

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

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August 21, 2014

## 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., 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.

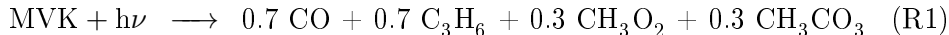
### S2.1 Photolysis

Photolysis was parameterised as a function of the solar zenith angle as per the MCM approach (Saunders et al., 2003). Mechanism species with a direct MCM v3.2 counterpart

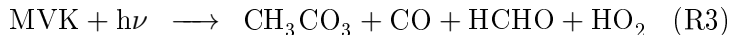
were assigned the corresponding MCM v3.2 photolysis rate parameter. Otherwise the  
 22 mechanism’s literature was used to determine the appropriate MCM v3.2 photolysis rate  
 parameter. In some cases this was the MCM v3.2 photolysis rate parameter closest in  
 24 magnitude to that specified in the mechanism.

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

Photolysis of a mechanism species was sometimes represented by more than one  
 30 MCM v3.2 photolysis reaction. The product yield of the original mechanism reaction  
 was preserved by using a combination of the MCM v3.2 rate parameters. For example, the  
 32 photolysis of methyl vinyl ketone (MVK) in MOZART-4 is described by the reaction



34 Whereas in the MCM v3.2 it is described by two reactions



36 where the photolysis parameters for reactions (R2) and (R3) are designated as  $J_{23}$  and  
 $J_{24}$ , respectively. In order to keep the product yield as prescribed in MOZART-4, the  
 38 photolysis rate parameter assigned to MVK photolysis using the MOZART-4 mechanism  
 is  $0.7 J_{23} + 0.3 J_{24}$ .

## 40 **S2.2 Organic Peroxy Radical Self and Cross Reactions**

Reactions of organic peroxy radicals ( $\text{RO}_2$ ) with other organic peroxy radicals are  
 42 divided into self ( $\text{RO}_2 + \text{RO}_2$ ) and cross ( $\text{RO}_2 + \text{R}'\text{O}_2$ ) reactions. These reactions are  
 typically represented in chemical mechanisms as bimolecular reactions which would cause  
 44 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  
 46 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

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

Table S1: Ethyl peroxy radical ( $\text{C}_2\text{H}_5\text{O}_2$ ) 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
$\text{MO2} + \text{MO2}$	$0.74 \text{ HO2} + 1.37 \text{ HCHO} + 0.63 \text{ MOH}$	$9.4 \times 10^{-14} \exp(390/T)$ $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
$\text{MO2}$	$0.37 \text{ HO2} + 0.685 \text{ HCHO} + 0.315 \text{ MOH}$	$9.4 \times 10^{-14} \exp(390/T)*\text{RO2}$ $\text{s}^{-1}$
$\text{ETHP} + \text{MO2}$	$\text{HO2} + 0.75 \text{ HCHO} + 0.75 \text{ ACD}$ $+ 0.25 \text{ MOH} + 0.25 \text{ EOH}$	$1.18 \times 10^{-13} \exp(158/T)$ $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
$\text{ETHP}$	$0.63 \text{ HO2} + 0.065 \text{ HCHO} + 0.75 \text{ ACD}$ $+ 0.25 \text{ EOH}$	$1.18 \times 10^{-13} \exp(158/T)*\text{RO2}$ $\text{s}^{-1}$

Table S2: 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.

48 whose rate constant includes a factor ‘RO2’ which was the sum of the mixing ratios of all organic peroxy radicals (Saunders et al., 2003).

50 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 52 for the MOZART-4 treatment of the ethyl peroxy radical in Table S1. 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 S2 54 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 56 as outlined above using the  $\text{MO}_2 + \text{MO}_2$  reaction. The  $\text{MO}_2$  product yields are then subtracted from the  $\text{EHP} + \text{MO}_2$  reaction. Any products having a negative yield were 58 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 60 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 62 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  $\text{CH}_3\text{C}(\text{O})\text{O}_2$ .

64 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 66 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.

## 68 **S2.3 Dry Deposition**

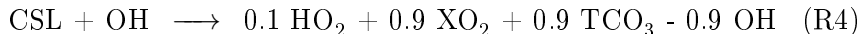
Dry deposition velocities were taken from the MCM v3.2. The dry deposition velocity of 70 MCM v3.2 species of the same chemical functional group was used for mechanism species without direct MCM v3.2 analogues. For example, the dry deposition velocity of PAN 72 species in all mechanisms was equivalent to that of the PAN species in the MCM v3.2.

## **S2.4 Negative Product Yield Treatment**

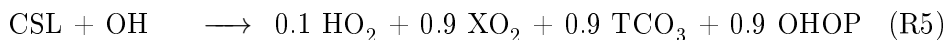
74 Some mechanisms include reactions where certain products have a negative yield. These reactions were re-written including an operator species with a positive yield as the analysis 76 tools used in this study does not allow use of negative product yields. The operator species

acts as a sink for the original product by immediately reacting with the original product  
 78 generating a ‘NULL’ product.

For example, in RADM2 the reaction of cresol (CSL) with OH has negative OH yield  
 80 (R4).



82 The negative OH yield was adapted to a positive operator (OHOP) yield (R5) which  
 then immediately reacts with OH giving a ‘NULL’ product with a rate constant of  
 84  $8.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (R6). Thus preserving the OH yields using the original mechanism.



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

The RADM2, RACM and RACM2 octane TOPP value time series presented in the paper  
 88 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,  
 90 RADM2, RACM and RACM2 to the number of carbon atoms of the degradation products  
 is depicted in Figure S1.

92 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  
 94 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  
 96 down so quickly that it cannot reach maximum  $\text{O}_x$  production on the second day, which  
 is a feature of alkane degradation.

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

The paper showed that the CRI v2 maximum daily toluene TOPP value is reached on the  
 100 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  
 102 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.

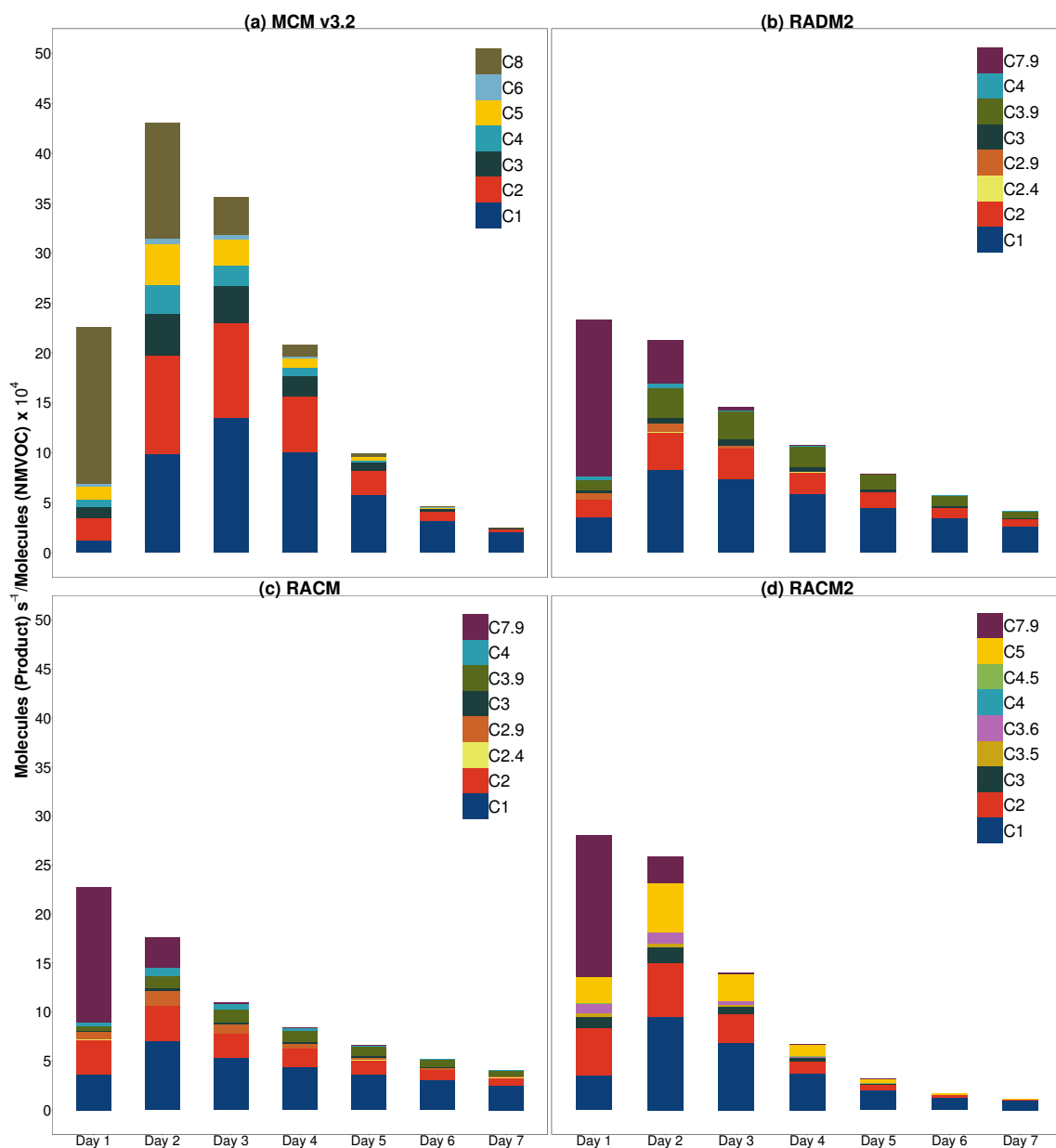


Figure S1: The  $O_x$  production budgets from octane degradation attributed to the number of carbon atoms in (a) MCM v3.2, (b) RADM2, (c) RACM and (d) RACM2.

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 S3: Glyoxal photolysis in MCM v3.2 and CRI v2 with specified rate parameters.

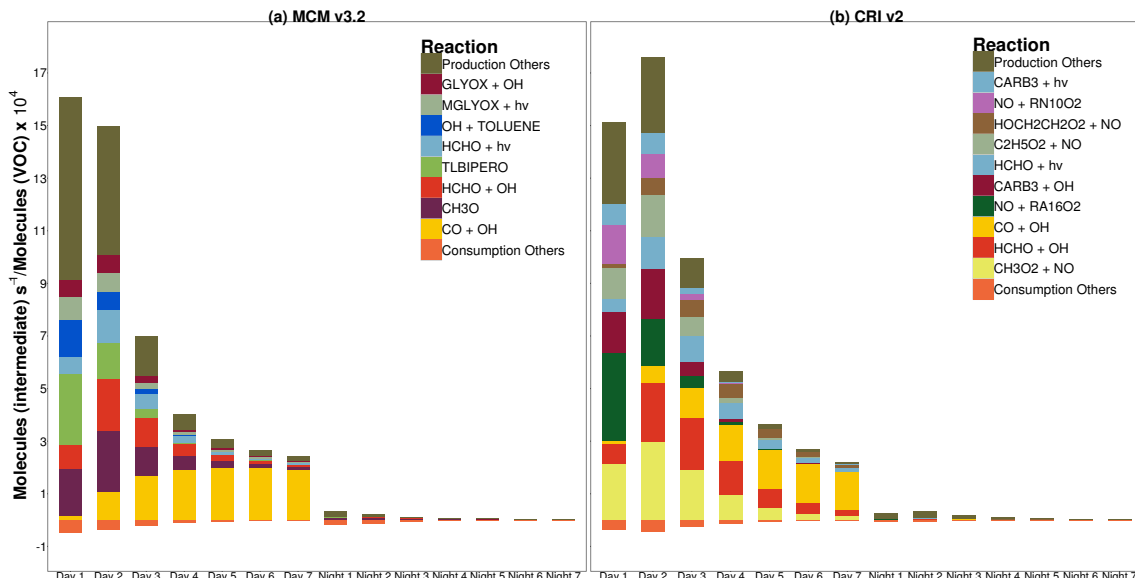


Figure S2: The  $\text{HO}_{2x}$  production budgets from toluene degradation attributed to the responsible reactions in (a) MCM v3.2 and (b) CRI v2.

104 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  
106 produced from aromatic degradation whilst GLYOX is a degradation product of many  
other non-aromatic NMVOCs in MCM v3.2.

108 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  
110 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.  
112 These photolysis pathways and their rate parameters are outlined in Table S3. The  
additional photolysis pathways in MCM v3.2 are non- $\text{HO}_{2x}$  producing pathways leading  
114 to less  $\text{HO}_{2x}$  production.

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

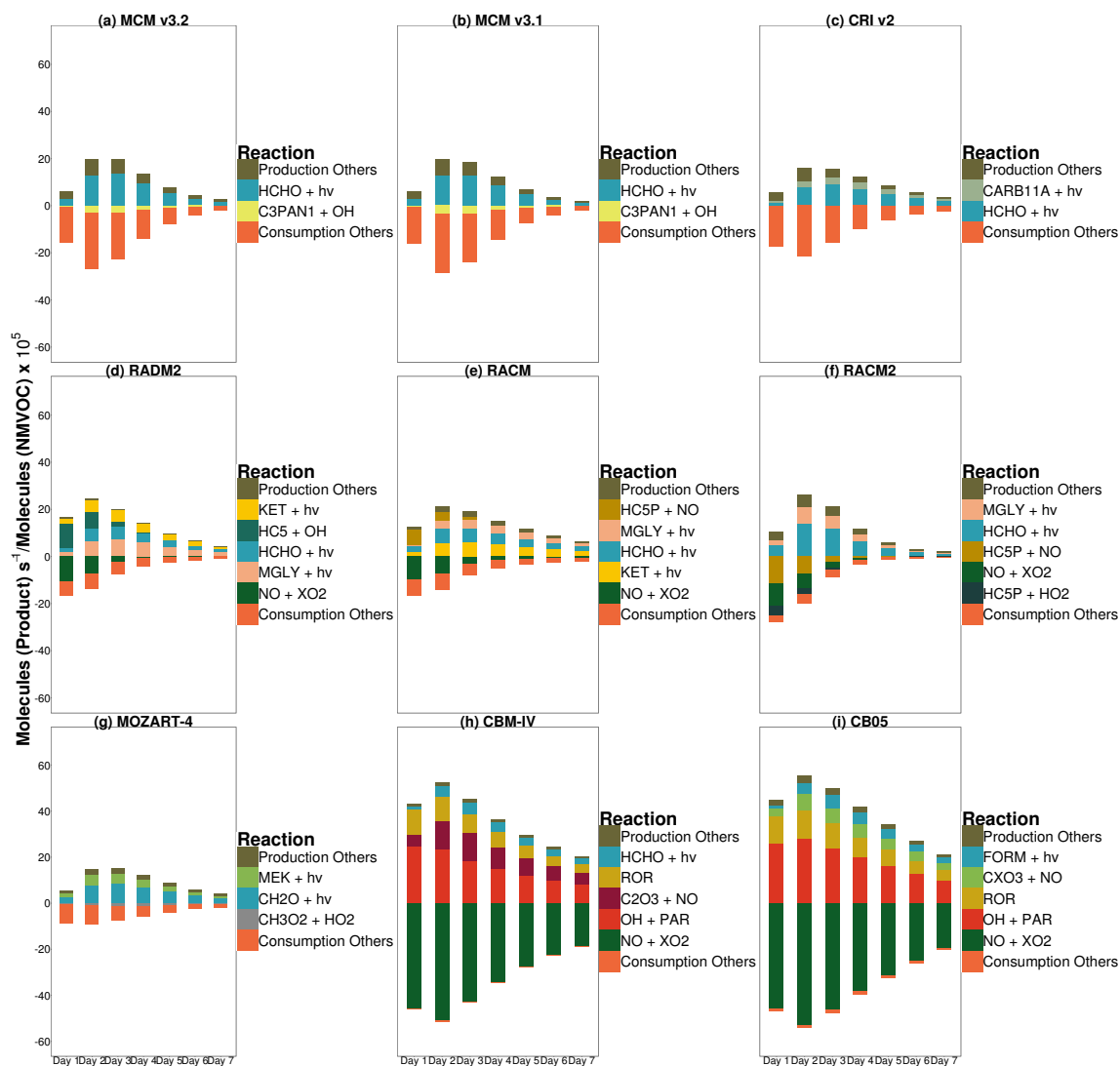


Figure S3: The radical family production and loss budgets from pentane degradation attributed to the responsible reactions in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.



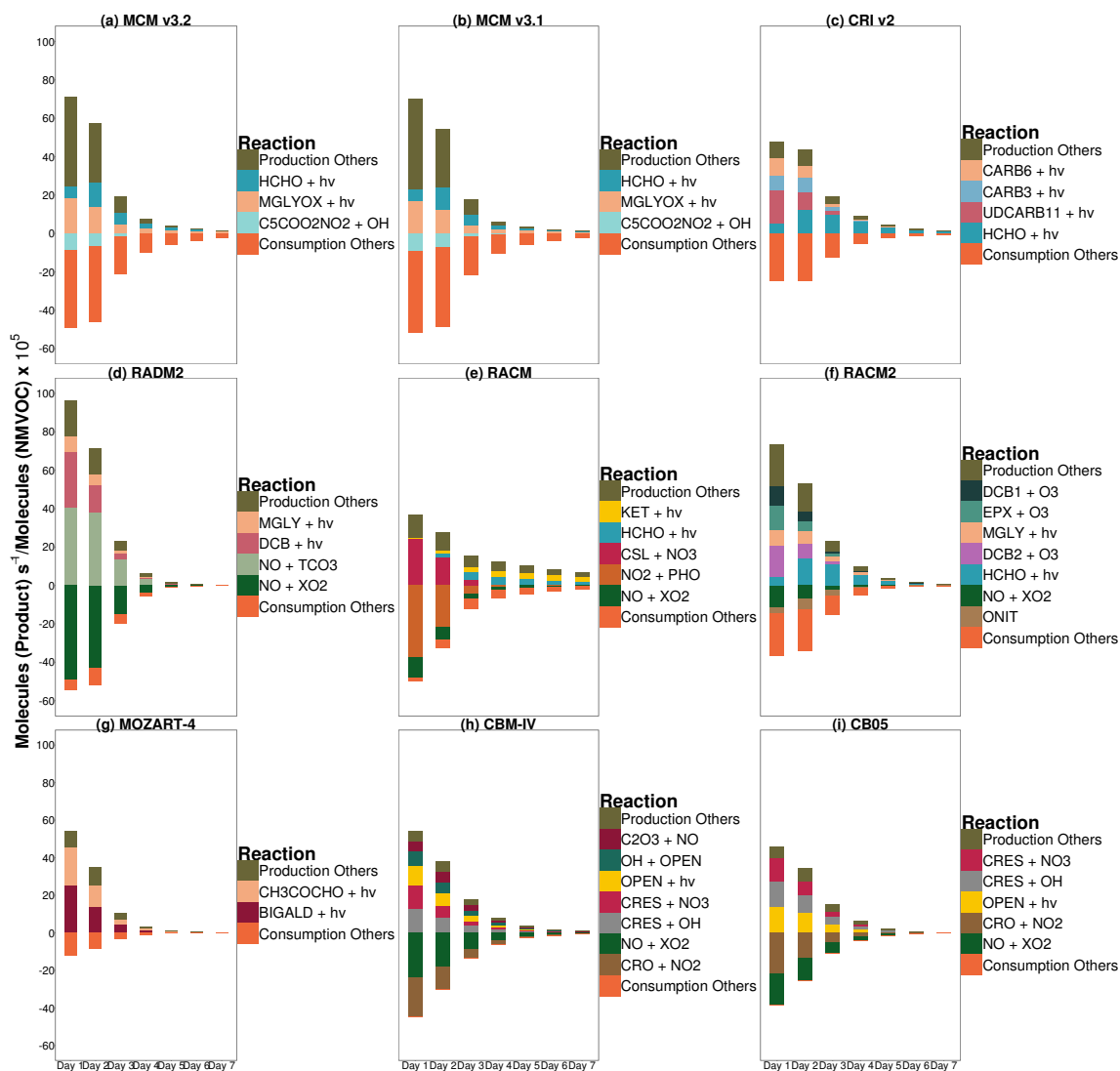


Figure S4: The radical family production and loss budgets from toluene degradation attributed to the responsible reactions in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

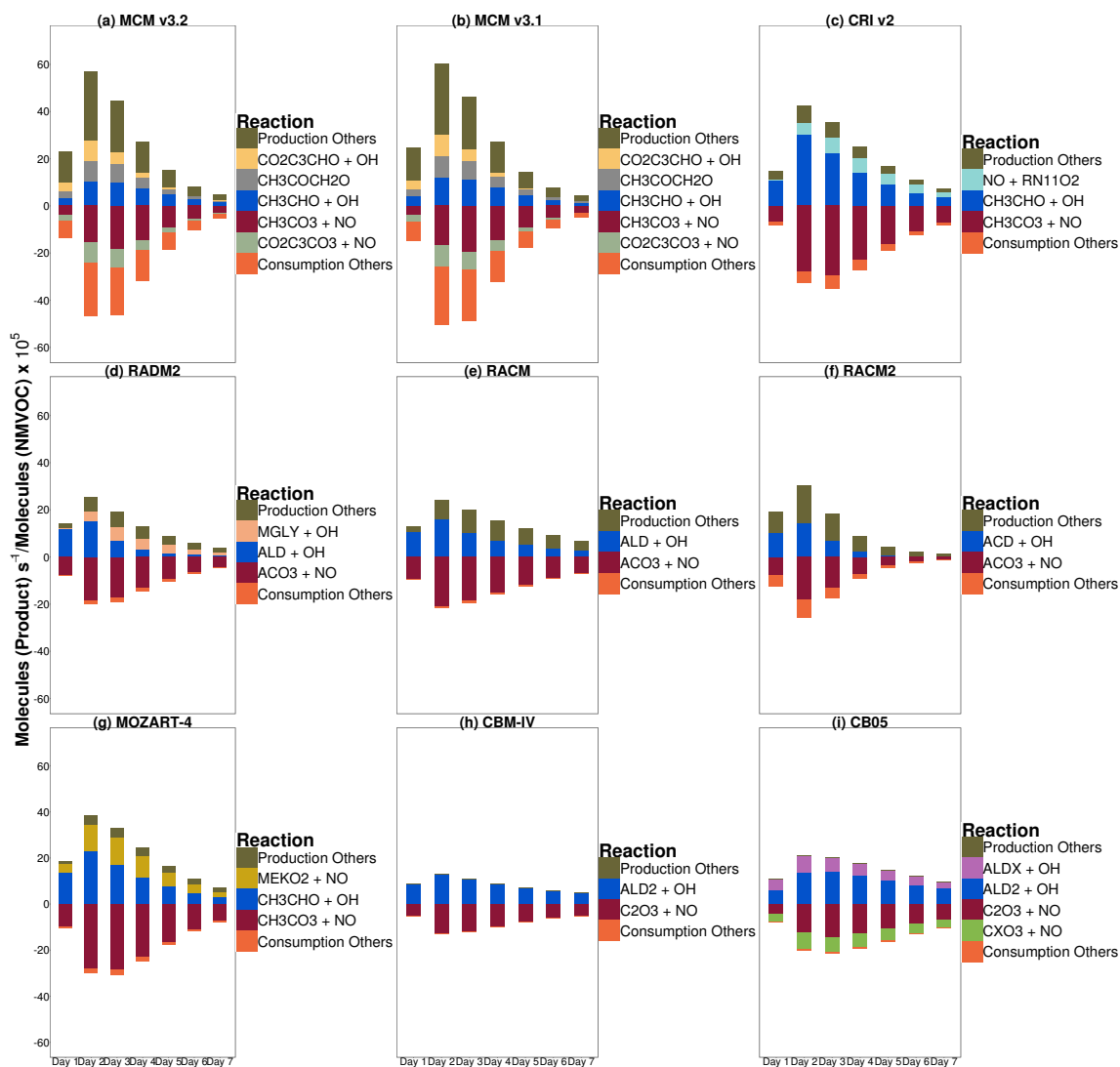


Figure S5: The PAN family production and loss budgets from pentane degradation attributed to the responsible reactions in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

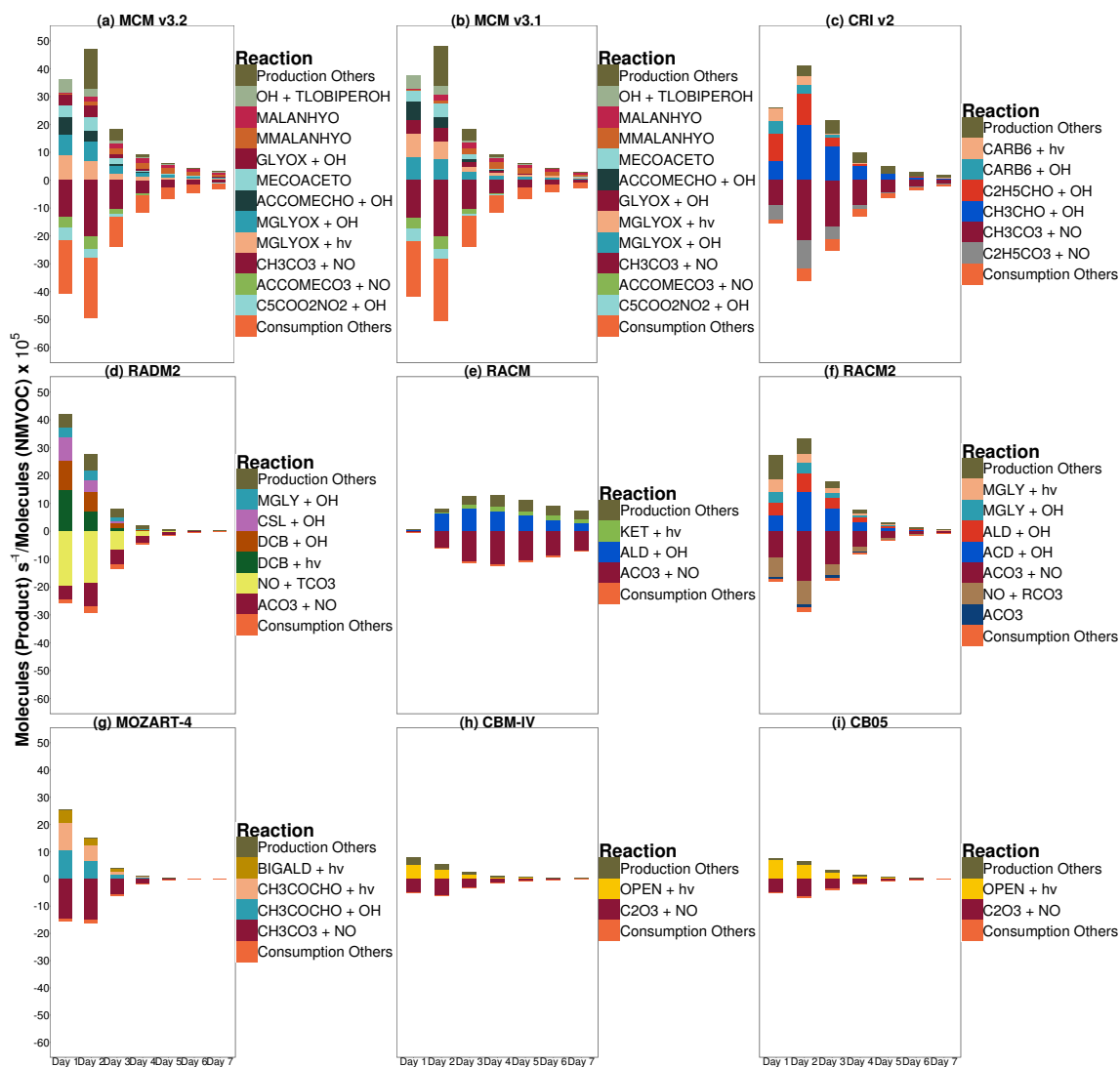


Figure S6: The PAN family production and loss budgets from toluene degradation attributed to the responsible reactions in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

## 118 **S5 Radical and PAN Family Budgets – Additional Plots**

In the paper, net radical and PAN family production budgets from alkane, alkene and  
120 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  
122 from each mechanism was attributed to the responsible processes. These processes are  
further broken down to the individual reactions.

124 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  
126 responsible for PAN family production and consumption are illustrated in Figure S5 and  
Figure S6.

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