

Dear Dr. Richter,

Thank you for assuming the role of editor for our manuscript and for your comments, which are highlighted in blue below with our responses and changes.

We hope that with this revisions that the manuscript will be suitable for publication in Atmospheric Measurement Techniques. Please feel free to contact me if you have any additional questions.

Very truly yours,

Philip S. Stevens
James H. Rudy Professor
Indiana University

Even after your revisions, I'm confused by the discussion of NO flow rates. While you explain in the replies to the reviewers, that the nominal flow rate during MCMA was the same as used in your tests, the last paragraph on page 20 as well as the last sentence on page 21 appear to state something different. Can you please clarify?

Thank you for pointing out the inconsistencies in this section of the manuscript. We have revised the paragraph on page 20 (page 13 in the revised manuscript) as follows for clarification:

“Because the HO₂-to-OH conversion efficiency of 80% in these experiments was approximately 20% lower than the conversion efficiency measured during the campaign (Dusanter et al., 2008; Dusanter et al., 2009a), the relative peroxy radical contributions illustrated in this figure are likely lower limits to the actual contribution during the campaign.”

We have also revised the last sentence on page 21 (page 14 of the revised manuscript) as follows:

“As discussed above, the modeled HO₂* is likely a lower limit given that the RO₂-to-HO₂ conversion efficiencies during the campaign may be greater than shown in Table 2 due to the higher HO₂-to-OH conversion efficiency measured during the campaign.”

Why is NO concentration given in table 1? In all other places you discuss NO flow so I'm wondering if you did this intentionally to provide additional information. I assume that these values are just computed from the measured NO flow?

We included the concentration of NO in this table to provide additional information that could be compared to the NO concentrations reported previously by Fuchs et al. (2011) and Whalley et al. (2012). We have clarified in the table that these concentrations are computed from the measured 1scm NO flow.

I'm not convinced that there is a difference in error propagation between adding modelled interferences to modelled HO₂ or subtracting modelled interferences from measured HO₂ as stated on page 21. I would expect that there is actually no difference either way. Please comment.*

Subtracting the modeled RO₂ interference from the measured HO₂* to obtain a measured HO₂ concentration would increase the uncertainty associated with the resulting measured HO₂ concentration compared

to the HO₂* measurement uncertainty. We have clarified this on page 14 in the revised manuscript as follows:

“While it is possible to subtract the modeled speciated RO₂ concentrations from the measured HO₂* and compare the results to the modeled HO₂, this method increases the uncertainty associated with the measured concentrations due to the additional uncertainty associated with the modeled RO₂ concentrations as well as the uncertainties associated with the measured RO₂-to-HO₂ conversion efficiencies.”

page 16, line 12: Thus is possible => Thus it is possible

This has been corrected on page 9 of the revised manuscript.

page 18, line 19: duplicate "possible"

This has been corrected on page 11 of the revised manuscript.

page 21, line 22: We estimate that ... to be => We estimate ... to be

This has been corrected on page 14 line 20 of the revised manuscript.

Measurement of interferences associated with the detection of the hydroperoxy radical in the atmosphere using laser-induced fluorescence

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1 **Abstract.** One technique used to measure concentrations of the hydroperoxy radical (HO_2) in the atmosphere
2 involves chemically converting it to OH by addition of NO and subsequent detection of OH. However, some
3 organic peroxy radicals (RO_2) can also be rapidly converted to HO_2 (and subsequently OH) in the presence of
4 NO, interfering with measurements of ambient HO_2 radical concentrations. This interference must be
5 characterized for each instrument to determine to what extent various RO_2 radicals interfere with measurements
6 of HO_2 and to assess the impact of this interference on past measurements. The efficiency of RO_2 to HO_2
7 conversion for the Indiana University Laser-Induced Fluorescence – Fluorescence Assay by Gas Expansion (IU-
8 FAGE) instrument was measured for a variety of RO_2 radicals. Known quantities of OH and HO_2 radicals were
9 produced from the photolysis of water vapor at 184.9 nm, and RO_2 radicals were produced by the reaction of
10 several volatile organic compounds with OH. The conversion efficiency of RO_2 radicals to HO_2 was measured
11 when NO was added to the sampling cell for conditions employed during several previous field campaigns. For
12 these conditions, approximately 80% of alkene derived RO_2 radicals and 20% of alkane derived RO_2 radicals were
13 converted to HO_2 . Based on these measurements, interferences from various RO_2 radicals contributed to
14 approximately 35% of the measured HO_2 signal during the Mexico City Metropolitan Area (MCMA) 2006
15 campaign, where the measured VOCs consisted of a mixture of saturated and unsaturated species. However, this
16 interference can contribute more significantly to the measured HO_2 signal in forested environments dominated by
17 unsaturated biogenic emissions such as isoprene.

1 **1 Introduction**

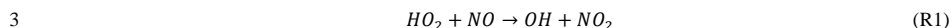
2 The hydroxyl radical (OH) is one of the primary oxidants in the atmosphere (Levy, 1972). The reaction of OH
3 radicals with volatile organic compounds (VOCs) leads to the production of peroxy radicals, both the hydroperoxy
4 radical (HO₂) and organic peroxy radicals (RO₂), which in the presence of nitrogen oxides (NO_x = NO + NO₂)
5 can lead to the production of ozone and secondary organic aerosols in the atmosphere. As a consequence, the
6 development of effective control strategies for the formation of these pollutants requires an accurate understanding
7 of the OH, HO₂, and RO₂ radical chemistry in the atmosphere. Measurements of OH and HO₂ (together HO_x) can
8 provide a robust test of our understanding of this complex oxidation chemistry.

9 Multiple field campaigns have been conducted over the years measuring OH and HO₂ radicals in both
10 urban and forested environments. While much attention has been focused on discrepancies between measured and
11 modeled OH concentrations (Rohrer et al., 2014), the agreement between measured and modeled HO₂
12 concentrations has been highly variable. In urban environments, measured HO₂ concentrations were sometimes
13 found to agree with model predictions (Shirley et al., 2006; Emmerson et al., 2007; Dusanter et al., 2009b;
14 Michoud et al., 2012; Lu et al., 2013; Ren et al., 2013; Griffith et al., 2016), while other times the measurements
15 were found to be both lower (George et al., 1999; Konrad et al., 2003) and higher than model predictions (Martinez
16 et al., 2003; Ren et al., 2003; Emmerson et al., 2005; Kanaya et al., 2007a; Chen et al., 2010; Sheehy et al., 2010;
17 Czader et al., 2013; Griffith et al., 2016). In forested environments, measured HO₂ concentrations were sometimes
18 found to agree with model predictions (Tan et al., 2001; Ren et al., 2005; 2006), but were often found to be either
19 lower (Carslaw et al., 2001; Kanaya et al., 2007b; Whalley et al., 2011; Kanaya et al., 2012; Mao et al., 2012;
20 Griffith et al., 2013), or higher than model predictions (Carslaw et al., 2001; Kubistin et al., 2010; Kim et al.,
21 2013; Hens et al., 2014).

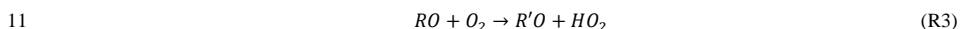
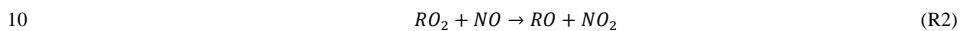
22 These results question our understanding of HO_x radical chemistry and the ability of models to simulate
23 future changes in the chemical composition of the atmosphere. However, a recent intercomparison of several
24 instruments measuring HO₂ found that the agreement between the different instruments was variable, although
25 the measurements were highly correlated (Fuchs et al., 2010). While the differences were within the combined
26 uncertainties of the measurements, there were several measurement periods when the differences could not be
27 explained by instrumental uncertainties. These results suggested the possibility of potential interferences in the
28 HO₂ measurement technique.

29 Laser-induced fluorescence using the Fluorescence Assay by Gas Expansion technique (LIF-FAGE) is a
30 common method for measuring HO₂ radicals in the atmosphere. In this technique HO₂ radicals are measured

1 indirectly after sampling ambient air at low pressure through chemical conversion to OH by addition of NO as
2 shown in reaction R1 and subsequent detection of OH by LIF:



4 It was previously believed that the detection of HO₂ radicals using the LIF-FAGE technique was free from
5 interferences from the reaction of RO₂ radicals with NO, as model simulations and measurements suggested that
6 the rate of conversion of RO₂ radicals to HO₂ by reactions R2 and R3 and subsequent conversion to OH through
7 reaction R1 was negligible due to the slow rate of reaction R3 under the reduced oxygen concentration in the low
8 pressure LIF-FAGE cell and the short reaction time between injection of NO and detection of OH (Heard and
9 Pilling, 2003).



12 For example, RO₂ radicals produced from the OH-initiated oxidation of small alkanes were found to produce a
13 negligible yield of HO₂ (Stevens et al., 1994; Kanaya et al., 2001; Tan et al., 2001; Creasey et al., 2002; Holland
14 et al., 2003).

15 However, recent laboratory studies have shown that there are interferences associated with measurements
16 of HO₂ using this technique from the conversion of RO₂ radicals derived from the OH-initiated oxidation of
17 alkenes and aromatics to HO₂ (and subsequently OH) by reaction with NO. Measured RO₂ to HO₂ conversion
18 efficiencies of 95% for the peroxy radicals derived from the OH-initiated oxidation of propene and 86% for the
19 peroxy radicals derived from the OH-initiated oxidation of benzene have been reported (Fuchs et al., 2011). The
20 high conversion efficiency of alkene-based peroxy radicals to HO₂ is due to the ability of the β-hydroxyalkoxy
21 radicals produced from reaction R2 to rapidly decompose forming a hydroxyalkyl radical which then reacts rapidly
22 with O₂ leading to the production of a carbonyl compound and HO₂ (Fuchs et al., 2011; Whalley et al., 2013). The
23 conversion efficiency depends on the instrumental characteristics and the configurations employed (Fuchs et al.,
24 2011; Whalley et al., 2013). As a result, this interference must be characterized for all LIF-FAGE instruments for
25 the accurate analysis of ambient HO₂.

26 This paper will describe the characterization of the RO₂ interferences associated with the Indiana
27 University LIF-FAGE instrument under several past campaign configurations. These include the Mexico City
28 Metropolitan Area (MCMA) campaign in 2006 (Dusanter et al., 2009a; 2009b), the Community Atmosphere-
29 Biosphere Interactions EXperiment (CABINEX) in 2009 (Griffith et al., 2013), and the California Research at
30 the Nexus of Air Quality and Climate Change campaign in Los Angeles (CalNex-LA) in 2010 (Griffith et al.,

1 2016). The impact of this interference on the previously published results from the MCMA-2006 campaign and a
2 reanalysis of these HO₂ measurements will be discussed.

3 **2 Experimental Section**

4 **2.1 Instrument description**

5 The Indiana University LIF-FAGE instrument (IU-FAGE) has been described in detail previously (Dusanter et
6 al., 2008; 2009a; Griffith et al., 2013; 2016). In the LIF-FAGE technique, OH radicals are detected by laser-
7 induced fluorescence after expansion of ambient air to low pressure. This enhances the OH fluorescence lifetime,
8 allowing temporal filtering of the fluorescence from laser scatter (Heard and Pilling, 2003). A diagram of the IU-
9 FAGE detection cell is illustrated in Fig. 1. Ambient air is expanded through an orifice between 0.635 mm and
10 1.016 mm diameter located at the top of a cylindrical nozzle (5 cm in diameter and 20 cm long). The size of the
11 orifice was kept unchanged during each campaign but was varied between the different campaigns reported here.
12 Two scroll pumps (Edwards XDS 35i) connected in parallel maintain a pressure inside the cell between 4 and 7.5
13 Torr depending on the sampling size of the orifice and the pumping speed, resulting in a flow rate between 3 and
14 10 SLPM through the sampling nozzle.

15 The original IU-FAGE laser system used in this study and in the MCMA-2006 campaign consisted of a
16 Spectra Physics Navigator II YHP40-532Q diode-pumped Nd:YAG laser that produced approximately 5.5W of
17 radiation at 532 nm at a repetition rate of 5 kHz. This laser pumped a Lambda Physik Scanmate 1 dye laser
18 (Rhodamine 640, 0.25 g L⁻¹ in isopropanol) that produced tunable radiation around 616 nm, which was frequency
19 doubled to generate 2 to 20 mW of radiation at 308 nm (~20 ns pulse width). This laser system was recently
20 replaced with a Spectra Physics Navigator II YHP40-532Q that produces approximately 8 W of radiation at 532
21 nm at a repetition rate of 10 kHz that pumps a Sirah Credo Dye laser (255 mg/L of Rhodamine 610 and 80 mg/L
22 of Rhodamine 101 in ethanol), resulting in 40 to 100 mW of radiation at 308 nm. Measurements of the conversion
23 efficiencies were similar for the two laser systems. After exiting the dye laser, the beam was focused onto the
24 entrance of a 12 m optical fiber to transmit the radiation to the sampling cell. In the detection cell, the laser crosses
25 the expanded air perpendicular to the flow in a White cell configuration with approximately 24 passes.

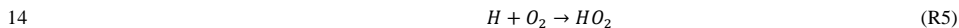
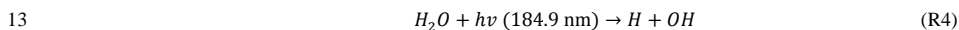
26 OH radicals are excited using the $A^2\Sigma^+ \nu'=0 \leftarrow X^2\Pi \nu''=0$ transition near 308 nm (Stevens et al., 1994).
27 The net signal is measured by turning the wavelength on- and off-resonance in successive modulation cycles. A
28 reference cell where OH is produced by thermal dissociation of water vapor is used to ensure that the laser is tuned
29 on and off the OH transition. The OH fluorescence is detected using a microchannel plate photomultiplier tube

1 (MCP-PMT) detector (Hamamatsu R5946U-50), a preamplifier (Stanford Research System SR445) and a gated
2 photon counter (Stanford Research Systems SR 400). The MCP-PMT is switched off during the laser pulse
3 through the use of electronic gating allowing the OH fluorescence to be temporally filtered from laser scattered
4 light.

5 A Teflon injector located approximately 2.5 cm below the inlet and 17.5 cm above the detection axis
6 (Fig. 1) allowed for the addition of NO (Matheson, 99.8%) to convert ambient HO₂ to OH through reaction R1.
7 The fraction of HO₂ (C_{HO₂}) converted into OH was measured during calibration experiments (Dusanter et al.,
8 2008). The NO flow (approximately 1-3×10¹³ cm⁻³) maximized the conversion of HO₂ into OH while minimizing
9 the removal of OH by the OH + NO reaction.

10 2.2 Instrument Calibration for OH and HO₂

11 The IU-FAGE instrument is calibrated by producing known quantities of OH and HO₂ radicals from the photolysis
12 of water vapor in air (reactions R4 and R5) (Dusanter et al., 2008):

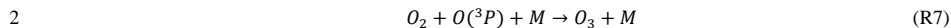
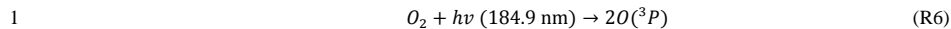


15 The calibration source consists of an aluminum flow reactor (1.27×1.27×30 cm) equipped with quartz windows
16 on two sides (Fig. 2). The light source consists of a low-pressure mercury lamp (UVP Inc.) housed in an aluminum
17 cartridge that is continuously purged with dry nitrogen to prevent light absorption by gases in addition to helping
18 to stabilize the lamp temperature. The radiation from the lamp passes through a bandpass filter centered at 185
19 nm (Acton Research) prior to entering the reactor and is detected by a photodiode. The lamp housing can be
20 adjusted along the length of the calibrator to measure the loss of radicals between the source region and the exit
21 of the calibrator.

22 The concentration of OH and HO₂ radicals produced by the calibration source can be determined from
23 the following equation:

$$24 \quad [OH] = [HO_2] = [H_2O] \cdot \sigma_{H_2O} \cdot \phi_{OH+H} \cdot F \cdot t \quad (1)$$

25 In this equation ϕ_{OH+H} is the quantum yield of OH from water photolysis, and σ_{H_2O} is the absorption cross section
26 of water (7.14×10^{-20} cm² molecule⁻¹ (Cantrell et al., 1997; Hofzumahaus et al., 1997; Creasey et al., 2000)). The
27 product of the photon flux (F) and the photolysis time (t) can be determined from oxygen actinometry, as the
28 photolysis of oxygen at 185 nm leads to the production of ozone (reactions R6 and R7) (Okabe, 1978):



3 The concentration of HO_x radicals can thus be calculated from measured concentrations of water and ozone using
4 Eq. (2) (Heard and Pilling, 2003; Holland et al., 2003):

5
$$[OH] = [HO_2] = [H_2O] \cdot \sigma_{H_2O} \cdot \varphi_{OH+H} \cdot \frac{[O_3]}{\varphi_{O_3} \cdot \sigma_{O_2} \cdot [O_2]}$$
 (2)

6 Here φ_{O_3} is the quantum yield of O₃ from oxygen photolysis and σ_{O_2} is the absorption cross sections of O₂,
7 which must be experimentally determined for each penlamp due to the overlap of the highly structured absorption
8 spectrum of O₂ and the lineshape of the emission at 184.9 nm. The lineshape depends on the operating conditions
9 of the lamp as a result of line reversal and potential fluorescence of the fused silica envelope (Cantrell et al., 1997;
10 Hofzumahaus et al., 1997; Lanzendorf et al., 1997).

11 2.3 Measurement of the RO₂ conversion efficiency to HO₂

12 Various alkenes (isoprene, methyl vinyl ketone, methacrolein, methyl ethyl ketone, ethene, trans-2-butene,
13 tetramethylethylene), alkanes (propane, butane, octane), and aromatic compounds (toluene) were used to measure
14 the conversion efficiency of RO₂ radicals to HO₂. These VOCs were added to the main calibrator flow, either by
15 direct addition of a gas mixture or by bubbling air through the liquid compound (Tables S1 and S2), approximately
16 190 ms prior to the radical source to ensure that the added VOC was well mixed into the humid air flow before
17 photolysis within the calibration source. The concentration of each VOC added to the calibrator was increased to
18 react and remove the majority of the OH produced in the calibrator, resulting in RO₂ concentrations that were
19 approximately equal to the concentration of OH reacted away. These RO₂ radicals are then sampled into the IU-
20 FAGE instrument. Addition of NO inside the detection axis converts a fraction of the RO₂ radicals to HO₂ through
21 reactions R2 and R3. Since RO₂ is produced together with HO₂ in the calibrator, there is a subsequent conversion
22 of both RO₂ and HO₂ into OH in the IU-FAGE cell, which is then detected by LIF.

23 Figure 3 illustrates two typical experiments designed to measure the conversion efficiency of RO₂
24 radicals to HO₂ in the IU-FAGE instrument. The total HO_x signal is defined as the sum of the total OH (S_{OH}) and
25 HO₂ (S_{HO2}) produced by the mercury penlamp in the absence of the added VOC (Eq. (3)):

26
$$S_{HO_x} = S_{HO_2} + S_{OH}$$
 (3)

1 The OH concentration produced by the penlamp is measured at the beginning, middle, and at the end of each
 2 experiment to ensure that the concentrations remained stable (experimental mode 1 in Fig. 3). Once the OH signal
 3 (S_{OH}) stabilizes, NO is added internally to the detection cell to convert HO_2 into OH and measure the total HO_x
 4 signal (S_{HO_x}) (mode 2 in Fig. 3). The conversion efficiency of HO_2 to OH is defined by Eq. (4):

$$5 \quad C_{HO_2 \rightarrow OH} = \frac{S_{HO_x} - S_{OH}}{S_{OH_0}} = \frac{S_{HO_2}}{S_{OH_0}} \quad (4)$$

6 S_{OH_0} is the OH signal after accounting for the loss of OH on the walls of the calibrator (approximately 20%). The
 7 wall loss for HO_2 is negligible in the calibrator (Dusanter et al., 2008).

8 Next, internal NO addition is stopped and the OH signal is measured again to ensure the stability of
 9 radical production during the experiment. The VOC is then added to the calibration system resulting in a decrease
 10 in the observed OH signal (mode 3 in Fig. 3). The remaining OH signal in the presence of the VOC is denoted as
 11 S_{OH+VOC} . For alkenes such as isoprene, the fast reaction with OH results in an almost total removal of OH radicals
 12 from the calibration source and S_{OH+VOC} is close to zero. However, for less reactive alkanes such as butane, the
 13 added VOC concentration was often not sufficient to completely remove OH radicals due to the short reaction
 14 time in the calibrator, resulting in a non-zero S_{OH+VOC} signal. The conversion efficiency in which OH radicals are
 15 converted to RO_2 radicals ($C_{OH \rightarrow RO_2}$) is defined by Eq. (5), derived from integrating the expressions for the rate of
 16 OH loss and the rate of RO_2 production from the OH + VOC reaction:

$$17 \quad C_{OH \rightarrow RO_2} = \frac{[RO_2]}{[OH]_0} = \frac{F_{OH} - k_w t}{F_{OH}} (1 - e^{-F_{OH}}) \quad F_{OH} = \ln \left(\frac{S_{OH_0}}{S_{OH+VOC}} \right) \quad (5)$$

18 Here $k_w t$ is the product of the rate constant for reaction of OH radicals on the wall of the calibration source with
 19 the reaction time t , reflecting the measured loss of OH on the walls of the calibrator (Dusanter et al., 2008).

20 The subsequent addition of NO to the detection cell will convert a fraction of RO_2 radicals and HO_2
 21 radicals to OH (mode 4 in Fig. 3). The conversion efficiency of RO_2 to OH ($C_{RO_2 \rightarrow OH}$) is determined by
 22 multiplying the fraction of RO_2 radicals converted to HO_2 ($f_{RO_2 \rightarrow HO_2}$) with the conversion efficiency of HO_2 to
 23 OH ($C_{HO_2 \rightarrow OH}$):

$$24 \quad C_{RO_2 \rightarrow OH} = f_{RO_2 \rightarrow HO_2} \cdot C_{HO_2 \rightarrow OH} \quad (6)$$

25 The signal due to RO_2 radicals (S_{RO_2}) is defined as the original OH signal (S_{OH_0}) multiplied by the conversion
 26 efficiency of OH radicals to RO_2 radicals ($C_{OH \rightarrow RO_2}$) and multiplied by the conversion efficiency of RO_2 to OH
 27 ($C_{RO_2 \rightarrow OH}$) (Eq. (7)):

1
$$S_{RO_2} = S_{OH_0} \cdot C_{OH \rightarrow RO_2} \cdot C_{RO_2 \rightarrow OH} \quad (7)$$

2 For OH +VOC reactions that lead to the production of HO₂ with a yield of y (OH + benzene and toluene for
3 example (Klotz et al., 1998; Nehr et al., 2011)), the OH to RO₂ conversion efficiency (C_{OH+VOC}) must be multiplied
4 by the overall yield (1-y) of RO₂ radicals produced from the OH +VOC reaction. Taking this yield into account,
5 the signals due to RO₂ and HO₂ radicals become:

6
$$S_{RO_2} = S_{OH_0} \cdot C_{OH \rightarrow RO_2} \cdot (1 - y) \cdot C_{RO_2 \rightarrow OH} \quad (7a)$$

7
$$S_{HO_2 \text{ total}} = S_{OH_0} \cdot C_{OH \rightarrow RO_2} \cdot y \cdot C_{HO_2 \rightarrow OH} + S_{HO_2} \quad (8)$$

8 The measured OH signal under these conditions (S_{ROx}) reflects the contribution of RO₂, HO₂, and unreacted OH
9 radicals (experimental mode 4):

10
$$S_{RO_x} = S_{RO_2} + S_{HO_2 \text{ total}} + S_{OH+VOC} \quad (9)$$

11
$$S_{RO_x} = (S_{OH_0} \cdot C_{OH \rightarrow RO_2} \cdot (1 - y) \cdot C_{RO_2 \rightarrow OH}) + (S_{OH_0} \cdot C_{OH \rightarrow RO_2} \cdot y \cdot C_{HO_2 \rightarrow OH} + S_{HO_2}) + S_{OH+VOC} \quad (9a)$$

12 Combining equations 3, 6, and 9a results in an expression for the fraction of RO₂ radicals converted to HO₂
13 (f_{RO₂→HO₂}) that can be expressed as the measured signals for each experimental mode (S_{OH}, S_{HOx}, S_{OH+VOC},
14 S_{ROx}) as seen in Eq. (10):

15
$$f_{RO_2 \rightarrow HO_2} = \frac{S_{RO_x} - S_{HO_x} + S_{OH} - S_{OH+VOC} - S_{OH_0} \cdot C_{OH \rightarrow RO_2} \cdot y \cdot C_{HO_2 \rightarrow OH}}{S_{OH_0} \cdot C_{OH \rightarrow RO_2} \cdot (1 - y) \cdot C_{RO_2 \rightarrow OH}} \quad (10)$$

16 When the yield of HO₂ from the OH + VOC reaction is zero (y = 0), and under conditions where all the OH
17 radicals are converted to RO₂ (S_{OH+VOC} = 0), the above equation (with Eq. 3 and 4) simplifies to the following:

18
$$f_{RO_2 \rightarrow HO_2} = \frac{S_{RO_x} - S_{HO_x} + S_{OH}}{S_{OH_0} \cdot C_{OH \rightarrow RO_2} \cdot C_{HO_2 \rightarrow OH}} = \frac{S_{RO_x} - S_{HO_x} + S_{OH}}{(S_{HO_x} - S_{OH}) \cdot C_{OH \rightarrow RO_2}} \quad (11)$$

19 Because this method cannot distinguish between the different peroxy radicals that could be produced from each
20 OH + VOC reaction, the measured conversion efficiency reflects the average conversion efficiency of all peroxy
21 radicals for a given VOC.

1 3 Results

2 The pressure and flow conditions for the three campaigns conducted with the IU LIF-FAGE instrument are
3 summarized in Table 1. For each characterization, the flow rate of NO addition was kept constant at 1 sccm in
4 order to determine the impact of the different operating conditions on the measured RO₂-to-HO₂ conversion
5 efficiencies. This is the NO flow rate used during the MCMA-2006, CABINEX and CalNex campaigns, and
6 resulted in HO₂-to-OH conversion efficiencies that were similar to that measured during both the CABINEX and
7 the CalNex campaigns. However, the measured HO₂-to-OH conversion efficiency for the MCMA-2006 campaign
8 configuration in these experiments was approximately 20% lower than that previously reported (Dusanter et al.,
9 2008; 2009a). The reason for this discrepancy is unclear, and may indicate problems in precisely recreating the
10 flow conditions during this campaign in these laboratory experiments. In addition, the NO flow rate was varied
11 during MCMA-2006 in order to maximize the HO₂-to-OH conversion efficiency and to quantify the photolytic
12 interference associated with high NO concentrations in the detection cell. Thus it is possible that the actual flow
13 rate used to maximize the conversion efficiency was slightly greater than the 1 sccm reported. Since it is not
14 known whether the flow was greater than the 1 sccm that was measured, or whether the flow conditions led to
15 more efficient mixing, we chose to conduct the experiments using the measured 1 sccm flow rate. It is difficult to
16 quantify how the higher HO₂-to-OH conversion efficiency measured during MCMA-2006 would translate into
17 the various RO₂-to-HO₂ conversion efficiencies, although it is likely that many of them would be larger. As a
18 result, the conversion efficiencies measured in this study for the MCMA-2006 configuration may represent a
19 lower limit to the actual conversion efficiencies during the campaign.

20 The RO₂ conversion efficiency into HO₂ ($f_{\text{RO}_2 \rightarrow \text{HO}_2}$) measured for the inlet conditions for the MCMA
21 2006, CABINEX, and CalNex campaigns are summarized in Table 2 and represent the results of several
22 experiments similar to those illustrated in Fig. 3, with the uncertainty representing one standard error of the mean
23 of the measurements. The largest RO₂ interference was observed for the CalNex inlet conditions where alkenes
24 produced interferences ranging from $83 \pm 7\%$ for isoprene-based peroxy radicals to $96 \pm 6\%$ for
25 tetramethylethylene (TME)-based peroxy radicals, while the conversion efficiency of aromatic, aldehydes, and
26 ketone compounds ranged from $54 \pm 4\%$ for methacrolein (MACR) to $91 \pm 4\%$ for methyl vinyl ketone (MVK).
27 The RO₂ to HO₂ conversion efficiency of a number of alkanes ranged from an average measured value of $15 \pm$
28 3% for propane-based peroxy radicals to $62 \pm 4\%$ for octane-based peroxy radicals, with the RO₂ to HO₂
29 conversion efficiency increasing with the carbon number. The inlet configuration and conditions used during the
30 MCMA 2006 campaign generally resulted in lower RO₂ interferences likely due to the higher flow rate (and
31 shorter reaction time) in the detection cell and the lower NO concentration (Table 1), although the measured

1 conversion efficiency was found to be somewhat greater for some VOCs. Under these inlet conditions the RO₂ to
2 HO₂ conversion efficiency for propane-based peroxy radicals was measured to be 22 ± 11% while the conversion
3 efficiency for octane-based peroxy radicals was 30 ± 5%. Because the CABINEX campaign occurred in a remote
4 forested environment, measurements of the RO₂-to-HO₂ conversion efficiency focused on characterizing
5 interferences from peroxy radicals produced from isoprene and its oxidation products (MVK and MACR), as
6 isoprene peroxy radicals were predicted to contribute to more than 80% of the total RO₂ concentration during the
7 campaign (Griffith et al., 2013). The inlet and instrumental configuration during CABINEX resulted in a higher
8 pressure and slower sampling rate compared to the MCMA 2006 configuration. For this instrumental
9 configuration, the RO₂-to-HO₂ conversion efficiency was found to be 91 ± 5% for isoprene-based peroxy radicals,
10 while the conversion efficiencies for MVK and MACR were found to be 62 ± 5% and 30 ± 7%, respectively.

11 These observations are consistent with results reported for other FAGE instruments (Fuchs et al., 2011;
12 Whalley et al., 2011), and assumes that the photolysis of each VOC does not contribute to the production of
13 radicals in these experiment. However, tests to determine whether photolysis of the various VOCs resulted in the
14 formation of HO_x radicals in the absence of water vapor revealed that the photolysis of methyl vinyl ketone
15 (MVK), methacrolein (MACR), methyl ethyl ketone (MEK), and toluene can lead to the production of HO_x
16 radicals. The radical signals from the photolysis of methacrolein, and toluene were small and negligible relative
17 to the total HO_x signal produced from the photolysis of water. However, the signal from the photolysis of MVK
18 and MEK during these tests was significant and could interfere with the measurements of the RO₂-to-HO₂
19 conversion efficiency. These results are in contrast to that reported by Fuchs et al. (2011), who found that the
20 photolysis of VOCs during similar tests in dry air did not produce any radicals. The reason for this discrepancy is
21 unclear, but may be related to differences in the UV flux produced by the different mercury lamps or impurities
22 associated with the VOC samples (Tables S1 and S2). Addition of water vapor may reduce the HO_x radical
23 production from photolysis of these VOCs due to quenching of the excited VOC, and as a result it is difficult to
24 quantify the interference in these experiments. However, any interference from HO_x radicals produced from the
25 photolysis of MVK and MEK would result in higher apparent conversion efficiencies, as they could represent an
26 additional source of HO_x radicals when the VOCs are added, and could contribute to the higher RO₂-to-HO₂
27 conversion efficiency reported here for MVK compared to that reported by Fuchs et al. (2011).

28 As previously observed, the RO₂-to-HO₂ conversion efficiency of alkene-based β-hydroxyalkyl peroxy
29 radicals was found to be greater than the conversion efficiency of alkane-based alkyl peroxy radicals (Fuchs et
30 al., 2011). As discussed above, this is due to the ability of the β-hydroxyalkoxy radicals produced from the
31 RO₂ + NO reaction to rapidly decompose to form a hydroxyalkyl radical. The hydroxyalkyl radical reacts rapidly

1 with O₂ in the FAGE detection cell leading to the production of a carbonyl compound and HO₂. However, the
2 ability of large alkoxy radicals to rapidly isomerize and decompose (Atkinson, 1997; Finlayson-Pitts and Pitts Jr.,
3 2000) also results in a rapid production of HO₂ radicals and a larger conversion efficiency.

4 In general, reducing the reaction time in the IU-FAGE instrument reduces the conversion of these peroxy
5 radicals to HO₂, as illustrated by the reduced conversion efficiencies between the CalNex and MCMA operating
6 conditions for the majority of the VOCs tested. However, the measured conversion efficiencies of some of the
7 tested VOCs did not always display this behavior and the reasons for the discrepancies are unclear. For example,
8 the conversion efficiency for ethene peroxy radicals was lower for the CalNex configuration compared to the
9 CABINEX and MCMA configurations even though the overall flow rate was slower for the CalNex configuration.
10 However, the HO₂-to-OH conversion efficiency was also lower for this inlet configuration, suggesting that
11 reaction time may not be the only factor limiting the conversion efficiency under these instrument conditions.
12 Similarly, the conversion efficiency of MVK and MACR measured for the CABINEX instrument configuration
13 was lower than that measured for the MCMA inlet configuration, even though the overall slower flow rate in the
14 CABINEX configuration leads to a longer reaction time in the IU-FAGE detection cell. This may suggest that the
15 chemistry of peroxy radicals produced from the OH-initiated oxidation of MVK and MACR is different than that
16 of the peroxy radicals produced from the OH-initiated oxidation of alkenes and alkanes, with competing channels
17 that result in a more complex dependence on reaction time. As discussed in Fuchs et al. (2011), the fates of the
18 peroxy radicals produced by the OH initiated oxidation of MVK and MACR are not well known. For the peroxy
19 radicals produced from the OH-initiated oxidation of MVK, three decomposition channels are possible, with two
20 channels potentially leading to fast HO₂ production and one likely leading to slower HO₂ production (Fuchs et al.,
21 2011). For the peroxy radicals produced from the OH-initiated oxidation of MACR, the channel that leads to the
22 formation of a hydroxyalkyl peroxy radical likely leads to fast HO₂ production, while the channel that leads to the
23 formation of an acyl peroxy radical would lead to much slower HO₂ production (Fuchs et al., 2011).

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24 4 Discussion

25 4.1 RO₂ Radical Concentrations during MCMA 2006

26 The previous analysis of the HO₂ radical concentrations during the Mexico City Metropolitan Area (MCMA)
27 2006 did not take into account interferences from RO₂ radicals (Dusanter et al., 2009b). As discussed above, the
28 instrumental conditions during MCMA-2006 resulted in the conversion of a fraction of RO₂ radicals to HO₂,
29 resulting in the measurements reflecting HO₂* = HO₂ + αRO₂ and overestimating the actual HO₂ concentrations.

1 To determine the fraction (α) of RO₂ radicals likely detected during the HO₂ measurements, the RO₂ radical
2 concentrations during MCMA-2006 that were previously modeled using the Regional Atmospheric Chemistry
3 Mechanism (RACM) were used to calculate the modeled HO₂* concentrations (Dusanter et al., 2009b).

4 As discussed in Dusanter et al. (2009b), the RACM model is a condensed chemical mechanism that
5 describes the gas-phase oxidation of 17 inorganic and 32 organic species. Kinetic parameters for the reactions of
6 OH, O₃ and NO₃ with inorganic species and for reactions involving organic species treated explicitly in RACM
7 (methane, ethane, ethene, formaldehyde, glyoxal, methyl peroxide and isoprene) were updated using the JPL
8 database (Sanders et al., 2006). Rate constants and branching ratios for OH, O₃ and NO₃ reactions with surrogate
9 species were used as described in the RACM model (Stockwell et al., 1997). Heterogeneous chemistry, such as
10 the incorporation of trace gases into aerosols, was not included.

11 The peroxy radical fractions calculated by the model are illustrated in Fig. 4 for 9 am, 12 pm, 6pm (local
12 times) and the overall diurnal average. Alkane-based peroxy radicals (red shades) include methyl peroxy (RACM
13 category CH3O2), ethyl peroxy (ETHP), peroxy radicals formed from the oxidation of alkanes, esters, and alkynes
14 exhibiting OH rate constants lower than $3.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (HC3P), peroxy radicals formed from
15 alkanes, esters, and alkynes characterized by OH rate constants ranging from 3.4×10^{-12} to $6.8 \times 10^{-12} \text{ cm}^3$
16 $\text{molecule}^{-1} \text{ s}^{-1}$ (HC5P), and peroxy radicals formed from alkanes, esters, and alkynes whose OH rate constants are
17 larger than $6.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (HC8P). Alkene-based peroxy radicals (blue shades) include peroxy
18 radicals from the oxidation of ethene (ETEP), external olefins (OLTP), internal olefins (OLIP), isoprene (ISOP),
19 and from α -pinene and other cyclic terpenes with one double bond (APIP). Aromatic peroxy radicals (green
20 shades) include species produced during the oxidation of toluene (TOLP), xylenes (XYLP), and cresol (CSLP).
21 The carbonyl-based peroxy radicals (grey shades) include saturated (ACO3) and unsaturated (TCO3) acyl peroxy
22 radicals.

23 The total average modeled RO₂ concentration from 9:00 am to 6:00 pm consisted of 54% alkane-based,
24 27% alkene-based, and 14% aromatic-based peroxy radicals (Fig. 4). On average, the modeled composition of
25 peroxy radicals was relatively constant throughout the day during the MCMA campaign. The modeled relative
26 contribution of aromatic-based peroxy radicals was greater in the morning, consistent with the observed elevated
27 concentrations of benzene and toluene during the morning hours (Dusanter et al., 2009b).

28 **4.2 Implications of RO₂ interferences for HO₂ measurements during MCMA 2006**

29 The modeled diurnal average concentrations of total RO₂ radicals during MCMA is shown in Fig. 5, along with
30 the modeled HO₂ concentrations and the measured HO₂* concentrations. As discussed in Dusanter et al. (2009b),

1 the modeled HO₂ concentrations were in good agreement with the measurements during the afternoon but the
2 model underestimated the measured HO₂ concentrations during the morning hours by a factor of approximately 2
3 to 5. However, these conclusions were based on the assumption that the measured HO₂ concentrations were free
4 from interferences and could be compared to the modeled HO₂ concentrations. Based on the conversion
5 efficiencies reported for RO₂ radicals in the present study, it is clear that the MCMA measurements represent an
6 upper limit to the actual HO₂ concentrations and should be compared to the modeled HO₂* = HO₂ + αRO₂
7 concentrations.

8 The RACM modeled HO₂* concentrations were calculated by applying the measured RO₂-to-HO₂
9 conversion efficiencies for the instrumental conditions reported in Table 2 for MCMA-2006 using Eq. 12:

$$\begin{aligned} 10 \quad HO_2^* = HO_2 + & (0.84 \cdot ISOP + 0.68 \cdot OLIP + 0.68 \cdot OLTP + 0.86 \cdot ETEP + 0.32 \cdot TOLP + 0.32 \cdot XYLP + \\ 11 \quad & 0.32 \cdot CSLP + 0.72 \cdot APIP + 0.22 \cdot HC3P + 0.22 \cdot HC5P + 0.30 \cdot HC8P + 0.05 \cdot CH3O2 + 0.07 \cdot ETHP \\ 12 \quad & + 0.32 \cdot ACO3 + 0.32 \cdot TCO3 + 0.72 \cdot KETP \end{aligned} \quad (12)$$

13 The contribution for isoprene peroxy radicals (ISOP), ethene peroxy radicals (ETEP), and toluene peroxy radicals
14 (TOLP) were taken directly from Table 2. The average RO₂-to-HO₂ conversion efficiency for *trans*-2-butene and
15 tetramethylethylene-based peroxy radicals was used for the conversion efficiency of peroxy radicals from internal
16 olefins (OLIP), and external olefins (OLTP), while the conversion efficiency for *trans*-2-butene was used for the
17 conversion efficiency for α-pinene and other cyclic terpene peroxy radicals (APIP). The measured conversion
18 efficiency for toluene-based peroxy radicals was used to represent the conversion efficiency for xylene (XYLP)
19 and cresol (CSLP) peroxy radicals. The conversion efficiency of methacrolein-based peroxy radicals was used to
20 represent the conversion efficiency of acetyl peroxy and higher saturated acyl peroxy radicals (ACO3) as well as
21 unsaturated acyl peroxy radicals (TCO3), while the conversion efficiency of methyl vinyl ketone-based peroxy
22 radicals was used to represent the efficiency of ketone-based peroxy radicals (KETP).

23 The overall average contribution of peroxy radicals to the modeled HO₂* and the relative contribution of
24 each RACM peroxy radical category to the RO₂ interference are shown in Fig. 6. Because the HO₂-to-OH
25 conversion efficiency of 80% in these experiments was approximately 20% lower than the conversion efficiency
26 measured during the campaign (Dusanter et al., 2008; Dusanter et al., 2009a), the relative peroxy radical
27 contributions illustrated in this figure are likely lower limits to the actual contribution during the campaign.

28 On average, RO₂ radicals contributed to approximately 35% of the total modeled HO₂* (Fig. 6). While
29 alkanes compose the majority of the modeled peroxy radicals (Fig. 4), they only contributed to about 29% of the
30 RO₂ interference, while alkenes contributed to approximately 51% to the interference (Fig. 6). While isoprene

Deleted: the NO flow rate used in characterizing the conversion efficiencies in Table 2 was generally lower than the flow rates used during the campaign, the relative peroxy radical contributions illustrated in this figure are likely lower limits to the actual contribution during the campaign, as the HO₂-to-OH conversion efficiency of 80% in these experiments was approximately 20% lower than the conversion efficiency measured during the campaign

1 peroxy radicals contributed to only 5% of the total RO₂ concentration, they contributed approximately 11% to the
2 interference.

3 The overall contribution of RO₂ radicals to the measured HO₂* concentrations in this environment is
4 similar to that observed during the CalNex campaign, where RO₂ radicals were modeled to contribute to
5 approximately 30% of the measured HO₂* concentrations, although during CalNex peroxy radicals from isoprene
6 (ISOP) and its oxidation products accounted for approximately 40-50% of the modeled interference and olefins
7 (OLTP, OLIP) contributed approximately 20-30% (Griffith et al., 2016). Unlike these urban environments, in
8 forested environments where the OH reactivity is dominated by isoprene and other unsaturated biogenic
9 emissions, isoprene and other biogenic hydroxyl alkyl peroxy radicals can be the dominant peroxy radicals and
10 can make a significant contribution to the measured HO₂* concentrations due to their high conversion efficiency
11 to HO₂ in the FAGE detection cell (Table 2). For example, during the CABINEX campaign in a northern Michigan
12 forest, isoprene peroxy radicals were modeled to be the dominant peroxy radical in this environment and the main
13 contributor to the interference, contributing to approximately 50% of the modeled HO₂* concentrations during
14 the daytime (Griffith et al., 2013). As a result, previous measurements of HO₂ in these environments by LIF-
15 FAGE or other chemical conversion techniques are likely influenced by an interference from β-hydroxyalkyl
16 peroxy radicals such as those produced by the OH-initiated oxidation of isoprene and other biogenic emissions.

17 While it is possible to subtract the modeled speciated RO₂ concentrations from the measured HO₂* and compare
18 the results to the modeled HO₂, this method increases the uncertainty associated with the measured concentrations
19 due to the uncertainty associated with the modeled RO₂ concentrations as well as the uncertainties associated with
20 the measured RO₂-to-HO₂ conversion efficiencies. We estimate the uncertainty associated with the RACM
21 modeled RO₂ to be approximately ±70% (2σ), similar to that for the modeled HO₂ (Dusanter et al., 2009b). As a
22 result, we prefer to compare the modeled HO₂* to the measured HO₂*.

23 The diurnal average modeled HO₂* concentrations for the MCMA-2006 campaign are also shown in Fig.
24 5. As can be seen in this figure, the model overestimates the measured HO₂* by approximately 35% between
25 12:00 and 17:00 CST, although the modeled results are generally close to the upper bound of the calibration
26 accuracy (36%, 2σ) (Dusanter et al., 2009b). As discussed above, the modeled HO₂* is likely a lower limit given
27 that the RO₂-to-HO₂ conversion efficiencies during the campaign may be greater than shown in Table 2 due to the
28 higher HO₂-to-OH conversion efficiency measured during the campaign. Although, the measured HO₂* are still
29 likely to be within the overall uncertainty of the model, which was estimated to be approximately a factor of 1.7
30 (Dusanter et al., 2009b), these results suggest that the model likely overestimates the measured concentrations
31 during the afternoon.

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1 These results are in contrast to the results from the CalNex campaign, where the simulations using the
2 RACM2 model tended to underestimate the measured HO₂* concentrations during the week, when NO mixing
3 ratios were greater than 4 ppb (Griffith et al., 2016). The reason for this difference between the campaigns is
4 unclear, but may be related to the relative concentrations of dicarbonyl species and their treatment in the RACM
5 and RACM2 models. Dusanter et al. (2009b) demonstrated that the RACM model results for MCMA-2006 were
6 highly sensitive to the concentrations of dicarbonyl species in the model, with the model significantly
7 overpredicting the concentration of HO_x radicals when unmeasured concentrations of these species were not
8 constrained. Daytime average measured glyoxal mixing ratios during MCMA-2006 were approximately 0.4 ppb
9 (Dusanter et al., 2009b), which were greater than the maximum daytime mixing ratios of 0.16 ppb during CalNex
10 (Washenfelder et al., 2011), suggesting that the MCMA-2006 results may be more sensitive to the treatment of
11 dicarbonyl chemistry compared to CalNex. Additional analysis and modeling will be needed to resolve this issue.

12 While the model tends to overestimate the measured HO₂* concentrations during the afternoon, it
13 underestimates the measured HO₂* concentrations in the morning by a factor of 3 between 9-11 am. As discussed
14 in Dusanter et al. (2009b), this may suggest that a significant radical source may be missing from current
15 atmospheric models under polluted conditions. Similar results were observed in Wangdu, China by Tan et al.
16 (2017). In this study, total peroxy radical concentrations were measured by chemical conversion to HO₂ in an
17 external reactor with subsequent detection of HO₂ (after chemical conversion to OH) in an LIF-FAGE instrument.
18 They also measured HO₂ radicals using a second LIF-FAGE detection axis that minimized interferences from
19 RO₂ radicals. They found that a model using the updated RACM2 mechanism was able to reproduce the observed
20 HO₂ concentrations during the day, but underestimated the observed total RO₂ concentration by a factor of 3 to 5
21 in the morning when NO concentrations were higher than 1 ppbv. The observed RO₂ concentrations could be
22 explained by a missing RO₂ source of 2 ppbv h⁻¹ (Tan et al., 2017).

23 Dusanter et al. (2009b) also compared the measured HO₂*/OH ratio to the RACM modeled HO₂/OH
24 ratio and found that the model underpredicted the observed ratio, especially under conditions where the mixing
25 ratio of NO was greater than 5 ppb. At NO mixing ratios of 10 ppb, the model underestimated the measured ratio
26 by a factor of 2 (Dusanter et al., 2009b). However, comparing the measured HO₂*/OH ratio to the modeled
27 HO₂*/OH ratio improves the agreement even though the model tends to overpredict both OH and HO₂* in the
28 afternoon (Fig. 7). This may indicate that there is either a missing sink of HO_x radicals in the model or a
29 miscalculation of the relative rates of initiation and/or termination. At an NO mixing ratio of 10 ppb the modeled
30 HO₂*/OH ratio is in good agreement with the measurements, although it still underestimates the measured
31 HO₂*/OH ratio at higher NO mixing ratios by as much as a factor of 4, and may also overestimate the HO₂*/OH

1 ratio for mixing ratios of NO less than 5 ppb by as much as a factor of 2 (Fig. 7). It is interesting to note that a
2 model underestimation of the total OH reactivity at high NO mixing ratios may contribute to this discrepancy.
3 Unfortunately, total OH reactivity was not measured during MCMA-2006 and the reliability of the model to
4 simulate it could not be assessed. Similar results were observed for the CalNex campaign (Griffith et al., 2016),
5 which included direct measurements of the total OH reactivity. Although accounting for the missing reactivity in
6 the analysis of the CalNex data improved the agreement between the measured and modeled HO₂*/OH ratio, the
7 model still underestimates the measured ratio at high mixing ratios of NO (Griffith et al., 2016). These results
8 suggest that our understanding of the radical propagation chemistry under high NO conditions may be incomplete.

9 **5. Summary and Conclusions**

10 The RO₂ interference associated with measurements of HO₂ by the IU-FAGE instrument was
11 characterized for three different instrument configurations that were used in previous field campaigns (MCMA
12 2006, CABINEX 2009, and CalNex 2010). Similar to that reported for other LIF-FAGE instruments, the RO₂-to-
13 HO₂ conversion efficiency was highest for alkene- and aromatic-based RO₂ radicals, producing higher levels of
14 interference, while the conversion efficiency of alkane-based RO₂ radicals was less but increased with increasing
15 carbon number. In general, the conversion efficiency was higher for instrument configurations that involved
16 slower sampling flow rates and longer reaction times between the peroxy radicals and NO in the detection cell.

17 The similarities in the measured RO₂ conversion efficiencies reported here with those reported for other
18 LIF-FAGE instruments suggest that the main factor controlling the conversion efficiency is the rate of reaction of
19 RO₂ radicals with NO, and that increasing the efficiency of the conversion of HO₂ to OH will also increase the
20 RO₂-to-HO₂ conversion efficiency. Although the impact of differences in the characteristics of the low pressure
21 expansion in LIF-FAGE instruments cannot be ruled out, these results suggest that the interferences reported here
22 associated with measurements of HO₂ are likely similar for all instruments that measure HO₂ by chemical
23 conversion through reaction with NO. Previous measurements of HO₂ radicals by instruments using this method
24 were likely influenced by the conversion of RO₂ radicals, with measurements of HO₂ in forested environments
25 likely influenced by interferences from peroxy radicals derived from biogenic alkenes such as isoprene due to the
26 high RO₂-to-HO₂ conversion efficiencies of these radicals. Because of the lower conversion efficiencies of alkane-
27 based peroxy radicals, the impact on previous measurements in urban areas will depend on the relative
28 concentrations of alkanes versus alkenes and aromatics contributing to the overall pool of peroxy radicals in these
29 environments.

1 While this interference was taken into account to investigate the radical chemistry during CABINEX
2 (Griffith et al., 2013) and CalNex (Griffith et al., 2016), this issue was not known when the radical measurements
3 from the MCMA-2006 field campaign were published (Dusanter et al., 2009b). An analysis of the impact of this
4 interference on the results for the MCMA-2006 campaign suggests that the RO₂ radical contribution to the
5 measured HO₂* concentration was approximately 35% based on the RACM modeled RO₂ concentrations. Taking
6 this interference into account, the resulting modeled HO₂* concentrations were generally greater than the
7 measured concentrations by 35% during the afternoon, although the model results were within the calibration
8 uncertainty of the measurements (36% at 2σ). Given that the modeled HO₂* concentrations likely reflect a lower
9 limit to the interference during the campaign these results suggest that the model likely overestimates the measured
10 concentrations during the afternoon. However, the model still underestimates the HO₂* concentration by a factor
11 of 3 in the morning, suggesting that the model may be missing an important radical source in the morning.
12 Although the measured HO₂*/OH ratio was in better agreement with the modeled HO₂*/OH ratio compared to the
13 modeled HO₂/OH ratio, the model still significantly underestimates the HO₂*/OH ratio by up to a factor of 4 for
14 NO mixing ratios greater than 10 ppb, suggesting that our understanding of radical propagation under these
15 conditions is still incomplete.

16 Future measurements of peroxy radicals by the IU-FAGE instrument will involve measurements at lower
17 NO concentrations to minimize the RO₂-to-HO₂ conversion efficiency. Recent experiments have demonstrated
18 that the addition of an NO concentration of approximately 9×10¹¹ cm⁻³ results in an HO₂-to-OH conversion
19 efficiency of approximately 17% and a conversion efficiency of isoprene-based peroxy radicals to HO₂ of
20 approximately 10%. Even at this low HO₂-to-OH conversion efficiency, the resulting HO₂ signals are still
21 significantly greater than the limit of detection of the instrument, but at this low NO concentration, the subsequent
22 conversion of isoprene peroxy radicals to OH is negligible, allowing for measurements of ambient HO₂
23 concentrations without interferences from RO₂ radicals.

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Table 1. Configuration of the IU-FAGE instrument during various previous field campaigns.

	CalNex	CABINEX	MCMA-2006
Cell pressure (hPa)	5.5	10.0	7.2
Orifice diameter (mm)	0.64	1.02	1.02
Sample flow rate (SLPM)	3.4	8.5	10
NO (molecules/cm ³) <i>(for 1 sccm flow)</i>	2.9×10^{13}	2.1×10^{13}	1.3×10^{13}

Table 2. Average measured $f_{\text{RO}_2 \rightarrow \text{HO}_2}$ for various alkenes and alkanes under different inlet conditions. Uncertainties represents the standard error of the mean from all individual experiments, with the number of experiments shown in parentheses.

Compounds	4 Torr @ 3.4 SLPM (CalNex)	7.5 Torr @ 8.5 SLPM (CABINEX)	5 Torr @ 10 SLPM (MCMA 2006)	Fuchs et al. ^a	Whalley et al. ^b
C(HO ₂ →OH)	0.67 ± 0.01 (67)	0.90 ± 0.02 (47)	0.80 ± 0.01 (81)	—	—
Isoprene	0.83 ± 0.07 (5)	0.91 ± 0.05 (9)	0.84 ± 0.05 (6)	0.79 ± 0.05	0.92 ± 0.04
MVK	0.91 ± 0.04 (10)	0.62 ± 0.05 (21)	0.72 ± 0.04 (15)	0.60 ± 0.06	—
MACR	0.54 ± 0.04 (4)	0.30 ± 0.07 (5)	0.32 ± 0.07 (11)	0.58 ± 0.17	—
MEK	0.57 ± 0.06 (6)	0.62 ± 0.01 (2)	0.51 ± 0.07 (9)	—	—
Ethene	0.65 ± 0.05 (18)	0.81 ± 0.06 (7)	0.86 ± 0.06 (9)	0.85 ± 0.05	1.00 ± 0.08
<i>trans</i> -2-butene	0.92 ± 0.04 (4)	—	0.72 ± 0.03 (6)	—	—
TME	0.96 ± 0.06 (2)	—	0.64 ± 0.06 (8)	—	—
Toluene	0.65 ± 0.07 (4)	—	0.32 ± 0.10 (6)	—	—
Propane	0.15 ± 0.03 (4)	—	0.22 ± 0.11 (2)	—	0.03 ± 0.01
n-butane	0.31 ± 0.03 (4)	0.30 ± 0.03 (3)	0.23 ± 0.05 (4)	—	0.18 ± 0.01
n-octane	0.62 ± 0.04 (5)	—	0.30 ± 0.05 (5)	—	—

^aFraction of conversion for RO₂ to HO₂ conversion for the Julich LIF instrument (Fuchs et al., 2011)

^b Conversion efficiencies of RO₂ to OH for the Leeds LIF instrument referenced to ethene (Whalley et al., 2013)

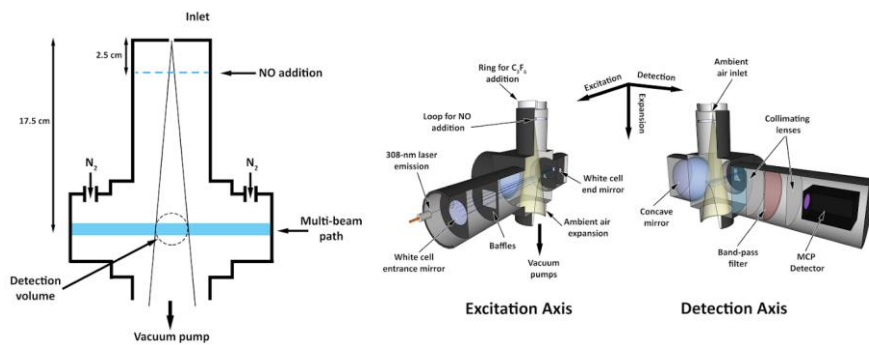


Figure 1. Indiana University LIF-FAGE cross section (left) and a schematic of the sampling/excitation axis and the sampling detection axis (right) (Dusanter et al., 2008)

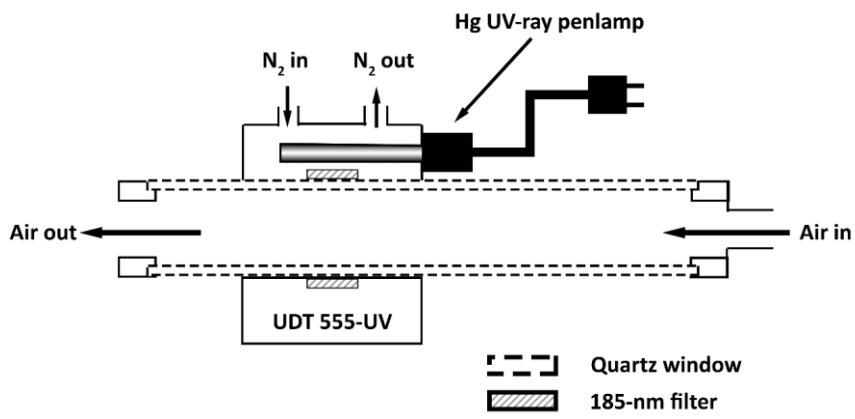


Figure 2. Cross-section of Indiana University calibration source for the IU-FAGE instrument

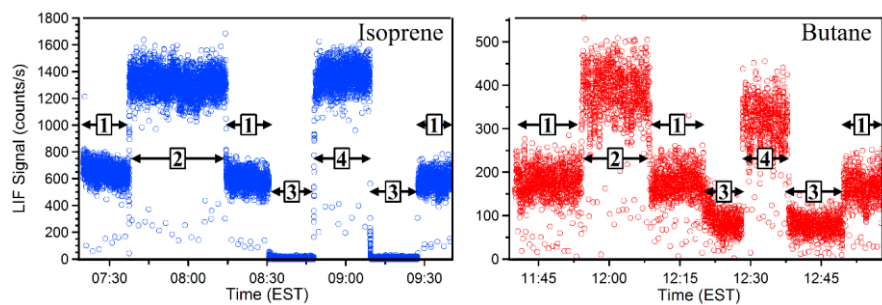


Figure 3. RO₂ interference measurement experiment for isoprene (left—with an OH reactivity of approximately 290 s⁻¹) and butane (right—with an OH reactivity of approximately 30 s⁻¹). The boxed numbers within the figure represents the various experimental modes: (1) S_{OH}, (2) S_{Hox} with internal NO addition, (3) S_{OH + VOC} with VOC added, (4) S_{ROx} with VOC added and internal NO addition.

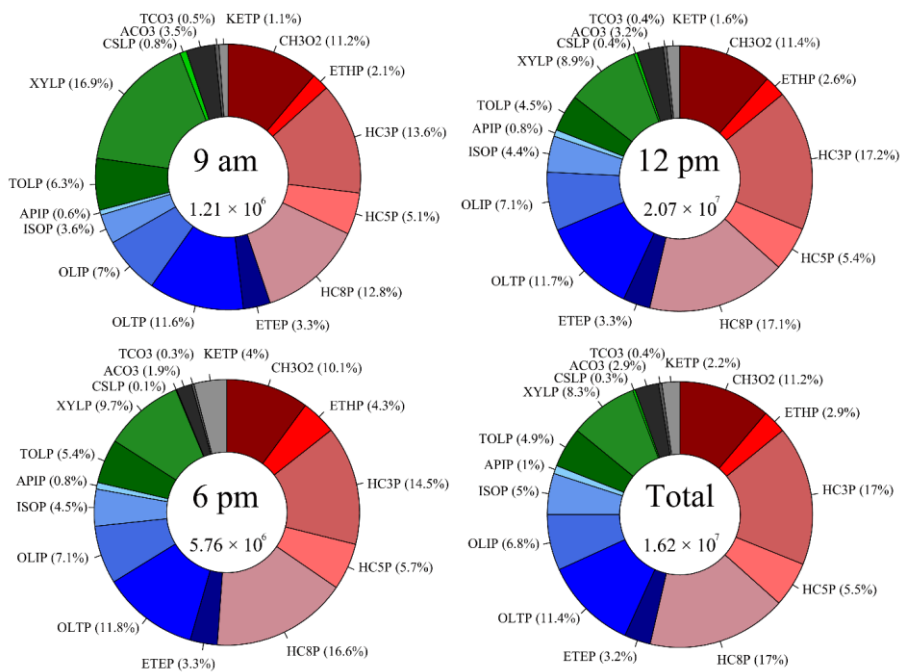


Figure 4. Modeled average peroxy radical contributions for the MCMA 2006 field campaign at 9:00 am (top left), 12:00 pm (top right), 6:00 pm (bottom left), and for the average campaign (bottom right). Shades of red represent alkanes, shades of blue represent alkenes, shades of green represent aromatics, and shades of grey represent acyl peroxy radicals. Individual RACM peroxy radical categories are defined in Section 4.2.

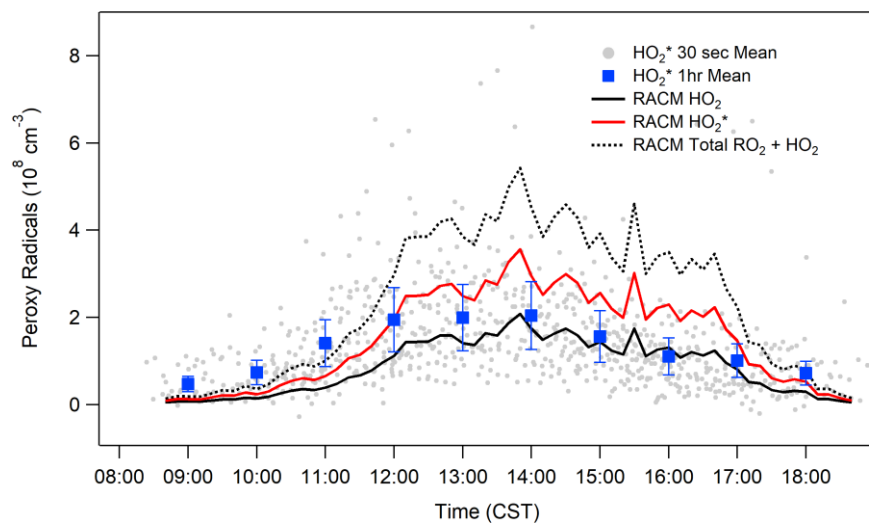


Figure 5. Diurnal average HO₂* measurements from MCMA 2006. The grey solid circles are 30 sec averages and solid blue square symbols are binned 1 hour averages. The solid black line represents the RACM modeled HO₂, the solid red line represents the modeled HO₂*, and the dotted black line represents the total modeled RO₂ + HO₂. The error bars reflect the calibration accuracy of the measurements ($\pm 36\%$, 2σ).

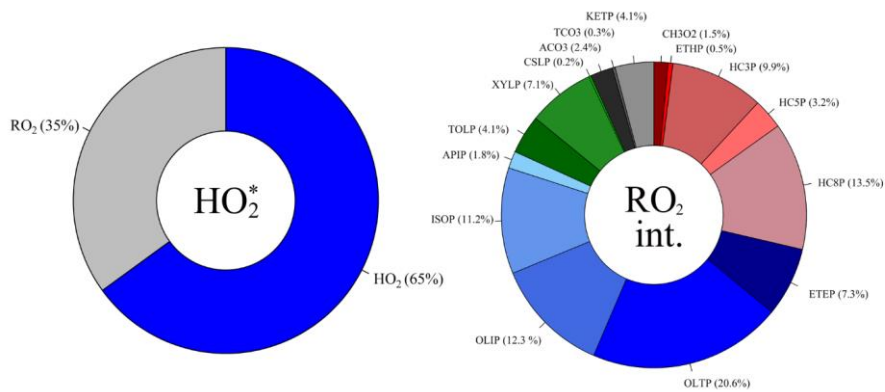


Figure 6. Modeled speciation of the RO₂ interference for MCMA 2006. The pie chart on the left is the modeled HO₂* composition after adding the fraction of RO₂ interference to the modeled HO₂. The pie chart on the right is the composition of the RO₂ interference.

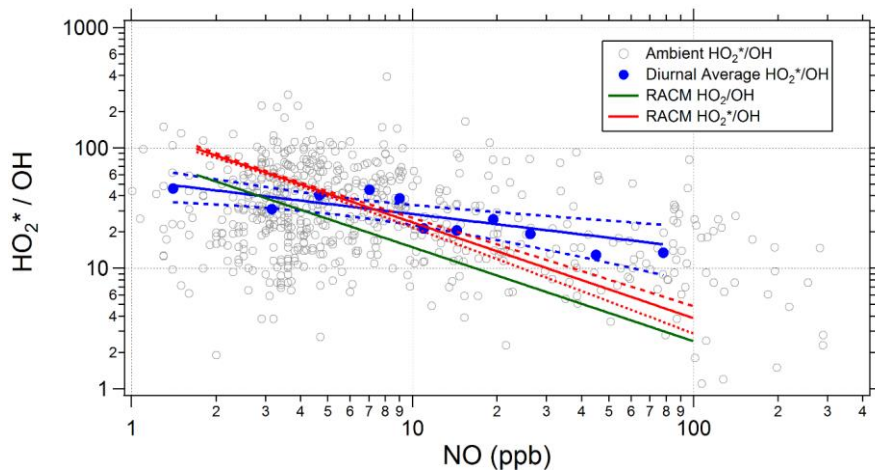


Figure 7. Correlation plot for $\text{HO}_2^* / \text{OH}$ vs. NO . Small grey circles are individual measurements recorded for the whole campaign. Large blue circles are average values calculated on binned NO data and the blue line is a fit to the average measurements. The model-calculated $\text{HO}_2^* / \text{OH}$ ratio is displayed by the green line for the campaign averaged measurements, while the red line represents the modeled $\text{HO}_2^* / \text{OH}$ ratio. Dashed lines are the 95% confidence interval from the non-linear power regressions.