

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

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 NO_x 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 NO_x 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 HO₂).