Response to interactive comments on "Speciation of OH reactivity above the canopy of an isoprene-dominated forest" by J. Kaiser et al.

We thank the reviewers for the thorough reading and helpful comments. Below, we address each remark individually. Original comments are in green, and our response follows, indented and in black. Our pagination refers to the pdf of the discussion paper. Beyond the changes to the manuscript outlined below, please note a change in supplement "entrainment" scenario which corrects a previous error in the calculations for the dilution sensitivity test. These changes have no impact on our analysis or conclusions.

Referee #1

(1) The abstract does not contain any quantitative information about the level of agreement between model and measured OH reactivity, which is the main result. There is a long introduction to the abstract and it is not until line 18 that any points specifically relevant to the results of this study are presented. Lines 10-17 need to be moved to the introductory material in the main paper, and some of the main results from the study (overall level of agreement (i.e. that the model underpredicts), slopes of main correlation plots, OH reactivity versus isoprene calculated reactivity, diurnal behaviour, statement that there are large model overprediction of OVOCs with values etc.) need to be stated. The abstract needs to be extended considerably in terms of summarising the main results.

> We have substantially changed the abstract to eliminate much of the background and add a more quantitative and detailed summarization. The new abstract reads:
>
> *Measurements of OH reactivity, the inverse lifetime of the OH-radical, can provide a top-down estimate of the total amount of reactive carbon in an airmass. Using a comprehensive measurement suite, we examine the measured and modeled OH reactivity above an isoprene-dominated forest in the South East United States during the 2013 Southern Oxidant and Aerosol Study (SOAS) field campaign. Measured and modeled species account for the vast majority of average daytime reactivity (80-95%), and a smaller portion of night-time and early morning reactivity (68-80%). The largest contribution to total reactivity consistently comes from primary biogenic emissions, with isoprene contributing ~60% in the afternoon, ~30-40% at night, and monoterpenes contributing ~15-25% at night. By comparing total reactivity to the reactivity stemming from isoprene alone, we find that ~20% of the discrepancy is temporally related to isoprene reactivity, and an additional constant ~1 s^{-1} offset accounts for the remaining portion. The model typically overestimates measured OVOC concentrations, indicating that unmeasured oxidation products are unlikely to influence measured OH reactivity.*

> *Instead, we suggest that unmeasured primary emissions may influence the OH reactivity at this site. While the magnitude of OH reactivity is related to RO2 production and subsequent ozone formation, determining the molecular structure of compounds related to missing reactivity is essential to understanding its impact.*

Paper

(1) Page 7 (there are no page numbers, so pages here refer to pages with the cover page as page 1) lines 2-3. In the measurement of OH reactivity, how was the zero of the instrument determined, and what is the value? Also, presumably in this environment the level of NO is low enough that any corrections for recycling of OH from HO2+NO within the sampling airstream are not necessary? If this is the case it should be stated. It would also be worth stating how the accuracy of the instrument is checked using known OH sinks.

> The operating procedures for the OH reactivity instrument are described in Mao et al. (2009). The OH reactivity instrument zero is determined by measuring the wall loss of the OH radical while using a clean carrier gas. The uncertainty in the zero is 0.5 s^{-1}, with 2 σ confidence. The recycling of OH from HO_2+NO was corrected by taking into account measured HO_2 decays. The accuracy of the instrument was verified using gasses with well-known reaction rate coefficients (C_3F_6 in the field, and CO, propane, propene, and isoprene in the lab).
>
> In the manuscript, we now state the value of the instrument offset during SOAS and refer the reader to Mao et al. (2009) for a description of the measurement technique.

(2) Page 7, line 25, MCM (not MVM).

> This has been corrected.

(3) Page 8, line 29. Would any process immediately regenerate OH? The timescale may be fast compared with the OH decay, but the actual values should be compared, and one shown to be much faster than the other, rather than just this statement.

> According to the version of the MCM used here, some processes immediately regenerate OH, most notably the reactions of some hydroperoxides with OH. For example, the product of ISOPOOH + OH reaction is IEPOX + OH. Because loss and production of OH is simultaneous, the ISOPOOH + OH reaction would not impact the measured OH decay. We have clarified this in the manuscript.

(4) Page 9, line 1. Small is subjective, please give a % value here to evidence this.

> We now state that the average total calculated reactivity of species that immediately regenerate OH is 0.6 ± 0.3 s^{-1}.

(5) Although not the subject of this paper (and measured OH is used to constrain the model), it would be useful to state the level of agreement between the model and measured OH and other measured radicals (HO2 and maybe RO2). It would be useful just to confirm how the model performs for these species (given that the model comparison for OVOCs is discussed later).

We cannot provide a comparison of measured and modeled OH or RO_2 because our model is constrained to measured OH values and RO_2 measurements are not available.

HO_2 was not constrained and can be compared to measurements. Our results are shown below. A manuscript comparing measured and modeled OH and HO_2 has recently been submitted to J. Atmos. Sci. (Feiner et al. 2016). Slightly different model configurations and selection of days results in a small difference between studies, but both show similar results for HO_2. Feiner et al. also find good agreement for OH (chemically zeroed measurement) and model values. We direct readers to the Feiner et al. paper for a more complete discussion of the HO_X budget for this campaign.

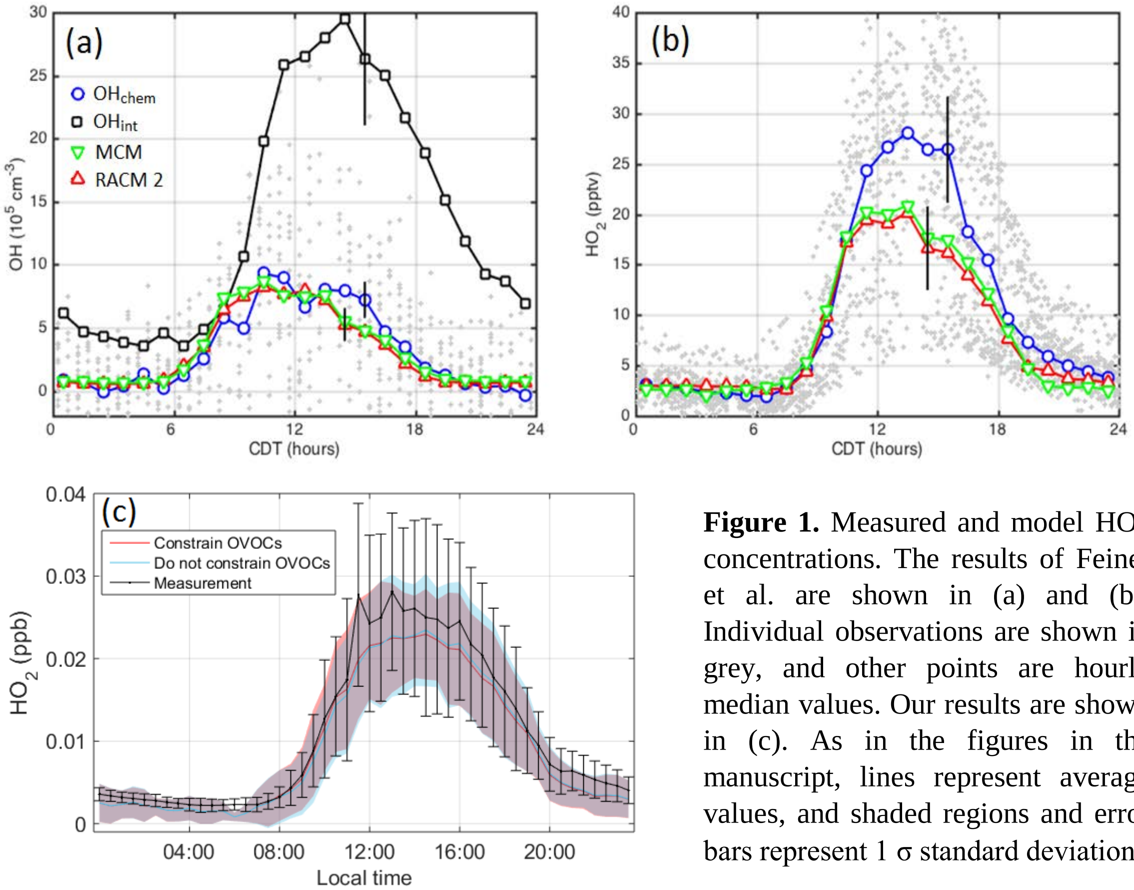

Figure 1. Measured and model HO_X concentrations. The results of Feiner et al. are shown in (a) and (b). Individual observations are shown in grey, and other points are hourly median values. Our results are shown in (c). As in the figures in the manuscript, lines represent average values, and shaded regions and error bars represent 1 σ standard deviation.

(6) Page 10, line 1. The largest discrepancy is observed at 0700 LT (32%). Can the authors comment on the general shape of Figure 2?

The general shape of Figure 2, including the peak of missing reactivity in the early morning, is addressed in the discussions section (page 8, starting at line 13).

(7) Page 10, line 16. It is stated that the slopes are not much larger than one. This is rather subjective as the observed slope of measured OH reactivity versus that from isoprene itself is 1.43, which although not a factor of 3, 5 etc., is significantly greater than 1 (by almost 50%). This statement ought to be qualified. It can be seen clearly from Fig 3 that at times the reactivity due to isoprene is considerably less than the total measured OH reactivity.

This sentence has been eliminated, as the numbers themselves adequately convey the relationship between total reactivity and isoprene.

(8) Page 12, line 3. Not slope of fig 3? You mean slope of fig 4?

This has been corrected to refer to Figure 4.

(9) It is difficult to compare the temperature dependence observed with that of Di Carlo et al., as the range of values of temperature only seem to have a limited range where they overlap. The parameterisation of Di Carlo seems to stop at 300 K, and in this region the current work's function does not change much. It is only above 300 K that the function for this work becomes significantly steeper than that of Di Carlo. Some further discussion of this is needed, and the parameterisation of Di Carlo needs extending to higher temperatures compare easily.

The parameterization shown in DiCarlo et al. (2004) is based on observations at the lower temperature range shown. Because extrapolating the fit may misrepresent the observations and conclusions of Di Carlo et al., we do not extend their parameterization to higher temperatures. However, we now highlight that the parameterizations are based on different ranges of temperatures.

(10) Page 12. The paper states that ". . .the model is missing ~ 1 s-1 that is temporally unrelated to the oxidation of . . ... (Figure 3)". However, inspection of Figure 3 suggests that the difference between the measured OH reactivity (black points) and the cumulative modelled reactivity is more than 1 s-1? It looks more like between 2 and 5 s-1 (depending on time of day). Some modification of this statement is therefore needed.

While the total missing reactivity is larger than 1 s^{-1}, we differentiate between the portion temporally related to isoprene (slope in Figure 4) and the offset (intercept in Figure 4). Increasing the effective reactivity of isoprene by 20% and adding 1 s^{-1} would account for the entirety of the 2-5 s^{-1} of missing reactivity. In our discussion, we address separately the difference in slope and intercept. This has been clarified in the manuscript.

(11) Page 12, line 12, missing "of"

This has been corrected.

(12) Page 13, line 2. Again 1s-1 seems to be a significant underestimate of the difference between measured and modelled shown in Figure 3. The amount of sesquiterpenes would therefore need to be more than ~ 200 ppt.

See response to comment 10.

(13) Page 13, line 22. The values quoted here are not consistent with the values quoted on page 10. The measured slope was quoted as 1.43 there, and modelled slope 1.22. Also, it says +/- 02 (should be 0.02).

We have corrected this error.

(14) Table 1. Glyoxal row, space between 9% (1 s)

This has been corrected.

(15) Figure 1. Please plot this graph from the origin (0,0) as it will be more informative. At present it is rather misleading as it suggests the points go to the origin.

We have remade the figure as suggested.

(16) Figure 1. The slope of the linear least squares fit weighted by uncertainty must be stated in the caption. This is one of the most important results of the paper.

The caption now includes the equation of the linear fit.

(17) Caption for Fig 2, second line, "Points the in gray. . ." needs correction

This has been corrected.

(18) Figure 3. As commented above the difference is considerably more than 1s-1 quoted in the text (seems to be 2-5 s-1 depending on time of day). Suggest reversing the order of the legend. At present the measurement is at the bottom, with Inorganics at the top, whereas the figure is measurement at the top, and Inorganic at the bottom.

See response to comment 10. The figure has been remade as suggested.

(19) Figure 4. Given the text gives the slopes at 1.43 and 1.22 (note inconsistency with page 13), the equation given on the figure needs to reflect this quoted accuracy. What does "weighted by uncertainty" mean?

The figure has been remade as suggested. The uncertainty in OH reactivity measurements (20%) and in the model (20%, based on the uncertainty in isoprene measurements) is noted in the manuscript. References for linear regression given uncorrelated errors are provided.

(20) Figure 6. See comments above about the degree of overlap in T for the solid and dashed lines. What is the value of Greek alpha for each?

See response to comment 9. DiCarlo et al. (2004) provide only a β value in the text of their manuscript, and we can therefore not provide an α value. The data shown here was taken from Figure 2 of their manuscript and replotted.

Referee #2

The main thrust of the paper is that the modeled reactivity agrees well with the measured reactivity when constrained to measured OVOCs and that primary emissions dominate the OH reactivity at this site, in contrast to previous studies in similar environments. However this conclusion is not highlighted clearly enough in the paper and the authors attempt to extend this conclusion to our understanding of RO2 production and O3 production without providing sufficient modeling studies to support this conclusion. The fact that the model significantly overestimates the measured OVOCs suggests that our understanding of RO2 chemistry and O3 production is still incomplete.

Unfortunately, there is little discussion as to potential reasons why the model significantly overestimates the observed OVOCs, although the paper mentions that uncertainties associated with modeled dilution rates of these species may be responsible. The paper would benefit from an expanded discussion of potential reasons for the model overprediction of OVOCs and their implications.

> Because other manuscripts focus on OVOCs (Su et al., 2015; Xiong et al., 2015) and on the HO_X budget (Feiner et al., 2016), we specifically focus only on OH reactivity given a well constrained model. OH reactivity inherently has implications for RO_2 production, which are briefly discussed but not the major focus of this paper. The largest uncertainty influencing OVOC concentrations is dilution, which is discussed in depth in the supplement.

Specific comments:

1) As discussed above, a main conclusion of the paper appears to be that because the modeled OH reactivity (constrained to the OVOCs) agrees well with the measured OH reactivity that the total RO2 production rate and therefore O3 production is well understood (page 9 lines 10-11).

> As stated by the manuscript title, the focus of this work is on the speciation of measured and modeled OH reactivity. The extension to RO_2 production (and SOA formation) is an implication that is derived from this work, but it is not the main focus. Our abstract has been rewritten to better reflect our primary focus and summarize our findings.

However, the fact that the model overestimates isoprene oxidation products and other OVOCs suggests that when the model is not constrained to measurements of these compounds that the model may not be able to reproduce total RO2 production, as many of these OVOCs are produced from RO2/HO2 chemistry, such as ISOPOOH and HPALD. The authors need to provide more information to justify this conclusion.

> It is true that when the model is not constrained to measured OVOCs that RO_2 production is likely represented less accurately. However, because these measurements are available, we are able to better constrain our model. As a well constrained model can capture OH reactivity, then the essential RO_2 production rate (essentially given by the

OH + VOC reaction rate) is likely also captured in this scenario. We do not imply that an unconstrained model would accurately capture the RO_2 production rate.

2) One test of the ability of the model to reproduce the observed OH reactivity would be to unconstrain the model to the measured OH and the measured OVOCs. It's not clear from the information given in the paper whether unconstraining the model to the measured OH impacts the modeled OH reactivity as the paper does not state how well the model is able to reproduce the measured OH when constrained to the measured species, or how sensitive the modeled OH reactivity is to the OH concentration. The paper would be stronger if the authors provided several model scenarios to compare to the measured OH reactivity, such as i) a base scenario where the model is constrained only by the traditional measured VOCs, NOx, etc., ii) a scenario where the model is further constrained by the measured OH but not constrained by the measured OVOCs, and iii) the scenario where the model is constrained by all measured species.

One of the primary goals of this manuscript is to determine if there is a large source of missing reactive carbon in our set of measured and modeled species. We therefore focus on the ability of a well-constrained model to capture OH reactivity, and if not, on potential sources of discrepancies. For this reason, we constrain to measurements whenever possible. This includes constraining to measured OH.

A manuscript comparing measured and modeled OH and HO_2 has recently been submitted to J. Atmos. Sci. (Feiner et al. 2016). Slightly different model configurations and selection of days results in a small difference between studies, but the results are similar to ours (see below). Because measured and modeled OH and HO_2 are in good agreement, and because measured species contribute most substantially to OH reactivity, constraining these radicals has minimal impact on OH reactivity. We direct the reader to the Feiner et al. manuscript for a more complete discussion of radical chemistry.

3) It is surprising that the authors chose to constrain the model to the measured OH but not to the measured HO_2, given the importance of peroxy radical chemistry to the formation of OVOCs such as ISOPOOH and HPALD. Were HO_2 measurements not available?

We did not constrain our model HO_2 measurements due to the higher than typical uncertainty (±40% at 2σ confidence level) stemming from the methods used to suppress the RO_2 interferences.

Does constraining the model to the measured OH reproduce the measured HO2? Or does this model scenario overestimate HO2 leading to the overestimation of the observed OVOCs? If the model is constrained to both measured OH and HO2, are the modeled OVOCs in better agreement with the measurements? These and other tests of the model would provide important information regarding the reasons for the model's inability to reproduce the observed OVOCs.

Shown below are our model results for OH and HO_2 as well as the results those of Feiner et al. (2016). Measured and modeled OH and HO_2 are in good agreement and have minimal impact on OVOC concentrations. As other studies have focused on the measured/modeled agreement of OVOCs, we focus instead on an OVOC-constrained model to examine OH reactivity. However, we now show our results in the supplement.

It is important to note that compared to the effects of constraining/not constraining HO_X, the range of dilution scenarios shown in the supplement is by far the largest source of uncertainty in modeled OVOC concentrations. OVOCs are highly sensitive to the assumed magnitude and diurnal variability of the dilution rate, which is typically not well parameterized in 0-D box models.

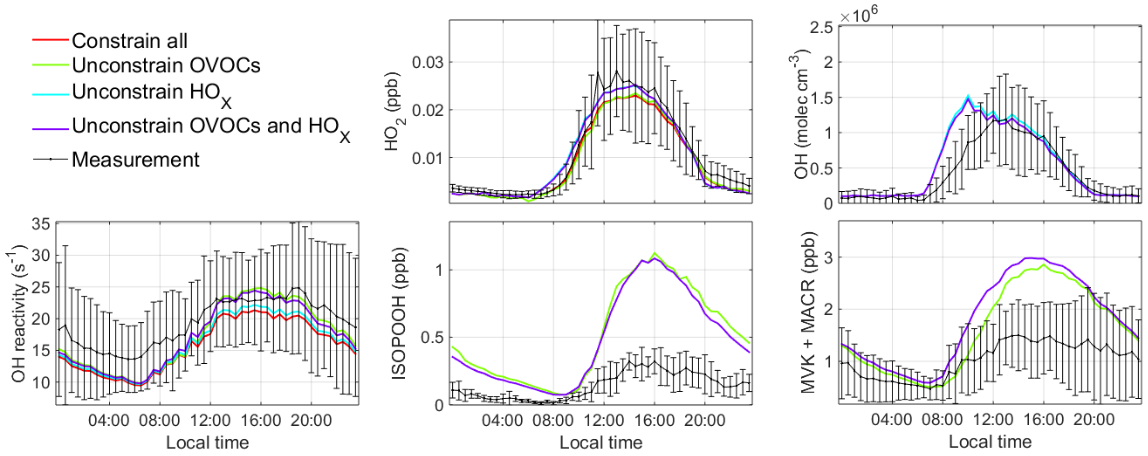

Figure 1. Model results of constraining or calculating OVOCs and HO_X on OH reactivity, HO_X, and specified OVOCs. Error bars on the measurement represent 1σ diurnal variability. All scenarios use a constant dilution rate of 4 day^{-1}.

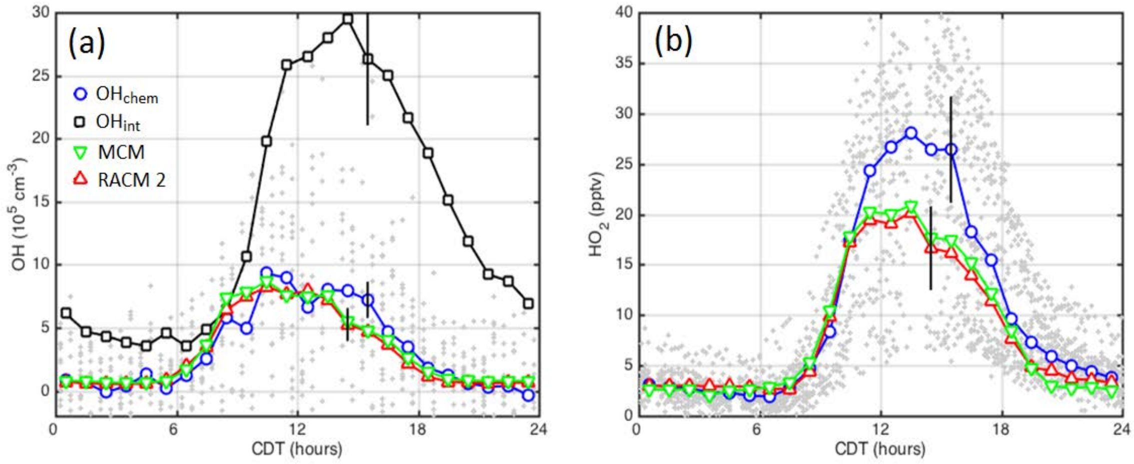

Figure 2. HO_X budget as studied by Feiner et al. (2016).

References

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

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Abstract. Measurements of OH reactivity, the inverse lifetime of the OH-radical, can provide a top-down estimate of the total amount of reactive carbon in an airmass. ~~Because OH reactivity is tied to the RO_2 production rate, the absolute value of OH reactivity has direct implications for ozone production. Additionally, as molecular structure determines volatility, the speciation of reactivity affects the production of secondary organic aerosol (SOA). Several studies have focused on the agreement of measured and calculated or modeled OH reactivity above and within the canopy of isoprene-dominated forests, as well as the relative contributions of volatile organic compounds (VOCs) and oxidized VOCs (OVOCs). Drawing definitive conclusions about the identity of the missing OH reactivity has been limited by the availability of VOC and OVOC measurements.~~ U~~In this work, u~~sing a comprehensive measurement suite, we examine the measured and ~~model~~modeled OH reactivity above an isoprene-dominated forest in the South East United States during the 2013 Southern Oxidant and Aerosol Study (SOAS) field campaign. Measured and modeled species account for the vast majority of average daytime reactivity (80-95%), and a smaller portion of night-time and early morning reactivity (68-80%). ~~We find good agreement between measured and modeled OH reactivity, with~~ T~~t~~he largest contribution to total reactivity consistently ~~coming~~ comes from primary biogenic emissions, with isoprene contributing ~60% in the afternoon, ~30-40% at night, and

monoterpenes contributing ~15-25% at night. By comparing total reactivity to the reactivity stemming from isoprene alone, we find that ~20% of the discrepancy is temporally related to isoprene reactivity, and an additional constant ~1 s^{-1} offset accounts for the remaining portion. The model typically overestimates measured OVOC concentrations, indicating that unmeasured oxidation products are unlikely to influence measured OH reactivity. ~~In contrast, there are small but significant discrepancies in the increase in OH reactivity per isoprene. As the model typically overestimates OVOCs, we do not attribute this discrepancy to unmeasured oxidation products.~~ Instead, we suggest that unmeasured primary emissions may influence the OH reactivity at this site. While the magnitude of OH reactivity is related to RO_2 production and subsequent ozone formation, determining the molecular structure of compounds related to missing reactivity is essential to understanding its impact.

1 Introduction

Biogenic emissions of volatile organic compounds (VOCs) constitute the largest source of reactive carbon in the atmosphere (Guenther et al., 2012). During the daytime, oxidation of VOCs by the OH radical can drive the formation of secondary pollutants. Under high NO_X ($NO + NO_2$) conditions, ~~the~~ peroxy radicals (RO_2) generated from VOC oxidation ~~can~~ convert NO to NO_2, which ultimately photolyzes to form ozone. Additionally, oxidized VOCs (OVOCs) are typically less volatile than their precursors, and can contribute to the formation of secondary organic aerosol (SOA). Therefore, it is important to understand the total VOC + OH reaction rate and the fate of the resultant OVOC to understand the formation of ~~secondary pollutants such as~~ tropospheric ozone and SOA.

While measuring every VOC and oxidation product ~~OVOCs~~ is not feasible, measurement of OH reactivity (the loss rate of the OH radical divided by the OH concentration) provides an alternative to the bottom-up molecular approach (Kovacs and Brune, 2001). The absolute value of OH reactivity can be used ~~as a top-down~~to estimate ~~of~~ the total amount of reactive carbon in an airmass, or the RO_2 production rate. The speciation of the reactivity carries air-quality relevant implications as SOA yield is directly tied to molecular properties such as volatility, hygroscopicity, viscosity, and condensed-phase reactivity.

One half of the annual non-methane VOC emissions is in the form of isoprene (C_5H_8), making it the dominant biogenic VOC globally (Guenther et al., 2012). Due to isoprene's abundance and high reactivity, the chemistry of isoprene and its resulting oxidation products ~~have~~ has been the focus of numerous field studies. OH reactivity has been examined in four isoprene-dominated forests, with some studies suggesting missing primary emissions or missing OVOCs, and others finding good agreement between measurements and calculations.

In a deciduous forest in Northern Michigan, ~~For example, using measured VOCs and OVOCs,~~ Di Carlo et al. (2004) could account for only 50% of the OH reactivity measured above the canopy in ~~of a deciduous forest in northern Michigan in~~ the summer of 2000. As OVOCs calculated by a model did not significantly increase calculated OH reactivity, and as the missing reactivity fit a terpenoid-like emission profile, unmeasured terpene emissions were cited as a large source of reactive carbon in this environment. However, later measurements of monoterpenes and sesquiterpenes at this site suggested that only ~20% of the missing reactivity could be attributed to these primary VOCs~~, leaving a total of ~40% unaccounted measured reactivity~~ (Kim et al., 2009). Additionally, Kim et al. (2011) found that measurements and calculations of OH reactivity in branch enclosures of isoprene-emitting trees at the same site were in good agreement. ~~They calculated ~8% of the missing reactivity could be attributed to unmeasured isoprene oxidation products. Recently, from~~Using ~~2009~~ measurements taken at this~~e same~~ site during 2009, Hansen et al. (2014) found that isoprene accounted for 60-70% of afternoon OH reactivity both within and above the forest canopy. Because in-canopy OH reactivity calculations and measurements were in good agreement, the authors concluded that there are unlikely to be unmeasured primary VOCs at this site. However, above-canopy comparisons show a large missing fraction of reactivity, suggesting unmeasured oxidation products may contribute at longer processing times.

In a downy oaks forest in the Mediterranean south east of France, Zannoni et al. (2015) examined OH~~-~~ reactivity both within and above the canopy ~~a downy oaks forest in the Mediterranean south east of France~~. Measured and calculated OH reactivity were in good agreement at both heights during the daytime, with isoprene contributing 83% within the canopy and 74% above the canopy. However, more than 50% of nighttime reactivity was missing on a subset of days. The authors conclude that unmeasured, higher-generation isoprene oxidation products ~~are~~ account for part of the nighttime discrepancy, ~~as well~~alongside unmeasured OVOCs ~~from~~ produced from the ~~reactions~~ ozonolysis of large, non-isoprene biogenic VOCs ~~and ozone~~.

~~In contrast, i~~In a tropical rainforest ~~on~~ in Borneo, unmeasured isoprene-derived OVOCs were a more dominant contribution to the observed reactivity than isoprene itself, at nearly 50% (Edwards et al., 2013). OH reactivity measured from a clearing atop a hill surrounded by forest was significantly underestimated by a model (~60% at noon). The authors concluded missing primary emissions were unlikely to contribute significantly to OH reactivity, and an underrepresentation of secondary multifunctional OVOCs is a likely source of discrepancies.

Finally, in the tropical rainforest of Suriname, in-canopy OH reactivity measured ~~in the tropical rainforest of Suriname~~ could not be reached by summing the contributions from measured isoprene, methyl-vinyl ketone, methacrolein, acetone, and acetaldehyde. The authors called for more comprehensive measurement suite to investigate the large discrepancy (65%) (Sinha et al., 2008).

Each forest examined ~~used~~ in these studies is composed of a unique species of trees, potentially leading to different relative contributions of non-isoprene~~relative~~ ~~biogenic VOC~~primary emissions. Furthermore, different meteorological conditions and canopy structures may lead to different processing times and resultant contributions of isoprene-derived OVOCs. While these differences may make the above studies difficult to generalize, they all address an underlying question: are isoprene-derived OVOCs a substantial source of missing reactive carbon? If so, after what degree of processing? ~~What is the impact of NO$_x$?~~

To assess the contribution of unmeasured oxidation products, ideally, one would explicitly model all isoprene OVOCs and include modeled species in the summation. Additionally, several OVOC measurements would be available to test the reliability of model concentrations. This sort of analysis has been performed in a chamber study of the oxidation of isoprene (Nölscher et al., 2014), but as initial concentrations of reactants were orders of magnitude greater than those found in the atmosphere, and as physical processes such as deposition onto plant surfaces are not captured in chamber studies, chamber experiments may not capture the ~~behavior~~behaviour of OH reactivity observed in a forest.

Of the above field studies, several rely only on the concentration of measured species in the calculation of OH reactivity (Sinha et al., 2008; Hansen et al., 2014 (part 2 will include a ~~comprehensive modeling~~modeling study); Zannoni et al., 2015). While studies that employ model OVOC concentrations have a more complete representation of oxidation products (Di Carlo et al., 2004; Edwards et al., 2013), neither of these studies compare measured and ~~modeled~~modeled OVOC mixing ratios. Additionally, as isoprene hydroxyl hydroperoxide (ISOPOOH) and isoprene hydroxy nitrate (ISPN) standards have only recently become available (Rivera et al., 2014; Lee et al., 2014), first-generation oxidation product measurements are often incomplete.

With high isoprene emissions, the South East United States is an ideal location to reassess questions of missing OH reactivity and speciation of observed reactivity. In addition to measurements of OH reactivity, the 2013 Southern Oxidant and Aerosol Study (SOAS) field campaign provides a comprehensive suite of VOC and OVOC measurements, enabling a more constrained analysis of the contribution from isoprene-derived OVOCs than previously available. This includes first-generation isoprene oxidation products for both low-NO and high-NO oxidation, such as ISOPOOH, ISOPN, isoprene hydroperoxy aldehydes (HPALD), the sum of methyl-vinyl ketone (MVK) and methacrolein (MACR), as well as several smaller oxidation products. Furthermore, dry deposition rates of isoprene's OVOCs are measured and parameterized for this site (Nguyen et al., 2015), enabling us to reduce some of the uncertainty related to physical losses of carbon. Speciated and total monoterpene measurements provide additional insight into reactive carbon not stemming from isoprene.

~~As a detailed analysis of isoprene photo-oxidation at this site is provided by Su et al. (2015) and Xiong et al. (2015), this work focuses primarily on the total amount and speciation of OH reactivity above the forest canopy.~~ Using a 0-D box model, we investigate the sources of reactive carbon and compare the summation of ~~modeled~~ calculated species with measured OH reactivity. We then discuss our findings in the context of previous studies, and briefly discuss the air quality relevant implications. Further discussion on the isoprene oxidation mechanism and product formation can be found in Su et al. (2015) and Xiong et al. (2015), and modeled OH and HO_2 are discussed more fully in Feiner et al. (2016).

2 ~~Section (as Heading 1)~~Methods

2.1 SOAS Measurements

Measurements were performed from 1 June to 15 July at the SouthEastern Aerosol Research and CHaracterization (SEARCH) Centreville (CTR) site near Brent, Alabama as part of the 2013 Southern Oxidant and Aerosol Study (SOAS) field campaign (soas2013.rutgers.edu/). CTR is a rural site surrounded by mixed deciduous-evergreen forests, at times experiencing urban-influence from Birmingham, Montgomery, or Tuscaloosa AL. The long term and regional chemical tends observed at this site have been discussed in detail elsewhere (Blanchard et al., 2013; Hidy et al. 2014). We restrict our analysis to the time frame of good instrumental overlap (11 June to 16 July 2013). All observations shown here are binned to 30 min time intervals. A discussion of missing data interpolation can be found in the supplement.

Table 1 summarizes the chemical measurements used in this analysis and their related uncertainties. Most chemical measurements and solar radiation were acquired from a walk-up tower with a height of ~20 m, approximately 10 m above the forest canopy. CO, Gas Chromatograph-Electron Capture Detector (GC-ECD) measurements and meteorological parameters (relative humidity, temperature, pressure, and boundary layer height) were acquired from a nearby trailer.

Key measurements to this analysis are OH reactivity, VOCs, and OVOCs. OH reactivity was measured by adding OH to an airstream using a moveable wand, and monitoring the decay of the OH radical by laser-induced fluorescence (Mao et al., 2009). Measurement accuracy (Table 1) and zero (0.5 s^{-1} at 2 σ confidence) were determined using the methods described in Mao et al. (2009). Most VOCs were measured by gas chromatography-mass spectrometry (GC-MS), which provided 5 min samples every 30 min (Gilman et al., 2010). Due to possible line-losses for oxygenated species in GC-MS measurements, Proton-Transfer-Reaction Time of Flight Mass Spectrometry (PTR-TOFMS, Ionicon Analytik model PTR-TOF 8000) measurements are used for the sum of MVK and MACR (Jordan et al., 2009). The PTR-TOFMS also provided measurements of the total monoterpene mixing ratio. Unspeciated monoterpenes are defined as the difference between PTR-TOFMS measurement of total monoterpenes and the sum of individual species ~~provided~~ measured by the GC-MS (α-pinene, β-pinene, limonene, mycrene, and camphene).

Glycolaldehyde, ISOPOOH, and isoprene dihydroxy epoxides (IEPOX) were measured by CF_3O^- triple quadrupole chemical ionization mass spectrometry (Paulot et al., 2009; St. Clair et al., 2010; St. Clair et al., 2014). ISOPN, HPALD, the sum of MVK and MACR nitrates ($MACNO_3$ + $MVKNO_3$), hydroxyacetone, and peroxyacetic acid were measured by chemical ionization time of flight mass spectrometry (Crounse et al., 2006; Lee et al., 2014). Formaldehyde (HCHO) was measured by fiber-laser-induced-fluorescence, (Hottle et al., 2008; DiGangi et al., 2011), and glyoxal was measured by Laser-Induced Phosphorescence (Huisman et al., 2008). Additional speciated organic nitrates were measured by gas chromatography-electron capture detector (Roberts et al., 2002).

2.2 Model simulations

A 0-D box model analysis was performed using the University of Washington Chemical Box Model (UWCM) (Wolfe and Thornton, 2011), incorporating the Master Chemical Mechanism, ~~MVM~~ MCM v3.2 (Jenkin et al., 1997; Saunders et al., 2003, website: http://mcm.leeds.ac.uk/MCM), updated to include the isoprene alkyl radical-O_2 adduct equilibria (Peeters and Muller, 2010), isoprene peroxy radical isomerizations (Crounse et al., 2011; da Silva et al., 2010), revised ISOPOOH+OH rate constant (St. Clair et al., 2015), and HPALD photolysis and OH reaction rates (Wolfe et al., 2012). Monoterpenes reactions for species not included in the MCM (i.e., mycrene, camphene, and unspeciated monoterpenes) are described in Wolfe et al. (2011). At each time step, photolysis rates are scaled according to the ratio of measured radiation and the maximum observed radiation at that time of day.

Dry deposition is included for H_2O_2, organic hydroperoxides, nitrates, and the isoprene-derived epoxides (IEPOX). Measured deposition velocities are used for H_2O_2, IEPOX and ISOPN. For other hydroperoxides and organic nitrates, noontime deposition velocities are calculated according to the relationship with mass shown by Nguyen et al. (2015). Diurnal variability of deposition velocities are scaled according to the measured variation for representative species (ISOPOOH for peroxides, methacrolein nitrate for nitrates).

Dilution is assumed to occur with air with a concentration of zero for all species. This dilution represents entrainment with free tropospheric air and any decrease in concentrations related to unrepresented deposition or advection processes. A constant, empirically determined rate of 4 day^{-1} is used in all analysis presented here, giving a 6 h lifetime with respect to dilution. Sensitivity analysis of this dilution rate is provided in the supplement. The model is initiated with a two day spin up period using diurnal averages of measured species to account for the buildup of unmeasured intermediate species.

Two separate model configurations are used to examine OH reactivity and OVOC concentrations. In all discussions of modeled OH reactivity, OVOC concentrations are constrained to their measurements to ensure the most complete representation of measured OH reaction partners. This includes constraining ISOPN, ISOPOOH, MVK+MACR, $MVKNO_3$+$MACNO_3$, HPALD, and IEPOX by applying modeled isomeric distributions to measured concentrations. Due to partial conversion of ISOPOOH to MVK+MACR in the PTR-TOFMS inlet (Rivera et al., 2014), this represents an upper limit on MVK and MACR measurements. However, because daytime ISOPOOH concentrations are a factor of >5 lower than MVK+MACR, and because the sensitivity to ISOPOOH is only ~30% of that of MVK+MACR, the effect of ISOPOOH on MVK+MACR signal is expected to be negligible. It should be noted that all species that react with OH are included in the calculated reactivity, whereas species that immediately regenerate OH as a reaction product (such as ISOPOOH + OH → IEPOX + OH), would not contribute to measured OH reactivity. ~~However, the~~ The average total contribution from such species to calculated reactivity is small (0.6 ± 0.3 s^{-1})~~small~~. The scenario for comparing modeled and measured OVOCs is identical, except that OVOCs are not constrained. Because OVOC concentrations are calculated in a separate model scenario, any discrepancy between measured and modeled OVOC concentrations does not translate to a discrepancy in calculated reactivity.

In both model configurations, OH, NO, NO_2, CO, O_3, H_2O_2, HNO_3, and all primary VOCs are constrained to their measurements. Primary VOCs are defined as any species that are likely to have a significant contribution from direct emissions. This includes alkanes, alkenes, aromatic compounds, and some oxygenated species (methanol, ethanol, acetone, methyl-ethyl-ketone, acetaldehyde, biacetyl, propanal, hydroxyacetone, and formic acid). Table 1 provides a listing of constraints for each model scenario.

The model ability to reproduce OH and HO_2 observations is shown in the supplement, and not discussed in depth here. Results are similar to those shown in Feiner et al. (2016), with HO_2 and OH in good agreement with measurements and having minimal impact on OH reactivity and OVOC concentrations.

3 Results

3.1 Measured and Modeled OH reactivity

Figure 1 shows a comparison between measured and modeled OH reactivity for the constrained-OVOC scenario. Modeled and measured values are well correlated (r^2=0.85), with a slope of 0.80 ± 0.02. The average missing reactivity for all measurement points is 16 ± 18%. An uncertainty of 20% is assigned to model reactivity based on the uncertainty in isoprene, which comprises the majority of modeled reactivity. Propagating measurement uncertainty (20%) and model uncertainty (20%) yields at least 28% uncertainty in the missing fraction of OH reactivity. As both the slope and average discrepancy agree with measurement within 28%, on average, we find no significant discrepancy between modeled and measured OH reactivity. A subset of points that correspond to high β-pinene concentrations fall outside of this range. Most of these points occur early in the measurement period, from 11 June – 17 June. To investigate the sources of these discrepancies, we examine both the diurnal variability and composition of OH reactivity.

Figure 2 shows the diurnal variability of the missing portion of reactivity. In the afternoon, the model typically captures >90% of OH reactivity. At night, the model typically captures ~80% of measured reactivity. Early morning discrepancies show the largest average discrepancies, reaching an average of 32% missing reactivity at 7:00 L.T.

The average diurnal speciation of observed reactivity is shown in Figure 3. Primary biogenic VOCs make up the largest fraction of modeled OH reactivity throughout the entire day, with isoprene contributing ~60% in the afternoon and ~30-40% at night, and monoterpenes contributing ~15-25% at night. Oxygen containing VOCs contribute less significantly at all time points (~20-28%), and the largest individual contributors are measured species such as HCHO (~3-4%), MVK, and MACR (~2-4%). Unmeasured oxidation products contribute ~6-10% of total modeled reactivity, and are most prominent at night.

As discussed in Edwards et al. (2013), the increase in total reactivity with increase in isoprene is another useful parameter when considering OH reactivity speciation. In a plot of total OH reactivity plotted against the contribution from isoprene alone, the slope is related to the contribution from short-lived isoprene-derived OVOCs and VOCs co-emitted with isoprene. Figure 4 shows this relationship for measured and modeled OH reactivity, still referring to the OVOC-constrained scenario. Both observed and modeled OH reactivity are tightly correlated with OH reactivity from isoprene ($r^2 \geq 0.81$). ~~The slopes are not much larger than one, again demonstrating that isoprene (rather than its oxidation products) dominates daytime reactivity at this site.~~ The difference between model (1.22 ± 0.02) and observed (1.~~43~~ 44 ± 0.02) slope is small but significant. This amounts to 15% of reactivity correlated with isoprene reactivity not captured by measured species or modeled unmeasured oxidation products. The y-intercept from measurements (6.~~3~~ 4 ± 0.1 s^{-1}) and model (5.~~2~~ 4 ± 0.1) also show a small but significant difference. This indicates a missing reactivity of ~1 s^{-1} that is temporally distinct from isoprene reactivity.

3.2 Measured and Modeled OVOCs

By investigating the model's ability to capture measured OVOC concentrations, we can ~~determine~~ assess the ~~reliability~~ likely accuracy of model predictions of unmeasured species. As the model is constrained to measured OVOC concentrations when calculating model OH reactivity, the contribution of unmeasured species to total reactivity will be different in these two scenarios. However, the ~~assessment~~ evaluation of model performance can be extended to the constrained-OVOC scenario.

Figure 5 shows the model's prediction of several measured OVOC concentrations. Isoprene's first generation oxidation products MVK+MACR, ISOPOOH, ISOPN, and HPALD are over-predicted in the afternoon. Though the uncertainties in each of these measurements is large (40-70%), all model concentrations are much higher than measurements. The model overestimates daytime HPALD observations by a factor of ~~~-~~6, ISOPOOH by a factor of ~4, and ISOPN by a factor of ~~~-~~3. This translates to an overprediction of IEPOX and $MACNO_3$+$MVKNO_3$, which are formed in the oxidation of ISOPOOH and ISOPN, respectively. For MVK+MACR, the daytime over-prediction is approximately a factor of two. Daytime agreement for MPAN, which is formed from MACR, is comparatively good. In general, smaller oxidation products (i.e., glyoxal, glycolaldehyde, and HCHO) are less susceptible to overprediction.

~~Model OVOC concentrations are highly sensitive to the assumed dilution scheme (see full discussion in Supplement). However, i~~In an investigation of isoprene photochemistry and turbulent mixing during this campaign, the ~~a more complex~~ mixed layer chemical model (MXLCH) predicts similarly high ~~peak~~ values for ISOPOOH (1.5 ppb), MVK+MACR (3.0 ppb), and ISOPN (80 ppt) in the convective mixed boundary layer (Su et al., 2015). The MXLCH MVK+MACR mixing ratios are substantially higher than ground-based measurements, but comparable to measurements from the Long-EZ research plane flying at altitudes from 100 – 1000 m a.g.l.

Model OVOC concentrations are highly sensitive to the assumed dilution scheme (see full discussion in Supplement). ~~Flight based measurements were relatively uniform throughout the boundary layer.~~ In order for dilution alone to account for the low concentrations of first generation oxidation products, extremely high dilution rates would need to be incorporated. For ISOPOOH, a constant rate of 40 day^{-1}, (roughly five times the photochemical loss rate) would be needed. Most importantly, when OVOCs are constrained, the assumed dilution scheme has very little effect on the model OH reactivity (Figure S2), as measured species dominate total reactivity.

4. Discussion

While on average the model largely captures the absolute value of OH reactivity at SOAS (Fig 1), there are small but significant differences (15%) in the increase of total reactivity and reactivity from isoprene alone (slope of Fig ~~3~~4). While most measured species have uncertainties >15%, it is unlikely that all measured species are systematically low, suggesting this discrepancy is likely the result of unmeasured species. When given a constrained precursor, the model either reproduces or overpredicts the resulting oxidation products (Fig 5, Fig S4). As isoprene and its oxidation products are heavily constrained, we conclude that~~e~~ unmeasured primary species co-emitted with isoprene (and those species' oxidation products) are the likely source of this small discrepancy.

As observed daytime isoprene concentrations increase with temperature, the difference in slope also represents a temperature-dependent daytime missing reactivity. The temperature dependence observed at SOAS is greater than that observed by Di Carlo et al. (2004) and the dependence of monoterpene emissions, though it is important to note the different range of temperatures included in each set of observations (Figure 6). Emissions which depend both on temperature and light are likely to have stronger net temperature dependence, as temperature increases with increasing solar radiation. Therefore, a portion of the total missing emissions could~~is~~ likely be characterized by both a light and temperature dependence.

Furthermore, the model is missing ~1 s^{-1} reactivity that is temporally unrelated to the oxidation of isoprene and co-emitted species (intercept of Figure ~~3~~4). This is consistent with the diurnal variability of missing reactivity, with larger portions occurring at night and in the early morning (Figure 2). Likely, missing nighttime reactivity is composed of a mixture of unmeasured primary emissions, unmeasured oxidation products, and long-lived unmeasured species mixed in from the residual layer. Xiong et al. (2015) show that 27% of the early morning increase in ISOPN results from downward mixing from the residual layer during this campaign. Similarly, there may be unmeasured OH reaction partners stored in the nocturnal boundary layer that lead to an increase in OH reactivity upon breakup of the inversion. Like β-pinene, anthropogenic VOCs such as toluene and benzene are highest at night. However, these species were not unusually high during the 11 June – 16 June period which demonstrated the highest missing reactivity, and therefore unmeasured anthropogenic VOCs are unlikely the major source of discrepancy. Sesquiterpenes ($C_{15}H_{24}$) are another class of VOC which typically follow the emission patterns of monoterpenes. The total sesquiterpene emission rate from broadleaf trees is estimated to be ~67% of the emission rate of total monoterpenes in terms of total mass (Sakulyanontittaya et al., 2008). Assuming a reaction rate with OH of β-caryophyllene, ~200 ppt of sesquiterpenes would provide the 1 s^{-1} offset in reactivity temporally separated from isoprene.

Much like the previous work of Zannoni et al. (2015), we find good daytime agreement between measured and modeled reactivity above the forest canopy, and that the majority of reactivity can be attributed to primary emissions. Using measurements of first and later generation OVOCs as a constraint on the amount of total unmeasured oxidation products, we find no evidence of substantial contributions of unmeasured OVOCs to above-canopy OH reactivity. This is in contrast to studies of Edwards et al. (2013) and Hansen et al. (2014), who showed that these species may contribute significantly to OH reactivity directly above the forest canopy. Varying amounts of intra-canopy oxidation are likely to result in these different conclusions, as secondary compounds will quickly become more important than the primary isoprene emissions at higher altitudes or farther downwind of the forest.

Based on measured OH concentrations, the measured concentrations of OVOCs suggest surprisingly little intracanopy oxidation of primary VOCs at this site. Furthermore, advection does not appear to bring in processed isoprene emissions. Despite measuring ~10 m above the forest canopy in a relatively homogeneous area, OH reactivity is primarily composed of measured primary species. Our model overpredicts concentrations of isoprene's first generation oxidation products by at least a factor of two. If these species and other OVOCs were not constrained by measurements, these overpredictions would lead to problematic conclusions about the speciation of reactivity. In the relationship of reactivity from isoprene to total reactivity, the modeled slope (1.~~43~~ 22 ± 0.02) and measured slope (1.~~44~~ 44 ± 0.02) would show no discrepancy. While the true observed missing contribution is small, it highlights the contribution from primary species whose oxidation may be important downwind.

5. Conclusions

In summary, the discrepancies in the absolute value of measured and modeled OH reactivity are rarely significant at this site. This suggests that the total RO_2 production rate and resulting O_3 formation are likely well understood. In contrast, small but significant discrepancies in the observed and calculated trend in OH reactivity with increasing isoprene suggest missing sources of reactive carbon. The model fails to capture a portion of reactivity that is temporally related to isoprene, as well as a portion unrelated to local isoprene oxidation. As isoprene oxidation products are heavily constrained and the model does not typically underestimate OVOCs, we propose that missing primary emissions and their oxidation products are likely candidates for both sources of reactive carbon. While these missing emissions do not lead to significant inconsistencies between measured and modeled OH reactivity, at larger total emissions, the trending discrepancy may lead to larger missing fractions of OH reactivity.

Additionally, the speciation of this missing carbon source has air quality relevant implications. For example, though monoterpenes are much less abundant than isoprene, they can substantially effect SOA formation. Ayres et al. (2015) found that organic nitrate aerosol from NO_3 + monoterpenes is a substantial contribution to observed particulate matter at this site, with a SOA molar yield of 23-44%. In contrast, the comparable isoprene nitrate is primarily a gas-phase product. Through positive matrix factorization analysis of aerosol mass spectrometer measurements, Xu et al. (2015) found monoterpene + NO_3 chemistry contributes 50% to total nighttime organic aerosol formation at this site, whereas IEPOX-derived SOA constitutes 19-34% total organic aerosol. Additionally, Su et al. (2015) cite aerosol uptake and condensed phase reactivity as a possible explanation for the large discrepancy between observed and modeled ISOPOOH at this site, which implies a large loss of total carbon to the aerosol phase. While the magnitude of OH reactivity is well captured, continued efforts in speciated OVOC and VOC measurements are vital to fully understand the SOA contribution from various primary emissions.

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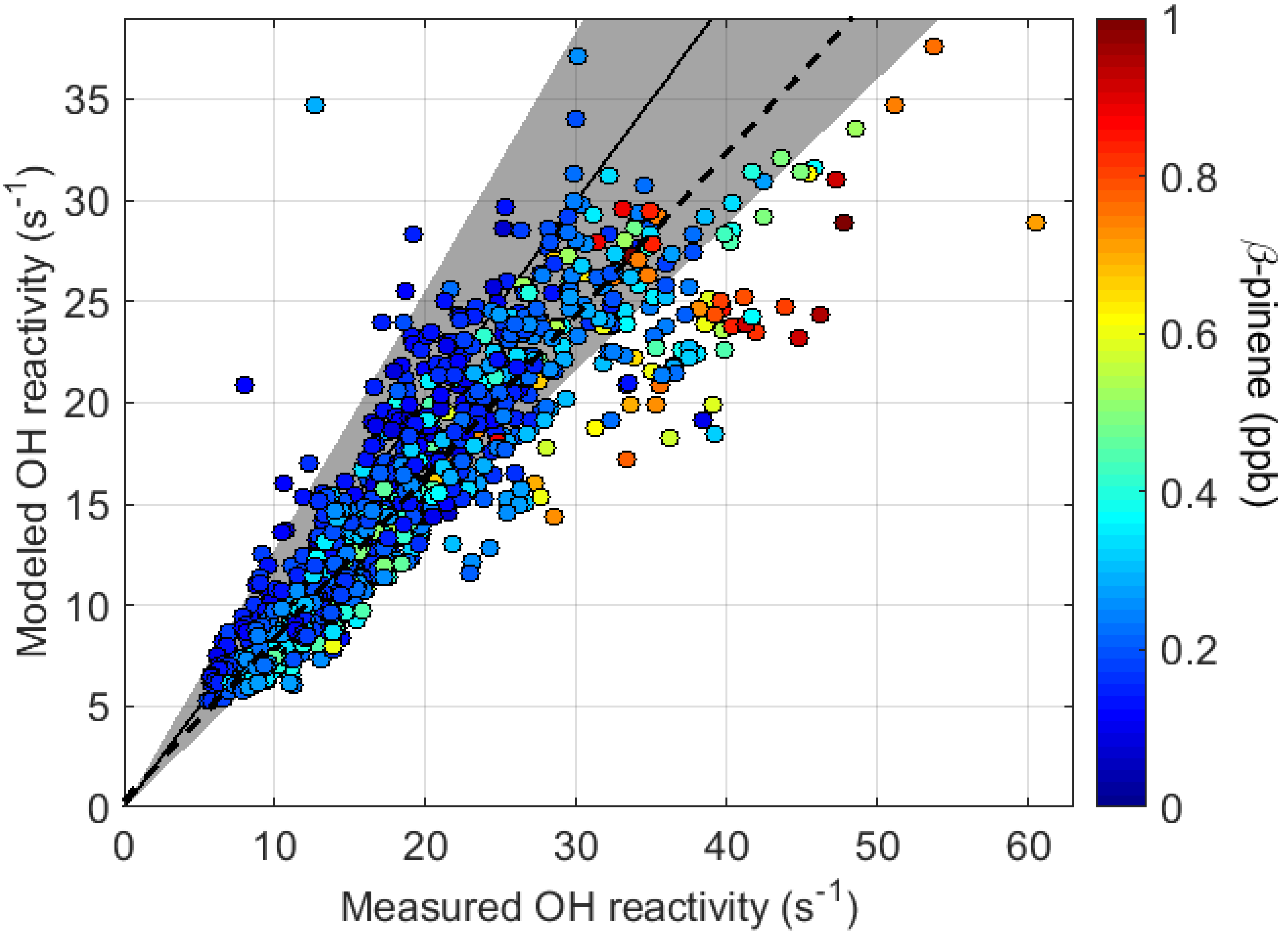
Table 1. SOAS measurements used in this study

Instrument	Parameters[a]	1 σ uncertainty	Reference/Model number
OH Laser-induced fluorescence	OH[b] OH reactivity	16% (30 min) 10% (30 sec)	Mao et al., 2009
Tropospheric Airborne Chromatograph for Oxy-hydrocarbons	VOCs[b]	20% (30 min)	Gilman et al., 2010
Proton-transfer-reaction time-of flight mass spectrometer	Total monoterpenes[b] MVK+MACR	20% (1 min) 40% (1 min)	Jordan et al., 2009
CF_3O^- triple quadrupole chemical ionization mass spectrometry	ISOPOOH, IEPOX, Glycolaldehyde	100 ppt + 70% (0.5 sec)	St. Clair et al., 2010
Fiber-Laser-Induced-Fluorescence	HCHO	15% (1 s)	Hottle et al., 2008; DiGangi et al., 2011
Madison Laser-Induced-Phosphorescence	Glyoxal	9% (1 s)	Huisman et al., 2008
Gas Chromatograph-Electron Capture Detector	PAN, PPN, MPAN	20% (20 min)	Roberts et al., 2002
CF_3O^- compact time of flight mass spectrometer	HCOOH[b], H_2O_2[b], HNO_3[b], ISOPN, Hydroxyacetone, Peroxyacetic acid, HPALD, $MACNO_3$+$MVKNO_3$	100 ppt + 30-50% (5 sec)	Crounse et al., 2006
Absorption of IR with Gas Filter Correlation	CO[b]	7.4% (5 min)	Thermo Scientific Model 48i-TLE
Nitrogen Oxides by Cavity Ring Down	O_3[b] NO[b] NO_2[b]	3% (1 min) 8% (1 min) 3% (1 min)	Fuchs et al., 2009; Wild et al., 2014

[a] All species listed are constrained when calculating OH reactivity.

[b] Denotes species constrained when calculating both OH reactivity and OVOC mixing ratios.


Modeled OH reactivity (s^{-1})
Measured OH reactivity (s^{-1})
0
5
10
15
20
25
30
35
0
10
20
30
40
50
60
β-pinene (ppb)
0
0.2
0.4
0.6
0.8
1

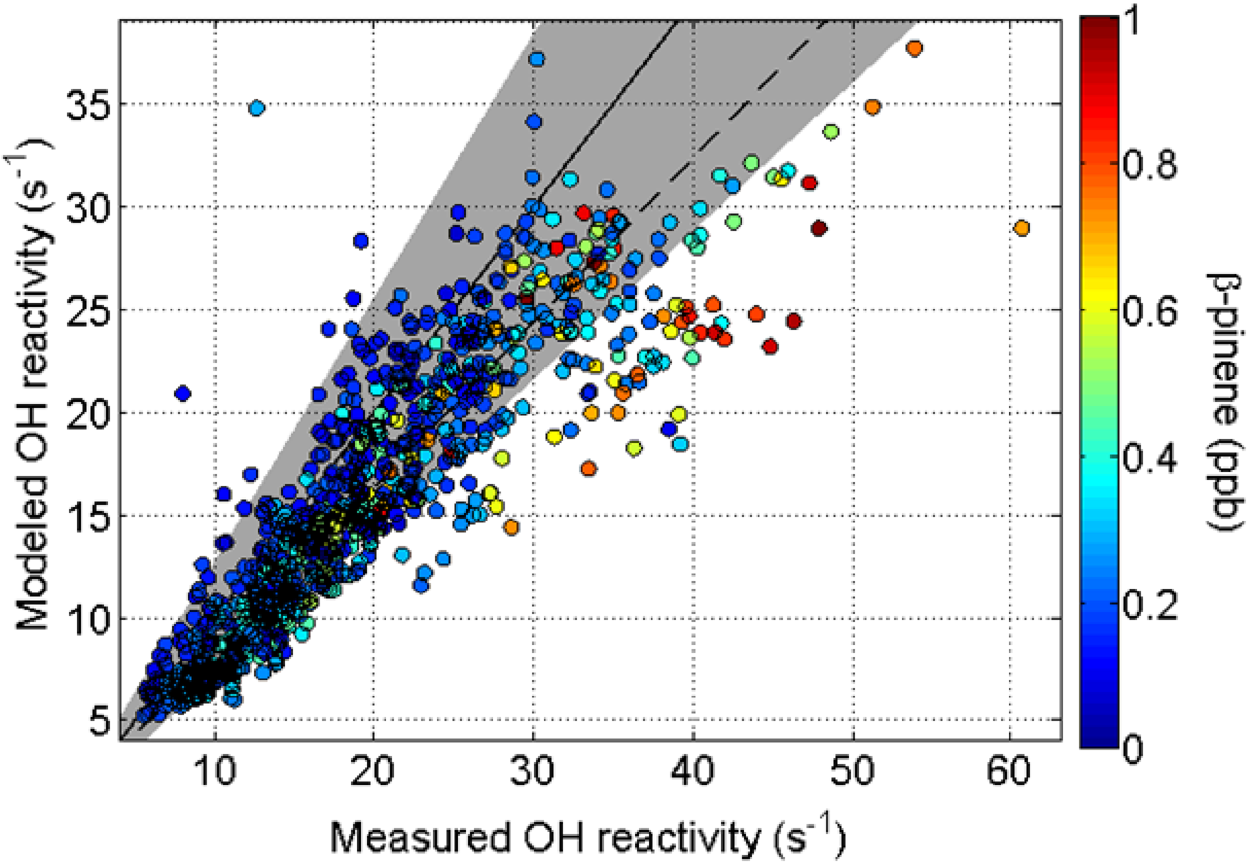


Figure 1. Comparison of measured and modeled OH reactivity colored by measured β-pinene concentrations. The solid line represents 1:1 agreement, and the dashed line (y=0.80x+0.36) ~~-~~represents the linear least squares fit weighted by uncertainty (York et al., 2004; Thirumalai et al., 2011). The grey shaded area represents ~~points~~ the region with ~~within combined~~ 28% uncertainty of 1:1 agreement. ~~(± 28%).~~

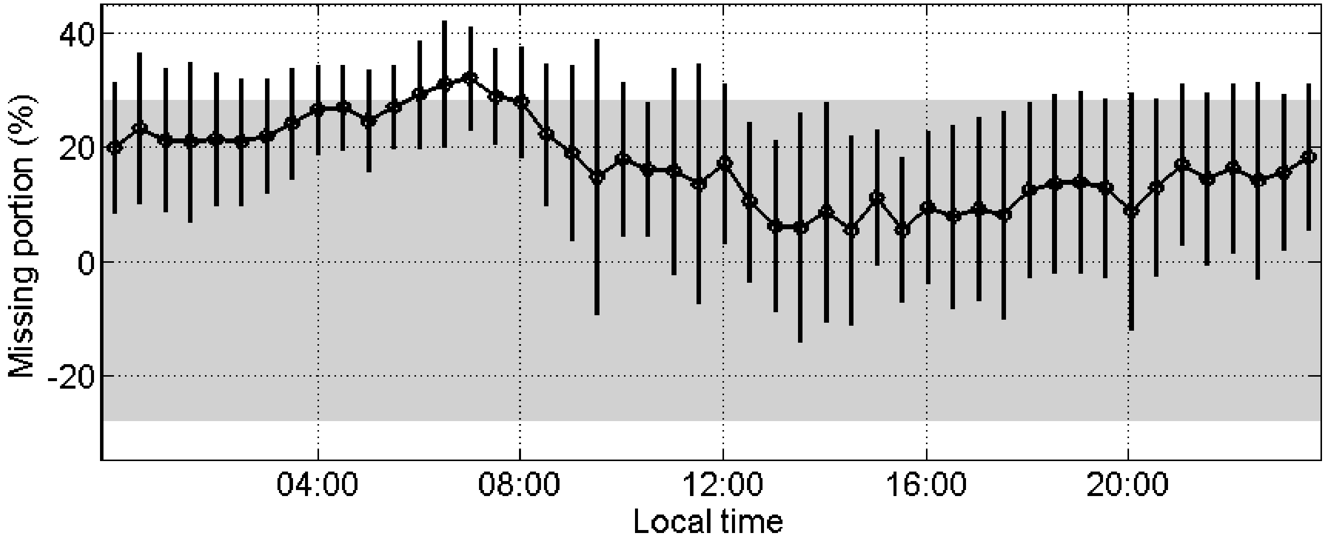


Figure 2. Diurnal profile of the discrepancy between measured and modeled OH reactivity. Error bars represent 1 σ standard deviation of diurnal variability. Points in the ~~in~~ gray shaded area are within the range of agreement considering combined measurement and model uncertainty (±28%).

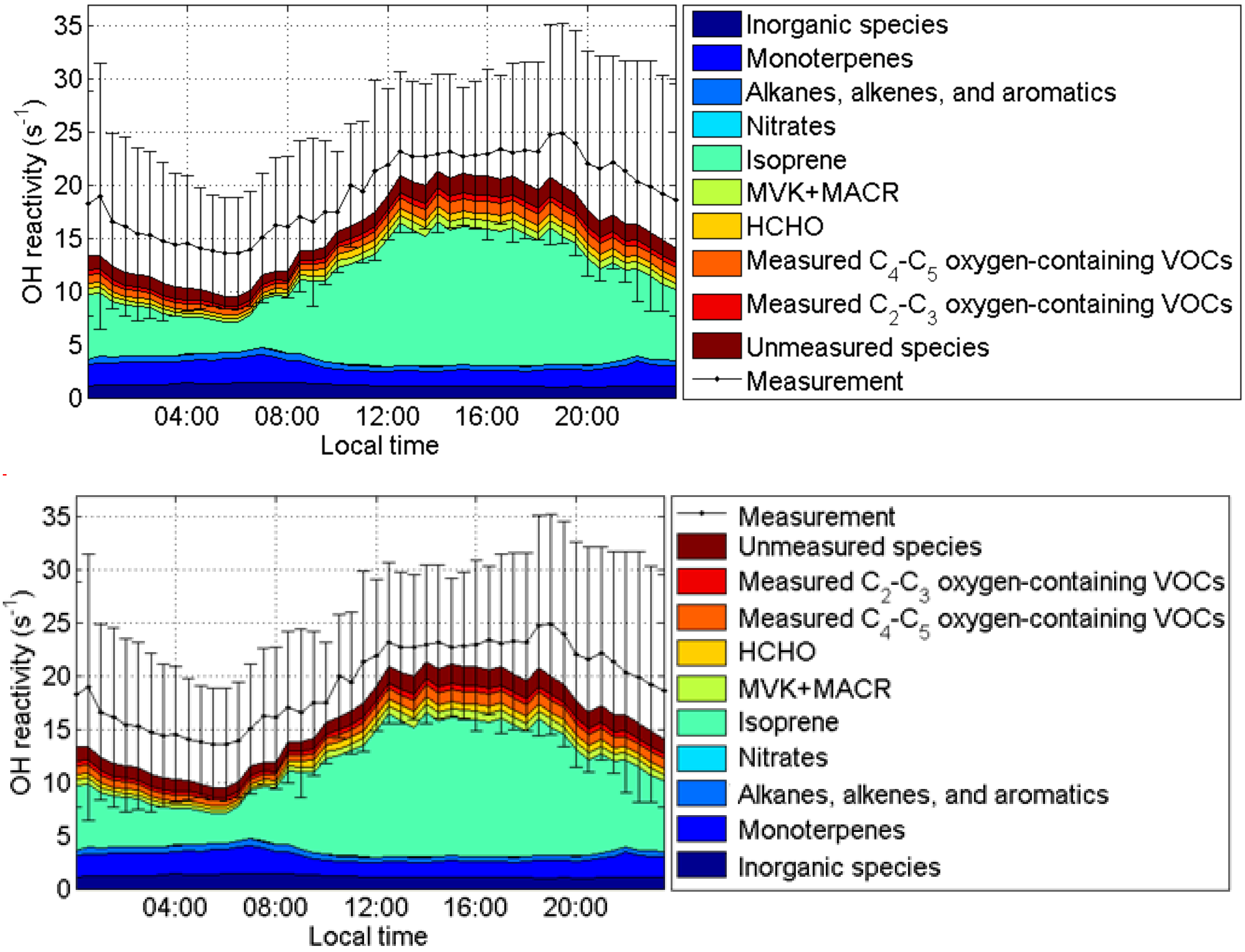
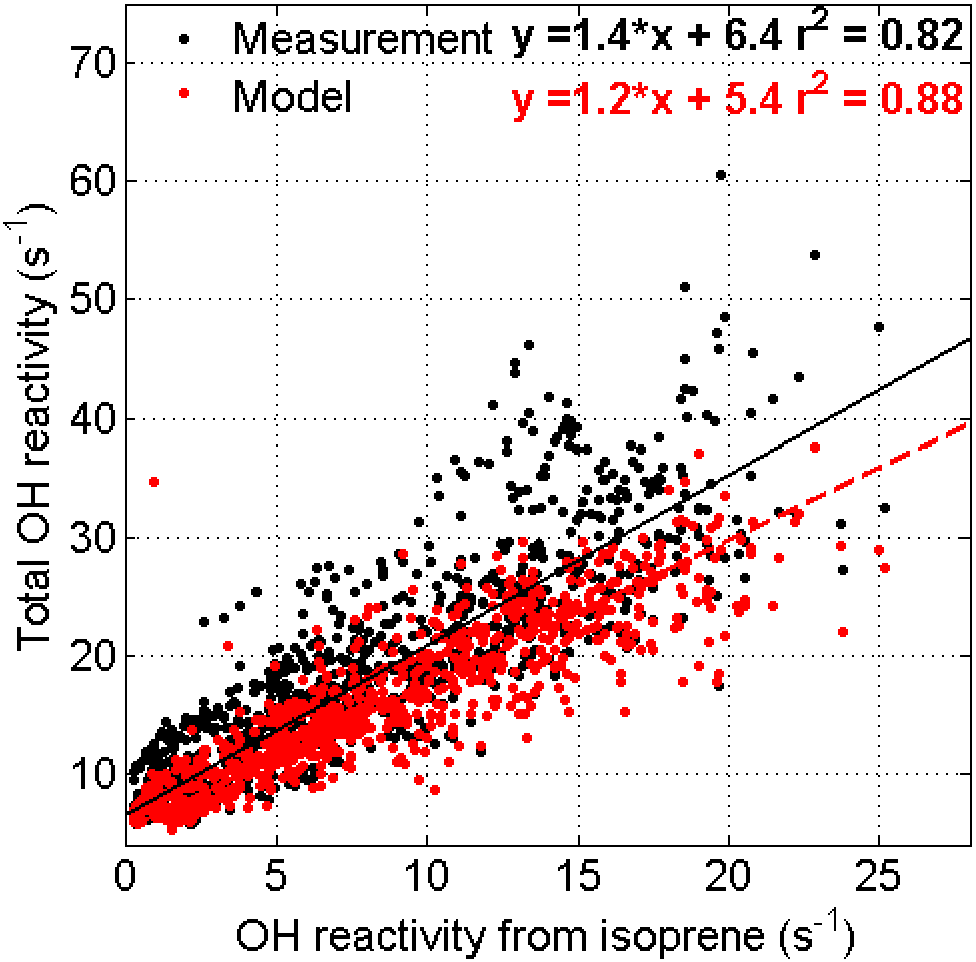


Figure 3. Diurnal profile of measured and modeled OH reactivity. Error bars represent 1 σ standard deviation of diurnal variability.


• Measurement y =1.4*x + 6.4 r^2 = 0.82
• Model y =1.2*x + 5.4 r^2 = 0.88
Total OH reactivity (s^{-1})
70
60
50
40
30
20
10
0
5
10
15
20
25
OH reactivity from isoprene (s^{-1})

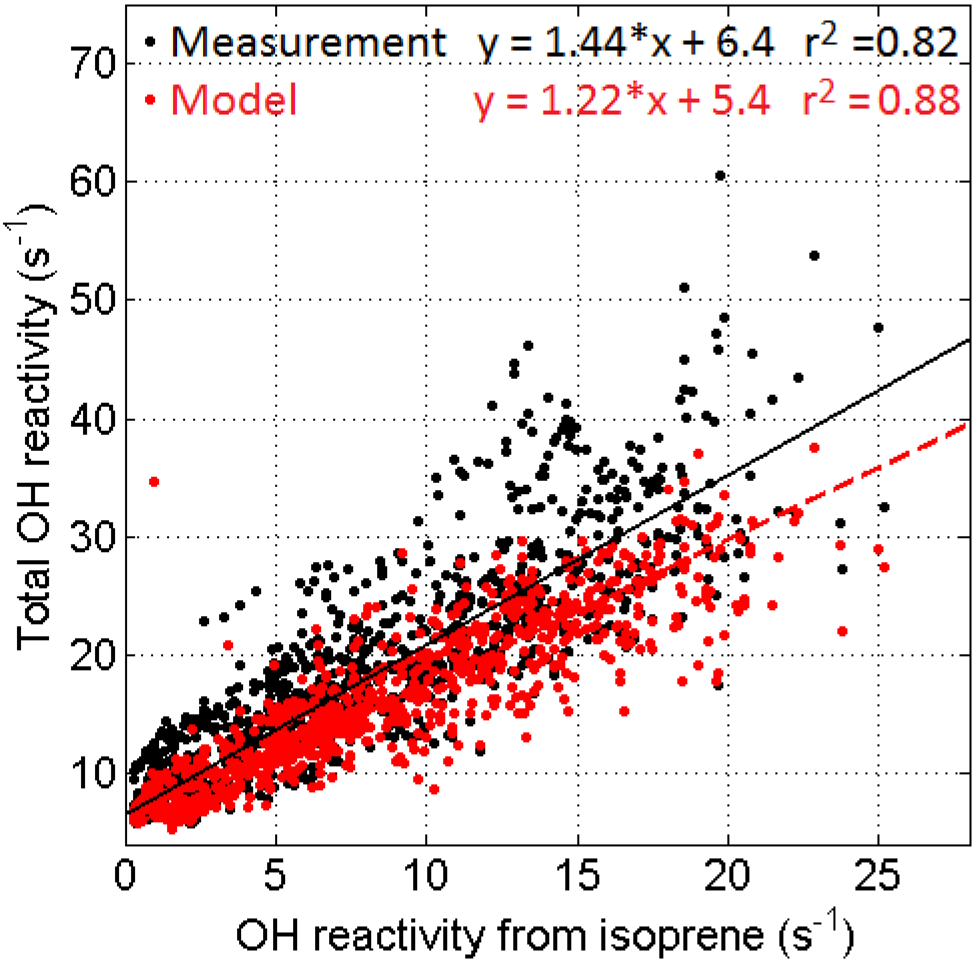


Figure 4. Total measured and modeled OH reactivity as a function of the OH reactivity calculated from isoprene alone. Lines represent least square linear fits weighted by uncertainty (York et al., 2004; Thirumalai et al., 2011) for measured (solid) and model (red dashed) OH reactivity.

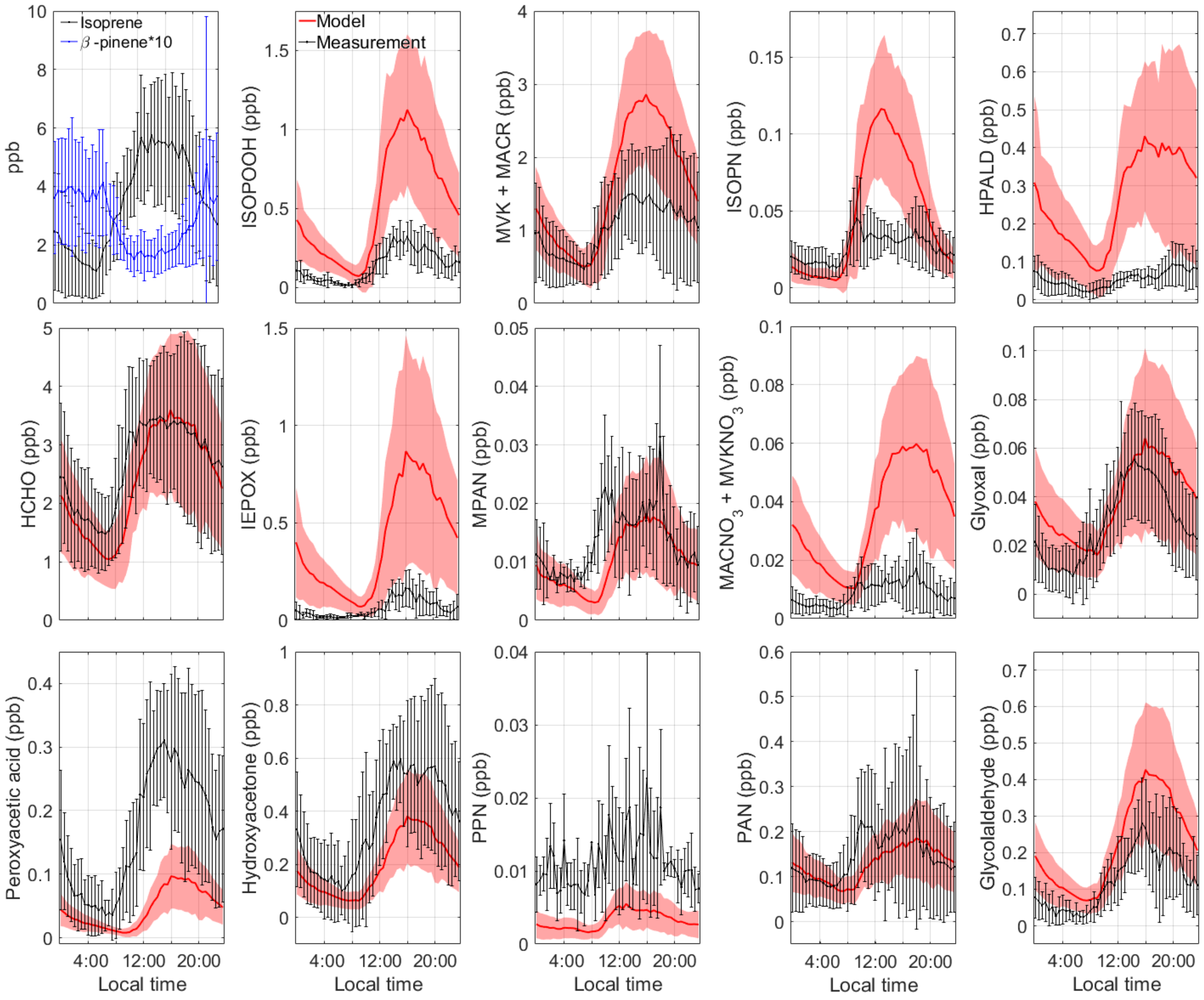


Figure 5. Average measured and modeled diurnal profiles of ~~mixing ratios for~~ isoprene, β-pinene, and several measured oxidation products~~ calculated by the model~~. Error bars and shaded area represent 1 σ standard deviation of diurnal variability. For each species, model results are not included for points where measurements are missing.

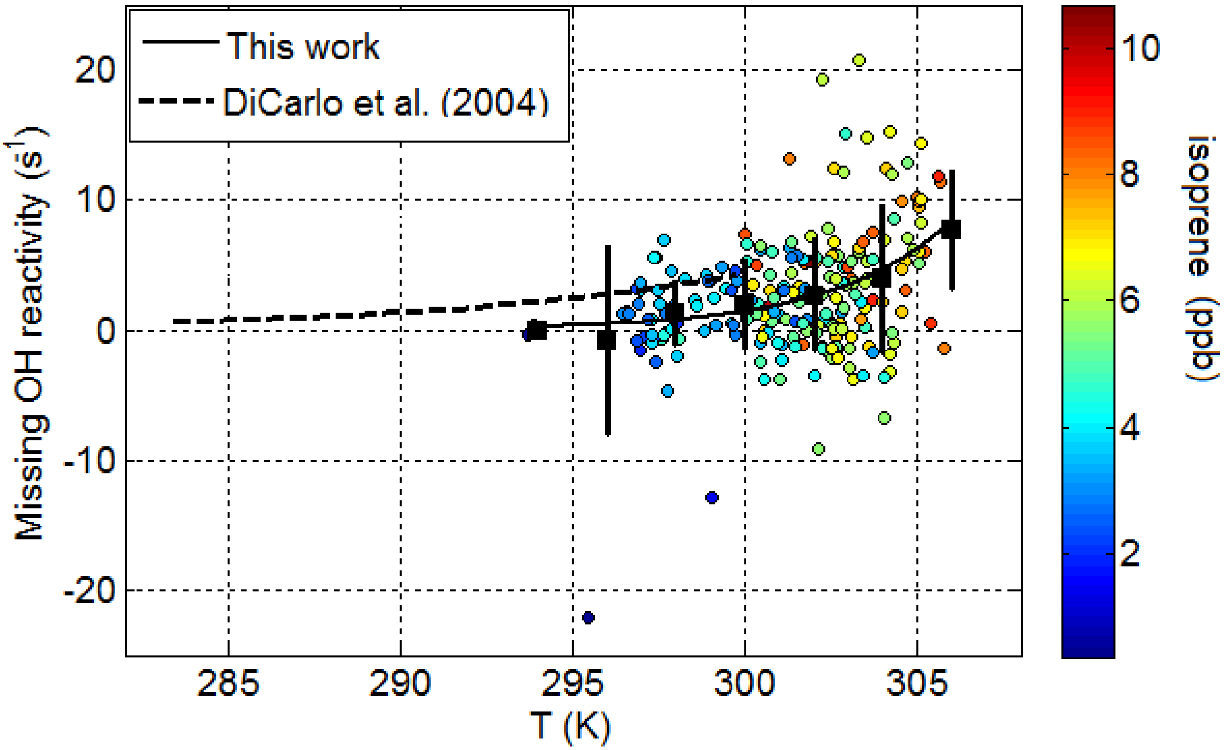


Figure 6. Daytime (10:00-16:00 L.T.) missing reactivity as a function of temperature and isoprene. Black squares represent 2 degree averages and standard deviations. All daytime points are fit according to the function y=α*exp(β(x-293)). The temperature dependence observed at SOAS (β = 0.30) is greater than that observed by Di Carlo et al. (2004) and the dependence of monoterpene emissions (β = 0.11).

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:

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

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:

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

Integrating yields:

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

We model OVOC concentrations and OH reactivity for three different dilution scenarios: (1) Applying the calculated entrainment rate k_e to all days, with no other dilution, and ignoring dilution where $k_e<0$. 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. (2) Applying a dilution constant that scales according to the ratio of observed BLH and maximum BLH, and (3) Using a constant dilution rate of either 2 $day^{-1,}$ 4 day^{-1}, and 40 day^{-1}. Calculated dilution rates are shown in Figure S1. As in the manuscript, measured VOCs are constrained when calculating OH reactivity. Results are shown in Figures S2 and S3.

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~~All scenarios~~ 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.

In contrast to OH reactivity, model OVOCs are largely a function of dilution rate. The rate of 4 day^{-1} is empirically determined based on the resultant agreement with several measured species including HCHO, glyoxal, glycolaldehyde, and PAN. Further support of this is the good agreement between measured and model IEPOX when ISOPOOH is constrained using this rate constant (Figure S4), and the agreement with the ISOPOOH, MVK+MACR, and ISOPN results from the mixed layer chemistry model presented by Su et al. (2015).

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 (Figure 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.~~18~~15	~~4~~7.~~92~~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

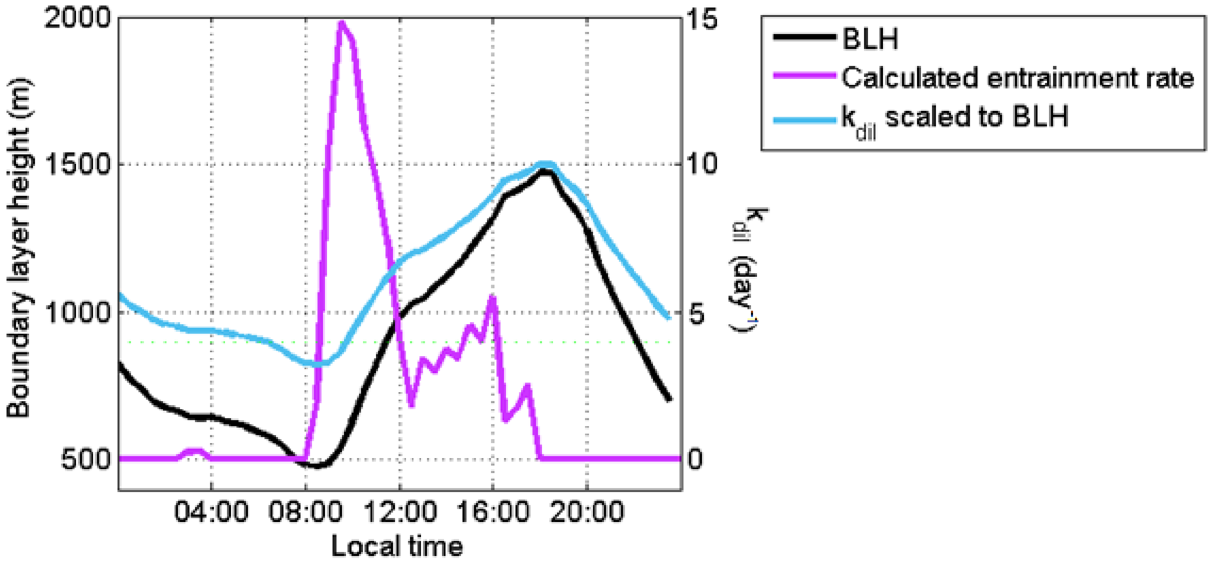
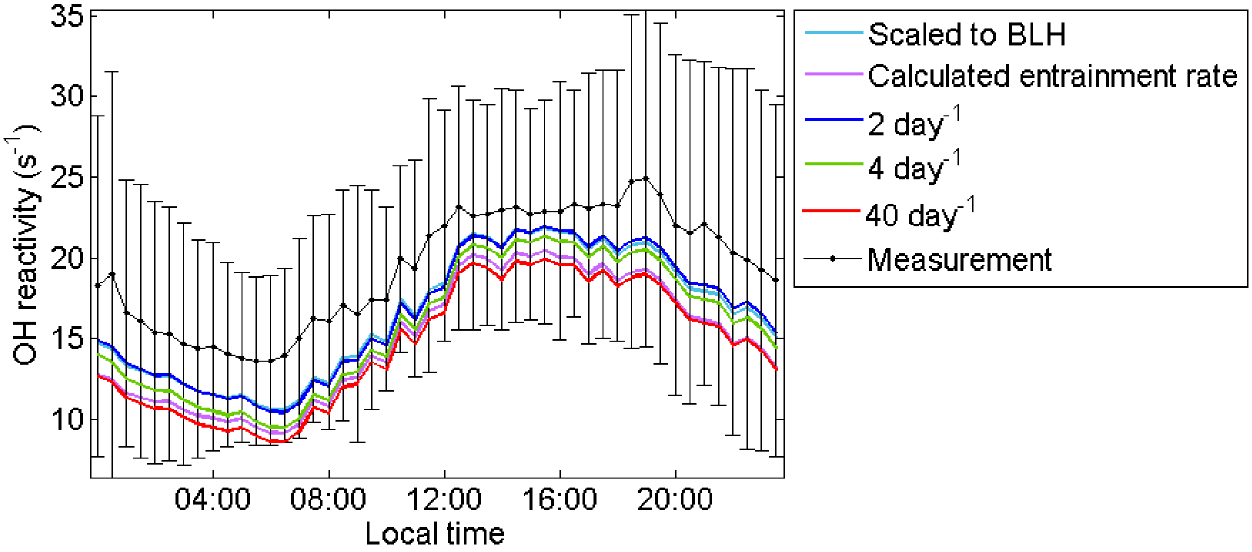


Figure S1. Diurnal average of boundary layer, smoothed over 2.5 hours, resultant dilution constant calculated according to Eq. 2, and dilution constant calculated from the ratio of BLH to maximum observed BLH.



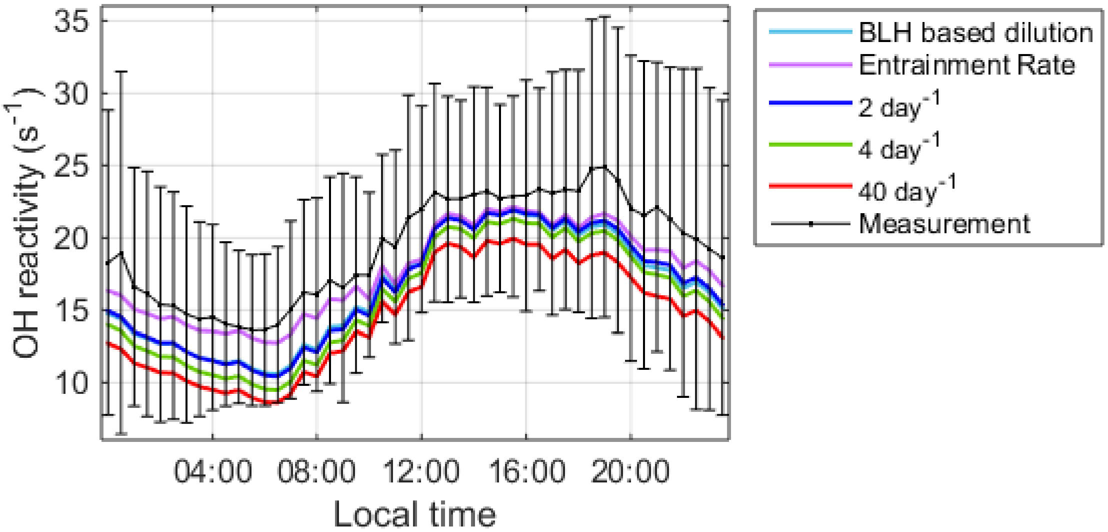
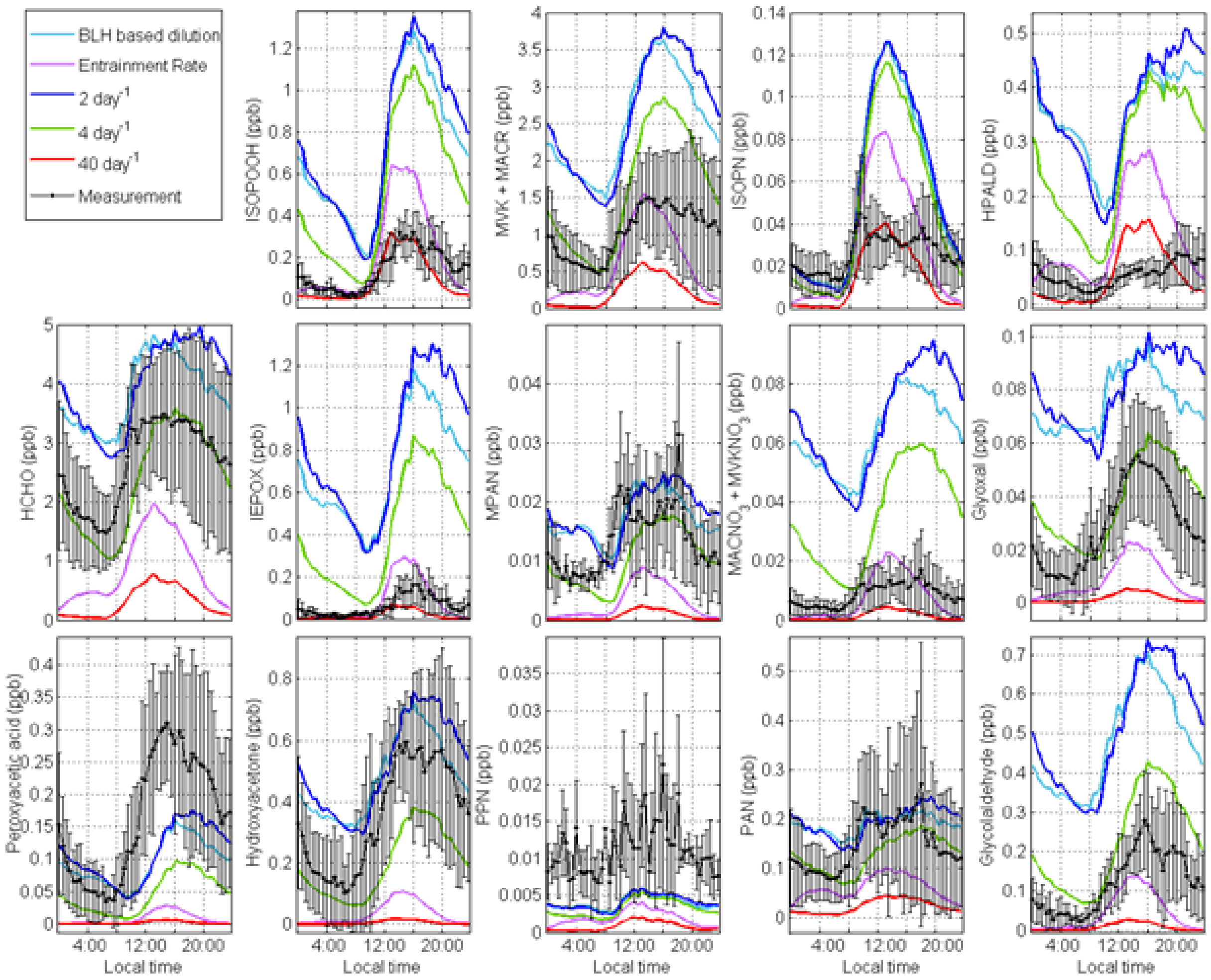


Figure S2. Sensitivity analysis for variability in the assumed dilution rate for OH reactivity. All measured species are constrained in this analysis. Error bars represent 1 σ diurnal variability in measurements. For clarity, diurnal variability is not shown in model results.


BLH based dilution
Entrainment Rate
2 day^{-1}
4 day^{-1}
40 day^{-1}
Measurement
ISOPOOH (ppb)
MVK + MACR (ppb)
ISOPN (ppb)
HPALD (ppb)
HCHO (ppb)
IEPOX (ppb)
MPAN (ppb)
MACNO$_3$ + MVKNO$_3$ (ppb)
Glyoxal (ppb)
Peroxyacetic acid (ppb)
Hydroxyacetone (ppb)
PPN (ppb)
PAN (ppb)
Glycolaldehyde (ppb)
4:00
12:00
20:00
Local time

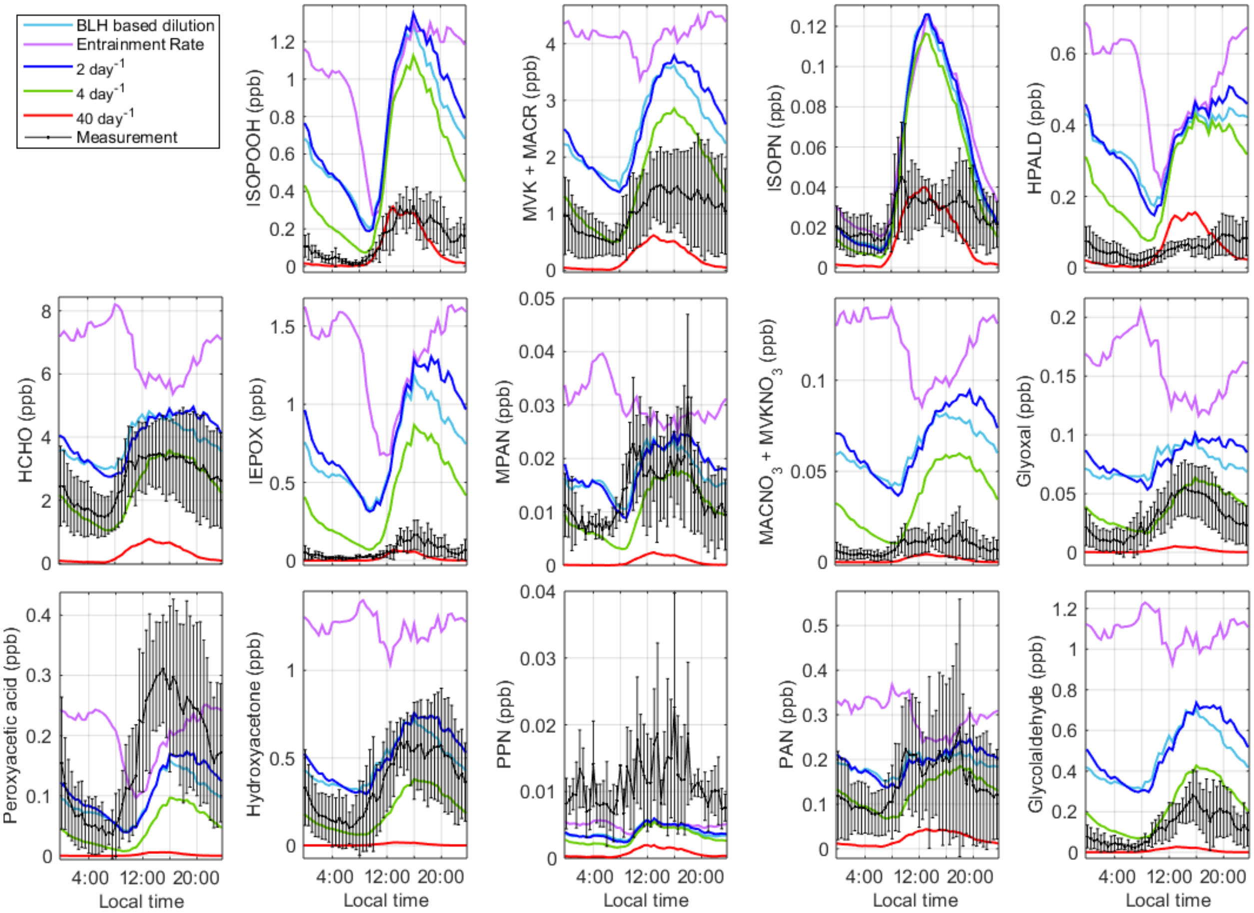


Figure S3. Sensitivity analysis for variability in the assumed dilution rate for OVOCs. Error bars represent 1 σ diurnal variability in measurements. For clarity, diurnal variability is not shown in model results. For each species, model results are not included for points where measurements are missing.

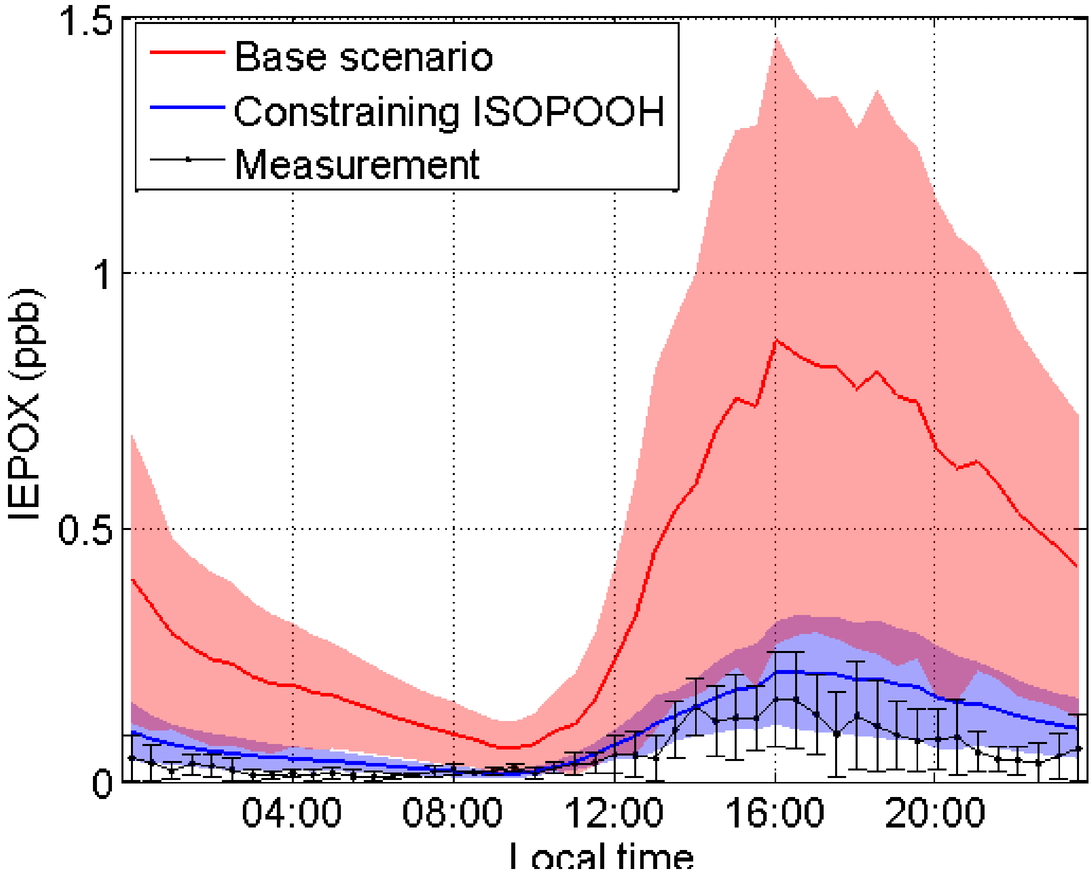


Figure S4. Comparison of measured and modeled concentrations of IEPOX with and without ISOPOOH constrained. Error bars and shaded area represent 1σ standard deviation of diurnal variability.

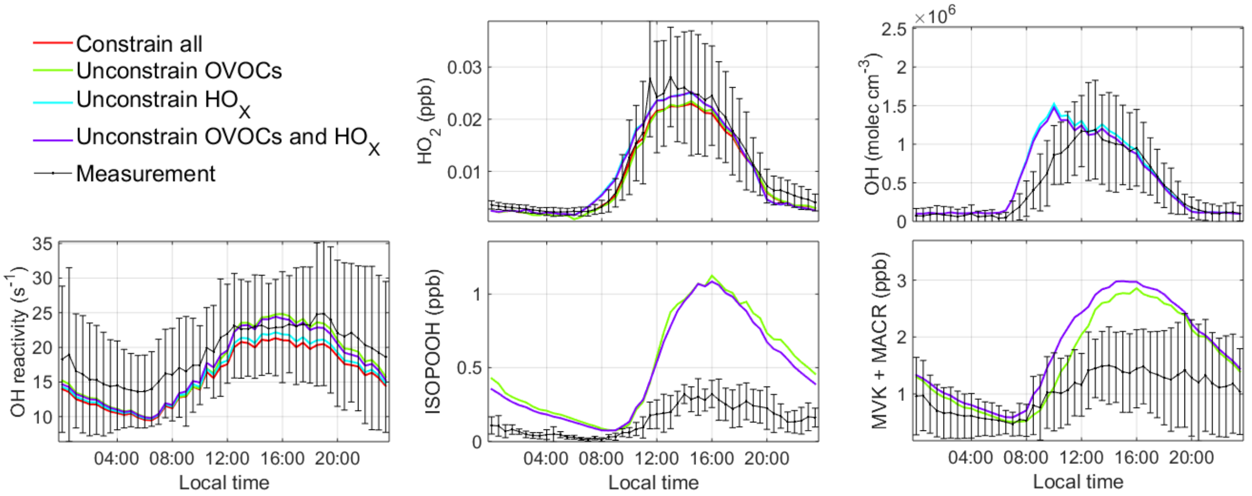


Figure S5. Model results of constraining or calculating OVOCs and HO_X on OH reactivity, HO_X, and specified OVOCs. Error bars on the measurement represent 1 σ diurnal variability. All scenarios use a constant dilution rate of 4 day^{-1}.