Atmos. Chem. Phys. Discuss., 15, C11034–C11036, 2016
www.atmos-chem-phys-discuss.net/15/C11034/2016/
© Author(s) 2016. This work is distributed under
the Creative Commons Attribute 3.0 License.

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric OH reactivity in central London: observations, model predictions and estimates of in situ ozone production" *by* L. K. Whalley et al.

Anonymous Referee #2

Received and published: 2 January 2016

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 measure-

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

ments 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 HO_2. The measured total RO_2 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.

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.

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

4) The authors state that the majority of the missing reactivity is due primarily to model

ACPD
15, C11034–C11036, 2016

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.

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 HO_2 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, NO_2, O_3, HONO) are not changing during the 15 minutes? If they are changing it could impact the modeled radical concentrations including the propagation of HO_2 to OH and could explain some of the model discrepancies described in this section.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 31247, 2015.