Response to Dr Stockwell's Review

We would like to thank Dr Stockwell for the review of our paper and feel that this review has enable us to improve our paper. Our responses to the review are below.

Review Point 1: The comparison of the RADM2 (mislabeled in the paper as RADM, an earlier mechanism), RACM and RACM2 mechanisms was particularly interesting to me. The available laboratory has vastly increased from what was available in 1990 and 1997 when the RADM2 and RACM mechanisms were published. Now RADM2 and RACM are relics of the past. RACM2 is based on much more recent data especially for aromatic compounds. We only use RACM2 for air quality simulations in my research group. Likewise the US EPA has implemented RACM2 in its most recent version of the Community Multi-scale Air Quality Model (CMAQ) and does not include the earlier obsolete versions. Much the same could be said about the other series of mechanisms.

Author Response: We agree with Dr Stockwell that older versions of the chemical mechanisms in our study are relics of the past. However, as highlighted in the recent review by Baklanov et al. (2014), all versions of the chemical mechanisms used in our study are actively used for modelling studies. We have updated Section 2.1 (page 12395, line 12) to include: *The recent review by Baklanov et al. (2014) shows that each chemical mechanism used in this study are actively used by modelling groups.*

Furthermore, we have updated Table 1 to include a column labelled *Recent Study* which includes the examples of studies using each chemical mechanism. The studies cited are: *Koss et al. (2015) for the MCM v3.2, Lidster et al. (2014) for the MCM v3.1, Derwent et al. (2015) for the CRI v2, Li et. al. (2014) for RADM2, Ahmadov et al. (2015) with RACM, Goliff et. al. (2015) using RACM2, Hou et al. (2015) using MOZART-4, Foster et al. (2014) with the CBM-IV and Dunker et. al. (2015) which uses the CB05.*

Dr Stockwell mentions that we have incorrectly referred to the RADM2 mechanism as RADM. In our paper, we have used the acronyms for the different chemical mechanisms provided by the base literature listed in Table 1 of the research article. Stockwell et al. (1990) is the base reference for RADM2 and we have accordingly used this acronym. We have checked our paper and find no instance of any mechanism being called RADM.

Review Point 2: One problem with the paper is that the authors appear to assume that the MCM is "correct". There is a vast difference between being more explicit and having a greater content of laboratory based information. Actually the authors are comparing three different approaches to developing air quality mechanisms: explicit, aggregation by functional group and aggregation by molecule (or reactivity). The most recent versions of all these mechanisms were developed from the same laboratory databases. Even though the MCM has thousands of reactions, its information content is not much more than the reduced mechanisms; my guess is that MCMs information advantage is probably not much more information than 10 to 20%.

Author Response: We also agree with Dr Stockwell that the MCM should not be considered "correct". Based on this review and comments from the second reviewer (Dr Jenkin), we have updated Section 2.1 (page 12395, line 15) of the manuscript: *The MCM v3.2 is the reference mechanism in this study due to its level of detail (*16 349 *organic reactions). Despite this level of detail, the MCM had difficulties in reproducing the results of chamber study experiments involving aromatic VOC (Bloss et al., 2005).*

Review Point 3: This raises and interesting discussion question: Have highly explicit mechanisms taught us anything new and important about the production of air pollutants? For ozone the answer is a resounding "NO" while for secondary organic aerosols its probably "Maybe".

Author Response: As mentioned by Dr Stockwell, our paper compares the effects on ozone production from different approaches to simplifying the detailed atmospheric chemistry. Our results show that the approach used to create the chemical mechanism rather than its explicitness influences ozone production. For example, in Fig. 1 of our paper, the ozone mixing ratios obtained using the Carbon Bond mechanisms (CBM-IV and CB05) compare well with the MCM despite both Carbon Bond mechanisms being less explicit than the MCM. Also, the ozone mixing ratios from RACM2 and RADM2 show similar absolute differences from that of the MCM despite RACM2 being more explicit than RADM2. Accordingly, we have added the following text to Section 3.1 (page 12399, line 22): *The O_3 mixing ratios in Fig. 1 are influenced by the approaches used in developing the chemical mechanisms and not a function of the explicitness of the chemical mechanism. For example, the O_3 mixing ratios obtained using the Carbon Bond mechanisms (CBM-IV and CB05) compare well with the MCM despite both Carbon Bond mechanisms having* ~ 1 % *of the number of reactions in the MCM v3.2. Also, the O_3 mixing ratios from RACM2 and RADM2 show similar absolute differences from that of the MCM despite RACM2 having more than double the number of reactions of RADM2.*

Response to Dr Jenkin's Review

We would like to thank Dr Jenkin for the helpful review that will enable us to improve our manuscript; our responses to the review points and comments are found below.

Review Point 1: Given that some inventory speciations contain several hundred VOCs for typical urban sources, it could be argued that this is already a substantially lumped representation or maybe more correctly an incomplete speciation, as it is based on reported measurements of a subset of species (although probably the generally more important ones). As a result, the reference MCM simulations are themselves already a reduction, using only a subset of the mechanism. The numbers of species and reactions listed for MCM v3.2 and MCM v3.1 (and CRI v2) in Table 1 should therefore probably more correctly correspond to the VOC speciation, as many species in the complete mechanisms are not participating in the chemistry. These can be obtained using the subset mechanism assembling facilities at the relevant MCM and CRI websites (see end of review). If the authors also wish to keep the existing full mechanism numbers, the subset numbers could be included in a footnote.

Author Response: We agree with Dr Jenkin that it would be more complete stating the number of organic reactions used in our study for each mechanism listed in Table 1. We have updated Section 2.1 (page 12395, line 10) of the manuscript stating : *We used a subset of each chemical mechanism containing all the reactions needed to fully describe the degradation of the VOC in Table 2.*

Accordingly, we have updated Table 1 in the manuscript with the number of organic species and reactions need to fully describe the degradation of the VOC used in the study for each mechanism. The caption of Table 1 has been updated with a further clarification: *The number of organic species and reactions needed to fully oxidise the VOC in Table 2 for each mechanism are also included.*. We have retained the information on the total number of organic reactions in each mechanism by updating the mechanism description in Section 2.1 to include this information.

Specific additions include: page 12395, line 15 (*due to its level of detail (16349 organic reactions).*); page 12395, line 16 (*with 1145 organic reactions*); page 12395, line 19 (*(12691 organic reactions)*); page 12395, line 26 (*Tropospheric chemistry is described by 145 organic reactions in MOZART-4*); page 12396, line 1 (*using 145 organic reactions*); page 12396, line 5 (*(193 organic reactions)*); page 12396, line 7 (*(315 organic reactions)*); page 12396, line 8 (*CBM-IV uses 46 organic reactions to simulate polluted urban conditions*); page 12396, line 15 (*and has 99 organic reactions*).

Review Point 2: On page 12400 (line 12) the high Ox formation from propane degradation in RACM2 is attributed to the mechanism species HC3 producing about 17 times the amount of acetaldehyde that is produced from propane in MCM v3.2. This high ratio arises because acetaldehyde is not a significant first generation product of propane degradation, and therefore not formed in MCM v3.2 until the second-generation chemistry (specifically the further oxidation of the relatively minor product, propanal). Acetaldehyde is therefore formed in RACM2 instead of other products formed in MCM v3.2 (mainly acetone, and some propanal). Acetone, has a low OH reactivity (and photolysis rate) and is not significantly oxidised on the several day timescale of these calculations, thereby largely halting Ox formation after the first-generation chemistry. I suggest it is therefore the failure of RACM2 to represent the high yield of an unreactive product that results in its overestimate in Ox. Although the high relative formation of acetaldehyde on day 1 with RACM2 and MCM v3.2 is one consequence of this, it is not itself the source of the Ox overestimate with RACM2.

Author Response: We would first like to thank Dr Jenkin for further insight into the differences in Ox production between RADM2 and MCM v3.2. As Dr Jenkin suggests, the yield of the less reactive ketone products during propane degradation is lower than in the MCM v3.2. We have updated Section 3.1 of the manuscript (page 12400, line 11) as follows: *Propane is represented as HC3 in RADM2 (Stockwell et al., 1990) and the degradation of HC3 has a lower yield of the less reactive ketones compared to the MCM. The further degradation of ketones hinders Ox production due to the low OH reactivity and photolysis rate of ketones. Secondary degradation of HC3 proceeds through the degradation of acetaldehyde (CH_3CHO) propogating Ox production through the reactions of CH_3CO_3 and CH3O2 with NO. Thus the lower ketone yields leads to increased Ox production from propane degradation in RADM2 compared to the MCM v3.2.*

Section 3.2.2 (page 12403, line 26) was also updated as follows: *The secondary chemistry of HC3 is tailored to produce O_x from these different VOC and differs from alkane degradation in the MCM v3.2 by producing less ketones in RADM2.*

Review Point 2-Cont: On page 12402 (line 28), where the second day maximum in Ox from toluene degradation with RACM2 and CRI v2 is attributed to "..increased C2H5O2 production from degradation of unsaturated dicarbonyls; C2H5O2 is not produced during degradation of unsaturated dicarbonyls in the MCM v3.2." I am particularly familiar with CRI v2, and I agree that a likely contributor to the discrepancy is that the formation of the (relatively reactive) unsaturated dicarbonyls (UDCARB8 and UDCARB11) is too efficient. C2H5O2 is indeed used as a representative peroxy radical, formed from one channel of the oxidation of UDCARB8 -

this being the surrogate for butenedial (MALDIAL) in MCM v3.2. However, MALDIAL is also oxidised to peroxy radicals (MALDIALO2 and MALDIALCO3) in MCM v3.2, with the fraction not leading to anhydride formation being represented by C2H5O2 in CRI v2. I therefore do not think this is an unreasonable assignment (note that contributions of MALDIALO2 + NO and MALDIALCO3 + NO are probably hidden within the large "production others" category for MCM v3.2). It is more that the formation of the unsaturated dicarbonyls is too efficient in CRI v2, and that their degradation produces Ox, regardless of which peroxy radicals are used as representatives. Although the fluxes through the reactions of NO with the specific peroxy radicals (C2H5O2 from UDCARB8 and RN10O2 from UDCARB11) are how this is quantified in the present study, I think that highlighting increased production of C2H5O2 as the sole specific cause is not particularly instructive, as it is once again a consequence of the real cause.

Author Response: Again, we would like to thank Dr Jenkin for his insight into the approach of toluene degradation in CRI v2. Based on this insight, we have revised Section 3.2.1 (page 12402, line 29) of the manuscript to: *The second day maximum of O_x production in CRI v2 and RACM2 from toluene degradation results from more efficient production of unsaturated dicarbonyls than the MCM v3.2. The degradation of unsaturated dicarbonyls produces peroxy radicals such as $C_2H_5O_2$ which promote O_x production via reactions with NO.*

Minor Comments 1: General "Volatile organic compounds" seems to be abbreviated as either "VOC" or "VOCs" at different points in the manuscript. Given that the original definition on line 3 of the Introduction is "VOCs", I would suggest using this consistently throughout, unless talking about an individual VOC.

Author Response: We have corrected the manuscript to defined volatile organic compounds as VOC (page 12390, line 22), and updated the manuscript to use this acronym consistently. Changes were made to page 12391, line 22; page 12397 lines 3 and 10; and to the caption of Table 3. We added the text: *a number of VOC* to page 12393, line 14 for clarification.

Minor Comments 2: Page 12391, line 22: perhaps it should be stated that VOCs are oxidised mainly by reaction with the OH radical, to acknowledge the existence of other initiation pathways.

Minor Comments 3: Page 12392: perhaps it should be clarified that Reaction (R4) specifically illustrates the abstraction of H from a VOC by reaction with OH, as occurs exclusively for alkanes. The main routes for the reactions of OH with alkenes and aromatics proceed by OH addition.

Author Response to Minor Comments 2 and 3: We have updated page 12391, line 22 to: *VOC (RH) are mainly oxidised in the troposphere by the hydoxyl radical (OH) forming peroxy radicals (RO_2) in the presence of O_2. For example, (Reaction R4) describes the OH-oxidation of alkanes proceeding though abstraction of an H from the alkane. In high-NO_x conditions,*

Minor Comments 4: Page 12394, line 13: As stated, the full CRI v2 does lump degradation products into common representatives. Although not used in the present study, its further reduced variants (e.g. CRI v2-R5) also lump emitted VOCs using POCP as a criterion (Watson et al., 2008), so that they are subsets of the full mechanism. As indicated in comment 1 above, the present work also uses a subset of the full mechanism, so I'm not sure that use of the "full CRI" can be claimed on page 12395, line 19.

Author Response: Our subset of the CRI v2 was taken from the full CRI not any of the reduced variants of the CRI that use further reduction techniques as described in Watson et al. (2008). We have updated page 12395, line 19 as follows: *The CRI v2 is available in more than one reduced variant, described in Watson et al. (2008). We used a subset of the full version of the CRI v2 (`http://mcm.leeds.ac.uk/CRI`).*

Minor Comments 5: Page 12398, line 9: The use of a family of Ox species is a sensible approach. However, it might be worth giving a formal definition of "other species involved in fast cycling with NO2", as those shown have a wide range of cycling lifetimes. Are PANs sufficiently short-lived?

Author Response: In our study, we simulate the conditions within the planetary boundary layer thus PAN chemistry is dominated by its production and thermal decomposition. Ox budgets when not including PAN as part of the Ox family are thus dominated by these cycles of PAN formation and thermal decompostion. For this reason we include PANs as part of the Ox family.

Other Comments 1: Page 12395, lines 13-22: MCM v3.2 is used as the reference mechanism in this study, with MCM v3.1 also considered for completeness, because it was the reference for the original development of CRI v2 (Jenkin et al., 2008). Because an overview description of MCM v3.2 has never been published in the open literature, I provide here a short summary of the updates. This is mainly for information, and not necessarily for reproduction in the paper, unless deemed helpful by the authors.

Because there is no overview publication, the authors have used the citation "Rickard et al. (2015)" for the MCM v3.2 website. I suggest the author list of this citation is expanded to include those listed as "current contributors" on the citation tab of the MCM v3.2 website (`http://mcm.leeds.ac.uk/MCMv3.2/contributors.htt`).

Author Response: We would like to thank Dr Jenkin for providing the updates from the

MCM v3.1 to MCM v3.2, and we shall update the reference to the MCM v3.2 to (Rickard et al., 2015) including those listed as current contributors to the MCM v3.2.

Other Comments 2: I note from the response to another reviewer (Coates and Butler, Atmos. Chem. Phys. Discuss., 15, C3816, 2015) that the authors are proposing to include references to the studies of Bloss et al. (2005) and Pinho et al. (2005) to illustrate that the MCM has had difficulties in reproducing the results of chamber studies for aromatic VOCs and isoprene. Whilst I agree with this for aromatics, the main conclusion of Pinho et al. (2005) was that the MCM v3 isoprene scheme (written in 2001) performed very well. The major factor responsible for deviations in performance of the MCM v3 scheme from the SAPRC chamber data was the absence of the reaction of O(3P) with isoprene in MCM v3, this reaction being insignificant under atmospheric conditions. A number of other less important refinements were also identified by Pinho et al. (2005), and these were all implemented long before release of MCM v3.2 in 2011. I therefore think it is misleading to report that the MCM has had difficulties in reproducing the results of traditional chamber studies for isoprene.

Author Response: Based upon the comments of Dr Jenkin, we shall not include the Pinho et al. (2005) study as an example of the MCM having difficulties reproducing chamber study results. We have updated page 12395, line 15 of the manuscript accordingly: *The MCM v3.2 is the reference mechanism in this study due to its level of detail (*16 349 *organic reactions). Despite this level of detail, the MCM had difficulties in reproducing the results of chamber study experiments involving aromatic VOC (Bloss et al., 2005).*

Additional Changes

Figure 5 has been updated to increase the font size of the legend, as the legend in Figure 5 of the discussion manuscript was difficult to read.

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A comparison of chemical mechanisms using Tagged Ozone Production Potential (TOPP) analysis

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Abstract

Ground-level ozone is a secondary pollutant produced photochemically from reactions of NO_x with peroxy radicals produced during VOC degradation. Chemical transport models use simplified representations of this complex gas-phase chemistry to predict O_3 levels and inform emission control strategies. Accurate representation of O_3 production chemistry is vital for effective predictions. In this study, VOC degradation chemistry in simplified mechanisms is compared to that in the near-explicit MCM mechanism using a boxmodel and by "tagging" all organic degradation products over multi-day runs, thus calculating the Tagged Ozone Production Potential (TOPP) for a selection of VOC representative of urban airmasses. Simplified mechanisms that aggregate VOC degradation products instead of aggregating emitted VOC produce comparable amounts of O_3 from VOC degradation to the MCM. First day TOPP values are similar across mechanisms for most VOC, with larger discrepancies arising over the course of the model run. Aromatic and unsaturated aliphatic VOC have largest inter-mechanisms differences on the first day, while alkanes show largest differences on the second day. Simplified mechanisms break down VOC into smaller sized degradation products on the first day faster than the MCM impacting the total amount of O_3 produced on subsequent days due to secondary chemistry.

1 Introduction

Ground-level ozone (O_3) is both an air pollutant and a climate forcer that is detrimental to human health and crop growth (Stevenson et al., 2013). O_3 is produced from the reactions of volatile organic compounds (~~VOCs~~VOC) and nitrogen oxides ($NO_x = NO + NO_2$) in the presence of sunlight (Atkinson, 2000).

Background O_3 concentrations have increased during the last several decades due to the increase of overall global anthropogenic emissions of O_3 precursors (HTAP, 2010). Despite decreases in emissions of O_3 precursors over Europe since 1990, EEA (2014) reports that 98 % of Europe's urban population are exposed to levels exceeding the WHO air quality guideline of $100\,\mu g\,m^{-3}$ over an 8 h mean. These exceedances result from local and regional O_3 precursor gas emissions, their intercontinental transport and the non-linear relationship of O_3 concentrations to NO_x and VOC levels (EEA, 2014).

Effective strategies for emission reductions rely on accurate predictions of O_3 concentrations using chemical transport models (CTMs). These predictions require adequate representation of gas-phase chemistry in the chemical mechanism used by the CTM. For reasons of computational efficiency, the chemical mechanisms used by global and regional CTMs must be simpler than the nearly-explicit mechanisms which can be used in box modelling studies. This study compares the impacts of different simplification approaches of chemical mechanisms on O_3 production chemistry focusing on the role of VOC degradation products.

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \text{(R1)}$$

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad \text{(R2)}$$

$$O_2 + O(^3P) + M \rightarrow O_3 + M \qquad \text{(R3)}$$

The photochemical cycle (Reactions R1–R3) rapidly produces and destroys O_3. NO and NO_2 reach a near-steady state via Reactions (R1) and (R2) which is disturbed in two cases. Firstly, via O_3 removal (deposition or Reaction R1 during night-time and near large NO sources) and secondly, when O_3 is produced through VOC–NO_x chemistry (Sillman, 1999).

~~VOCs~~ VOC (RH) are mainly oxidised in the troposphere by the hydoxyl radical (OH) forming peroxy radicals (RO_2) in the presence of O_2. For example, (Reaction R4) describes the OH-oxidation of alkanes proceeding though abstraction of an H from the alkane. In high-NO_x conditions, typical of urban environments, RO_2 react with NO (Reaction R5) to form alkoxy radicals (RO), which react quickly with O_2 (Reaction R6) producing a hydroperoxy radical (HO_2) and a carbonyl species (R′CHO). The secondary chemistry of these first generation carbon-containing oxidation products is analogous to the sequence (Reactions R4–R6), producing further HO_2 and RO_2 radicals. Subsequent generation oxidation products can continue to react, producing HO_2 and RO_2 until they have been completely oxidised to CO_2 and H_2O. Both RO_2 and HO_2 react with NO to produce NO_2 (Reactions R5 and R7) leading to O_3 production via Reactions (R2) and (R3). Thus the amount of O_3 produced from VOC degradation is related to the number of NO to NO_2 conversions by RO_2 and HO_2 radicals formed during VOC degradation (Atkinson, 2000).

$$RH + OH + O_2 \rightarrow RO_2 + H_2O \tag{R4}$$

$$RO_2 + NO \rightarrow RO + NO_2 \tag{R5}$$

$$RO + O_2 \rightarrow R'CHO + HO_2 \tag{R6}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{R7}$$

Three atmospheric regimes with respect to O_3 production can be defined (Jenkin and Clemitshaw, 2000). In the NO_x-sensitive regime, VOC concentrations are much higher than those of NO_x and O_3 production depends on NO_x concentrations. On the other hand, when NO_x concentrations are much higher than those of VOC (VOC-sensitive regime), VOC concentrations determine the amount of O_3 produced. Finally, the NO_x-VOC-sensitive regime produces maximal O_3 and is controlled by both VOC and NO_x concentrations.

These atmospheric regimes remove radicals through distinct mechanisms (Kleinman, 1991). In the NO_x-sensitive regime, radical concentrations are high relative to NO_x leading to radical removal by radical combination Reaction (R8) and bimolecular destruction Reaction (R9) (Kleinman, 1994).

$$RO_2 + HO_2 \rightarrow ROOH + O_2 \tag{R8}$$

$$HO_2 + OH \rightarrow H_2O + O_2 \tag{R9}$$

Whereas in the VOC-sensitive regime, radicals are removed by reacting with NO_2 leading to nitric acid (HNO_3) (Reaction R10) and PAN species (Reaction R11).

$$NO_2 + OH \rightarrow HNO_3 \tag{R10}$$

$$RC(O)O_2 + NO_2 \rightarrow RC(O)O_2NO_2 \tag{R11}$$

The NO_x-VOC-sensitive regime has no dominant radical removal mechanism as radical and NO_x amounts are comparable. This chemistry results in O_3 concentrations being a non-linear function of NO_x and VOC concentrations.

Individual VOC impact O_3 production differently through their diverse reaction rates and degradation pathways. These impacts can be quantified using Ozone Production Potentials (OPP) which can be calculated through incremental reactivity (IR) studies using photochemical models. In IR studies, VOC concentrations are changed by a known increment and the change in O_3 production is compared to that of a standard VOC mixture. Examples of IR scales are the Maximal Incremental Reactivity (MIR) and Maximum Ozone Incremental Reactivity (MOIR) scales in Carter (1994), as well as the Photochemical Ozone Creation Potential (POCP) scale of Derwent et al. (1996, 1998). The MIR, MOIR and POCP scales were calculated under different NO_x conditions, thus calculating OPPs in different atmospheric regimes.

Butler et al. (2011) calculate the maximum potential of a number of VOC to produce O_3 by using NO_x conditions inducing NO_x-VOC-sensitive chemistry over multi-day scenarios using a “tagging” approach – the Tagged Ozone Production Potential (TOPP). Tagging involves labelling all organic degradation products produced during VOC degradation with the name of the emitted VOC. Tagging enables the attribution of O_3 production from VOC degradation products back to the emitted VOC, thus providing a detailed insight into VOC degradation chemistry. Butler et al. (2011), using a near-explicit chemical mechanism, showed that some VOC, such as alkanes, produce maximum O_3 on the second day of the model run; in contrast to unsaturated aliphatic and aromatic VOC which produce maximum O_3 on the first day. In this study, the tagging approach of Butler et al. (2011) is applied to several chemical mechanisms of reduced complexity, using conditions of maximum O_3 production (NO_x-VOC-sensitive regime), to compare the effects of different representations of VOC degradation chemistry on O_3 production in the different chemical mechanisms.

A near-explicit mechanism, such as the Master Chemical Mechanism (MCM) (Jenkin et al., 2003; Saunders et al., 2003; Bloss et al., 2005), includes detailed degradation chemistry making the MCM ideal as a reference for comparing chemical mechanisms. Reduced mechanisms generally take two approaches to simplifying the representation of VOC degradation chemistry: lumped structure approaches; and lumped molecule approaches (Dodge, 2000).

Lumped structure mechanisms speciate VOC by the carbon bonds of the emitted VOC, examples are the Carbon Bond mechanisms, CBM-IV (Gery et al., 1989) and CB05 (Yarwood et al., 2005). Lumped molecule mechanisms represent VOC explicitly or by aggregating (lumping) many VOC into a single mechanism species. Mechanism species may lump VOC by functionality (MOdel for Ozone and Related chemical Tracers, MOZART-4, Emmons et al., 2010) or OH-reactivity (Regional Acid Deposition Model, RADM2 (Stockwell et al., 1990), Regional Atmospheric Chemistry Mechanisms, RACM (Stockwell et al., 1997) and RACM2 (Goliff et al., 2013)). The Common Representative Intermediates mechanism (CRI) lumps the degradation products of VOC rather than the emitted VOC (Jenkin et al., 2008).

Many comparison studies of chemical mechanisms consider modelled time series of O_3 concentrations over varying VOC and NO_x concentrations. Examples are Dunker et al. (1984); Kuhn et al. (1998) and Emmerson and Evans (2009). The largest discrepancies between the time series of O_3 concentrations in different mechanisms from these studies arise when modelling urban rather than rural conditions and are attributed to the treatment of radical production, organic nitrate and night-time chemistry. Emmerson and Evans (2009) also compare the inorganic gas-phase chemistry of different chemical mechanisms, differences in inorganic chemistry arise from inconsistencies between IUPAC and JPL reaction rate constants.

Mechanisms have also been compared using OPP scales. OPPs are a useful comparison tool as they relate O_3 production to a single value. Derwent et al. (2010) compared the near-explicit MCM v3.1 and SAPRC-07 mechanisms using first-day POCP values calculated under VOC-sensitive conditions. The POCP values were comparable between the mechanisms. Butler et al. (2011) compared first day TOPP values to the corresponding published MIR, MOIR and POCP values. TOPP values were most comparable to MOIR and POCP values due to the similarity of the chemical regimes used in their calculation.

In this study, we compare TOPP values of VOC using a number of mechanisms to those calculated with the MCM v3.2, under standardised conditions which maximise O_3 production. Differences in O_3 production are explained by the differing treatments of secondary VOC degradation in these mechanisms.

2 Methodology

2.1 Chemical mechanisms

The nine chemical mechanisms compared in this study are outlined in Table 1 with a brief summary below. We used a subset of each chemical mechanism containing all the reactions needed to fully describe the degradation of the VOC in Table 2. The reduced mechanisms in this study were chosen as they are commonly used in 3-D models and apply different approaches to representing secondary VOC chemistry. The recent review by Baklanov et al. (2014) shows that each chemical mechanism used in this study are actively used by modelling groups.

The MCM (Jenkin et al., 1997, 2003; Saunders et al., 2003; Bloss et al., 2005; Rickard et al., 2015) is a near-explicit mechanism describing the degradation of 125 primary VOC. The MCM v3.2 is the reference mechanism in this study due to its level of detail (16 349 organic reactions). Despite this level of detail, the MCM had difficulties in reproducing the results of chamber study experiments involving aromatic VOC (Bloss et al., 2005).

The CRI (Jenkin et al., 2008) is a reduced chemical mechanism with 1145 organic reactions describing the oxidation of the same primary VOC as the MCM v3.1 (12 691 organic reactions). VOC degradation in the CRI is simplified by lumping the degradation products of many VOC into mechanism species whose overall O_3 production reflects that of the MCM v3.1. The CRI v2 is available in more than one reduced variant, described in Watson et al. (2008). We used a subset of the full version of the CRI v2 (http://mcm.leeds.ac.uk/CRI)~~is used in this study~~. Differences in O_3 production between the CRI v2 and MCM v3.2 may be due to changes in the MCM versions rather than the CRI reduction techniques, hence the MCM v3.1 is also included in this study.

MOZART-4 represents global tropospheric and stratospheric chemistry (Emmons et al., 2010). Explicit species exist for methane, ethane, propane, ethene, propene, isoprene and α-pinene. All other VOC are represented by lumped species determined by the functionality of the VOC. Tropospheric chemistry is described by 145 organic reactions in MOZART-4.

RADM2 (Stockwell et al., 1990) describes regional scale atmospheric chemistry using 145 organic reactions with explicit species representing methane, ethane, ethene and isoprene. All other VOC are assigned to lumped species based on OH-reactivity and molecular weight. RADM2 was updated to RACM (Stockwell et al., 1997) with more explicit and lumped species representing VOC as well as revised chemistry (193 organic reactions). RACM2 is the updated RACM version (Goliff et al., 2013) with substantial updates to the chemistry, including more lumped and explicit species representing emitted VOC (315 organic reactions).

CBM-IV (Gery et al., 1989) ~~simulates~~ uses 46 organic reactions to simulate polluted urban conditions and represents ethene, formaldehyde and isoprene explicitly while all other emitted VOC are lumped by their carbon bond types. All primary VOC were assigned to lumped species in CBM-IV as described in Hogo and Gery (1989). For example, the mechanism species PAR represents the C–C bond. Pentane, having five carbon atoms, is represented as 5 PAR. A pentane mixing ratio of $1200\,\mathrm{pptv}$ would be assigned to $6000\ (= 1200 \times 5)$ pptv of PAR in CBM-IV. CBM-IV was updated to CB05 (Yarwood et al., 2005) by including further explicit species representing methane, ethane and acetaldehyde, and has 99 organic reactions. Other updates include revised allocation of primary VOC and updated rate constants.

2.2 Model Setup

The modelling approach and set-up follows the original TOPP study of Butler et al. (2011). The approach is summarised here; further details can be found in the Supplement and in Butler et al. (2011). We use the MECCA boxmodel, originally described by Sander et al. (2005), and as subsequently modified by Butler et al. (2011) to include MCM chemistry. In this study, the model is run under conditions representative of 34° N at the equinox (broadly representative of the city of Los Angeles, USA).

Maximum O_3 production is achieved in each model run by balancing the chemical source of radicals and NO_x at each timestep by emitting the appropriate amount of NO. These NO_x conditions induce NO_x-VOC-sensitive chemistry. Ambient NO_x conditions are not required as this study calculates the maximum potential of VOC to produce O_3. Future work should verify the extent to which the maximum potential of VOC to produce O_3 is reached under ambient NO_x conditions.

~~VOCs~~ VOC typical of Los Angeles and their initial mixing ratios are taken from Baker et al. (2008), listed in Table 2. Following Butler et al. (2011), the associated emissions required to keep the initial mixing ratios of each VOC constant until noon of the first day were determined for the MCM v3.2. These emissions are subsequently used for each mechanism, ensuring the amount of each VOC emitted was the same in every model run. Methane (CH_4) was fixed at 1.8 ppmv while CO and O_3 were initialised at 200 and 40 ppbv and then allowed to evolve freely.

The ~~VOCs~~ VOC used in this study are assigned to mechanism species following the recommendations from the literature of each mechanism (Table 1), the representation of each VOC in the mechanisms is found in Table 2. Emissions of lumped species are weighted by the carbon number of the mechanism species ensuring the total amount of emitted reactive carbon was the same in each model run.

The MECCA boxmodel is based upon the Kinetic Pre-Processor (KPP) (Damian et al., 2002). Hence, all chemical mechanisms were adapted into modularised KPP format. The inorganic gas-phase chemistry described in the MCM v3.2 was used in each run to remove any differences between treatments of inorganic chemistry in each mechanism. Thus differences between the O_3 produced by the mechanisms are due to the treatment of organic degradation chemistry.

The MCM v3.2 approach to photolysis, dry deposition of VOC oxidation intermediates and RO_2-RO_2 reactions was used for each mechanism; details of these adaptations can be found in the Supplement. Some mechanisms include reactions which are only important in the stratosphere or free troposphere. For example, PAN photolysis is only important in the free troposphere (Harwood et al., 2003) and was removed from MOZART-4, RACM2 and CB05 for the purpose of the study, as this study considers processes occurring within the planetary boundary layer.

2.3 Tagged Ozone Production Potential (TOPP)

This section summarises the tagging approach described in Butler et al. (2011) which is applied in this study.

2.3.1 O_x family and tagging approach

O_3 production and loss is dominated by rapid photochemical cycles, such as Reactions (R1)–(R3). The effects of rapid production and loss cycles can be removed by using chemical families that include rapidly inter-converting species. In this study, we define the O_x family to include O_3, $O(^3P)$, $O(^1D)$, NO_2 and other species involved in fast cycling with NO_2, such as HO_2NO_2 and PAN species. Thus, production of O_x can be used as a proxy for production of O_3.

The tagging approach follows the degradation of emitted VOC through all possible pathways by labelling every organic degradation product with the name of the emitted VOC. Thus, each emitted VOC effectively has its own set of degradation reactions. Butler et al. (2011) showed that O_x production can be attributed to the VOC by following the tags of each VOC.

O_x production from lumped mechanism species are re-assigned to the VOC of Table 2 by scaling the O_x production of the mechanism species by the fractional contribution of each represented VOC. For example, TOL in RACM2 represents toluene and ethylbenzene with fractional contributions of 0.87 and 0.13 to TOL emissions. Scaling the O_x production from TOL by these factors gives the O_x production from toluene and ethylbenzene in RACM2.

Many reduced mechanisms use an operator species as a surrogate for RO_2 during VOC degradation enabling these mechanisms to produce O_x while minimising the number of RO_2

species represented. O_x production from operator species is assigned as O_x production from the organic degradation species producing the operator. This allocation technique is also used to assign O_x production from HO_2 via Reaction (R7).

2.3.2 Definition of the Tagged Ozone Production Potential (TOPP)

Attributing O_x production to individual VOC using the tagging approach is the basis for calculating the TOPP of a VOC, which is defined as the number of O_x molecules produced per emitted molecule of VOC. The TOPP value of a VOC that is not represented explicitly in a chemical mechanism is calculated by multiplying the TOPP value of the mechanism species representing the VOC by the ratio of the carbon numbers of the VOC to the mechanism species. For example, CB05 represents hexane as 6 PAR, so the TOPP value of hexane in the CB05 is 6 times the TOPP of PAR. MOZART-4 represents hexane by the five carbon species BIGALK. Thus hexane emissions are represented molecule for molecule as $\frac{6}{5}$ of the equivalent number of molecules of BIGALK, and the TOPP value of hexane in MOZART-4 is calculated by multiplying the TOPP value of BIGALK by $\frac{6}{5}$.

3 Results

3.1 Ozone time series and O_x production budgets

Figure 1 shows the time series of O_3 mixing ratios obtained with each mechanism. There is an 8 ppbv difference in O_3 mixing ratios on the first day between RADM2, which has the highest O_3, and RACM2, which has the lowest O_3 mixing ratios when not considering the outlier time series of RACM. The difference between RADM2 and RACM, the low outlier, was 21 ppbv on the first day. The O_3 mixing ratios in the CRI v2 are larger than those in the MCM v3.1, which is similar to the results in Jenkin et al. (2008) where the O_3 mixing ratios of the CRI v2 and MCM v3.1 are compared over a five day period.

The O_3 mixing ratios in Fig. 1 are influenced by the approaches used in developing the chemical mechanisms and not a function of the explicitness of the chemical mechanism.

For example, the O_3 mixing ratios obtained using the Carbon Bond mechanisms (CBM-IV and CB05) compare well with the MCM despite both Carbon Bond mechanisms having ∼ 1 % of the number of reactions in the MCM v3.2. Also, the O_3 mixing ratios from RACM2 and RADM2 show similar absolute differences from that of the MCM despite RACM2 having more than double the number of reactions of RADM2.

The day-time O_x production budgets allocated to individual VOC for each mechanism are shown in Fig. 2. The relationships between O_3 mixing ratios in Fig. 1 are mirrored in Fig. 2 where mechanisms producing high amounts of O_x also have high O_3 mixing ratios. The conditions in the box model lead to a daily maximum of OH that increases with each day leading to an increase on each day in both the reaction rate of the OH-oxidation of CH_4 and the daily contribution of CH_4 to O_x production.

The first day mixing ratios of O_3 in RACM are lower than other mechanisms due to a lack of O_x production from aromatic VOC on the first day in RACM (Fig. 2). Aromatic degradation chemistry in RACM results in net loss of O_x on the first day, described later in Sect. 3.2.1.

RADM2 is the only reduced mechanism producing higher O_3 mixing ratios than the more detailed mechanisms (MCM v3.2, MCM v3.1 and CRI v2). Higher mixing ratios of O_3 in RADM2 are produced due to increased O_x production from propane compared to the MCM v3.2; on the first day, the O_x production from propane in RADM2 is triple that of the MCM v3.2 (Fig. 2). Propane is represented as HC3 in RADM2 (Stockwell et al., 1990) and ~~on the first day HC3 degradation produces about 17 times the amount of acetaldehyde () produced by the MCMv3.2. The OH-oxidation of~~ the degradation of HC3 has a lower yield of the less reactive ketones compared to the MCM. The further degradation of ketones hinders O_x production due to the low OH reactivity and photolysis rate of ketones. Secondary degradation of HC3 proceeds through the degradation of acetaldehyde (CH_3CHO~~starts a degradation chain that produces O_x~~) propogating O_x production through the reactions of CH_3CO_3 and CH_3O_2 with NO~~; thus the higher amounts of in RADM2 during propane degradation~~. Thus the lower ketone yields leads to increased O_x production from propane degradation in RADM2 compared to the MCM v3.2.

3.2 Time dependent O_x production

Time series of daily TOPP values for each VOC are presented in Fig. 3 and the cumulative TOPP values at the end of the model run obtained for each VOC using each of the mechanisms, normalised by the number of atoms of C in each VOC are presented in Table 3. In the MCM and CRI v2, the cumulative TOPP values obtained for each VOC show that by the end of the model run larger alkanes have produced more O_x per unit of reactive C than alkenes or aromatic VOC. By the end of the runs using the lumped structure mechanisms (CBM-IV and CB05), alkanes produce similar amounts of O_x per reactive C while aromatic VOC and some alkenes produce less O_x per reactive C than the MCM. Whereas in lumped molecule mechanisms (MOZART-4, RADM2, RACM, RACM2), practically all VOC produce less O_x per reactive C than the MCM by the end of the run. This lower efficiency of O_x production from many individual VOC in lumped molecule and structure mechanisms would lead to an underestimation of O_3 levels downwind of an emission source, and a smaller contribution to background O_3 when using lumped molecule and structure mechanisms.

The lumped intermediate mechanism (CRI v2) produces the most similar O_x to the MCM v3.2 for each VOC, seen in Fig. 3 and Table 3. Higher variability in the time dependent O_x production is evident for VOC represented by lumped mechanism species. For example, 2-methylpropene, represented in the reduced mechanisms by a variety of lumped species, has a higher spread in time dependent O_x production than ethene, which is explicitly represented in each mechanism.

In general, the largest differences in O_x produced by aromatic and alkene species are on the first day of the simulations, while the largest inter-mechanism differences in O_x produced by alkanes are on the second and third days of the simulations. The reasons for these differences in behaviour will be explored in Sect. 3.2.1 which examines differences in first day O_x production between the chemical mechanisms and Sect. 3.2.2 which examines the differences in O_x production on subsequent days.

3.2.1 First day ozone production

The first day TOPP values of each VOC from each mechanism, representing O_3 production from freshly emitted VOC near their source region, are compared to those obtained with the MCM v3.2 in Fig. 4. The root mean square error (RMSE) of all first day TOPP values in each mechanism relative to those in the MCM v3.2 are also included in Fig. 4. The RMSE value of the CRI v2 shows that O_x production on the first day from practically all the individual VOC matches that in the MCM v3.2. All other reduced mechanisms have much larger RMSE values indicating that the first day O_x production from the majority of the VOC differs from that in the MCM v3.2.

The reduced complexity of reduced mechanisms means that aromatic VOC are typically represented by one or two mechanism species leading to differences in O_x production of the actual VOC compared to the MCM v3.2. For example, all aromatic VOC in MOZART-4 are represented as toluene, thus less reactive aromatic VOC, such as benzene, produce higher O_x whilst more reactive aromatic VOC, such as the xylenes, produce less O_x in MOZART-4 than the MCM v3.2. RACM2 includes explicit species representing benzene, toluene and each xylene resulting in O_x production that is the most similar to the MCM v3.2 than other reduced mechanisms.

Figure 3 shows a high spread in O_x production from aromatic VOC on the first day indicating that aromatic degradation is treated differently between mechanisms. Toluene degradation is examined in more detail by comparing the reactions contributing to O_x production and loss in each mechanism, shown in Fig. 5. These reactions are determined by following the “toluene” tags in the tagged version of each mechanism.

Toluene degradation in RACM includes several reactions consuming O_x that are not present in the MCM resulting in net loss of O_x on the first two days. Ozonolysis of the cresol OH-adduct mechanism species ADDC contributes significantly to O_x loss in RACM. This reaction was included in RACM due to improved cresol product yields when comparing RACM predictions with experimental data (Stockwell et al., 1997). Other mechanisms that include cresol OH-adduct species do not include ozonolysis and these reactions are not included in the updated RACM2.

The total O_x produced on the first day during toluene degradation in each reduced mechanism is less than that in the MCM v3.2 (Fig. 5). Less O_x is produced in all reduced mechanisms due to a faster break down of the VOC into smaller fragments than the MCM, described later in Sect. 3.3. Moreover in CBM-IV and CB05, less O_x is produced during toluene degradation as reactions of the toluene degradation products CH_3O_2 and CO do not contribute to the O_x production budgets, which is not the case in any other mechanism (Fig. 5).

Maximum O_x production from toluene degradation in CRI v2 and RACM2 is reached on the second day in contrast to the MCM v3.2 which produces peak O_x on the first day. The second day maximum of O_x production in CRI v2 and RACM2 from toluene degradation results from ~~increased production from degradation of unsaturated dicarbonyls; is not produced during degradation~~ more efficient production of unsaturated dicarbonyls ~~in the MCM~~than the MCM v3.2. The degradation of unsaturated dicarbonyls produces peroxy radicals such as $C_2H_5O_2$ which promote O_x production via reactions with NO.

Unsaturated aliphatic VOC generally produce similar amounts of O_x between mechanisms, especially explicitly represented VOC, such as ethene and isoprene. On the other hand, unsaturated aliphatic VOC that are not explicitly represented produce differing amounts of O_x between mechanisms (Fig. 3). For example, the O_x produced during 2-methylpropene degradation varies between mechanisms; differing rate constants of initial oxidation reactions and non-realistic secondary chemistry lead to these differences, further details are found in the Supplement.

Non-explicit representations of aromatic and unsaturated aliphatic VOC coupled with differing degradation chemistry and a faster break down into smaller size degradation products results in different O_x production in lumped molecule and lumped structure mechanisms compared to the MCM v3.2.

3.2.2 Ozone production on subsequent days

Alkane degradation in CRI v2 and both MCM mechanisms produces a second day maximum in O_x that increases with alkane carbon number (Fig. 3). The increase in O_x production on the second day is reproduced for each alkane by the reduced mechanisms; except octane in RADM2, RACM and RACM2. However, larger alkanes produce less O_x than the MCM on the second day in all lumped molecule and structure mechanisms.

The lumped molecule mechanisms (MOZART-4, RADM2, RACM and RACM2) represent many alkanes by mechanism species which may lead to unrepresentative secondary chemistry for alkane degradation. For example, three times more O_x is produced during the degradation of propane in RADM2 than the MCM v3.2 on the first day (Fig. 2). Propane is represented in RADM2 by the mechanism species HC3 which also represents other classes of VOC, such as alcohols. The secondary chemistry of HC3 is tailored to produce O_x from these different VOC and differs from alkane degradation in the MCM v3.2 by producing ~~more~~ less ketones in RADM2.

As will be shown in Sect. 3.3, another feature of reduced mechanisms is that the breakdown of emitted VOC into smaller sized degradation products is faster than the MCM. Alkanes are broken down quicker in CBM-IV, CB05, RADM2, RACM and RACM2 through a higher rate of reactive carbon loss than the MCM v3.2 (shown for pentane and octane in Fig. 8); reactive carbon is lost through reactions not conserving carbon. Despite many degradation reactions of alkanes in MOZART-4 almost conserving carbon, the organic products have less reactive carbon than the organic reactant also speeding up the breakdown of the alkane compared to the MCM v3.2.

For example, Fig. 6 shows the distribution of reactive carbon in the reactants and products from the reaction of NO with the pentyl peroxy radical in both MCM mechanisms and each lumped molecule mechanism. In all the lumped molecule mechanisms, the individual organic products have less reactive carbon than the organic reactant. Moreover, in RADM2, RACM and RACM2 this reaction does not conserve reactive carbon leading to faster loss rates of reactive carbon.

The faster breakdown of alkanes in lumped molecule and structure mechanisms on the first day limits the amount of O_x produced on the second day, as less of the larger sized degradation products are available for further degradation and O_x production.

3.3 Treatment of degradation products

The time dependent O_x production of the different VOC in Fig. 3 results from the varying rates at which VOC break up into smaller fragments (Butler et al., 2011). Varying break down rates of the same VOC between mechanisms could explain the different time dependent O_x production between mechanisms. The break down of pentane and toluene between mechanisms is compared in Fig. 7 by allocating the O_x production to the number of carbon atoms in the degradation products responsible for O_x production on each day of the model run in each mechanism. Some mechanism species in RADM2, RACM and RACM2 have fractional carbon numbers (Stockwell et al., 1990, 1997; Goliff et al., 2013) and O_x production from these species was reassigned as O_x production of the nearest integral carbon number.

The degradation of pentane, a five-carbon VOC, on the first day in the MCM v3.2 produces up to 50 % more O_x from degradation products also having five carbon atoms than any reduced mechanism. Moreover, the contribution of the degradation products having five carbon atoms in the MCM v3.2 is consistently higher throughout the model run than in reduced mechanisms (Fig. 7). Despite producing less total O_x, reduced mechanisms produce up to double the amount of O_x from degradation products with one carbon atom than in the MCM v3.2. The lower contribution of larger degradation products indicates that pentane is generally broken down faster in reduced mechanisms, consistent with the specific example shown for the breakdown of the pentyl peroxy radical in Fig. 6.

The rate of change in reactive carbon during pentane, octane and toluene degradation was determined by multiplying the rate of each reaction occurring during pentane, octane and toluene degradation by its net change in carbon, shown in Fig. 8. Pentane is broken down faster in CBM-IV, CB05, RADM2, RACM and RACM2 by losing reactive carbon more quickly than the MCM v3.2. MOZART-4 also breaks pentane down into smaller sized products quicker than the MCM v3.2 as reactions during pentane degradation in MOZART-4 have organic products whose carbon number is less than the organic reactant, described in Sect. 3.2.2. The faster break down of pentane on the first day limits the amount of reactive carbon available to produce further O_x on subsequent days leading to lower O_x production after the first day in reduced mechanisms.

Figure 3 showed that octane degradation produces peak O_x on the first day in RADM2, RACM and RACM2 in contrast to all other mechanisms where peak O_x is produced on the second day. Octane degradation in RADM2, RACM and RACM2 loses reactive carbon much faster than any other mechanism on the first day so that there are not enough degradation products available on the second day to produce peak O_x on the second day (Fig. 8). This loss of reactive carbon during alkane degradation leads to the lower accumulated ozone production from these VOC shown in Table 3.

As seen in Fig. 3, O_x produced during toluene degradation has a high spread between the mechanisms. Figure 7 shows differing distributions of the sizes of the degradation products that produce O_x. All reduced mechanisms omit O_x production from at least one degradation fragment size which produces O_x in the MCM v3.2, indicating that toluene is also broken down more quickly in the reduced mechanisms than the more explicit mechanisms. For example, toluene degradation in RACM2 does not produce O_x from degradation products with six carbons, as is the case in the MCM v3.2. Figure 8 shows that all reduced mechanisms lose reactive carbon during toluene degradation faster than the MCM v3.2. Thus the degradation of aromatic VOC in reduced mechanisms are unable to produce similar amounts of O_x as the explicit mechanisms.

4 Conclusions

Tagged Ozone Production Potentials (TOPPs) were used to compare O_x production during VOC degradation in reduced chemical mechanisms to the near-explicit MCM v3.2. First day mixing ratios of O_3 are similar to the MCM v3.2 for most mechanisms; the O_3 mixing ratios in RACM were much lower than the MCM v3.2 due to a lack of O_x production from the degradation of aromatic VOC. Thus, RACM may not be the appropriate chemical mechanism when simulating atmospheric conditions having a large fraction of aromatic VOC.

The lumped intermediate mechanism, CRI v2, produces the most similar amounts of O_x to the MCM v3.2 for each VOC. The largest differences between O_x production in CRI v2 and MCM v3.2 were obtained for aromatic VOC, however overall these differences were much lower than any other reduced mechanism. Thus, when developing chemical mechanisms the technique of using lumped intermediate species whose degradation are based upon more detailed mechanism should be considered.

Many VOC are broken down into smaller sized degradation products faster on the first day in reduced mechanisms than the MCM v3.2 leading to lower amounts of larger sized degradation products that can further degrade and produce O_x. Thus, many VOC in reduced mechanisms produce a lower maximum of O_x and lower total O_x per reactive C by the end of the run than the MCM v3.2. This lower O_x production from many VOC in reduced mechanisms leads to lower O_3 mixing ratios compared to the MCM v3.2.

Alkanes produce maximum O_3 on the second day of simulations and this maximum is lower in reduced mechanisms than the MCM v3.2 due to the faster break down of alkanes into smaller sized degradation products on the first day. The lower maximum in O_3 production during alkane degradation in reduced mechanisms would lead to an underestimation of the O_3 levels downwind of VOC emissions, and an underestimation of the VOC contribution to tropospheric background O_3 when using reduced mechanisms in regional or global modelling studies.

This study has determined the maximum potential of VOC represented in reduced mechanisms to produce O_3, this potential may not be reached as ambient NO_x conditions may not induce NO_x-VOC-sensitive chemistry. Moreover, the maximum potential of ~~the~~ VOC to produce O_3 may not be reached when using these reduced mechanisms in 3-D models due to the influence of additional processes, such as mixing and meteorology. Future work shall examine the extent to which the maximum potential of VOC to produce O_3 in reduced chemical mechanisms is reached using ambient NO_x conditions and including processes found in 3-D models.

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Table 1. The chemical mechanisms used in the study, MCM v3.2 is the reference mechanism. The number of organic species and reactions needed to fully oxidise the VOC in Table 2 for each mechanism are also included.

Chemical Mechanism	Number of Organic Species	Number of Organic Reactions	Type of Lumping	Reference	Recent Study
MCM v3.2	1884	5621	No lumping	Rickard et al. (2015)	Koss et al. (2015)
MCM v3.1	1677	4862	No lumping	Jenkin et al. (1997) Saunders et al. (2003) Jenkin et al. (2003) Bloss et al. (2005)	Lidster et al. (2014)
CRI v2	189	559	Lumped intermediates	Jenkin et al. (2008)	Derwent et al. (2015)
MOZART-4	61	135	Lumped molecule	Emmons et al. (2010)	Hou et al. (2015)
RADM2	42	105	Lumped molecule	Stockwell et al. (1990)	Li et al. (2014)
RACM	51	152	Lumped molecule	Stockwell et al. (1997)	Ahmadov et al. (2015)
RACM2	92	244	Lumped molecule	Goliff et al. (2013)	Goliff et. al. (2015)
CBM-IV	19	47	Lumped structure	Gery et al. (1989)	Foster et al. (2014)
CB05	33	86	Lumped structure	Yarwood et al. (2005)	Dunker et. al. (2015)

Table 2. VOC present in Los Angeles, mixing ratios are taken from Baker et al. (2008) and their representation in each chemical mechanism. The representation of the VOC in each mechanism is based upon the recommendations of the literature for each mechanism (Table 1).

NMVOC	Mixing Ratio (pptv)	MCM v3.1, v3.2, CRI v2	MOZART-4	RADM2	RACM	RACM2	CBM-IV	CB05
Alkanes								
Ethane	6610	C2H6	C2H6	ETH	ETH	ETH	0.4 PAR	ETHA
Propane	6050	C3H8	C3H8	HC3	HC3	HC3	1.5 PAR	1.5 PAR
Butane	2340	NC4H10	BIGALK	HC3	HC3	HC3	4 PAR	4 PAR
2-Methylpropane	1240	IC4H10	BIGALK	HC3	HC3	HC3	4 PAR	4 PAR
Pentane	1200	NC5H12	BIGALK	HC5	HC5	HC5	5 PAR	5 PAR
2-Methylbutane	2790	IC5H12	BIGALK	HC5	HC5	HC5	5 PAR	5 PAR
Hexane	390	NC6H14	BIGALK	HC5	HC5	HC5	6 PAR	6 PAR
Heptane	160	NC7H16	BIGALK	HC5	HC5	HC5	7 PAR	7 PAR
Octane	80	NC8H18	BIGALK	HC8	HC8	HC8	8 PAR	8 PAR
Alkenes								
Ethene	2430	C2H4	C2H4	OL2	ETE	ETE	ETH	ETH
Propene	490	C3H6	C3H6	OLT	OLT	OLT	OLE + PAR	OLE + PAR
Butene	65	BUT1ENE	BIGENE	OLT	OLT	OLT	OLE + 2 PAR	OLE + 2 PAR
2-Methylpropene	130	MEPROPENE	BIGENE	OLI	OLI	OLI	PAR + FORM + ALD2	FORM + 3 PAR
Isoprene	270	C5H8	ISOP	ISO	ISO	ISO	ISOP	ISOP
Aromatics								
Benzene	480	BENZENE	TOLUENE	TOL	TOL	BEN	PAR	PAR
Toluene	1380	TOLUENE	TOLUENE	TOL	TOL	TOL	TOL	TOL
m-Xylene	410	MXYL	TOLUENE	XYL	XYL	XYM	XYL	XYL
p-Xylene	210	PXYL	TOLUENE	XYL	XYL	XYP	XYL	XYL
o-Xylene	200	OXYL	TOLUENE	XYL	XYL	XYO	XYL	XYL
Ethylbenzene	210	EBENZ	TOLUENE	TOL	TOL	TOL	TOL + PAR	TOL + PAR

Table 3. Cumulative TOPP values at the end of the model run for all ~~VOCs~~ VOC with each mechanism, normalised by the number of C atoms in each VOC.

NMVOC	MCM v3.2	MCM v3.1	CRI v2	MOZART-4	RADM2	RACM	RACM2	CBM-IV	CB05
Alkanes									
Ethane	0.9	1.0	0.9	0.9	1.0	1.0	0.9	0.3	0.9
Propane	1.1	1.2	1.2	1.1	1.8	1.8	1.4	0.9	1.0
Butane	2.0	2.0	2.0	1.7	1.8	1.8	1.4	1.7	2.1
2-Methylpropane	1.3	1.3	1.3	1.7	1.8	1.8	1.4	1.7	2.1
Pentane	2.1	2.1	2.2	1.7	1.5	1.6	1.1	1.7	2.1
2-Methylbutane	1.6	1.6	1.5	1.7	1.5	1.6	1.1	1.7	2.1
Hexane	2.1	2.1	2.2	1.7	1.5	1.6	1.1	1.7	2.1
Heptane	2.0	2.1	2.2	1.7	1.5	1.6	1.1	1.7	2.1
Octane	2.0	2.0	2.2	1.7	1.2	1.0	1.0	1.7	2.1
Alkenes									
Ethene	1.9	1.9	1.9	1.4	2.0	2.0	2.2	1.9	2.2
Propene	1.9	2.0	1.9	1.7	1.5	1.6	1.5	1.2	1.4
Butene	1.9	2.0	2.0	1.5	1.5	1.6	1.5	0.8	0.9
2-Methylpropene	1.1	1.2	1.2	1.5	1.1	1.5	1.6	0.5	0.5
Isoprene	1.8	1.8	1.8	1.3	1.2	1.6	1.7	1.9	2.1
Aromatics									
Benzene	0.8	0.8	1.1	0.6	0.9	0.6	0.9	0.3	0.3
Toluene	1.3	1.3	1.5	0.6	0.9	0.6	1.0	0.3	0.3
m-Xylene	1.5	1.5	1.6	0.6	0.9	0.6	1.7	0.9	1.0
p-Xylene	1.5	1.5	1.6	0.6	0.9	0.6	1.7	0.9	1.0
o-Xylene	1.5	1.5	1.6	0.6	0.9	0.6	1.7	0.9	1.0
Ethylbenzene	1.3	1.4	1.5	0.6	0.9	0.6	1.0	0.2	0.3

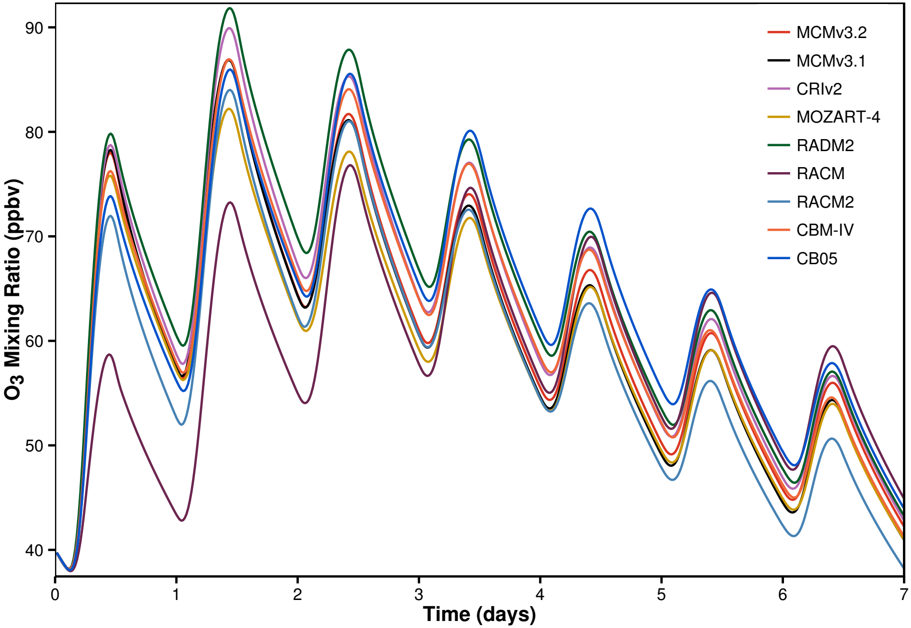

Figure 1. Time series of O_3 mixing ratios obtained using each mechanism.

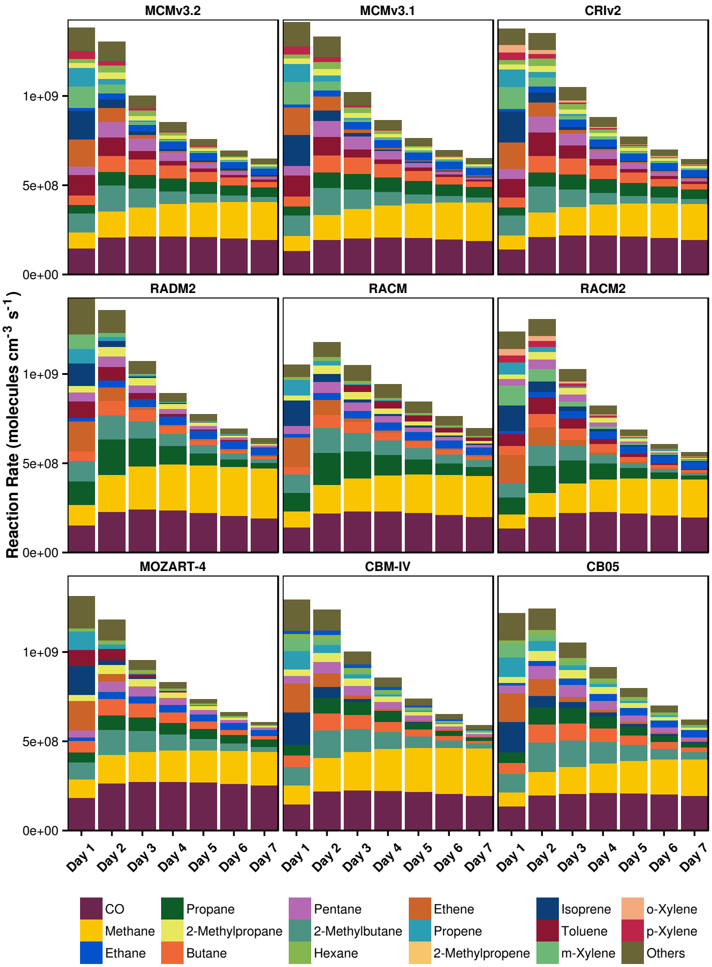

Figure 2. Day-time O_x production budgets in each mechanism allocated to individual VOC.

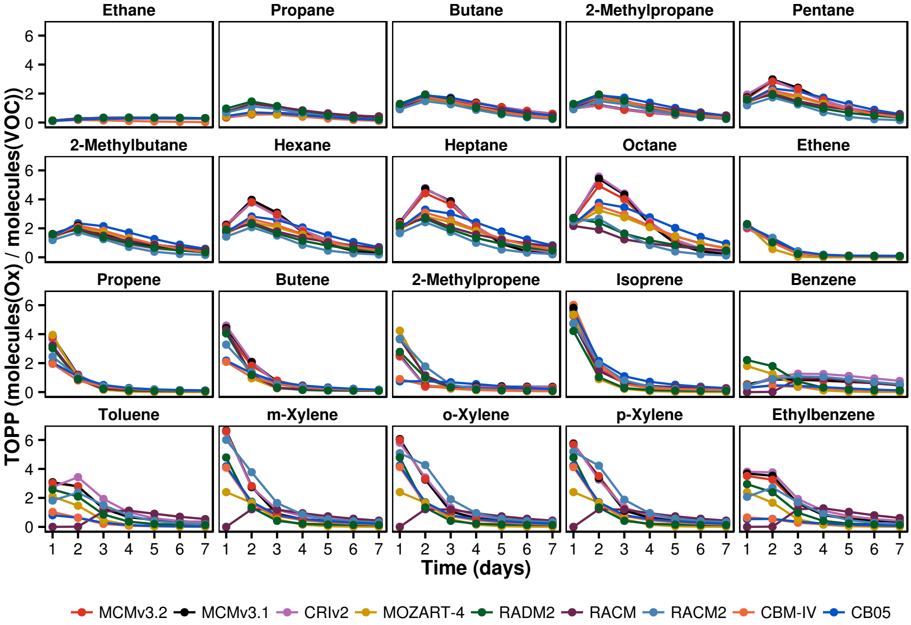

Figure 3. TOPP value time series using each mechanism for each VOC.

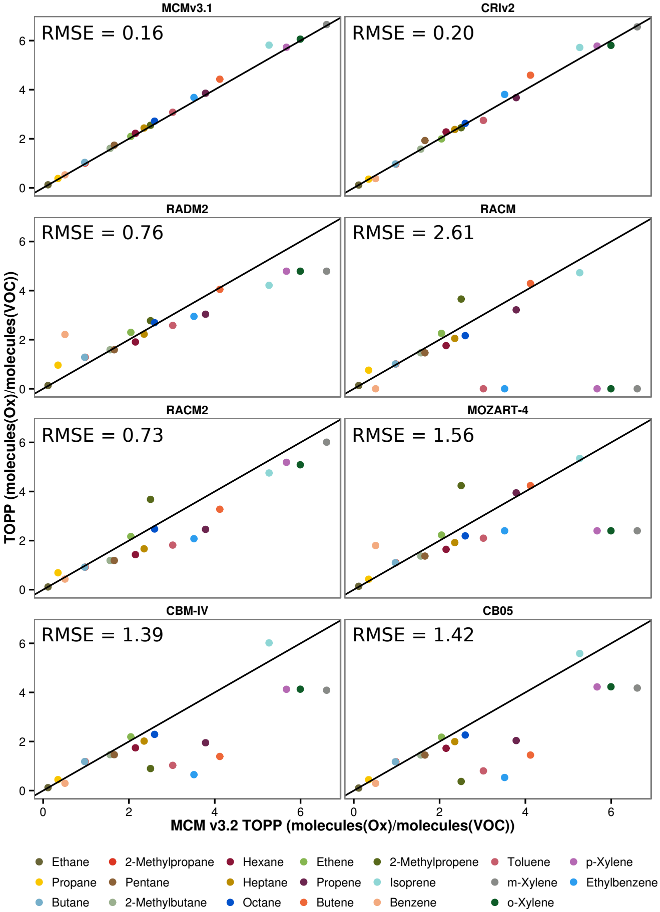

Figure 4. The first day TOPP values for each VOC calculated using MCM v3.2 and the corresponding values in each mechanism. The root mean square error (RMSE) of each set of TOPP values is also displayed. The black line represents the 1 : 1 line.

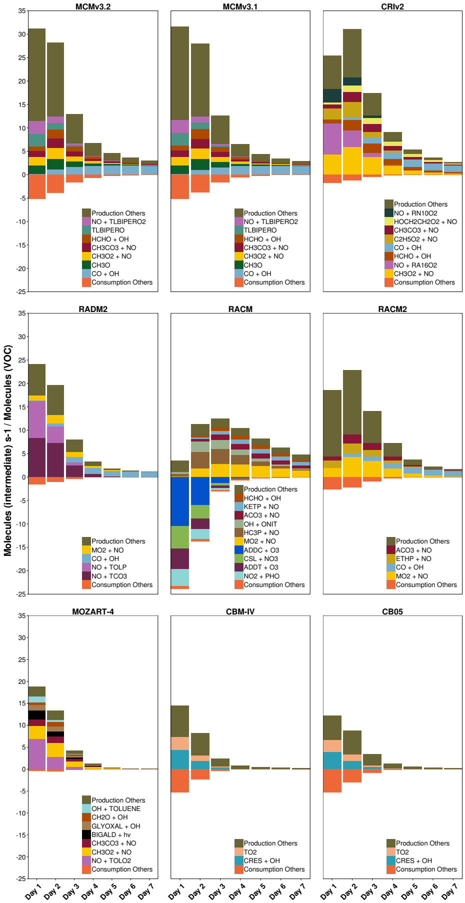

Figure 5. Day-time O_x production and loss budgets allocated to the responsible reactions during toluene degradation in all mechanisms. These reactions are presented using the species defined in each mechanism Table 1.

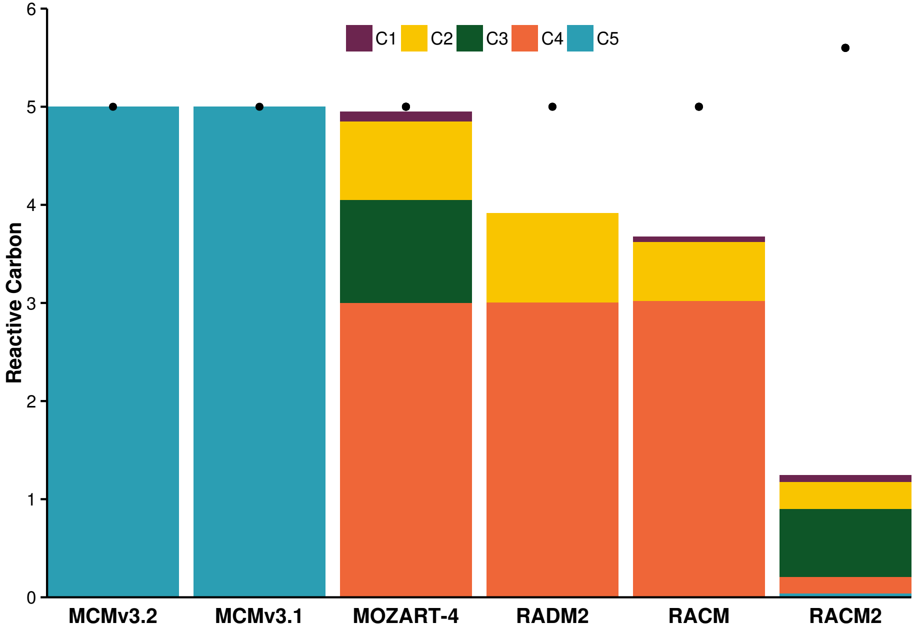

Figure 6. The distribution of reactive carbon in the products of the reaction between NO and the pentyl peroxy radical in lumped molecule mechanisms compared to the MCM. The black dot represents the reactive carbon of the pentyl peroxy radical.

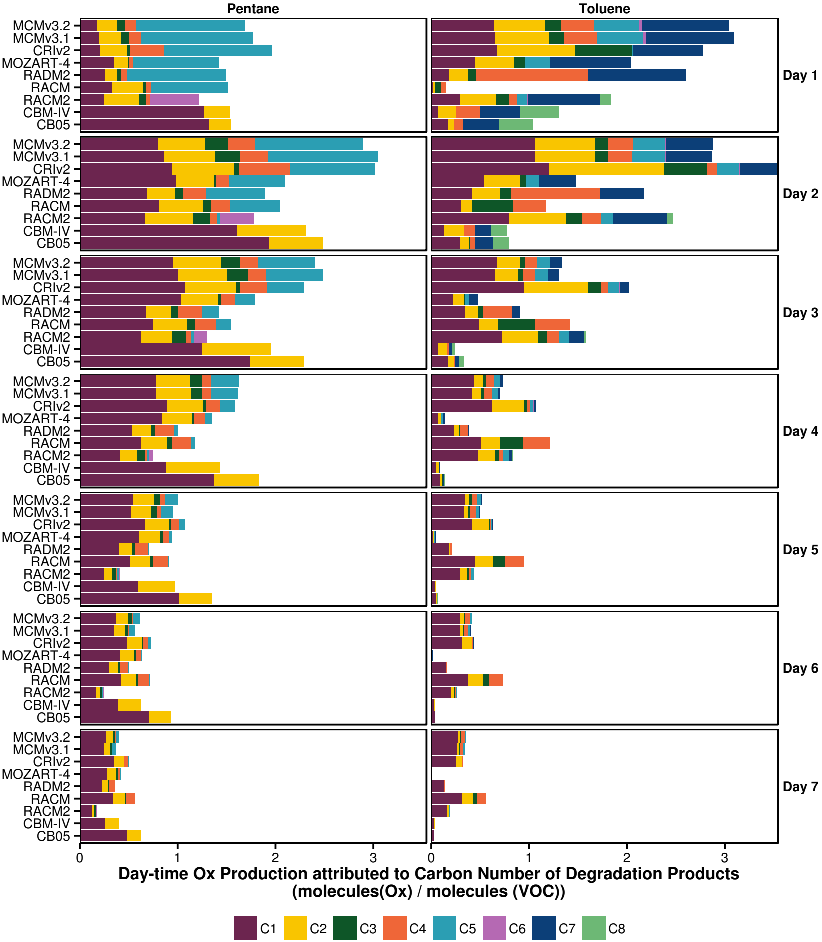

Figure 7. Day-time O_x production during pentane and toluene degradation is attributed to the number of carbon atoms of the degradation products for each mechanism.

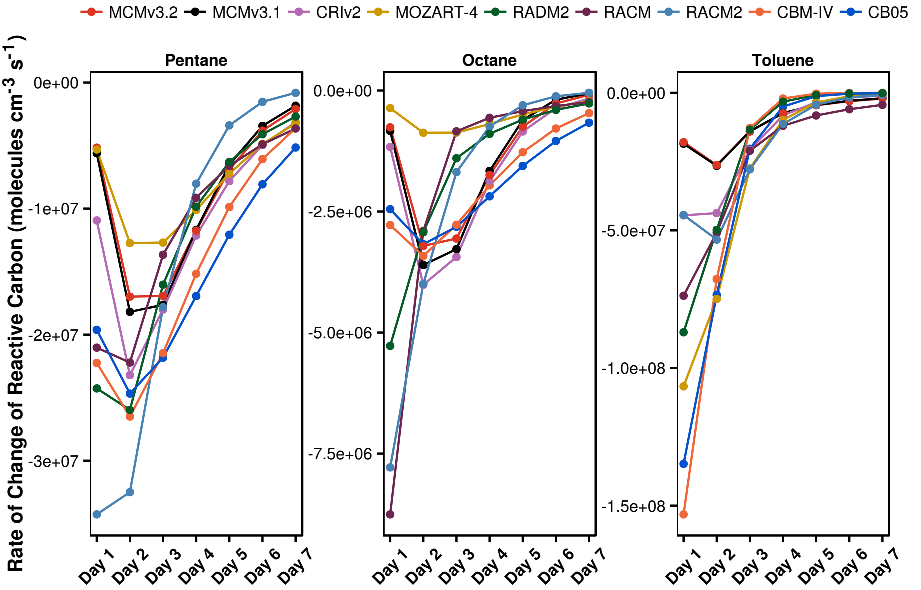

Figure 8. Daily rate of change in reactive carbon during pentane, octane and toluene degradation. Octane is represented by the five carbon species, BIGALK, in MOZART-4.