

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 the reactions of nitrogen oxides with peroxy radicals produced during volatile organic compound (VOC) degradation. Chemical transport models use simplified representations of this complex gas-phase chemistry to predict O_3 levels and inform emission control strategies. Thus an accurate representation of O_3 production chemistry is vital for effective predictions, VOC degradation chemistry in MCM v3.1, CRI v2, MOZART-4, RADM2, RACM, RACM2, CBM-IV and CB05 were compared to that of the near-explicit MCM v3.2 mechanism. This chemistry was compared by tagging all organic degradation products over multi-day runs and calculating the Tagged Ozone Production Potential (TOPP) for each VOC. First day TOPP values were similar for most VOCs, larger discrepancies arose over the model run. O_x production was attributed to the number of carbon atoms in each degradation product showing that reduced mechanisms break down the emitted VOC quicker than more explicit mechanisms. Analysing the radical and PAN net production budgets illustrated that inclusion of production sources not included in the MCM v3.2 impacts O_x production.

1 Introduction

Ground-level ozone (O_3) is both an air pollutant and a short-lived climate forcing pollutant (SLCP) that is detrimental to human health and crop growth (EEA, 2013). O_3 is a

secondary pollutant as it is not directly emitted but produced from the reactions of volatile organic compounds (VOCs) and nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) in the presence of sunlight (Atkinson, 2000).

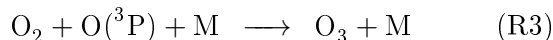
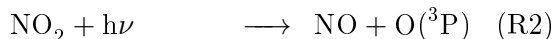
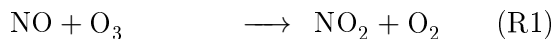
Emissions of O_3 precursors have been steadily decreasing over Europe, however 98% of Europe's urban population are exposed to levels that exceed the World Health Organization (WHO) air quality guideline of $100 \mu\text{g}/\text{m}^3$ over an 8-hour mean (WHO, 2006). These exceedances are the result of local and regional emissions of O_3 precursor gases, their intercontinental transport and the non-linear relationship of O_3 concentrations on NO_x and VOC levels (EEA, 2013).

Effective emission reduction strategies require accurate predictions of O_3 concentrations using chemical transport models (CTMs). This requires adequate representation of gas-phase chemistry in the chemical mechanism used by the CTM. Solving the concentrations of each chemical species is very computationally expensive and in regional and 3-D models simplified chemical mechanisms are used. Many chemical mechanisms are available, these were developed using differing streamlining approaches to gas-phase chemistry resulting in varying levels of simplification. This study compares the impacts of these different simplified representations on O_3 production levels with a focus on the treatment of VOC degradation product chemistry by the chemical mechanism.

re-word

There is also a need to improve the accuracy of modelling studies from a scientific perspective. Abbatt et al. (2014) stresses the need to focus on the three fundamentals of atmospheric chemistry: observations, laboratory and modelling.

O_3 is primarily produced and destroyed in the fast photochemical NO – NO_2 – O_3 cycle (R1)–(R3).

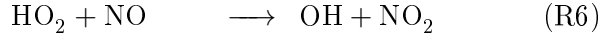
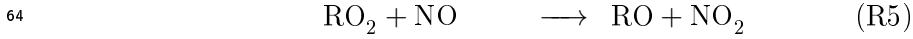


NO and NO_2 reach a near-steady state via (R1) and (R2) which is disturbed in two cases. Firstly, when O_3 is removed via (R1) which occurs during night-time or near large NO sources – NO_x -titration. Secondly, when O_3 is produced through VOC– NO_x chemistry (Sillman, 1999).

The odd oxygen family, O_x , is used to remove the influence of NO_x -titration on O_3

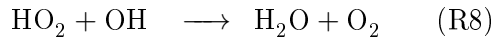
chemistry. In this study O_x is defined to include O_3 , NO_2 , $\text{O}(^3\text{P})$, $\text{O}(^1\text{D})$ and other
 56 chemical species that are involved in fast photochemical cycles with O_3 and NO_2 .

Emitted VOCs (RH) are typically oxidised in the atmosphere by reacting with the
 58 hydroxyl radical (OH) forming peroxy radicals (RO_2) in the presence of O_2 (R4). Further
 reactions of VOC degradation products produces RO_2 and hydroperoxy radicals (HO_2).
 60 Both RO_2 and HO_2 radicals react with NO to produce NO_2 ((R5)–(R6)) leading directly to
 O_3 production via (R2) and (R3). Thus the amount of O_3 produced from the degradation
 62 of a VOC is directly related to the number of NO to NO_2 conversions by peroxy and
 hydroperoxy radicals (Atkinson, 2000).

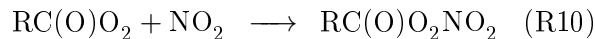
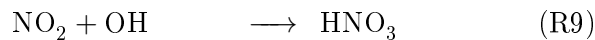


This chemistry leads to O_3 concentration being a non-linear function of the NO_x and
 66 VOCs concentrations. Three distinct atmospheric regimes with respect to O_3 production
 can be defined (Jenkin and Clemitshaw, 2000). In the NO_x -sensitive regime, VOC
 68 concentrations are much higher than those of NO_x and O_3 production is dependant on NO_x
 concentrations. On the other hand, when NO_x concentration is much higher than that of
 70 VOCs, it is the VOC concentration that determines the amount of O_3 produced. This is
 the VOC-sensitive regime. Finally, in the NO_x -VOC-sensitive regime there is maximal O_3
 72 production which is controlled by both VOC and NO_x concentrations.

These different atmospheric regimes give rise to distinct radical removal mechanisms
 74 (Kleinman, 1991). In the NO_x -sensitive regime, the concentration of radicals is very high
 relative to NO_x causing radical removal by either radical combination reactions (R7) or
 76 bimolecular destruction reactions (R8) (Kleinman, 1994).



Whereas in the VOC-sensitive regime, high NO_x concentrations lead to radical removal
 by reaction with NO_2 . These reactions lead to nitric acid (R9) and peroxy acetyl nitrate
 80 (PAN) species production (R10).



82 In the NO_x -VOC-sensitive regime, the amount of radicals is comparable to the amount
of NO_x leading to no dominant radical removal mechanism. Hence, radical and PAN
84 chemistry play an important role in O_3 production as radical production helps fuel O_3
production and PAN acts as a reservoir species for both radicals and NO_2 .

86 VOCs impact O_3 production in different ways due to their diverse reaction rates
and degradation pathways. Ozone Production Potentials (OPP) quantify the effect
88 of individual VOCs on O_3 production. OPPs are typically been calculated through
incremental reactivity (IR) studies. This involves changing the concentration of a particular
90 VOC by a known increment and calculating the resulting change in O_3 .

Examples of IR scales are the Maximal Incremental Reactivity (MIR) and Maximum
92 Ozone Incremental Reactivity (MOIR) scales in Carter (1994), as well as the Photochemical
Ozone Creation Potential (POCP) scale of Derwent et al. (1996) and Derwent et al. (1998).
94 Different NO_x conditions were used when calculating these IR scales thus calculating the
OPPs of VOCs in different atmospheric regimes.

96 IR calculations lack detailed mechanistic information about the processes affecting O_3
formation and combine both the direct and indirect effects of VOC degradation on O_3
98 production. The direct effect is the impact of the increased VOC concentration on O_3
production. This is related to the number of NO to NO_2 conversions from RO_2 produced
100 during VOC degradation. Whereas the indirect effect is the influence of the increased
radical species availability between the base VOC-mix and the increased VOC-mix on O_3
102 production.

OPPs have been calculated using a tagging approach in Butler et al. (2011). All organic
104 degradation products of a VOC are labelled with the name of the parent VOC enabling
attribution of O_x production back to the emitted VOC. The Tagged Ozone Production
106 Potential (TOPP) of a VOC is obtained by normalising the total daily O_x production by
the total emissions of the VOC. The tagging approach follows each degradation pathway
108 of each VOC making this approach ideal to compare the chemistry of different chemical
mechanisms. Full details of the TOPP calculation is found in Section 2.

110 Chemical mechanisms represent atmospheric chemistry in chemical transport models.
All mechanisms have some level of simplification due to the computational resources needed
112 for gas-phase chemistry calculations. These levels of simplification arise from the different

scopes of modelling studies, for example a global CTM requires a more computational
114 efficient mechanism than a boxmodel.

A near-explicit mechanism such as the Master Chemical Mechanism (MCM) (Jenkin
116 et al., 2003; Saunders et al., 2003; Bloss et al., 2005) includes a large amount of mechanistic
details ($\sim 12,000$ reactions). This makes the MCM ideal as a reference mechanism when
118 comparing chemical mechanisms. The latest version, MCM v3.2, (Rickard et al., 2014) is
the reference mechanism in this study.

120 Further simplification is achieved by using either a lumped structure or a lumped
molecule approach (Dodge, 2000). Lumped structure mechanisms speciate VOCs by the
122 carbon bonds of the emitted VOC. Whilst in lumped molecule mechanisms, VOCs are
represented by a specific organic or mechanism species representing a number of VOCs.
124 Different lumped molecule mechanisms use diverse approaches to creating mechanism
species representing emitted VOCs.

126 Other chemical mechanism comparison studies consider O_3 concentration time series
over varying VOC and NO_x concentrations. Examples of such studies are Dunker et al.
128 (1984); Kuhn et al. (1998); Gross and Stockwell (2003) and Emmerson and Evans (2009).
A common outcome is that the largest discrepancies in O_3 concentration times series arise
130 when modelling urban rather than rural conditions. Other atmospheric species, such as
PAN or H_2O_2 , also show large concentration time series deviations between mechanisms.

132 IR scales have also been used as a tool for mechanism comparison. In Derwent et al.
(2010), the near-explicit mechanisms MCM v3.1 and SAPRC-07 were compared using
134 first-day POCP values calculated under VOC-sensitive conditions. In general, the POCP
values were comparable between the mechanisms.

136 OPPs are a useful mechanism comparison tool as they relate O_3 production to a
single number. In this study, TOPPs calculated for a number of VOCs using different
138 mechanisms are compared to those calculated with the MCM v3.2. TOPPs are ideal for
such a mechanism comparison study as they address multi-day scenarios and the tagging
140 approach allows a detailed comparison of the VOC degradation chemistry between the
mechanisms.

142 The chemical mechanisms compared and the methodology are described in Section
2. Section 3 presents the comparison of the first-day TOPPs and their time series.

Chemical Mechanism	Number of Organic Species	Number of Organic Reactions	Type of VOC Lumping
MCM v3.2	5708	16349	No lumping
MCM v3.1	4351	12691	No lumping
CRI v2	411	1145	No lumping*
MOZART-4	69	145	Lumped molecule
RADM2	44	103	Lumped molecule
RACM	58	193	Lumped molecule
RACM2	99	315	Lumped molecule
CBM-IV	20	45	Lumped structure
CB05	37	99	Lumped structure

Table 1: The chemical mechanisms used in the study, MCM v3.2 is the reference mechanism. References for the mechanisms are found within the main text. *The full CRI v2 is used and this has no lumping of the primary VOCs.

Detailed analysis of O_x production chemistry as well as the treatment of radical and PAN chemistry is compared in Section 4. Finally the conclusions and further work are in outlined Section 5.

2 Methodology

2.1 Chemical Mechanisms

The chemical mechanisms used in this study are outlined in Table 1. This includes the reference mechanism (MCM v3.2) and other mechanisms that are used for both global and regional modelling.

The Master Chemical Mechanism (MCM) (Jenkin et al., 1997, 2003; Saunders et al., 2003; Bloss et al., 2005; Rickard et al., 2014) is a near-explicit mechanism that describes the degradation of 125 primary VOCs. Whilst the large number of reactions makes the MCM computationally inefficient for use in regional or 3-D models, it is ideal as a reference in mechanism comparison studies. The latest version, MCM v3.2, is the reference mechanism in this study.

The second version of the Common Representative Intermediates (CRI v2) (Jenkin et al., 2008) is a reduced chemical mechanism which describes the oxidation of the same

primary VOCs as the MCM v3.1. VOC degradation is represented through degradation species whose O_3 production reflects that of the MCM v3.1. The full version of the CRI v2 (<http://mcm.leeds.ac.uk/CRI>) was used in this study.

Differences in O_3 production between the CRI v2 and MCM v3.2 may be due to differences between the MCM versions rather than the reduction techniques used in the CRI v2. For this reason, the MCM v3.1 is also included in this study.

The Model for OZone and Related chemical Tracers version 4 (MOZART-4) is a global chemical transport model including its own representation of tropospheric and stratospheric chemistry (Emmons et al., 2010). Methane, ethane, propane, ethene, propene, isoprene and α -pinene are represented by non-lumped model species. The mechanism species BIGALK, BIGENE and TOLUENE represent all other VOC. The choice of mechanism species is based on the functional group of the VOC.

The second generation Regional Acid Deposition Model (RADM2) was developed for regional scale modelling of atmospheric chemistry (Stockwell et al., 1990). Methane, ethane, ethene and isoprene are represented by separate model species. All other VOCs are split into lumped model species based upon OH-reactivity and molecular weight.

RADM2 was updated to the Regional Atmospheric Chemistry Mechanism (RACM) (Stockwell et al., 1997). Updates include more mechanism species representing individual VOCs as well as revised rate constants and product yields. Aromatic, PAN and isoprene chemistry was also revised.

RACM2 is the most current version of the RACM mechanism (Goliff et al., 2013) with substantial updates to aromatic and ketone chemistry. More mechanism species representing emitted VOC are included in RACM2 leading to a more detailed mechanism than its previous versions.

The Carbon Bond Mechanism version four (CBM-IV) was developed for simulations of urban polluted conditions (Gery et al., 1989). Ethene, formaldehyde and isoprene are the only VOCs represented by specific species. All other emitted VOC are lumped according to their carbon bond types.

Initial concentrations of primary VOCs are split into the appropriate representation using the method described in Hogo and Gery (1989). For example, pentane has five single carbon bonds and is represented as 5 PAR. An initial concentration of 1,200 pptv would

be assigned as 6,000 ($= 1,200 \times 5$) pptv in CBM-IV.

192 The fifth version of the Carbon Bond Mechanism (CB05) (Yarwood et al., 2005)
includes the mechanism species representing methane, ethane and acetaldehyde. The
194 chemistry schemes were revised to include peroxide formation that occurs in VOC-sensitive
regions. There were also updates in the allocation of some primary VOC to mechanism
196 species.

2.2 Model Setup

198 The modelling approach and set-up followed that of the original TOPP study of Butler
et al. (2011). A summary is provided, further details are found in the supplement to
200 this paper and (Butler et al., 2011). Maximum O_3 production was achieved by emitting
the amount of NO required to balance the source of radicals at each time step and was
202 calculated following Kleinman (1991). The NO source was determined separately for each
model run ensuring conditions of maximum O_3 production for each mechanism.

204 The NMVOC and their initial mixing ratios are those typical of Los Angeles and taken
from Baker et al. (2008). The initial NMVOC mixing ratios were held constant until
206 midday of the first day and then left to react freely. Methane (CH_4) was held fixed at 1.8
ppmv throughout. Carbon monoxide (CO) and O_3 were initialised at 200 ppbv and 40
208 ppbv respectively and then allowed to evolve freely.

Table 2 outlines the NMVOC used in the study, their initial mixing ratios and
210 representation in the different mechanisms. Initial mixing ratios were weighted by carbon
number of the mechanism species when lumping NMVOC into mechanism species. This
212 ensured the amount of reactive carbon was constant between the model runs.

2.2.1 Mechanism Implementation

214 The MECCA boxmodel (Sander et al., 2011) is based upon the Kinetic Pre-Processor
(KPP) (Damian et al., 2002). Hence, all chemical mechanisms were adapted into the
216 modularised KPP format from their original format.

The MCM v3.2 inorganic chemistry reactions were used in each model run to focus on
218 the treatment of organic NMVOC degradation chemistry between mechanisms. Inorganic
gas-phase chemistry is well-known and any differences are typically due to inconsistencies

NMVOG	Mixing Ratio (ppbv)	MCM v3.1, v3.2 and 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	2 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 2: Typical NMVOCs present in Los Angeles and their respective mixing ratios (Baker et al., 2008) as well as their representation in each chemical mechanism. The representation of the VOCs in each mechanism is based upon the recommendations of the respective literature.

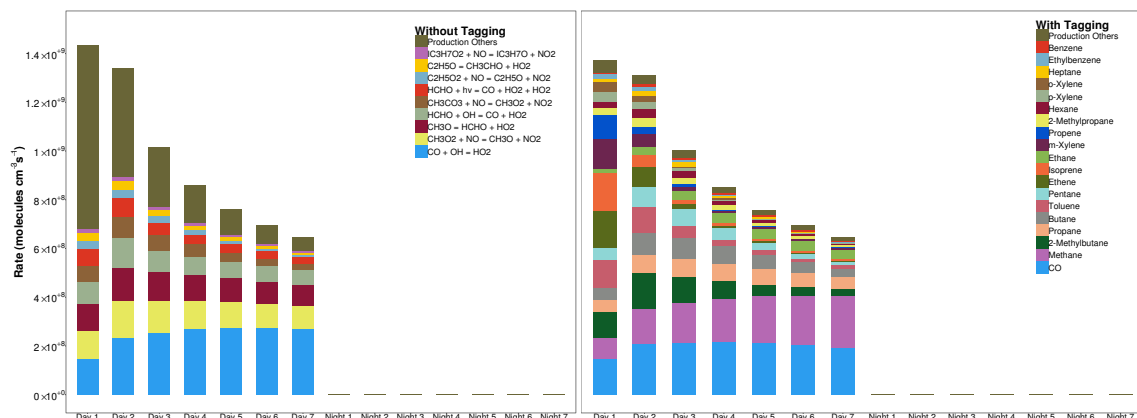


Figure 1: The O_x production budgets using the MCM v3.2 (a) without tagging and (b) with tagging, where O_x production is attributed to the emitted VOCs.

220 between IUPAC and JPL reaction rate constants (Emmerson and Evans, 2009).

Some mechanisms include reactions which are of importance only in the stratosphere or
 222 free troposphere. As this study is concerned with processes below the planetary boundary
 layer, these reactions were not included. For example, PAN photolysis was removed from
 224 MOZART-4, RACM2 and CB05 as it is only important in the free troposphere (Harwood
 et al., 2003).

226 The MCM v3.2 approach to photolysis, dry deposition and peroxy radical – peroxy
 radical reactions was used for each mechanism. The supplement to this article contains a
 228 detailed description of how this was implemented.

2.3 Tagged Ozone Production Potential (TOPP)

230 This section summarises the tagging methodology described in Butler et al. (2011) which
 should be consulted for more details.

2.3.1 Tagging Approach and Application to O_x Family

Tagging follows the degradation of all NMVOCs in Table 2 through all possible degradation
 234 pathways. This is achieved by labelling every organic degradation product produced during
 NMVOC degradation with the name of the emitted NMVOC. Thus, each NMVOC has its
 236 own set of degradation reactions.

The tagging approach allows allocation of production and consumption budgets to

emitted NMVOCs. Without tagging, the individual reactions responsible for O_x production are determined but not the NMVOC source of the organic reactants. The NMVOC source can be determined by exploiting the tags and this is illustrated in Figure 1.

2.3.2 Tagged Ozone Production Potential (TOPP) Definition

The daily Tagged Ozone Production Potential (TOPP) of a VOC is its total daily contribution to O_x production normalised by its total emissions on the first day of the model run. The O_x production of each VOC is determined by means of the tags as described in Section 2.3.1. The TOPP is a measure of the number of O_x molecules produced per molecule of emitted VOC.

3 Mechanism Comparison: Overall Results

3.1 First Day TOPP Value Comparison

The first day TOPP values calculated from each mechanism are compared to those calculated with the MCM v3.2 in Figure 2. The reduced mechanisms generally reproduce the MCM v3.2 first day TOPP values. However the TOPP values resulting from aromatic VOC degradation is underestimated in the reduced mechanisms.

Aromatic chemistry has always been difficult to represent in chemical mechanisms as many products, their yields and reactions are not known or are subject to uncertainties (Vereecken and Francisco, 2012). Thus, greater variation is expected between the TOPP values of aromatic VOCs. The largest discrepancies are the zero TOPP values of toluene and xylene in RACM. This is unrealistic as aromatic VOCs contribute significantly to O_x production (Derwent et al., 1998). Section 3.2.1 outlines the chemistry responsible for these results.

The first day TOPP values of 2-methylpropene in RACM, RACM2, CBM-IV and CB05 indicate that its degradation is treated very differently to the MCM v3.2. The variation between RACM, RACM2 and MCM v3.2 arise from the differences between the rate constants of the 2-methylpropene ozonolysis reactions. In MCM v3.2, this rate constant at 273 K is $1 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ whereas in RACM and RACM2 it is about 25 times faster at $2.5 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$. This leads to more radical and hence O_x production

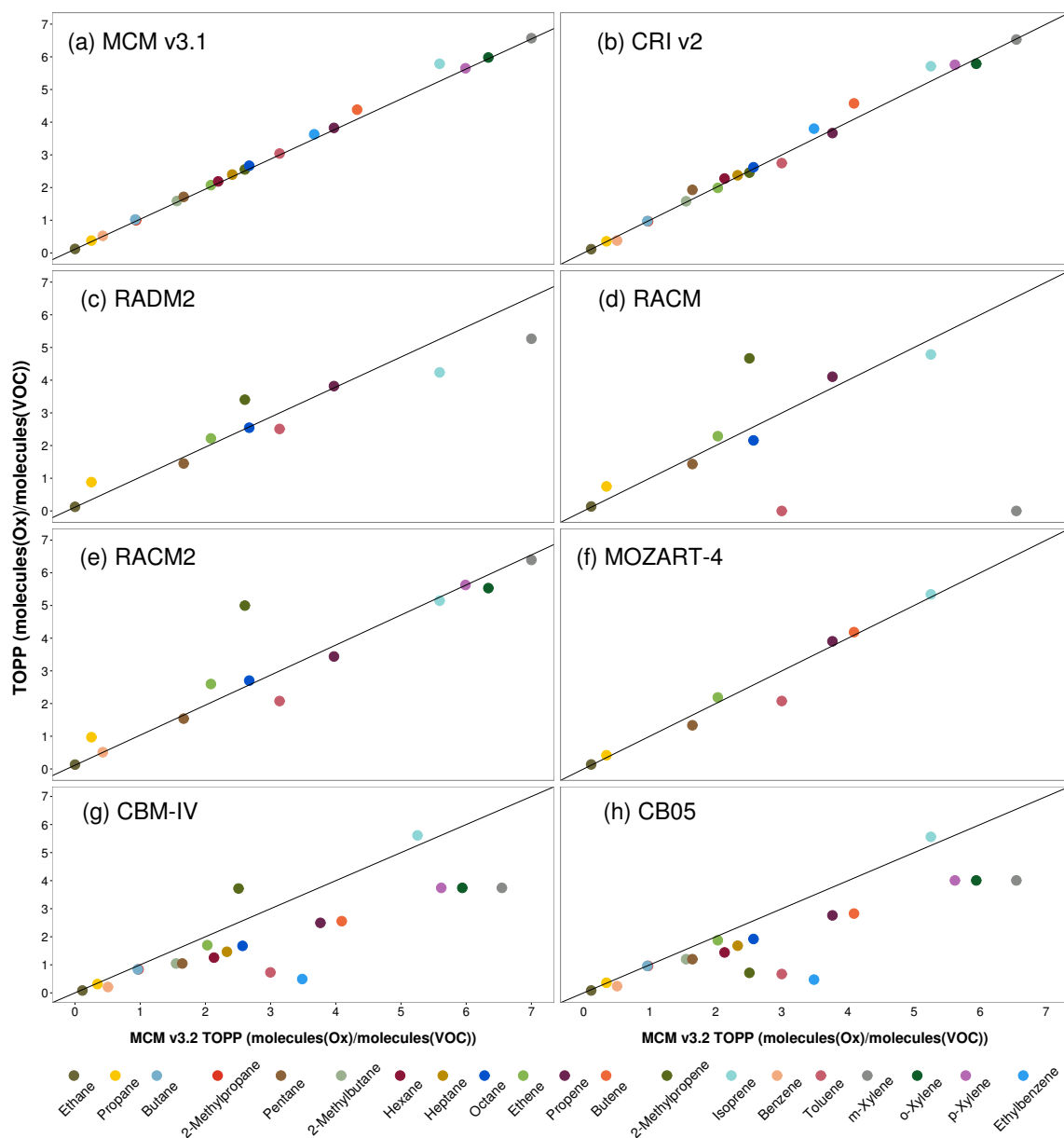


Figure 2: First day TOPP values obtained using (a) MCM v3.1, (b) CRI v2, (c) MOZART-4, (d) RADM2, (e) RACM, (f) RACM2, (g) CBM-IV and (h) CB05 mechanisms compared to the corresponding MCM v3.2 values.

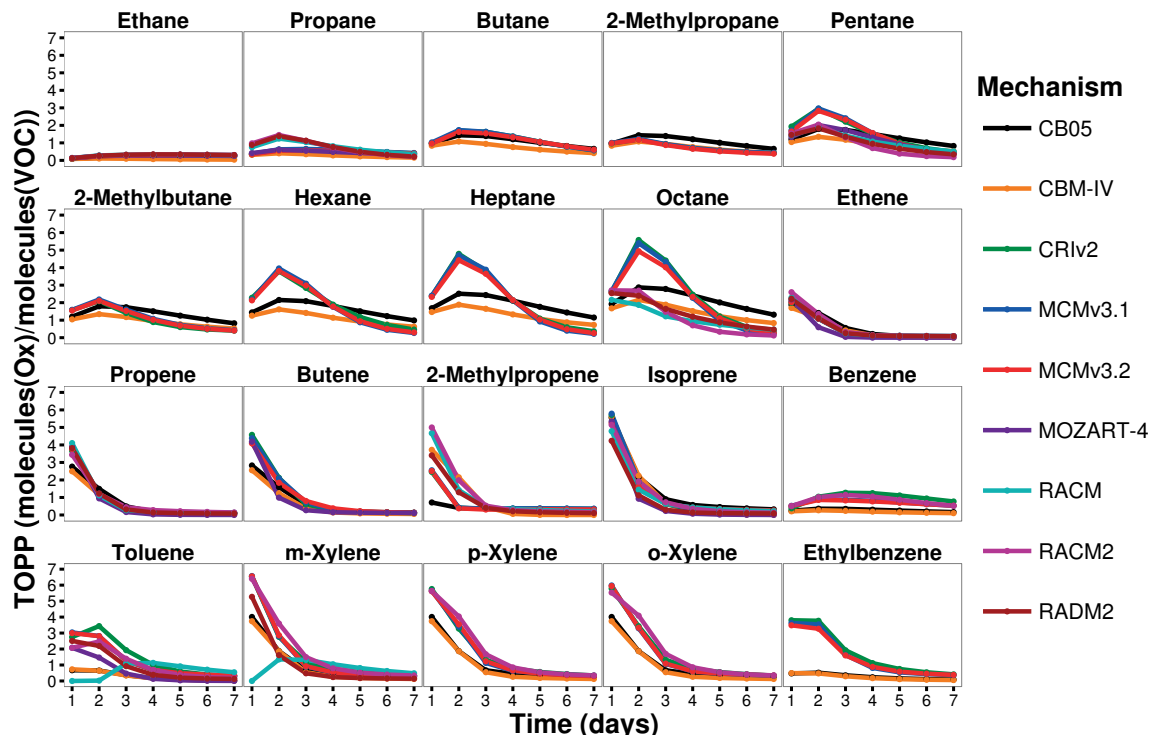


Figure 3: TOPP value time series for the NMVOC in Table 2 using the mechanisms of Table 1.

than in the MCM v3.2.

In CBM-IV, 2-methylpropene is represented by the mechanism species ALD2, which is a surrogate for aldehydes with more than one carbon atom. ALD2 reacts very quickly with OH forming CH_3CO_3 , leading to O_x production. Furthermore, photolysis of ALD2 promotes radical and in turn O_x production. This is not a degradation pathway for 2-methylpropene in any other mechanism. The choice of 2-methylpropene representation gives rise to more O_x production than in the MCM v3.2.

2-methylpropene representation was updated in CB05 to $\text{FORM} + 3 \text{ PAR}$, where FORM represents formaldehyde and PAR the paraffin C–C bond. The initial oxidation reactions of formaldehyde are similar to ALD2 whilst PAR is a slow reacting species. This slows down the O_x production resulting in lower O_x production than in the MCM v3.2.

3.2 TOPP Values Time Series

The time series of the daily TOPP values for all NMVOCs in Table 2 are presented in Figure 3. NMVOCs, such as ethene, whose degradation is described using dedicated

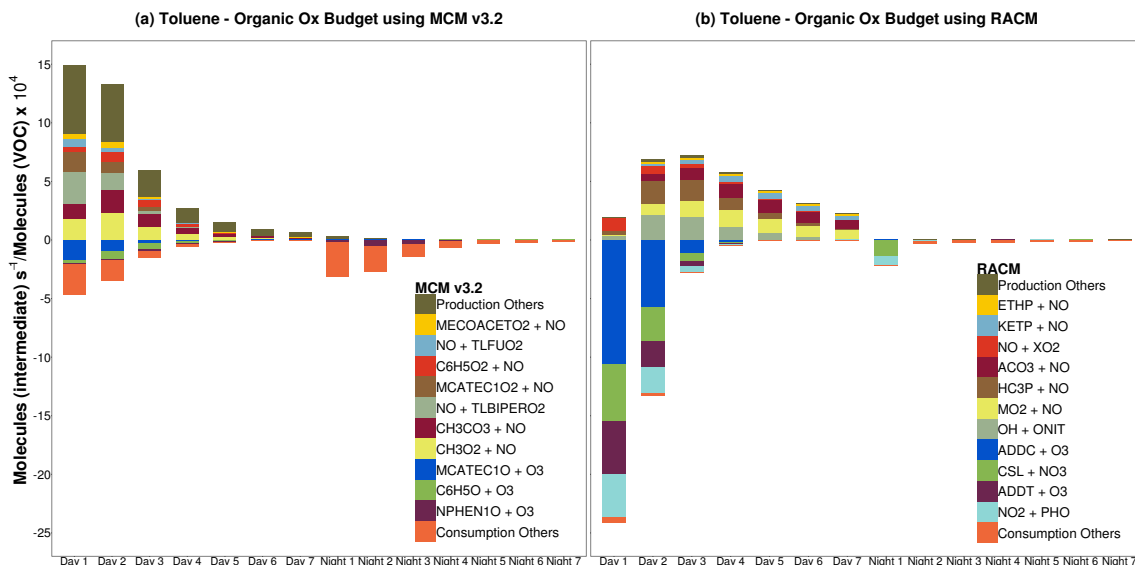


Figure 4: The O_x production and consumption budgets from toluene degradation in (a) MCM v3.2 and (b) RACM.

mechanism species have a narrow spread between their time series. Higher variability emerges between the time series of those NMVOCs, such as pentane, that are lumped mechanism species.

The second day maximum of all alkane TOPP time series is reproduced by all mechanisms except the RADM2, RACM and RACM2 representation of octane. O_x production is attributed to the carbon number of the NMVOC degradation products in Section 4.1 demonstrating that the reduced mechanisms break down the emitted NMVOC into species with a lower number of carbon atoms quicker than more detailed mechanisms. In the case of octane, this break down proceeds so quickly that its TOPP value maximum is on the first day. The supplement to this paper contains details of the octane analysis.

The TOPP time series of aromatic NMVOCs show the highest variability between mechanisms. In particular, TOPP values of zero are obtained for both toluene and m-xylene when using RACM and this is explained in Section 3.2.1. The rapid toluene break down in CBM-IV and CB05 results in a low TOPP time series. This impacts on the ethylbenzene TOPP value time series since it is represented as TOL + PAR.

3.2.1 RACM Aromatic Chemistry

296 The O_x production and consumption budgets due to toluene degradation in MCM v3.2
and RACM are depicted in Figure 4. The tagging approach allows attribution of these
298 budgets to the responsible organic reactions.

RACM chemistry results in net O_x consumption on the first two days in contrast to the
300 MCM v3.2 which has net O_x production throughout. O_x consumption is mainly through
reaction of the cresol OH-adduct mechanism species ADDC with O_3 . A fast rate constant
302 ($5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) was assigned to the this reaction making it the main reaction pathway
of ADDC. This reaction was included in RACM due to improved cresol product yields
304 when comparing RACM predictions with experimental data (Stockwell et al., 1997).

All other mechanisms that include cresol OH-adduct species do not include reaction
306 with O_3 . The inclusion of aromatic OH-adduct species ozonolysis in RACM results in
non-representative O_x production. This has been updated in RACM2 where aromatic
308 OH-adduct species ozonolysis is no longer included.

4 NMVOC Degradation Analysis

310 4.1 Carbon Number of O_x Producing Degradation Products

The timing and amount of O_x produced throughout NMVOC degradation depends on how
312 quickly the final degradation products of CO_2 and H_2O are reached (Butler et al., 2011).
The day-time O_x production of pentane and toluene in all mechanisms is attributed to
314 the number of carbon atoms of the degradation products in Figures 5 and 6 respectively.
This allows comparison of how quickly the emitted NMVOC is broken down into smaller
316 degradation products.

Figure 5 indicates that O_x production from degradation products having the same
318 number of carbon atoms as the emitted NMVOC has a larger influence in the near-explicit
mechanisms than reduced mechanisms. This is compensated by an increased amount of O_x
320 production from degradation products having two or less carbon atoms. Thus the emitted
VOC is broken down into smaller degradation products quicker in reduced mechanisms
322 and cannot produce similar amounts of O_x to near-explicit mechanisms.

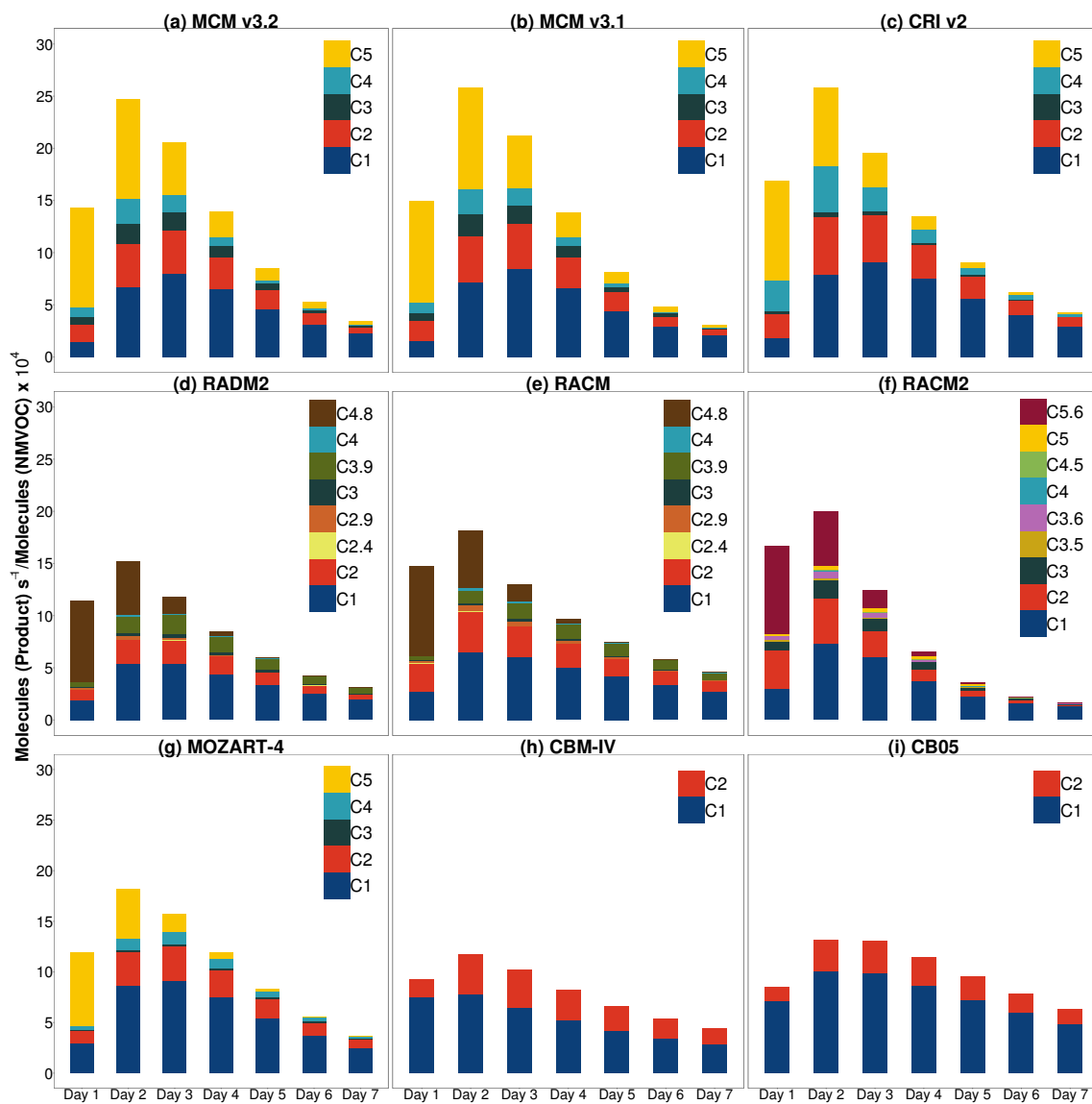


Figure 5: O_x production attributed to carbon number of degradation products during pentane degradation in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

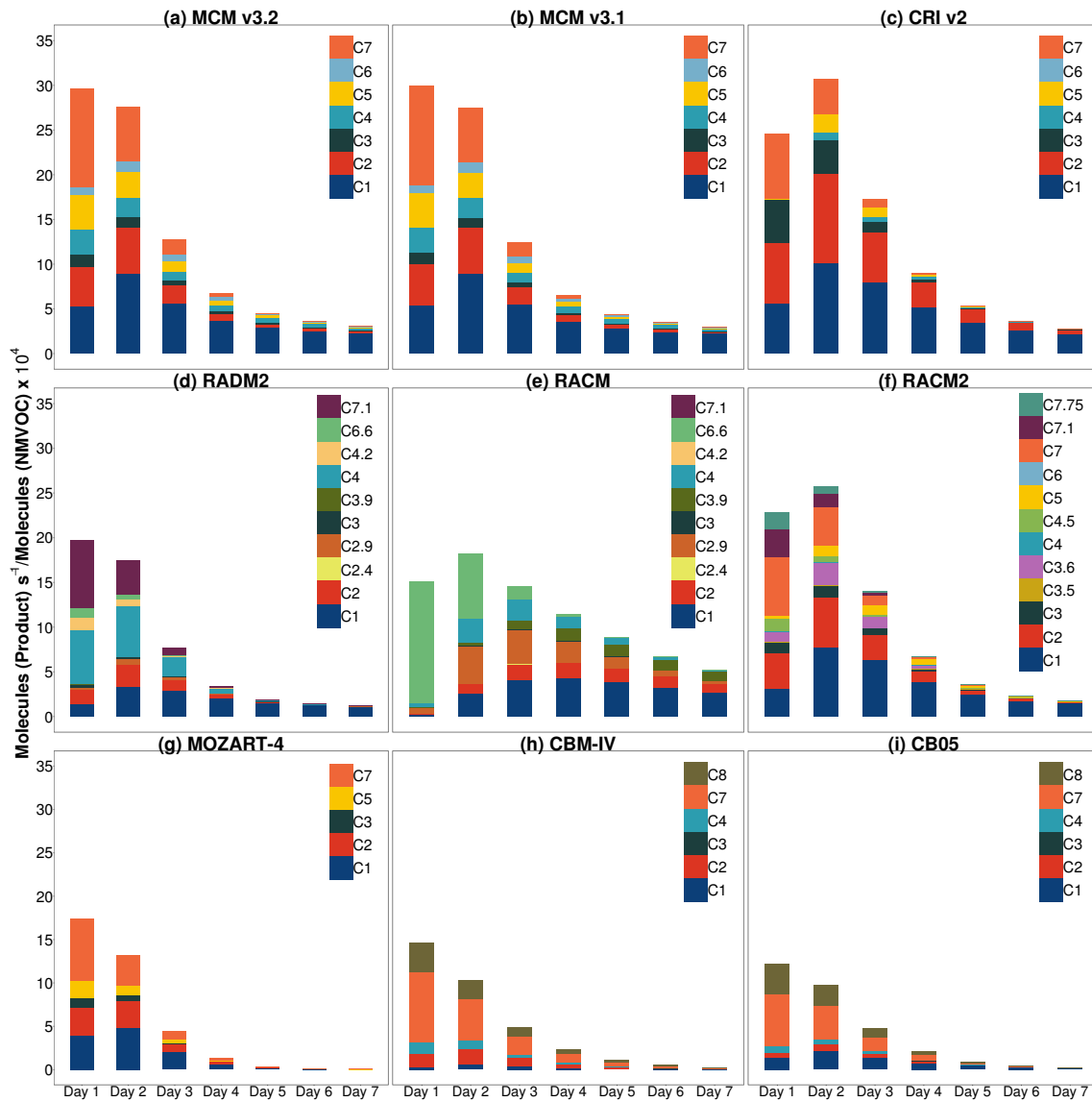


Figure 6: O_x production distributed by carbon number of degradation products during toluene degradation in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) MOZART-4, (e) RADM2, (f) RACM, (g) RACM2, (h) CBM-IV and (i) CB05. In RACM, net O_x consumption on the first two days is obtained as shown in Figure 4 and described in Section 3.2.1.

An extreme case is the toluene degradation in MOZART, CBM-IV and CB05 shown
324 in Figure 6. Toluene is immediately broken down into degradation products having two
or less carbon atoms. This results in much lower O_x production and TOPP values than
326 other reduced mechanisms.

Toluene degradation in CRI v2 differs from all other mechanisms as it has maximum O_x
328 production on the second day. Larger O_x production from species having carbon number
three or less than in the MCM v3.2 is responsible. This increase originates from extra HO_2
330 produced from the reaction of the carbonyl mechanism species CARB3 with OH. This is
discussed further in the supplement to this paper. Jenkin et al. (2008) also acknowledge
332 that reducing the MCM v3.1 chemistry of monoalkyl-substituted benzenes, such as toluene,
was the most challenging and the resulting reduced chemistry over-estimates the O_3 mixing
334 ratios.

RACM2 toluene degradation also reaches maximum O_x production on the second day.
336 O_x production from degradation products of a similar or higher carbon number to toluene
indicate that toluene is broken down at slower in RACM2 than in MCM v3.2.

338 4.2 Radical Production and Consumption Budgets

O_x production is directly to the conversion of NO to NO_2 by peroxy radicals. Moreover, in
340 this study maximum O_3 production was achieved by emitting the amount of NO required
to balance the radical source at each time step. A radical family for each mechanism
342 was used to investigate the processes affecting production and loss budgets. This radical
family includes all radical species and species involved in quick production and consumption
344 cycles, such as PAN species and HO_2NO_2 .

The day-time net radical production and loss budgets due to alkane, alkene and
346 aromatic degradation is shown in Figure 7. The largest differences arise from alkane
and aromatic degradation. Pentane and toluene radical budgets are attributed to the
348 responsible processes in Figures 8 and 9 to determine the source of these differences.

In general, photolysis is the major radical production process and the reactions of
350 radicals with other species, such as NO and HO_2 , is the main radical sink. Reduced
mechanisms include other processes to maintain radical production.

352 Figure 8 shows that initial VOC oxidation contributes to radical production in RADM2.

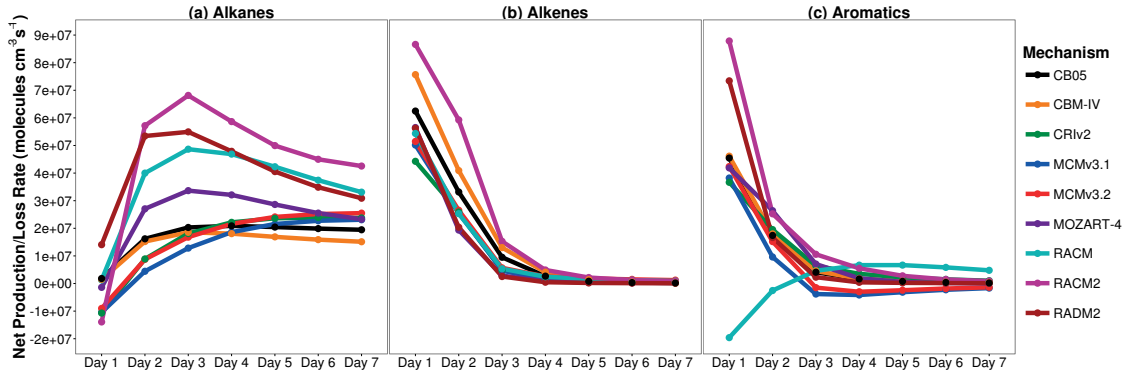
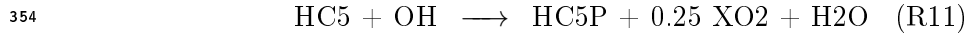


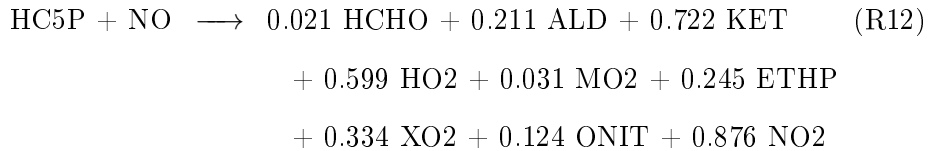
Figure 7: The day-time net budget contribution of (a) alkane, (b) alkene and (c) aromatic degradation on the radical family in each mechanism.

This is represented by



where HC5P is the pentyl peroxy radical and XO2 is an operator species which accounts for extra NO to NO₂ conversions. XO2 is included in the radical family as it functions as a peroxy radical. This additional radical production pathway is responsible for the net first day radical production in RADM2.

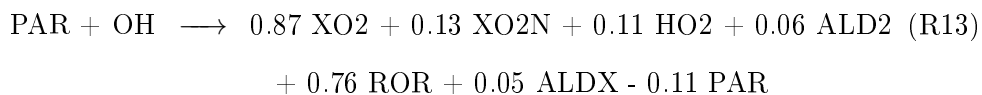
The reactions of radicals lead to large net radical production in RACM after the first day. The main source being the reaction of HC5P with NO,



where HO2, MO2, ETHP and XO2 are the produced radical species. The larger net RADM2 and RACM radical production in Figure 7 is traced back to the extra radical production from reactions (R11) and (R12) respectively.

Radical production in CBM-IV and CB05 is largely impacted by NMVOC initial oxidation and production from other radical reactions. Pentane degradation in these mechanisms is very similar and the CB05 reactions are considered here.

Initial pentane degradation is via the PAR reaction with OH,



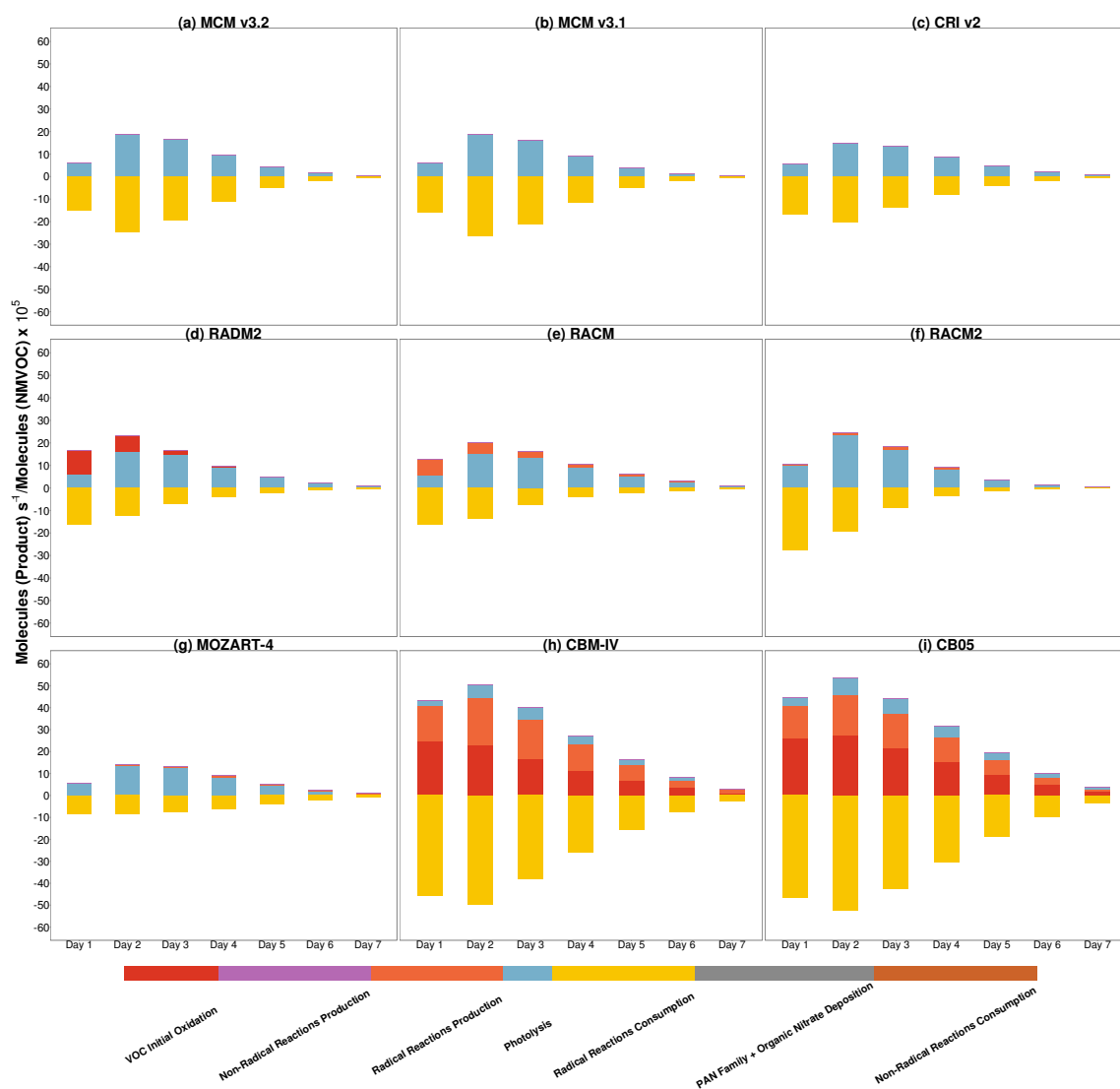


Figure 8: The processes influencing the radical family production and consumption budgets during pentane degradation are illustrated for (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

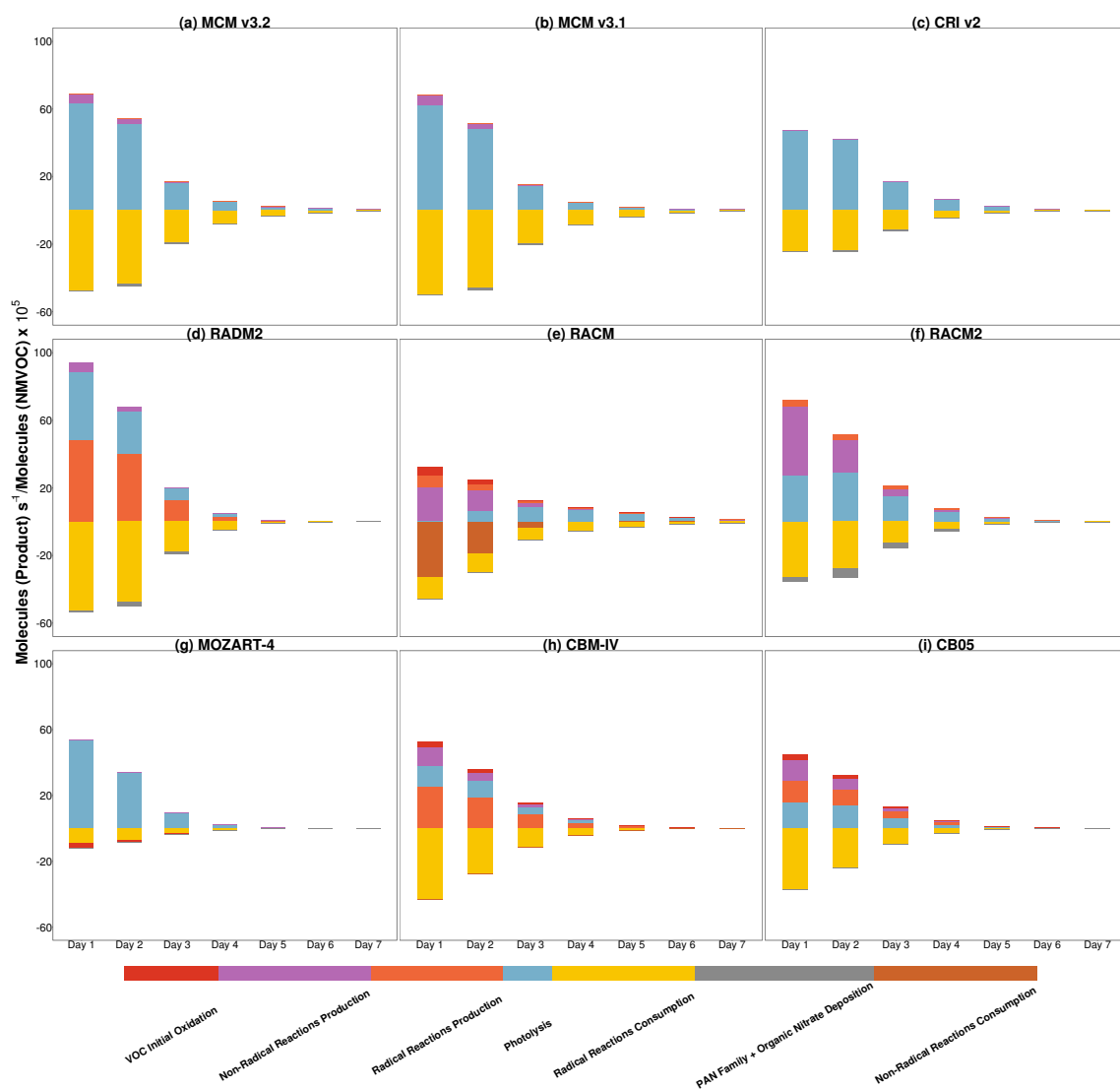


Figure 9: The processes influencing the radical family production and consumption budgets during toluene degradation is illustrated for (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

370 where XO₂, HO₂ and ROR are the produced radical species. The
mechanism species ROR decomposes immediately to either HO₂ or
372 $0.96 \text{ XO}_2 + 0.04 \text{ XO}_2\text{N} + 0.94 \text{ HO}_2 + 0.6 \text{ ALD}_2 + 0.02 \text{ ROR} + 0.5 \text{ ALDX} - 2.1 \text{ PAR}$,
once again XO₂, HO₂ and ROR are the produced radical species. The very fast
374 decomposition of ROR and the use of XO₂ to rapidly convert NO to NO₂ leads to a rapid
loss of radicals. The large production and consumption processes are balanced so that the
376 net radical production correlates with that of the MCM v3.2.

The first day net radical production due to aromatic degradation are overestimated
378 using RADM2 and RACM2 chemistry and underestimated in RACM. The RACM
underestimation results from the degradation chemistry discussed in Section 3.2.1.

380 Figure 9 indicates that the RACM2 overestimation is due to radical production from
reactions that do not involve radicals. The ozonolysis of the unsaturated dicarbonyl
382 mechanism species DCB1 and DCB2 as well as the epoxy mechanism species EPX are
additional reactions used to produce radicals.

384 The MCM v3.2 species TLEPOXMUC is analogous to EPX in RACM2. The ozonolysis
rate constants are 5×10^{-18} and $1 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ respectively. The RACM2 rate
386 constant is 20 times larger than that of the MCM v3.2 leading to excess radical production
in RACM.

388 The ozonolysis of dicarbonyl species are included in RACM2 based on the
recommendations of Bierbach et al. (1994). Dicarbonyl ozonolysis was not included in
390 the MCM due to the uncertainties of these reactions (Bloss et al., 2005). This additional
radical source leads to larger net radical production.

392 4.3 PAN Production and Consumption Budgets

PAN chemistry influences O_x production as it is both a radical and NO_x sink (Fischer et al.,
394 2014). PAN production and consumption budgets were compared using a PAN family for
each mechanism. This PAN family included all PAN species and associated acyl peroxy
396 radicals.

Figure 10 shows the net day-time budgets of the PAN family from alkane, alkene and
398 aromatic degradation. The PAN production and consumption budgets due to pentane
and toluene degradation are expressed in terms of the contributing processes in Figures 11

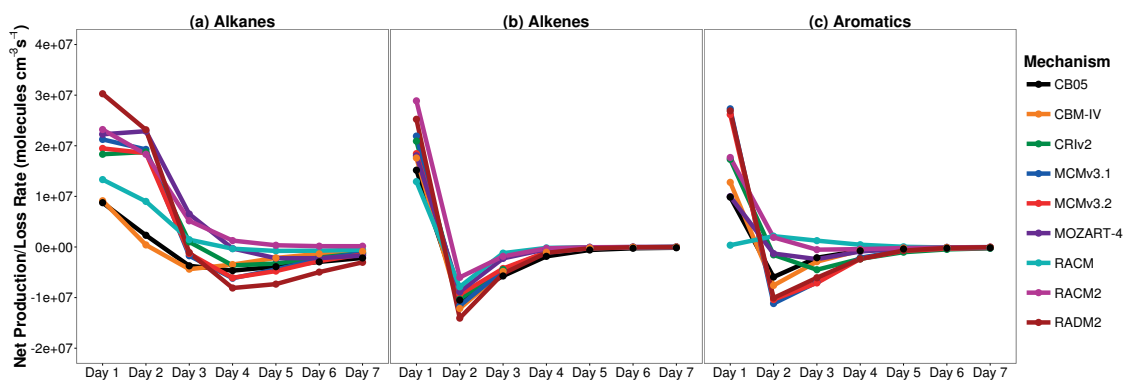


Figure 10: The day-time net budget contribution of (a) alkane, (b) alkene and (c) aromatic degradation on the PAN family in each mechanism.

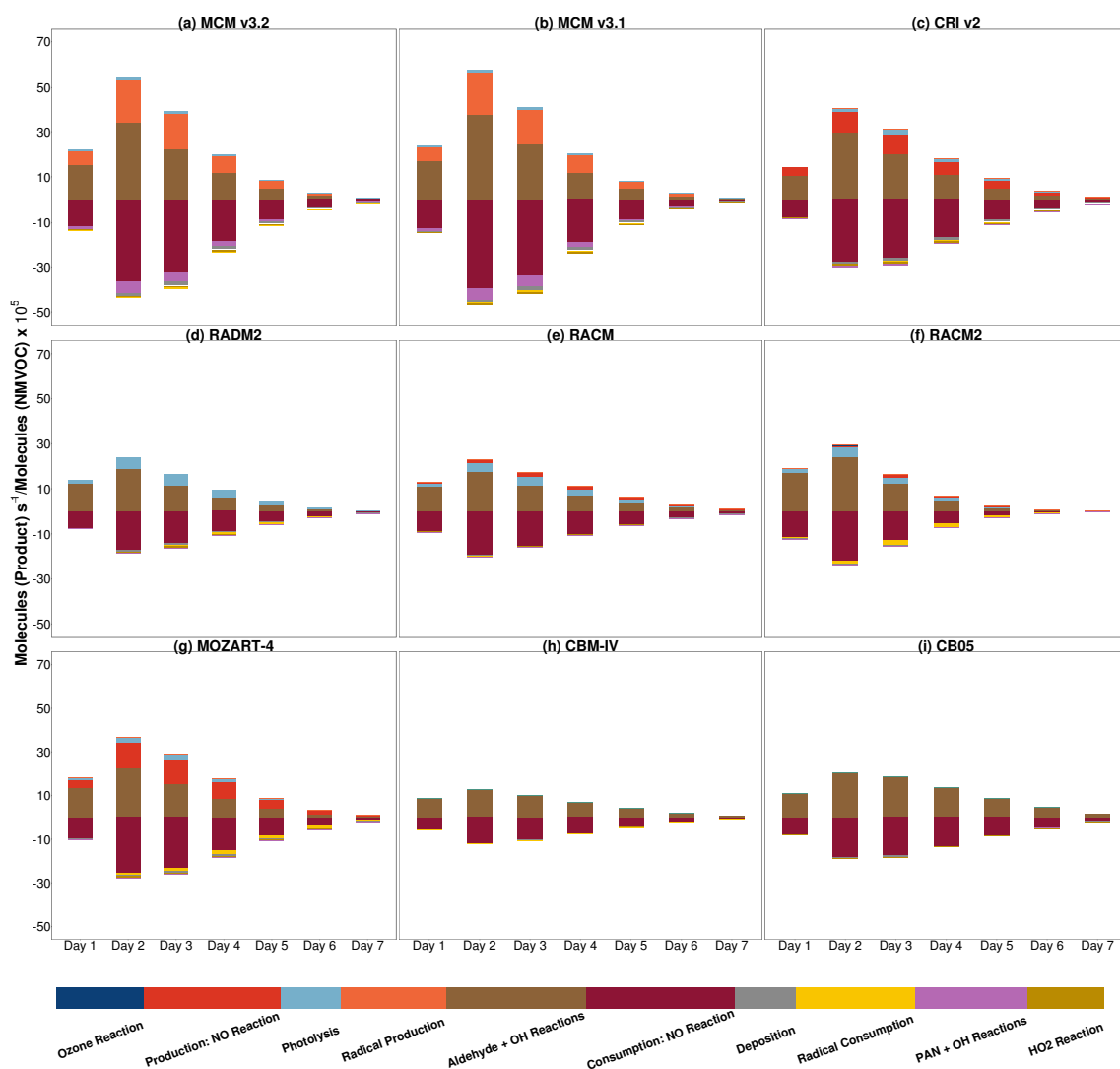


Figure 11: The processes influencing the PAN family production and loss budgets during pentane degradation are illustrated for (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

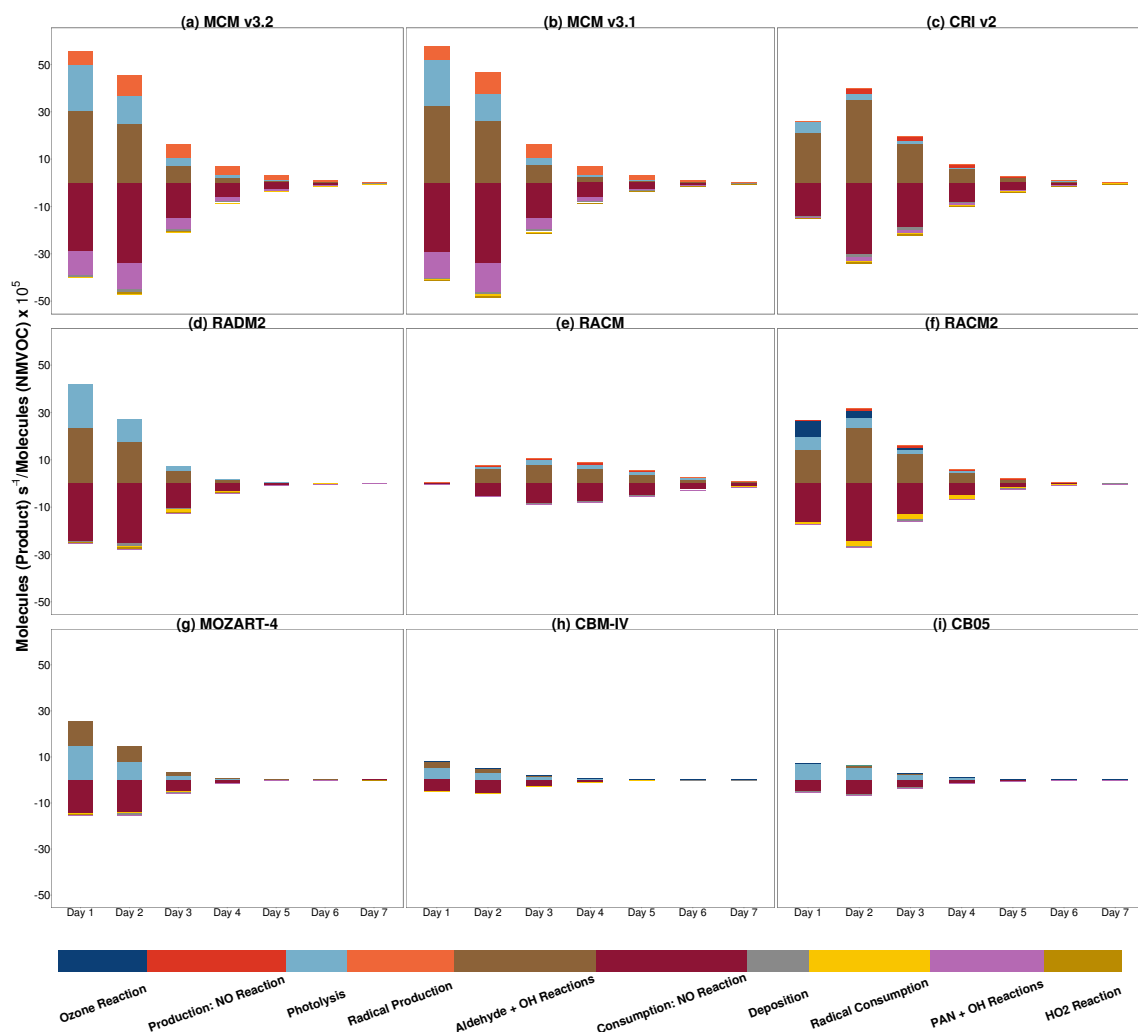
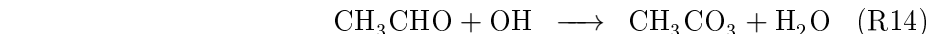


Figure 12: The processes contributing to PAN family production and loss during toluene degradation are shown for (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

400 and 12 respectively. Similar to the net radical budget analysis in Section 4.2, the largest differences are from alkane and aromatics degradation.

402 Overall, reactions of aldehydes with OH are the main PAN family source with (R14) being the most prominent. The reaction of NO with acyl peroxy radicals is the major
404 sink where (R15) is the main contributor. Other processes also impact production and consumption and these differ between mechanisms.

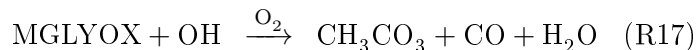
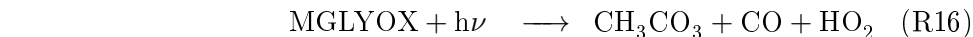


PAN family production in both MCM mechanisms is further fuelled by alkoxy radical
408 decomposition. This process is not included in any reduced mechanism and additional PAN family production is obtained through photolysis and reactions involving NO or O₃.

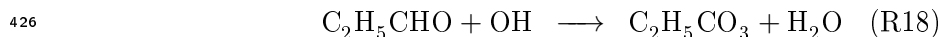
410 CBM-IV and CB05 do not include any additional PAN family sources in alkane degradation. Whilst during aromatic degradation the additional PAN family source due
412 to photolysis is minor. This results in lower net PAN family production compared to other mechanisms.

414 RADM2 has large net PAN family production regardless of the NMVOC type. The (R15) rate constant is $\sim 60\%$ slower than that of the MCM v3.2 rate constant resulting
416 in less PAN family consumption. This rate constant was updated in RACM whilst the rate constant of (R14) was not significantly changed. This leads to more PAN family
418 consumption in RACM and lower net PAN family production.

The detailed aromatic degradation chemistry of the MCM mechanisms produces the
420 largest net PAN family production. The main sources of PAN family in the MCM are methyl glyoxal photolysis (R16) and reaction with OH (R17).



In RADM2 and MOZART-4, (R16) and (R17) are also the main PAN family production
424 sources. This contrasts to CRI v2 and RACM2 where these reactions are not as significant as PAN family production from (R14) and (R18).



The PAN family production budgets in CRI v2 and RACM2 in Figure 12 peak on
428 the second day rather than the first, similar to their O_x production budgets in Figure
6. As outlined in Section 4.1, CRI v2 toluene degradation has a larger contribution from
430 degradation products with a carbon number three or less. This is reflected in CRI v2
PAN family production where the largest contributions are from reactions of CH_3CHO
432 and C_2H_5CHO .

The RACM2 ozonolysis reactions of unsaturated dicarbonyls are an additional PAN
434 family source not included in other mechanisms. These reactions have a double contribution
to PAN family production. Firstly, the mechanism acyl peroxy radical species RO3 is
436 produced which sets off a reaction chain with CH_3CHO , represented as ALD in RACM2,
being produced. These additional reactions result in a very different PAN family budget
438 when compared to MCM v3.2.

5 Conclusions

440 Tagged Ozone Production Potentials (TOPPs) were used to compare the NMVOC
degradation in reduced chemical mechanisms to the near-explicit MCM v3.2. The first
442 day NMVOC TOPP values in all mechanisms are generally comparable to those of the
MCM v3.2. TOPP value time series over multi-day scenarios have larger differences. Thus
444 differences in O_x production between reduced mechanisms and near-explicit mechanisms
has a larger impact over multi-day scenarios.

446 The largest discrepancies from the MCM v3.2 are the zero TOPP values of toluene
and m-xylene in RACM. These are due to the net O_x consumption from ozonolysis of
448 aromatic-OH adduct species.

Attributing O_x production budgets to the number of carbon atoms of each degradation
450 species showed that reduced mechanisms break down NMVOCs faster than near-explicit
mechanisms. This leads to reduced mechanisms being unable to reach the O_x levels of
452 near-explicit mechanisms.

Radical and PAN family production and consumption budgets were analysed in detail
454 through tagging. Photolysis is the main radical source in the MCM v3.2 whilst reduced
mechanisms also produce radicals by thermal reactions. This leads to larger net radical

456 production than in MCM v3.2.

Alkoxy radical decomposition is a PAN family production source in the MCM v3.2
458 that is substituted by thermal reactions or photolysis in reduced mechanisms. This leads
to different PAN family chemistry in reduced mechanisms which impacts both radical and
460 O_x production.

The tagging approach and TOPP calculation over multi-day scenarios have proven to
462 be a useful tool in comparing the chemical degradation pathways in chemical mechanisms.
This approach could be used to further investigate how mechanisms treat degradation
464 chemistry under more realistic NO_x conditions or a range of NO_x conditions, simulating
different atmospheric regimes.

466

Acknowledgem
section

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