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Supplement of

Speciation of OH reactivity above the canopy of an isoprene-dominated forest

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Supplemental Information

1 Missing data interpolation

Overall, the SOAS dataset is very complete with very few gaps in observations; however; in order to constrain the model, all gaps must be filled. If the period of missing data is less than 2 hours, a cubic interpolation of the entire time series is used to replace the missing points. If the data gap is larger, the missing points are replaced in one of the following ways:

(1) For species with no clear diurnal cycle, the measurement average is used. This primarily applies to anthropogenic VOCs with low concentrations (i.e. xylenes).

(2) For species that exhibit clear, consistent diurnal cycle but may have entire days with missing data, the diurnal average is used. This primarily applies to OVOCs (i.e. IEPOX).

(3) For isoprene, missing data is filled using a standard least squares regression of temperature and measured mixing ratios for all measurement points (r^2=0.68). Similarly, standard least squares regression of isoprene and MVK+MACR is used to fill missing MVK+MACR data (r^2=0.55).

(4) For NO, NO_2, and O_3, missing data were filled using measurements from an instrument in a nearby trailer. For HNO_3, a standard least squares regression between ground and tower observations is used to fill data gaps (r^2=0.51).

For all figures and analysis, model outputs are not included for time periods during with gaps in OH, OH reactivity, or isoprene measurements. Results are also not included for 28 June, 9 July, and 10 July are also excluded as PTR-MS and GC isoprene measurements could not be reconciled on these days.

2 Sensitivity to dilution rate

Ideally, a time-dependent dilution constant would be applied that represents mixing in of the residual layer, strong boundary layer growth throughout the morning, a maximum boundary layer height in the afternoon boundary layer height, and little vertical mixing at night. The entrainment rate into the boundary layer is given by:

$$\text{Entrainment Rate} = \frac{v}{BLH}([X]_{FT} - [X]_{BL}) \quad (1)$$

Where *BLH* is the boundary layer height, $[X]_{BLH}$ and $[X]_{FT}$ refer to the concentration of a given species in the boundary layer and the free troposphere, and v is the entrainment velocity. The entrainment rate constant (k_e) is v/BLH. As v is equivalent to the change of BLH with time, we arrive at:

$$k_e = \frac{1}{BLH} d[BLH]/dt \quad (2)$$

Integrating yields:

$$k_e = \ln\left(\frac{BLH_{t1}}{BLH_{t2}}\right)/dt \quad (3)$$

The calculated k_e from BLH measurements is very sensitive to measurement noise. Therefore, we calculate k_e by taking a smoothed version of the diurnal average BLH measurement acquired by ceilometer. Dilution is ignored where $k_e<0$.

As OH reactivity is dominated by measured species, k_{dil} has minimal impact on the calculated OH reactivity. In the relationship between total OH reactivity and reactivity from isoprene, the model slope and intercept are both slightly dependent on the dilution rate (Table S1). However, under nearly all model scenarios, the slope and intercept are slightly underestimated. The intercept for the entrainment scenario is higher than the measurement case because of the inaccurately high calculated nighttime OVOC concentrations (Fig. S3). The more accurate representations of dilution are consistent with the primary conclusions: (1) the contribution to total OH reactivity from unmeasured, unconstrained OVOCs is small (2) there is a small but significant discrepancy in the relationship between observed and modeled total reactivity and reactivity from isoprene alone.

3 Sensitivity to OH and HO_2 concentrations

A full discussion of the OH and HO_2 budget during this campaign can be found in Feiner et al. (2016). Importantly, our model concentrations are similar to theirs, and have minimal impact on OH reactivity and OVOC concentrations (Fig. S5).

Table S1. Least squares linear fit for model OH reactivity as a function of the OH reactivity from isoprene alone under different assumed dilution rates.

Dilution Rate	**Slope**	**Intercept (s^{-1})**
Calculated entrainment rate	1.15	7.43
Scaled to BLH	1.22	6.08
2 day^{-1}	1.22	6.04
4 day^{-1}	1.22	5.36
40 day^{-1}	1.17	4.65
Measurement	1.44	6.43

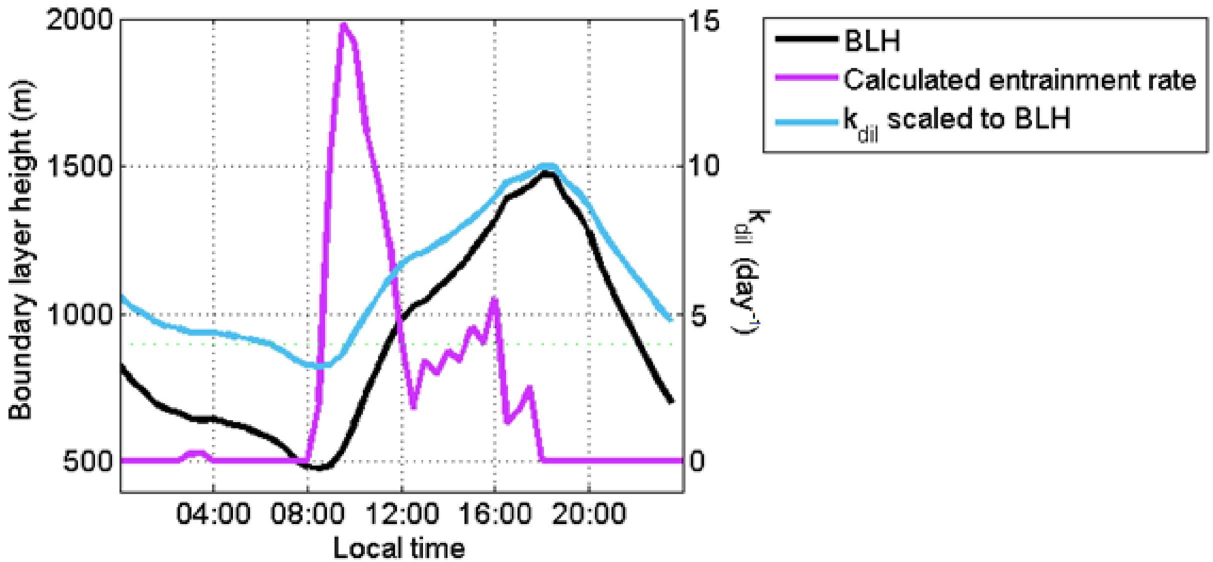

Figure S1. Diurnal average of boundary layer, smoothed over 2.5 hours, resultant dilution constant calculated according to Eq. 2, and dilution constant calculated from the ratio of BLH to maximum observed BLH.

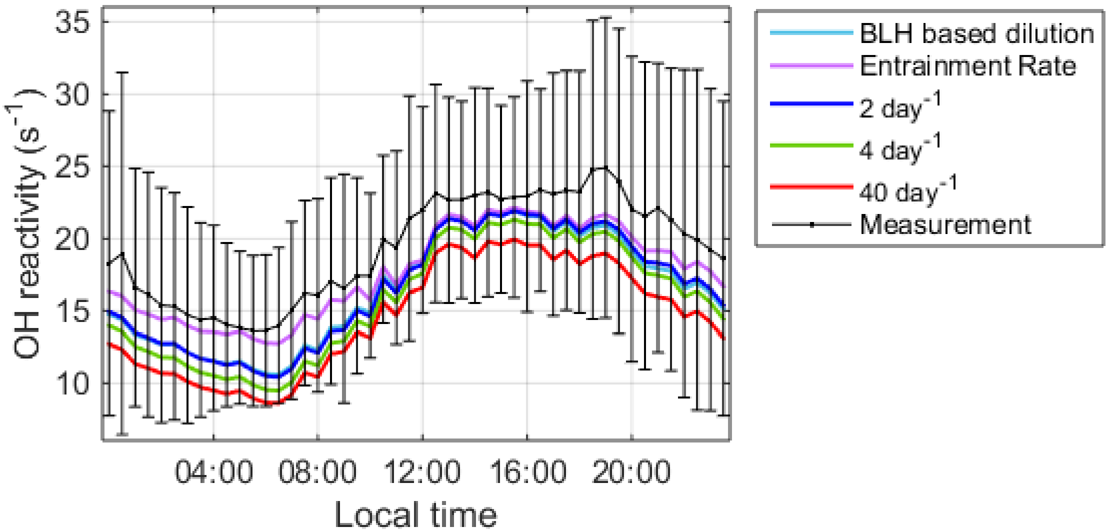

Figure S2. Sensitivity analysis for variability in the assumed dilution rate for OH reactivity. All measured species are constrained in this analysis. Error bars represent 1 σ diurnal variability in measurements. For clarity, diurnal variability is not shown in model results.

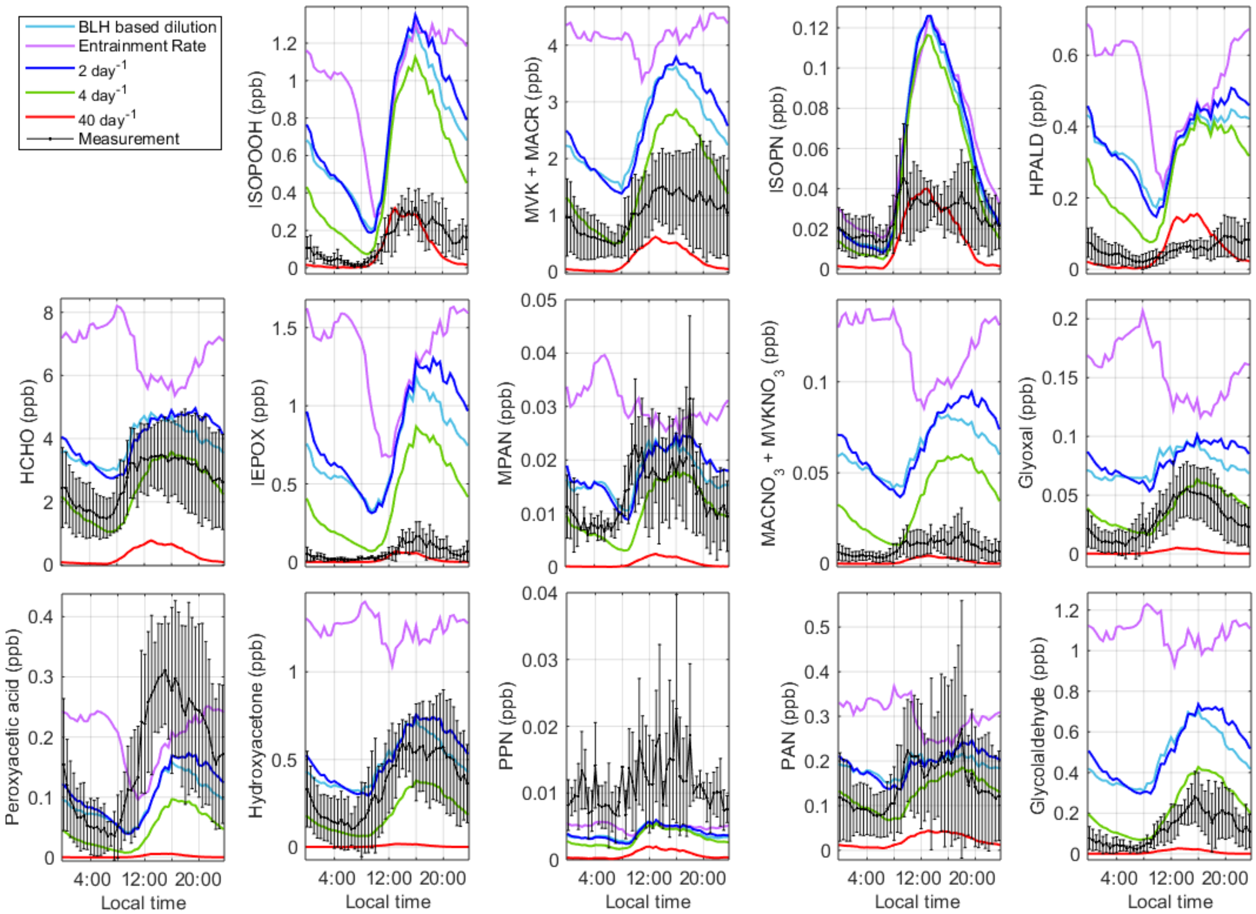

Figure S3. Sensitivity analysis for variability in the assumed dilution rate for OVOCs. Error bars represent 1 σ diurnal variability in measurements. For clarity, diurnal variability is not shown in model results. For each species, model results are not included for points where measurements are missing.

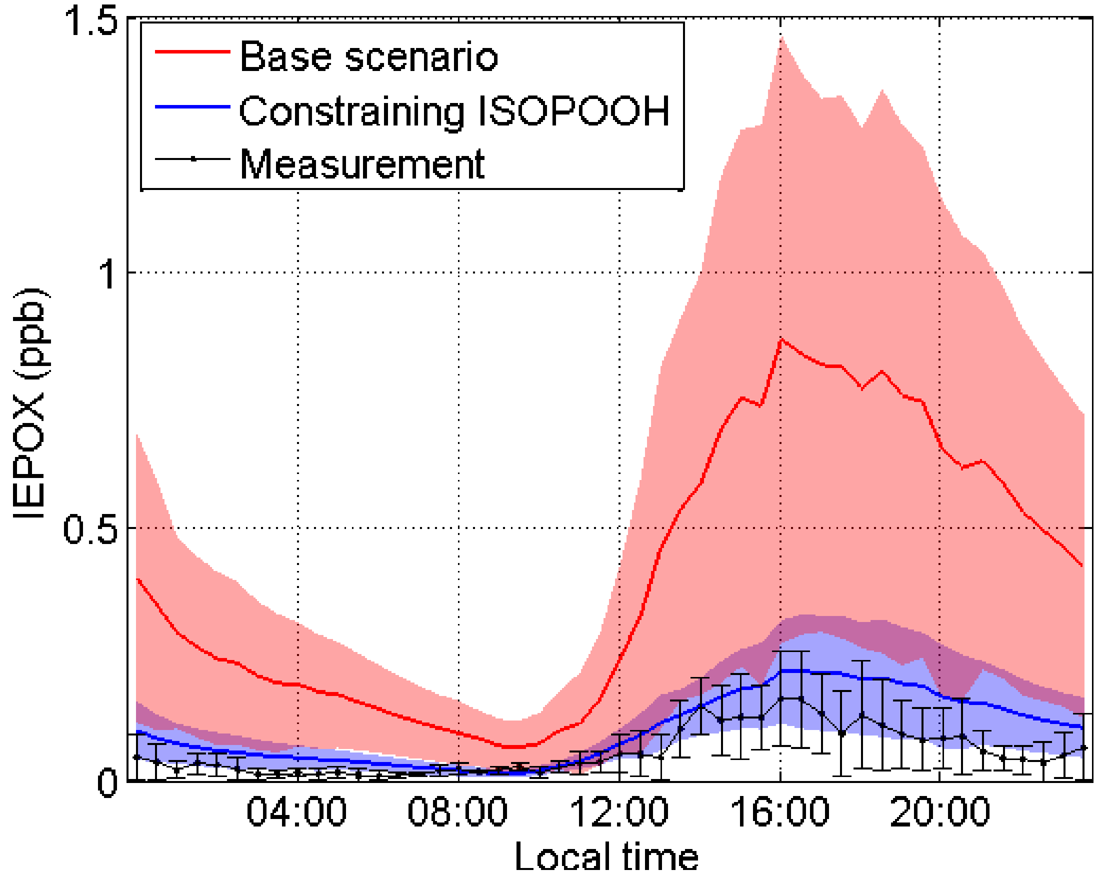

Figure S4. Comparison of measured and modeled concentrations of IEPOX with and without ISOPOOH constrained. Error bars and shaded area represent 1σ standard deviation of diurnal variability.

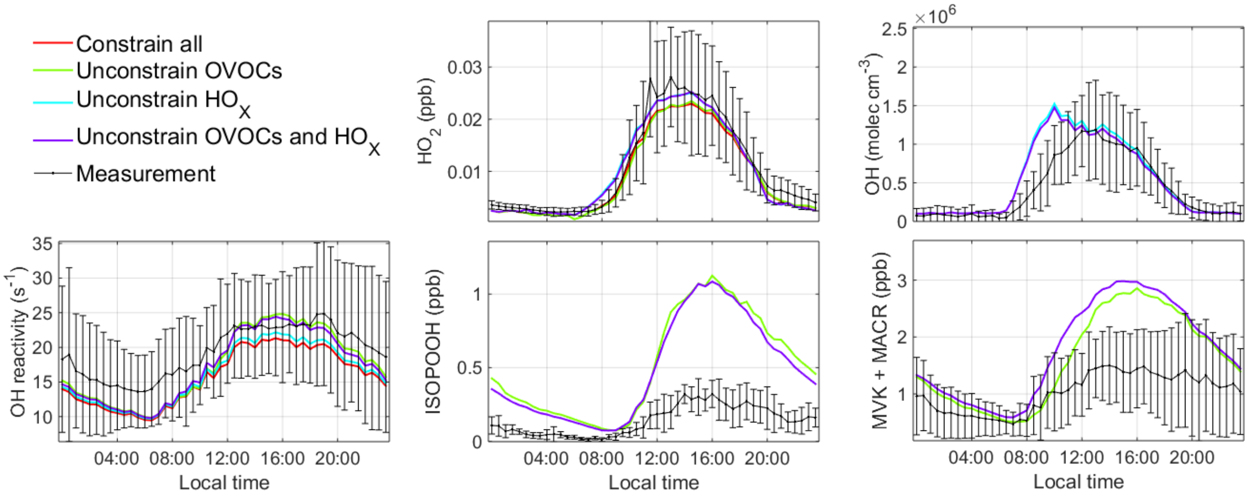

Figure S5. Model results of constraining or calculating OVOCs and HO_X on OH reactivity, HO_X, and specified OVOCs. Error bars on the measurement represent 1 σ diurnal variability. All scenarios use a constant dilution rate of 4 day^{-1}.