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MEASUREMENTS OF HYDROPEROXY & TOTAL ORGANIC PEROXY RADICALS IN AN INDIANA FOREST USING LASER INDUCED-FLUORESCENCE

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AMBIENT CHEMISTRY OF HYDROPEROXY (HO₂) AND PEROXY (RO₂) RADICALS

The OH radical initiates the oxidation of volatile organic compounds (VOCs), leading to HO₂ and RO₂ radicals whose chemistry, in the presence of nitrogen oxides (NO_x), can lead to the formation of ozone and secondary organic aerosols in the environment. Previous measurements of these radicals in forest environments characterized by high mixing ratios of isoprene and low mixing ratios of NO_x have shown serious discrepancies with modeled predictions, bringing into question our understanding of isoprene oxidation in the atmosphere.

LASER-INDUCED FLUORESCENCE-FLUORESCENCE ASSAY BY GAS EXPANSION (LIF-FAGE)

- Measures OH & HO₂ by excitation and fluorescence of OH at 308 nm. Fluorescence is detected by a micro-channel plate PMT (Fig. 1).
- Air is sampled via an inlet and is expanded under vacuum (~3.5 to 4 Torr).
- HO₂ in the detection cell is measured by addition of NO to produce OH within the cell: HO₂ + NO → OH + NO₂
- A low NO concentration (~3.6 to 7 × 10¹¹ cm⁻³) is used in the detection cell for HO₂ measurements to minimize interference from RO₂ radicals (Lew, 2018). HO₂ to OH conversion efficiency in the detection cell is ~14%.

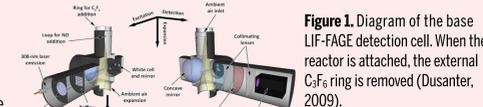


Figure 1. Diagram of the base LIF-FAGE detection cell. When the reactor is attached, the external C₂F₆ ring is removed (Dusanter, 2009).

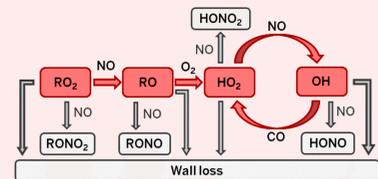


Figure 2. Chemistry in the reactor flow tube. Propagation reactions are shown in red, while termination reactions are shown in gray. Loss reactions are mostly wall losses or recombination with NO.

ROxLIF configuration

- LIF-FAGE inlet was modified by attaching a 45-cm reactor flow tube (Fig. 3, right) to convert RO_x and HO_x species to HO₂, which is detected in the detection cell (Fuchs, Holland et al. 2008).
- RO_x and HO_x modes are achieved by addition of CO and NO (Fig. 2), under low pressure conditions (~30 Torr) before reaching the detection cell.
- Detection limits for HO₂ and RO₂ were (2-4) × 10⁷ cm⁻³, and (1.5-3) × 10⁷ cm⁻³, respectively, for S/N = 1 and 5-minute measurements.

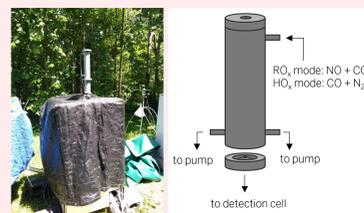


Figure 3. (Left) ROxLIF deployed to the IURTP site. (Right) Diagram of the ROxLIF attachment. The top inlet is a pinhole while the bottom inlet is conical. From here, the sample is directed to the detection cell shown in Fig. 1.

Conversion Efficiency and Sensitivity of ROxLIF

- OH is converted to HO₂ by the addition of CO: OH + CO → H + CO₂
 H + O₂ → HO₂
- RO₂ is measured by adding NO into the reactor: RO₂ + NO → RO + NO₂
 RO + O₂ → R'O + HO₂

- Known concentrations of OH and HO₂ were generated using the calibration source shown in Fig 4a. To generate RO₂, ethane was added to the calibration source and react with OH and introduced into the reactor. The RO₂ concentration was assumed to be equal to the initial OH concentration.
- Sensitivity to RO₂, C_{RO2}, was calculated from ethane-RO₂ measurements (Fig 4b).
- Chemistry within the reactor have been modeled using Master Chemical Mechanism v3.3.1, wall loss rate constants from experiments and literature (Fuchs, 2008; Mihele, 1999; Sander, 2003). Residence times of RO₂ species generated from methane, toluene and isoprene have been found to be within 10% of the residence time for ethane-RO₂. Thus, it is reasonable to assume a generic C_{RO2} for these RO₂ species.

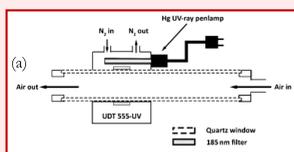


Figure 4. (a, top) Calibration source used to generate HO₂ and RO₂ radicals (Lew, 2018) (b, right) Calculated RO₂ and HO₂ sensitivity as function of water %.

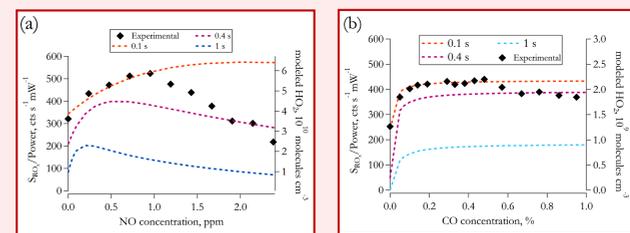
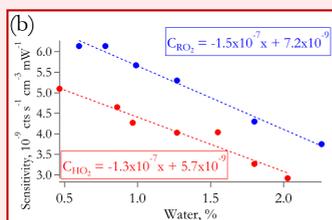


Figure 5. Measured (points) and modeled (dotted lines) instrument response to RO₂ as function of (a) NO and (b) CO concentration added to reactor. Models were done for different residence times in the reactor. For the measured RO₂, ethane was used as source of RO₂.

PREVIOUS VS. CURRENT MEASUREMENTS AT THE IURTP SITE

- The Indiana University Research and Teaching Preserve (IURTP) is a mixed deciduous forest consisting of sugar maple, sycamore, tulip polar, ash and hickory trees (Lew et al., 2019).
- It is located ~2.5 km NE of the center of the Indiana University campus, and 1 km from the IN 45/46 bypass at the northern perimeter.

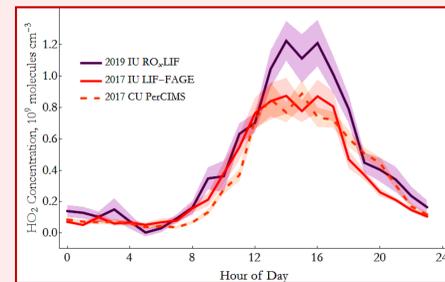


Figure 6. HO₂ measurements at the IURTP site using three different techniques: ROxLIF in 2019, Peroxy Radical Chemical Ionization Mass Spectrometry (PerCIMS) in 2017 and LIF-FAGE in 2017. PerCIMS was operated by University of Colorado-Boulder.

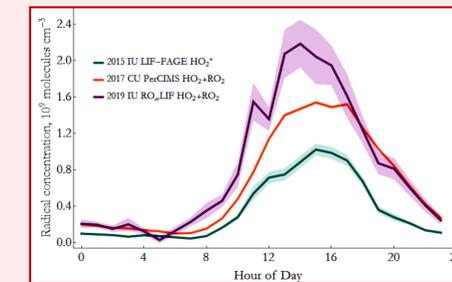


Figure 7. Total HO₂+RO₂ measurements at the IURTP site in 2017 and 2019 compared with HO₂* measurements by the LIF-FAGE in 2015. HO₂* is HO₂ + αRO₂, where α is a fraction of alkene and aromatic hydrocarbons.

- Isoprene concentrations in 2019 were greater than that measured in 2017, but similar to that measured in 2015 (Fig. 8c). NO₂ concentrations in 2019 were lower than measurements in both 2015 and 2017 (Fig. 8b) suggesting that NO concentrations were also lower compared to 2015 and 2017.
- The higher HO₂ and RO₂ concentrations observed in 2019 may be consistent with lower NO concentrations at this site compared with 2017 and 2015 (Figs. 6 and 7).

Supporting Measurements: Isoprene, Ozone and NO_x

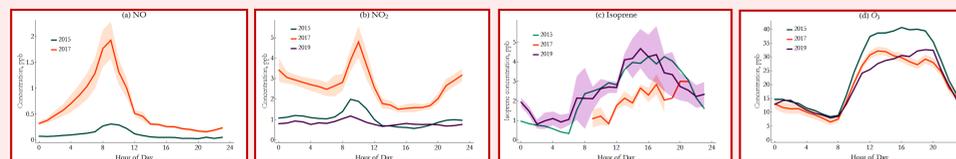


Figure 8. Concentrations of (a) NO, (b) NO₂, (c) Isoprene and (d) ozone at the IURTP site in 2015, 2017 and 2019. NO concentrations in 2019 are below LOD and are not shown in (a). Shaded areas, when visible, stand for standard error.

DAILY MEASUREMENTS & MODEL COMPARISONS

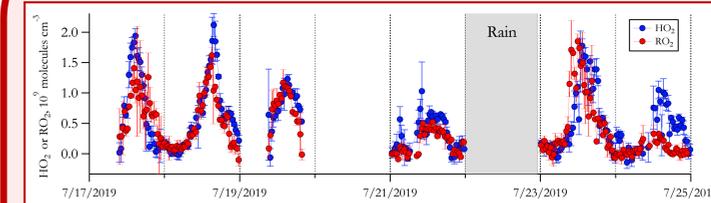


Figure 9. Time series of HO₂ and RO₂ measurements during the campaign.

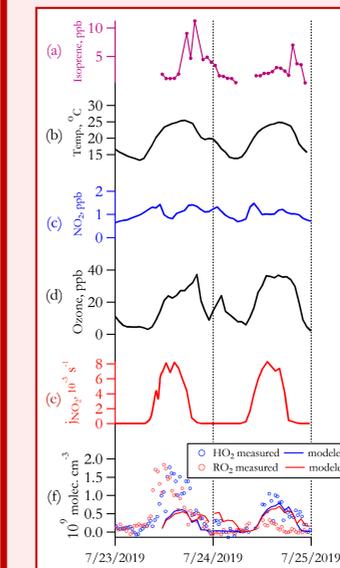


Figure 10. Measured and modeled HO₂ and RO₂ concentrations are shown on (f), while the top panels (a-e) show the supporting measurements used as model constraints.

- HO₂ and RO₂ show a strong diurnal trend that is characteristic of photolytically-driven reactions.
- For most days, measured HO₂ = RO₂ except for July 24th (Fig 9). This day, isoprene was lower than the previous days (Fig 10a).
- To constrain a zero-dimensional box model based on the Master Chemical Mechanism (MCM) v3.3.1, supporting measurements of photolysis rates, VOCs, O₃ and NO₂ (Fig. 10a-e) were used.
- Calculations were done using the Framework for 0-D Atmospheric Modeling (FOAM) (Wolfe, 2016).
- The model underestimates HO₂ concentrations on the 23rd, but seem to reproduce them well on the 24th.
- On the other hand, RO₂ is underestimated on the 23rd but overestimated on the 24th especially during the night.

CONCLUSIONS

This work presents the first successful ambient measurements of HO₂ and RO₂ in a forested environment by the newly constructed IU ROxLIF-FAGE system. The conversion efficiency for different RO₂ species within the flow tube have been estimated to be within ~10% of each other and have been detected using the ROxLIF method. Ambient concentrations of HO₂ and RO₂ were found to be around 4 × 10⁸ to 2 × 10⁹ molecules cm⁻³, similar to previous measurements at this site. Modeled HO₂ concentrations using MCM v3.3.1 agree or underestimate the measurements on two days, while modeled RO₂ concentrations either under- or overestimate the measurements by a factor of two.

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