

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).

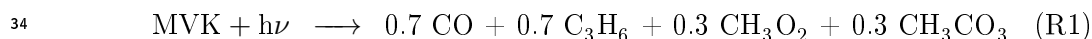
The MCM v3.2 (Jenkin et al., 1997, 2003; Saunders et al., 2003; Bloss et al., 2005; Rickard et al., 2014) was the reference mechanism. Its approach to inorganic chemistry, dry deposition, photolysis and treatment of peroxy radical–peroxy radical reactions were applied to all mechanisms.

S2.1 Photolysis

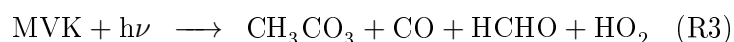
20 Photolysis was parameterised as a function of the solar zenith angle as per the MCM
approach (Saunders et al., 2003). Mechanism species with a direct MCM v3.2 counterpart
22 were assigned the corresponding MCM v3.2 photolysis rate parameter. Otherwise the
mechanism’s literature was used to determine the appropriate MCM v3.2 photolysis rate
24 parameter. In some cases this was the MCM v3.2 photolysis rate parameter 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 rate
28 parameters ($J_{51} - J_{57}$). The rate parameter J_{54} was the most similar and this was assigned
as the ONIT photolysis rate parameter in RACM2.

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



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



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

S2.2 Organic Peroxy Radical Self and Cross Reactions

42 Reactions of organic peroxy radicals (RO_2) with other organic peroxy radicals are
divided into self ($\text{RO}_2 + \text{RO}_2$) and cross ($\text{RO}_2 + \text{R}'\text{O}_2$) reactions. These reactions are
44 typically represented in chemical mechanisms as bimolecular reactions which would cause
ambiguities when implementing the tagging scheme. Namely, which tag to be used for the

Mechanism	Reaction	Rate Constant
MCM v3.2	$\text{C}_2\text{H}_5\text{O}_2 = \text{C}_2\text{H}_5\text{O}$	$k^*\text{RO}_2*0.6 \text{ s}^{-1}$
	$\text{C}_2\text{H}_5\text{O}_2 = \text{C}_2\text{H}_5\text{OH}$	$k^*\text{RO}_2*0.2 \text{ s}^{-1}$
	$\text{C}_2\text{H}_5\text{O}_2 = \text{CH}_3\text{CHO}$	$k^*\text{RO}_2*0.2 \text{ s}^{-1}$
MOZART-4	$\text{C}_2\text{H}_5\text{O}_2 + \text{CH}_3\text{O}_2 = 0.7 \text{ CH}_2\text{O} + 0.8 \text{ CH}_3\text{CHO} + \text{HO}_2$ $+ 0.3 \text{ CH}_3\text{OH} + 0.2 \text{ C}_2\text{H}_5\text{OH}$	$2 \times 10^{-13} \text{ cm}^3$ $\text{molecules}^{-1} \text{ s}^{-1}$
	$\text{C}_2\text{H}_5\text{O}_2 + \text{C}_2\text{H}_5\text{O}_2 = 1.6 \text{ CH}_3\text{CHO} + 1.2 \text{ HO}_2$ $+ 0.4 \text{ C}_2\text{H}_5\text{OH}$	$6.8 \times 10^{-14} \text{ cm}^3$ $\text{molecules}^{-1} \text{ s}^{-1}$
MOZART-4 modified	$\text{C}_2\text{H}_5\text{O}_2 = 0.8 \text{ CH}_3\text{CHO} + 0.6 \text{ HO}_2 + 0.2 \text{ C}_2\text{H}_5\text{OH}$	$2 \times 10^{-13}*\text{RO}_2 \text{ s}^{-1}$

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 RO_2 is the sum of all organic peroxy radical mixing ratios.

Reactants	Products	Rate Constant
$\text{MO}_2 + \text{MO}_2$	$0.74 \text{ HO}_2 + 1.37 \text{ HCHO} + 0.63 \text{ MOH}$	$9.4 \times 10^{-14} \exp(390/T)$ $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
MO_2	$0.37 \text{ HO}_2 + 0.685 \text{ HCHO} + 0.315 \text{ MOH}$	$9.4 \times 10^{-14} \exp(390/T)*\text{RO}_2$ s^{-1}
$\text{ETHP} + \text{MO}_2$	$\text{HO}_2 + 0.75 \text{ HCHO} + 0.75 \text{ ACD}$ $+ 0.25 \text{ MOH} + 0.25 \text{ EOH}$	$1.18 \times 10^{-13} \exp(158/T)$ $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
ETHP	$0.63 \text{ HO}_2 + 0.065 \text{ HCHO} + 0.75 \text{ ACD}$ $+ 0.25 \text{ EOH}$	$1.18 \times 10^{-13} \exp(158/T)*\text{RO}_2$ s^{-1}

Table S2: Dermination of ETHP pseudo-unimolecular reaction and rate constant in RACM2 including rate constants. RO_2 is the sum of all organic peroxy radical mixing ratios.

46 products of reactions between RO_2 having different tags. To avoid such ambiguities, the
MCM v3.2 approach to self and cross RO_2 reactions is used – all RO_2 react with RO_2 and
48 $\text{R}'\text{O}_2$ at a single uniform rate. This was represented as a pseudo-unimolecular reaction
whose rate constant includes a factor ‘RO2’ which was the sum of the mixing ratios of all
50 organic peroxy radicals (Saunders et al., 2003).

The pseudo-unimolecular reaction products and their yields were determined either
52 by using the $\text{RO}_2 + \text{RO}_2$ reaction and halving the product yields. This is demonstrated
for the MOZART-4 treatment of the ethyl peroxy radical in Table S1. Alternatively, the
54 $\text{RO}_2 + \text{CH}_3\text{O}_2$ reaction was used and the products due to CH_3O_2 were removed. Table S2
outlines the steps taken to determine the EHP pseudo-unimolecular reaction in RACM2.

56 First the products due to MO_2 , which represents CH_3O_2 in RACM2, are determined
as outlined above using the $\text{MO}_2 + \text{MO}_2$ reaction. The MO_2 product yields are then
58 subtracted from the EHP + MO_2 reaction. Any products having a negative yield were
not included in the final pseudo-unimolecular reaction.

60 The methyl acyl peroxy radical ($\text{CH}_3\text{C}(\text{O})\text{O}_2$) was the exception to the above
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
62 pseudo-unimolecular reaction was derived by subtracting the CH_3O_2 product yields from
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
64 is the most significant reaction for $\text{CH}_3\text{C}(\text{O})\text{O}_2$.

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

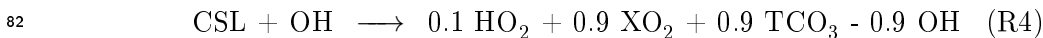
S2.3 Dry Deposition

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

74 S2.4 Negative Product Yield Treatment

Some mechanisms include reactions where certain products have a negative yield. These
 76 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
 78 acts as a sink for the original product by immediately reacting with the original product
 generating a ‘NULL’ product.

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



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



S3 Octane O_x Budget Analysis

88 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
 90 the second day. The attribution of O_x production from octane degradation in MCM v3.2,
 RADM2, RACM and RACM2 to the number of carbon atoms of the degradation products
 92 is depicted in Figure S1.

First day O_x production is similar between the mechanisms. However second day O_x
 94 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 O_x
 96 production from degradation products having six carbon atoms. Thus octane is broken
 down so quickly that it cannot reach maximum O_x production on the second day, which
 98 is a feature of alkane degradation.

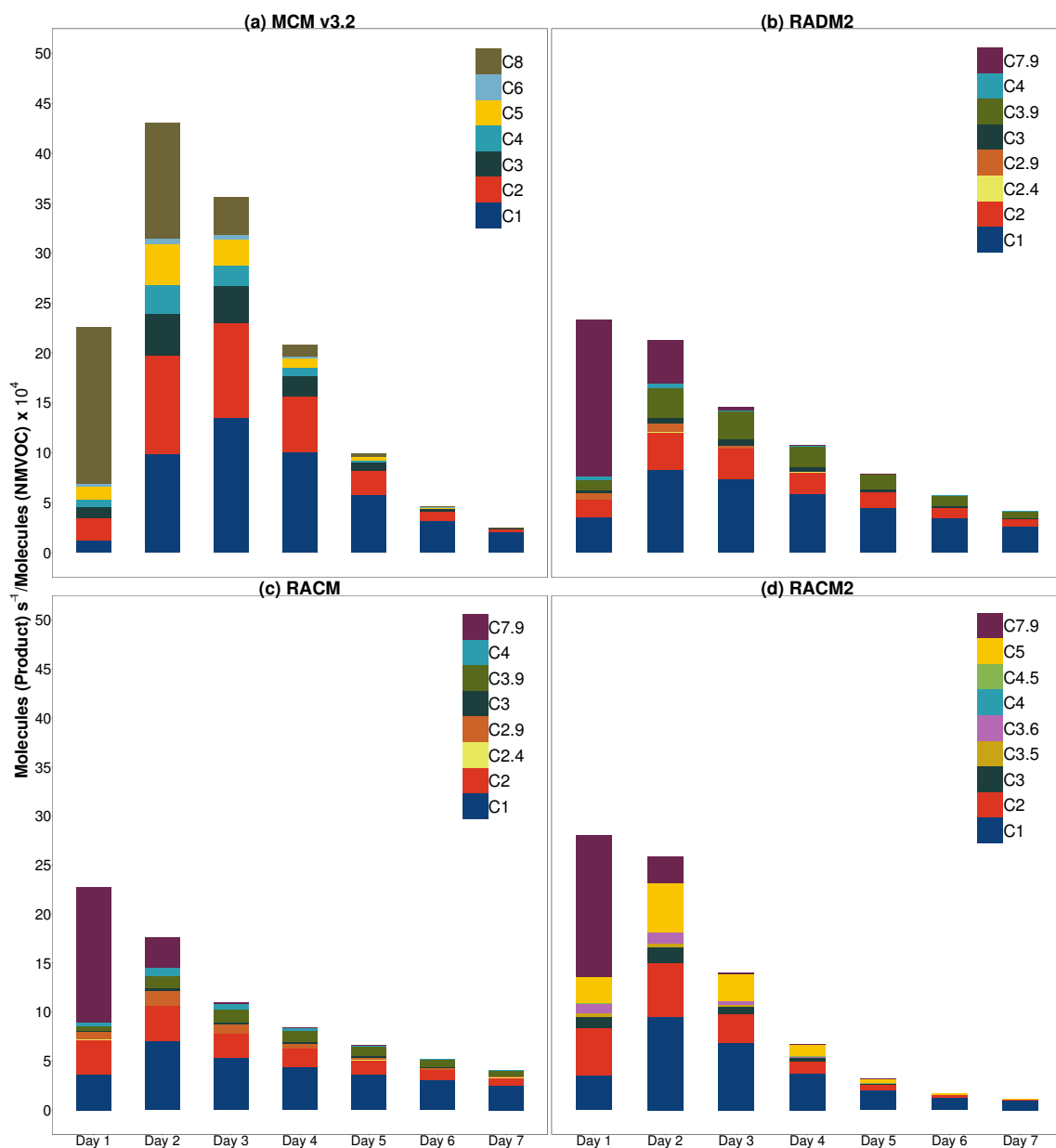


Figure S1: The O_x production budgets from octane degradation attributed to the number of carbon atoms in (a) MCM v3.2, (b) RADM2, (c) RACM and (d) RACM2.

Mechanism	Photolysis Pathway	Rate Parameter
MCM v3.2	GLYOX + hv = CO + CO + H ₂	J ₃₁
	GLYOX + hv = HCHO + CO	J ₃₂
	GLYOX + hv = CO + CO + HO ₂ + HO ₂	J ₃₃
CRI v2	CARB3 + hv = CO + CO + HO ₂ + HO ₂	J ₃₃

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

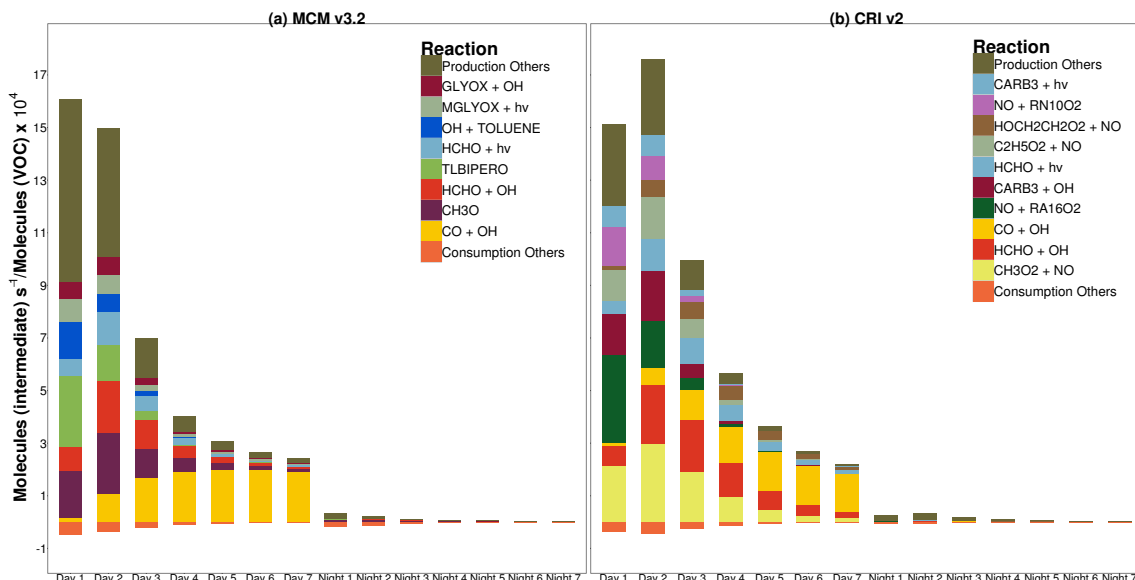


Figure S2: The HO_{2x} production budgets from toluene degradation attributed to the responsible reactions in (a) MCM v3.2 and (b) CRI v2.

S4 Toluene 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 HO_{2x} production budget allocated to the responsible reactions for both the MCM v3.2 and CRI v2. The 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 S3. The additional photolysis pathways in MCM v3.2 are non- HO_{2x} producing pathways leading to less HO_{2x} production.

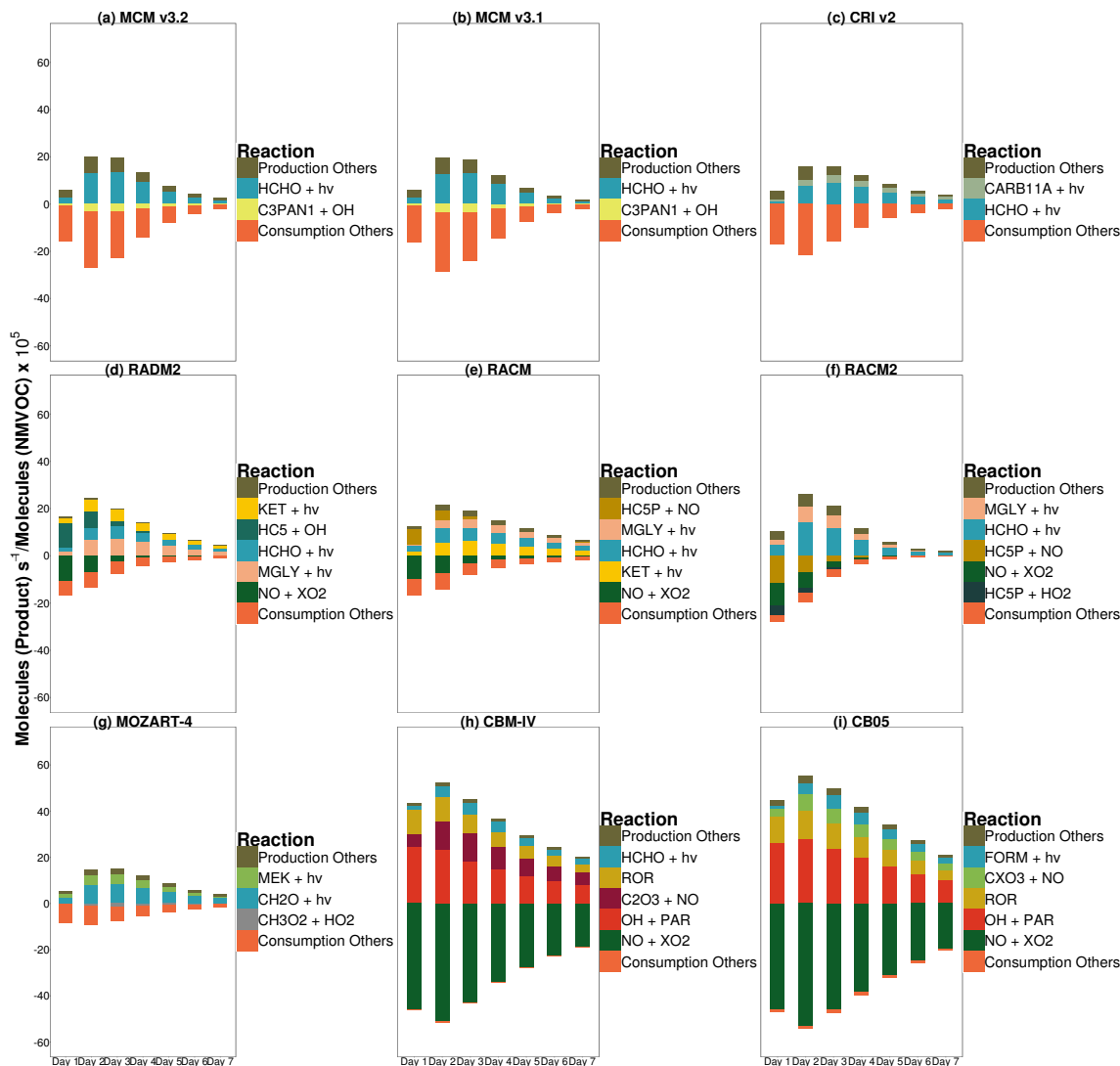


Figure S3: The radical family production and loss budgets from pentane degradation attributed to the responsible reactions in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

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

S5 Radical and PAN Family Budgets – Additional Plots

120 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
 122 to alkane and aromatic degradation, the pentane and toluene production and loss budgets

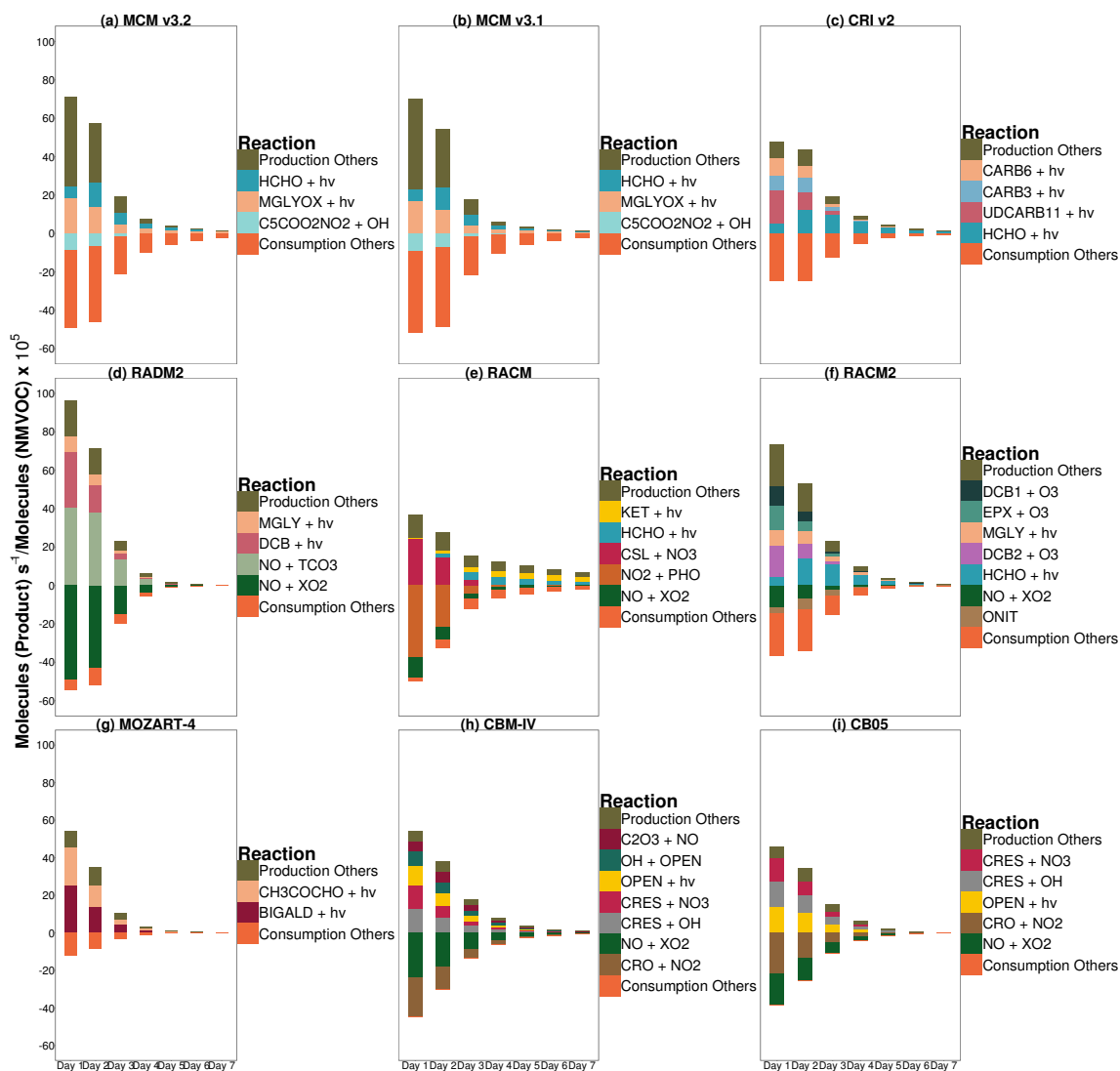


Figure S4: The radical family production and loss budgets from toluene degradation attributed to the responsible reactions in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

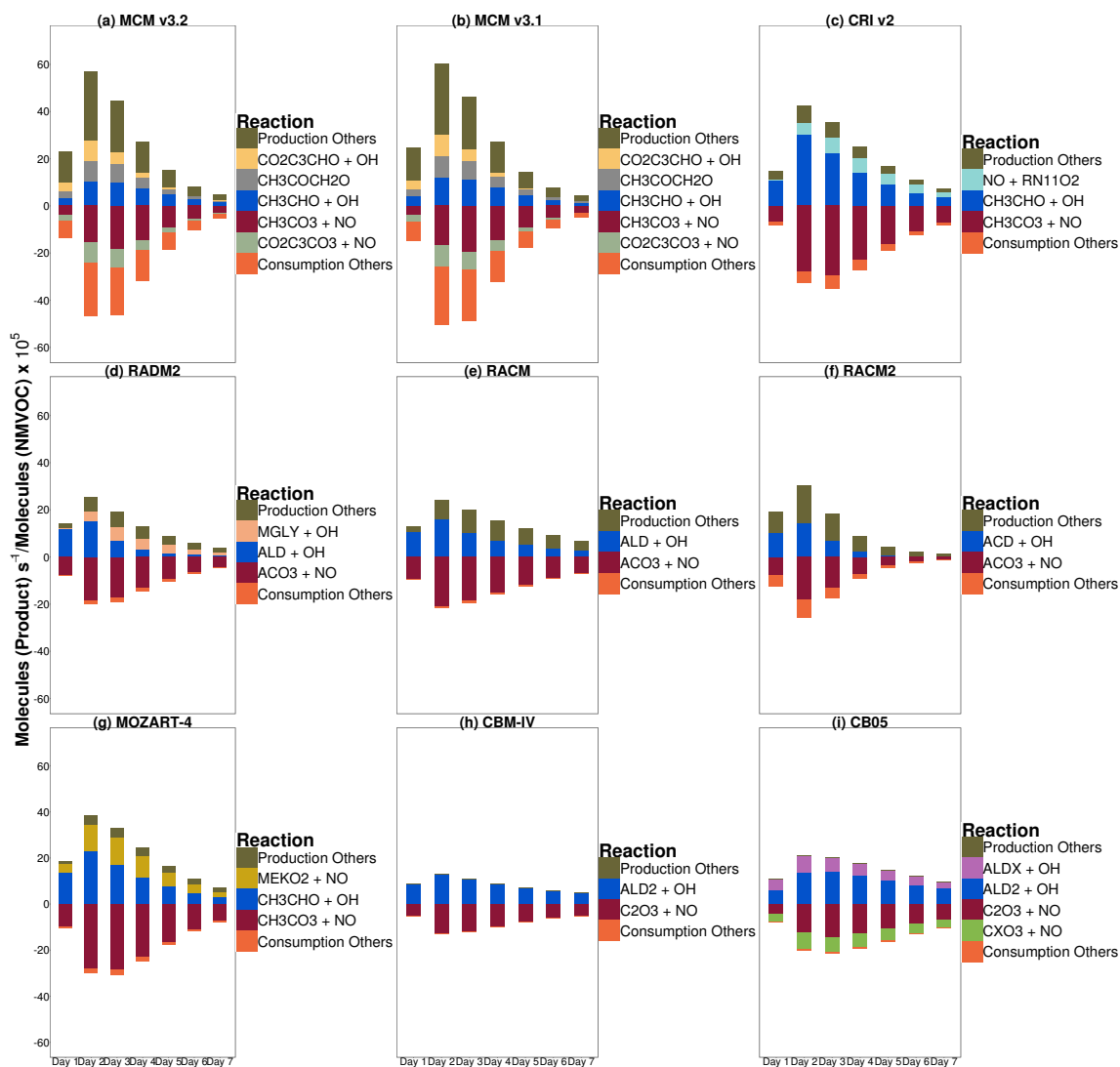


Figure S5: The PAN family production and loss budgets from pentane degradation attributed to the responsible reactions in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

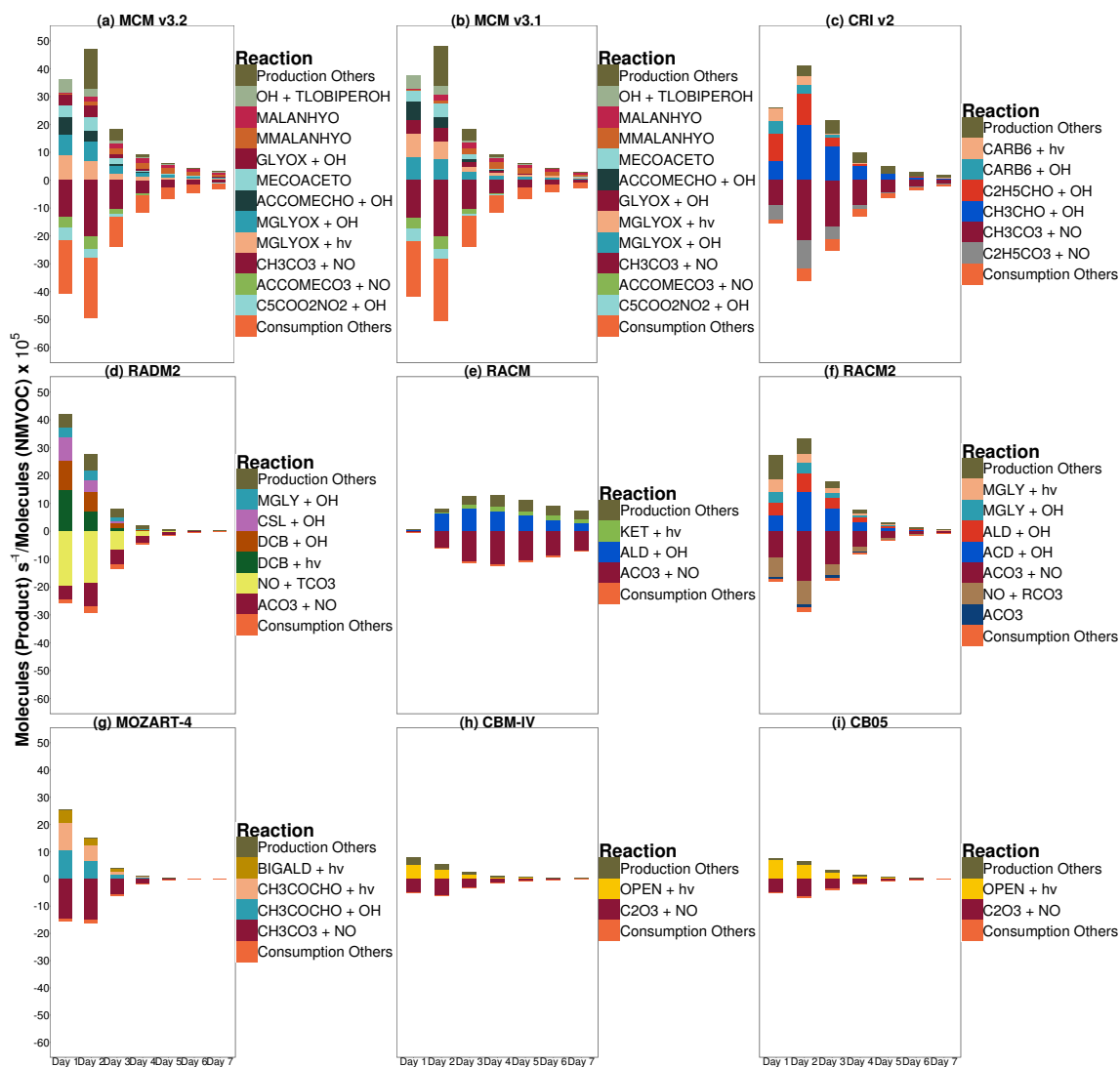


Figure S6: The PAN family production and loss budgets from toluene degradation attributed to the responsible reactions in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

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

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

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