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 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 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 a 1-2 days but the resulting HO_x converts to H_2O_2, so that 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 time scale 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 time scale of the order of one 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 that 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 pptv in the marine boundary layer and 100pptv 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, $8x10^4$ *M* atm^{-1} and $3x10^2$ *M* atm^{-1} at room temperature [*O'Sullivan et al.*, 1996], one would expect H_2O_2 but not CH_3OOH 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.*, 1998]. 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^oN to 72^oS. Most of the data were collected between 0^oS and 30^oS 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_2O_2, CH_3OOH, CH_3I, and a number of other species. We use CH_3I 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 CH_3I as a chemical clock to determine the time scale 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 (CH_3I) is emitted ubiquitously by the oceans. Though biological production of CH_3I 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 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 marine tracers such as DMS. Biomass burning is thought to be a much smaller source of CH_3I 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 CH_3I is sufficiently low (K_H=0.14 M atm^{-1} at room temperature [*Moore et al.*, 1995]) that rainout is negligible.

Observations in PEM-Tropics (A) indicate relatively uniform concentrations of CH_3I in the marine boundary layer (MBL) over the south tropical 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 CH_3I 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 concentration, 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^o-30^oS), 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 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^oE). Mixing ratios of CH_3I over this region decline by only a factor of two 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 PEM-West (A) campaign over the western equatorial Pacific [*Hoell et al.*, 1996] and the 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 PEM-Tropics (A) [*Schultz et al.*, 1998]. 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), indicating 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 (CH_3I>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.*, 1998]. *Schultz et al*. [1998] 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 $O(^1D) + H_2O$ 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 $CH_3O_2 + HO_2$ reaction [*DeMore et al.*, 1997].

The role of convection in enhancing CH_3OOH concentrations in the upper troposphere is evident from Table 1. The mean CH_3OOH mixing ratio above 8 km is 6 times higher in convective outflow than in background air. The mean H_2O_2 mixing ratio in convective outflow is also elevated but by less than a factor of 2. The CH_3OOH / CH_3I concentration ratio in fresh convective outflow is similar to that in the boundary layer, indicating no significant scavenging of CH_3OOH in the precipitation associated with deep convection.

We estimate the scavenging efficiency of H_2O_2 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 air (BL) and background upper tropospheric air (UT). The fraction β of UT air in this mixture represents a dilution factor for the convected air and is given by:

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

where X is the mixing ratio of an insoluble tracer such as $CHBr_3$, CH_3OOH, or CH_3I 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

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

and rearrangement yields an expression for the scavenging efficiency α:

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

Scavenging efficiencies for H_2O_2, H_2O, and SO_2 in deep convection are given in Table 2 using the mean observations in Table 1 and either of the reference tracers $CHBr_3$, CH_3OOH, or CH_3I 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 H_2O_2 scavenging efficiency of 55-70%. A higher scavenging efficiency is found for SO_2 (65-95%), presumably reflecting oxidation by H_2O_2 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

Once injected in the upper troposphere, the peroxides decay and supply a source of HO_x (Figure 1). The time scale for decay of the peroxide enhancement following a convective event can be estimated in the PEM-Tropics (A) data by plotting the peroxide mixing ratios versus the CH_3I mixing ratio taken as a time coordinate (Figure 6). Also shown in Figure 6 are results from a time-dependent, 0-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_2O, 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

6.7×10^{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_3I coordinate to time. The trend of peroxide vs. CH_3I 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_3OOH decline on a time scale of 1-2 days following a convective event. In contrast, observed concentrations of H_2O_2 show no significant decline for ~5 days following convection and then decline to steady state. We explain the longer persistence of H_2O_2 as reflecting the cycling within the HO_y family (Figure 1); recycling of peroxides from HO_x in the upper troposphere favors H_2O_2 over CH_3OOH because of the dominance of CO over CH_4 as a sink for OH.

The dominant sink of HO_y in fresh convective outflow in the model is the oxidation of CH_3OOH by OH:

$$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O \qquad (4)$$

while the dominant sink in background air is the reaction of OH with HO_2:

$$OH + HO_2 \rightarrow H_2O + O_2 \qquad (5)$$

The time scale for relaxation of HO_y to steady state following the convective perturbation can be inferred from the trend in the sum of H_2O_2 and CH_3OOH, 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 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 CH_4 to produce CH_2O; photolysis of this CH_2O 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 O_3 columns and higher NO_x concentrations (which facilitate reaction *(5)* by increasing the OH / HO_2 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 O_3 columns, and high humidities, which maintained a large rate of primary HO_x production from the $O(^1D)+H_2O$ 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 CH_3OOH. Concentrations of CH_3O_2 are almost twice as high in convective outflow as in background air due to the source from convected CH_3OOH. 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 CH_3I and elevated relative humidity. CH_3I 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 C_2H_2. Though not used extensively in this study, $CHBr_3$ exhibits similar traits to CH_3I and could also serve as a tracer of marine convection.

We found that concentrations of CH_3OOH in convective outflow at 8-12 km altitude were elevated by a factor of 6 relative to the upper tropospheric background, while concentrations of H_2O_2 were elevated by less than a factor of 2. Scavenging by precipitation in the convective updraft was negligible for CH_3OOH and 55-70% for H_2O_2. 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 CH_2O were made in PEM-Tropics (A). If boundary layer CH_2O mixing ratios were 600-1000 pptv, as found in some shipboard measurements over the equatorial Pacific [*Arlander et al.*, 1990], then convective pumping of CH_2O would be of comparable importance to peroxides as a source of HO_x in convective outflow. However, models and most observations indicate CH_2O mixing ratios of 100-300 pptv in the tropical marine boundary layer [*Jacob et al.*, 1996]. At these levels, transport of CH_2O 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 by using concurrent observations of H_2O_2, CH_3OOH, and CH_3I concentrations, with CH_3I serving as a photochemical clock. Results were compared to a photochemical model simulation. Concentrations of CH_3OOH 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 CH_3OOH was recycled to H_2O_2. Concentrations of H_2O_2 thus did not decline for about 5 days following convective injection. The perturbation to HO_x from the convective injection of peroxides decayed on a time scale of 2-3 days; this time-scale 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 O_3 because the outflow contains low concentrations of NO_x. In continental convection, by contrast, convective injection of peroxides and CH_2O leads to rapid O_3 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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Figure captions

figure 1: Schematic of the convective injection of peroxides and the cycling of HO_y in the upper troposphere

figure 2: Vertical profiles of the 24-hour average photolysis frequency of CH_3I for three different latitudes. Calculations were done for a solar declination angle of 0^o (equinox), an ozone column of 280 DU, and cloud-free conditions. Absorption cross-sections for CH_3I 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.

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^o-30^oS latitude. Squares represent median values and lines represents interquartile ranges. In (a), darkened circles represent the subset of CH_3I mixing ratios over the West Pacific Warm Pool, west of 170^oE and north of 15^oS, 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.

figure 6: Mixing ratios of (a) CH_3OOH, (b) H_2O_2, and (c) the sum of peroxides vs. the CH_3I mixing ratio measured in PEM-Tropics (A) at 0^o-30^oS latitude. Plus signs denote individual observations, large crosses are mean values and standard deviations for CH_3I octiles. Data with strong biomass burning influence (C_2H_2 > 80 pptv) were excluded. Open circles are results from a photochemical model calculation (see text); each circle represents an aging time of one day in the model starting from fresh convective outflow.

Table 1: Air mass compositions at 0-2 km and 8-12 km altitude over the tropical South Pacific

	0-2 km boundary layer n=253	8-12 km high CH_3I fresh convective outflow n=23	8-12 km high CH_3I aged convective outflow n=27	8-12 km high CH_3I biomass burning pollution n=5	8-12 km background n=355
CH_3I (pptv)	0.36 ± 0.14	0.15 ± 0.03	0.15 ± 0.03	0.18 ± 0.04	0.05 ± 0.02
CH_3OOH (pptv)	1080 ± 410	500 ± 280	230 ± 130	110 ± 40	80 ± 80
H_2O_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[a](pptv)	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 (ppbv)	25 ± 11	27 ± 7	29 ± 8	61 ± 29	51 ± 22
Water vapor (ppmv)	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_2H_2 (pptv)	44 ± 33	33 ± 10	37 ± 10	130 ± 90	57 ± 34

Means and standard deviations of concentrations measured at 0^o-30^oS latitude during PEM-Tropics (A). The following selection criteria were applied: Recent marine convection: CH_3I and relative humidity both in the top octiles of measurements at 8-12 km altitude (i.e., CH_3I > 0.11pptv, relative humidity > 50%). All cases meeting these criteria also had low biomass burning influence (C_2H_2 < 80pptv). Aged convective outflow: CH_3I > 0.11 pptv, relative humidity < 50%, and C_2H_2 < 80 pptv. Biomass burning pollution: CH_3I > 0.11 pptv, relative humidity < 50%, and C_2H_2 > 80pptv. The rest of the data (i.e. CH_3I < 0.11 pptv and relative humidity< 50%) were labeled background conditions.

[a] $NO_x = NO + NO_2$; NO_2 is calculated with a photochemical steady state model [*Schultz et al.*, 1998].

[b] Relative humidity is defined with respect to ice.

[c] Detection limit for the DMS measurements.

Table 2: Scavenging efficiencies of gases during deep convection

	Reference Tracer		
	$CHBr_3$	CH_3OOH	CH_3I
Dilution factor β	0.36	0.58	0.68
Scavenging efficiency α			
H_2O_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 $CHBr_3$, CH_3OOH, or CH_3I to derive the dilution factor β by equation (1).

Table 3: Sources and sinks of HO_x at 8-12 km altitude

	fresh convective outflow	background
HO_x concentrations, 10^7 molecules cm^{-3}		
total HO_x	7.4	5.0
HO_2	5.2	3.7
CH_3O_2	2.1	1.2
OH	0.11	0.11
HO_x sources, 10^4 molecules cm^{-3} s^{-1}		
$O(^1D)+H_2O$	4.9	2.1
H_2O_2 + hv	3.1	1.7
CH_2O + hv	2.9	2.3
CH_3OOH + hv	2.5	0.9
Acetone + hv	0.5	0.5
HO_x sinks, 10^4 molecules cm^{-3} s^{-1}		
HO_2 + HO_2	5.1	2.3
HO_2 + CH_3O_2	4.4	1.5
OH + HO_2	3.4	2.5
other	1.0	1.2

24-hour mean concentrations, sources and sinks of HO_x obtained in a photochemical model [*Schultz et al.*, 1998] 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).

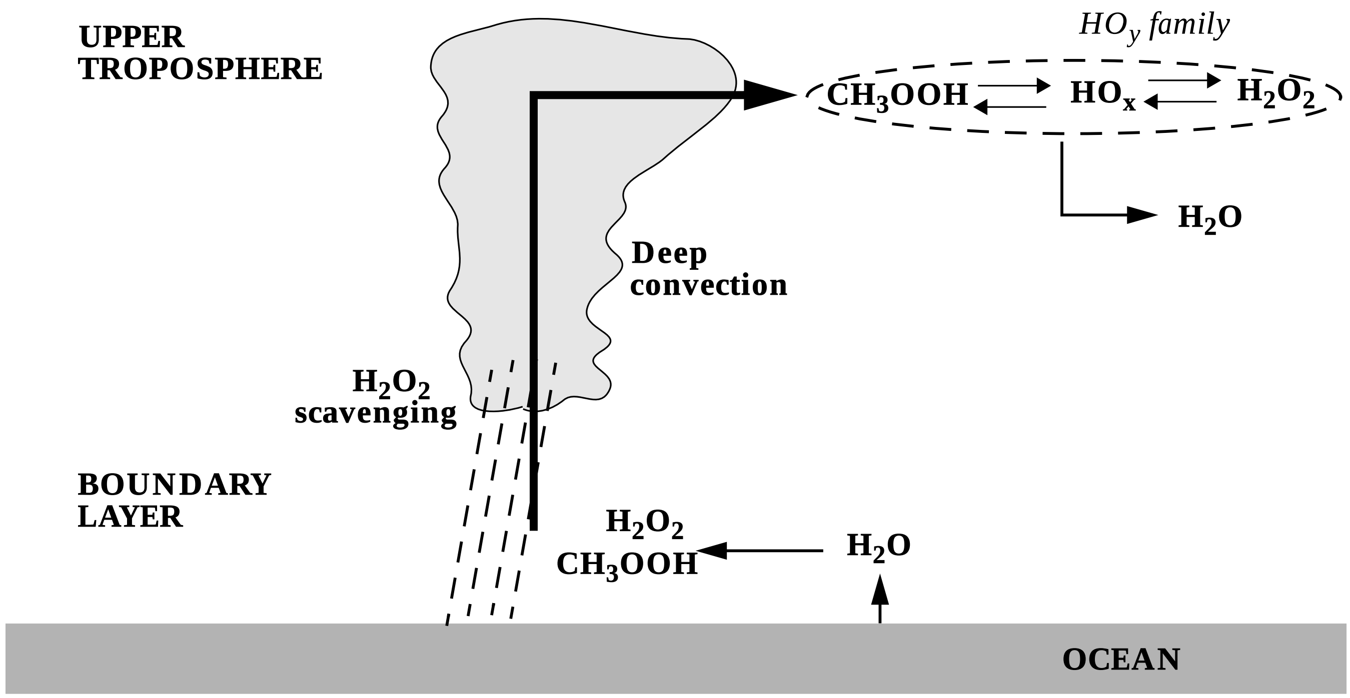
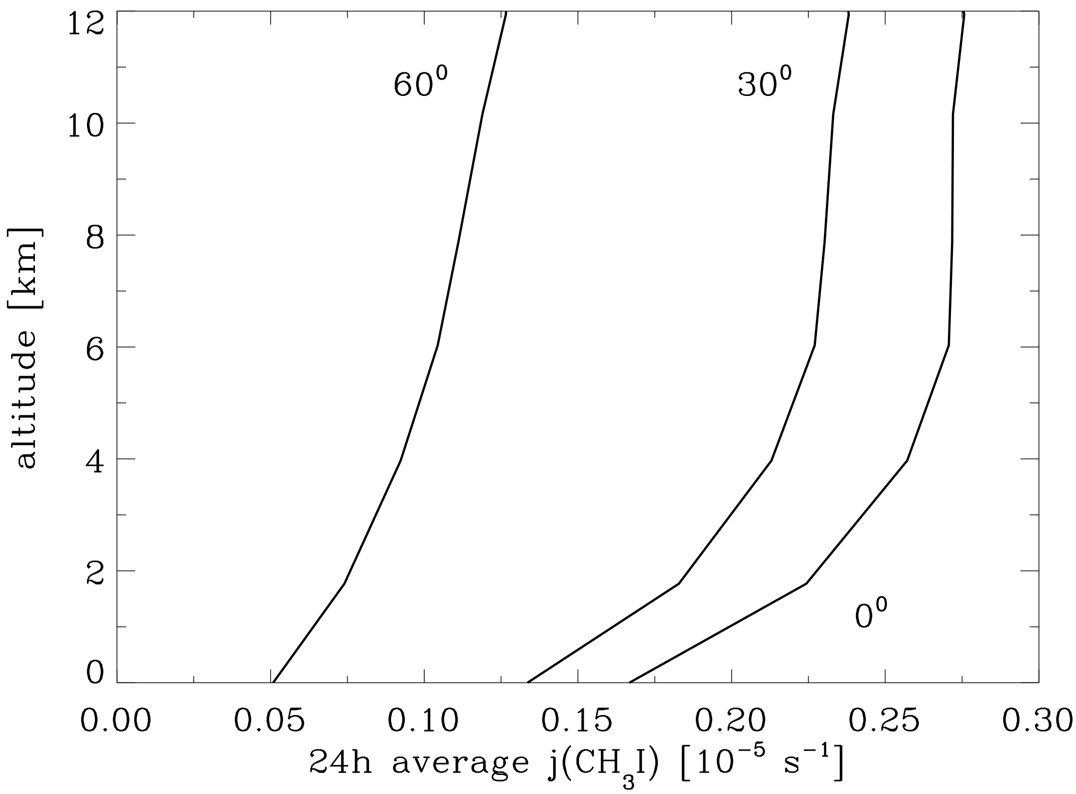

HOy family
UPPER
TROPOSPHERE
CH3OOH
HOx
H2O2
H2O
Deep
convection
H2O2
scavenging
BOUNDARY
LAYER
H2O2
CH3OOH
H2O
OCEAN

Figure 1.



Cohan1998:figure02, 05/13/1998 13:55

figure 2

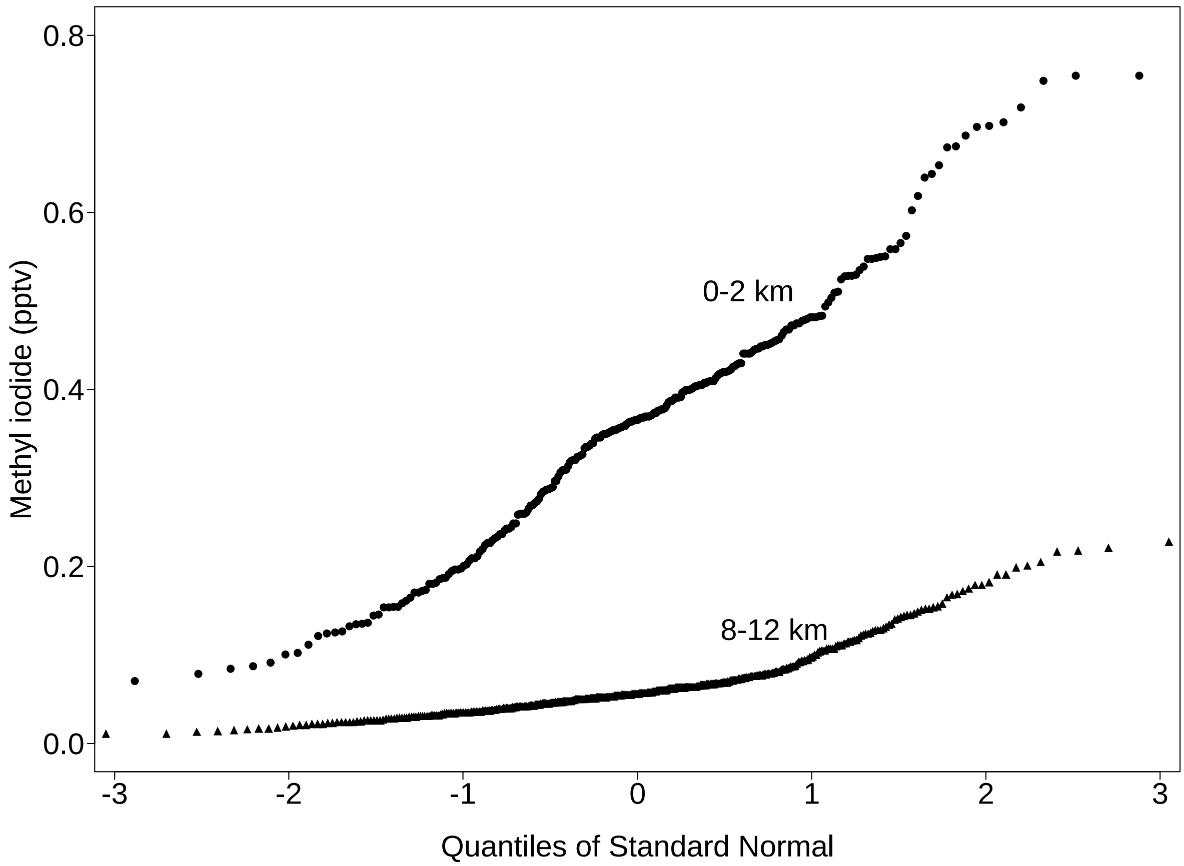
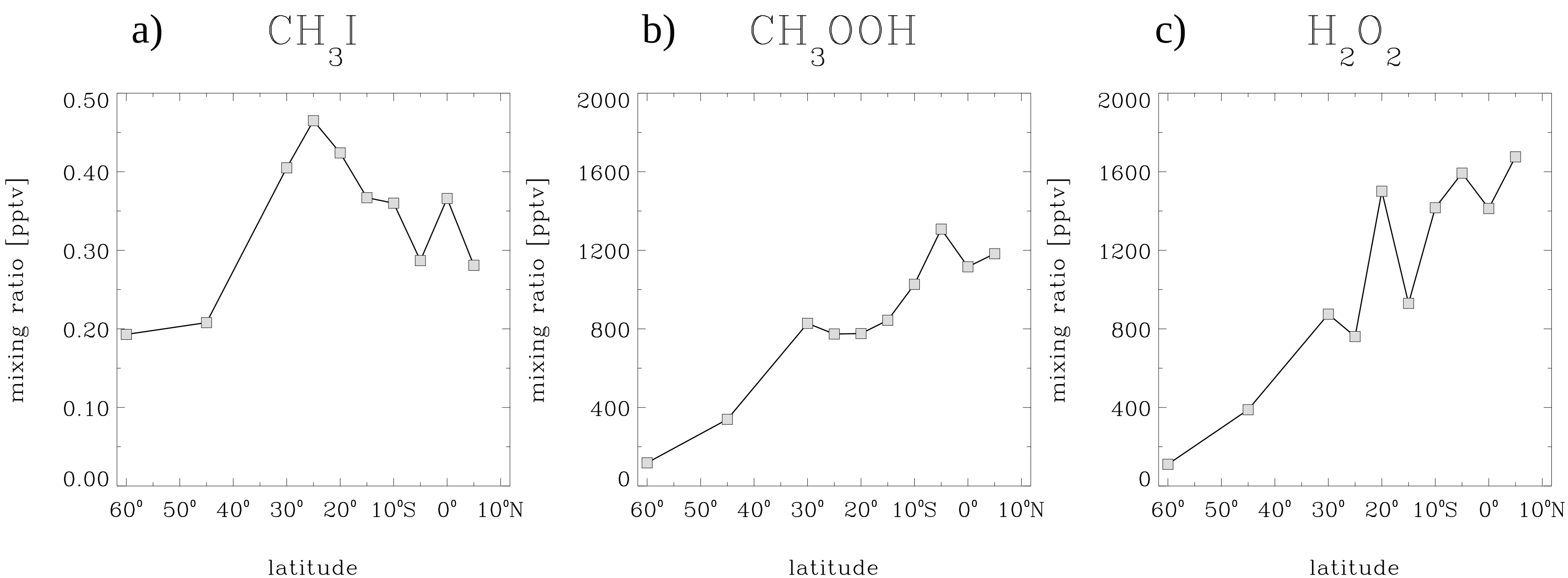

0.8
0.6
0.4
0.2
0.0
Methyl iodide (pptv)
0-2 km
8-12 km
-3
-2
-1
0
1
2
3
Quantiles of Standard Normal

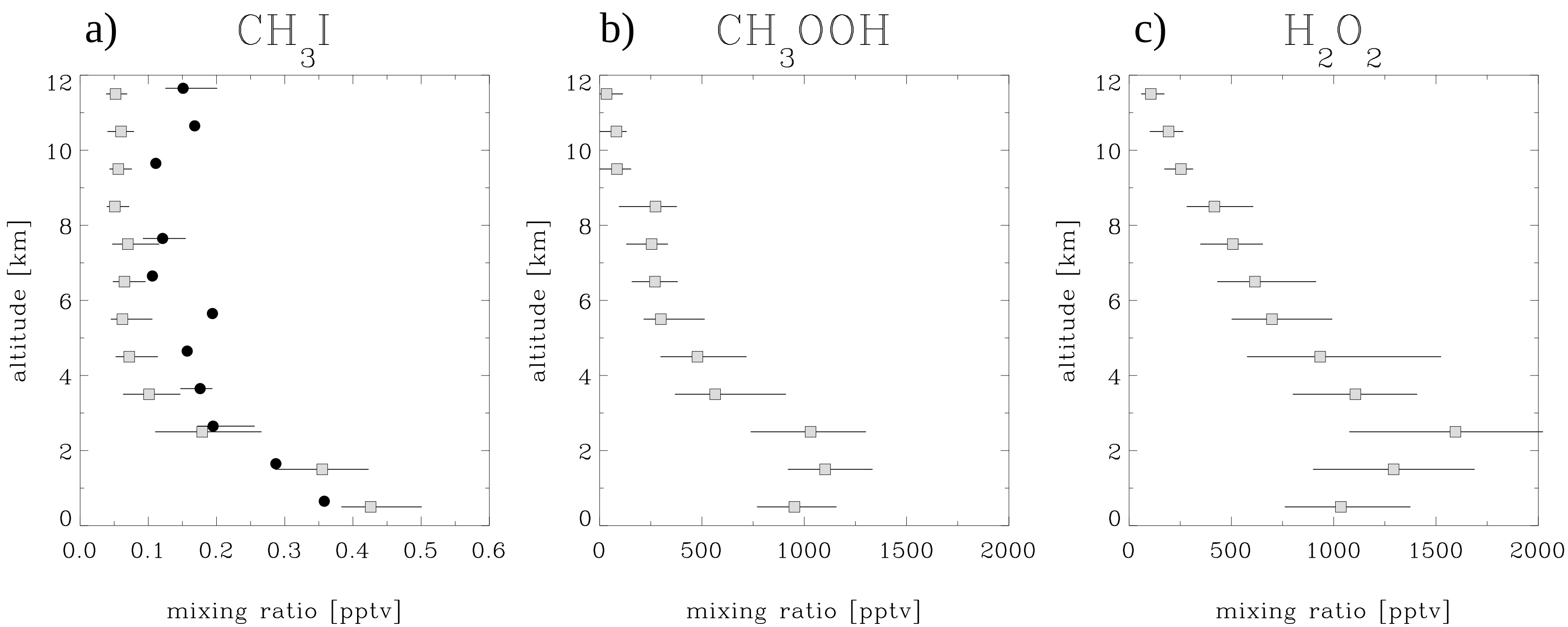
figure 3

Figure 4



a)
CH3I
b)
CH3OOH
c)
H2O2
mixing ratio [pptv]
0.50
0.40
0.30
0.20
0.10
0.00
2000
1600
1200
800
400
0
60° 50° 40° 30° 20° 10°S 0° 10°N
latitude

Figure 5



a)
CH3I
b)
CH3OOH
c)
H2O2
altitude [km]
mixing ratio [pptv]
0 2 4 6 8 10 12
0.0 0.1 0.2 0.3 0.4 0.5 0.6
0 500 1000 1500 2000

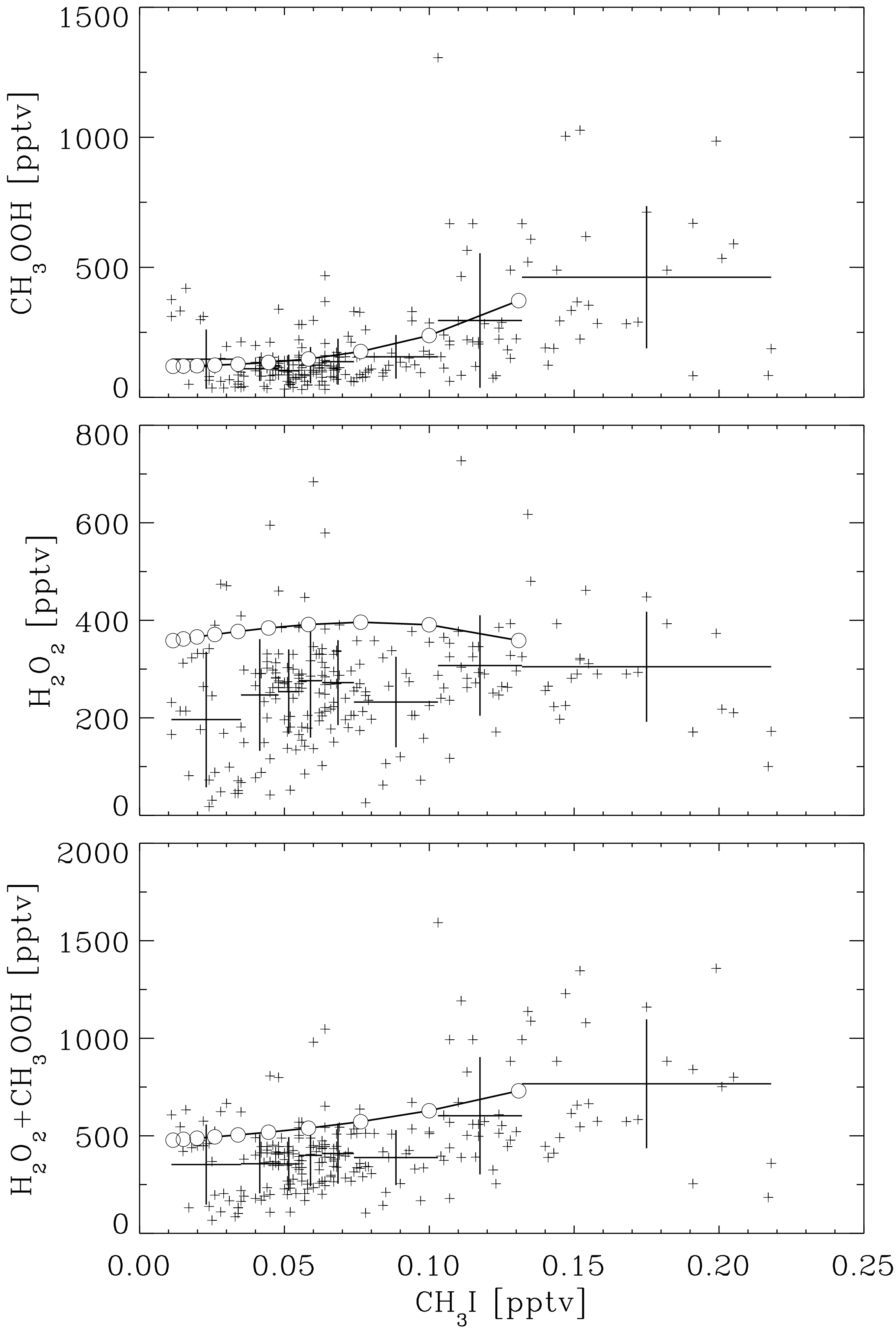

1500
1000
500
0
CH3OOH [pptv]
800
600
400
200
0
H2O2 [pptv]
2000
1500
1000
500
0
H2O2+CH3OOH [pptv]
0.00
0.05
0.10
0.15
0.20
0.25
CH3I [pptv]

figure 6