

1 **We would like to thank the two referees for their useful comments. We address these in bold**  
2 **below:**

3 **Referee 1:**

4 This papers reports on measurements of the total OH reactivity (kOH) in the megacity London.  
5 Measurements of kOH are sparse. Therefore, the presentation of these measurements are  
6 important. Measurements of kOH are completed in this campaign by the detection of a large set of  
7 different VOCs. The authors nicely show, to which extend contributions of all measured OH reactants  
8 can explain measured OH reactivity. If also contributions of unmeasured oxygenated VOCs that are  
9 calculated by models are taken into account, the authors can show that kOH is explained. As the  
10 authors emphasize, missing reactivity that is discussed in literature always needs to be seen in the  
11 context of the completeness of measurement of OH reactants. These messages are clearly presented  
12 in the manuscript. However, the focus of the paper on these points could be improved specifically in  
13 the second part of the manuscript. The authors should consider the following points:

14

15 (1) I assume that the measurement site was close to sources of VOCs. This may have consequences  
16 for the applicability of a box model, which assumes that oxygenated VOCs can accumulate. If the  
17 transport time between the source and the site is short, concentrations of products could be over-  
18 estimated.

19 **We have run the model both constrained and unconstrained to OVOCs that were measured**  
20 **(acetaldehyde, acetone as well as formaldehyde which is discussed in the paper) and find that the**  
21 **model has a tendency to under-estimates the concentration of these species, suggesting that**  
22 **there may be direct emissions of these species which are not considered in the model when run**  
23 **unconstrained. Therefore, unknown direct emissions of these species which would lead to model**  
24 **under-predictions may outweigh any expected model overprediction if full steady-state is not**  
25 **reached owing to short times between emission of parent VOCs and the site. We have discussed**  
26 **the sensitivity of the model predictions to the deposition term for all the unconstrained model**  
27 **species which determines the steady state concentrations reached and have shown the model to**  
28 **be reasonably insensitive to this.**

29 (2) In my opinion, the presentation of instruments that are used for the analysis is not well-balanced.  
30 The major progress of this work is that a large set of VOC measurements was detected. However,  
31 the authors present their FAGE system in much greater detail than their GC systems. The authors  
32 may want to move Fig. 4 in the context of a more detailed description of these instruments. It is not  
33 clear to me, if all details of the FAGE system that are currently given are required.

34 **The recent paper by Dunmore and co-authors (ACP, 15, 9983-9996, 2015) which we reference in**  
35 **the Experimental section details the VOC measurements and so we only provide a basic overview**  
36 **of these measurements in this paper. We do explicitly list all the VOCs individually included in the**  
37 **model in Table 1, however, which we feel is the key information for this manuscript. In the revised**  
38 **manuscript we will add further details on the effective saturation concentration range and**  
39 **sampling resolution of the GC systems. The details of the FAGE instrumentation was included as**

1 **we present OH and RO2 measurements from this instrument, however, in light of points (3) and**  
2 **(4) we will modify the FAGE details provided.**

3 (3) The authors discuss results of model calculations for HCHO, OH, HO2, and RO2. This discussion  
4 seems partly misplaced in this paper, especially because the authors announce to publish details of  
5 the comparison of modelled and measured radical concentrations in a separate paper. The context  
6 of the discussion is not always clear here and the information that is given to understand the results  
7 is not sufficient. I understand that the authors want to emphasize the importance of the increased  
8 number of VOC species that could be detected in this campaign. In this context, the discussion of  
9 HCHO might be justified. However, I do not see that the discussion of OH and RO2 makes much  
10 sense here. Only sparse information is given concerning important other species like for example  
11 ozone, HONO, details of NOx, HO2, CO that are needed to understand the production and  
12 destruction of radicals. Specifically, the model run of OH which is constrained to measured HO2  
13 requires at least to show the diurnal profile of measured HO2 and NO. I understand that this will be  
14 the topic of separate paper, but then I would suggest to remove the discussion here and to focus the  
15 paper on kOH.

16 **In this section of the paper we were aiming to demonstrate the impact of under-estimating OH**  
17 **reactivity on predicted OH (and, hence, the oxidising capacity), on the predicted HCHO and also on**  
18 **predicted ozone production. We think it is important to show the impact of this as many of the**  
19 **earlier publications which have compared modelled or calculated OH reactivity to observations**  
20 **have often constrained the model or calculation with only a limited VOC suite.**

21 **The aim of this section was not to model the observed OH and so, as the referee suggests, we will**  
22 **remove the OH model-measurement comparison (figure 9). We propose to restrict our discussion**  
23 **on the impact of under-estimating OH reactivity simply to stating the % change in modelled OH as**  
24 **a function of the three OH reactivity scenarios.**

25 **We also agree that it is not necessary to compare [RO<sub>2</sub>] calculated from OH reactivity to the**  
26 **observed [RO<sub>2</sub>] and so will remove Figure 10 (and remove the associated discussion) from the**  
27 **revised manuscript. We think it is important and relevant to discuss the impact the extra OH**  
28 **reactivity (that derives from the extended VOC suite or model generated intermediates) on ozone**  
29 **production, however, so we propose to still include discussion on the calculation of [RO<sub>2</sub>]<sub>ss</sub>.**

30 (4) The authors use measured OH to calculate steady state RO2, that is then used to calculate ozone  
31 production rate. It seems a bit arbitrary to use measured OH, but not to use measured RO2 instead  
32 of calculated RO2. If the calculated RO2 concentration is used, the reader needs more quantitative  
33 information, if simplifications in this calculation are justified.

34 **To evaluate the impact of the additional OH reactivity which derives from the extended VOC suite**  
35 **and model generated intermediates (which are not always considered when modelling or**  
36 **calculating OH reactivity) on ozone production we need to estimate the additional [RO<sub>2</sub>] that**  
37 **derives from these species. Using the observed [RO<sub>2</sub>] would not allow us to evaluate this.**

38 (5) Concerning the simplification of the calculation of the ozone production rate, it is not clear, why  
39 the authors do not include ozone production from HO2.

1 **As our aim was to show the impact on ozone production that arises from under-estimating the**  
2 **VOC fraction which contributes to the total OH reactivity, we chose not to include ozone**  
3 **production from HO<sub>2</sub>. We hope the revisions proposed above will make our main aims clearer in**  
4 **the revised manuscript.**

5 In my opinion, the discussion of the ozone production rate does not fit the topic of the paper well,  
6 because the only conclusion is that radical concentrations needs to be correct in the model. If RO<sub>2</sub> is  
7 measured like in this campaign, however, there is no need to use kOH at all.

8 **The aim was not to model (or calculate) ozone production rate – if we wanted to do this we would**  
9 **use our observations of RO<sub>2</sub> and HO<sub>2</sub>. The aim was to show the impact on ozone production of**  
10 **under-estimating the VOC fraction of the total OH reactivity. Substantial ozone production was**  
11 **observed during the campaign and understanding the influence of more-complex VOCs (which are**  
12 **not traditionally measured) and modelled intermediates have on this pollutant is important and a**  
13 **relevant discussion point.**

14 (6) Fig. 8 is mostly showing results that are already included in other figures. I would suggest to  
15 reduce this figure to the new aspects (physical loss, HO<sub>2</sub> constrained model).

16 **We will modify this figure accordingly.**

17 Why do the authors use the model run, in which HO<sub>2</sub> is constrained? If I understand the point  
18 correctly, the purpose is to get the modelled OH correct. In this case, however, the use of measured  
19 OH as constraint would make much more sense.

20 **Yes, we constrained the model to HO<sub>2</sub> to allow the model to predict OH correctly. We chose not to**  
21 **constrain to the measured OH so we could evaluate the model's ability to predict OH for diurnal**  
22 **comparisons presented in Figure 9. Regardless of the method chosen to reproduce the observed**  
23 **OH by the model, the impact of reducing the model OH on OH reactivity will be the same.**

24 (7) Technical remark regarding figures: The font size and thickness of lines may be not adequate in  
25 the final publication for one-column figures.

26 **We will assess this point at the production stage.**

1 **Referee 2:**

2

3 This paper presents measurements of total OH reactivity in central London during the ClearLo  
4 project in summer 2012. Similar to other studies, the authors find that the measured reactivity is  
5 greater than the reactivity calculated from a box model constrained to a standard set of VOC  
6 measurements consisting of C2-C8 hydrocarbons and a small selection of oxygenated VOCs.  
7 However, when the model is constrained to an extended set of measurements that included heavier  
8 molecular weight (up to C12) aliphatic VOCs, oxygenated VOCs and the biogenic VOCs of  $\alpha$ -pinene  
9 and limonene obtained using a two-dimensional GC instrument the modeled reactivity is in better  
10 agreement with the measurements. Including unidentified peaks in the GCxGC measurements  
11 further improves the agreement. Including the extended VOC measurements also improved the  
12 agreement between the measured and modeled OH concentrations, although the constrained  
13 model still overestimated the measured OH. Better agreement with the measured OH was achieved  
14 when the model was constrained to the measured HO<sub>2</sub>. The measured total RO<sub>2</sub> concentrations are  
15 also underpredicted by a steady-state calculation constrained by the modeled reactivity based on  
16 the standard VOC measurements, but are in better agreement with the measurements when the  
17 calculation is constrained by the modeled reactivity based on the extended VOC measurements.  
18 Because the missing reactivity appears to be mainly due to the contribution of  $\alpha$ -pinene and  
19 limonene and their oxidation products, the authors conclude that ozone control strategies for  
20 London should consider the impact of biogenic emissions. The paper is well written and suitable for  
21 publication in ACP. I have a few comments that the authors should consider in their revision of the  
22 manuscript.

23

24 1) The authors focus their discussion of missing reactivity on the diurnal average measurements.  
25 However, it would be interesting to examine some of the individual days in more detail. Are there  
26 days when the standard VOC measurements provide a reasonable estimated of the measured  
27 reactivity (perhaps days when the biogenic concentrations are lower), or do these measurements  
28 consistently underestimate the measured reactivity? The paper would benefit from an expanded  
29 discussion of the day-to-day agreement/disagreement of the measured and modeled reactivity.

30 **In Figure 6 we contrast the two air-mass scenarios encountered during the project. From these, it**  
31 **is evident that the contribution to the total reactivity made by an individual class of compounds**  
32 **does not change significantly between these two regimes, rather all classes represent bigger OH**  
33 **sinks during the more polluted phase. We have now looked at the breakdown in reactivity on a**  
34 **day by day basis in more detail. We note that the reactivity associated with the model**  
35 **intermediates deriving from the biogenic VOCs increases on the warmest days which were**  
36 **coincident with the easterly flows experienced at the beginning of the campaign. Temperatures**  
37 **were lower during the second easterly and, as a consequence, the model predicts a lower**  
38 **reactivity from model-generated intermediate species. On the 9<sup>th</sup> and 10<sup>th</sup> August (easterly flow,**  
39 **lower temperatures) a model constrained only with the standard VOC measurements provides a**  
40 **reasonable estimate of the total observed reactivity. When the influence on the biogenic species is**  
41 **strongest, i.e. during the first Easterly flow regime when it is warmer, only a model constrained to**  
42 **the extended VOC suite provides a reasonable estimate of the observed reactivity. As noted in the**

1 paper, at times (28<sup>th</sup> July – 5<sup>th</sup> Aug) during south westerly flows even a model constrained with the  
2 extended VOC suite is unable to entirely reconcile the observed reactivity. We hypothesised that  
3 there may be more undetected VOCs on these days or that the physical loss of the model  
4 generated intermediates should be treated differently during these two contrasting air-masses.  
5 The influence of biogenic species during the south westerly conditions was lower than during  
6 easterlies but non-negligible and inclusion of alpha pinene and limonene in the VOC model  
7 constraints improves the model measured agreement particularly from the 5<sup>th</sup> – 8<sup>th</sup> Aug and also  
8 from the 11<sup>th</sup> Aug until the end of the campaign.

9 In the revised manuscript we will include a discussion of the model performance day to day. We  
10 will add additional panels to Figure 1 showing the breakdown of modelled reactivity when only  
11 the standard VOC suite is considered and a panel showing the breakdown of modelled reactivity  
12 when the extended VOC suite is used to aid this discussion.

13 2) Related to the above, including a time series of the VOC and NO<sub>x</sub> measurements would assist in  
14 the interpretation of the information shown in Figure 1. In addition, showing the time series of the  
15 calculated reactivity based on the standard VOC measurements in addition to that modeled with the  
16 addition 2DGC VOC measurements would be useful.

17 We will include these additional time-series as suggested. We will separate the VOCs into biogenic  
18 and non-biogenic (excluding CH<sub>4</sub>). We will also include a time-series of temperature which we  
19 think helps to highlight what is driving the chemical composition observed on the warmer days.

20 3) The caption to Figure 1 states that days with easterly flow are highlighted. However, this is not  
21 clear in the Figure.

22 The clarity of this will be improved in the revised manuscript.

23 4) The authors state that the majority of the missing reactivity is due primarily to model generated  
24 intermediates from the oxidation of  $\alpha$ -pinene and limonene. Although they identify pinonaldehyde  
25 as a significant contributor, it would be useful to identify some of the other major contributors.

26 As we mention in the paper there are close to 2600 reactions included in the extended VOC model  
27 run which destroy OH and the reaction of OH with the different model-generated intermediate  
28 species accounts for >90% of these reactions so to list all these reactions explicitly would  
29 overwhelm the reader and wouldn't be very informative. We will extend this discussion to include  
30 the top 10 model-intermediate species and the % each contribute to reactivity.

31 5) It appears that the MCM model is unable to reproduce the observed OH concentrations even  
32 when the modeled OH reactivity is in agreement with the measured reactivity, perhaps due to the  
33 an overestimation of the HO<sub>2</sub> concentration. The authors state that the model constraints were re-  
34 initialized in the model every 15 minutes. Given the rapid propagation rates under these relatively  
35 high NO<sub>x</sub> concentrations, are the authors confident that the modeled constraints (especially NO,  
36 NO<sub>2</sub>, O<sub>3</sub>, HONO) are not changing during the 15 minutes? If they are changing it could impact the  
37 modeled radical concentrations including the propagation of HO<sub>2</sub> to OH and could explain some of  
38 the model discrepancies described in this section.

- 1 **We don't think this is the case, as rapidly changing model constraints would not result in a wholly**
- 2 **positive bias as we see (i.e. the model consistently over-predicts HO<sub>2</sub>).**
- 3

1 **Atmospheric OH reactivity in central London:**  
2 **observations, model predictions and estimates of *in situ***  
3 **ozone production**

4  
5 **L. K. Whalley<sup>1,2</sup>, D. Stone<sup>1</sup>, B. Bandy<sup>3</sup>, R. Dunmore<sup>4</sup>, J. F. Hamilton<sup>4</sup>, J.**  
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7  
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16  
17

18 **Abstract**

19 Near-continuous measurements of OH reactivity in the urban background atmosphere of  
20 central London during the summer of 2012 are presented. OH reactivity behaviour is seen to  
21 be broadly dependent on air mass origin with the highest reactivity and the most pronounced  
22 diurnal profile observed when air had passed over central London to the East, prior to  
23 measurement. Averaged over the entire observation period of 26 days, OH reactivity peaked  
24 at  $\sim 27 \text{ s}^{-1}$  in the morning with a minimum of  $\sim 15 \text{ s}^{-1}$  during the afternoon. A maximum OH  
25 reactivity of  $116 \text{ s}^{-1}$  was recorded on one day during morning rush hour. A detailed box  
26 model using the Master Chemical Mechanism was used to calculate OH reactivity, and was  
27 constrained with an extended measurement dataset of volatile organic compounds (VOCs)  
28 derived from GC-FID and a two-dimensional GC instrument which included heavier  
29 molecular weight (up to  $\text{C}_{12}$ ) aliphatic VOCs, oxygenated VOCs and the biogenic VOCs of  
30  $\alpha$ -pinene and limonene. Comparison was made between observed OH reactivity and  
31 modelled OH reactivity using (i) a standard suite of VOC measurements ( $\text{C}_2$ - $\text{C}_8$  hydrocarbons  
32 and a small selection of oxygenated VOCs) and (ii) a more comprehensive inventory  
33 including species up to  $\text{C}_{12}$ . Modelled reactivities were lower than those measured (by 33%)

1 when only the reactivity of the standard VOC suite was considered. The difference between  
2 measured and modelled reactivity was improved, to within 15%, if the reactivity of the higher  
3 VOCs ( $\geq C_9$ ) was also considered, with the reactivity of the biogenic compounds of  $\alpha$ -pinene  
4 and limonene and their oxidation products almost entirely responsible for this improvement.  
5 Further improvements in the model's ability to reproduce OH reactivity (to within 6%) could  
6 be achieved if the reactivity and degradation mechanism of unassigned two-dimensional GC  
7 peaks were estimated. Neglecting the contribution of the higher VOCs ( $\geq C_9$ ) (particularly  $\alpha$ -  
8 pinene and limonene) and model-generated intermediates decreases the modelled OH  
9 concentrations by 41%, and the magnitude of *in situ* ozone production calculated from the  
10 production of RO<sub>2</sub> was significantly lower (60%). This work highlights that any future ozone  
11 abatement strategies should consider the role that biogenic emissions play alongside  
12 anthropogenic emissions in influencing London's air quality.

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## 15 **1 Introduction**

16 It has been estimated that there may be in excess of 10<sup>5</sup> different VOC species present in the  
17 atmosphere globally (Goldstein and Galbally, 2007) and it is the hydroxyl radical which is  
18 primarily responsible for the processing and eventual removal of these compounds. In an  
19 urban setting, rich with vehicular emissions, the task of accurately quantifying the total rate  
20 of reactive OH loss using measurements of each individual VOC present is unfeasible. Yet  
21 underestimations of the loss rate of OH can lead to inaccuracies in predicting the OH  
22 concentration and oxidation capacity and, in NO<sub>x</sub>-rich areas, such as urban centres, ozone  
23 production resulting from the reaction between peroxy radicals (formed during OH oxidation  
24 of VOCs and CO) and NO may be under-estimated.

25

26 It is possible to measure the total OH reactivity, defined as:

27

$$28 \quad k_{OH} = \sum_i k_{OH+X_i} [X_i] \quad (1)$$

29

30 where [X<sub>i</sub>] represents the concentration of species which react with OH (VOC, NO<sub>2</sub>, CO etc)  
31 and  $k_{OH+X_i}$  is the corresponding bimolecular rate constant.

32



1 The techniques used to determine  $k_{OH}$  include the flow tube with sliding injector method  
2 pioneered by Brune and co-workers (Kovacs and Brune, 2001), a comparative rate method  
3 (Sinha et al., 2008), and a laser flash photolysis pump-probe technique (Sadanaga et al.,  
4 2004). These techniques have been used in a variety of environments and the reader is  
5 referred to the overview of previous measurements provided by Lou et al. (2010). Both the  
6 flow-tube with sliding injector and comparative rate method rely on H<sub>2</sub>O vapour photolysis at  
7 185 nm using a lamp which generates OH and HO<sub>2</sub> simultaneously. As a consequence,  
8 corrections must be made when ambient NO concentrations reach ~1 ppbV or more to  
9 account for OH recycled by reaction of this generated HO<sub>2</sub> with NO. The recycled OH, if left  
10 uncorrected, effectively slows the rate of the first order decay of OH (Ingham et al., 2009)  
11 leading to an underestimation of the OH reactivity. Using the flash photolysis technique, OH  
12 is generated by photolysing ozone at 266 nm followed by reaction of O(<sup>1</sup>D) with H<sub>2</sub>O vapour.  
13 HO<sub>2</sub> is not formed initially by this method, so it is possible to measure OH reactivity at  
14 significantly higher NO concentrations before a correction becomes necessary, making this  
15 technique well suited to urban measurements of OH reactivity (Sadanaga et al., 2005).

16  
17 There have now been several observations of OH reactivity in urban environments (Kovacs et  
18 al., 2003; Ren et al., 2003; Sadanaga et al., 2005; Shirley et al., 2006; Yoshino et al., 2006;  
19 Ren et al., 2006; Sinha et al., 2008; Mao et al., 2010; Chatani et al., 2009; Dolgorouky et al.,  
20 2012) with some of the highest ever observed values of >120 s<sup>-1</sup> recorded in megacities such  
21 as Mexico City (Shirley et al., 2006) and Paris (Dolgorouky et al., 2012). In many cities  
22 (Houston, New York City, Mexico City), OH reactivity has been found to be dominated by  
23 anthropogenic hydrocarbons, CO and NO<sub>x</sub>. Oxygenated VOCs (OVOCs) have been  
24 highlighted as significant OH sinks in a number of urban studies, contributing between 11–  
25 24% during summertime (Mao et al., 2010).

26  
27 The short-lived OH radical is in photostationary steady state, with its rates of production,  
28  $P_{OH}$ , and destruction,  $D_{OH}$ , balanced:

29  
30 
$$P_{OH} = D_{OH} = k_{OH} [OH] \quad (2)$$

31  
32 and hence simultaneous measurements of OH reactivity and OH concentrations permits a  
33 field measurement of  $P_{OH}$  and, by comparison with a model constrained using the measured  
34 OH precursors, an assessment of the completeness of the model radical sources can be

1 obtained. This type of OH budget analysis has proved particularly effective in highlighting  
2 large missing OH sources in low NO<sub>x</sub>, biogenically influenced regions, such as tropical  
3 forests (Whalley et al., 2011). In a number of urban studies conducted in different US cities  
4 and Mexico City (Mao et al., 2010), this type of OH budget analysis has identified that during  
5 the morning rush hour the rate of OH production exceeds that of destruction ( $P_{OH}/D_{OH} > 1$ )  
6 suggesting uncertainties in either the chemistry used in the model or in the measurements of  
7 the precursors of OH under elevated levels of NO<sub>x</sub> which lead to an overestimation of  $P_{OH}$ .

8  
9 OH reactivity measurements themselves are often compared to calculated values simply  
10 using equation (1) with  $[X_i]$  restricted to those species which are measured in the field, and  
11 with knowledge of laboratory kinetic data. In some cases comparison is also made with  
12 modelled OH reactivity which also includes unmeasured OH sinks which are often  
13 oxygenated VOCs formed following the oxidative degradation of directly emitted  
14 hydrocarbon species. Measurements of OH reactivity are typically higher than those  
15 predicted (Lou et al., 2010), with the difference between the measured OH reactivity and that  
16 either calculated or modelled referred to as the missing OH reactivity. Analysis of the  
17 magnitude of this disagreement when calculated and modelled OH reactivity are used to  
18 compare with field determined  $k_{OH}$ , enables some distinction to be made between the fraction  
19 of missing OH reactivity due to missing primary emissions and that due to unmeasured  
20 oxidised intermediates.

21  
22 Missing reactivity is often largest in forested environments, e.g. (Edwards et al., 2013), with  
23 both missing primary emissions (Di Carlo et al., 2004) and oxidised intermediates (Edwards  
24 et al., 2013) considered as potential contributors. In contrast, analysis made during a number  
25 of urban studies has demonstrated good agreement between measured OH reactivity and that  
26 calculated using equation (1) from individually measured OH sinks (Ren et al., 2003; Di  
27 Carlo et al., 2004; Mao et al., 2010). In almost all urban studies to date, the measured OH  
28 reactivity has been compared to calculated OH reactivity only rather than modelled reactivity;  
29 the latter would include an estimate of the contribution that model-generated intermediates  
30 make to the total loss rate. The fact that closure has previously been obtained using calculated  
31 reactivity from primary emissions alone suggests that oxidised intermediates do not always  
32 contribute significantly to the total OH reactivity in certain cities. This is not the case at all  
33 urban sites, for example Chatani et al. (2009) reported a missing reactivity of ~ 30% in Tokyo  
34 during the summer determined by comparing the measured OH reactivity with that calculated

1 from measured sinks, and concluded that oxidised intermediates likely contributed to the  
2 missing fraction. Similarly, Dolgorouky et al. (2012) reported a missing reactivity of 75%  
3 when continental air was sampled in Paris during the wintertime MEGAPOLI project and  
4 only measured sinks were used to calculate  $k_{\text{OH}}$ . The closure of the OH reactivity budget in  
5 certain cities such as Houston (Mao et al., 2010) and New York (Ren et al., 2003) may reflect  
6 the dominance of  $\text{NO}_x$  acting as main OH sink; a species from which no model-generated  
7 intermediates will derive (in New York the reaction of OH with NO and  $\text{NO}_2$  accounted for  
8 50% of the total OH reactivity (Ren et al., 2003)). The VOC classes which dominate in  
9 different cities may also be substantially different (and, hence, their propensity to generate  
10 intermediates may differ). For example, aromatics account for up to 15% of the total  
11 reactivity in Houston (Mao et al., 2010) where local petrochemical industries can influence  
12 the local air-mass composition. In contrast, aromatics accounted for just 5% of the total  
13 reactivity in Tokyo (Yoshino et al., 2012) during the summer of 2007. During the PRIDE-  
14 PRD campaign in southern China, OH reactivity was modelled using the Regional  
15 Atmospheric Chemistry Model (RACM) and, alongside calculated OH reactivity from  
16 measured sinks, was compared to measured OH reactivity. Lou et al. (2010) found that the  
17 calculated OH reactivity was a factor of two less than the measured value, whereas the  
18 RACM modelled OH reactivity reproduced the observations well, suggesting that  
19 unmeasured secondary species (mainly thought to be OVOCs) do make a significant  
20 contribution to the total observed OH reactivity. During the daytime the PRIDE-PRD site was  
21 heavily influenced by biogenic emissions, in contrast to some of the urban sites discussed  
22 above, which may in part explain the differences of the missing OH reactivity reported.

23

24 Care is needed when comparing the missing OH reactivity reported in the literature, as the  
25 chemical detail and range of measured VOCs and inorganic (e.g.,  $\text{NO}_x$ , CO,  $\text{O}_3$ ) species  
26 which have been used to calculate OH reactivity varies significantly between projects.  
27 Oxygenated VOCs or biogenic VOCs (in addition to isoprene) are often measured, although  
28 this is not always the case as in the urban studies reported by (Lou et al., 2010; Kovacs et al.,  
29 2003; Ren et al., 2003; Mao et al., 2010; Dolgorouky et al., 2012).

30

31 This paper presents an extensive dataset of OH reactivity measured in London during the  
32 summer of 2012 as part of the Clean air for London (ClearLo) project (Bohnenstengel,  
33 2014). Alongside OH reactivity, an extremely comprehensive speciated VOC dataset was  
34 measured and used to constrain a zero dimensional box model based on the Master Chemical

1 Mechanism v3.2 in order to model OH reactivity. By comparing modelled and measured  
2 reactivity the level of missing OH reactivity is quantified. By also constraining the model  
3 with a subset of the VOCs comprising the more commonly reported C<sub>2</sub>-C<sub>8</sub> VOCs (measured  
4 using a dual-channel gas chromatography system), we assess which classes of VOC are  
5 controlling the OH reactivity in London. Using the model we also investigate the impact of  
6 various classes of VOC on the concentration of peroxy radical species and consequently on  
7 the magnitude of *in situ* O<sub>3</sub> production.

8

## 9 **2 Experimental**

### 10 **2.1 Site description**

11 The ClearfLo campaign ran from 22<sup>nd</sup> July to 18<sup>th</sup> August and overlapped with the London  
12 2012 summer Olympics. An extensive suite of instrumentation was deployed and operated  
13 from the grounds of Sion Manning School in North Kensington (51°31'61" N, 0°12'48" W),  
14 which is located adjacent to a long-term air quality monitoring site in North Kensington (Bigi  
15 and Harrison, 2010). Further details on the campaign and location may be found in the  
16 ClearfLo overview paper (Bohnenstengel, 2014). The inlets for the OH reactivity instrument  
17 and those for measuring OH sinks were within 5 m of one another horizontally, and 1 m  
18 vertically.

19

### 20 **2.2 OH reactivity measurements**

21

22 OH reactivity measurements were made using the laser flash photolysis pump-probe  
23 technique (Sadanaga et al., 2004), and the instrument is described in detail in Stone et al.  
24 (2015). Ambient air was drawn into a reaction cell (85 cm in length; 5 cm internal diameter),  
25 at a flow rate of 12 slm, by an extraction fan situated at the far end of the reaction cell to the  
26 inlet. A flow of 0.5 slm of humidified ultra-high purity air (BTCA 178, BOC Special Gases)  
27 was passed across a low pressure Hg lamp, generating ~ 50 ppb O<sub>3</sub>, and mixed with the  
28 ambient air flow. Laser photolysis of O<sub>3</sub> at 266 nm gave uniform production of OH along the  
29 length of the reaction cell following the reaction of O(<sup>1</sup>D) with water vapour.

30

31 Changes in OH radical concentrations owing to pseudo-first-order loss with species present in  
32 ambient air were monitored by sampling air from the reaction cell through a 0.8 mm pin-hole  
33 into a FAGE (fluorescence assay by gas expansion) detection cell maintained at a pressure of

1 ~1.5 Torr by a Roots blower backed by a Rotary pump. The 308 nm probe laser, operating at  
2 a pulse-repetition-frequency of 5 kHz, was passed across the gas flow in the FAGE cell to  
3 excite OH radicals, with the subsequent laser-induced fluorescence (LIF) signal at ~308 nm  
4 detected by a gated channel photomultiplier tube (CPM). The OH decay profile owing to  
5 reactions with species in ambient air is thus detected in real time.

6  
7 Decay profiles were averaged for 5-minute periods, and fitted to a first-order rate equation to  
8 find the rate coefficient describing the observed loss of OH ( $k_{\text{loss}}$ ). The OH reactivity,  $k_{\text{OH}}$ ,  
9 was determined by subtracting the rate coefficient describing physical losses of OH ( $k_{\text{phys}}$ )  
10 from the observed loss of OH in ambient air, with a small correction to account for the  
11 dilution of ambient air with the small flow of O<sub>3</sub>-containing humidified ultra-high purity air.  
12 The rate coefficient,  $k_{\text{phys}}$ , was determined by monitoring the loss of OH when sampling ultra-  
13 high purity air (BTCA 178, BOC Special Gases, passed through scrubbers to remove trace  
14 amounts of NO<sub>x</sub>, H<sub>2</sub>, CO and CO<sub>2</sub>) containing the same small flow of O<sub>3</sub>-containing  
15 humidified ultra-high purity air as for the measurements sampling ambient air, and was found  
16 to be  $1.1 \pm 1.0 \text{ s}^{-1}$ .

17  
18 The accuracy of the OH reactivity measurements were verified in the laboratory by  
19 measuring the bimolecular rate coefficients for reactions of OH with CO and CH<sub>4</sub> under  
20 pseudo-first-order conditions at 293 K. For reaction of OH with CO, a bimolecular rate  
21 coefficient of  $(2.4 \pm 0.2) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  was determined, in agreement with the literature  
22 value of  $2.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  (Atkinson et al., 2006), and for OH + CH<sub>4</sub>, a rate coefficient of  
23  $(5.5 \pm 0.6) \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$  was determined, in agreement with the literature value of  $5.8 \times 10^{-15}$   
24  $\text{cm}^3 \text{ s}^{-1}$  (Atkinson et al., 2006). The  $1\sigma$  uncertainty of the measurements was, on average,  $\pm 3.2$   
25  $\text{s}^{-1}$  reflecting the combined uncertainties from the fits of the observed OH decays,  
26 determinations of  $k_{\text{phys}}$  and uncertainties in the dilution factor.

### 28 2.3 VOC measurements

29 Two gas chromatography (GC) instruments were deployed as part of the summer ClearLo  
30 campaign for *in situ* VOC measurements: a dual channel GC, (DC)-GC-FID, measuring the  
31 very volatile VOCs (C<sub>2</sub>-C<sub>8</sub> hydrocarbons and a small selection of OVOCs) with effective  
32 saturation concentrations ranging from  $3 \times 10^7$  to  $1.4 \times 10^{12} \mu\text{g m}^{-3}$ , and a comprehensive  
33 two-dimensional GC (GC×GC-FID) which measured the less volatile fraction, (C<sub>6</sub>-C<sub>13</sub> and a

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1 large group of OVOCS) with effective saturation concentrations ranging from  $1.8 \times 10^6$  to  $2.4$   
2  $\times 10^9 \mu\text{g m}^{-3}$ . The combined sampling and separation time of the systems allowed a time  
3 resolution of approximately 1 hour. The details of these two instruments and the time-series  
4 of the VOC measurements during ClearFlo are presented in Dunmore et al. (2015). A total of  
5 64 VOCs were individually identified and quantified and used to constrain a zero  
6 dimensional box model; these are listed in Table 1. Many hundreds more were included in a  
7 carbon number and functionality grouping in an attempt to quantify as much of the reactive  
8 carbon loading as possible (Dunmore et al., 2015).

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## 11 2.4 Model description

12 A zero dimensional box model, utilising a subset of the chemistry described within the  
13 Master Chemical Mechanism MCMv3.2 (Jenkin et al., 2012), has been used to predict OH  
14 reactivity for comparison with the measured reactivity. In its entirety, the MCM treats the  
15 degradation of 135 VOCs following oxidation by OH, O<sub>3</sub> and NO<sub>3</sub>, and for alkanes only,  
16 oxidation by Cl atoms, and contains ~6,700 species and ~17,000 reactions. Complete details  
17 of the kinetic and photochemical data used in the mechanism are available at the MCM  
18 website (MCM, <http://mcm.leeds.ac.uk/MCM/home>).

19  
20 The model was constrained to measurements of NO, NO<sub>2</sub>, O<sub>3</sub>, HONO, CO, CH<sub>4</sub>, PAN,  
21 HCHO, VOCs (details given in Table 1), water vapour, temperature, pressure, photolysis  
22 frequencies (using actinic fluxes measured by a spectral radiometer) and aerosol surface area.  
23 A constant H<sub>2</sub> concentration of 500 ppbV was assumed.

24  
25 The model inputs were updated every 15 minutes. For species measured more frequently,  
26 data were averaged to 15 minute intervals, whilst those measured at a lower time resolution,  
27 for example the VOCs (Table 1), were interpolated. By this method, a model time-series was  
28 produced which could be directly compared with the OH reactivity and radical observations  
29 and from which diurnal averages were also generated.

30  
31 The loss of all non-constrained, model generated species by deposition was represented by a  
32 deposition velocity equivalent to 1 cm s<sup>-1</sup>. The mixing height was constrained to

Deleted: ~~Radical measurements~~  
OH, HO<sub>2</sub> and RO<sub>2</sub> radical concentrations were measured using the FAGE technique (Stone et al., 2012). In the case of HO<sub>2</sub> and RO<sub>2</sub>, the radicals were first titrated with NO to OH before FAGE detection. The current mode of operation is described further in Whalley et al., (2013), including details of the ROxLIF method used to determine RO<sub>2</sub>. Two measurement axes were operated simultaneously during the ClearFlo deployment. In the first, air was sampled through a 1 mm diameter pin-hole into a FAGE cell which was dedicated to sequential measurements of OH and HO<sub>2</sub>. In the second axis, air was sampled, again through a 1 mm diameter pinhole, into an 83 cm long flow reactor coupled to a second FAGE cell via a 4 mm diameter pinhole, which permitted detection of the sum of all RO<sub>2</sub> radicals (Whalley et al., 2013). Both detection FAGE cells were held at 1.1 Torr, whilst the flow reactor, which was differentially pumped, was held at ~30 Torr. A fast-flow rate through each fluorescence cell was achieved using a Roots blower backed by a Rotary pump. The two fluorescence cells were joined by a tube containing a quartz window, and so shared a single laser optical axis. The instrument was calibrated twice weekly on average using photolysis of a known concentration of water vapour at 185 nm within a turbulent flow tube to generate OH and HO<sub>2</sub>, with the product of the photon flux at 185 nm and the water vapour photolysis residence time measured using a chemical actinometer (Commane et al., 2010). For calibration of RO<sub>2</sub>, methane (BOC, CP grade, 99.5%) was added to the humidified air flow in sufficient quantity to rapidly convert OH to CH<sub>3</sub>O<sub>2</sub>. The limit of detection (LOD) at a signal-to-noise ratio of one for one data acquisition cycle lasting 7 minutes was  $\sim 4.5 \times 10^5$  molecule cm<sup>-3</sup> for OH,  $\sim 2.1 \times 10^6$  molecule cm<sup>-3</sup> for HO<sub>2</sub> and  $\sim 6.9 \times 10^6$  molecule cm<sup>-3</sup> for CH<sub>3</sub>O<sub>2</sub> at a typical laser power of 13 mW in each cell. The measurements were recorded with 1 s time-resolution, and the accuracy of the measurements was ~26% (2σ). The HO<sub>2</sub> measurements were subject to a small interference from RO<sub>2</sub> (typically < 3% for all RO<sub>2</sub>), which was quantified as described in Whalley et al. (2013).¶

1 measurements made by a LIDAR instrument (Barlow et al., 2011) and was observed to  
2 rapidly increase after sunrise up to a height of ~1800 m from a minimum of ~ 330 m at ~4am.  
3 The model was run for the entirety of the campaign in overlapping 7 day segments. To allow  
4 all the unmeasured, model generated intermediate species time to reach steady state  
5 concentrations the model was initialised with inputs from the first measurement day (22<sup>nd</sup>  
6 July 2012) for 5 days before comparison to measurements were made. Comparison of these 5  
7 spin-up days demonstrated that the concentration of model generated species rapidly  
8 converged and there was less than a 1% difference in (for example) modelled OH  
9 concentration by the second spin up day. As a result of this, the model segments were run so  
10 as to overlap for 2 days only to reduce the computing time.

11  
12

### 13 **3 Results**

14 Near continuous OH reactivity measurements were made in London from 22<sup>nd</sup> July to 17<sup>th</sup>  
15 August 2012 and a comprehensive suite of individually measured inorganic and organic OH  
16 sink species were made alongside, as detailed in Table 1. The OH reactivity time-series is  
17 presented in Figure 1**b and c**. Typically, South Westerly winds ranging from less than 1 ms<sup>-1</sup>  
18 during the night to between 4 – 6 ms<sup>-1</sup> in the afternoon were encountered. However, close to  
19 the start of the campaign (24<sup>th</sup> – 27<sup>th</sup> July) and also later in the campaign (8<sup>th</sup> – 10<sup>th</sup> August),  
20 the wind direction switched to an Easterly flow, bringing air that had passed over Central  
21 London to the site, and wind speeds dropped. Fine weather prevailed during these Easterly  
22 flows, with enhancements in air temperature and solar radiation observed (Bohnenstengel,  
23 2014). During these periods, radical concentrations were elevated, as were the concentration  
24 of a number of other species such as NO<sub>x</sub>, formaldehyde, ozone and many of the individually  
25 detected VOCs. OH reactivity was also observed to increase during the Easterly flows with a  
26 peak reactivity of 116 s<sup>-1</sup> recorded on the morning (7am, GMT, which is local time (BST) – 1  
27 hour) of the 24<sup>th</sup> July.

28

29 On all days a distinct diurnal trend was apparent in OH reactivity, which peaked between 6  
30 and 7 am (GMT) and then dropped to a minimum during the afternoon as shown in Figure 2.  
31 A broader, less distinct secondary peak in reactivity was observed after 6 pm continuing  
32 throughout the night. This trend is typical of the OH reactivity profile observed at urban sites,  
33 e.g. (Dolgorouky et al., 2012; Sadanaga et al., 2005; Chatani et al., 2009; Lou et al., 2010),

1 and closely follows the observed  $\text{NO}_x$  profile. The mean reactivity for the campaign was 18.1  
2  $\text{s}^{-1}$  and on average the reaction of OH with NO and  $\text{NO}_2$  accounted for 4.5  $\text{s}^{-1}$  (25%) of the  
3 reactivity observed. The reaction with CO accounted for a further 1.3  $\text{s}^{-1}$  (7%) and so it is  
4 evident, by considering the reactivity that remains unaccounted for, that the combined  
5 contribution made by organic compounds must be significant. The model was initially run  
6 constrained to the standard set of VOCs measured by the (DC)-GC-FID. The rate of loss of  
7 OH by reaction with each individual VOC compound is extremely small, so by grouping  
8 individual VOCs detected by the (DC)-GC-FID by class (alcohol, alkanes, alkenes and  
9 alkynes, aromatics, carbonyls and dialkenes) the influence of different VOC types on the  
10 removal of OH and hence their influence on the oxidising capacity can be evaluated. Using  
11 this approach, for the carbonyl class of VOCs the reactivity towards OH is dominated by  
12 formaldehyde (40%) and acetaldehyde (54%), and when considered as a whole, makes a  
13 similar contribution as  $\text{NO}_2$  to the total OH reactivity. The other organic classes contribute  
14 less to total reactivity (between 0.2 – 0.6  $\text{s}^{-1}$  on average), with reactivity from most of the  
15 classes exhibiting a weak diurnal profile similar to that of  $\text{NO}_x$ . In contrast, the contribution  
16 to OH reactivity made by the dialkene class, which itself is dominated by isoprene, peaks at  
17 noon suggesting a dominance of a temperature/sunlight driven biogenic signature as opposed  
18 to a traffic signature for this class.

19  
20 Combined, the contribution of  $\text{NO}_x$ , CO and all measured organic classes cannot reconcile  
21 the OH reactivity observed, with an average missing reactivity of 6.7  $\text{s}^{-1}$  which equates to  
22 37% of the total measured value. Even when model-generated intermediates are considered,  
23 which are made up largely by oxygenated compounds such as methylglyoxal, glyoxal and  
24 glycoaldehyde which derive from aromatic species, isoprene and methyl vinyl ketone, on  
25 average 6.0  $\text{s}^{-1}$  of OH reactivity (33% of the total measured) remains unaccounted for, as  
26 shown in Figure 2.

27  
28 An extended range of VOCs (24 additional compounds), consisting of *n*-alkanes, substituted  
29 aromatic and carbonyl compounds and the monoterpenes of  $\alpha$ -pinene and limonene, were  
30 detected using a GCxGC-FID instrument. The missing reactivity determined in the modelling  
31 exercise above (which included only VOCs from the (DC)-GC-FID) may derive from these  
32 additional VOCs which, historically, are not typically detected by traditional GC  
33 methodologies. As shown in Figure 3, the reaction of OH with the biogenic species of  $\alpha$ -



1 pinene and limonene alone (not including any model-derived intermediates) increases the  
2 total calculated OH reactivity by  $0.25 \text{ s}^{-1}$ , and similar increases are calculated by inclusion of  
3 the additional *n*-alkanes detected (Table 1). Overall, however, calculated OH reactivity  
4 increases by just  $0.7 \text{ s}^{-1}$  on average when these additional contributions are considered  
5 without including model-derived intermediates. Interestingly, the contribution that the model-  
6 derived intermediates make to OH reactivity when the model is run constrained to the  
7 extended VOC suite is much more significant than previously presented in Figure 2. When  
8 combined, the model-generated intermediates contribute  $3.2 \text{ s}^{-1}$  on average to the OH  
9 reactivity in the model run constrained to the extended VOC measurements, compared to just  
10  $0.7 \text{ s}^{-1}$  in the model run constrained just with the standard VOC measurements.

11  
12 In total there are close to 2600 reactions included in the extended VOC model run which  
13 destroy OH and the reaction of OH with the different model-generated intermediate species  
14 accounts for more than 90% of these reactions. Pinonaldehyde (an oxidation product of  $\alpha$ -  
15 pinene formed both during ozonolysis and OH-initiated oxidation reactions) is the most  
16 destructive model intermediate species with respect to OH and this single species is found to  
17 contribute approximately 7.5% to the total OH reactivity of the modelled intermediates at  
18 noon. Considering the top ten most destructive model intermediates which account for  
19 roughly 30% of the total model intermediate reactivity, nine out of the ten derive from  
20 biogenic species. Species which derive from  $\alpha$ -pinene account for two thirds of the reactivity  
21 of the top ten intermediate species, whilst those which derive from limonene account for  
22 approximately one third. 3-Hydroxypropanal which derives from the alkane class and is the  
23 tenth most destructive model intermediate contributes ~1.5% to the total reactive of the  
24 intermediates on average. To determine the absolute impact of the biogenic species on OH  
25 reactivity, a model was run constrained to all (DC)-GC-FID and GCxGC-FID VOC  
26 measurements apart from  $\alpha$ -pinene and limonene. The model-generated intermediates from  
27 this run contributed  $1.04 \text{ s}^{-1}$  to total OH reactivity on average, demonstrating that although the  
28 contribution to total OH reactivity from the measured biogenic class (considering only  
29 reaction with the parent VOCs) was small ( $0.25 \text{ s}^{-1}$ ), the oxidation products from just  $\alpha$ -  
30 pinene and limonene alone account for  $2.2 \text{ s}^{-1}$  of the OH reactivity. The total concentration of  
31  $\text{C}_9 - \text{C}_{12}$  alkanes is ~5 times greater than the combined concentration of the biogenics on  
32 average. Despite this, the model intermediates generated during the oxidation of these larger  
33 alkanes ( $\text{C}_9 - \text{C}_{12}$ ) which derive from diesel emissions (Dunmore et al., 2015), and the

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1 intermediates generated from the additional aromatic and carbonyl species detected by  
2 GCxGC-FID, contribute only  $0.34 \text{ s}^{-1}$  to total reactivity on average. The rate of reaction of  
3 OH with  $\alpha$ -pinene ( $5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298K) is approximately 4.5 times faster  
4 (and the reaction with limonene ( $1.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298K) is an order of  
5 magnitude faster) than the analogous reactions with the  $\text{C}_9 - \text{C}_{12}$  alkanes ( $\sim 1.2 \times 10^{-11} \text{ cm}^3$   
6  $\text{molecule}^{-1} \text{ s}^{-1}$  at 298K). Furthermore, the initial reaction of these biogenic species with ozone  
7 can also contribute to the formation of the biogenic-derived model intermediates species. The  
8 biogenic intermediates themselves remain highly reactive towards OH, with the rate  
9 coefficient for the reaction of OH with pinonaldehyde being similar to the rate coefficient for  
10 the reaction of OH with  $\alpha$ -pinene itself ( $4 \times 10^{-11}$  and  $5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  respectively  
11 at 298K). These factors combined lead to the biogenic species strongly influencing OH  
12 reactivity.

13

14 The contribution that modelled intermediates derived from the larger VOCs (measured by the  
15 GCxGC-FID) make to the total OH reactivity is significant, and is able to largely close the  
16 gap between modelled and observed OH reactivity, with  $\sim 15\%$  missing reactivity remaining.  
17 Good agreement both in terms of the magnitude and variability from day-to-day (Fig. 1) and  
18 campaign average diurnal profile (Fig. 3) is achieved by the model when constrained to the  
19 extended VOC measurements. This result highlights the impact of biogenic VOCs in London  
20 when the oxidised secondary products are considered. The role of biogenic VOCs (excluding  
21 isoprene) in increasing the OH reactivity has not previously been demonstrated at urban sites.  
22 Often biogenic VOCs other than isoprene are not measured at urban sites when OH reactivity  
23 has been reported e.g. (Kovacs et al., 2003; Ren et al., 2003; Mao et al., 2010; Lou et al.,  
24 2010; Dolgorouky et al., 2012) and even if they are measured, the contribution they make to  
25 total OH reactivity is deemed small if only the reaction of the parent measured biogenic  
26 species with OH is considered, e.g. (Chatani et al., 2009). The ultimate fate of these oxidised  
27 intermediates derived from biogenic VOCs is highly uncertain, but if they remain in the gas-  
28 phase, as opposed to partitioning onto particles, their potential to increase the rate of radical  
29 propagation and in situ ozone production is significant.

30

31 Even when the contribution made to reactivity from the additional VOCs measured by the  
32 GCxGC-FID is taken into account, a small missing reactivity ( $\sim 15\%$  on average) remains.  
33 This missing reactivity could suggest that the physical loss of model generated intermediates

1 may actually be slower than imposed in the model (see Sect. 3.2) or this under-prediction in  
2 OH reactivity could also reflect further missing primary OH sinks, for example, higher  
3 molecular weight carbon ( $\geq C_{13}$ ) that is not detected by either the (DC)-GC-FID or GCxGC-  
4 FID methods employed. It is known that  $\geq C_{13}$  makes up a large fraction of diesel emissions  
5 and diesel-related hydrocarbons have been shown to dominate the gas phase carbon (in terms  
6 of mass) in London (Dunmore et al., 2015).

7

8 The complexity of London's air can be observed in the GCxGC-FID chromatogram shown in  
9 Figure 4. In addition to the many identified VOCs, there are many others that can be grouped  
10 according to chemical class through their position on the chromatogram, but are not identified  
11 explicitly. Ten groups are shown in Figure 4, with areas 1-8 representing branched and cyclic  
12 alkanes, area 9 represents unidentified monoterpenes and area 10 is the  $C_4$ -substituted  
13 monoaromatics species. The highly branched alkane species can be incorporated into the  
14 model by approximating the reactivity to be the same as for the straight-chain alkane  
15 equivalent. For example, for an unidentified branched alkane which contains six carbon  
16 atoms it has been estimated that it would have the same reactivity with respect to OH as *n*-  
17 hexane (and the same, subsequent, degradation mechanism). For unidentified monoterpenes,  
18 a reaction rate coefficient (and the subsequent degradation mechanism) the same as that for  
19 the reaction between OH and  $\alpha$ -pinene is assumed, whilst for unidentified substituted  
20 aromatics the reaction rate coefficient with respect to OH (and degradation mechanism) is  
21 taken to be the same as that for propyl-benzene. Inclusion of this additional reactive carbon in  
22 the model leads to a  $0.4 \text{ s}^{-1}$  increase in the alkane contribution and only a small increase of  
23  $\sim 0.1 \text{ s}^{-1}$  due to increasing the carbon in the biogenic and aromatic classes combined. Despite  
24 the small contribution made by increasing the effective  $\alpha$ -pinene present, this increase in  
25 biogenic carbon leads to a further  $1.1 \text{ s}^{-1}$  increase in the contribution from model  
26 intermediates. Figure 5 compares the total modelled OH reactivity alongside the measured  
27 values when these additional unidentified species are included. Overall, this additional carbon  
28 (which is known to be present but cannot be fully identified) improves the overall model-to-  
29 measured agreement with just 6% of the total reactivity now unaccounted for.

30 Considering the breakdown in modelled OH reactivity on a day by day basis (Figure 1b and  
31 c), the reactivity associated with the model intermediates deriving from the biogenic VOCs  
32 increases on the warmest days which were coincident with the easterly flows experienced at  
33 the beginning of the campaign (24<sup>th</sup> – 27<sup>th</sup> July). Di Carlo and co-workers (2004) found in a

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1 forested environment that missing reactivity increased with temperature and hypothesised  
2 that unknown reactive biogenic VOCs, possibly unmeasured mono-terpenes, accounted for  
3 this missing reactivity. They observed little difference between calculated reactivity and  
4 modelled reactivity suggesting that the oxidation products of these biogenic species do not  
5 increase OH reactivity significantly. This finding is in contrast to the model predictions  
6 presented here and demonstrates that the higher levels of NO present in London relative to a  
7 forested environment promotes more efficient model propagation and the generation of  
8 reactive model intermediates. Lower temperatures and, consequently, lower biogenic VOC  
9 concentrations were observed (Figure 1a) during the easterly flow experienced between 8<sup>th</sup> -  
10 10<sup>th</sup> August relative to the first easterly period. The model predicts a lower reactivity from the  
11 model-generated intermediate species during this period despite [NO<sub>x</sub>] being similar to those  
12 experienced during the first easterly. On the 9<sup>th</sup> and 10<sup>th</sup> August, during the second of the  
13 easterly flow periods captured, a model constrained only with the standard VOC  
14 measurements provided a reasonable estimate of the total observed reactivity (Figure 1b).  
15 When the influence on the biogenic species is predicted to be the strongest, i.e. during the  
16 first easterly flow regime, only a model constrained to the extended VOC suite provides a  
17 reasonable estimate of the observed reactivity. From Figure 1c it is evident that the largest  
18 fraction of missing reactivity occurs during the south-westerly flow conditions encountered  
19 between the 28<sup>th</sup> July – 5<sup>th</sup> August and even considering the 1σ uncertainty of the OH  
20 reactivity measurements of ±3.2 s<sup>-1</sup>, the missing reactivity during this period is significant.  
21 The propensity of the model to under-estimate reactivity during this south westerly flow is  
22 further highlighted when the modelled averaged diurnal reactivity is taken for south westerly  
23 and easterly conditions separately (Fig. 6). The contribution to the total reactivity made by  
24 any individual class of compounds does not change significantly between these two regimes,  
25 rather, all classes represent bigger OH sinks during the more polluted phase. The diurnal  
26 profile is much more distinct during the polluted phase demonstrating a stronger traffic-based  
27 source, likely in combination with more significant boundary layer height changes over the  
28 course of the day during low wind speed periods. There is a very slight over-prediction  
29 during the Easterly flow in OH reactivity during the afternoon and during the morning rush-  
30 hour, but overall the agreement between model and measurements is excellent during the  
31 Easterlies. In contrast, an under-prediction in the observed OH reactivity throughout the day  
32 during south-westerly conditions is apparent suggesting either there are more undetected  
33 VOCs during south-westerly flows than during the easterly flows or that the physical loss of  
34 the model generated intermediates should be treated differently during these two contrasting

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1 air-masses. The sensitivity of model predictions to the physical loss term of the model-  
2 generated intermediates is investigated in Sect. 3.2.

3

### 4 **3.1 Ability of the model to reconcile the observed formaldehyde concentration**

5 Thus far, all model runs have been constrained to the observed formaldehyde (HCHO)  
6 concentration. HCHO is formed during the oxidation of nearly every VOC and so may be  
7 considered a useful target species against which to assess atmospheric oxidation schemes. A  
8 model run constrained to (DC)-GC-FID VOCs only, but now unconstrained to HCHO  
9 significantly under-predicts (by 60% on average) the observed HCHO concentration (Fig. 7).  
10 The ability of the model to capture the observed HCHO in terms of magnitude is substantially  
11 improved (to with 32% of the observations) when the model is constrained to the extended  
12 VOC suite (including the contribution from the unidentified GCxGC-FID VOC species). This  
13 improved predicative capability of the model in terms of HCHO (as for OH reactivity) is  
14 almost entirely due to the inclusion of the biogenics. Even constrained to the extended VOC  
15 observations (and the unidentified GCxGC-FID VOC species), the model is unable to capture  
16 the HCHO concentration observed with the discrepancy greatest during the morning hours.  
17 This under-prediction may reflect inaccuracies in the physical deposition of HCHO in the  
18 model (discussed further in Sect. 3.2) but may also reflect a missing primary source of  
19 HCHO in the model. Similar findings are reported from field observations in the Po Valley in  
20 Italy where the discrepancy between modelled and measured OH reactivity was found to be  
21 small, but HCHO concentrations were substantially under-predicted by a 1-D model,  
22 demonstrating an unidentified non-photochemical ground-level source of HCHO (Kaiser et  
23 al., 2015). The unidentified source of HCHO in the Po Valley was postulated to be a direct  
24 emission from agricultural land. In London, the missing HCHO peaks at ~8am and may  
25 reflect a missing source directly emitted from vehicular exhausts.

26

### 27 **3.2 Sensitivity of model-generated intermediates to parameterisation of the** 28 **rate of physical loss**

29 There is considerable uncertainty associated with the concentration of model species which  
30 are generated by reaction in the model rather than constrained to observations. Model species  
31 can undergo gas-phase reactions, may be lost via wet or dry deposition (at different rates  
32 depending on the particular species), be taken up on aerosol surfaces, or if their lifetime is

1 sufficiently long, there may be a net movement of these species either into or out of the  
2 model box.

3

4 In the model runs considered above, the deposition rate for all intermediate species (including  
5 HCHO in the model runs with HCHO unconstrained) was set equal to  $1 \text{ cm s}^{-1}$  which is  
6 equivalent to a lifetime of  $\sim 27$  hrs in a 1000 m boundary layer. The boundary layer varied  
7 from a minimum of 330 m at night to 1800 m in the afternoon. By treating the modelled  
8 physical loss as a function of boundary layer height, a dry deposition of species to the surface  
9 is reasonably well represented, but this method does not represent possible ventilation from  
10 the model box very well (as wind-speeds picked up during the afternoon hours for example).  
11 Setting the boundary layer height in the model to a constant 300 m throughout effectively  
12 enhances the physical loss rate of intermediates during the afternoon when the boundary layer  
13 was previously set higher. Figure 8 highlights that this does modestly improve the overall  
14 modelled agreement with observed reactivity during the afternoon hours, but the reduction in  
15 modelled reactivity is small. This demonstrates that although the treatment of physical loss  
16 remains a highly uncertain model parameter, the concentration of model intermediates and  
17 their impact on modelled reactivity is not particularly sensitive to this term, with large  
18 changes in the lifetime of the intermediates (from  $\sim 50$  hrs to  $\sim 8$  hrs during the afternoon)  
19 only leading to a reduction of  $0.6 \text{ s}^{-1}$  (or 4%) in the modelled reactivity at 2 pm. It should be  
20 noted that this enhanced physical loss of intermediates would lead to further disagreement  
21 between the modelled and measured OH reactivity during south westerly flow.

22 For the model to better represent the observed HCHO concentrations, a reduction in the  
23 physical loss of this species is needed. Reducing the deposition rate from  $1 \text{ cm s}^{-1}$  to  $0.3 \text{ cm}$   
24  $\text{s}^{-1}$  in the model (Fig. 7) enhances the modelled HCHO leading to an improved model  
25 representation of this species at night. The model still under-estimates the concentration of  
26 HCHO during the day (total underestimate of 16% on average) which may reflect the  
27 uncertainty in the treatment of the physical loss of other model-generated intermediates  
28 which go on to form HCHO themselves, or may reflect the small under-estimation of OH  
29 reactivity (6%) which remains, or may reflect a small direct emission of HCHO not  
30 accounted for by the model (as discussed above). Despite the small under-prediction of  
31 [HCHO], this analysis demonstrates that the majority of the HCHO observed (84%) can be  
32 accounted for by considering the oxidative degradation of the VOCs detected in London's  
33 atmosphere, and the HCHO concentration will be significantly under-estimated if the VOC

1 model constraints under-represent the actual VOC composition (particularly, if the  
2 contribution of the biogenics is neglected).

### 3.3 Impact of the different VOC constraints on modelled OH

5 As may be expected, with an increase in the modelled OH reactivity moving from the model  
6 run with standard VOC constraints to a run with the extended VOC constraints, the OH  
7 concentration predicted by the model is concomitantly reduced by 41% (standard VOC suite  
8 to extended VOC suite including contribution from unassigned peaks). This analysis  
9 demonstrates that neglecting the contribution of the higher VOCs ( $\geq C_9$ ) (particularly  $\alpha$ -  
10 pinene and limonene) and model-generated intermediates can impact a model's ability to  
11 predict the oxidising capacity accurately.

12 It is also worth considering the influence that modelled OH concentrations have upon the  
13 predicted OH reactivity. Lowering the modelled OH concentration by ~ factor of 3 reduces  
14 the modelled OH reactivity, due to the competition which exists between the rate of OH  
15 initiated production of model generated intermediates and physical loss of these species  
16 (Edwards et al., 2013). As shown in Figure 8, despite these substantial reductions in modelled  
17 OH concentrations, the modelled OH reactivity is only reduced by  $0.24 \text{ s}^{-1}$  (or 2%) at 2 pm  
18 (GMT). These results demonstrate that the modelled reactivity is not particularly sensitive to  
19 the [OH], perhaps as a result of OH influencing both the rate of production and loss of these  
20 intermediates (the latter by further reaction with OH).

## 4 Atmospheric implications and the influence on the rate of *in-situ* ozone production

24 The definition of total OH reactivity as defined by Eq. 1 may be expanded to breakdown the  
25 contribution of organic and inorganic reactions:

$$27 \quad k_{\text{OH}} = \sum k_{\text{OH}+\text{VOC}}[\text{VOC}] + k_{\text{OH}+\text{NO}_2}[\text{NO}_2] + k_{\text{OH}+\text{NO}}[\text{NO}] + k_{\text{OH}+\text{O}_3}[\text{O}_3] + k_{\text{OH}+\text{CO}}[\text{CO}] + \\ 28 \quad k_{\text{OH}+\text{HCHO}}[\text{HCHO}] \quad (3)$$

30 The reaction of OH with NO (to form HONO) or NO<sub>2</sub> (to form HNO<sub>3</sub>) may be viewed as  
31 either a temporary or permanent radical sink, respectively, dependent upon the lifetime of the  
32 reservoir species formed. In contrast, the reaction of OH with VOCs, O<sub>3</sub>, CO or HCHO is the

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1 rate determining step producing peroxy radicals and, in the presence of NO, net ozone  
2 production via the production and subsequent photolysis of NO<sub>2</sub>.

3

4 Assuming the steady-state approximation, an expression can be determined for the  
5 concentration of RO<sub>2</sub> radicals, which derive from the reaction of OH with VOC from a  
6 measurement of the total OH reactivity (with the contribution of inorganic reactions and any  
7 HO<sub>2</sub> formation reactions subtracted), an [OH] measurement and an RO<sub>2</sub> sink term  
8 represented as the average rate coefficient for reaction of RO<sub>2</sub> with NO (under the conditions  
9 in London other loss routes for RO<sub>2</sub> are ignored):

10

$$11 [RO_2]_{ss} = \frac{(k_{OH} - (k_{OH+NO_2}[NO_2] + k_{OH+NO}[NO] + k_{OH+O_3}[O_3] + k_{OH+CO}[CO] + k_{OH+HCHO}[HCHO]))[OH]}{k_{RO_2+NO}[NO]} \quad (4)$$

12

13 The rate of *in situ* ozone production resulting from [RO<sub>2</sub>]<sub>ss</sub> may then be estimated using:

14

$$15 P(O_3) = k_{RO_2+NO}[RO_2]_{ss}[NO] - k_{OH+NO_2}[OH][NO_2] \quad (5)$$

16

17 Eq. 5 considers the production of NO<sub>2</sub> (and upon photolysis, O<sub>3</sub>) by reaction of RO<sub>2</sub> radicals  
18 with NO only (ignoring HO<sub>2</sub>). The loss of NO<sub>2</sub> by reaction, for example with OH, rather than  
19 photolysis which generates O<sub>3</sub>, must also be taken into account when determining net  
20 production.

21

22 Using this methodology, an [RO<sub>2</sub>]<sub>ss</sub> diurnal profile peaking at ~ 6×10<sup>7</sup> molecule cm<sup>-3</sup> is  
23 derived from total OH reactivity. From this [RO<sub>2</sub>]<sub>ss</sub>, an average *in situ* ozone production  
24 during the day (from RO<sub>2</sub> + NO) of ~ 22 ppbV d<sup>-1</sup> is estimated. This analysis can be repeated  
25 using k<sub>OH</sub> calculated from the standard VOC suite measured with the (DC)-GC-FID alone  
26 (with the contribution from model intermediates and heavier weight VOCs omitted). The  
27 [RO<sub>2</sub>]<sub>ss</sub> is reduced by ~ 45% and consequently the calculated *in situ* O<sub>3</sub> production from RO<sub>2</sub>  
28 is reduced to ~ 9 ppbV d<sup>-1</sup>.

29 Despite a number of approximations, this analysis suggests that *in situ* ozone predictions may  
30 be substantially underestimated if either oxidised VOC intermediate species are not  
31 considered or if the measured VOC suite does not sufficiently represent the actual primary  
32 VOC emissions.

33

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Deleted: as shown in Figure 10, and compares reasonably well with the total [RO<sub>2</sub>] that was measured by the FAGE technique during the campaign. The steady state derived [RO<sub>2</sub>], however, does not consider RO<sub>2</sub> formed from direct photolysis of carbonyl species or RO<sub>2</sub> from thermal decomposition of PAN species, which will also be contributing to the RO<sub>2</sub> concentration that was measured. The sink term used in Eq. 4 is also a lower estimate which does not consider, for example, RO<sub>2</sub> loss via PAN formation or other sink reactions such as RO<sub>2</sub>+HO<sub>2</sub>, and so good agreement should not necessarily be expected, unless the missing source terms and sinks terms coincidentally balance one another, as they seem to do at certain times.¶

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## 1 **Conclusions**

2 | The ability of the model to replicate the observed OH reactivity in London only when the  
3 reactivity of the extended suite of VOCs is considered demonstrates the role played by the  
4 heavier weight VOC fraction, particularly biogenics, in modifying the oxidising capacity of  
5 this Megacity and the ability of these VOCs to drive up local ozone production. In contrast to  
6 a number of urban OH reactivity comparisons reported from other cities (e.g. (Ren et al.,  
7 2003; Di Carlo et al., 2004; Mao et al., 2010)), the observed OH reactivity in London can  
8 only be reconciled by consideration of model-generated intermediates. We have  
9 demonstrated that the oxidation products of  $\alpha$ -pinene and limonene contribute most  
10 significantly to the reactivity of the model-generated intermediate class and so differences in  
11 the abundances of these monoterpenes in different cities may influence how well OH  
12 reactivity can be calculated from the measured primary emissions before model-derived  
13 species need to be considered also. Similar to London, in Tokyo where monoterpenes have  
14 been observed, a 30% under-prediction of OH reactivity was reported when observations  
15 were compared to calculated OH reactivity only (Chatani et al., 2009).

16 During the ClearfLo study, ozone exceeded 60 ppbV on several days during Easterly  
17 conditions and peaked at 100 ppbV during the afternoon of the 25<sup>th</sup> July. Future ozone  
18 abatement strategies will need to consider the role both anthropogenic and biogenic emissions  
19 play in contributing to ozone production even for relatively temperate locations such as  
20 London.

21

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28

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31

1 **Table 1:** Species used as input to the model, the class each species is grouped into, the  
 2 average contribution ( $s^{-1}$  and %) of each class to OH reactivity and the detection method for  
 3 each species. The OH reactivity when the concentration of the unassigned GCxGC-FID peaks  
 4 is also considered is given in parentheses.

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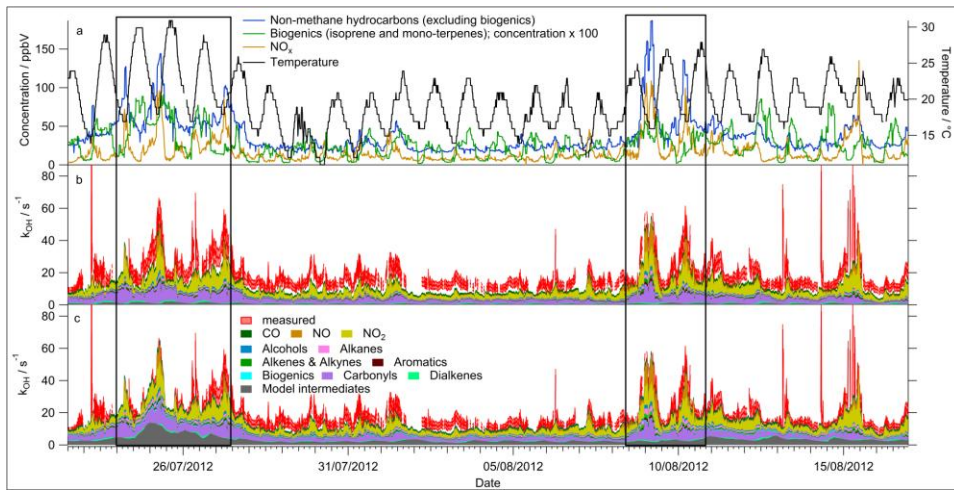
Species (MCM name)	Class	Contribution to OH reactivity ( $s^{-1}$ )	Contribution to OH reactivity (%)	Instrument
O3	O <sub>3</sub>	0.05 <sup>#</sup>	0.3	Thermo 49 Series
NO	NO	0.76	4.2	Air Quality Design Inc. Chemiluminescence with LED NO <sub>2</sub> converter
NO2	NO <sub>2</sub>	3.82	21.1	
CO	CO	1.31	7.2	Ametek monitor
H2	H <sub>2</sub>	0.08 <sup>#</sup>	0.4	-
HONO HNO3 PAN	NO <sub>2</sub>	0.04 <sup>#</sup>	0.2	LOPAP CIMS GC-ECD
CH3OH C2H5OH NPROPOL NBUTOL	Alcohol	0.54	3.0	(DC)-GC-FID (DC)-GC-FID (DC)-GC-FID (DC)-GC-FID
CH4 C2H6 C3H8 IC4H10 NC4H10 IC5H12 NC5H12 NC6H14 NC7H16 NC8H18 M2PE NC9H20	Alkane	0.81 (1.22)	4.5 (6.7)	(DC)-GC-FID (DC)-GC-FID (DC)-GC-FID (DC)-GC-FID (DC)-GC-FID (DC)-GC-FID (DC)-GC-FID (DC)-GC-FID & GCxGC-FID (DC)-GC-FID & GCxGC-FID (DC)-GC-FID & GCxGC-FID (DC)-GC-FID GCxGC-FID

NC10H22				GCxGC-FID
NC11H24				GCxGC-FID
NC12H26				GCxGC-FID
CH2CL2				GCxGC-FID
C2H2	Alkene and Alkyne	0.47	2.6	(DC)-GC-FID
C2H4				(DC)-GC-FID
C3H6				(DC)-GC-FID
TBUT2ENE				(DC)-GC-FID
BUT1ENE				(DC)-GC-FID
MEPROPENE				(DC)-GC-FID
CBUT2ENE				(DC)-GC-FID
PENT2ENE				(DC)-GC-FID
PENT1ENE				(DC)-GC-FID
TRICLETH				GCxGC-FID
BENZENE	Aromatic	0.235 (0.24)	1.3 (1.3)	(DC)-GC-FID
TOLUENE				(DC)-GC-FID
EBENZ				(DC)-GC-FID
MXYL				(DC)-GC-FID
PXYL				(DC)-GC-FID
OXYL				(DC)-GC-FID
TM123B				(DC)-GC-FID & GCxGC-FID
TM135B				(DC)-GC-FID & GCxGC-FID
TM124B				(DC)-GC-FID & GCxGC-FID
STYRENE				GCxGC-FID
IPBENZ				GCxGC-FID
PBENZ				GCxGC-FID
METHTOL				GCxGC-FID
PETHTOL				GCxGC-FID
OETHTOL				GCxGC-FID
BENZAL				GCxGC-FID
APINENE	Biogenic	0.25 (0.33)	1.4 (1.8)	GCxGC-FID
LIMONENE				GCxGC-FID
HCHO	Carbonyl	3.45	19.1	Aerolaser 4021 analyser

CH3CHO				(DC)-GC-FID
CH3COCH3				(DC)-GC-FID
MACR				(DC)-GC-FID & GCxGC-FID
MVK				(DC)-GC-FID & GCxGC-FID
IPRCHO				GCxGC-FID
ETHACET				GCxGC-FID
MEK				GCxGC-FID
C3H7CHO				GCxGC-FID
MPRK				GCxGC-FID
C4H9CHO				GCxGC-FID
MIBK				GCxGC-FID
HEX2ONE				GCxGC-FID
CYHEXONE				GCxGC-FID
C4H6	Dialkene	0.32	1.8	(DC)-GC-FID
C5H8				(DC)-GC-FID
Model intermediates	Model intermediates	3.2 (4.3)	17.7 (23.8)	-

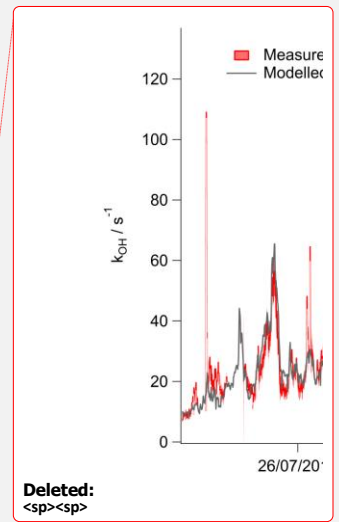
- 1 #The contributions of classes which account for less than 0.1 s<sup>-1</sup> OH reactivity are not plotted
- 2 in Fig. 2, 3, 5 and 6 for clarity.

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**Figure 1a:** Time-series of non-methane hydrocarbons (excluding biogenics), biogenics (isoprene and mono-terpenes), NO<sub>x</sub> and temperature and **b:** Measured OH reactivity time-series and breakdown of modelled OH reactivity when only the standard set of VOCs are used as model constraints and **c:** Measured OH reactivity time-series and breakdown of modelled OH reactivity when VOCs measured by the dual-channel-GC-FID and GCxGC-FID instruments are used as model constraints (see Table 1 for details). Periods of more polluted Easterly flows are highlighted. The averaging period is 15 minutes. The 1 $\sigma$  uncertainty of the OH reactivity measurements (red shading) was, on average,  $\pm 3.2 \text{ s}^{-1}$ .



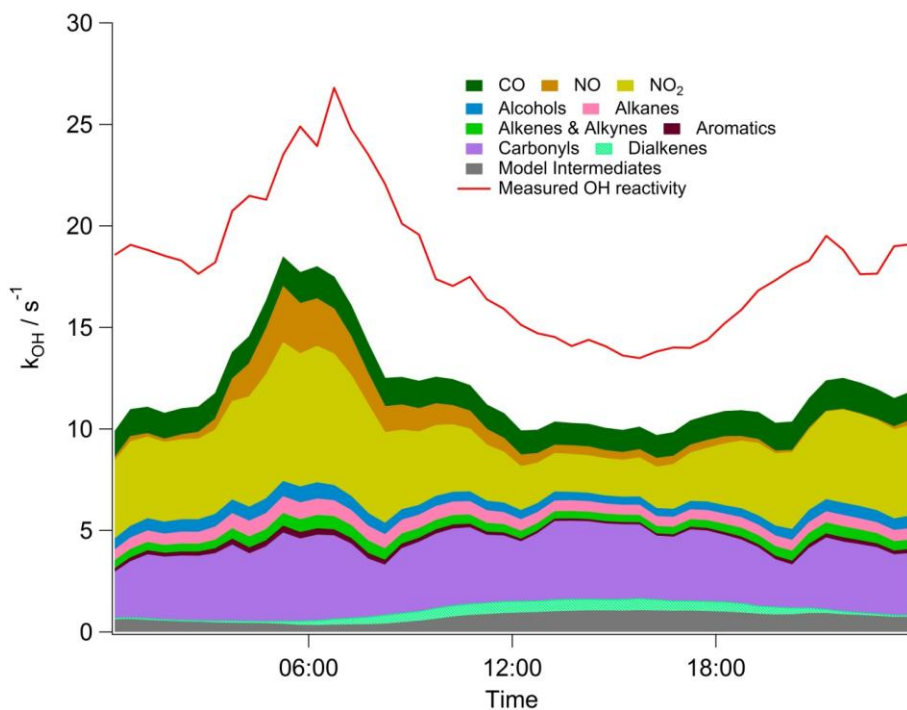
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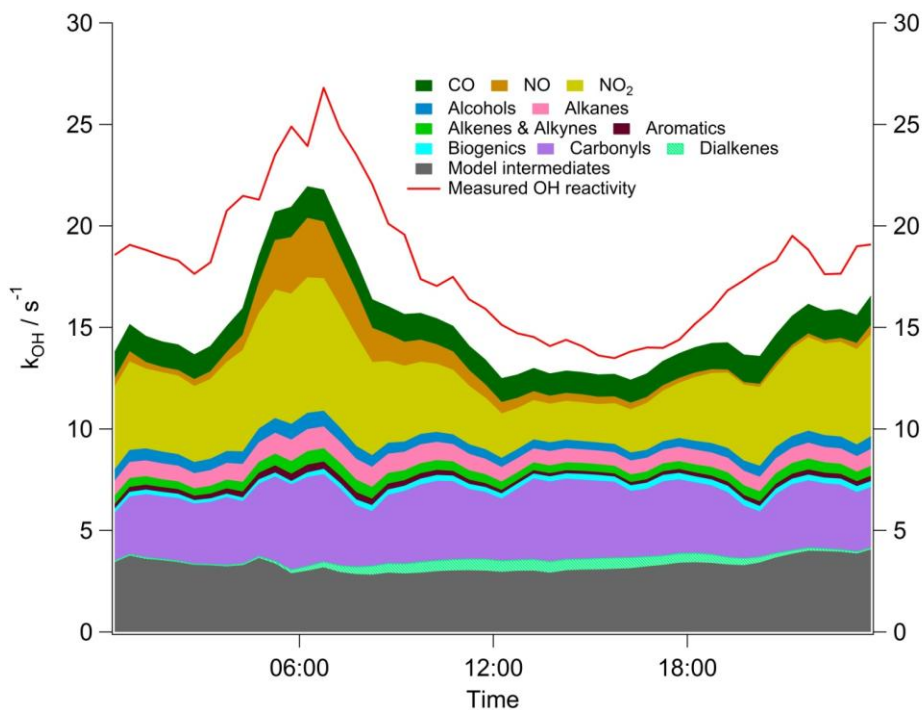
**Deleted:** The model represents the OH reactivity calculated from the VOCs measured by the (DC)-GC-FID and GCxGC-FID instruments (see Table 1 for details), and the additional VOCs derived from unassigned peaks from the GCxGC-FID chromatographs as explained in the text, plus all model intermediates deriving from these species.





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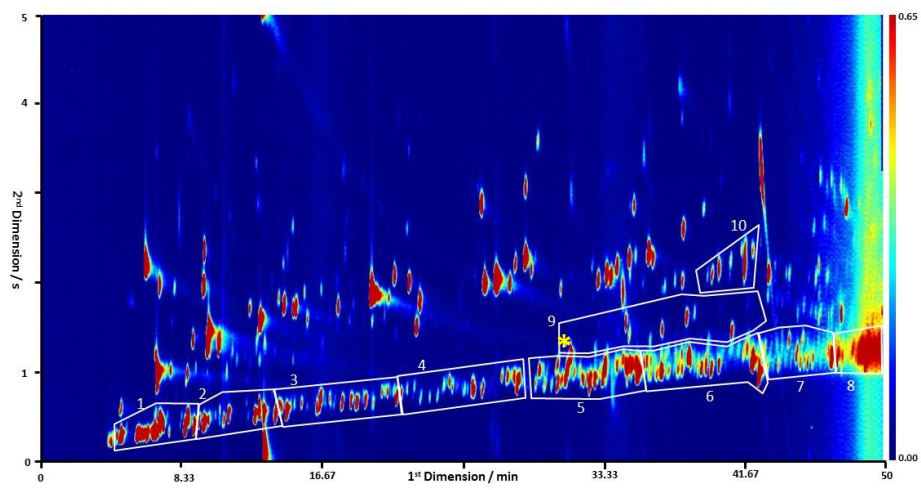
2 **Figure 2:** Average diurnal profile of measured reactivity for the entire ClearfLo campaign  
 3 and a breakdown of modelled reactivity into inorganic and organic classes when the model is  
 4 constrained to the standard VOC suite measured by the (DC)-GC-FID instrument. See Table  
 5 1 for details of the individual VOCs that were measured.



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2 **Figure 3:** Average diurnal profile of measured reactivity and a breakdown of modelled  
 3 reactivity into inorganic and organic classes when the model is constrained to the standard  
 4 VOC suite measured by the (DC)-GC-FID and additional VOCs (including  $\alpha$ -pinene and  
 5 limonene, see Table 1 for details) measured with by GCxGC-FID.

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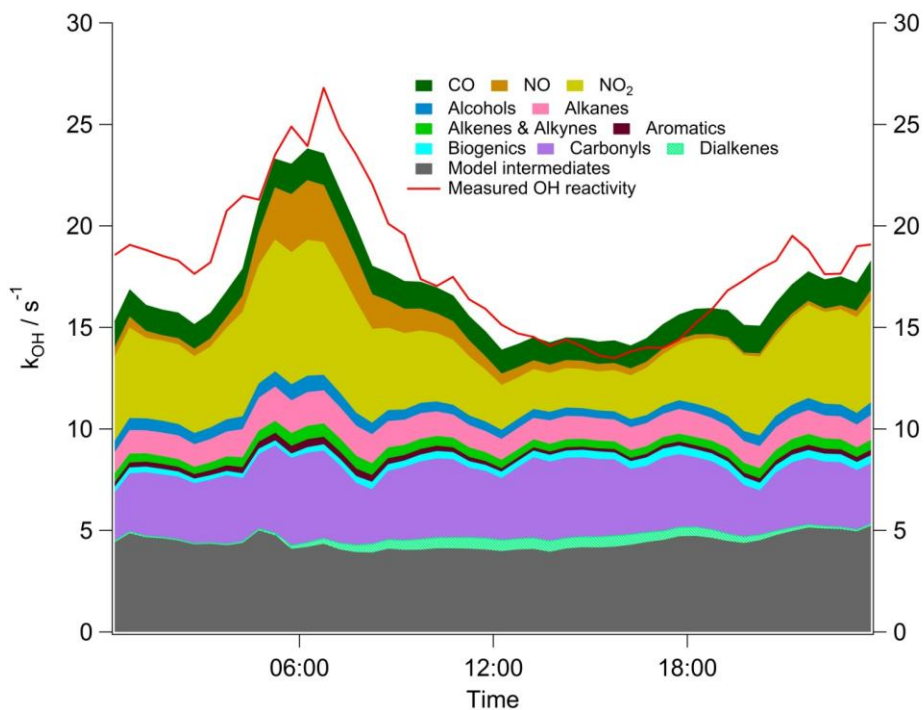


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2 **Figure 4:** A typical GC×GC chromatogram from the summer ClearfLo campaign. The  
 3 retention times from column 1 (separation based on volatility) and column 2 (separation  
 4 based on polarity) are the x and y axis respectively, and compound intensity is the coloured  
 5 contour. Labelled groups are identified as follows; (1-8) aliphatic groups from C<sub>6</sub> to C<sub>13</sub>, (9)  
 6 C<sub>10</sub> monoterpenes with \* corresponding to α-pinene which is the start of that group and (10)  
 7 C<sub>4</sub> substituted monoaromatics.

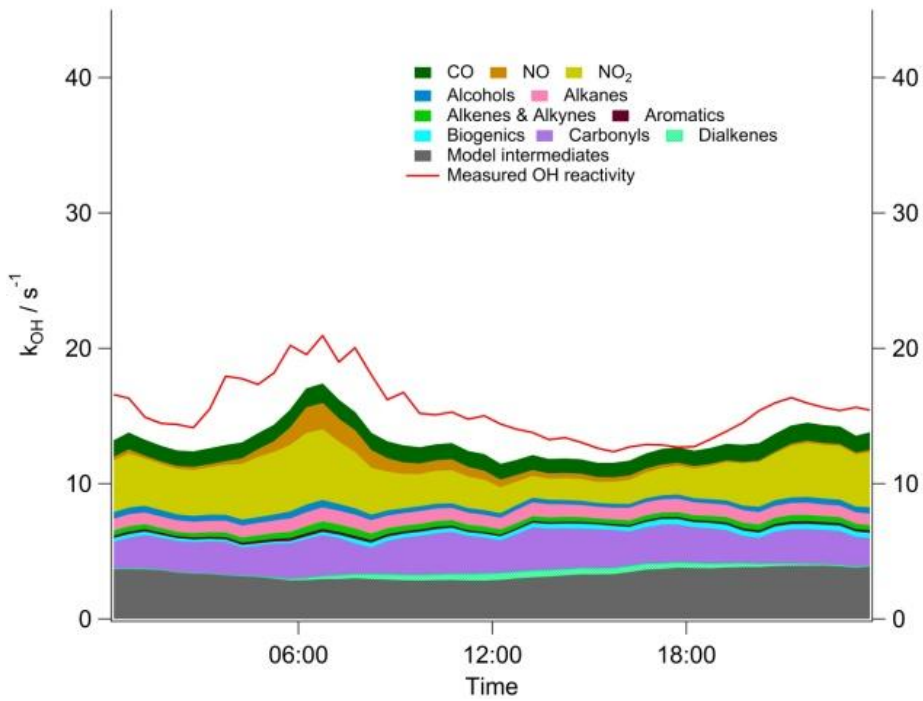
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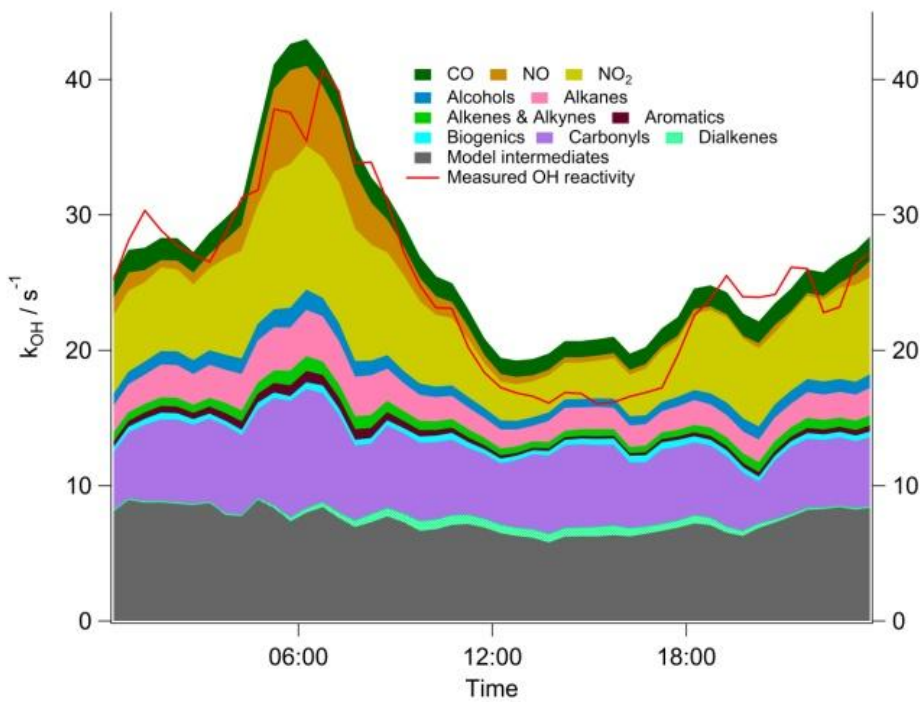


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 2 **Figure 5:** Average diurnal profile of measured reactivity and a breakdown of modelled  
 3 reactivity into inorganic and organic classes when the model is constrained to the standard  
 4 VOC suite measured by the dual-channel (DC)-GC-FID, the additional identified VOCs  
 5 (including  $\alpha$ -pinene and limonene, see Table 1 for details) measured with by GCxGC-FID  
 6 and the unassigned GCxGC-FID peaks.

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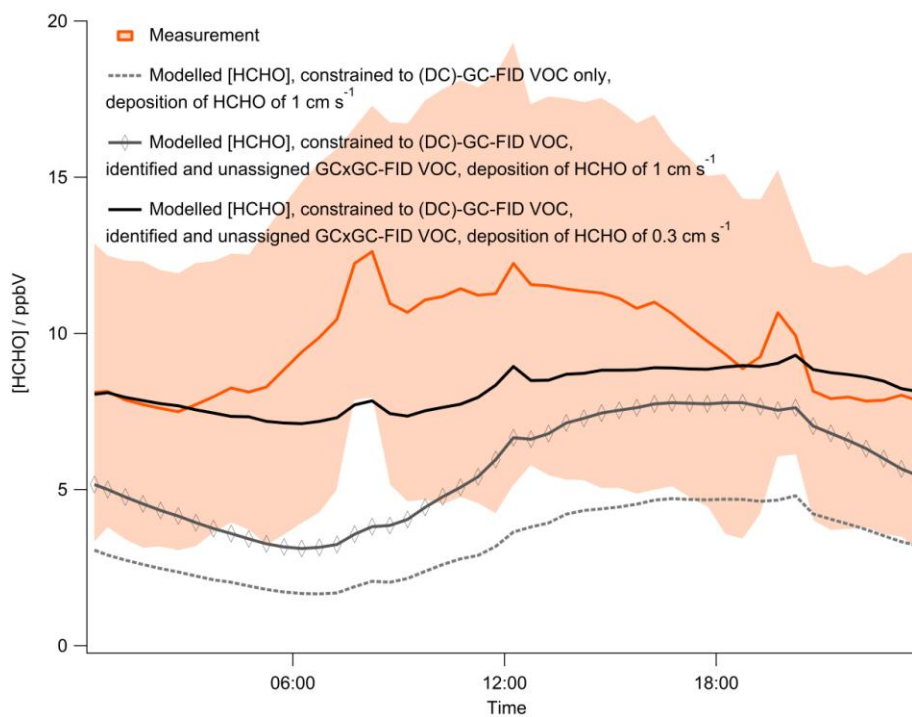
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1 **Figure 6:** Average diurnal profile of measured reactivity and a breakdown of modelled  
2 reactivity into inorganic and organic classes when the model is constrained to the standard  
3 VOC suite measured by the dual-channel (DC)-GC-FID, additional VOCs (including  $\alpha$ -  
4 pinene and limonene, see Table 1 for details) measured with by GCxGC-FID and unassigned  
5 GCxGC-FID peaks. Top: Average diurnal during south westerly flows and Bottom: Average  
6 diurnal during easterly flows.

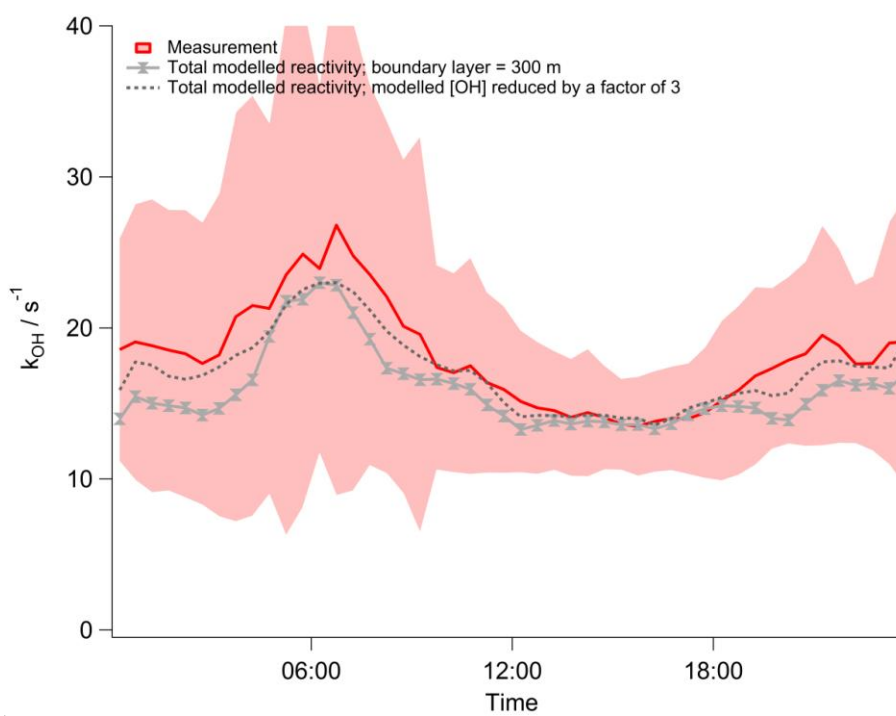
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 2 **Figure 7:** Average diurnal profile of the observed HCHO and modelled HCHO for different  
 3 model scenarios (see text for further details). The shading represents the  $1\sigma$  variability of the  
 4 measurements; with each data point representing 30 min averaged data.

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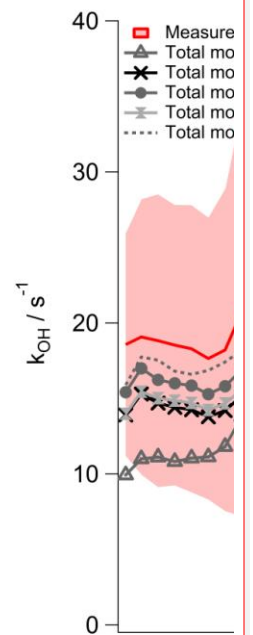


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4 **Figure 8:** Average diurnal profile of the total modelled and measured OH reactivity for  
5 different model scenarios (see text for further details); the level of agreement shown here can  
6 be compared to the model-measured agreement presented in figure 5. The shading represents  
7 the  $1\sigma$  variability of the measurements, with each data point representing 30 min averaged  
8 data.

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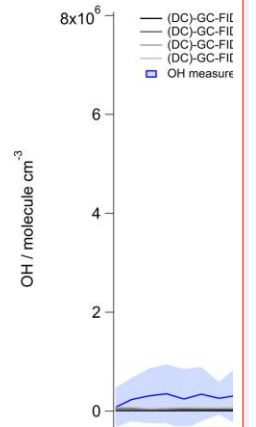
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**Deleted:** **Figure 9:** Average diurnal profile of modelled and measured [OH]. The shading represents the 1σ variability of the measurements; with each data point representing 30 min averaged data. See text for details of the different model scenarios.¶

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$1.2 \times 10^8$   
1.0  
0.8  
0.6  
0.4  
0.2  
0.0

$\text{RO}_2 / \text{molecule cm}^{-3}$

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**Deleted: Figure 10:** Average diurnal profile of measured  $\text{RO}_2$  (green) and steady state calculated  $\text{RO}_2$  using equation 3 (black, solid line =  $[\text{RO}_2]_{\text{ss}}$  derived from the observed total OH reactivity and grey, dashed line =  $[\text{RO}_2]_{\text{ss}}$  derived from calculated OH reactivity using (DC)-GC-FID VOC only. The shading represents the  $1\sigma$  variability of the measurements; with each data point representing 30 min averaged data.