CH$_3$I as a tracer of marine convection. Most measurements of elevated CH$_3$I at 8-12 km altitude (>0.11 pptv, top octile) displayed corroborating signs of recent marine convection: high humidity, high mixing ratios of bromoform, and low O$_3$ mixing ratios (Table 1). However, as shown in Table 1, some of the high-CH$_3$I measurements were associated with low humidity (<10% with respect to ice) and high C$_2$H$_2$ mixing ratios (80-300 pptv), indicating biomass burning pollution rather than marine convection as the source of CH$_3$I. To distinguish recent marine convection from biomass burning pollution in the PEM-Tropics A data at 8-12 km altitude, we used relative humidity as a corroborating tracer of convection (Table 1). All points with both CH$_3$I and relative humidity in the top octile (CH$_3$I > 0.11 pptv, relative humidity >50% with respect to ice) also had elevated mixing ratios of bromoform as well as low C$_2$H$_2$, O$_3$, and NO.

3. Convective Pumping and Scavenging of Peroxides

Latitudinal and vertical distributions of the peroxides measured in PEM-Tropics A are shown in Figures 4 and 5. The large-scale spatial trends follow the trends in the photochemical source [Logan et al., 1981; O'Sullivan et al., this issue]. Schultz et al. [this issue] examined the extent to which the peroxide concentrations measured in PEM-Tropics A could be explained from a photochemical steady-state model calculation constrained with the local aircraft observations of chemical, radiative, and meteorological variables. Primary sources of HO$_x$ in that calculation included the O(D) + H$_2$O reaction and the photolysis of acetone (for which a constant mixing ratio of 400 pptv was assumed). They found that the steady-state calculation reproduces observed peroxide concentrations to within 35% on average below 8 km altitude but underestimates CH$_3$OOH by a factor of 2 and H$_2$O$_2$ by 30%, on average, at 8-12 km. Convective transport would be a likely explanation for the underestimate of CH$_3$OOH at high altitude, although the magnitude of the bias is within the uncertainty of the low-temperature rate constant for the CH$_3$O$_2$ + HO$_2$ reaction [DeMore et al., 1997].
Table 1. Air Mass Compositions at 0-2 km and 8-12 km Altitude Over Tropical South Pacific

<table>
<thead>
<tr>
<th></th>
<th>Boundary Layer</th>
<th>High CH₃I</th>
<th>High CH₃I</th>
<th>High CH₃I</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0-2 km</td>
<td>Fresh</td>
<td>Aged</td>
<td>Biomass</td>
<td>8-12 km</td>
</tr>
<tr>
<td>n = 253</td>
<td>8-12 km</td>
<td></td>
<td></td>
<td></td>
<td>n = 355</td>
</tr>
<tr>
<td>n = 23</td>
<td>n = 27</td>
<td></td>
<td></td>
<td></td>
<td>n = 5</td>
</tr>
<tr>
<td>CH₃I, pptv</td>
<td>0.36 ± 0.14</td>
<td>0.15 ± 0.03</td>
<td>0.15 ± 0.03</td>
<td>0.18 ± 0.04</td>
<td>0.05 ± 0.02</td>
</tr>
<tr>
<td>CH₃OOH, pptv</td>
<td>1080 ± 410</td>
<td>500 ± 280</td>
<td>230 ± 130</td>
<td>110 ± 40</td>
<td>80 ± 80</td>
</tr>
<tr>
<td>H₂O₂, pptv</td>
<td>1340 ± 710</td>
<td>330 ± 140</td>
<td>270 ± 80</td>
<td>190 ± 150</td>
<td>200 ± 110</td>
</tr>
<tr>
<td>NO, pptv</td>
<td>2.4 ± 4.4</td>
<td>19 ± 16</td>
<td>29 ± 25</td>
<td>74 ± 35</td>
<td>56 ± 43</td>
</tr>
<tr>
<td>NOₓ, pptv</td>
<td>7.1 ± 16.4</td>
<td>22 ± 19</td>
<td>34 ± 28</td>
<td>125 ± 26</td>
<td>60 ± 52</td>
</tr>
<tr>
<td>HNO₃, pptv</td>
<td>36 ± 53</td>
<td>25 ± 15</td>
<td>43 ± 18</td>
<td>100 ± 58</td>
<td>75 ± 59</td>
</tr>
<tr>
<td>Ozone, pptv</td>
<td>25 ± 11</td>
<td>27 ± 7</td>
<td>29 ± 8</td>
<td>61 ± 29</td>
<td>51 ± 22</td>
</tr>
<tr>
<td>Water vapor, pptv</td>
<td>15100 ± 6500</td>
<td>700 ± 520</td>
<td>160 ± 150</td>
<td>70 ± 70</td>
<td>130 ± 110</td>
</tr>
<tr>
<td>Rel. humidity b</td>
<td>75% ± 19%</td>
<td>82% ± 14%</td>
<td>21% ± 14%</td>
<td>6% ± 1%</td>
<td>13% ± 12%</td>
</tr>
<tr>
<td>DMS, pptv</td>
<td>48 ± 54</td>
<td>7 ± 11</td>
<td>2 ± 5</td>
<td>2 ± 2</td>
<td>&lt; 0.8c</td>
</tr>
<tr>
<td>CHBr₃, pptv</td>
<td>1.0 ± 0.4</td>
<td>0.76 ± 0.13</td>
<td>0.44 ± 0.18</td>
<td>0.61 ± 0.38</td>
<td>0.33 ± 0.17</td>
</tr>
<tr>
<td>SO₂, pptv</td>
<td>31 ± 29</td>
<td>13 ± 6</td>
<td>14 ± 5.5</td>
<td>18 ± 3</td>
<td>18 ± 15</td>
</tr>
<tr>
<td>CO, pptv</td>
<td>62 ± 13</td>
<td>57 ± 4</td>
<td>61 ± 4</td>
<td>92 ± 31</td>
<td>64 ± 13</td>
</tr>
<tr>
<td>C₂H₂, pptv</td>
<td>44 ± 33</td>
<td>33 ± 10</td>
<td>37 ± 10</td>
<td>130 ± 90</td>
<td>57 ± 34</td>
</tr>
</tbody>
</table>

Means and standard deviations of concentrations measured at 0ø-30øS latitude during PEM-Tropics A. The following selection criteria were applied:

- Recent marine convection: CH₃I and relative humidity both in the top octiles of measurements at 8-12 km altitude (i.e., CH₃I > 0.11 pptv, relative humidity > 50%). All cases meeting these criteria also had low biomass burning influence (C₉_H₉_ < 80 pptv).
- Aged convective outflow: CH₃I > 0.11 pptv, relative humidity < 50%, and C₉_H₉_ < 80 pptv.
- Biomass burning pollution: CH₃I > 0.11 pptv, relative humidity < 50%, and C₉_H₉_ > 80 pptv. The rest of the data (i.e., CH₃I < 0.11 pptv and relative humidity < 50%) were labeled background conditions.

a NOₓ = NO + NO₉_; NO₉_ is calculated with a photochemical steady-state model [Schultz et al., this issue].

b Relative humidity is defined with respect to ice.
c Detection limit for the DMS measurements.

The role of convection in enhancing CH₃OOH concentrations in the upper troposphere is evident from Table 1. The mean CH₃OOH mixing ratio above 8 km is 6 times higher in convective outflow than in background air. The mean H₂O₂ mixing ratio in convective outflow is also elevated but by less than a factor of 2. The CH₃OOH/CH₃I concentration ratio in fresh convective outflow is similar to that in the boundary layer, indicating no significant scavenging of CH₃OOH in the precipitation associated with deep convection.

We estimate the scavenging efficiency of H₂O₂ in deep convection by modeling the observed composition of the fresh convective outflow (conv) in Table 1 as a two-component mixture of boundary layer (BL) air and background upper tropospheric (UT) air. The fraction B of UT air in this mixture represents a dilution factor for the convected air and is given by

![Equation](1) $\beta = \frac{X_{BL} - X_{conv}}{X_{BL} - X_{UT}}$

where X is the mixing ratio of an insoluble tracer, such as CHBR₃, CH₃OOH, or CH₃I, that is conserved during convective transport. Consider a water-soluble species (mixing ratio Y) scavenged with an efficiency $\alpha$ during convective transport. Our two-component model gives

![Equation](2) $Y_{conv} = (1 - \alpha)(1 - \beta)Y_{BL} + \beta Y_{UT}$

and rearrangement yields an expression for the scavenging efficiency $\alpha$:

![Equation](3) $\alpha = 1 - \frac{Y_{conv} - \beta Y_{UT}}{(1 - \beta)Y_{BL}}$

Scavenging efficiencies for H₂O₂, H₂O, and SO₂ in deep convection are given in Table 2 using the mean observations in Table 1 and either of the reference tracers CHBr₃, CH₃OOH, or CH₃I to derive the dilution factor $\beta$. Changes in $\alpha$ depending on the reference tracer used give some measure of the uncertainty of the approach. We derive in this manner an H₂O₂ scavenging efficiency of 55-70%. A higher scavenging efficiency is found for SO₂ (65-95%), presumably reflecting oxidation by H₂O₂ in convective clouds. Water vapor is even more efficiently scavenged (90%) because of its low vapor pressure at convective outflow temperatures.

4. Fate of Peroxides in the Upper Troposphere

When injected in the upper troposphere, the peroxides decay and supply a source of HOₓ (Figure 1). The timescale for decay of the peroxide enhancement following a convective event can be estimated in the PEM-Tropics A data by plotting
Table 2. Scavenging Efficiencies of Gases During Deep Convection

<table>
<thead>
<tr>
<th>Reference Tracer</th>
<th>CHBr$_3$</th>
<th>CH$_3$OOH</th>
<th>CH$_3$I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilution factor $\beta$</td>
<td>0.36</td>
<td>0.58</td>
<td>0.68</td>
</tr>
<tr>
<td>Scavenging efficiency $\alpha$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>70%</td>
<td>62%</td>
<td>55%</td>
</tr>
<tr>
<td>Water vapor</td>
<td>93%</td>
<td>90%</td>
<td>87%</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>67%</td>
<td>80%</td>
<td>94%</td>
</tr>
</tbody>
</table>

The scavenging efficiency $\alpha$ is defined as the fraction of species scavenged by precipitation in air convected from the marine boundary layer to 8-12 km altitude. Values are calculated from equation (3) using the mean air mass compositions from Table 1 and either of the reference tracers CHBr$_3$, CH$_3$OOH, or CH$_3$I to derive the dilution factor $\beta$ by equation (1).

The peroxide mixing ratios versus the CH$_3$I mixing ratio taken as a time coordinate (Figure 6). Also shown in Figure 6 are results from a time-dependent, zero-dimensional photochemical model simulation [Schultz et al., 1998] for an air parcel initialized with the fresh convective outflow composition in Table 1. Acetone and CH$_2$O, not measured in PEM-Tropics A, are initialized with mixing ratios of 400 pptv and 60 pptv, respectively [Wang et al., 1998]. The NO$_x$ concentration is held constant in the simulation and no dilution of the air parcel with time is allowed. The O$_3$ column is $6.7 \times 10^{18}$ molecules cm$^{-2}$, average of tropical observations in PEM-Tropics A. Circles plotted every 24 hours on the model curves in Figure 6 convert the CH$_3$I coordinate to time. The trend of peroxide versus CH$_3$I concentrations computed with the model is roughly consistent with the observations although the scatter in the observations is large.

We see from Figure 6 that observed concentrations of CH$_3$OOH decline on a timescale of 1-2 days following a convective event. In contrast, observed concentrations of H$_2$O$_2$ show no significant decline for ~5 days following convection and then decline to steady state. We explain the longer persistence of H$_2$O$_2$ as reflecting the cycling within the HO$_x$ family (Figure 1); recycling of peroxides from HO$_x$ in the upper troposphere favors H$_2$O$_2$ over CH$_3$OOH because of the dominance of CO over CH$_4$ as a sink for OH.

The dominant sink of HO$_x$ in fresh convective outflow in the model is the oxidation of CH$_3$OOH by OH:

$$\text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O} \quad (4)$$

while the dominant sink in background air is the reaction of OH with HO$_2$:

$$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (5)$$

The timescale for relaxation of HO$_x$ to steady state following the convective perturbation can be inferred from the trend in the sum of H$_2$O$_2$ and CH$_3$OOH, which account for about 95% of total HO$_x$ in the model. Results in Figure 6 indicate an effective e-folding lifetime of 2-3 days for HO$_x$, both in the model and in the observations.

This e-folding lifetime is longer than the standard lifetime computed in the model from the ratio of the HO$_x$ concentration to the 24-hour average HO$_x$ loss rate, which varies from 1.3 to 1.5. The e-folding lifetime is also shorter than the estimate from the observed HO$_x$ decline of 2-3 days, consistent with the observed HO$_x$ decline in fresh convective outflow in the model.

Figure 6. Mixing ratios of (a) CH$_3$OOH, (b) H$_2$O$_2$, and (c) the sum of peroxides versus the CH$_3$I mixing ratio measured in PEM-Tropics A at $0^\circ-30^\circ$S latitude. Plus signs denote individual observations, large crosses are mean values and standard deviations for CH$_3$I octiles. Data with strong biomass-burning influence (C$_2$H$_2$ > 80 pptv) were excluded. Circles are results from a photochemical model calculation (see text); each circle represents an aging time of 1 day in the model starting from fresh convective outflow.
days in fresh convective outflow to 1.5 days in aged air. The reason is that photolysis of the peroxides in the outflow produces OH, which oxidizes CH4 to produce CH2O; photolysis of this CH2O then regenerates HOy, thus sustaining the HOy enhancement in the outflow for longer than would be expected from the standard calculation of HOy lifetime. The effective e-folding lifetime of the HOy enhancement for the PEM-Tropics A conditions is still much shorter than the 6-day value reported by daegld et al. [1997] in model calculations for the wintertime upper troposphere over Hawaii. Higher Sun angles in PEM-Tropics A are the principal factor for this difference; lower O3 columns and higher NOx concentrations (which facilitate reaction (5) by increasing the OH/HO2 concentration ratio) also contribute.

We find in our model that HOy concentrations in convective outflow are 50% higher than in the background upper troposphere (Table 3). About half of this enhancement is due to convected water vapor, and half is due to convected peroxides (we do not account for convective enhancements of acetone or formaldehyde due to lack of observations). Larger relative enhancements of HOy in convective outflow were found in previous studies [Jaeglé et al., 1997, 1998]. The weaker effect in PEM-Tropics A is due to high Sun angles, low O3 columns, and high humidities, which maintained a large rate of primary HOy production from the O(1D) + H2O reaction in background air up to the 12 km ceiling of the aircraft. We see from Table 3 that concentrations of HOy are not enhanced in the convective outflow, because the added source of HOy is balanced by the additional OH sink from oxidation of convected CH3OOH. Concentrations of CH3O2 are almost twice as high in convective outflow as in background air due to the source from convected CH3OOH. Although the role of convective injection of peroxides in enhancing HOx concentrations is relatively small for the PEM-Tropics A conditions, the general results obtained here regarding the convective injection, scavenging, and decay of peroxides should be applicable to other upper tropospheric regions where the effect on HOy is more important.

### 5. Summary and Conclusions

We used aircraft observations over the tropical South Pacific up to 12 km altitude to examine the deep convective injection of peroxides to the upper troposphere and the subsequent chemical decay of these peroxides. Convective outflow at 8-12 km was identified by a combination of elevated CH3I and elevated relative humidity. CH3I is an excellent tracer of marine convection in the upper troposphere because of its relatively uniform marine boundary layer concentrations, its relatively well-defined atmospheric lifetime (photolysis is the main sink, with a lifetime of about 4 days in the tropics), and its low detection limit. Interference from biomass burning pollution is a problem but can be screened out using concurrent observations of high relative humidity and C2H2. Though not used extensively in this study, CHBr3 exhibits similar traits to CH3I and could also serve as a tracer of marine convection.

We found that concentrations of CH3OOH in convective outflow at 8-12 km altitude were elevated by a factor of 6 relative to the upper tropospheric background, while concentrations of H2O2 were elevated by less than a factor of 2. Scavenging by precipitation in the convective updraft was negligible for CH3OOH and 55-70% for H2O2. Photolysis of convected peroxides was a major source of HOy in the convective outflow.

Formaldehyde is an additional HOx precursor injected to the upper troposphere by deep convection, but no measurements of CH3O were made in PEM-Tropics A. If boundary layer CH2O mixing ratios were 600-1000 pptv, as found in some shipboard measurements over the equatorial Pacific [Arlander et al., 1990], then convective pumping of CH2O would be of comparable importance to peroxides as a source of HOx in convective outflow. However, models and most observations indicate CH2O mixing ratios of 100-300 pptv in the tropical marine boundary layer [Jacob et al., 1996]. At these levels, transport of CH2O in deep marine convection provides only a minor source of HOy in the upper troposphere [Prather and Jacob, 1997; Jaeglé et al., 1997].

We estimated the rate of chemical decay of the peroxides in the upper troposphere following convective injection using concurrent observations of H2O2, CH3OOH, and CH3I concentrations, with CH3I serving as a photochemical clock. Results were compared to a photochemical model simulation. Concentrations of CH3OOH declined with an e-folding lifetime of 1-2 days due to losses from photolysis and reaction with OH. The HOy produced from photolysis of CH3OOH was recycled to H2O2. Concentrations of H2O2 thus did not decline for about 5

### Table 3. Sources and Sinks of HOx at 8-12 km Altitude

<table>
<thead>
<tr>
<th>Source/Sink</th>
<th>Fresh Convective Outflow</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total HOx</td>
<td>7.4 5.0</td>
<td>7.4 5.0</td>
</tr>
<tr>
<td>HO2</td>
<td>5.2 3.7</td>
<td>5.2 3.7</td>
</tr>
<tr>
<td>CH3O2</td>
<td>2.1 1.2</td>
<td>2.1 1.2</td>
</tr>
<tr>
<td>OH</td>
<td>0.11 0.11</td>
<td>0.11 0.11</td>
</tr>
<tr>
<td>HO2 + HO2</td>
<td>5.1 2.3</td>
<td>5.1 2.3</td>
</tr>
<tr>
<td>HO2 + CH3O2</td>
<td>4.4 1.5</td>
<td>4.4 1.5</td>
</tr>
<tr>
<td>OH + HO2</td>
<td>3.4 2.5</td>
<td>3.4 2.5</td>
</tr>
<tr>
<td>Other</td>
<td>1.0 1.2</td>
<td>1.0 1.2</td>
</tr>
</tbody>
</table>

Twenty-four-hour mean concentrations, sources, and sinks of HOy obtained in a photochemical model [Schultz et al., this issue] constrained with the mean observations for fresh convective outflow and background upper tropospheric air over the tropical South Pacific in PEM-Tropics A (Table 1).
days following convective injection. The perturbation to HOx from the convective injection of peroxides decayed on a timescale of 2-3 days; this timescale is relatively short because of the intense radiation over the tropical South Pacific.

Photochemical model results for the PEM-Tropics A conditions indicate a 50% enhancement of HOx in convective outflow relative to background air at 8-12 km altitude. Half of this enhancement is due to convected water vapor and half is due to convected peroxides. As pointed out by Folkins et al. [1998], convective enhancement of HOx in the upper troposphere by deep marine convection is in general inefficient as a source of O3 because the outflow contains low concentrations of NOx. In continental convection, by contrast, convective injection of peroxides and CH2O leads to rapid O3 production because of the large concurrent source of NOx from lightning and pumping of continental pollution [Jaeglé et al., 1998].

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References


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