



*Supplement of*

## **Missing peroxy radical sources within a summertime ponderosa pine forest**

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# Missing Peroxy Radical Sources within a Summertime Ponderosa Pine Forest

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## *Supplementary Information*

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### Correction of MBO and Monoterpenes for In-Canopy Gradients

As mentioned in Sect. 2.3 of the main text, MBO and speciated monoterpene (MT) measurements were recorded at 25 m by the PTR-TOF-MS and TOGA instruments, respectively. It is preferable to constrain the model with these observations due to their temporal coverage (and speciation, in the case of MTs); however, as these species are directly emitted, they must first be corrected for the vertical gradient in mixing ratios. Figure S2 illustrates this correction, which involves three steps:

- 1) Mean diel cycles of MBO and total MT from the NCAR quadrupole PTR-MS at 4 m and 23 m are interpolated from their reporting interval of 90 min to the model time step of 30 min.
- 2) The ratio of measurements at these two heights is used to generate a time-dependent gradient correction factor.
- 3) This correction factor is applied to MBO (PTR-TOF-MS) and speciated MT (TOGA) observations at 25 m to estimate their within-canopy concentrations.

In-canopy gradients of these compounds can be significant, with correction factors ranging from 0.9 to 1.5 for MBO and from 1.2 to 1.8 for monoterpenes (Fig. S2).

### Estimation of Model Uncertainty

Uncertainty in model-calculated mixing ratios arises mainly from confidence in observational constraints. The primary drivers of model-predicted peroxy radical concentrations in the present work are NO, VOCs, O<sub>3</sub>, photolysis frequencies and OH (for scenarios where OH is constrained). Uncertainties for these measurements are listed in Table S1. To quantify the corresponding model uncertainty, a series of sensitivity runs were performed where each constraint was set to its lower or upper uncertainty limit while holding all other parameters at their nominal values. In the case of VOCs, including HCHO and CHOCHO, all constraints were taken simultaneously to their lower or upper limit (as opposed to a separate model run for each compound). Figure S3 shows the percentage change in HO<sub>2</sub><sup>\*</sup>, RO<sub>2</sub><sup>\*</sup>, total peroxy radicals and OH for each sensitivity experiment. Also shown is the total uncertainty, calculated by adding all of the upper and lower uncertainty limits in quadrature. For peroxy radicals, confidence in OH observations is the largest contributor to model uncertainty. Technically this contribution is absent when OH is not constrained to observations, which significantly decreases the total calculated uncertainty; however, we still use the total uncertainty from the base case as an upper limit for the uncertainty in the ModOH case. For OH, NO is the largest driver of uncertainty, followed by

VOC mixing ratios. The total uncertainties shown in Figure S3 correspond to error bars for model mixing ratios in the main text.

### Model-Assisted Separation of HO<sub>2</sub> and RO<sub>2</sub> Measurements

As discussed in the main text, the signal from the nominal HO<sub>2</sub> channel (high NO/O<sub>2</sub> mode) of the PerCIMS measurement likely includes a positive artifact due to fast conversion of certain organic peroxy radicals to HO<sub>2</sub>. In particular,  $\beta$ -hydroxyalkylperoxy radicals, formed via OH-addition to alkenes, are known to cause such interferences (Fuchs et al., 2011; Hornbrook et al., 2011). Given that unsaturated biogenic hydrocarbons comprise a major fraction of reactive VOC during BEACHON-ROCS, we expect such radicals to be abundant in this environment. While the primary PerCIMS observations of HO<sub>2</sub>\* and HO<sub>2</sub> + RO<sub>2</sub> provide a useful separation of the peroxy radical pool, it would be advantageous to also have an observational constraint on HO<sub>2</sub>. Using 0-D box model results, we can explore potential corrections to the PerCIMS measurements to obtain an estimate of ambient HO<sub>2</sub> mixing ratios. Here we investigate four calculations:

- 1) Correction of measured HO<sub>2</sub>\* with modeled  $\beta$ -hydroxyalkylperoxy radical concentrations;
- 2) Correction of measured HO<sub>2</sub> + RO<sub>2</sub> with the modeled HO<sub>2</sub>/(HO<sub>2</sub> + RO<sub>2</sub>) ratio;
- 3) Correction of measured HO<sub>2</sub>\* with the modeled HO<sub>2</sub>/HO<sub>2</sub>\* ratio; and
- 4) Correction of PerCIMS sensitivities using the modeled RO<sub>2</sub> distribution.

The first three methods are relatively straightforward. Subtraction of modeled  $\beta$ -hydroxyalkylperoxy radicals from measured HO<sub>2</sub>\* is the simplest method, though this will overestimate HO<sub>2</sub> if the model underestimates concentrations of these radicals or if additional RO<sub>2</sub> also contribute to the HO<sub>2</sub>\* signal. The second and third calculations assume that the model adequately represents the relative distribution of peroxy radicals, even though absolute abundances are too low. This partitioning is largely controlled by the competition of HO<sub>2</sub> sinks via reaction with NO, HO<sub>2</sub> and RO<sub>2</sub>. As noted in the main text (see e.g. Fig. 4), the HO<sub>2</sub>/(HO<sub>2</sub> + RO<sub>2</sub>) ratio tends to decrease with higher peroxy radical levels, reflecting the somewhat faster rate of RO<sub>2</sub> + HO<sub>2</sub> relative to HO<sub>2</sub> + HO<sub>2</sub>. In contrast, reaction with NO is less sensitive to the nature of the peroxy radical and forces this ratio to approach a value of 0.5 due to the fast cycling between RO<sub>2</sub>, HO<sub>2</sub> and OH. Thus, since peroxy radicals are under-predicted during the day, we might expect the modeled HO<sub>2</sub>/(HO<sub>2</sub> + RO<sub>2</sub>) ratio to be too high, resulting in an over-estimate of HO<sub>2</sub>. Non-cycling radical sources (e.g. oVOC photolysis or decomposition of PAN-like compounds) could

also influence this estimate if they were sufficiently strong. Similar qualifications hold for the HO<sub>2</sub>/HO<sub>2</sub>\* method. Additionally, this calculation is tied to our assumptions regarding which RO<sub>2</sub> to include in the model HO<sub>2</sub>\* family. A list of these species is provided in Table S2.

The last method is more sophisticated as it involves manipulation of raw instrument signals. Following equations (5) – (12) of Hornbrook et al. (2011), the PerCIMS signals in low and high NO/O<sub>2</sub> modes are related to ambient concentrations as

$$S_{low}F_{low} = [HO_2] + \alpha_{low}[RO_2] \quad (S1)$$

$$S_{high}F_{high} = [HO_2] + \alpha_{high}[RO_2] \quad (S2)$$

Here,  $S$  is the background-corrected instrument signal,  $F$  is the calibrated sensitivity to HO<sub>2</sub>, and  $\alpha$  is the empirically-determined ratio of the calibration factor for RO<sub>2</sub> relative to that for HO<sub>2</sub>. By default, concentrations of HO<sub>2</sub> and HO<sub>2</sub> + RO<sub>2</sub> are calculated by inverting these equations and using the  $\alpha$  values determined for CH<sub>3</sub>O<sub>2</sub> ( $\alpha_{low} = 1.22$ ,  $\alpha_{high} = 0.17$ ). We can improve upon this calculation by estimating  $\alpha$  as the weighted sum of contributions from each RO<sub>2</sub>:

$$\alpha_{weighted} = \sum_i \alpha_i [RO_2]_i / \sum_i [RO_2]_i \quad (S3)$$

Unfortunately,  $\alpha$  values have only been determined for a handful of peroxy radicals, mostly those derived from anthropogenic alkanes and alkenes (Hornbrook et al., 2011). For this analysis, we assume that all  $\beta$ -hydroxyalkylperoxy radicals (Table S2) exhibit the same sensitivity as isoprene ( $\alpha_{low} = 1.18$ ,  $\alpha_{high} = 1.12$ ), while other RO<sub>2</sub> behave like CH<sub>3</sub>O<sub>2</sub>. Using the RO<sub>2</sub> distribution from the base model simulation (Fig. 4), we calculate new values (averaged over 24 hours) of  $\alpha_{low} = 1.201 \pm 0.001$  and  $\alpha_{high} = 0.61 \pm 0.02$ . Equations (S1) and (S2) are first used to deconvolute  $S_{low}F_{low}$  and  $S_{high}F_{high}$  from observations (using  $\alpha$ -values for CH<sub>3</sub>O<sub>2</sub>). New concentrations for HO<sub>2</sub> and HO<sub>2</sub> + RO<sub>2</sub> are then calculated with the weighted  $\alpha$ -values.

Figure S6 compares the HO<sub>2</sub> and RO<sub>2</sub> mixing ratios calculated from all methods with the measured HO<sub>2</sub>\* and RO<sub>2</sub>\*. Note that total peroxy radical concentrations remain the same in all cases. The first three methods decrease HO<sub>2</sub> to near or just below the lower uncertainty limit throughout the day, though the decrease is relatively smaller at midday for the  $\beta$ -RO<sub>2</sub> subtraction (first) method. HO<sub>2</sub> derived from these corrections generally maintains the same diel shape as HO<sub>2</sub>\*, though from the changes to RO<sub>2</sub> it is clear that these methods preferentially shift HO<sub>2</sub> into RO<sub>2</sub> at noontime, with

comparatively smaller changes in the afternoon. HO<sub>2</sub> estimated via the sensitivity correction (fourth) method is similar to that from the ratio-scaling methods at mid-day but significantly lower in the morning and afternoon. The profile of this corrected HO<sub>2</sub> seems unexpectedly sharp, especially when considering other observations such as OH concentrations. This may indicate that 1) the model overpredicts the contribution of  $\beta$ -hydroxyalkylperoxy radicals to total RO<sub>2</sub> at these times, or 2) it is not appropriate to use isoprene-peroxy radicals as a proxy for all  $\beta$ -hydroxyalkylperoxy radicals. In either case, the accumulation of uncertainties from measurements and model results makes it difficult to utilize the derived HO<sub>2</sub> and RO<sub>2</sub> mixing ratios with sufficient confidence.

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Table S1. BEACHON-ROCS 2010 observations used in this study

Parameter	Instrument/Technique <sup>a</sup>	Uncertainty	Height (m)	Reference
HO <sub>2</sub> , RO <sub>2</sub> + HO <sub>2</sub>	PeRCIMS	35%	1.6	(Hornbrook et al., 2011)
OH	CIMS	35%	1.6	(Tanner et al., 1997)
OH reactivity	Laser pump-probe LIF	5%	4	(Sadanaga et al., 2004)
NO	Chemiluminescence	15%	2	Eco Physics CLD 88 p
NO <sub>2</sub>	Conversion to NO	15%	2	Droplet Technologies Blue Light Converter
O <sub>3</sub>	UV absorption	2%	2	2B Technology
CO	IR absorption	15%	3	Thermo Scientific Model 48i
VOC	PTRMS-TOF <sup>b</sup>	15%	25	(Graus et al., 2010)
	TOGA (Gas Chromatography) <sup>c</sup>	15%	25	(Apel et al., 2010)
	PTRMS-Quad <sup>d</sup>	15%	4, 23	(Karl et al., 2009)
HCHO	LIF	20%	9	(Hottle et al., 2009) (DiGangi et al., 2011)
Glyoxal	Laser-Induced Phosphorescence	20%	2	(Huisman et al., 2008)
PAN, PPN	Thermal Dissociation CIMS	20%	25	(Slusher et al., 2004)
J(NO <sub>2</sub> )	Filter Radiometer	11%	1.6, 25 <sup>e</sup>	(Shetter et al., 2003)
T, P, RH	-	-	2	Vaisala WXT-520

<sup>a</sup>CIMS: chemical ionization mass spectrometry; LIF: laser-induced fluorescence; PTRMS: proton transfer mass spectrometer; TOF: time-of-flight.

<sup>b</sup>Includes MBO, benzene, toluene and acetaldehyde.

<sup>c</sup>Includes isoprene,  $\alpha$ -pinene,  $\beta$ -pinene, limonene, camphene, non-specified monoterpenes, acetone, methanol, methyl vinyl ketone, methacrolein, propanal, n-butanal and 1,3-butadiene.

<sup>d</sup>MBO and total monoterpene gradients used to correct PTRMS-TOF and gas chromatography data (see text for details).

<sup>e</sup>Measured downwelling J(NO<sub>2</sub>) multiplied by 1.05 to account for upwelling radiation as determined from a single day of observations.

Table S2. Contribution of model species to HO<sub>2</sub>\*

Species	Parent VOC	% of HO <sub>2</sub> * <sup>a</sup>
HO2	-	62.2
MBOAO2 MBOBO2	MBO	22.7
ISOPAO2 ISOPBO2 ISOPCO2 ISOPDO2	Isoprene	4.5
APINAO2 APINBO2 APINCO2	α-pinene	0.8
BPINAO2 BPINBO2 BPINCO2	β-pinene	2.8
LIMAO2 LIMBO2 LIMCO2	Limonene	2.3
LIMALO2 LIMALAO2 LIMALBO2	Limal	2.7
MT02	Camphene, Unspeciated MT	0.6
HMVKA02 HMKVBO2	MVK	1.1
MACRO2 MACROHO2	MACR	0.1
BUTDBO2 BUTDCO2	Butadiene	0.1
ACO3B	Acrolein	0.01
BZBIPERO2	Benzene	0.003
PHENO2	Phenol	0.0005
TLBIPERO2	Toluene	0.04
CRESO2	Cresol	0.002

<sup>a</sup>24-hour average from base model simulation.

Table S3. Very reactive VOC reaction mechanism

Reaction <sup>a</sup>	$k(298K)^b$ ( $\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ )	Notes
$\text{VRVOC} + \text{OH} \rightarrow \text{VRO21}$	$2.0 \times 10^{-10}$	-
$\text{VRVOC} + \text{O}_3 \rightarrow 0.1\text{VRO22} + 0.1\text{OH} + 0.9\text{VROX}$	$1.2 \times 10^{-14}$	Assumes 10% radical yield
$\text{VRVOC} + \text{NO}_3 \rightarrow 0.9\text{VRO23} + 0.1\text{VROX}$	$2.2 \times 10^{-11}$	Assumes 10% alkyl nitrate yield
$\text{VRO2n} + \text{NO} \rightarrow \text{VROX} + 0.76\text{NO}_2 + 0.76\text{HO}_2$	$9.0 \times 10^{-12}$	Assumes 24% alkyl nitrate yield
$\text{VRO2n} + \text{HO}_2 \rightarrow \text{VROX}$	$2.1 \times 10^{-11}$	-
$\text{VRO2n} + \text{RO}_2 \rightarrow \text{VROX} + 0.7\text{HO}_2$	$9.0 \times 10^{-14}$	-

<sup>a</sup>Reactions follow Wolfe et al. (2011), except that initial VRO2 are speciated according to oxidant. All VRO2 are assigned the same loss processes. VROX is a generic oxidized product that does not undergo further chemistry.

<sup>b</sup>Rate constants are equal to those of  $\beta$ -caryophyllene for VRVOC and BPINAO2 for VRO2.

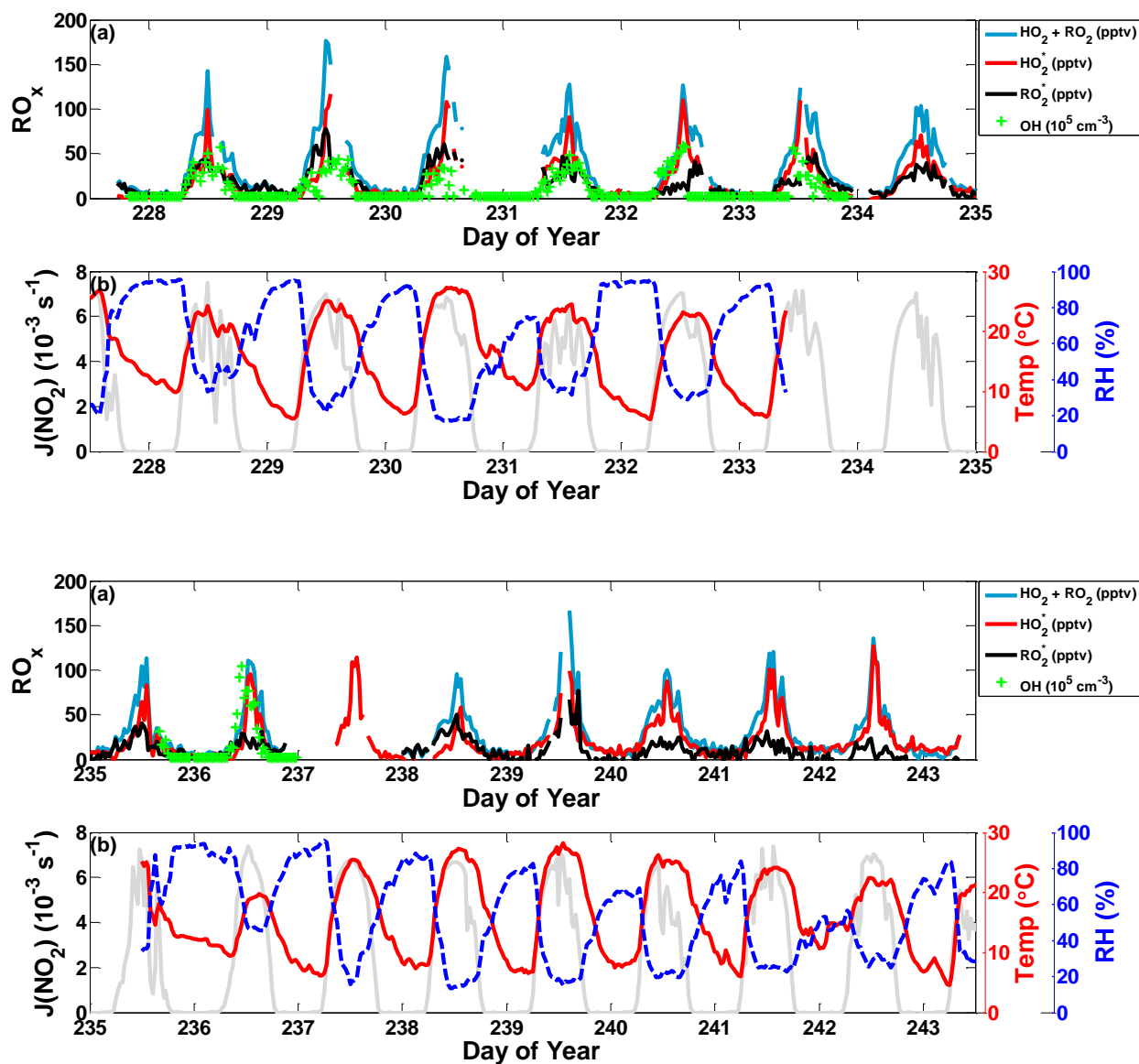


Figure S1. Full time series for observations of peroxy radicals and meteorology during BEACHON-ROCS. (a) Total peroxy radicals (blue line), HO<sub>2</sub>\* (red line), RO<sub>2</sub>\* (black line) and OH (green crosses). Peroxy radicals units are pptv, and OH units are 10<sup>5</sup> molec cm<sup>-3</sup>. (b) Above-canopy NO<sub>2</sub> photolysis frequencies (gray solid line), air temperature (red solid line) and relative humidity (blue dashed line). All data are displayed as 30-minute averages. OH values below the instrument detection limit (5 × 10<sup>5</sup> cm<sup>-3</sup>) are nominally set to half of this value.

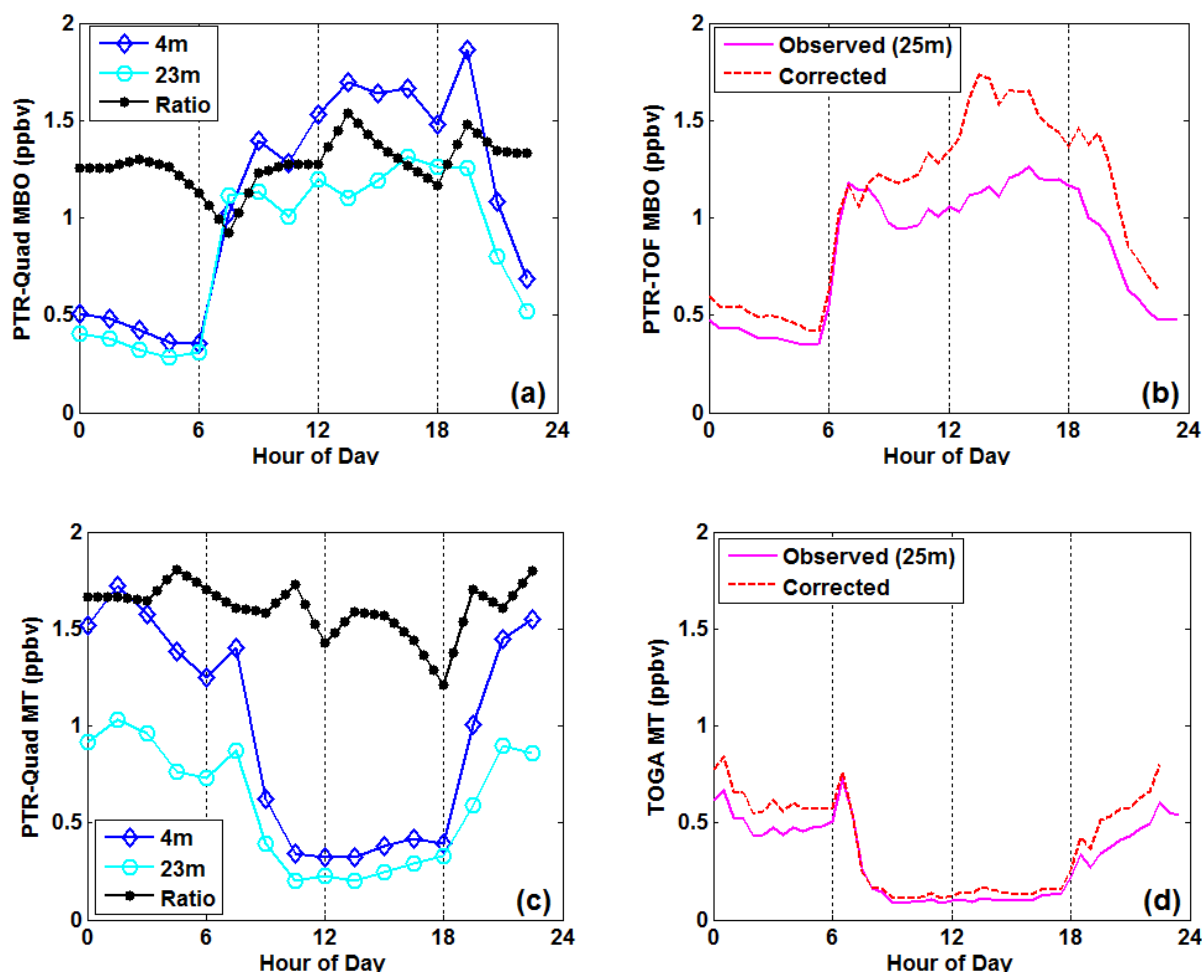


Figure S2. Demonstration of vertical gradient corrections for MBO (a, b) and monoterpenes (c, d). The left panels show diurnal mean observations of MBO and total monoterpenes from the PTR-quadrupole instrument, with inlet heights at 4m (blue diamonds) and 23 m (cyan circles). Also shown is the ratio of the 4m measurement to the 23m measurement, which defines the correction factor described in the SI text. The right panels show observations of MBO and total monoterpenes taken at 25m via the PTR-TOF and TOGA instruments, respectively. Total monoterpenes represent the sum of  $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, myrcene, limonene, 1,8-cineole, camphene and a group of unspeciatiated monoterpenes. Observations (solid magenta line) are multiplied by the correction factor to give gradient-corrected values (dashed red line), which are used in model calculations.

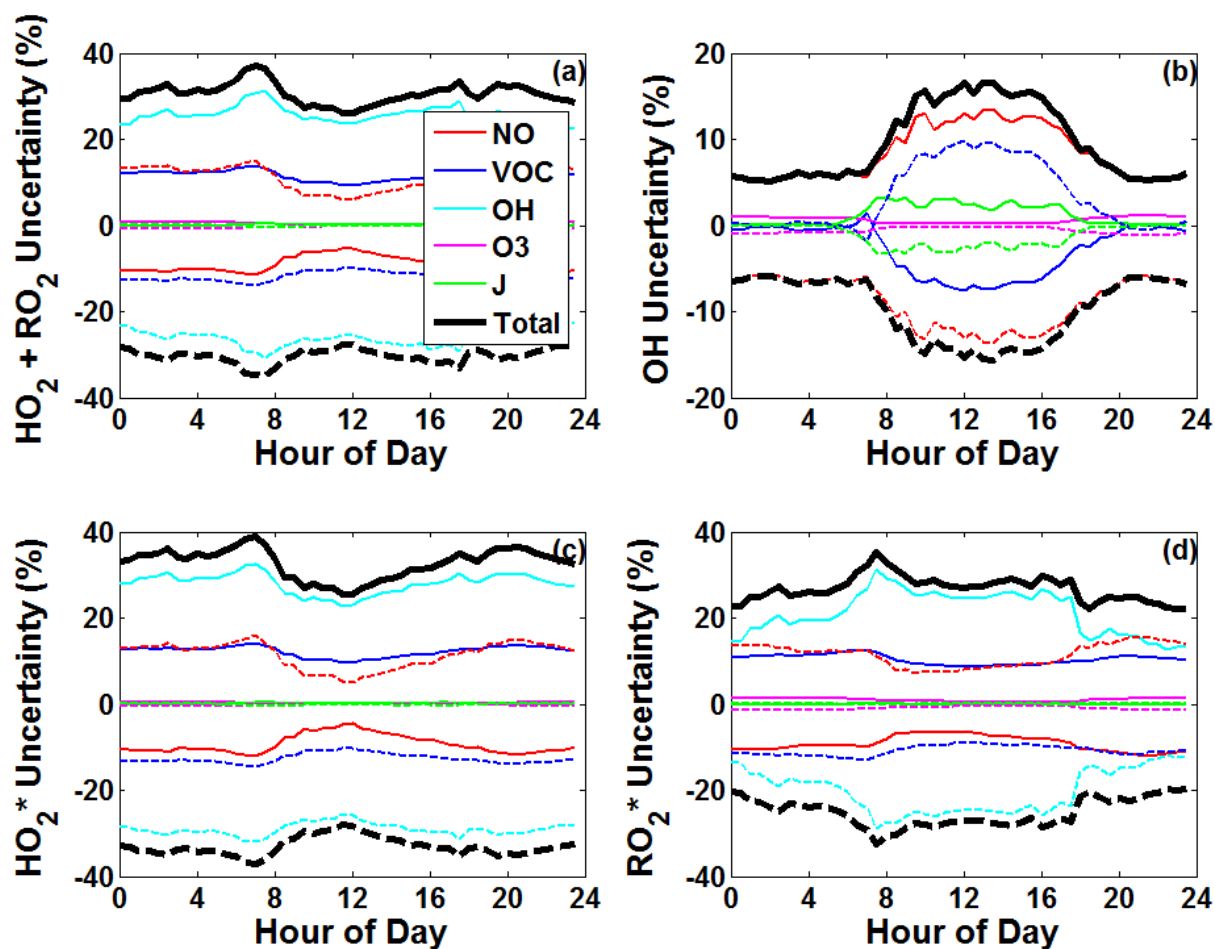


Figure S3. Results of sensitivity runs for estimating model uncertainty stemming from observational constraints for (a) total peroxy radicals, (b) OH, (c)  $\text{HO}_2^*$  and (d)  $\text{RO}_2^*$ . Thin lines represent percentage change in modeled concentrations when setting each listed species (NO, VOC, OH,  $\text{O}_3$ , or photolysis frequencies) to their upper (solid lines) or lower (dashed lines) limits. For peroxy radicals, the base model scenario is used as the reference case, while for OH the “ModOH” scenario is used. Thick black lines denote the total uncertainty, calculated by summing up all positive or negative uncertainties in quadrature.

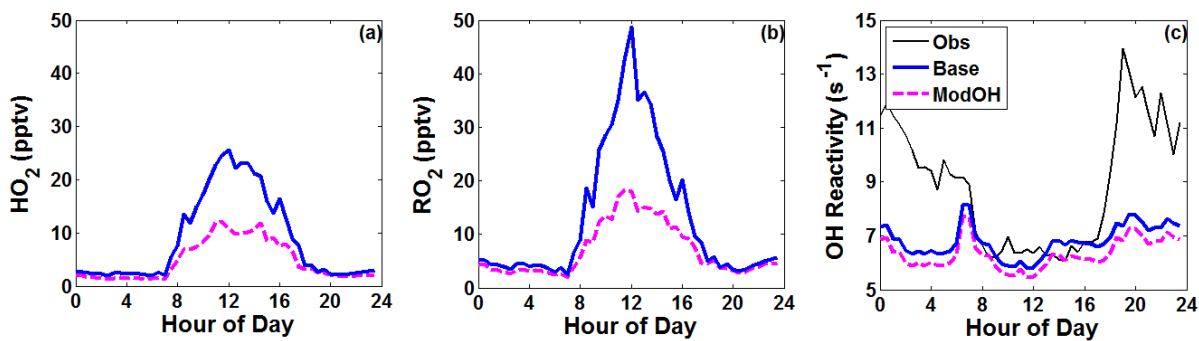


Figure S4. Additional 0-D model results: (a)  $\text{HO}_2$ , (b) total  $\text{RO}_2$  and (c) OH reactivity. Model results are shown for the base scenario (solid blue line) and ModOH scenario (dashed magenta line). Total observed OH reactivity is also shown (solid black line). Total  $\text{RO}_2$  represents the sum of 347 model species. Modeled OH reactivity is calculated by summing the loss rate of OH from all relevant reactions (1014 total) and dividing by the OH concentration.

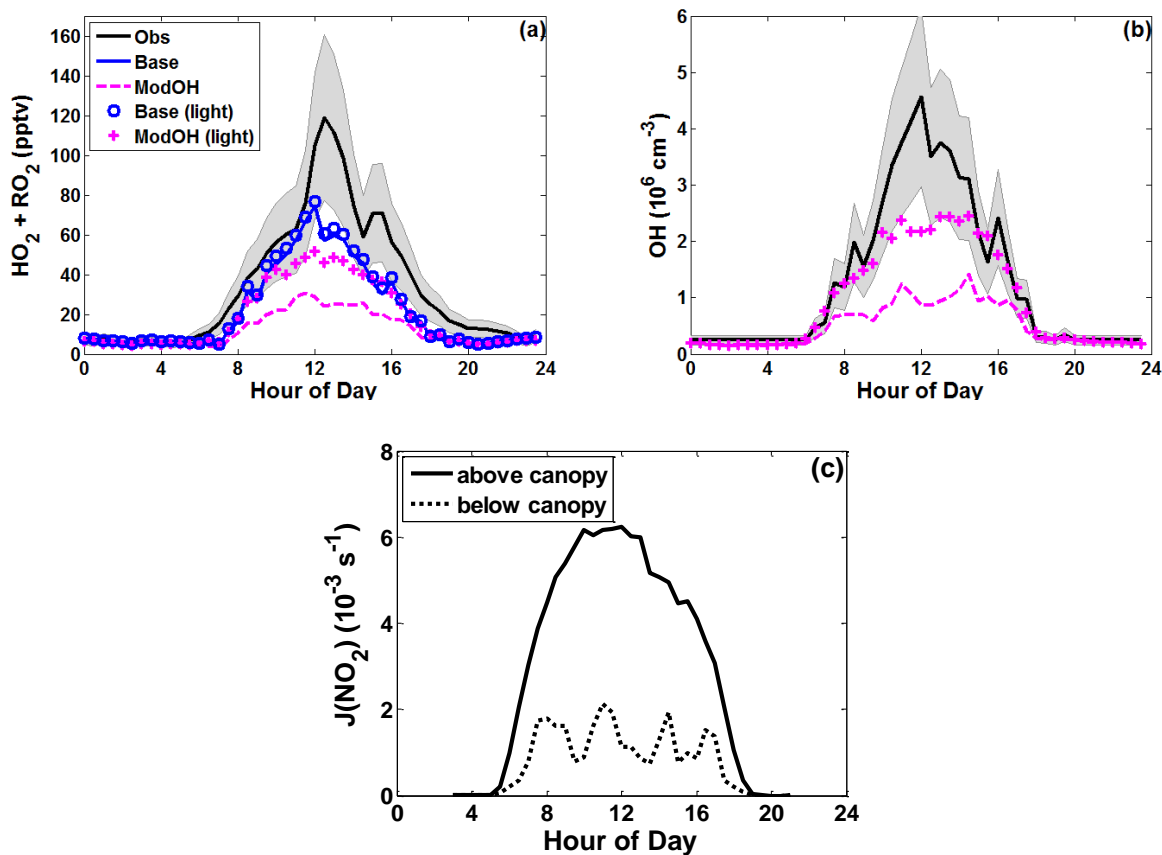


Figure S5. Comparison of model output for (a) total peroxy radicals and (b) OH concentrations under varying sunlight conditions. Solid black lines with shaded gray areas represent observations and their associated uncertainties. Colored lines denote model results with photolysis frequencies constrained by below-canopy  $J(\text{NO}_2)$  measurements and include the base (solid blue line) and ModOH (dashed magenta line) scenarios. Symbols denote results for scenarios constrained by  $J(\text{NO}_2)$  measured above the canopy (blue circles: base, magenta crosses: ModOH). Observed  $\text{NO}_2$  photolysis frequencies are also shown (c).



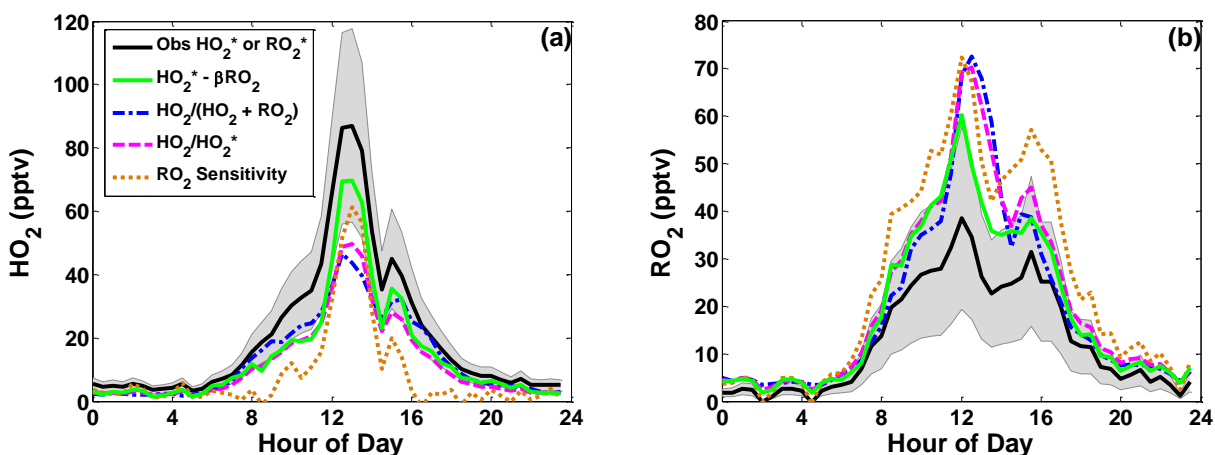


Figure S6. Comparison of model-assisted corrections to peroxy radical observations. Black lines with shaded areas denote observations and their associated uncertainties; note that the  $\text{RO}_2$  uncertainty is 50% due to combined uncertainties of the  $\text{HO}_2^*$  and  $\text{HO}_2 + \text{RO}_2$  measurements (35% each). Correction methods include subtraction of modeled  $\beta$ -hydroxyalkylperoxy radicals (solid green line), scaling by modeled  $\text{HO}_2/(\text{HO}_2 + \text{RO}_2)$  (dash-dotted blue line), scaling by modeled  $\text{HO}_2/\text{HO}_2^*$  (dashed magenta line) and correction of PerCIMS sensitivities with the modeled  $\text{RO}_2$  distribution (dotted orange line).

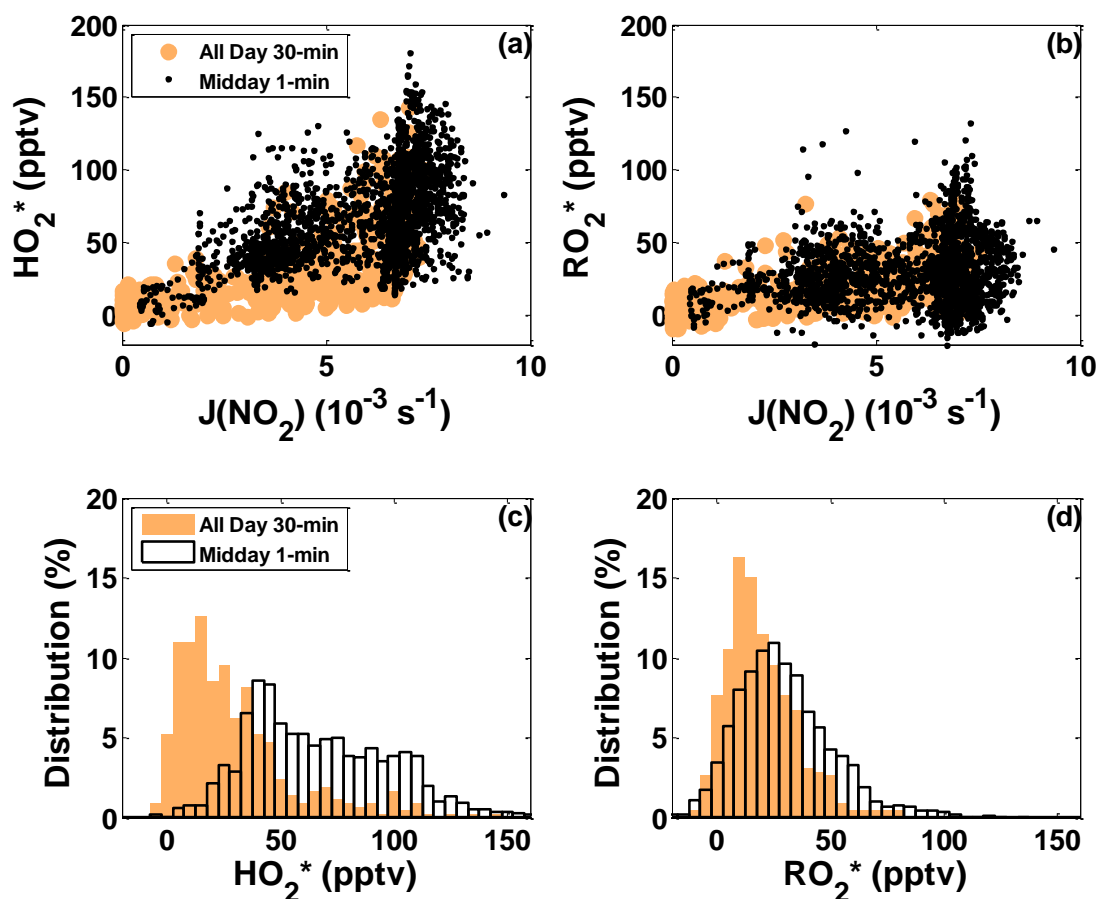


Figure S7. (a-b) Scatter plots of observed peroxy radical mixing ratios and above-canopy (25 m)  $\text{NO}_2$  photolysis frequencies (a proxy for solar radiation). Orange circles represent all daytime data ( $J(\text{NO}_2) > 2 \times 10^{-6} \text{ s}^{-1}$ ), averaged to 30 minute intervals to effectively damp out fast changes. Black points represent 1 minute averaged data from hours 11:30 to 14:30 only. Correlation coefficients ( $r^2$ ) for scatter plots are 0.41 and 0.26 for  $\text{HO}_2^*$  30-min and 1-min and 0.30 and 0.03 for  $\text{RO}_2^*$  30-min and 1-min, respectively. (c-d) Distribution of peroxy radical mixing ratios for all 30 minute averaged daytime data (solid orange) and 1 minute averaged midday data (black outline).

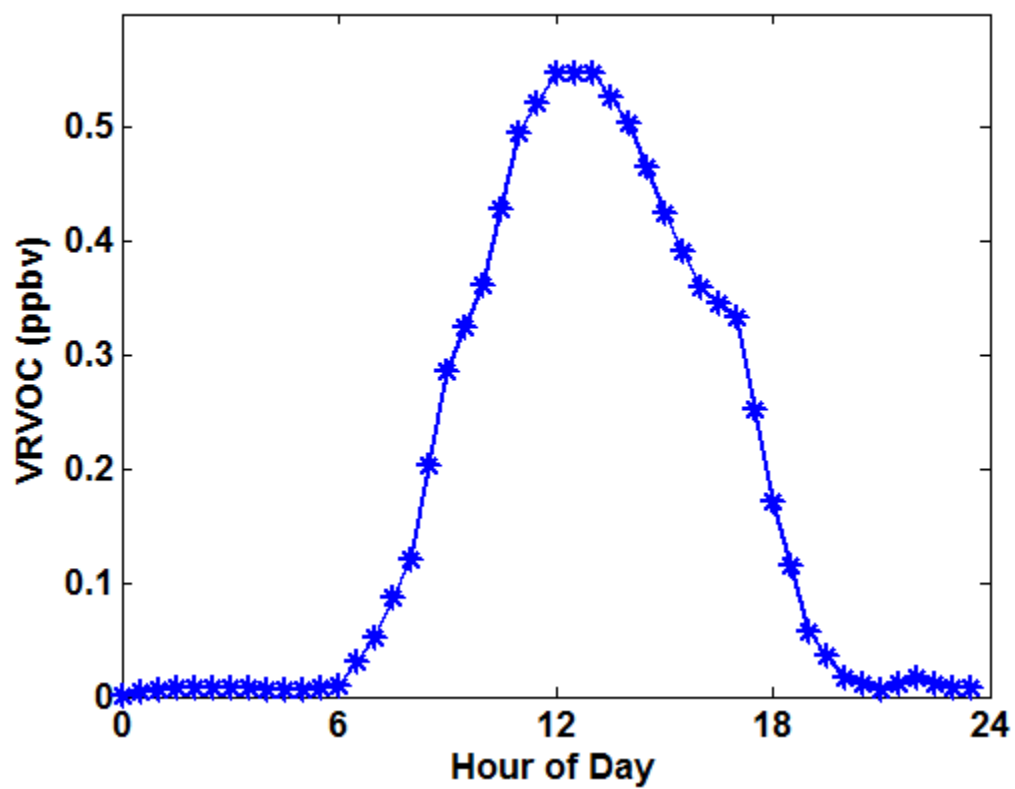


Figure S8. Mixing ratio of very reactive VOC (VRVOC) used to constrain the model scenario described in section 5.2 of the main text.



Figure S9. Picture of  $\text{HO}_x$  inlet setup during BEACHON. The PerCIMS inlet is on the left end of the trailer, and the OH inlet is on the right. The inlets are pointing roughly southeast.