Supplementary Material

Measurements of Total Hydroxyl Radical Reactivity during CABINEX 2009 – Part 1: Field Measurements

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S1. Characterization of the IU-TOHLM Instrument

S1.1 Measurement of k_b

To test the effects of impurities from the carrier N_2 source on k_b, measurements of k_b were performed alternately with nitrogen from an industrial-grade N_2 dewar (Indiana Oxygen) and VOC-free nitrogen (purity of 99.9995%, Matheson). The average difference between the k_b values from these two sources was 0.24 s^{-1}, which corresponds to approximately 7% of the k_b measured in these tests.

S1.2 Inlet Tests

To confirm that the sampling inlet (described in section 2.1) did not have an effect on the OH reactivity measurements, various sections of inlet were added in the field during CABINEX. The same location was sampled with both inlet configurations. For the CABINEX campaign, an additional inlet section (7 m long) was attached to a sampling inlet of 6.7 m, doubling the inlet length. The added section of inlet was alternately attached and removed every 30 min. The difference in reactivity between the 13.7 m inlet and the 6.7 m inlet was 0.32 ± 0.5 s^{-1} (n = 9).

S1.3 Determination of flow characteristics

The flow velocity profile was measured approximately 2 cm upstream of the exit of the flow tube. Measurements of flow velocity were made at increments of 2 mm along the internal diameter of the flow tube. The flow velocity was uniform throughout the inner diameter of the flow tube, with a 10% higher flow velocity at the center and sharp drop-offs near the wall of the flow tube. This profile matches the characteristics of turbulent flow as described by Seeley et al. (1993).

S2. Instrument operation

The IU-TOHLM instrument shares a laser with the IU FAGE instrument (Dusanter et al., 2009; Griffith et al., 2012). For the IU-FAGE instrument, which measures ambient HO_x concentrations, the laser must be tuned on and off the OH transition multiple times over the course of an OH reactivity measurement. This is necessary to achieve the time resolution necessary for the ambient HO_x measurements. These successive on- and off-resonant measurements can be seen on the OH decay displayed in Fig. S2.

S3. Trends of temperature and $J(NO_2)$ during CABINEX

Ambient temperatures (black trace, panels a in Figures S3-S5) span the same range of values among the three heights (10–26°C). However, ambient temperatures measured at the 21m (17.9°C on average) and 31m (18.4°C on average) heights are generally higher on average than those measured at the 6m height (16.2°C on average). Values of $J(NO_2)$ from the 31 m height (red trace, panels a in Figures S3-S5) serve as a metric of UV radiation and as an indicator of cloud cover; the impact of cloud cover can be assessed by comparing the measured $J(NO_2)$ to that calculated under clear sky conditions by the Tropospheric Ultraviolet and Visible radiation model (TUV), version 4.4 (shown as a dashed line on panels a). The cloud cover was low ($J(NO_2) \approx 8 \times 10^{-3}\ s^{-1}$) for most of the campaign, although there were several cloudy days as shown by the significant differences observed between measured and calculated values of $J(NO_2)$ on 7, 15, 18, 22, 23, and 30 July as well as 1, 3, and 8 August.

References

Dusanter, S., Vimal, D., Stevens, P. S., Volkamer, R., and Molina, L. T.: Measurements of OH and HO_2 concentrations during the MCMA-2006 field campaign - Part 1: Deployment of the Indiana University laser-induced fluorescence instrument, Atmos. Chem. Phys., 9, 1665-1685, 2009.

Griffith, S. M., Hansen, R. F., Dusanter, S., Stevens, P. S., Alaghmand, M., Bertman, S. B., Carroll, M. A., Erickson, M., Galloway, M., Grossberg, N., Hottle, J., Hou, J., Jobson, B. T., Kammrath, A., Keutsch, F. N., Lefer, B. L., Mielke, L. H., O'Brien, A., Shepson, P. B., Thurlow, M., Wallace, W., Zhang, N., and Zhou, X. L.: OH and HO_2 radical chemistry during PROPHET 2008 and CABINEX 2009 - Part 1: Measurements and model comparison, Atmos. Chem. Phys. Discuss., 12, 2012.

Seeley, J. V., Jayne, J. T., and Molina, M. J.: High-Pressure Fast-Flow Technique for Gas Kinetics Studies, Int. J. Chem. Kinet., 25, 571-594, 1993.

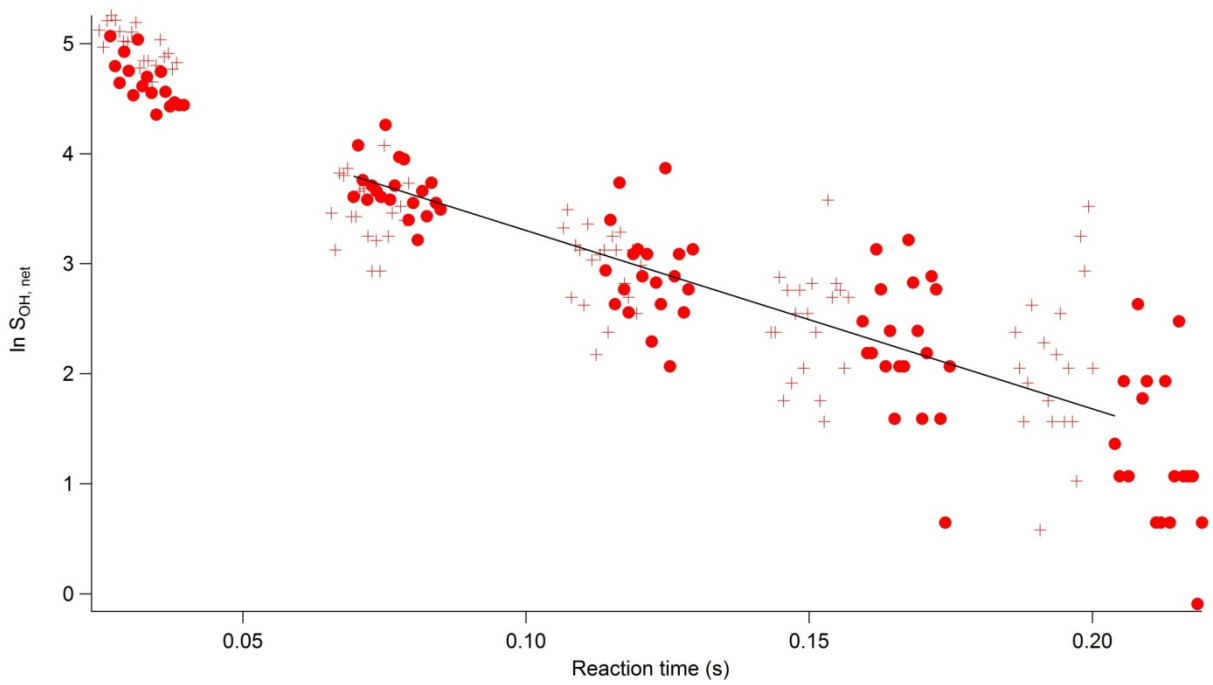

Figure S1. Two subsequent OH decays from CABINEX, one measured in the forward (crosses) and one measured in the reverse (circles) directions on 10 July 2009. The solid line shows a linear fit yielding a value of OH reactivity of 16.4 s^{-1}.

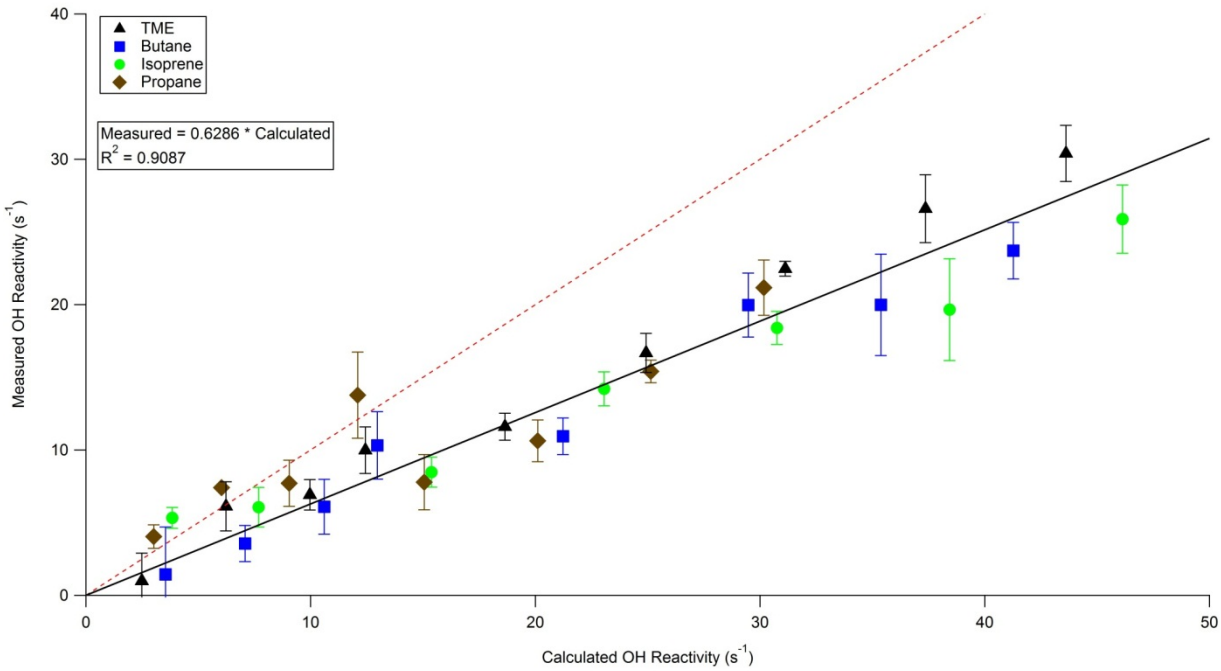

Figure S2. Summary of laboratory characterizations of IU-TOHLM instrument. The dashed line represents the 1:1 line; the solid line is a linear fit of the data. Error bars represent 1σ standard deviation of the average values.

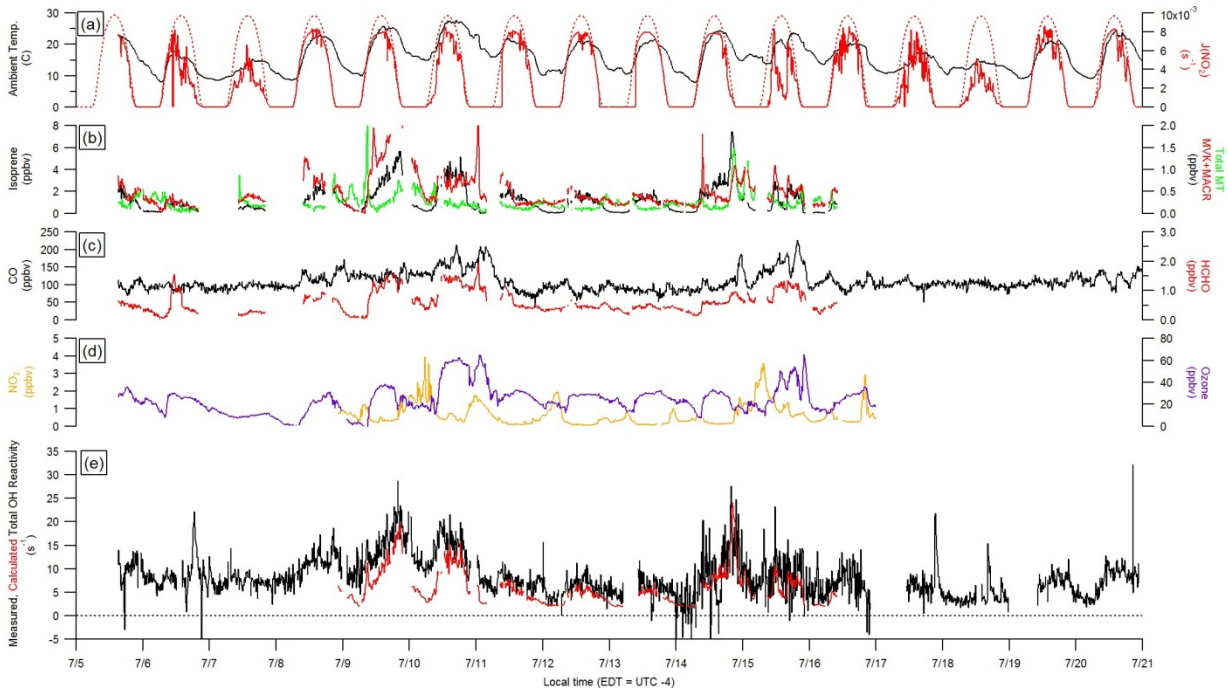

Figure S3. Time series of 10-minute averages for the 6m height. The dashed line in panel a indicates values of $J(NO_2)$ calculated by the TUV 4.4 model for clear sky conditions.

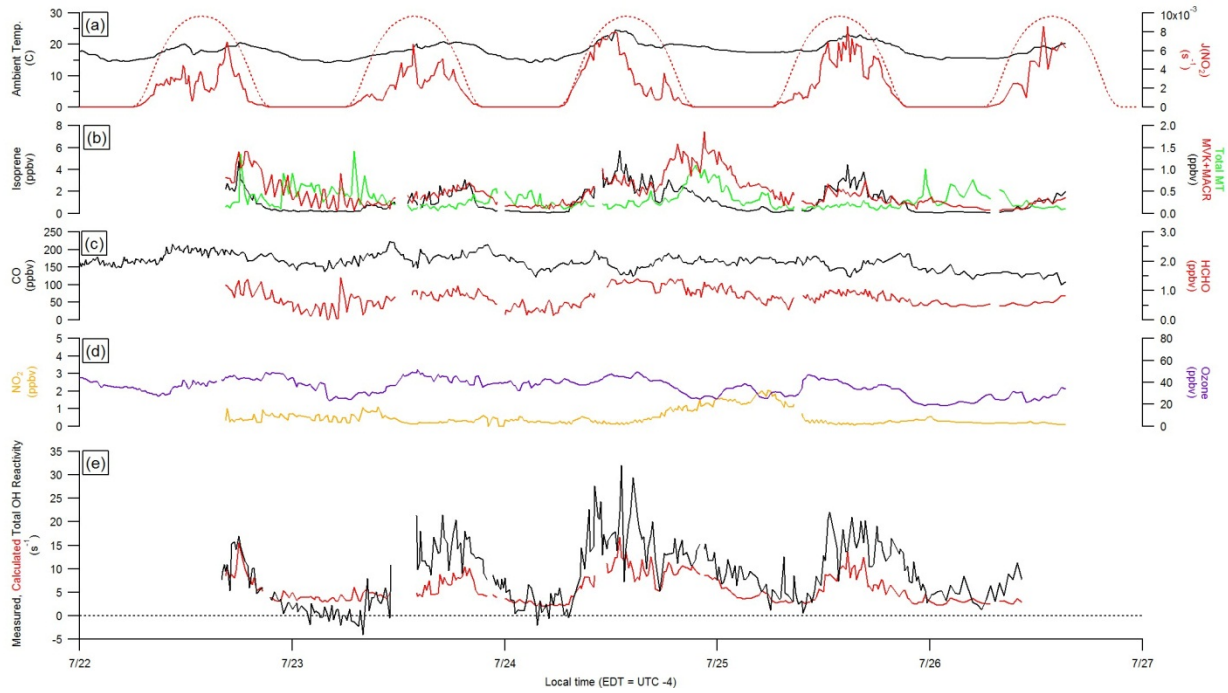

Figure S4. Time series of 10-minute averages for the 21m height.

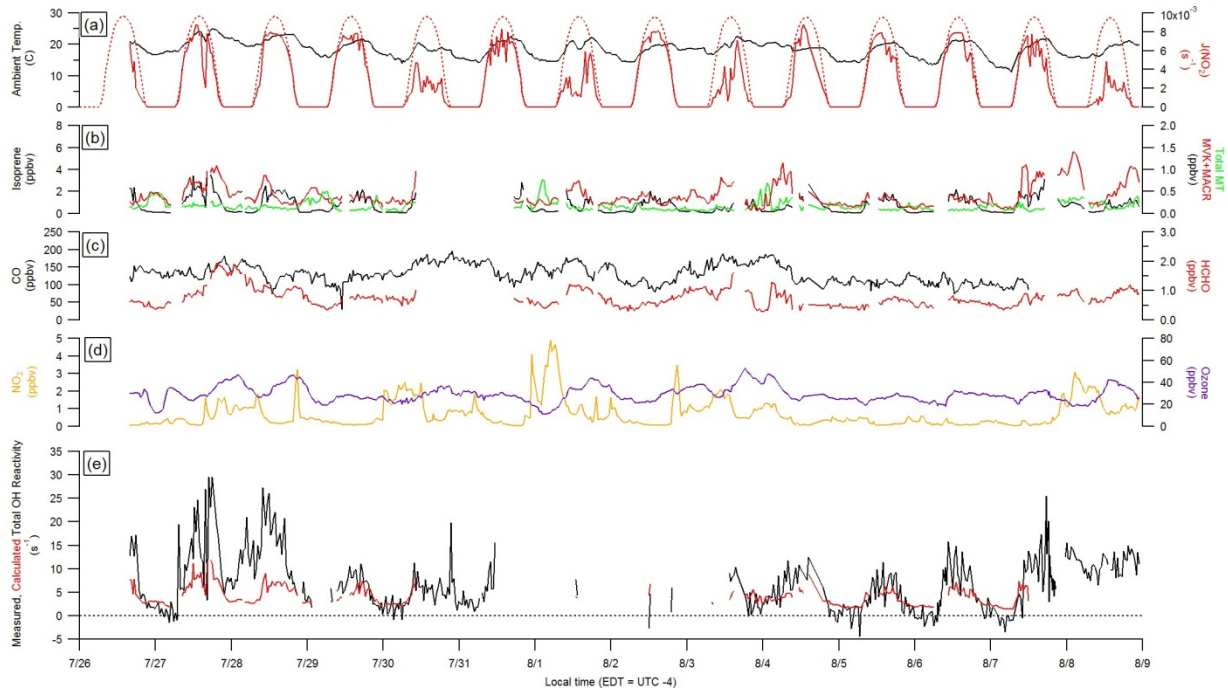

Figure S5. Time series of 10-minute averages for the 31m height.

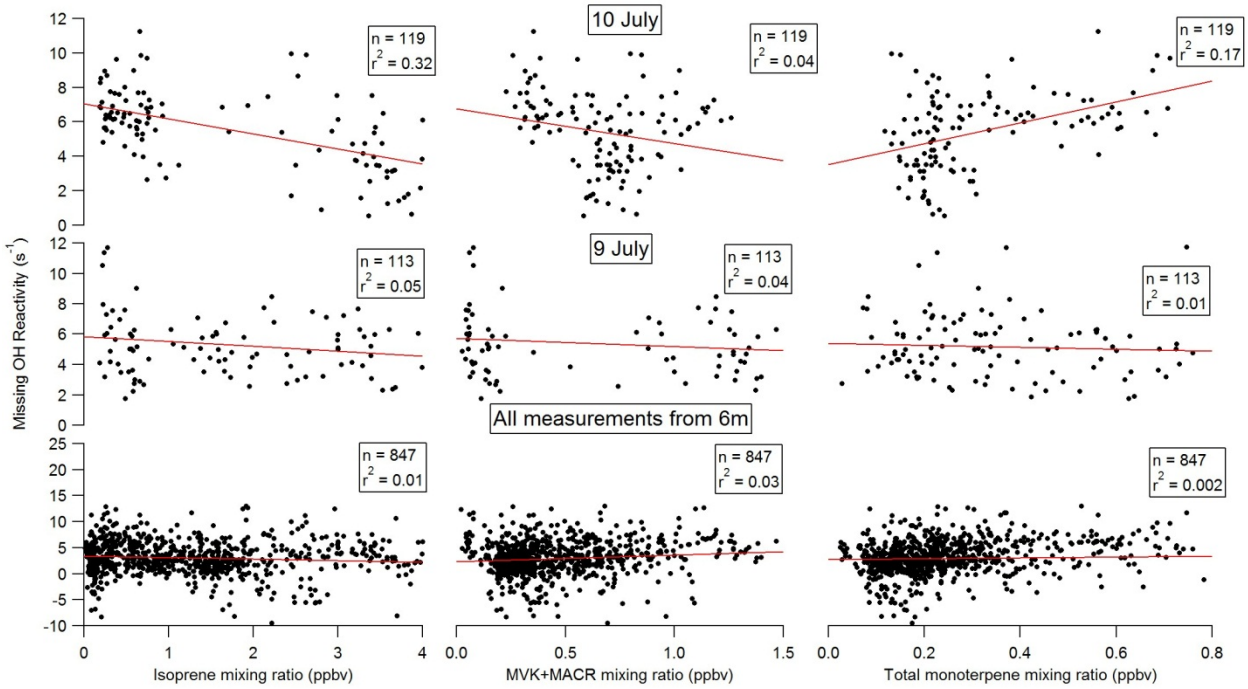

Figure S6. Plots of missing OH reactivity from the 6 m height as a function of ambient isoprene, MVK + MACR, and total monoterpene mixing ratios for 10 July (top panels), 9 July (middle panels), and the entire 6 m dataset (bottom panels).