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*Supplement of*

## **OH and HO<sub>2</sub> radical chemistry in a midlatitude forest: measurements and model comparisons**

**Michelle M. Lew et al.**

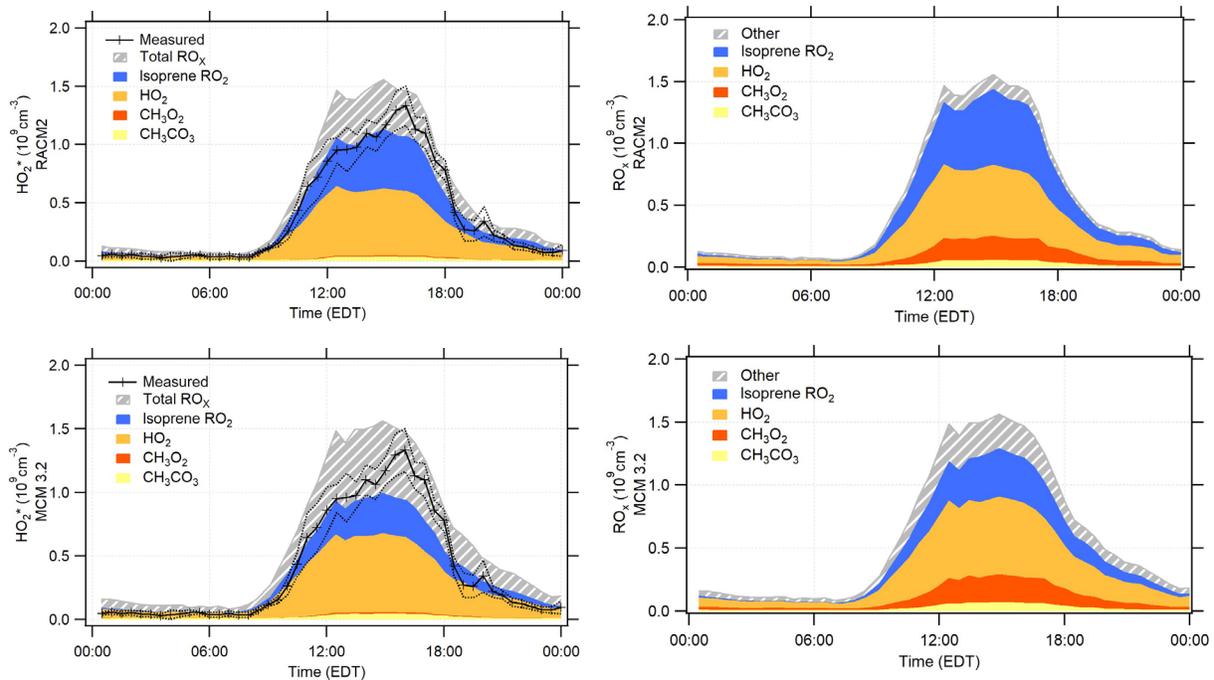
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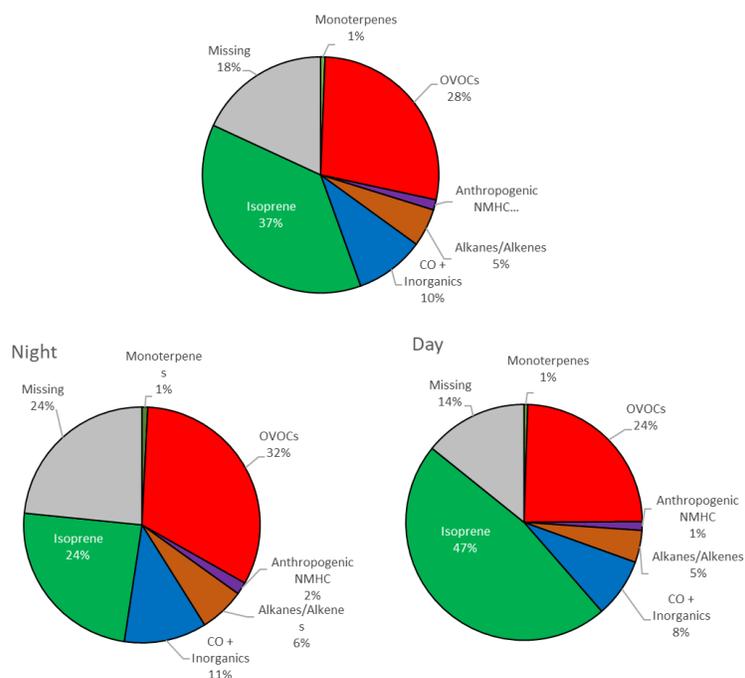
**Table S1:** Characterization of measured compounds by various institutions (IU: Indiana University, UMass: University of Massachusetts, LD: IMT Lille Douai) into RACM2 groups.

RACM2	VOCs	Source	RACM2	VOCs	Source
<b>NO</b>	NO	UMass	<b>HCHO</b>	Formaldehyde	LD
<b>NO2</b>	NO <sub>2</sub>	UMass	<b>ACD</b>	Acetaldehyde	LD
<b>H2O</b>	Water vapor	IU	<b>ACT</b>	Acetone	LD
<b>HONO</b>	Nitrous Acid	IU	<b>EOH</b>	Ethanol	LD
			<b>ACE</b>	Acetylene	LD
<b>CH4</b>	Methane	est	<b>ISO</b>	Isoprene	LD
<b>ETH</b>	Ethane	LD	<b>MACR</b>	Methacrolein	est*
<b>HC3</b>	Propane, isobutene, butane, neopentane, 2,2-dimethylbutane, 2,2-dimethylpentane	LD	<b>MEK</b>	Methyl ethyl ketone	LD
<b>HC5</b>	Isopentane, pentane, propyne, 2-methylpentane, 3-methylpentane, hexane, 2,4-dimethylpentane, 2,2,3-trimethylbutane, 3,3-dimethylpentane, 2,3-dimethylpentane, isooctane	LD	<b>MVK</b>	Methyl vinyl ketone	LD
<b>HC8</b>	Butyne, cyclopentane + 2,3-dimethylbutane, cyclohexane, 2-methylhexane, heptane, octane, nonane, undecane, dodecane, nC13, nC14	LD	<b>API</b>	$\alpha$ -pinene, $\beta$ -pinene, 3-carene	LD
<b>ETE</b>	Ethene	LD	<b>ROH</b>	Borneol	LD
<b>OLT</b>	Propene, 1-butene, isobutene, 3-methyl-1-butene, 1-pentene, 2-methyl-1-butene, hexene	LD	<b>BENZENE</b>	Benzene	LD
<b>OLI</b>	trans-2-butene, cis-2-butene, trans-2-pentene, 2-methyl-2-butene, 1-pentene, cis-2-pentene, cyclopentane	LD	<b>TOL</b>	Toluene, chlorobenzene, ethylbenzene, styrene, isopropylbenzene, n-propylbenzene, 2-ethyltoluene, n-butylbenzene	LD
<b>DIEN</b>	1,3-butadiene, 3-methyl-1,4-pentadiene	LD	<b>MXYL/PXYL</b>	m+p xylene, 3-ethyltoluene, 4-ethyltoluene, 1,3,5-trimethylbenzene + camphene, 1,2,4-trimethylbenzene + nC10, 1,2,3-trimethylbenzene + $\alpha$ -terpinene	LD
<b>KET</b>	Nopinone	LD	<b>OXYL</b>	o-xylene	LD
			<b>ORA1</b>	Formic Acid	LD

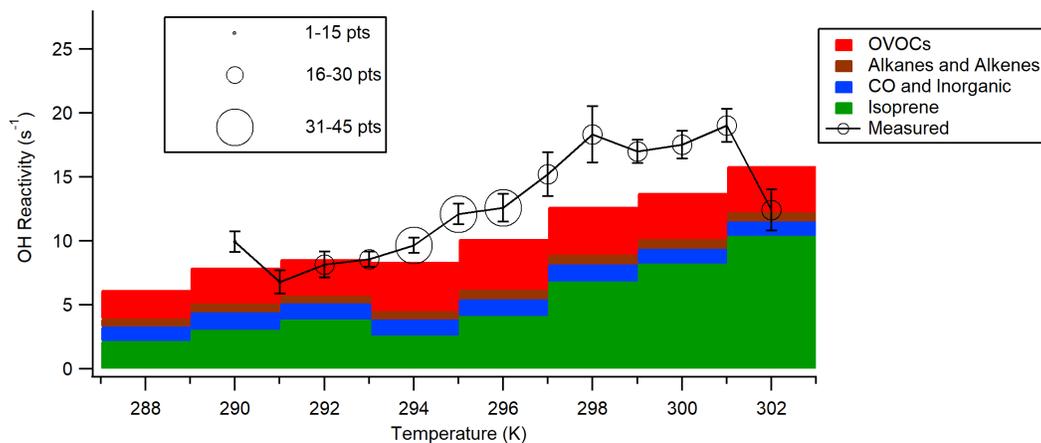
\*Mixing ratios of CO were estimated based on published emission ratios of CO with benzene (Warneke et al., 2007). Mixing ratios of methacrolein were estimated based on measured MVK/MACR ratios (Apel et al., 2002)



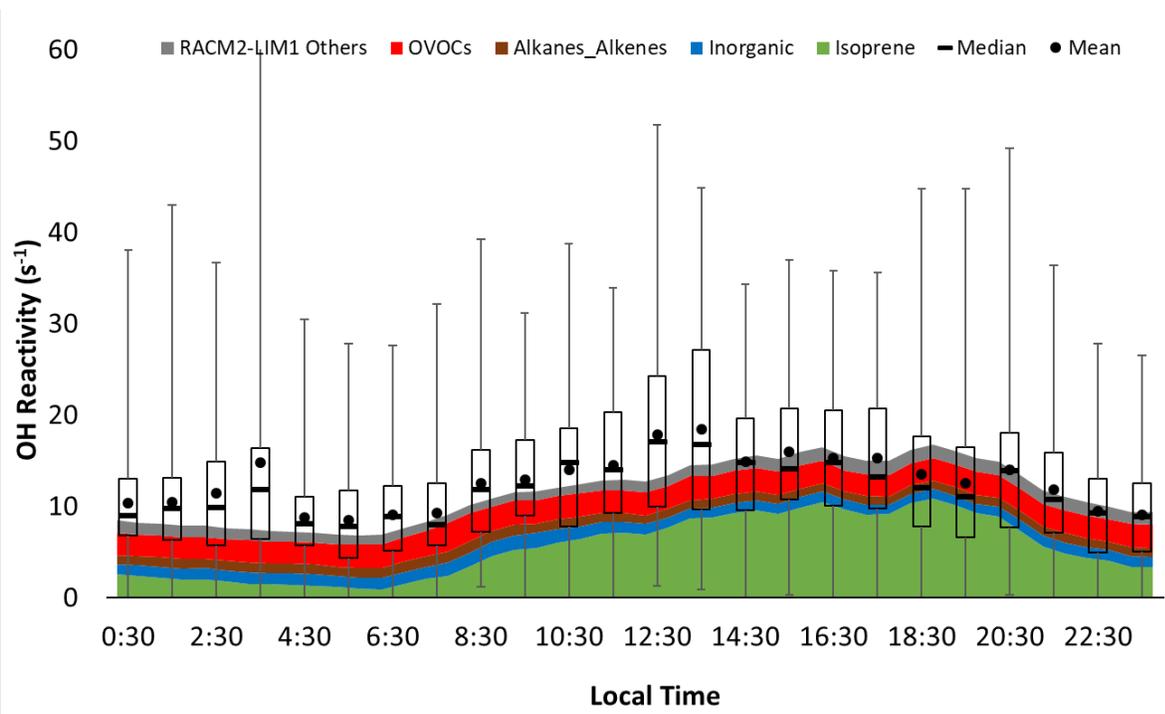
**Figure S1.** The RACM2 and MCM 3.2 diurnal average modeled peroxy radical concentration and composition for the days when NO was measured simultaneously (see text). Left panels show the modeled contribution to the HO<sub>2</sub>\* concentrations. Measured 30-min mean HO<sub>2</sub>\* is shown by the black line with  $\pm 1\sigma$  standard error shown by the dotted lines. The calibration uncertainty of the measurements (not shown) is 38% ( $2\sigma$ ). Right panels show the total RO<sub>x</sub> (RO<sub>2</sub> +HO<sub>2</sub>) composition predicted by each model.



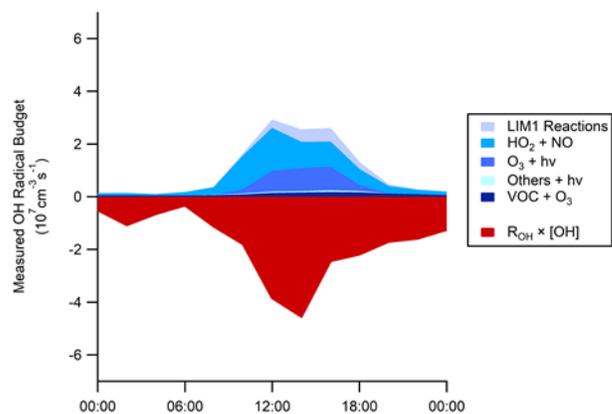
**Figure S2.** The diurnal average components of the mean calculated OH reactivity over the course of the campaign (top), as well as that during daytime (08:00-20:00 hours) and nighttime (20:00-08:00 hours).



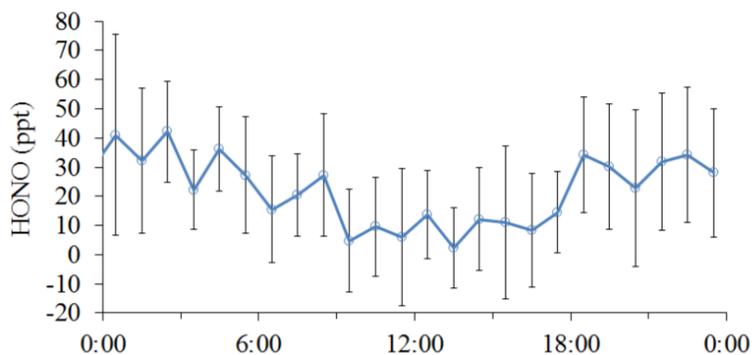
**Figure S3.** Median measured and calculated OH reactivity separated by the measured components over the observed temperature range. Size of the measured symbol indicates the number of measurements in each temperature bin. Error bars represent  $\pm 1\sigma$  standard error.



**Figure S4.** Diurnal box and whiskers plot of observed total OH reactivity showing the mean and median values for each hour with the mean calculated values from the measured OH sinks as well as the unmeasured oxidation products from the RACM2-LIM1 model results. Error bars show range of measurements and bars show Q1 and Q3 for the measured OH reactivity.



**Figure S5:** Experimental daytime OH radical budget for the days when NO was measured based on measured production and loss rates. Concentrations of HO<sub>2</sub> used to calculate the HO<sub>2</sub> + NO production rate were estimated based on the measured concentrations of HO<sub>2</sub>\* and the modeled HO<sub>2</sub>/HO<sub>2</sub>\* ratio for these days (approximately 0.6). The modeled LIM1 contribution to OH production is included for reference. The OH loss rate is based on the average total OH reactivity measurements for this period.



**Figure S6.** Diurnal average measurements of HONO during the IRRONIC 2015 campaign. Error bars represent the standard error of the measurements.

## References

Apel, E. C. et al., Measurement and interpretation of isoprene fluxes and isoprene, methacrolein, and methyl vinyl ketone mixing ratios at the PROPHET site during the 1998 Intensive, *J. Geophys. Res.*, 107(D3), doi:10.1029/2000jd000225, 2002.

Warneke, C., et al., Determination of urban volatile organic compound emission ratios and comparison with an emissions database, *J. Geophys. Res.*, 112, D10S47, doi:10.1029/2006JD007930, 2007.