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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_2O_2 and CH_3OOH in the upper troposphere is investigated using aircraft observations from the NASA Pacific Explorer 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 mixing ratios 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 a major source of the HO_x 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_3I as a chemical clock and is interpreted using photochemical model calculations. Decline of CH_3OOH takes place on a timescale of a 1-2 days, but the resulting HO_x converts to H_2O_2 , so H_2O_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_2O_2 and CH_3OOH 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_2SO_4 [Chatfield and Crutzen, 1984; Prather and Jacob, 1997]. Jaeglé *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_3I , H_2O_2 , and CH_3OOH 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_3I provides a sensitive tracer of deep marine convection.

The peroxides H_2O_2 and CH_3OOH are produced in the atmosphere by combination reactions of the HO_x radicals, $HO_2 + HO_2$ and $CH_3O_2 + HO_2$, 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_2O_2 and CH_3OOH 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_2O_2 and CH_3OOH , $8 \times 10^4 M atm^{-1}$ and $3 \times 10^2 M atm^{-1}$ at room temperature [O'Sullivan *et al.*, 1996], one would expect H_2O_2 but not

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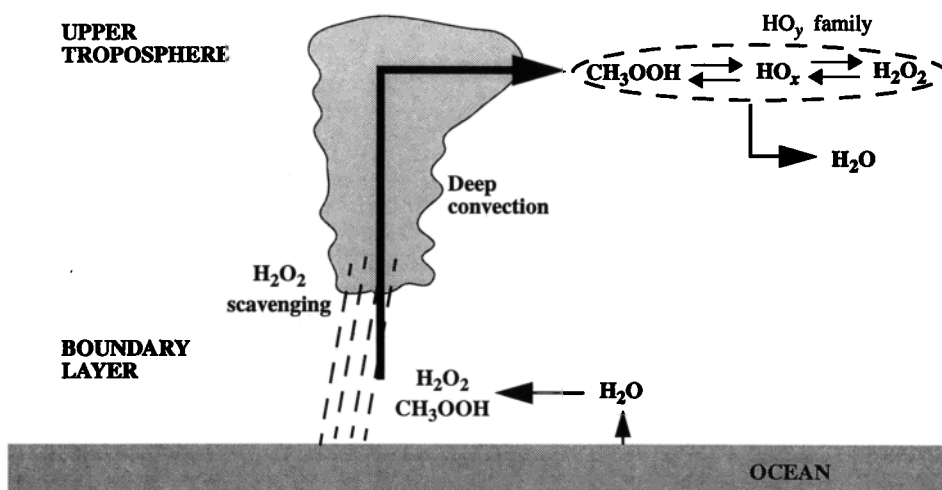


Figure 1. Schematic of the convective injection of peroxides and the cycling of HO_y in the upper troposphere.

CH₃OOH 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_y family (sum of HO_x and peroxides). Eventual conversion of HO_y back to water vapor terminates the process. A schematic of the resulting life cycle for HO_y 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 atmospheric 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 H₂O₂, CH₃OOH, CH₃I, and a number of other species. We use CH₃I 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 precipitation associated with deep convection (section 3). We then use CH₃I as a chemical clock to determine the timescale for decay of HO_y in the upper troposphere following convection and interpret 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 (CH₃I) is emitted ubiquitously by the oceans. Though biological production of CH₃I may be important 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 Zafriou, 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 marine tracers such as DMS. Biomass burning is thought to be a much smaller source of CH₃I 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 troposphere (Figure 2). Oxidation by OH accounts for only ~1% of the loss from photolysis. The Henry's Law constant of CH₃I 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 uniform concentrations of CH₃I 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 tracers, such as DMS, which have highly variable biological sources [Andreae *et al.*, 1985]. Atmospheric measurements of CH₃I concentrations can be made with high sensitivity (detection limit of 0.01 pptv) [D. Blake *et al.*, 1996]. The combination of relatively uniform boundary layer concentra-

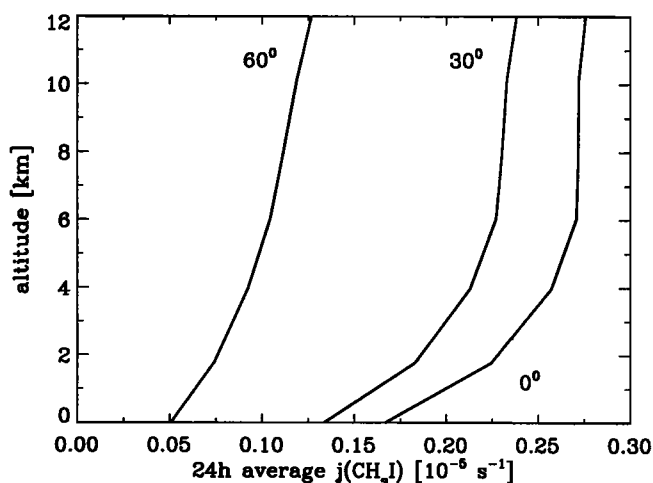


Figure 2. Vertical profiles of the 24-hour average photolysis frequency of CH₃I for three different latitudes. Calculations were done for a solar declination angle of 0° (equinox), an ozone column of 280 DU, and cloud-free conditions. Absorption cross sections for CH₃I are taken from Roehl *et al.* [1997], and a quantum yield of unity for photolysis is assumed.

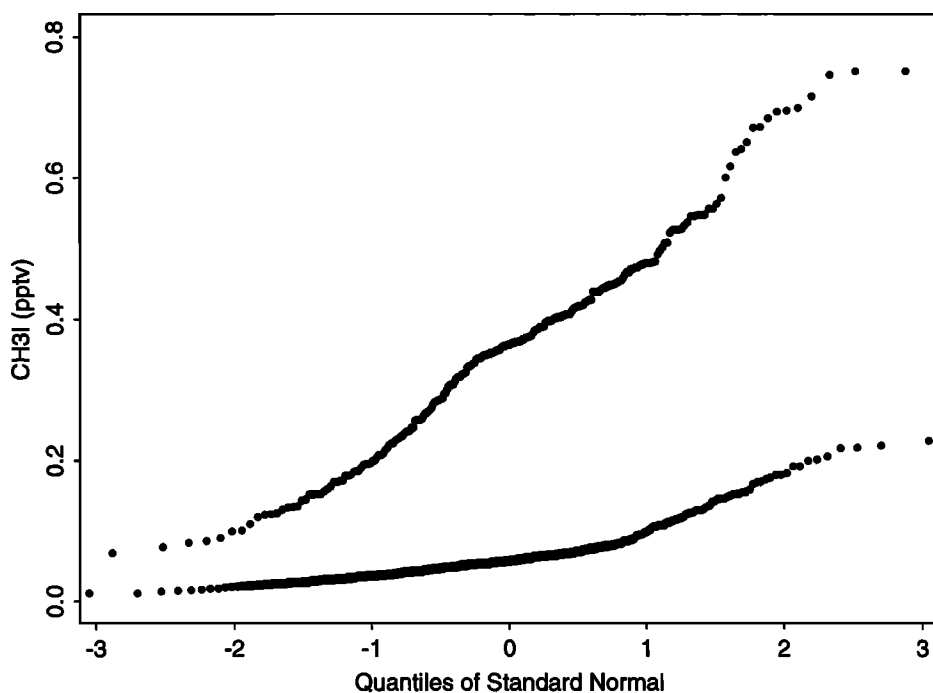


Figure 3. Probability distribution of CH_3I concentrations over the tropical South Pacific at 0–2 km altitude (circles) and at 8–12 km altitude (triangles). The abscissa is a normal probability scale that a normal distribution would plot as a straight line with standard deviations indicated as the quantiles of standard normal.

tion, relatively well defined lifetime, and low limit of detection makes CH_3I an attractive tracer for deep marine convection and the age of air in the upper troposphere. A parallel can be drawn to the radioisotope ^{222}Rn , which is emitted by soils and provides a sensitive tracer of continental convection [Jacob *et al.*, 1997].

Figure 4a shows the latitudinal distribution of CH_3I 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 CH_3I 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

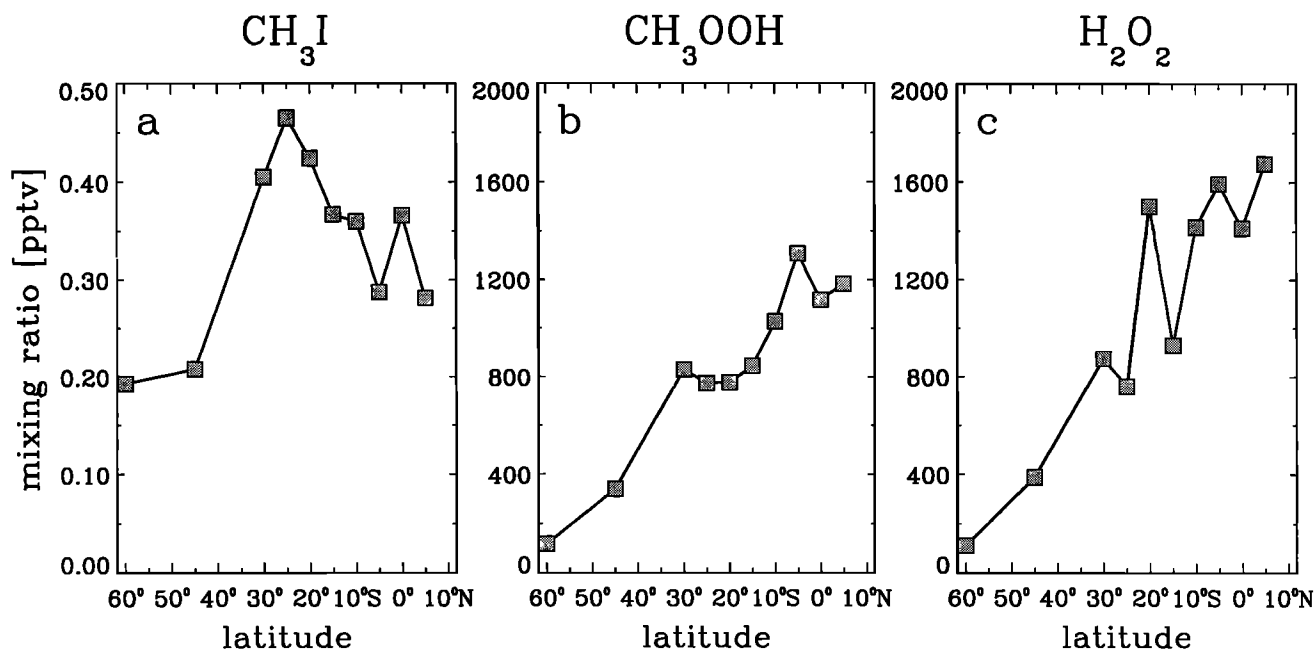


Figure 4. Latitudinal distributions of median mixing ratios of (a) CH_3I , (b) CH_3OOH , and (c) H_2O_2 at 0–2 km altitude in PEM-Tropics A. Each symbol contains at least 10 samples.

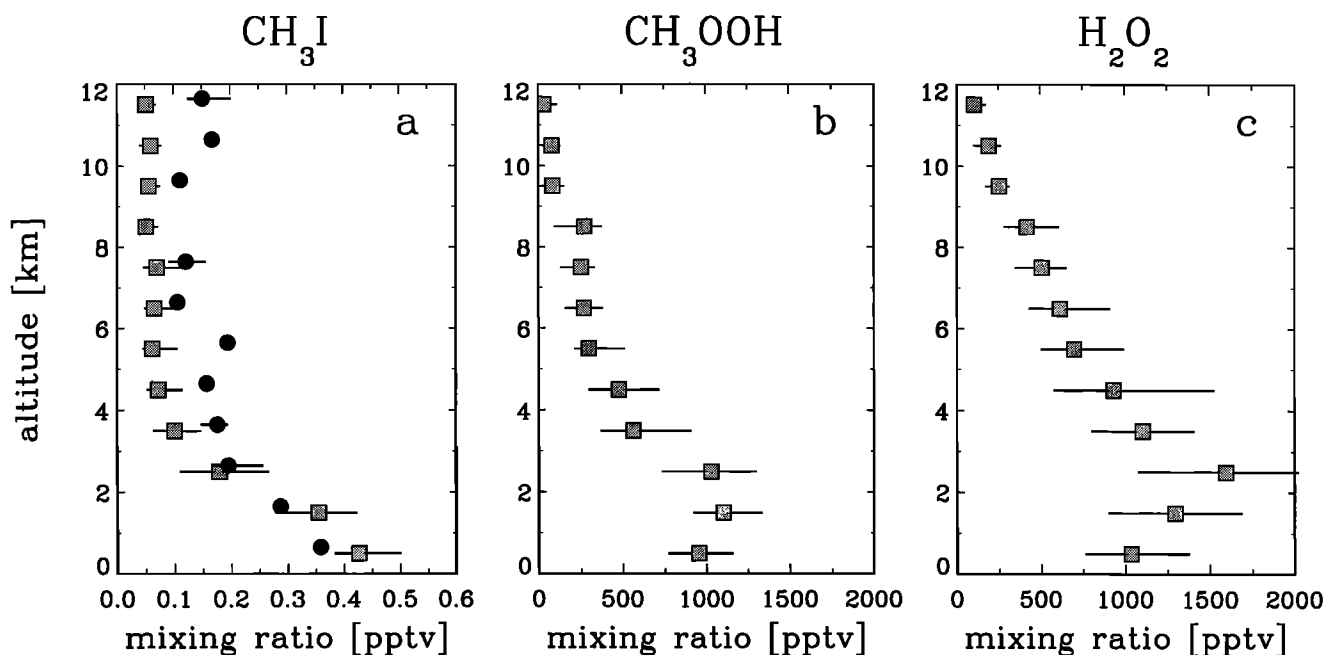


Figure 5. Vertical profiles of mixing ratios of (a) CH_3I , (b) CH_3OOH , and (c) H_2O_2 measured in PEM-Tropics A at 0° - 30°S latitude. Squares represent median values and lines represent interquartile ranges. In Figure 5a, circles represent the subset of CH_3I mixing ratios over the West Pacific Warm Pool, west of 170°E and north of 15°S , an area of particularly intense convection. Each square contains at least 80 samples, each circle contains at least 5 samples; the interquartile range is not shown if there were less than 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_3I 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_3I 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_3I 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_3I 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_3I 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_3I as a tracer of marine convection. Most measurements of elevated CH_3I 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_3I measurements were associated with low humidity ($<10\%$ with respect to ice) and high C_2H_2 mixing ratios (80-300 pptv), in-

dicating biomass burning pollution rather than marine convection as the source of CH_3I . 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_3I and relative humidity in the top octile ($\text{CH}_3\text{I} > 0.11$ pptv, relative humidity $>50\%$ with respect to ice) also had elevated mixing ratios of bromoform as well as low C_2H_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 $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ 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_3OOH by a factor of 2 and H_2O_2 by 30%, on average, at 8-12 km. Convective transport would be a likely explanation for the underestimate of CH_3OOH at high altitude, although the magnitude of the bias is within the uncertainty of the low-temperature rate constant for the $\text{CH}_3\text{O}_2 + \text{HO}_2$ reaction [DeMore *et al.*, 1997].

Table 1. Air Mass Compositions at 0–2 km and 8–12 km Altitude Over Tropical South Pacific

	Boundary Layer 0–2 km <i>n</i> = 253	High CH ₃ I Fresh Convective Outflow 8–12 km <i>n</i> = 23	High CH ₃ I Aged Convective Outflow 8–12 km <i>n</i> = 27	High CH ₃ I Biomass Burning Pollution 8–12 km <i>n</i> = 5	Background 8–12 km <i>n</i> = 355
CH ₃ I, pptv	0.36 ± 0.14	0.15 ± 0.03	0.15 ± 0.03	0.18 ± 0.04	0.05 ± 0.02
CH ₃ OOH, pptv	1080 ± 410	500 ± 280	230 ± 130	110 ± 40	80 ± 80
H ₂ O ₂ , pptv	1340 ± 710	330 ± 140	270 ± 80	190 ± 150	200 ± 110
NO, pptv	2.4 ± 4.4	19 ± 16	29 ± 25	74 ± 35	56 ± 43
NO _x , pptv ^a	7.1 ± 16.4	22 ± 19	34 ± 28	125 ± 26	60 ± 52
HNO ₃ , pptv	36 ± 53	25 ± 15	43 ± 18	100 ± 58	75 ± 59
Ozone, pptv	25 ± 11	27 ± 7	29 ± 8	61 ± 29	51 ± 22
Water vapor, pptv	15100 ± 6500	700 ± 520	160 ± 150	70 ± 70	130 ± 110
Rel. humidity ^b	75% ± 19%	82% ± 14%	21% ± 14%	6% ± 1%	13% ± 12%
DMS, pptv	48 ± 54	7 ± 11	2 ± 5	2 ± 2	< 0.8 ^c
CHBr ₃ , pptv	1.0 ± 0.4	0.76 ± 0.13	0.44 ± 0.18	0.61 ± 0.38	0.33 ± 0.17
SO ₂ , pptv	31 ± 29	13 ± 6	14 ± 5.5	18 ± 3	18 ± 15
CO, pptv	62 ± 13	57 ± 4	61 ± 4	92 ± 31	64 ± 13
C ₂ H ₂ , pptv	44 ± 33	33 ± 10	37 ± 10	130 ± 90	57 ± 34

Means and standard deviations of concentrations measured at 0°–30°S 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 (C₂H₂ < 80 pptv). Aged convective outflow: CH₃I > 0.11 pptv, relative humidity < 50%, and C₂H₂ < 80 pptv. Biomass burning pollution: CH₃I > 0.11 pptv, relative humidity < 50%, and C₂H₂ > 80 pptv. The rest of the data (i.e., CH₃I < 0.11 pptv and relative humidity < 50%) were labeled background conditions.

^a NO_x = NO + NO₂; NO₂ 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 β of UT air in this mixture represents a dilution factor for the convected air and is given by

$$\beta = \frac{X_{\text{BL}} - X_{\text{conv}}}{X_{\text{BL}} - X_{\text{UT}}} \quad (1)$$

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 α during convective transport. Our two-component model gives

$$Y_{\text{conv}} = (1 - \alpha)(1 - \beta)Y_{\text{BL}} + \beta Y_{\text{UT}} \quad (2)$$

and rearrangement yields an expression for the scavenging efficiency α:

$$\alpha = 1 - \frac{Y_{\text{conv}} - \beta Y_{\text{UT}}}{(1 - \beta)Y_{\text{BL}}} \quad (3)$$

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 β. Changes in α 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 HO_x (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

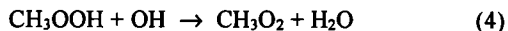
	Reference Tracer		
	CHBr ₃	CH ₃ OOH	CH ₃ I
Dilution factor β	0.36	0.58	0.68
Scavenging efficiency α			
H ₂ O ₂	70%	62%	55%
Water vapor	93%	90%	87%
SO ₂	67%	80%	94%

The scavenging efficiency α 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 CHBr₃, CH₃OOH, or CH₃I to derive the dilution factor β by equation (1).

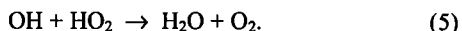
the peroxide mixing ratios versus the CH₃I mixing ratio taken as a time coordinate (Figure 6). Also shown in Figure 6 are results from a time-dependent, zero-dimensional photochemical model simulation [Schultz *et al.*, 1998] for an air parcel initialized with the fresh convective outflow composition in Table 1. Acetone and CH₂O, 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 O₃ column is 6.7×10^{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 CH₃I coordinate to time. The trend of peroxide versus CH₃I 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 CH₃OOH decline on a timescale of 1–2 days following a convective event. In contrast, observed concentrations of H₂O₂ show no significant decline for ~5 days following convection and then decline to steady state. We explain the longer persistence of H₂O₂ as reflecting the cycling within the HO_y family (Figure 1); recycling of peroxides from HO_x in the upper troposphere favors H₂O₂ over CH₃OOH because of the dominance of CO over CH₄ as a sink for OH.

The dominant sink of HO_y in fresh convective outflow in the model is the oxidation of CH₃OOH by OH:



while the dominant sink in background air is the reaction of OH with HO₂:



The timescale for relaxation of HO_y to steady state following the convective perturbation can be inferred from the trend in the sum of H₂O₂ and CH₃OOH, which account for about 95% of total HO_y in the model. Results in Figure 6 indicate an effective *e*-folding lifetime of 2–3 days for HO_y, 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_y concentration to the 24-hour average HO_y loss rate, which varies from 1.3

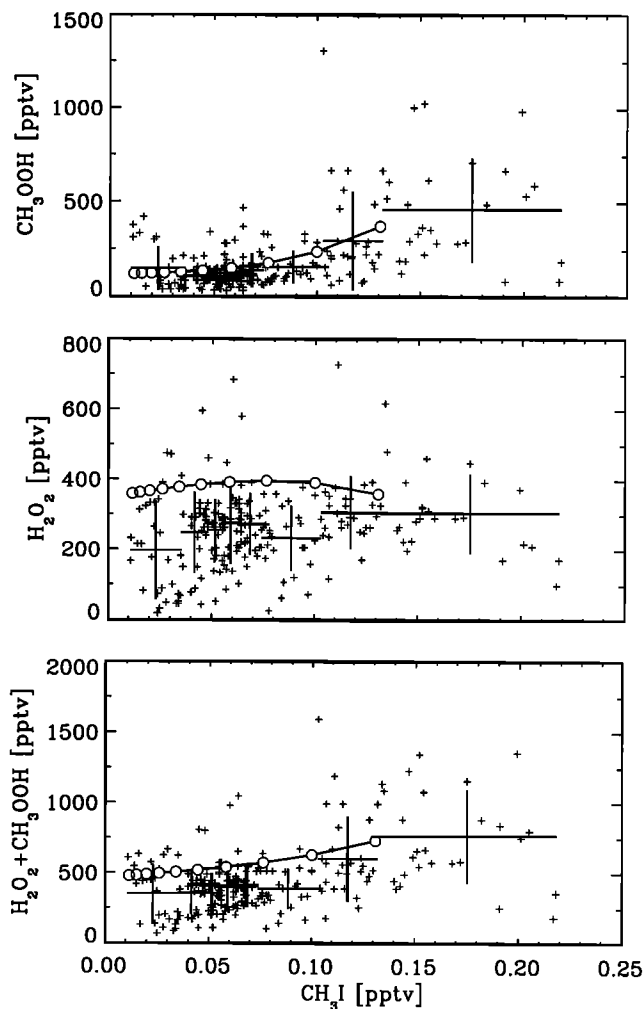


Figure 6. Mixing ratios of (a) CH₃OOH, (b) H₂O₂, and (c) the sum of peroxides versus the CH₃I mixing ratio measured in PEM-Tropics A at 0°–30°S latitude. Plus signs denote individual observations, large crosses are mean values and standard deviations for CH₃I octiles. Data with strong biomass-burning influence (C₂H₂ > 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 HO_y, thus sustaining the HO_y enhancement in the outflow for longer than would be expected from the standard calculation of HO_y lifetime. The effective *e*-folding lifetime of the HO_y enhancement for the PEM-Tropics A conditions is still much shorter than the 6-day value reported by Jaeglé *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 NO_x concentrations (which facilitate reaction (5) by increasing the OH/HO₂ concentration ratio) also contribute.

We find in our model that HO_x 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 HO_x 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 HO_x 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 OH are not enhanced in the convective outflow, because the added source of HO_x 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 HO_x 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 HO_x 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 HO_x in the convective outflow.

Formaldehyde is an additional HO_x precursor injected to the upper troposphere by deep convection, but no measurements of CH₂O 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 HO_x 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 HO_x 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 HO_x 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 HO_x at 8–12 km Altitude

	Fresh Convective Outflow	Background
<i>HO_x concentrations, 10⁷ molecules cm⁻³</i>		
Total HO _x	7.4	5.0
HO ₂	5.2	3.7
CH ₃ O ₂	2.1	1.2
OH	0.11	0.11
<i>HO_x sources, 10⁴ molecules cm⁻³ s⁻¹</i>		
O(¹ D) + H ₂ O	4.9	2.1
H ₂ O ₂ + <i>hν</i>	3.1	1.7
CH ₂ O + <i>hν</i>	2.9	2.3
CH ₃ OOH + <i>hν</i>	2.5	0.9
Acetone + <i>hν</i>	0.5	0.5
<i>HO_x sinks, 10⁴ molecules cm⁻³ s⁻¹</i>		
HO ₂ + HO ₂	5.1	2.3
HO ₂ + CH ₃ O ₂	4.4	1.5
OH + HO ₂	3.4	2.5
Other	1.0	1.2

Twenty-four-hour mean concentrations, sources, and sinks of HO_x 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 HO_x 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 HO_x 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 HO_x in the upper troposphere by deep marine convection is in general inefficient as a source of O₃ because the outflow contains low concentrations of NO_x. In continental convection, by contrast, convective injection of peroxides and CH₂O leads to rapid O₃ production because of the large concurrent source of NO_x from lightning and pumping of continental pollution [*Jaeglé et al.*, 1998].

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References

- Andreae, M.O., R.J. Ferek, F. Bermond, K.P. Byrd, R.T. Engstrom, S. Hardin, P.D. Houmère, F. LeMarrec, H. Raemdonck, and R.B. Chatfield, Dimethyl sulfide in the marine atmosphere, *J. Geophys. Res.*, **90**, 12,891-12,900, 1985.
- Andreae, M.O., et al., Methyl halide emissions from savanna fires in southern Africa, *J. Geophys. Res.*, **101**, 23,603-23,613, 1996.
- Arlander, D.W., D.R. Cronn, J.C. Farmer, F.A. Menzia, and H.H. Westberg, Gaseous oxygenated hydrocarbons in the remote marine troposphere, *J. Geophys. Res.*, **95**, 16,391-16,403, 1990.
- Blake, D.R., T.-Y. Chen, T.W. Smith Jr., C.J.-L. Wang, O.W. Wingenter, N.J. Blake, F.S. Rowland, and E.W. Mayer, Three-dimensional distribution of NMHCs and halocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Mission (PEM-West A), *J. Geophys. Res.*, **101**, 1763-1778, 1996.
- Blake, N.J., D.R. Blake, B.C. Sive, T.Y. Chen, F.S. Rowland, J.E. Collins, G.W. Sachse, and B.E. Anderson, Biomass burning emissions and vertical distribution of atmospheric methyl halides and other reduced carbon gases in the South Atlantic region, *J. Geophys. Res.*, **101**, 24,151-24,164, 1996.
- Brune, W.H., et al., Airborne in situ OH and HO₂ observations in the cloud-free troposphere and lower stratosphere during SUCCESS, *Geophys. Res. Lett.*, **25**, 1701-1704, 1998.
- Chatfield, R.B., and P.J. Crutzen, Sulfur dioxide in remote ocean air: Cloud transport of reactive precursors, *J. Geophys. Res.*, **89**, 7111-7132, 1984.
- 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.
- DeMore, W.B., S.P. Sander, D.M. Golden, R.F. Hampson, M.J. Kurylo, C.J. Howard, A.R. Ravishankara, C.E. Kolb, and M.J. Molina, Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publ. 97-4*, NASA Jet Propul. Lab., Pasadena, Calif., 1997.
- Fishman, J., J.M. Hoell, R.D. Bendura, R.J. McNeal, and V.W.J.H. Kirchhoff, NASA GTE TRACE A Experiment (September-October 1992): Overview, *J. Geophys. Res.*, **101**, 23,865-23,879, 1996.
- Folkins, I., R. Chatfield, H. Singh, Y. Chen, and B. Heikes, Ozone production efficiencies of acetone and peroxides in the upper troposphere, *Geophys. Res. Lett.*, **25**(9), 1305-1308, 1998.
- Happell, J.D., and D.W.R. Wallace, Methyl iodide in the Greenland/Norwegian Seas and the tropical Atlantic Ocean: Evidence for photochemical production, *Geophys. Res. Lett.*, **101**, 2105-2108, 1996.
- Heikes, B.G., et al., Hydrogen peroxide and methylhydroperoxide distributions related to ozone and odd hydrogen over the North Pacific in the fall of 1991, *J. Geophys. Res.*, **101**, 1891-1905, 1996.
- Hoell, J.M., D.D. Davis, S.C. Liu, R. Newell, M. Shipham, H. Akimoto, R.J. McNeal, R.J. Bendura, and J.W. Drewry, Pacific Exploratory Mission-West A (PEM-West A): September-October 1991, *J. Geophys. Res.*, **101**, 1641-1654, 1996.
- Hoell, J.M., D.D. Davis, D.J. Jacob, M.O. Rodgers, R.E. Newell, H.E. Fuelberg, R.J. McNeal, J.L. Raper, and R.J. Bendura, The Pacific Exploratory Mission in the Tropical Pacific: PEM-Tropics A, August-September 1996, *J. Geophys. Res.*, this issue.
- 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.*, **101**, 24,235-24,250, 1996.
- Jacob, D.J., et al., Evaluation and intercomparison of global atmospheric transport models using ²²²Rn and other short-lived tracers, *J. Geophys. Res.*, **102**, 5953-5970, 1997.
- Jaeglé, L., et al., Observed OH and HO₂ in the upper troposphere suggest a major source from convective injection of peroxides, *Geophys. Res. Lett.*, **24**, 3181-3184, 1997.
- Jaeglé, L., D.J. Jacob, W.H. Brune, A.J. Weinheimer, B.A. Ridley, T.L. Campos, and G.W. Sachse, Sources of HO_x and production of ozone in the upper troposphere over the United States, *Geophys. Res. Lett.*, **25**(10), 1709-1712, 1998.
- 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.
- Manley, S.L., and J.L. de la Cuesta, Methyl iodide production from marine phytoplankton cultures, *Limnology and Oceanography*, **42**, 142-147, 1997.
- Moore, R., and O. Zafiriou, Photochemical production of methyl iodide in seawater, *J. Geophys. Res.*, **99**, 16,415-16,420, 1994.
- Moore, R.M., C.E. Geen, and V.K. Tait, Determination of Henry's Law constant for a suite of naturally occurring halogenated methanes in seawater, *Chemosphere*, **30**, 1183-1191, 1995.
- O'Sullivan, D.W., M. Lee, B.C. Noone, and B.G. Heikes, Henry's Law constant determinations for hydrogen peroxide, methylhydroperoxide, hydroxymethylhydroperoxide, ethylhydroperoxide and peroxyacetic acid, *J. Phys. Chem.*, **100**, 3241-3247, 1996.
- O'Sullivan, D.W., B.G. Heikes, M. Lee, W. Chang, G. Gregory, D. Blake, and G. Sachse, The distribution of hydrogen peroxide and methylhydroperoxide over the Pacific and South Atlantic Oceans, *J. Geophys. Res.*, this issue.
- Prather, M.J., and D.J. Jacob, A persistent imbalance in HO_x and NO_x photochemistry of the upper troposphere driven by deep tropical convection, *Geophys. Res. Lett.*, **24**, 3189-3192, 1997.
- Roehl, C.M., et al., Temperature dependence of UV absorption cross sections and atmospheric implications of several alkyl iodides, *J. Geophys. Res.*, **102**, 12,819-12,829, 1997.
- Schultz, M.G., et al., On the origin of tropospheric ozone and NO_x over the tropical South Pacific, *J. Geophys. Res.*, this issue.
- Wang, Y., J.A. Logan, D.J. Jacob, and C.M. Spivakovsky, Global simulation of tropospheric O₃-NO_x-hydrocarbon chemistry, 2, Model evaluation and global ozone budget, *J. Geophys. Res.*, **103**, 10,713-10,725, 1998.
- Wennberg, P.O., et al., Hydrogen radicals, nitrogen radicals, and the production of O₃ in the middle and upper troposphere, *Science*, **279**, 49-52, 1998.
- Yokouchi, Y., H. Mukai, H. Yamamoto, A. Otsuki, C. Saitoh, and Y. Nojiri, Distribution of methyl iodide, ethyl iodide, bromoform, and dibromomethane over the ocean (east and southeast Asian Seas and the western Pacific), *J. Geophys. Res.*, **102**, 8805-8809, 1997.

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