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

Referee 1:
This papers reports on measurements of the total OH reactivity (kOH) in the megacity London. Measurements of kOH are sparse. Therefore, the presentation of these measurements are important. Measurements of kOH are completed in this campaign by the detection of a large set of different VOCs. The authors nicely show, to which extend contributions of all measured OH reactants can explain measured OH reactivity. If also contributions of unmeasured oxygenated VOCs that are calculated by models are taken into account, the authors can show that kOH is explained. As the authors emphasize, missing reactivity that is discussed in literature always needs to be seen in the context of the completeness of measurement of OH reactants. These messages are clearly presented in the manuscript. However, the focus of the paper on these points could be improved specifically in the second part of the manuscript. The authors should consider the following points:

(1) I assume that the measurement site was close to sources of VOCs. This may have consequences for the applicability of a box model, which assumes that oxygenated VOCs can accumulate. If the transport time between the source and the site is short, concentrations of products could be over-estimated. We have run the model both constrained and unconstrained to OVOCs that were measured (acetaldehyde, acetone as well as formaldehyde which is discussed in the paper) and find that the model has a tendency to under-estimates the concentration of these species, suggesting that there may be direct emissions of these species which are not considered in the model when run unconstrained. Therefore, unknown direct emissions of these species which would lead to model under-predictions may outweigh any expected model overprediction if full steady-state is not reached owing to short times between emission of parent VOCs and the site. We have discussed the sensitivity of the model predictions to the deposition term for all the unconstrained model species which determines the steady state concentrations reached and have shown the model to be reasonably insensitive to this.

(2) In my opinion, the presentation of instruments that are used for the analysis is not well-balanced. The major progress of this work is that a large set of VOC measurements was detected. However, the authors present their FAGE system in much greater detail than their GC systems. The authors may want to move Fig. 4 in the context of a more detailed description of these instruments. It is not clear to me, if all details of the FAGE system that are currently given are required. The recent paper by Dunmore and co-authors (ACP, 15, 9983-9996, 2015) which we reference in the Experimental section details the VOC measurements and so we only provide a basic overview of these measurements in this paper. We do explicitly list all the VOCs individually included in the model in Table 1, however, which we feel is the key information for this manuscript. In the revised manuscript we will add further details on the effective saturation concentration range and sampling resolution of the GC systems. The details of the FAGE instrumentation was included as
we present OH and RO2 measurements from this instrument, however, in light of points (3) and (4) we will modify the FAGE details provided.

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

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

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

We also agree that it is not necessary to compare [RO2] calculated from OH reactivity to the observed [RO2] and so will remove Figure 10 (and remove the associated discussion) from the revised manuscript. We think it is important and relevant to discuss the impact the extra OH reactivity (that derives from the extended VOC suite or model generated intermediates) on ozone production, however, so we propose to still include discussion on the calculation of [RO2]s.

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

To evaluate the impact of the additional OH reactivity which derives from the extended VOC suite and model generated intermediates (which are not always considered when modelling or calculating OH reactivity) on ozone production we need to estimate the additional [RO2] that derives from these species. Using the observed [RO2] would not allow us to evaluate this.

(5) Concerning the simplification of the calculation of the ozone production rate, it is not clear, why the authors do not include ozone production from HO2.
As our aim was to show the impact on ozone production that arises from under-estimating the VOC fraction which contributes to the total OH reactivity, we chose not to include ozone production from HO$_2$. We hope the revisions proposed above will make our main aims clearer in the revised manuscript.

In my opinion, the discussion of the ozone production rate does not fit the topic of the paper well, because the only conclusion is that radical concentrations needs to be correct in the model. If RO2 is measured like in this campaign, however, there is no need to use kOH at all.

The aim was not to model (or calculate) ozone production rate – if we wanted to do this we would use our observations of RO$_2$ and HO$_2$. The aim was to show the impact on ozone production of under-estimating the VOC fraction of the total OH reactivity. Substantial ozone production was observed during the campaign and understanding the influence of more-complex VOCs (which are not traditionally measured) and modelled intermediates have on this pollutant is important and a relevant discussion point.

(6) Fig. 8 is mostly showing results that are already included in other figures. I would suggest to reduce this figure to the new aspects (physical loss, HO2 constrained model).

We will modify this figure accordingly.

Why do the authors use the model run, in which HO$_2$ is constrained? If I understand the point correctly, the purpose is to get the modelled OH correct. In this case, however, the use of measured OH as constraint would make much more sense.

Yes, we constrained the model to HO$_2$ to allow the model to predict OH correctly. We chose not to constrain to the measured OH so we could evaluate the model’s ability to predict OH for diurnal comparisons presented in Figure 9. Regardless of the method chosen to reproduce the observed OH by the model, the impact of reducing the model OH on OH reactivity will be the same.

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

We will assess this point at the production stage.
Referee 2:

This paper presents measurements of total OH reactivity in central London during the ClearfLo project in summer 2012. Similar to other studies, the authors find that the measured reactivity is greater than the reactivity calculated from a box model constrained to a standard set of VOC measurements consisting of C2-C8 hydrocarbons and a small selection of oxygenated VOCs. However, when the model is constrained to an extended set of measurements that included heavier molecular weight (up to C12) aliphatic VOCs, oxygenated VOCs and the biogenic VOCs of α-pinene and limonene obtained using a two-dimensional GC instrument the modeled reactivity is in better agreement with the measurements. Including unidentified peaks in the GCxGC measurements further improves the agreement. Including the extended VOC measurements also improved the agreement between the measured and modeled OH concentrations, although the constrained model still overestimated the measured OH. Better agreement with the measured OH was achieved when the model was constrained to the measured HO2. The measured total RO2 concentrations are also underpredicted by a steady-state calculation constrained by the modeled reactivity based on the standard VOC measurements, but are in better agreement with the measurements when the calculation is constrained by the modeled reactivity based on the extended VOC measurements. Because the missing reactivity appears to be mainly due to the contribution of α-pinene and limonene and their oxidation products, the authors conclude that ozone control strategies for London should consider the impact of biogenic emissions. The paper is well written and suitable for publication in ACP. I have a few comments that the authors should consider in their revision of the manuscript.

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

In Figure 6 we contrast the two air-mass scenarios encountered during the project. From these, it is evident that the contribution to the total reactivity made by an individual class of compounds does not change significantly between these two regimes, rather all classes represent bigger OH sinks during the more polluted phase. We have now looked at the breakdown in reactivity on a day by day basis in more detail. We note that the reactivity associated with the model intermediates deriving from the biogenic VOCs increases on the warmest days which were coincident with the easterly flows experienced at the beginning of the campaign. Temperatures were lower during the second easterly and, as a consequence, the model predicts a lower reactivity from model-generated intermediate species. On the 9th and 10th August (easterly flow, lower temperatures) a model constrained only with the standard VOC measurements provides a reasonable estimate of the total observed reactivity. When the influence on the biogenic species is strongest, i.e. during the first Easterly flow regime when it is warmer, only a model constrained to the extended VOC suite provides a reasonable estimate of the observed reactivity. As noted in the
paper, at times (28th July – 5th Aug) during south westerly flows even a model constrained with the extended VOC suite is unable to entirely reconcile the observed reactivity. We hypothesised that there may be more undetected VOCs on these days or that the physical loss of the model generated intermediates should be treated differently during these two contrasting air-masses. The influence of biogenic species during the south westerly conditions was lower than during easterlies but non-negligible and inclusion of alpha pinene and limonene in the VOC model constraints improves the model measured agreement particularly from the 5th – 8th Aug and also from the 11th Aug until the end of the campaign.

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

2) Related to the above, including a time series of the VOC and NOx measurements would assist in the interpretation of the information shown in Figure 1. In addition, showing the time series of the calculated reactivity based on the standard VOC measurements in addition to that modeled with the addition 2DGC VOC measurements would be useful.

We will include these additional time-series as suggested. We will separate the VOCs into biogenic and non-biogenic (excluding CH4). We will also include a time-series of temperature which we think helps to highlight what is driving the chemical composition observed on the warmer days.

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

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

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

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

5) It appears that the MCM model is unable to reproduce the observed OH concentrations even when the modeled OH reactivity is in agreement with the measured reactivity, perhaps due to the an overestimation of the HO2 concentration. The authors state that the model constraints were re-initialized in the model every 15 minutes. Given the rapid propagation rates under these relatively high NOx concentrations, are the authors confident that the modeled constraints (especially NO, NO2, O3, HONO) are not changing during the 15 minutes? If they are changing it could impact the modeled radical concentrations including the propagation of HO2 to OH and could explain some of the model discrepancies described in this section.
We don’t think this is the case, as rapidly changing model constraints would not result in a wholly positive bias as we see (i.e. the model consistently over-predicts HO).
Atmospheric OH reactivity in central London: observations, model predictions and estimates of in situ ozone production

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Abstract

Near-continuous measurements of OH reactivity in the urban background atmosphere of central London during the summer of 2012 are presented. OH reactivity behaviour is seen to be broadly dependent on airmass origin with the highest reactivity and the most pronounced diurnal profile observed when air had passed over central London to the East, prior to measurement. Averaged over the entire observation period of 26 days, OH reactivity peaked at \( \sim 27 \) s\(^{-1}\) in the morning with a minimum of \( \sim 15 \) s\(^{-1}\) during the afternoon. A maximum OH reactivity of 116 s\(^{-1}\) was recorded on one day during morning rush hour. A detailed box model using the Master Chemical Mechanism was used to calculate OH reactivity, and was constrained with an extended measurement dataset of volatile organic compounds (VOCs) derived from GC-FID and a two-dimensional GC instrument which included heavier molecular weight (up to C\textsubscript{12}) aliphatic VOCs, oxygenated VOCs and the biogenic VOCs of \( \alpha \)-pinene and limonene. Comparison was made between observed OH reactivity and modelled OH reactivity using (i) a standard suite of VOC measurements (C\textsubscript{2}-C\textsubscript{8} hydrocarbons and a small selection of oxygenated VOCs) and (ii) a more comprehensive inventory including species up to C\textsubscript{12}. Modelled reactivities were lower than those measured (by 33\%).
when only the reactivity of the standard VOC suite was considered. The difference between measured and modelled reactivity was improved, to within 15%, if the reactivity of the higher VOCs (≥C₉) was also considered, with the reactivity of the biogenic compounds of α-pinene and limonene and their oxidation products almost entirely responsible for this improvement. Further improvements in the model’s ability to reproduce OH reactivity (to within 6%) could be achieved if the reactivity and degradation mechanism of unassigned two-dimensional GC peaks were estimated. Neglecting the contribution of the higher VOCs (≥C₉) (particularly α-pinene and limonene) and model-generated intermediates decreases the modelled OH concentrations by 41%, and the magnitude of in situ ozone production calculated from the production of RO₂ was significantly lower (60%). This work highlights that any future ozone abatement strategies should consider the role that biogenic emissions play alongside anthropogenic emissions in influencing London’s air quality.

1 Introduction

It has been estimated that there may be in excess of 10⁵ different VOC species present in the atmosphere globally (Goldstein and Galbally, 2007) and it is the hydroxyl radical which is primarily responsible for the processing and eventual removal of these compounds. In an urban setting, rich with vehicular emissions, the task of accurately quantifying the total rate of reactive OH loss using measurements of each individual VOC present is unfeasible. Yet underestimations of the loss rate of OH can lead to inaccuracies in predicting the OH concentration and oxidation capacity and, in NOₓ-rich areas, such as urban centres, ozone production resulting from the reaction between peroxy radicals (formed during OH oxidation of VOCs and CO) and NO may be under-estimated.

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

\[ k_{OH} = \sum_i k_{OH,i} [X_i] \]  

(1)

where \([X_i]\) represents the concentration of species which react with OH (VOC, NO₂, CO etc) and \(k_{OH,i} \) is the corresponding bimolecular rate constant.
The techniques used to determine $k_{OH}$ include the flow tube with sliding injector method pioneered by Brune and co-workers (Kovacs and Brune, 2001), a comparative rate method (Sinha et al., 2008), and a laser flash photolysis pump-probe technique (Sadanaga et al., 2004). These techniques have been used in a variety of environments and the reader is referred to the overview of previous measurements provided by Lou et al. (2010). Both the flow-tube with sliding injector and comparative rate method rely on $H_2O$ vapour photolysis at 185 nm using a lamp which generates $OH$ and $HO_2$ simultaneously. As a consequence, corrections must be made when ambient NO concentrations reach ~1 ppbV or more to account for $OH$ recycled by reaction of this generated $HO_2$ with $NO$. The recycled $OH$, if left uncorrected, effectively slows the rate of the first order decay of $OH$ (Ingham et al., 2009) leading to an underestimation of the $OH$ reactivity. Using the flash photolysis technique, $OH$ is generated by photolysing ozone at 266 nm followed by reaction of $O(1D)$ with $H_2O$ vapour. $HO_2$ is not formed initially by this method, so it is possible to measure $OH$ reactivity at significantly higher NO concentrations before a correction becomes necessary, making this technique well suited to urban measurements of $OH$ reactivity (Sadanaga et al., 2005).

There have now been several observations of $OH$ reactivity in urban environments (Kovacs et al., 2003; Ren et al., 2003; Sadanaga et al., 2005; Shirley et al., 2006; Yoshino et al., 2006; Ren et al., 2006; Sinha et al., 2008; Mao et al., 2010; Chatani et al., 2009; Dolgorouky et al., 2012) with some of the highest ever observed values of $>120$ s$^{-1}$ recorded in megacities such as Mexico City (Shirley et al., 2006) and Paris (Dolgorouky et al., 2012). In many cities (Houston, New York City, Mexico City), $OH$ reactivity has been found to be dominated by anthropogenic hydrocarbons, CO and $NO_x$. Oxygenated VOCs (OVOCs) have been highlighted as significant $OH$ sinks in a number of urban studies, contributing between 11–24% during summertime (Mao et al., 2010).

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

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

and hence simultaneous measurements of $OH$ reactivity and $OH$ concentrations permits a field measurement of $P_{OH}$ and, by comparison with a model constrained using the measured $OH$ precursors, an assessment of the completeness of the model radical sources can be
obtained. This type of OH budget analysis has proved particularly effective in highlighting large missing OH sources in low NOx, biogenically influenced regions, such as tropical forests (Whalley et al., 2011). In a number of urban studies conducted in different US cities and Mexico City (Mao et al., 2010), this type of OH budget analysis has identified that during the morning rush hour the rate of OH production exceeds that of destruction ($P_{OH}/D_{OH} >1$) suggesting uncertainties in either the chemistry used in the model or in the measurements of the precursors of OH under elevated levels of NOx which lead to an overestimation of $P_{OH}$.

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

Missing reactivity is often largest in forested environments, e.g. (Edwards et al., 2013), with both missing primary emissions (Di Carlo et al., 2004) and oxidised intermediates (Edwards et al., 2013) considered as potential contributors. In contrast, analysis made during a number of urban studies has demonstrated good agreement between measured OH reactivity and that calculated using equation (1) from individually measured OH sinks (Ren et al., 2003; Di Carlo et al., 2004; Mao et al., 2010). In almost all urban studies to date, the measured OH reactivity has been compared to calculated OH reactivity only rather than modelled reactivity; the latter would include an estimate of the contribution that model-generated intermediates make to the total loss rate. The fact that closure has previously been obtained using calculated reactivity from primary emissions alone suggests that oxidised intermediates do not always contribute significantly to the total OH reactivity in certain cities. This is not the case at all urban sites, for example Chatani et al. (2009) reported a missing reactivity of ~ 30% in Tokyo during the summer determined by comparing the measured OH reactivity with that calculated.
from measured sinks, and concluded that oxidised intermediates likely contributed to the missing fraction. Similarly, Dolgorouky et al. (2012) reported a missing reactivity of 75% when continental air was sampled in Paris during the wintertime MEGAPOLI project and only measured sinks were used to calculate $k_{OH}$. The closure of the OH reactivity budget in certain cities such as Houston (Mao et al., 2010) and New York (Ren et al., 2003) may reflect the dominance of NOx acting as main OH sink; a species from which no model-generated intermediates will derive (in New York the reaction of OH with NO and NO2 accounted for 50% of the total OH reactivity (Ren et al., 2003)). The VOC classes which dominate in different cities may also be substantially different (and, hence, their propensity to generate intermediates may differ). For example, aromatics account for up to 15% of the total reactivity in Houston (Mao et al., 2010) where local petrochemical industries can influence the local air-mass composition. In contrast, aromatics accounted for just 5% of the total reactivity in Tokyo (Yoshino et al., 2012) during the summer of 2007. During the PRIDE-PRD campaign in southern China, OH reactivity was modelled using the Regional Atmospheric Chemistry Model (RACM) and, alongside calculated OH reactivity from measured sinks, was compared to measured OH reactivity. Lou et al. (2010) found that the calculated OH reactivity was a factor of two less than the measured value, whereas the RACM modelled OH reactivity reproduced the observations well, suggesting that unmeasured secondary species (mainly thought to be OVOCs) do make a significant contribution to the total observed OH reactivity. During the daytime the PRIDE-PRD site was heavily influenced by biogenic emissions, in contrast to some of the urban sites discussed above, which may in part explain the differences of the missing OH reactivity reported.

Care is needed when comparing the missing OH reactivity reported in the literature, as the chemical detail and range of measured VOCs and inorganic (e.g., NOx, CO, O3) species which have been used to calculate OH reactivity varies significantly between projects. Oxygenated VOCs or biogenic VOCs (in addition to isoprene) are often measured, although this is not always the case as in the urban studies reported by (Lou et al., 2010; Kovacs et al., 2003; Ren et al., 2003; Mao et al., 2010; Dolgorouky et al., 2012).

This paper presents an extensive dataset of OH reactivity measured in London during the summer of 2012 as part of the Clean air for London (ClearfLo) project (Bohnenstengel, 2014). Alongside OH reactivity, an extremely comprehensive speciated VOC dataset was measured and used to constrain a zero dimensional box model based on the Master Chemical
Mechanism v3.2 in order to model OH reactivity. By comparing modelled and measured reactivity the level of missing OH reactivity is quantified. By also constraining the model with a subset of the VOCs comprising the more commonly reported C\textsubscript{2}-C\textsubscript{8} VOCs (measured using a dual-channel gas chromatography system), we assess which classes of VOC are controlling the OH reactivity in London. Using the model we also investigate the impact of various classes of VOC on the concentration of peroxy radical species and consequently on the magnitude of \textit{in situ} O\textsubscript{3} production.

2 Experimental

2.1 Site description

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

2.2 OH reactivity measurements

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

Changes in OH radical concentrations owing to pseudo-first-order loss with species present in ambient air were monitored by sampling air from the reaction cell through a 0.8 mm pin-hole into a FAGE (fluorescence assay by gas expansion) detection cell maintained at a pressure of
~1.5 Torr by a Roots blower backed by a Rotary pump. The 308 nm probe laser, operating at a pulse-repetition-frequency of 5 kHz, was passed across the gas flow in the FAGE cell to excite OH radicals, with the subsequent laser-induced fluorescence (LIF) signal at ~308 nm detected by a gated channel photomultiplier tube (CPM). The OH decay profile owing to reactions with species in ambient air is thus detected in real time.

Decay profiles were averaged for 5-minute periods, and fitted to a first-order rate equation to find the rate coefficient describing the observed loss of OH (kloss). The OH reactivity, kOH, was determined by subtracting the rate coefficient describing physical losses of OH (kphys) from the observed loss of OH in ambient air, with a small correction to account for the dilution of ambient air with the small flow of O3-containing humidified ultra-high purity air. The rate coefficient, kphys, was determined by monitoring the loss of OH when sampling ultra-high purity air (BTCA 178, BOC Special Gases, passed through scrubbers to remove trace amounts of NOx, H2, CO and CO2) containing the same small flow of O3-containing humidified ultra-high purity air as for the measurements sampling ambient air, and was found to be 1.1 ± 1.0 s⁻¹.

The accuracy of the OH reactivity measurements were verified in the laboratory by measuring the bimolecular rate coefficients for reactions of OH with CO and CH₄ under pseudo-first-order conditions at 293 K. For reaction of OH with CO, a bimolecular rate coefficient of (2.4 ± 0.2) x 10⁻¹³ cm³ s⁻¹ was determined, in agreement with the literature value of 2.3 x 10⁻¹³ cm³ s⁻¹ (Atkinson et al., 2006), and for OH + CH₄, a rate coefficient of (5.5 ± 0.6) x 10⁻¹⁵ cm³ s⁻¹ was determined, in agreement with the literature value of 5.8 x 10⁻¹⁵ cm³ s⁻¹ (Atkinson et al., 2006). The 1σ uncertainty of the measurements was, on average, ±3.2 s⁻¹ reflecting the combined uncertainties from the fits of the observed OH decays, determinations of kphys and uncertainties in the dilution factor.

### 2.3 VOC Measurements

Two gas chromatography (GC) instruments were deployed as part of the summer ClearFlo campaign for in situ VOC measurements: a dual channel GC, (DC)-GC-FID, measuring the very volatile VOCs (C₂-C₈ hydrocarbons and a small selection of OVOCs) with effective saturation concentrations ranging from 3 x 10⁷ to 1.4 x 10¹² µg m⁻³, and a comprehensive two-dimensional GC (GC×GC-FID) which measured the less volatile fraction, (C₉-C₁₃ and a
A large group of OVOCs with effective saturation concentrations ranging from $1.8 \times 10^6$ to $2.4 \times 10^9$ µg m$^{-3}$. The combined sampling and separation time of the systems allowed a time resolution of approximately 1 hour. The details of these two instruments and the time-series of the VOC measurements during ClearLo are presented in Dunmore et al. (2015). A total of 64 VOCs were individually identified and quantified and used to constrain a zero dimensional box model; these are listed in Table 1. Many hundreds more were included in a carbon number and functionality grouping in an attempt to quantify as much of the reactive carbon loading as possible (Dunmore et al., 2015).

### 2.4 Model description

A zero dimensional box model, utilising a subset of the chemistry described within the Master Chemical Mechanism MCMv3.2 (Jenkin et al., 2012), has been used to predict OH reactivity for comparison with the measured reactivity. In its entirety, the MCM treats the degradation of 135 VOCs following oxidation by OH, O$_3$, and NO$_3$, and for alkanes only, oxidation by Cl atoms, and contains ~6,700 species and ~17,000 reactions. Complete details of the kinetic and photochemical data used in the mechanism are available at the MCM website (MCM, http://mcm.leeds.ac.uk/MCM/home).

The model was constrained to measurements of NO, NO$_2$, O$_3$, HONO, CO, CH$_4$, PAN, HCHO, VOCs (details given in Table 1), water vapour, temperature, pressure, photolysis frequencies (using actinic fluxes measured by a spectral radiometer) and aerosol surface area. A constant H$_2$ concentration of 500 ppbV was assumed.

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

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

3 Results

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

On all days a distinct diurnal trend was apparent in OH reactivity, which peaked between 6 and 7 am (GMT) and then dropped to a minimum during the afternoon as shown in Figure 2. A broader, less distinct secondary peak in reactivity was observed after 6 pm continuing throughout the night. This trend is typical of the OH reactivity profile observed at urban sites, e.g. (Dolgorouky et al., 2012; Sadanaga et al., 2005; Chatani et al., 2009; Lou et al., 2010).
and closely follows the observed NO\textsubscript{x} profile. The mean reactivity for the campaign was 18.1 s\textsuperscript{-1} and on average the reaction of OH with NO and NO\textsubscript{2} accounted for 4.5 s\textsuperscript{-1} (25\%) of the reactivity observed. The reaction with CO accounted for a further 1.3 s\textsuperscript{-1} (7\%) and so it is evident, by considering the reactivity that remains unaccounted for, that the combined contribution made by organic compounds must be significant. The model was initially run constrained to the standard set of VOCs measured by the (DC)-GC-FID. The rate of loss of OH by reaction with each individual VOC compound is extremely small, so by grouping individual VOCs detected by the (DC)-GC-FID by class (alcohol, alkanes, alkenes and alkynes, aromatics, carbonyls and dialkenes) the influence of different VOC types on the removal of OH and hence their influence on the oxidising capacity can be evaluated. Using this approach, for the carbonyl class of VOCs the reactivity towards OH is dominated by formaldehyde (40\%) and acetaldehyde (54\%), and when considered as a whole, makes a similar contribution as NO\textsubscript{2} to the total OH reactivity. The other organic classes contribute less to total reactivity (between 0.2 – 0.6 s\textsuperscript{-1} on average), with reactivity from most of the classes exhibiting a weak diurnal profile similar to that of NO\textsubscript{x}. In contrast, the contribution to OH reactivity made by the dialkene class, which itself is dominated by isoprene, peaks at noon suggesting a dominance of a temperature/sunlight driven biogenic signature as opposed to a traffic signature for this class.

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

An extended range of VOCs (24 additional compounds), consisting of n-alkanes, substituted aromatic and carbonyl compounds and the monoterpenes of α-pinene and limonene, were detected using a GCxGC-FID instrument. The missing reactivity determined in the modelling exercise above (which included only VOCs from the (DC)-GC-FID) may derive from these additional VOCs which, historically, are not typically detected by traditional GC methodologies. As shown in Figure 3, the reaction of OH with the biogenic species of α-
pinene and limonene alone (not including any model-derived intermediates) increases the
total calculated OH reactivity by 0.25 s\(^{-1}\), and similar increases are calculated by inclusion of
the additional \(n\)-alkanes detected (Table 1). Overall, however, calculated OH reactivity
increases by just 0.7 s\(^{-1}\) on average when these additional contributions are considered
without including model-derived intermediates. Interestingly, the contribution that the model-
derived intermediates make to OH reactivity when the model is run constrained to the
extended VOC suite is much more significant than previously presented in Figure 2. When
combined, the model-generated intermediates contribute 3.2 s\(^{-1}\) on average to the OH
reactivity in the model run constrained to the extended VOC measurements, compared to just
0.7 s\(^{-1}\) in the model run constrained just with the standard VOC measurements.

In total there are close to 2600 reactions included in the extended VOC model run which
destroy OH and the reaction of OH with the different model-generated intermediate species.accounts for more than 90\% of these reactions. Pinonaldehyde (an oxidation product of \(\alpha\)-
pinene formed both during ozonolysis and OH-initiated oxidation reactions) is the most
destructive model intermediate species with respect to OH and this single species is found to
contribute approximately 7.5\% to the total OH reactivity of the modelled intermediates at
noon. Considering the top ten most destructive model intermediates which account for
roughly 30\% of the total model intermediate reactivity, nine out of the ten derive from
biogenic species. Species which derive from \(\alpha\)-pinene account for two thirds of the reactivity
of the top ten intermediate species, whilst those which derive from limonene account for
approximately one third. 3-Hydroxypropanal which derives from the alkane class and is the
ten most destructive model intermediate contributes \(\sim\)1.5\% to the total reactive of the
intermediates on average. To determine the absolute impact of the biogenic species on OH
reactivity, a model was run constrained to all (DC)-GC-FID and GCxGC-FID VOC
measurements apart from \(\alpha\)-pinene and limonene. The model-generated intermediates from
this run contributed 1.04 s\(^{-1}\) to total OH reactivity on average, demonstrating that although the
contribution to total OH reactivity from the measured biogenic class (considering only
reaction with the parent VOCs) was small (0.25 s\(^{-1}\)), the oxidation products from just \(\alpha\)-
pinene and limonene alone account for 2.2 s\(^{-1}\) of the OH reactivity. The total concentration of
\(\text{C}_9 - \text{C}_{12}\) alkanes is \(\sim\)5 times greater than the combined concentration of the biogenics on
average. Despite this, the model intermediates generated during the oxidation of these larger
alkanes (\(\text{C}_9 - \text{C}_{12}\)) which derive from diesel emissions (Dunmore et al., 2015), and the
intermediates generated from the additional aromatic and carbonyl species detected by GCxGC-FID contribute only 0.34 s\(^{-1}\) to total reactivity on average. The rate of reaction of OH with α-pinene (5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} at 298K) is approximately 4.5 times faster (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 magnitude faster) than the analogous reactions with the C\(_9–C\(_{12}\) alkanes (\textasciitilde 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} at 298K). Furthermore, the initial reaction of these biogenic species with ozone can also contribute to the formation of the biogenic-derived model intermediates species. The biogenic intermediates themselves remain highly reactive towards OH, with the rate coefficient for the reaction of OH with pinonaldehyde being similar to the rate coefficient for the reaction of OH with α-pinene itself (4 \times 10^{-11} and 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} respectively at 298K). These factors combined lead to the biogenic species strongly influencing OH reactivity.

The contribution that modelled intermediates derived from the larger VOCs (measured by the GCxGC-FID) make to the total OH reactivity is significant, and is able to largely close the gap between modelled and observed OH reactivity, with \textasciitilde 15\% missing reactivity remaining.

Good agreement both in terms of the magnitude and variability from day-to-day (Fig. 1) and campaign average diurnal profile (Fig. 3) is achieved by the model when constrained to the extended VOC measurements. This result highlights the impact of biogenic VOCs in London when the oxidised secondary products are considered. The role of biogenic VOCs (excluding isoprene) in increasing the OH reactivity has not previously been demonstrated at urban sites. Often biogenic VOCs other than isoprene are not measured at urban sites when OH reactivity has been reported e.g. (Kovacs et al., 2003; Ren et al., 2003; Mao et al., 2010; Lou et al., 2010; Dolgorouky et al., 2012) and even if they are measured, the contribution they make to total OH reactivity is deemed small if only the reaction of the parent measured biogenic species with OH is considered, e.g. (Chatani et al., 2009). The ultimate fate of these oxidised intermediates derived from biogenic VOCs is highly uncertain, but if they remain in the gas-phase, as opposed to partitioning onto particles, their potential to increase the rate of radical propagation and in situ ozone production is significant.

Even when the contribution made to reactivity from the additional VOCs measured by the GCxGC-FID is taken into account, a small missing reactivity (\textasciitilde 15\% on average) remains. This missing reactivity could suggest that the physical loss of model generated intermediates
may actually be slower than imposed in the model (see Sect. 3.2) or this under-prediction in OH reactivity could also reflect further missing primary OH sinks, for example, higher molecular weight carbon (≥C13) that is not detected by either the (DC)-GC-FID or GCxGC-FID methods employed. It is known that ≥C13 makes up a large fraction of diesel emissions and diesel-related hydrocarbons have been shown to dominate the gas phase carbon (in terms of mass) in London (Dunmore et al., 2015).

The complexity of London’s air can be observed in the GCxGC-FID chromatogram shown in Figure 4. In addition to the many identified VOCs, there are many others that can be grouped according to chemical class through their position on the chromatogram, but are not identified explicitly. Ten groups are shown in Figure 4, with areas 1-8 representing branched and cyclic alkanes, area 9 represents unidentified monoterpenes and area 10 is the C4-substituted monoaromatics species. The highly branched alkane species can be incorporated into the model by approximating the reactivity to be the same as for the straight-chain alkane equivalent. For example, for an unidentified branched alkane which contains six carbon atoms it has been estimated that it would have the same reactivity with respect to OH as n-hexane (and the same, subsequent, degradation mechanism). For unidentified monoterpenes, aromatics the reaction rate coefficient with respect to OH (and degradation mechanism) is taken to be the same as that for propyl-benzene. Inclusion of this additional reactive carbon in the model leads to a 0.4 s\(^{-1}\) increase in the alkane contribution and only a small increase of ~0.1 s\(^{-1}\) due to increasing the carbon in the biogenics and aromatic classes combined. Despite the small contribution made by increasing the effective α-pinene present, this increase in biogenic carbon leads to a further 1.1 s\(^{-1}\) increase in the contribution from model intermediates. Figure 5 compares the total modelled OH reactivity alongside the measured values when these additional unidentified species are included. Overall, this additional carbon (which is known to be present but cannot be fully identified) improves the overall model-to-measured agreement with just 6% of the total reactivity now unaccounted for.

Considering the breakdown in modelled OH reactivity on a day by day basis (Figure 1b and c), the reactivity associated with the model intermediates deriving from the biogenic VOCs increases on the warmest days which were coincident with the easterly flows experienced at the beginning of the campaign (24\(^{th}\) – 27\(^{th}\) July). Di Carlo and co-workers (2004) found in a
forested environment that missing reactivity increased with temperature and hypothesised that unknown reactive biogenic VOCs, possibly unmeasured mono-terpenes, accounted for this missing reactivity. They observed little difference between calculated reactivity and modelled reactivity suggesting that the oxidation products of these biogenic species do not increase OH reactivity significantly. This finding is in contrast to the model predictions presented here and demonstrates that the higher levels of NO present in London relative to a forested environment promotes more efficient model propagation and the generation of reactive model intermediates. Lower temperatures and, consequently, lower biogenic VOC concentrations were observed (Figure 1a) during the easterly flow experienced between 8th - 10th August relative to the first easterly period. The model predicts a lower reactivity from the model-generated intermediate species during this period despite [NOx] being similar to those experienced during the first easterly. On the 9th and 10th August, during the second of the easterly flow periods, captured, a model constrained only with the standard VOC measurements provided a reasonable estimate of the total observed reactivity (Figure 1b). When the influence on the biogenic species is predicted to be the strongest, i.e. during the first easterly flow regime, only a model constrained to the extended VOC suite provides a reasonable estimate of the observed reactivity. From Figure 1c it is evident that the largest fraction of missing reactivity occurs during the south-westerly flow conditions encountered between the 28th July – 5th August and even considering the 1σ uncertainty of the OH reactivity measurements of ±3.2 s⁻¹, the missing reactivity during this period is significant. The propensity of the model to under-estimate reactivity during this south westerly flow is further highlighted when the modelled averaged diurnal reactivity is taken for south westerly and easterly conditions separately (Fig. 6). The contribution to the total reactivity made by any individual class of compounds does not change significantly between these two regimes, rather, all classes represent bigger OH sinks during the more polluted phase. The diurnal profile is much more distinct during the polluted phase demonstrating a stronger traffic-based source, likely in combination with more significant boundary layer height changes over the course of the day during low wind speed periods. There is a very slight over-prediction during the Easterly flow in OH reactivity during the afternoon and during the morning rush-hour, but overall the agreement between model and measurements is excellent during the Easterlies. In contrast, an under-prediction in the observed OH reactivity throughout the day during south-westerly conditions is apparent suggesting either there are more undetected VOCs during south-westerly flows than during the easterly flows or that the physical loss of the model generated intermediates should be treated differently during these two contrasting
air-masses. The sensitivity of model predictions to the physical loss term of the model-generated intermediates is investigated in Sect. 3.2.

3.1 Ability of the model to reconcile the observed formaldehyde concentration

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

3.2 Sensitivity of model-generated intermediates to parameterisation of the rate of physical loss

There is considerable uncertainty associated with the concentration of model species which are generated by reaction in the model rather than constrained to observations. Model species can undergo gas-phase reactions, may be lost via wet or dry deposition (at different rates depending on the particular species), be taken up on aerosol surfaces, or if their lifetime is
sufficiently long, there may be a net movement of these species either into or out of the model box.

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

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

3.3 Impact of the different VOC constraints on modelled OH

As may be expected, with an increase in the modelled OH reactivity moving from the model-  
rung with standard VOC constraints to a run with the extended VOC constraints, the OH  
concentration predicted by the model is concomitantly reduced by 41% (standard VOC suite  
to extended VOC suite including contribution from unassigned peaks). This analysis  
demonstrates that neglecting the contribution of the higher VOCs (>C9) (particularly α-  
pinene and limonene) and model-generated intermediates can impact a model’s ability to  
predict the oxidising capacity accurately,

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

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

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

\[
k_{\text{OH}} = \sum k_{\text{OH} + \text{VOC}}[\text{VOC}] + k_{\text{OH} + \text{NO}_2}[\text{NO}_2] + k_{\text{OH} + \text{NO}}[\text{NO}] + k_{\text{OH} + \text{O}_3}[\text{O}_3] + k_{\text{OH} + \text{CO}}[\text{CO}] + \\
k_{\text{OH} + \text{HCHO}}[\text{HCHO}] 
\]  

(3)

The reaction of OH with NO (to form HONO) or NO₂ (to form HNO₃) may be viewed as  
either a temporary or permanent radical sink, respectively, dependent upon the lifetime of the  
reservoir species formed. In contrast, the reaction of OH with VOCs, O₃, CO or HCHO is the
rate determining step producing peroxo radicals and, in the presence of NO, net ozone production via the production and subsequent photolysis of NO₂.

Assuming the steady-state approximation, an expression can be determined for the concentration of RO₂ radicals which derive from the reaction of OH with VOC from a measurement of the total OH reactivity (with the contribution of inorganic reactions and any HO₂ formation reactions subtracted), an [OH] measurement and an RO₂ sink term represented as the average rate coefficient for reaction of RO₂ with NO (under the conditions in London other loss routes for RO₂ are ignored):

\[ [RO₂]_{SS} = \frac{(k_{OH} - (k_{OH+NO}[NO₂] + k_{OH+NO}[O₂] + k_{OH+CO}[CO] + k_{OH+HCHO}[HCHO]))[OH]}{k_{RO₂+NO}[NO]} \]  

(4)

The rate of in situ ozone production resulting from [RO₂]_{SS} may then be estimated using:

\[ P(O₃) = k_{RO₂+NO}[RO₂]_{SS}[NO] - k_{OH+NO₂}[OH][NO₂] \]  

(5)

Eq. 5 considers the production of NO₂ (and upon photolysis, O₃) by reaction of RO₂ radicals with NO only (ignoring HO₂). The loss of NO₂ by reaction, for example with OH, rather than photolysis which generates O₃, must also be taken into account when determining net production.

Using this methodology, an [RO₂]_{SS} diurnal profile peaking at ~ 6x10⁷ molecule cm⁻³ is derived from total OH reactivity. From this [RO₂]_{SS}, an average in situ ozone production during the day (from RO₂ + NO) of ~ 22 ppbV d⁻¹ is estimated. This analysis can be repeated using k_{OH} calculated from the standard VOC suite measured with the (DC)-GC-FID alone (with the contribution from model intermediates and heavier weight VOCs omitted). The [RO₂]_{SS} is reduced by ~ 45% and consequently the calculated in situ O₃ production from RO₂ is reduced to ~ 9 ppbV d⁻¹.

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

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

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

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

<table>
<thead>
<tr>
<th>Species (MCM name)</th>
<th>Class</th>
<th>Contribution to OH reactivity ($s^{-1}$)</th>
<th>Contribution to OH reactivity (%)</th>
<th>Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3</td>
<td>O$_3$</td>
<td>0.05$^a$</td>
<td>0.3</td>
<td>Thermo 49 Series</td>
</tr>
<tr>
<td>NO</td>
<td>NO</td>
<td>0.76</td>
<td>4.2</td>
<td>Air Quality Design Inc. Chemiluminescence with LED NO$_2$ converter</td>
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<td>21.1</td>
<td></td>
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<tr>
<td>CO</td>
<td>CO</td>
<td>1.31</td>
<td>7.2</td>
<td>Ametek monitor</td>
</tr>
<tr>
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<td>H$_2$</td>
<td>0.08$^a$</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>HONO</td>
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<td>0.2</td>
<td>LOPAP CIMS GC-ECD</td>
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<td>HNO$_3$</td>
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1 The contributions of classes which account for less than 0.1 s⁻¹ OH reactivity are not plotted in Fig. 2, 3, 5 and 6 for clarity.
Figure 1a: Time-series of non-methane hydrocarbons (excluding biogenics), biogenics (isoprene and mono-terpenes), NOx 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 1σ uncertainty of the OH reactivity measurements (red shading) was, on average, ±3.2 s⁻¹.
Figure 2: Average diurnal profile of measured reactivity for the entire ClearLo campaign and a breakdown of modelled reactivity into inorganic and organic classes when the model is constrained to the standard VOC suite measured by the (DC)-GC-FID instrument. See Table 1 for details of the individual VOCs that were measured.
Figure 3: Average diurnal profile of measured reactivity and a breakdown of modelled reactivity into inorganic and organic classes when the model is constrained to the standard VOC suite measured by the (DC)-GC-FID and additional VOCs (including α-pinene and limonene, see Table 1 for details) measured with by GCxGC-FID.
Figure 4: A typical GC×GC chromatogram from the summer ClearfLo campaign. The retention times from column 1 (separation based on volatility) and column 2 (separation based on polarity) are the x and y axis respectively, and compound intensity is the coloured contour. Labelled groups are identified as follows; (1-8) aliphatic groups from C$_6$ to C$_{13}$, (9) C$_{10}$ monoterpenes with * corresponding to α-pinene which is the start of that group and (10) C$_4$ substituted monoaromatics.
Figure 5: Average diurnal profile of measured reactivity and a breakdown of modelled reactivity into inorganic and organic classes when the model is constrained to the standard VOC suite measured by the dual-channel (DC)-GC-FID, the additional identified VOCs (including α-pinene and limonene, see Table 1 for details) measured with by GCxGC-FID and the unassigned GCxGC-FID peaks.
Figure 6: Average diurnal profile of measured reactivity and a breakdown of modelled reactivity into inorganic and organic classes when the model is constrained to the standard VOC suite measured by the dual-channel (DC)-GC-FID, additional VOCs (including α-pinene and limonene, see Table 1 for details) measured with by GCxGC-FID and unassigned GCxGC-FID peaks. Top: Average diurnal during south westerly flows and Bottom: Average diurnal during easterly flows.
Figure 7: Average diurnal profile of the observed HCHO and modelled HCHO for different model scenarios (see text for further details). The shading represents the 1σ variability of the measurements; with each data point representing 30 min averaged data.
Figure 8: Average diurnal profile of the total modelled and measured OH reactivity for different model scenarios (see text for further details); the level of agreement shown here can be compared to the model-measured agreement presented in figure 5. The shading represents the 1σ variability of the measurements, with each data point representing 30 min averaged data.
Figure 9: Average diurnal profile of modelled and measured $[\text{OH}]$. 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.
Figure 10: Average diurnal profile of measured RO$_2$ (green) and steady state calculated RO$_2$ using equation 3 (black, solid line = [RO$_2$]ss derived from the observed total OH reactivity and grey, dashed line = [RO$_2$]ss derived from calculated OH reactivity using (DC)-GC-FID VOC only. The shading represents the 1σ variability of the measurements, with each data point representing 30 min averaged data.