Hydrogen peroxide, methyl hydroperoxide, and formaldehyde over North America and the North Atlantic

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[1] Hydrogen peroxide (H2O2), methyl hydroperoxide (CH3OOH), and formaldehyde (CH2O) were measured over North America and the North Atlantic during the INTEX-NA, TOPSE, and SONEX aircraft campaigns. An overview of H2O2, CH3OOH, and CH2O across the geographic and temporal range of these campaigns is presented. H2O2, CH3OOH, and CH2O mixing ratios and variability were larger during INTEX-NA compared to TOPSE and SONEX. Mean H2O2, CH3OOH, and CH2O were 1390, 440, and 480 pptv, respectively, more than two times higher than TOPSE measurements and an order of magnitude higher than SONEX measurements. This is attributed to higher solar radiation levels and the more polluted conditions of INTEX-NA. Mixing ratios and variability decreased with altitude for all three gases and on all three campaigns, except for CH3OOH during TOPSE. The impact of convection on H2O2, CH3OOH, and CH2O is also discussed. Using the ratio H2O2/CH3OOH, convectively influenced air parcels were found to be enhanced in CH3OOH, CH2O, CO, NO, and NO2, while H2O2 and HNO3 were depleted by wet removal. Biomass burning was also shown to increase H2O2, CH3OOH, and CH2O mixing ratios up to 1.5, 2, and 1 ppbv, respectively, even after 4–5 days of transit. Results from this study show considerable variability in H2O2, CH3OOH, and CH2O throughout the North American and North Atlantic troposphere. The variability in the upper troposphere is driven by local photochemical production and transport via regional convection and long-range pathways, suggesting transport mechanisms are important factors to include in photochemical models simulating H2O2, CH3OOH, CH2O, and HOx.


1. Introduction

[2] The NASA Intercontinental Transport Experiment—North America (INTEX-NA) mission investigated the outflow of pollution from North America to the North Atlantic with a focus on understanding the transport and evolution of ozone (O3) and O3 precursors. INTEX-NA, the first phase of the NASA INTEX campaign, was conducted from June to August 2004 with twenty flights extending from California to the mid North Atlantic (Figure 1) [Singh et al., 2006]. A full suite of chemical species was investigated during this mission including HOx precursors, hydrogen peroxide (H2O2), methyl hydroperoxide (CH3OOH), and formaldehyde (CH2O). A critical analysis of the distribution of hydroxyl radical precursors, along with the hydroxyl radical (HO), the perhydroxyl radical (HO2), nitrogen oxides (NOx), and hydrocarbons (HCs), is necessary to understand O3 production over North America and the North Atlantic during the summer.

[3] H2O2, CH3OOH, and CH2O contribute about 30% of the gross odd-hydrogen production in the troposphere with the remainder of production coming from the photolysis of ozone in the presence of water vapor [Lee et al., 1997]. In regions where water vapor is limited, such as in the upper troposphere (UT), H2O2, CH3OOH, and CH2O become more important HOx reservoirs [Finlayson-Pitts and Pitts, 1986; Jaeglé et al., 2000, 1999; Tan et al., 2000]. CH3OOH has the potential to produce one HO and up to three HO2 molecules when photolyzed and the subsequent photolysis of CH2O is considered [Logan et al., 1981]. Hydrogen peroxide has a much smaller impact on UT HOx levels because of its high solubility and resulting removal by precipitation and in-cloud reactions with SO2 [O’Sullivan et al., 1999; Crawford et al., 2000]. However, low SO2
mixing ratios during INTEX-NA, indicate in-cloud reactions with SO$_2$ were not significant. As HO$_x$ sinks, their sequestration in H$_2$O and CH$_3$OOH followed by the loss of these compounds, results in the removal of three HO$_2$ radicals and an organic peroxy radical. This loss is a limit to net ozone production.

Typically H$_2$O$_2$, CH$_3$OOH, and CH$_2$O have lower mixing ratios at higher altitudes. Therefore determining how these gases become elevated in the UT is of great interest. One possible source of H$_2$O$_2$ and CH$_3$OOH to the UT is convective vertical transport [Prather and Jacob, 1997]. For example, strong convective uplift in thunderstorms, typhoons [Newell et al., 1996], and widespread convective activity in regions such as the South Pacific Convergence Zone (SPCZ) and Inter Tropical Convergence Zone (ITCZ) [Pickering et al., 1992; Cohan et al., 1999; Gregory et al., 1999] may be important mechanisms for transporting HO$_x$ precursors to the UT. UT enhancements of CH$_3$OOH in tropical and subtropical regions have been previously observed [Heikes et al., 1996a; Lee et al., 1995; Pickering et al., 1995; Newell et al., 1996; O’Sullivan et al., 1999] and these authors suggest convectively lifted boundary layer (BL) air, elevated in CH$_3$OOH, was the source of the observed enhancements. Although UT measurements of peroxydes and CH$_2$O are limited over continents, elevated CH$_3$OOH associated with tropical air [Snow et al., 2003] and elevated CH$_2$O associated with long-range transport of its precursors [Fried et al., 2003a; A. Fried et al., The role of convection in redistributing formaldehyde to the upper troposphere over North America and the North Atlantic during the summer 2004 INTEX campaign, unpublished manuscript, 2007, hereinafter referred to as Fried et al., unpublished manuscript, 2007] have been observed over North America.

Care must be exercised in the interpretation of elevated CH$_2$O at high altitudes. The lifetime of CH$_2$O with respect to photolysis and OH is at most a few hours under sunlit conditions. Elevated CH$_2$O near clouds may be from convective injection, but a more likely scenario is CH$_2$O is elevated because of the injection of reactive hydrocarbons therefore serving as a tracer of lofted boundary layer reactive hydrocarbons (J. Crawford, personal communication, 2006; Fried et al., unpublished manuscript, 2007).

Tropospheric photochemistry point models have been unable to exactly capture the vertical structure of HO$_x$, particularly in the UT where models both underestimate and overestimate HO$_x$ levels [Jaegle et al., 1997; Wang and Prinn, 2000; X. Ren et al., HOx observations and model comparison during INTEX-NA 2004, submitted to Journal of Geophysical Research, 2006, hereinafter referred to as Ren et al., submitted manuscript, 2006]. Model studies have shown that peroxydes impact HO$_x$ levels when they are introduced into the UT through transport [Lee et al., 1995; Jaegle et al., 1997; Prather and Jacob, 1997; Folkins et al., 1998; Cohan et al., 1999; Crawford et al., 2000]. The results in Crawford et al. [2000] showed elevated CH$_3$OOH
increased HO mixing ratios by 30–60% over a 50-hour period. Jaegle et al. [1997] predicted that the injection of CH$_3$OOH would cause large increases in UT HO$_x$ concentrations for more than a week downwind of the convective event. However, more recently, during INTEX-NA, point models under predicted HO$_2$ and HO by a factor of 3 above 8 km pointing to an unknown source of HO$_x$ (Ren et al., submitted manuscript, 2006). Studies have also shown CH$_2$O to be an important UT HO$_x$ source [McKeen et al., 1997]. In convective outflow over biomass burning regions, CH$_2$O is a significant source of HO$_x$ and may stimulate UT O$_3$ production [Lee et al., 1998]. Conclusions from model results indicate the injection of peroxides and CH$_2$O to the UT may be a source of not only local UT HO$_x$, but may also impact global HO$_x$ distributions [Jaegle et al., 1997].

It is important to note that these model studies [Lee et al., 1995; Jaegle et al., 1997; Prather and Jacob, 1997; Folkins et al., 1998; Cohan et al., 1999; Crawford et al., 2000] take place over tropical regions where peroxides and CH$_2$O are highly elevated in the BL and water vapor levels are relatively high. Over North America, HO$_x$ production is primarily dominated by reactions of O(D) and H$_2$O at low latitudes and by CH$_2$O at high latitudes [Weinstein-Lloyd et al., 1998; Cantrell et al., 2003; Snow et al., 2003]; H$_2$O$_2$ and CH$_2$OOH were shown to make only small contributions to the total UT HO$_x$ budget. However, previously recorded measurements of peroxides spanning the troposphere over North America are limited, making INTEX-NA an important addition to peroxide distributions in this region, particularly during the summer months when photochemical production of peroxides is at a maximum.

In this study we utilize in situ measurements from the INTEX-NA campaign and meteorological analyses to examine the hypothesis that convective transport is a source of HO$_x$ precursors, H$_2$O$_2$, CH$_3$OOH, and CH$_2$O to the UT over North America and the North Atlantic. A companion paper by Fried and colleagues (Fried et al., unpublished manuscript, 2007) further examines the role of CH$_2$O in this regard. In addition, this study compares the results of the INTEX-NA campaign to earlier aircraft campaigns, Tropospheric Ozone Production about the Spring Equinox (TOPSE) [Atlas et al., 2003; Cantrell et al., 2003; Snow et al., 2003] and Subsonic Assessment of Ozone and Nitrogen (SONEX) [Singh et al., 1999; Thompson et al., 2000], conducted over North America and the North Atlantic during different seasons (Figure 1).

2. Methods

2.1. H$_2$O$_2$ and CH$_3$OOH

Measurements of H$_2$O$_2$ and CH$_3$OOH were made using a technique described by Lee et al. [1995]. Ambient air was sampled through an inlet on the side of the NASA DC-8 and mixed with a collection solution in a continuous flow scrubbing coil. This technique scrubs peroxides from the ambient air into a collection solution (pH 6) based on the Henry’s Law equilibrium partitioning. The aqueous solution was then analyzed using high-performance liquid chromatography with C-18 columns. The separated peroxides were then reacted with peroxidase and p-hydroxyphenyl-acetic acid to produce a fluorescent hydroperoxide derivative that was quantified using fluorescence detection. The gas phase limits of detection (LOD) for H$_2$O$_2$ and CH$_3$OOH were 25 pptv and 20 pptv (2 sigma), respectively and the uncertainties were LOD ±30% of the ambient mixing ratios for 2 minute averaged samples. This technique has successfully been employed aboard the NASA DC-8, the NASA P3-B, and the NCAR C-130 research aircraft during previous airborne experiments [Heikes, 1992; Heikes et al., 1996a, 1996b; O’Sullivan et al., 1999, 2004; Snow et al., 2003]. H$_2$O$_2$ was also measured using a new CIMS technique [Crounse et al., 2006].

2.2. CH$_2$O

[10] CH$_2$O was measured using two separate techniques; the University of Rhode Island and United States Naval Academy (URI-USNA) group used a fluorometric method and the National Center for Atmospheric Research (NCAR) group used a tunable diode laser absorption spectroscopic (TDLAS) instrument (Fried et al., unpublished manuscript, 2007). A comparison of results from these two techniques is found in section 2.2.3.

2.2.1. CH$_2$O (URI-USNA)

[11] CH$_2$O was measured with an automated fluorometric method adapted from Lazorus et al. [1988]. Gas phase CH$_2$O is removed from the atmosphere by mixing ambient samples with a pH 2 collection solution in glass stripping coils. The CH$_2$O reacts with H$_2$O to form the adduct dihydroxymethane (CH$_3$OH$_2$) which in the presence of the catalyst formaldehyde dehydrogenase (FDH) reacts with nicotinamide adenine dinucleotide (NAD$^+$) to produce NADH. The fluorescence of NADH is proportional to the mixing ratio of CH$_2$O in the ambient sample. Prior to the mission, gas phase standards were added at the inlet under different pressures to calibrate the in-flight collection efficiency. Liquid standards were analyzed before each flight to calibrate the instrument. The CH$_2$O 2 sigma LOD was 50 pptv with an estimated uncertainty of 50 pptv ±30% of the ambient value for 1 minute averaged samples. The technique has been employed on previous aircraft and ground based experiments [Heikes, 1992; Lee et al., 1998; O’Sullivan et al., 2004].

2.2.2. CH$_2$O (NCAR)

[12] CH$_2$O was measured by the NCAR group using a tunable diode laser absorption spectroscopic (TDLAS) instrument. A detailed description of this instrument is found in Fried et al. [2003a, 2003b] and Wert et al. [2003]; therefore only a brief explanation will be given here. Sample air was pulled in through a heated PFA Teflon inlet (~35°C and 1.3 cm OD) at ~9 standard liters per minute. The air then passed through a multipass Herriott cell where it absorbed the infrared (IR) radiation (3.5 μm, 2831.6 cm$^{-1}$) from a tunable diode laser passing back and forth through the cell (total path length of 100 m). An IR detector was used to measure the amount of IR absorption by the ambient CH$_2$O. This technique, with minor modifications, has been previously used to measure CH$_2$O on a number of aircraft campaigns [e.g., Fried et al., 2003a, 2003b; Wert et al., 2003]. Averaged over the entire campaign, the 2 sigma LOD for 1-min measurements was 78 pptv. Starting with flight 14 on 31 July 2004 improvements in the mechanical stability of various optical components improved the LOD to 66 pptv. The systematic uncertainty at the 2 sigma level was estimated at 12% of
the ambient CH$_2$O mixing ratio, and the total uncertainty for
each measurement is determined from the quadrature addition
of the LOD with the systematic uncertainty (Fried et al.,
unpublished manuscript, 2007).

2.2.3. Comparison of CH$_2$O Measurements

Coincident CH$_2$O measurements by the URI-USNA
group and the NCAR group have occurred on several
aircraft missions providing a series of comparison data.
During INTEX-NA, URI-USNA CH$_2$O measurements were
approximately 70% of NCAR CH$_2$O, more in the UT, with
a weighted bivariate linear regression yielding an $r^2$ of 0.89
(Fried et al., unpublished manuscript, 2007). The agreement
between URI-USNA and NCAR also improved throughout
the INTEX-NA mission. This result is opposite of measure-
ments made during the NASA TRACE-P missions where
URI-USNA CH$_2$O was greater. However, at present we
have no explanation for the discrepancy and the apparent
change with mission or with time. For a more complete
explanation of the instrument comparison see Fried et al.
(unpublished manuscript, 2007).

3. Results and Discussion

H$_2$O$_2$, CH$_3$OOH, and CH$_2$O mixing ratios were
measured during three aircraft missions across North Amer-
ica and the North Atlantic covering a broad temporal range.
The flight tracks and dates of each mission are shown in
Figure 1. Singh et al. [2006], Atlas et al. [2003], and Singh
et al. [1999] and Thompson et al. [2000] provide overviews
of the INTEX-NA, TOPSE, and SONEX aircraft cam-
paigns, respectively.

3.1. Comparison of H$_2$O$_2$, CH$_3$OOH, and CH$_2$O

During INTEX-NA, TOPSE, and SONEX

The mean and median H$_2$O$_2$ measured during
INTEX-NA (1390 and 1070 pptv) were about ten times
larger than those observed during TOPSE and SONEX
(170, 150 and 120, 80 pptv) (Table 1). The higher
INTEX-NA mixing ratios are consistent with increased
photochemical production during the summer months com-
pared to production during the winter-spring sampling
period of TOPSE and the fall sampling period of SONEX.
In addition to the time of sampling, the relative locations of
each mission impacted the H$_2$O$_2$ mixing ratios. INTEX-NA
flew over continental regions and along the northeast coast
of the United States, often sampling in the BL, while
TOPSE sampled at higher latitudes and SONEX sampled
a larger portion of UT air. H$_2$O$_2$ mixing ratios are typically
lower at higher latitudes and higher altitudes and therefore
are expected to be lower during TOPSE and SONEX.
During INTEX-NA, H$_2$O$_2$ ranged from a minimum of
LOD (12.5 pptv) to a maximum of 13 ppbv. Previous

Table 1. Mean/Median and (Range) of H$_2$O$_2$, CH$_3$OOH, and CH$_2$O Mixing Ratios for Each Mission

<table>
<thead>
<tr>
<th></th>
<th>INTEX-NA</th>
<th>TOPSE</th>
<th>SONEX</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$_2$</td>
<td>1390/1070 (LOD-13180)</td>
<td>170/150 (LOD-1330)</td>
<td>120/80 (LOD-670)</td>
</tr>
<tr>
<td>CH$_3$OOH</td>
<td>440/350 (LOD-2150)</td>
<td>180/150 (LOD-1400)</td>
<td>50/30 (LOD-340)</td>
</tr>
<tr>
<td>CH$_2$O-URI-USNA</td>
<td>480/210 (LOD-4220)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$O-NCAR</td>
<td>790/360 (LOD-6780)</td>
<td>120/90 (LOD-1340)</td>
<td></td>
</tr>
</tbody>
</table>

*LOD indicates the value was below the limit of detection. Unit is parts per trillion by volume (pptv).*
higher than measurements made during the TOPSE and SONEX missions. During TOPSE and SONEX, maximum H$_2$O$_2$ measurements made above 6 km are less than the upper quartile of H$_2$O$_2$ measurements made during INTEX-NA. In the MT, H$_2$O$_2$ measurements reached 1 ppbv during TOPSE but never exceeded 500 pptv during SONEX. These results are not surprising given the different solar radiation levels during these campaigns and the influence of convection from the BL to the UT.

Regardless of the mission, H$_2$O$_2$ levels reach a maximum in the MT. A peak is typically found at ~2 km because of the combined impact of water vapor and solar radiation. This peak has been observed in the tropics [O’Sullivan et al., 1999], the North Pacific [Heikes et al., 1996a], and over continental regions including North America [Boatman et al., 1990; Daum et al., 1990; Heikes, 1992; Ray et al., 1992; Balasubramanian and Husain, 1997; Snow et al., 2003].

CH$_3$OOH mixing ratios during INTEX-NA were more variable than during TOPSE or SONEX. During all missions, the minimum CH$_3$OOH mixing ratio measured was LOD and the maximum mixing ratio measured during INTEX-NA, TOPSE, and SONEX were 2150, 1400, and 340 pptv respectively. The relatively small increase in CH$_3$OOH compared to H$_2$O$_2$ over the winter-spring to summer comparison can be explained by the existence of two seasonally dependent peroxide regimes. de Serves [1994] and Snow et al. [2003] showed an organically dominated peroxide regime, dominated primarily by CH$_3$OOH, during the winter-spring when lower sunlight, lower temperatures, and lower water vapor exist. H$_2$O$_2$ dominates during the summer when sunlight, temperatures, and water vapor increase. Therefore it is not surprising to find a different transition across this temporal range for CH$_3$OOH compared to H$_2$O$_2$ as is exhibited in the INTEX-NA-TOPSE comparison. Mixing ratios are much lower during SONEX because of the location of that mission; the majority of flights occurred in the UT [Singh et al., 1999; Thompson et al., 2000], where CH$_3$OOH is significantly lower when not perturbed by convection.

CH$_3$OOH mixing ratios showed a slight decrease with altitude during INTEX-NA (Figure 2b). Median mixing ratios in the BL were ~630 pptv and decreased to 600 pptv in the MT and to 200 pptv above 6 km. BL mixing ratios are lower than those observed by Weinstein-Lloyd et al. [1998] who found ~1–2 ppbv CH$_3$OOH between 0 and 3 km during the summer over urban and agricultural land in the Nashville region. The decrease with altitude is also unlike the TOPSE mission, where CH$_3$OOH mixing ratios above 6 km exceeded those in the MT and the UT median for INTEX-NA. Snow et al. [2003] attributed the elevated CH$_3$OOH mixing ratios to the transport of subtropical marine air containing high levels of CH$_3$OOH. Even with the transport of subtropical marine air during TOPSE, this result is somewhat surprising given the differences in solar radiation between these two missions. As with H$_2$O$_2$, the range of INTEX-NA BL and MT CH$_3$OOH measurements was larger than that observed in the UT; BL and MT
Figure 2b. CH$_3$OOH mixing ratios during INTEX-NA, TOPSE, and SONEX for three different altitude bins (<1 km, 1–6 km, and >6 km). Each box has lines at the lower quartile, median, and upper quartile values. The whiskers extend to 1.5 times the interquartile range. The notch in the box estimates the uncertainty about the median, and no overlap between the notches indicates a statistical difference between samples at the 95% confidence level.

Figure 2c. CH$_3$O mixing ratios during INTEX-NA, TOPSE, and SONEX for three different altitude bins (<1 km, 1–6 km, and >6 km). CH$_3$O measurements were made by URI-USNA and NCAR and the appropriate group is indicated along the y axis. Each box has lines at the lower quartile, median, and upper quartile values. The whiskers extend to 1.5 times the interquartile range. The notch in the box estimates the uncertainty about the median, and no overlap between the notches indicates a statistical difference between samples at the 95% confidence level.
CH$_3$OOH measurements ranged from the LOD to $\sim$2.5 ppbv while UT measurements were from the LOD to $\sim$1.5 ppbv. 

Measurements of CH$_3$OOH over marine regions compared to those over continental regions yielded a significant difference during INTEX-NA. Mean and median CH$_3$OOH over marine regions were $\sim$20% greater than measurements made over the North American continent in the BL and UT. This could be a result of continental outflow, however observations of enhanced H$_2$O$_2$ and CH$_3$O were not observed over marine regions. In fact, the opposite observation was made; H$_2$O$_2$ and CH$_3$O were elevated over the North American continent and decreased over marine regions (Fried et al., unpublished manuscript, 2007).

It is important to note that CH$_3$O was measured by two techniques. The two CH$_3$O techniques were used simultaneously only on INTEX-NA; CH$_3$O was measured by NCAR on TOPSE and by URI-USNA on SONEX. For ease of discussion, when referring to CH$_3$O measurements made during INTEX-NA, the authors will be referring to the URI-USNA measurements unless otherwise noted by the NCAR designation.

The comparison of CH$_3$O between field missions is similar to that of CH$_3$OOH with a larger range of mixing ratios observed during INTEX-NA; about a 4 ppbv range on INTEX-NA compared to $\sim$1 ppbv on TOPSE and $\sim$400 ppbv on SONEX. Nearly an order of magnitude difference was observed between the CH$_3$O mean and median during INTEX-NA (480 and 210 ppbv) compared to SONEX (70 and 30 ppbv). Mean and median CH$_3$O mixing ratios measured on INTEX-NA are higher by a factor of 3–4, but within an order of magnitude of those sampled on TOPSE (120 pptv and 90 pptv). During INTEX-NA, CH$_3$O decreased sharply above the BL dropping from a median of 1300 pptv to 600 pptv in the MT and 100 pptv in the UT (Figure 2c). These observations are about a factor of 3 higher than measurements made over the North Atlantic during the September NARE campaign [Fried et al., 2002]. This is also in contrast to TOPSE which had a slight peak in CH$_3$O mixing ratios in the MT. In all three campaigns, the lowest observed CH$_3$O levels were found in the UT. The variability in CH$_3$O also decreased with altitude during all three missions. INTEX-NA observed the largest variability in CH$_3$O mixing ratios ranging from LOD to 4200 ppbv in the BL, LOD to 3100 ppbv in the MT and LOD to 1800 ppbv in the UT. In contrast, SONEX observed the smallest variability with ranges from LOD to 500 ppbv in the MT and LOD to 700 ppbv in the UT. The range and magnitude of CH$_3$O observed on INTEX-NA is similar to measurements at surface sites over North America during the summer [Macdonald et al., 2001; Li et al., 2004] where variability and mixing ratios were controlled by regional meteorology and diurnal photochemical production. The effect of photochemical production is also clearly seen by the latitudinal distribution of CH$_3$O during INTEX-NA; CH$_3$O mixing ratios decreased by half from 30 to 50$^\circ$N.

### 3.2. Convective Influence in the Upper Troposphere

#### 3.2.1. Peroxide Influence ($H_2O_2/CH_3OOH$)

Convective events throughout the world have been identified by using the ratio of H$_2$O$_2$ to CH$_3$OOH [Heikes et al., 1996a; O’Sullivan et al., 1999; Snow et al., 2003]. Peroxides are generally higher in the BL than in the UT [Heikes et al., 1996a] making them excellent indicators of convective outflow. Furthermore, H$_2$O$_2$ is preferentially removed during convective events because of its high solubility in water, followed by precipitation or reaction with dissolved sulfur dioxide (SO$_2$). Cohan et al. [1999] estimated scavenging of H$_2$O$_2$ in deep convection was at least 60%. The removal of CH$_3$OOH during such events is negligible [Heikes et al., 1996a; Pickering et al., 1996; Cohan et al., 1999]. Therefore the H$_2$O$_2$/CH$_3$OOH ratio can be an excellent indicator of convection. O’Sullivan et al. [1999] observed ratios of $<1$ associated with the Inter Tropical Convergence Zone (ITCZ) and South Pacific Convergence Zone (SPCZ), between altitudes of 8 and 12 km, an indication CH$_3$OOH had been transported to the UT. Similar values were observed by Pickering et al. [1996] and were associated with tropical convection over Brazil. Snow et al. [2003] observed ratios of $<3$ associated with the transport of subtropical air to the central United States. The effectiveness of the H$_2$O$_2$/CH$_3$OOH ratio as a convective tracer is lost in $\sim$3 days because the lifetime of CH$_3$OOH is on the order of 1 to 2 days in the tropics, and slightly longer at higher latitudes [Cohan et al., 1999].
Figure 3
making the \( \text{H}_2\text{O}_2/\text{CH}_3\text{OOH} \) ratio uniquely suited for detecting recent convection.

[26] Table 2 shows the mean and median \( \text{H}_2\text{O}_2/\text{CH}_3\text{OOH} \) ratio in the BL, MT, and UT during INTEX-NA, TOPSE, and SONEX. The median peroxide ratio during TOPSE (0.7) was driven below 1 by the dominance of organic peroxides during the cold, dark winter periods [Snow et al., 2003]. The mean BL \( \text{H}_2\text{O}_2/\text{CH}_3\text{OOH} \) ratio poleward of 50° N in March was 0.7 indicating a strong dominance of \( \text{CH}_3\text{OOH} \). The ratio reached 1.2 by May but never exceeded 1.5 suggesting an increase in \( \text{H}_2\text{O}_2 \) due to increased solar radiation and a decrease in \( \text{CH}_3\text{OOH} \) due to a decrease in hydrocarbon mixing ratios at lower altitudes [Blake et al., 2003]. During INTEX-NA, the median BL \( \text{H}_2\text{O}_2/\text{CH}_3\text{OOH} \) ratio was 3.4. This indicates a peroxide regime dominated by \( \text{H}_2\text{O}_2 \). This also agrees well with de Serves [1994] who found a shift from an organic peroxide dominated to \( \text{H}_2\text{O}_2 \) dominated atmosphere when temperature and solar radiation increased.

[27] In the MT the median INTEX-NA \( \text{H}_2\text{O}_2/\text{CH}_3\text{OOH} \) ratio was 3.5, similar to the MT ratio observed during SONEX (3.4). An increase in the MT ratio was also observed during TOPSE although the ratio was still much lower, ~1. During TOPSE and SONEX, the median \( \text{H}_2\text{O}_2/\text{CH}_3\text{OOH} \) ratio decreased in the UT, suggesting some convective influence, but remained constant during INTEX-NA. The INTEX-NA UT ratio is surprisingly high given Bertram et al. [2006] estimated 30–56% of the atmosphere sampled during INTEX-NA had been cloud processed within the past two days, which is an indication of strong convective activity and would suggest removal of \( \text{H}_2\text{O}_2 \). However, it is possible that the UT \( \text{H}_2\text{O}_2/\text{CH}_3\text{OOH} \) ratio is being driven by local photochemistry. Crawford et al. [1999] suggest local photochemistry driven by high \( \text{H}_2\text{O} \) (666 ppmv) in tropical convective outflow, not convective transport itself, may be the most important factor in UT \( \text{H}_2\text{O}_2 \) variability. During INTEX-NA, however, the UT conditions were drier (median UT \( \text{H}_2\text{O} \) was 340 ppmv) and therefore would result in less photochemical production of \( \text{HO}_3 \), leading to lower \( \text{H}_2\text{O}_2 \). Another important factor is the low UT \( \text{SO}_2 \) observations (median UT \( \text{SO}_2 \) ~24 pptv), making heterogeneous removal of \( \text{H}_2\text{O}_2 \) by \( \text{SO}_2 \) small. In actuality, transport, local photochemical production, and heterogeneous reactions are most likely all factors controlling the \( \text{H}_2\text{O}_2/\text{CH}_3\text{OOH} \) ratio over North America.

### 3.2.2. Convective Enhancements During INTEX-NA

[28] Convective influence (CI) in the UT was defined as the \( \text{H}_2\text{O}_2/\text{CH}_3\text{OOH} \) ratio <1 and \( \text{O}_3 < 100 \) ppbv (to exclude stratospheric samples). The cut off point of 1 is consistent with other studies that have used the peroxide ratio to identify convection [Heikes et al., 1996a; O'Sullivan et al., 1999; Snow et al., 2003]. The distribution of the INTEX-NA \( \text{H}_2\text{O}_2/\text{CH}_3\text{OOH} \) ratio in the BL was used to determine the ratio for free unperturbed UT (FT) as the \( \text{H}_2\text{O}_2/\text{CH}_3\text{OOH} \) ratio >3 and \( \text{O}_3 < 100 \), ppbv above 6 km. Note that the definition of FT for this study means those samples not influenced by recent convection (within 3–4 days) or by the stratosphere. Using this definition of CI and FT, a comparison of soluble and less soluble species are presented in Figures 3a and 3b. The mean \( \text{H}_2\text{O}_2 \) and \( \text{HNO}_3 \)
levels in CI samples are lower than those samples identified as FT, the difference is statistically significant at the 95% confidence level. Soluble species such as H$_2$O$_2$ and HNO$_3$ are removed during the convective process through precipitation and cloud processing [Cohan et al., 1999; O'Sullivan et al., 1999] and the lower mixing ratio found in CI samples is expected. In contrast, less soluble species, such as CH$_3$OOH and CO, show a statistically higher mean in the CI samples than in the FT samples (Figure 3b) providing evidence of the UT enhancement of CH$_3$OOH via convective outflow. The difference between the mean of the two sample groups is significant at the 95% confidence level. With a lifetime of ~2 months [Warneck, 2000], CO is expected to be well mixed in the UT. However, given the peroxide ratio method detects fresh convection and most of the INTEX-NA storms occurred over the eastern United States where BL CO is highly elevated, it is not surprising to see a statistically higher median in CI samples compared to FT. Pooled URI-USNA and NCAR CH$_2$O observations were high in CI samples compared to FT samples. It is worth noting that the CH$_2$O increase between the CI and FT time periods is much larger in measurements acquired by the NCAR group. Lightning, an UT source of NO$_x$ [Luke et al., 1992], or anthropogenic emissions, a BL source of NO$_x$, are most likely responsible for the elevated levels of NO$_x$ observed in the CI samples.

Table 3 presents a comparison of CI air masses to FT air masses during aircraft campaigns over different regions. In general INTEX-NA measured relatively high O$_3$, CO, C$_2$Cl$_4$, and CH$_2$Cl$_2$ in CI samples compared to other studies. This is most likely due to the location of sampling; INTEX-NA sampled over continental regions where BL mixing ratios are higher than over marine regions. CH$_3$I and CHBr$_3$ were comparably lower during INTEX-NA, most likely due to the lack of marine influence on the convective outflow compared to the other aircraft missions, which took place over the Atlantic and Pacific Oceans.

3.3. Evidence of Convective Outflow: A Case Study of INTEX-NA Flights 7 and 18

Although convective influence was detected throughout the UT over North America and along the eastern coast during INTEX-NA, flights 7 and 18 present especially clear cases demonstrating the influence of convection on peroxides and CH$_2$O in the UT. Figure 4 shows the flight tracks of flights 7 and 18. Flight 7 occurred on 12 July and flew over the central United States and sampled fresh convective outflow along the southeastern leg of the flight over the southeastern United States. This region was dominated by a high-pressure system located over the northern Gulf of Mexico, just to the south of the flight track. The anticyclonic flow of this dominant system produced onshore southerly winds along the western Gulf coast and offshore northerly winds along the eastern Gulf coast. High-pressure conditions are typically associated with subsiding air and are not associated with significant convective activity. However, on 12 July, the winds were light, ranging from 5–20 knots at 3 km to ~20 knots at 10 km. The light UT winds, in particular, resulted in little movement of air previously lifted into the UT by convection up to 3 days earlier. Figure 5 shows the pathway of convected air parcels and potential convection cells on a GOES water vapor image taken 36 hours prior to sampling.
Figure 5. GOES water vapor image for 10 July at 0000 UTC, approximately 36 hours prior to the sampling of aged convective outflow on 12 July. The dark black line indicates the direction air masses moved between the GOES image and the time of the convective sampling. Possible convective cells that may have contributed to the aged outflow sampled during flight 7 are highlighted in the black box. The location where convective influenced air was sampled on flight 7 is shown as a white dot outlined in black.

Figure 6. Vertical profiles of H$_2$O$_2$, CH$_3$OOH, CH$_2$O, O$_3$, and CO for flight 7. Elevated CH$_3$OOH, CH$_2$O, O$_3$, and CO in the upper troposphere is indicative of convective lofting of boundary layer air. H$_2$O$_2$ is preferentially removed by precipitation because of its high solubility.
Using this meteorological analysis, the age of the convective outflow is determined to be \(~3\) days. The lifetime of \(\text{CH}_3\text{OOH}\) in the summer troposphere is \(~3\) days, within the age of this convected plume.

[31] Figure 6 shows an altitude profile collected as the aircraft approached the convective outflow. Both \(\text{H}_2\text{O}_2\) and \(\text{CH}_3\text{OOH}\) exhibited the typical decrease with altitude.

However, above \(8\) km, \(\text{H}_2\text{O}_2\) continued to decrease while \(\text{CH}_3\text{OOH}\) showed a slight enhancement of \(~200\) pptv. The \(\text{CH}_3\text{OOH}\) enhancement is a result of BL air, convectively lifted and transported to the UT while the same process subsequently removed \(\text{H}_2\text{O}_2\). \(\text{CH}_3\text{O}_2\) is enhanced above \(8\) km and reaches \(600\) pptv compared to \(50\) pptv observed between \(5\) and \(8\) km. Because the lifetime of \(\text{CH}_2\text{O}\) is

Figure 7. Flight track, where convective outflow was sampled, is overlaid onto a GOES water vapor image. (top) First half of the flight track and (bottom) second half. Both images show the aircraft flew very near a convective cell just upwind, to the south/southwest of the flight track.
Figure 8. Vertical profiles of \( \text{H}_2\text{O}_2 \), \( \text{CH}_3\text{OOH} \), \( \text{CH}_2\text{O} \), \( \text{O}_3 \), and \( \text{CO} \) for flight 18. Elevated \( \text{CH}_3\text{OOH} \), \( \text{CH}_2\text{O} \), \( \text{O}_3 \), and \( \text{CO} \) above 6 km suggests convective outflow of boundary layer air. \( \text{H}_2\text{O}_2 \) is preferentially removed by precipitation because of its high solubility.

Figure 9. Flight 9 flight track showing the location of the Alaskan fire plume with shaded dots.
several hours during sunlit conditions, these CH$_2$O enhancements are an indication of the photochemical production from reactive hydrocarbons and reflect the vertical transport of the hydrocarbons. Fried et al. (unpublished manuscript, 2007) provide a detailed discussion of the photochemical production of CH$_2$O within convective outflow. O$_3$, CO, and relative humidity (RH) also increase in the UT; O$_3$ averages $\sim$70 ppbv above 8 km but CO, which peaks at 115 ppbv, begins to decrease around 8.5 km. RH increased to $\geq$80% above 8 km providing further evidence that convective outflow was sampled. This event contrasts enhanced UT CH$_3$OOH cases during TOPSE which were a result of the transport of subtropical marine air that was relatively clean with low CO (100 ppbv) and O$_3$ (25 ppbv) and suggests convection over North America plays an important role in increasing UT CH$_2$O precursors, O$_3$, and possibly CO.

[32] Flight 18 made two distinct legs, one south across the western N. Atlantic and the other across the coastal waters of the eastern United States toward the central United States (Figure 4). Convective outflow was sampled at the beginning of the flight, as the aircraft headed north over New Brunswick. The dominant meteorological features were an occluded and a cold front extending south of a well-developed low-pressure system just north of the Great Lakes. East of the cold front, relatively warm air (surface temperatures were $\sim$70 F) moved to the north along the eastern seaboard while west of the cold front, relatively cold air (surface temperatures were $\sim$60 F) shifted from northwesterly to southwesterly flow following the cyclonic motion of the low pressure. Cold fronts are typically associated with convective activity and on 11 August, convective activity was scattered across the eastern seaboard ahead of the cold front. Figure 7 shows the flight track over a GOES water vapor image taken at the time of sampling. Convective storm cells, just upwind of the CI sampled air, are visible on these images. The convective outflow sampled during this flight was $\sim$4 hours old and was characterized by $\sim$100% RH and 100% cloudiness, indicating we flew through active convection.

Figure 10. Air mass back trajectories showing strong westerly flow originating over Alaska 5 days prior to flight 9.
The convectively lofted air mass sampled on flight 18 is shown above 6 km in Figure 8. At 6 km, \( \text{H}_2\text{O}_2 \) dropped from \( \sim 1000 \) pptv to \( \sim 500 \) pptv while \( \text{CH}_3\text{OOH} \) increased from \( \sim 500 \) pptv to \( \sim 1000 \) pptv shifting the \( \text{H}_2\text{O}_2/\text{CH}_3\text{OOH} \) ratio from 2 to 0.5. This is a strong indication that the sampled air was influenced by fresh convection. The use of the \( \text{H}_2\text{O}_2/\text{CH}_3\text{OOH} \) ratio to identify the convective outflow on flight 18 agrees well with Bertram et al. [2006]. These authors use an increase in the \( \text{NO}_x/\text{HNO}_3 \) ratio away from steady state as a tool for identifying fresh convection. Bertram et al. [2006] further note that increases in \( \text{SO}_2 \) (up to 700 pptv) are indicative of recent convective lofting of BL air and point to another possible removal mechanism for \( \text{H}_2\text{O}_2 \) during this event. Elevated short-lifetime species such as ethene (\( \sim 1.4 \) days) [Warneck, 2000] also support the conclusion that recent convective outflow was sampled along this portion of flight 18. In the outflow, \( \text{CH}_2\text{O} \) levels increased to 750 pptv, values similar to samples collected at 3 km. Since this outflow was older than \( \sim 2 \) hours, these enhancements most likely reflect the vertical transport of reactive hydrocarbons followed by the photochemical production of \( \text{CH}_2\text{O} \). \( \text{O}_3 \) also showed a slight enhancement of \( \sim 25 \) ppbv while CO showed a marked step increase at 6 km from 100 ppbv to 140 ppbv. Like flight 7, flight 18 shows clear evidence of UT enhancements of \( \text{CH}_3\text{OOH}, \text{CH}_2\text{O}, \text{O}_3 \), and CO associated with convective outflow.

3.4. Evidence of Biomass Burning: A Case Study of INTEX-NA Flight 9

Flight 9 left Bangor, ME crossing over New Brunswick and the western North Atlantic (Figure 9). A biomass burning plume was sampled during the northern most leg of this flight. Meteorological conditions during and prior to flight 9 (18 July) consisted of strong westerly flow north of the U.S.-Canada border. Figure 10 shows air mass back trajectories for the biomass-burning plume sampled on 18 July. The trajectories indicated consistent westerly flow up to 5 days prior to sampling and suggest the sampled air mass originated over Alaska between 4 and 5 days prior to 18 July.

An altitude profile of \( \text{H}_2\text{O}_2, \text{CH}_3\text{OOH}, \text{CH}_2\text{O}, \text{O}_3, \) and CO is shown in Figure 11. At 7 km, the aircraft clearly went through a thin layer of highly polluted air that was mixed up to 9 km. \( \text{H}_2\text{O}_2 \) and \( \text{CH}_3\text{OOH} \) increased by 1.4 ppbv, reaching 2 and 1.5 ppbv respectively, and remained elevated until 9 km. \( \text{CH}_2\text{O} \) (NCAR) reached 1 ppbv while CO reached 600 ppbv. \( \text{O}_3 \) mixing ratios peaked only slightly at 7 km and decreased just above the pollution layer. In addition, \( \text{CO}_2, \text{CH}_4, \) and NO, all typical fire emissions [Yokelson et al., 1996, 1997, 1999] were elevated in this plume. These results agree well with observations of other biomass burning plumes around the world [Lee et al., 1997, 1998; Yokelson et al., 1999]. Lee et al. [1998] found enhanced \( \text{H}_2\text{O}_2 \), organic hydroperoxides, and \( \text{CH}_2\text{O} \) within biomass burning plumes over the South Atlantic, Brazil, and southern Africa. Direct production within the fires and post photochemical production in the atmosphere produced \( \text{H}_2\text{O}_2 \) and \( \text{CH}_3\text{OOH} \) mixing ratios of up to 14 and 5 ppbv respectively. Unlike the biomass burning plume sampled on INTEX-NA, these samples were collected within the fires, not 4–5 days downwind of the fire, explaining the elevated observations.

\[ \text{H}_2\text{O}_2, \text{CH}_3\text{OOH}, \text{CH}_2\text{O} \text{ increased with CO similar to fire samples measured by Lee et al. [1997]. The} \]
4. Conclusions

[37] A comparison of H$_2$O$_2$, CH$_3$OOH, and CH$_3$O over North America and the North Atlantic during the INTEX-NA, TOPSE, and SONEX aircraft campaigns showed highly variable mixing ratios. Peroxides and CH$_3$O mixing ratios and variability were larger during INTEX-NA compared to TOPSE and SONEX. Mean H$_2$O$_2$, CH$_3$OOH, and CH$_3$O were 1390, 440, and 480 pptv respectively, more than two times higher than TOPSE measurements and an order of magnitude higher than SONEX measurements. This is attributed to higher solar radiation levels and the more polluted conditions of INTEX-NA. H$_2$O$_2$, CH$_3$OOH, and CH$_3$O mixing ratios and variability decreased with altitude for all three gases and on all three campaigns, except for CH$_3$OOH during TOPSE. In addition, the impact of convection on H$_2$O$_2$, CH$_3$OOH, and CH$_3$O mixing ratios was investigated. Using the H$_2$O$_2$/CH$_3$OOH ratio, convectively influenced air parcels were found to be enhanced in CH$_3$OOH, CH$_3$O, CO, NO, and NO$_2$ while H$_2$O$_2$ and HNO$_3$ were depleted by wet removal. Given that the lifetime of CH$_3$O during the summer is ~2 hours, the enhanced UT CH$_3$O in convective case studies represents the transport of and photochemical production by reactive hydrocarbons. In addition to convection, biomass burning was shown to enhance upper tropospheric peroxides and CH$_3$O up to 1.5, 2, and 1 pptv, respectively. Results from this study suggest the variability of the H$_2$O$_2$, CH$_3$OOH, and CH$_3$O in the UT is driven by the transport of convectively lofted air masses and nonregional sources in addition to local photochemistry. This implies transport mechanisms are important factors to include in photochemical models simulating upper troposphere H$_2$O$_2$, CH$_3$OOH, and CH$_3$O.

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