

# A Comparison of Chemical Mechanisms using Tagged Ozone Production Potential (TOPP) Analysis: Supplementary Material

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## S1 Introduction

This is the supplementary material to the research paper “A Comparison of Chemical Mechanisms using Tagged Ozone Production Potential (TOPP) Analysis”. It provides further information about the methodology and additional analysis.

## S2 Mechanism Setup

All chemical mechanisms were adapted into the modularised KPP (Damian et al., 2002) format from their original format for use in the MECCA boxmodel (Sander et al., 2005) as modified by (Butler et al., 2011).

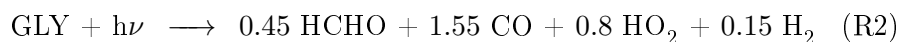
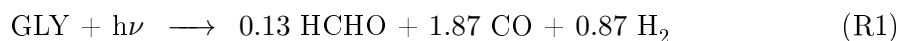
The MCM v3.2 (Jenkin et al., 1997, 2003; Saunders et al., 2003; Bloss et al., 2005; Rickard et al., 2014) was the reference mechanism. Its approach to inorganic chemistry, dry deposition, photolysis and treatment of peroxy radical–peroxy radical reactions were applied to all mechanisms.

## S2.1 Photolysis

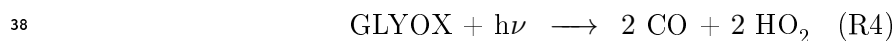
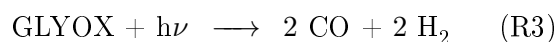
20 Photolysis was parameterised as a function of the solar zenith angle as per the MCM  
 approach (Saunders et al., 2003). Species from reduced mechanisms having a direct MCM  
 22 v3.2 counterpart were assigned the corresponding MCM v3.2 photolysis rate. Otherwise the  
 recommended mechanism rate was used to determine the appropriate MCM v3.2 photolysis  
 24 rate. In some cases this was the MCM v3.2 photolysis rate closest in magnitude to that  
 specified in the mechanism.

26 For example, in RACM2 the organic nitrate species ONIT has a photolysis rate of  
 $1.96 \times 10^{-6} \text{ s}^{-1}$  that was compared to the MCM v3.2 organic nitrate photolysis rates  
 28 ( $J_{51} - J_{57}$ ). The rate parameter  $J_{54}$  had the most similar magnitude and was assigned as  
 the ONIT photolysis rate in RACM2.

30 Photolysis of a reduced mechanism species was sometimes represented by more than  
 one MCM v3.2 photolysis reaction. The product yields of the original mechanism reaction  
 32 was preserved using combinations of the MCM v3.2 rates. This approach was used for  
 glyoxal photolysis in RADM2. Glyoxal photolysis in RADM2 is described by (R1) and  
 34 (R2).



36 Whereas in the MCM v3.2, (R3), (R4) and (R5) are prescribed for glyoxal photolysis with  
 the rates  $J_{31}$ ,  $J_{32}$  and  $J_{33}$  respectively.



The product yields of (R1) were retained using a photolysis rate of  $0.87 J_{31} + 0.13 J_{32}$ ,  
 40 whilst for (R2) the rate  $0.15 J_{31} + 0.45 J_{32} + 0.4 J_{33}$  was used. Table S1 illustrates the  
 product yield calculations.

## 42 S2.2 Organic Peroxy Radical Self and Cross Reactions

Reactions of organic peroxy radicals ( $\text{RO}_2$ ) with other organic peroxy radicals are  
 44 divided into self ( $\text{RO}_2 + \text{RO}_2$ ) and cross ( $\text{RO}_2 + \text{R}'\text{O}_2$ ) reactions. These reactions are

	Rate	MCM v3.2 Product Yields
(R1)	0.87 J <sub>31</sub>	1.74 CO + 0.87 H <sub>2</sub>
	0.13 J <sub>32</sub>	0.13 CO + 0.13 HCHO
	0.87 J <sub>31</sub> + 0.13 J <sub>32</sub>	1.87 CO + 0.13 HCHO + 0.87 H <sub>2</sub>
(R2)	0.15 J <sub>31</sub>	0.30 CO + 0.15 H <sub>2</sub>
	0.45 J <sub>32</sub>	0.45 CO + 0.45 HCHO
	0.4 J <sub>33</sub>	0.80 CO + 0.80 HO <sub>2</sub>
	0.15 J <sub>31</sub> + 0.45 J <sub>32</sub> + 0.4 J <sub>33</sub>	1.55 CO + 0.45 HCHO + 0.80 HO <sub>2</sub> + 0.15 H <sub>2</sub>

Table S1: Calculation of glyoxal MCM v3.2 photolysis rates keeping RADM2 glyoxyl product yields.

Mechanism	Reaction	Rate Constant
MCM v3.2	C2H5O2 = C2H5O	$k \cdot \text{RO2} \cdot 0.6 \text{ s}^{-1}$
	C2H5O2 = C2H5OH	$k \cdot \text{RO2} \cdot 0.2 \text{ s}^{-1}$
	C2H5O2 = CH3CHO	$k \cdot \text{RO2} \cdot 0.2 \text{ s}^{-1}$
MOZART-4	C2H5O2 + CH3O2 = 0.7 CH2O + 0.8 CH3CHO + HO2 + 0.3 CH3OH + 0.2 C2H5OH	$2 \times 10^{-13} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
	C2H5O2 + C2H5O2 = 1.6 CH3CHO + 1.2 HO2 + 0.4 C2H5OH	$6.8 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
MOZART-4 modified	C2H5O2 = 0.8 CH3CHO + 0.6 HO2 + 0.2 C2H5OH	$2 \times 10^{-13} \cdot \text{RO2} \text{ s}^{-1}$

Table S2: Ethyl peroxy radical (C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>) self and cross organic peroxy reactions in the MCM v3.2 and MOZART-4 mechanisms including rate constants.  $k = 2(6.6 \times 10^{-27} \exp(365/T))^{\frac{1}{2}} \text{ molecules}^{-1} \text{ s}^{-1}$  and RO2 is the sum of all organic peroxy radical mixing ratios.

Reactants	Products	Rate Constant
MO2 + MO2	0.74 HO2 + 1.37 HCHO + 0.63 MOH	$9.4 \times 10^{-14} \exp(390/T) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
MO2	0.37 HO2 + 0.685 HCHO + 0.315 MOH	$9.4 \times 10^{-14} \exp(390/T) \cdot \text{RO2} \text{ s}^{-1}$
ETHP + MO2	HO2 + 0.75 HCHO + 0.75 ACD + 0.25 MOH + 0.25 EOH	$1.18 \times 10^{-13} \exp(158/T) \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
ETHP	0.63 HO2 + 0.065 HCHO + 0.75 ACD + 0.25 EOH	$1.18 \times 10^{-13} \exp(158/T) \cdot \text{RO2} \text{ s}^{-1}$

Table S3: Dermination of ETHP pseudo-unimolecular reaction and rate constant in RACM2 including rate constants. RO2 is the sum of all organic peroxy radical mixing ratios.

typically represented in chemical mechanisms as bimolecular reactions which would cause  
46 ambiguities when implementing the tagging scheme. Namely, which tag to be used for the  
products of reactions between  $\text{RO}_2$  having different tags. To avoid such ambiguities, the  
48 MCM v3.2 approach to self and cross  $\text{RO}_2$  reactions is used – all  $\text{RO}_2$  react with  $\text{RO}_2$  and  
 $\text{R}'\text{O}_2$  at a single uniform rate. This was represented as a pseudo-unimolecular reaction  
50 whose rate constant includes a factor ‘RO2’ which was the sum of the mixing ratios of all  
organic peroxy radicals (Saunders et al., 2003).

52 The pseudo-unimolecular reaction products and their yields were determined either  
by using the  $\text{RO}_2 + \text{RO}_2$  reaction and halving the product yields. This is demonstrated  
54 for the MOZART-4 treatment of the ethyl peroxy radical in Table S2. Alternatively, the  
 $\text{RO}_2 + \text{CH}_3\text{O}_2$  reaction was used and the products due to  $\text{CH}_3\text{O}_2$  were removed. Table S3  
56 outlines the steps taken to determine the EHP pseudo-unimolecular reaction in RACM2.

First the products due to  $\text{MO}_2$ , which represents  $\text{CH}_3\text{O}_2$  in RACM2, are determined  
58 as outlined above using the  $\text{MO}_2 + \text{MO}_2$  reaction. The  $\text{MO}_2$  product yields are then  
subtracted from the EHP +  $\text{MO}_2$  reaction. Any products having a negative yield were  
60 not included in the final pseudo-unimolecular reaction.

The methyl acyl peroxy radical ( $\text{CH}_3\text{C}(\text{O})\text{O}_2$ ) was the exception to the above  
62 approach. Although most mechanisms include a  $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2$  reaction, its  
pseudo-unimolecular reaction was derived by subtracting the  $\text{CH}_3\text{O}_2$  product yields from  
64 the  $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{O}_2$ . This approach was used as the  $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{CH}_3\text{O}_2$  reaction  
is the most significant reaction for  $\text{CH}_3\text{C}(\text{O})\text{O}_2$ .

66 The rate constant for each pseudo-unimolecular reaction was taken as that of the  
 $\text{RO}_2 + \text{CH}_3\text{O}_2$  reaction multiplied by an ‘RO2’ factor, which is the sum of the mixing  
68 ratios of all organic peroxy radicals. The  $\text{RO}_2 + \text{CH}_3\text{O}_2$  rate constant was chosen as this  
is the most likely reaction to occur in the atmosphere.

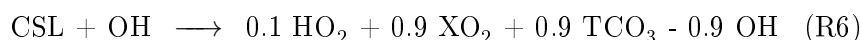
## 70 S2.3 Dry Deposition

Dry deposition velocities were taken from the MCM v3.2. The dry deposition velocity of  
72 MCM v3.2 species of the same chemical functional group was used for mechanism species  
without direct MCM v3.2 analogues. For example, the dry deposition velocity of PAN  
74 species in all mechanisms was equivalent to that of the PAN species in the MCM v3.2.

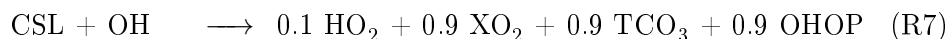
## S2.4 Negative Product Yield Treatment

Some mechanisms include reactions where certain products have a negative yield. These reactions were re-written including an operator species with a positive yield as the analysis tools used in this study does not allow use of negative product yields. The operator species acts as a sink for the original product by immediately reacting with the original product generating a ‘NULL’ product.

For example, in RADM2 the reaction of cresol (CSL) with OH has negative OH yield (R6).



The negative OH yield was adapted to a positive operator (OHOP) yield (R7) which then immediately reacts with OH giving a ‘NULL’ product with a rate constant of  $8.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (R8). Thus preserving the OH yields using the original mechanism.



## S3 Octane $\text{O}_x$ Budget Analysis

The RADM2, RACM and RACM2 octane TOPP value time series presented in the paper differ from the MCM v3.2 time series by not reaching their maximum TOPP value on the second day. The attribution of  $\text{O}_x$  production from octane degradation in MCM v3.2, RADM2, RACM and RACM2 to the number of carbon atoms of the degradation products is depicted in Figure S1.

First day  $\text{O}_x$  production is similar between the mechanisms. However second day  $\text{O}_x$  production in RADM2, RACM and RACM2 from octane degradation products having a carbon number between five and three is lower than in MCM v3.2. There is also no  $\text{O}_x$  production from degradation products having six carbon atoms. Thus octane is broken down so quickly that it cannot reach maximum  $\text{O}_x$  production on the second day, which is a feature of alkane degradation.

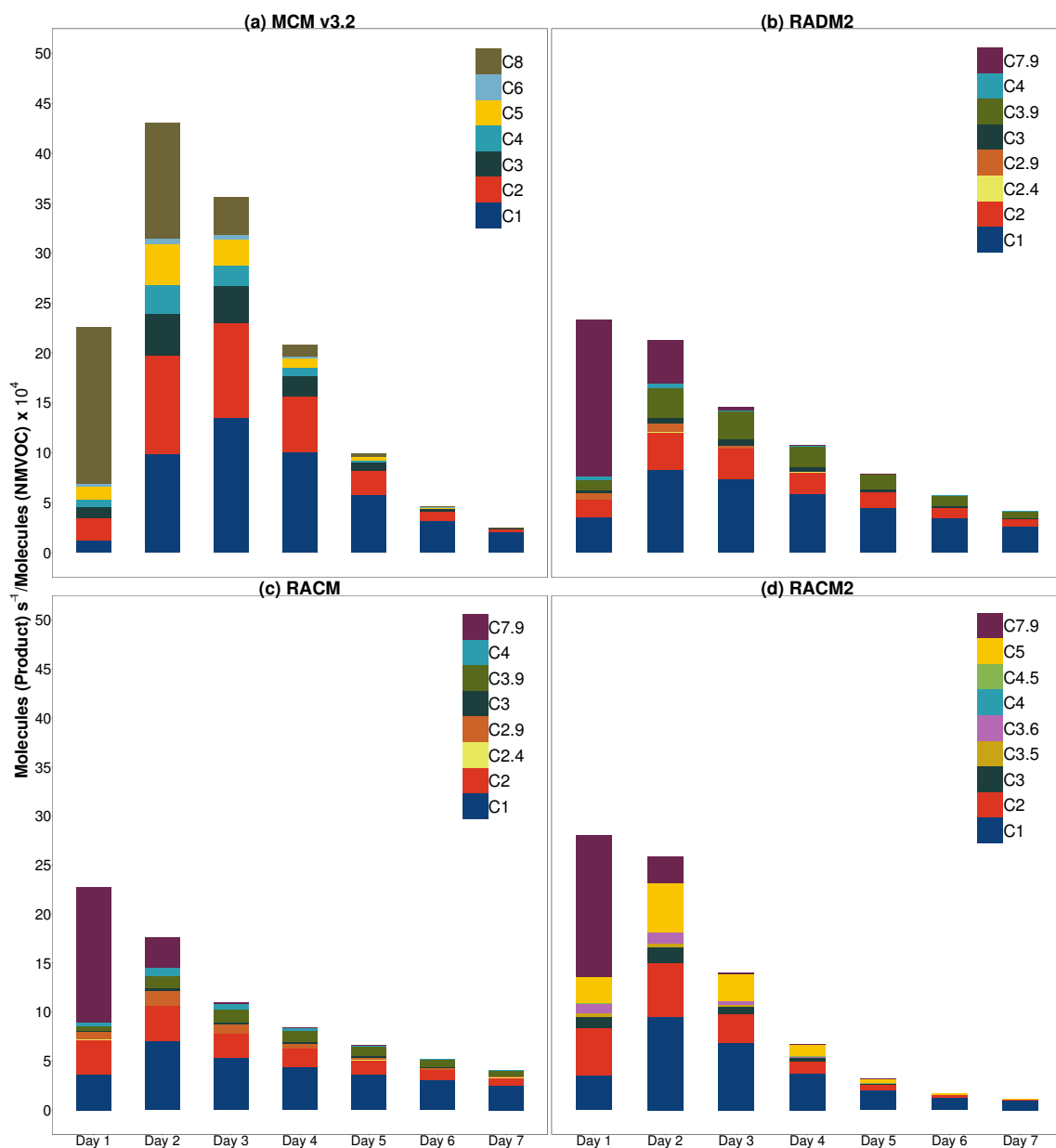


Figure S1: The  $O_x$  production budgets from octane degradation attributed to the number of carbon atoms in (a) MCM v3.2, (b) RADM2, (c) RACM and (d) RACM2.

Mechanism	Photolysis Pathway	Rate Parameter
MCM v3.2	$GLYOX + h\nu = CO + CO + H_2$	$J_{31}$
	$GLYOX + h\nu = HCHO + CO$	$J_{32}$
	$GLYOX + h\nu = CO + CO + HO_2 + HO_2$	$J_{33}$
CRI v2	$CARB3 + h\nu = CO + CO + HO_2 + HO_2$	$J_{33}$

Table S4: Glyoxal photolysis in MCM v3.2 and CRI v2 with specified rate parameters.

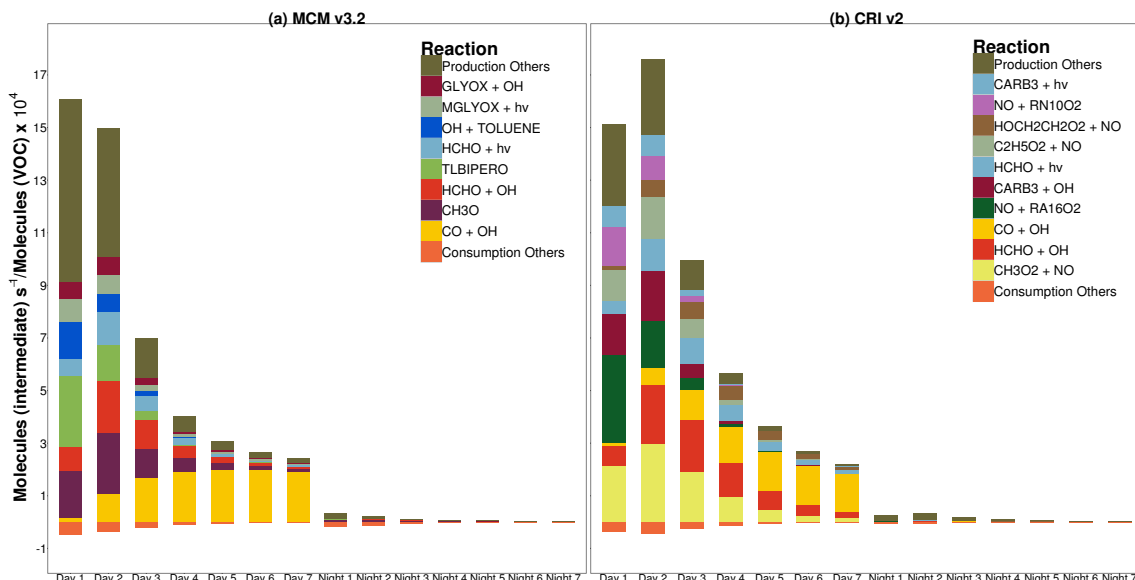


Figure S2: The  $\text{HO}_{2x}$  production budgets from toluene degradation attributed to the responsible reactions in (a) MCM v3.2 and (b) CRI v2.

## S4 Toluene $\text{HO}_{2x}$ Budget Analysis

The paper showed that the CRI v2 maximum daily toluene TOPP value is reached on the second day whilst in the MCM v3.2 this is reached on the first. Figure S2 illustrates the  $\text{HO}_{2x}$  production budget allocated to the responsible reactions for both the MCM v3.2 and CRI v2. The  $\text{HO}_{2x}$  production from the reaction of CARB3 and OH in CRI v2 has a larger contribution than its corresponding reaction ( $\text{GLYOX} + \text{OH}$ ) in the MCM v3.2.

Despite glyoxal being represented as CARB3 in CRI v2 and GLYOX in MCM v3.2, there are many differences in how glyoxal chemistry is treated. In CRI v2, CARB3 is only produced from aromatic degradation whilst GLYOX is a degradation product of many other non-aromatic NMVOCs in MCM v3.2.

Glyoxal degradation is through reaction with OH radical and photolysis in CRI v2. Extra degradation options are available in MCM v3.2. Moreover, the rate constant for the reaction with OH radical is  $\sim 15\%$  faster in CRI v2 than in MCM v3.2.

Glyoxal has three available photolysis pathways in MCM v3.2 and only one in CRI v2. These photolysis pathways and their rate parameters are outlined in Table S4. The additional photolysis pathways in MCM v3.2 are non- $\text{HO}_{2x}$  producing pathways leading to less  $\text{HO}_{2x}$  production.

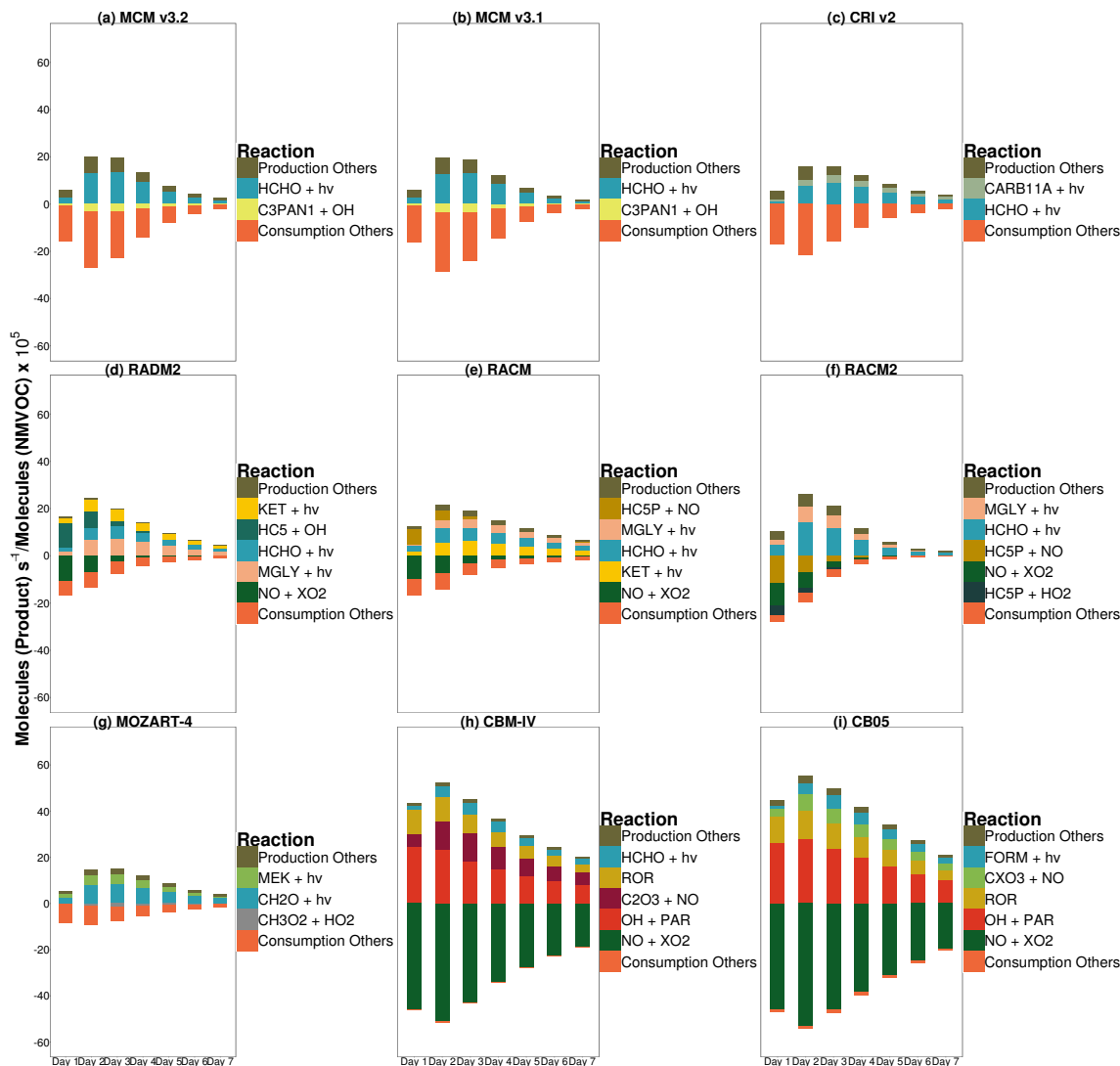


Figure S3: The radical family production and loss budgets from pentane degradation attributed to the responsible reactions in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

The combination of the higher rate constant for the glyoxal reaction with OH radical and additional  $\text{HO}_{2x}$  production during CRI v2 photolysis are responsible for the higher  $\text{HO}_{2x}$  production in CRI v2.

## S5 Radical and PAN Family Budgets – Additional Plots

In the paper, net radical and PAN family production budgets from alkane, alkene and aromatic degradation was analysed for all mechanisms. As the largest differences were due to alkane and aromatic degradation, the pentane and toluene production and loss budgets



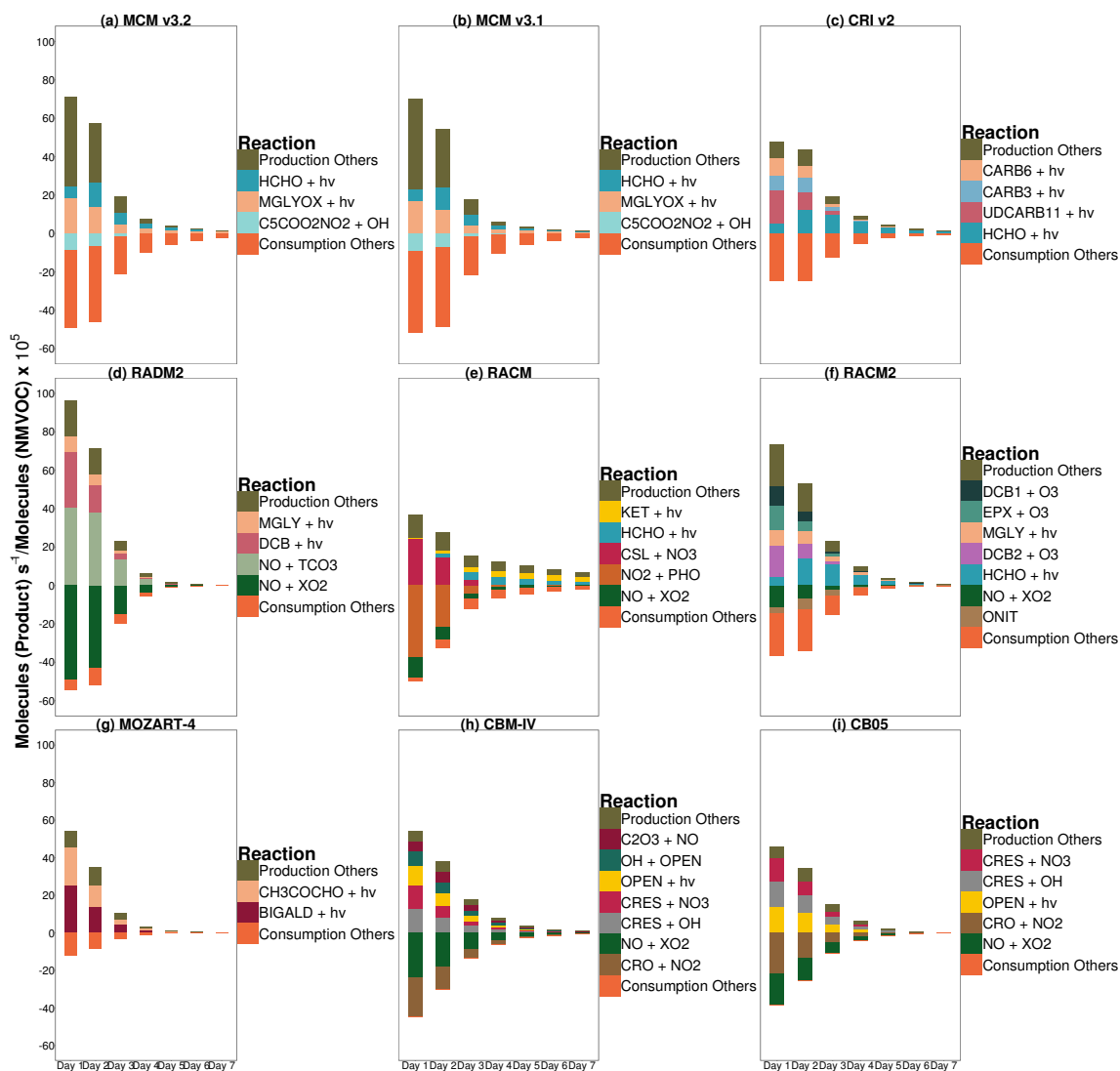


Figure S4: The radical family production and loss budgets from toluene degradation attributed to the responsible reactions in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

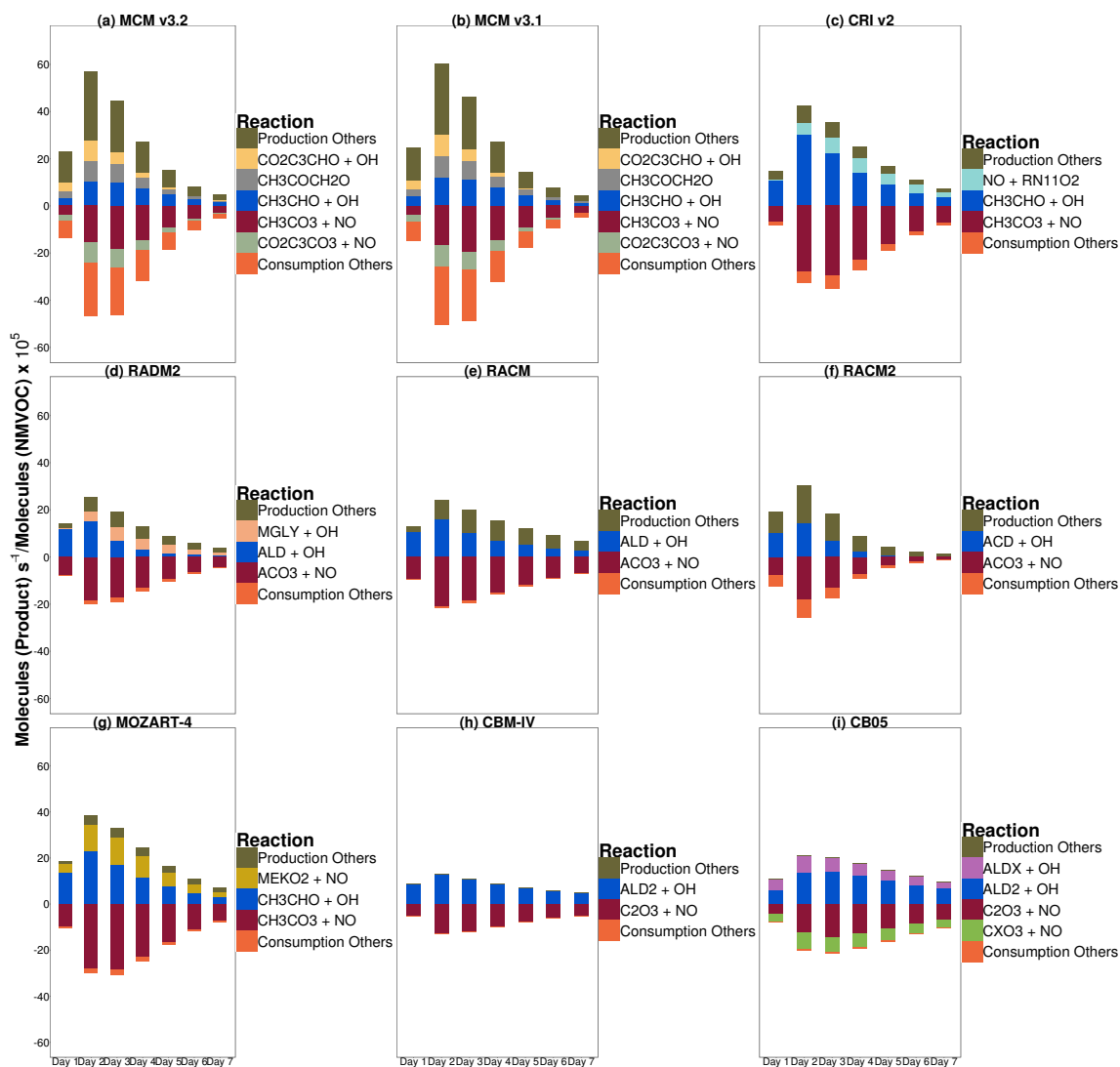


Figure S5: The PAN family production and loss budgets from pentane degradation attributed to the responsible reactions in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

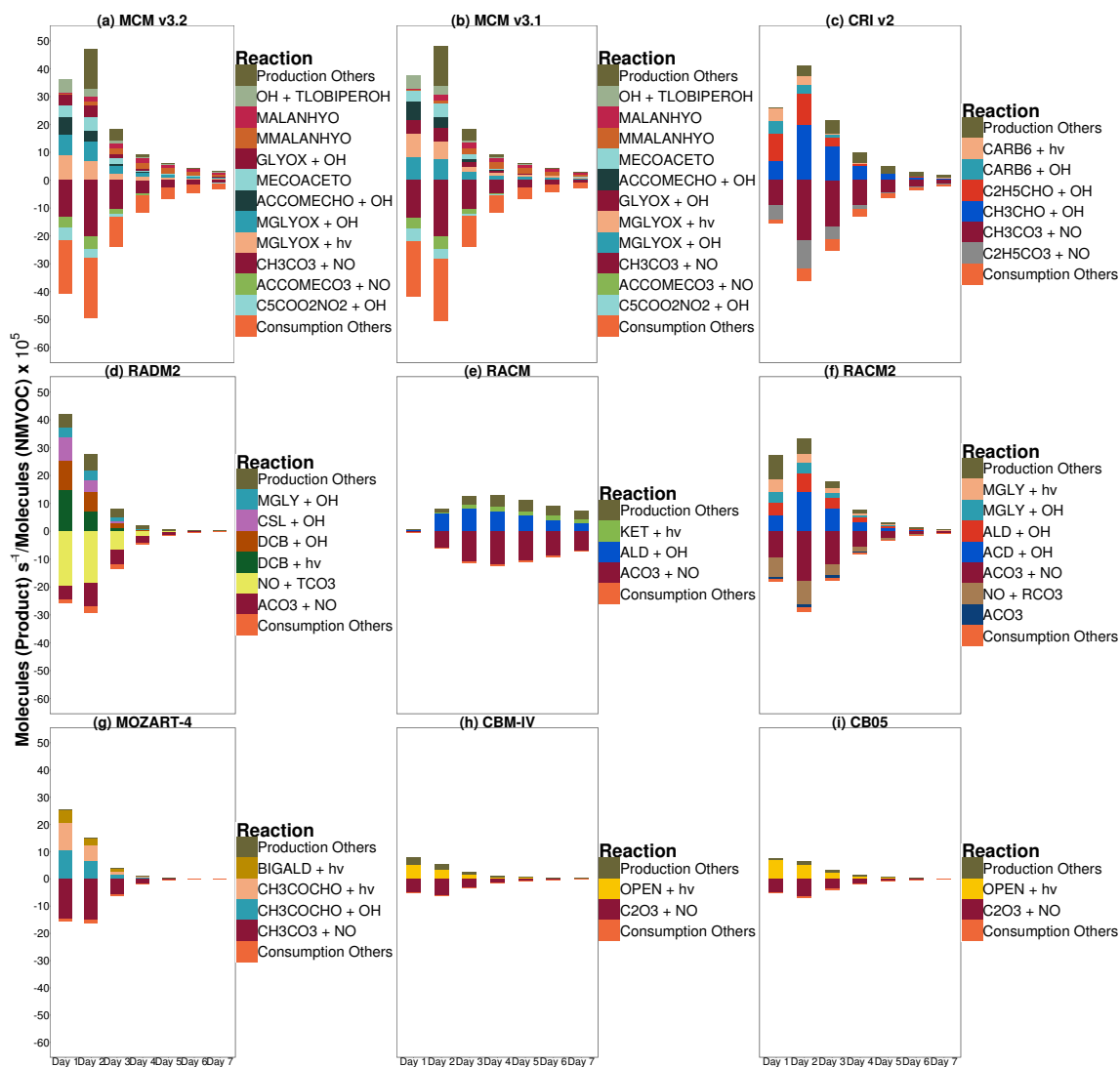


Figure S6: The PAN family production and loss budgets from toluene degradation attributed to the responsible reactions in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

124 from each mechanism was attributed to the responsible processes. These processes are  
further broken down to the individual reactions.

126 Figures S3 and S4 depict the reactions contributing to the radical family production  
and loss budgets of pentane and toluene degradation respectively. Whilst the reactions  
128 responsible for PAN family production and consumption are illustrated in Figure S5 and  
Figure S6.

## References

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