

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

J. Coates¹ and T. Butler¹

¹Institute for Advanced Sustainability Studies, Potsdam, Germany

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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., 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.

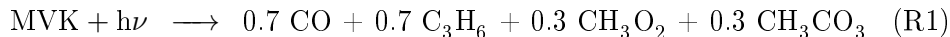
S2.1 Photolysis

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

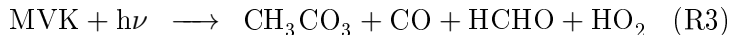
were assigned the corresponding MCM v3.2 photolysis rate parameter. Otherwise the
 22 mechanism’s literature was used to determine the appropriate MCM v3.2 photolysis rate
 parameter. In some cases this was the MCM v3.2 photolysis rate parameter closest in
 24 magnitude to that specified in the mechanism.

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 (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 RO_2 having different tags. To avoid such ambiguities, the
 46 MCM v3.2 approach to self and cross RO_2 reactions is used – all RO_2 react with 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
$\text{MO2} + \text{MO2}$	$0.74 \text{ HO2} + 1.37 \text{ HCHO} + 0.63 \text{ MOH}$	$9.4 \times 10^{-14} \exp(390/T)$ $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
MO2	$0.37 \text{ HO2} + 0.685 \text{ HCHO} + 0.315 \text{ MOH}$	$9.4 \times 10^{-14} \exp(390/T)*\text{RO2}$ s^{-1}
$\text{ETHP} + \text{MO2}$	$\text{HO2} + 0.75 \text{ HCHO} + 0.75 \text{ ACD}$ $+ 0.25 \text{ MOH} + 0.25 \text{ EOH}$	$1.18 \times 10^{-13} \exp(158/T)$ $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$
ETHP	$0.63 \text{ HO2} + 0.065 \text{ HCHO} + 0.75 \text{ ACD}$ $+ 0.25 \text{ EOH}$	$1.18 \times 10^{-13} \exp(158/T)*\text{RO2}$ 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 CH_3O_2 were removed. Table S2 54 outlines the steps taken to determine the EHP pseudo-unimolecular reaction in RACM2.

First the products due to MO_2 , which represents CH_3O_2 in RACM2, are determined 56 as outlined above using the $\text{MO}_2 + \text{MO}_2$ reaction. The 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 CH_3O_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

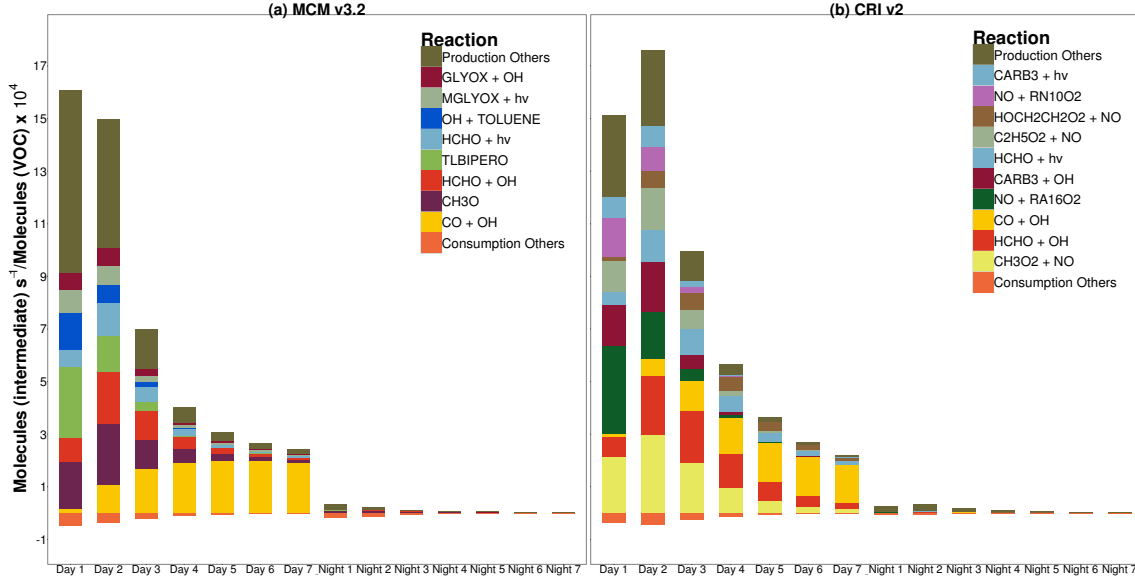
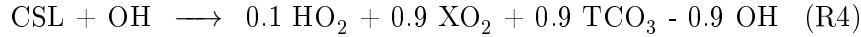


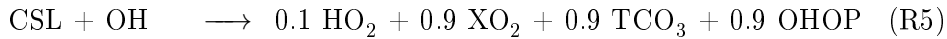
Figure S1: The HO_{2x} production budgets from toluene degradation attributed to the responsible reactions in (a) MCM v3.2 and (b) CRI v2.

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 Toluene HO_{2x} Budget Analysis

The paper showed that the CRI v2 maximum daily toluene TOPP value is reached on the
 88 second day whilst in the MCM v3.2 this is reached on the first. Figure S1 illustrates the
 HO_{2x} production budget allocated to the responsible reactions for both the MCM v3.2
 90 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.

Mechanism	Photolysis Pathway	Rate Parameter
MCM v3.2	GLYOX + hv = CO + CO + H2	J ₃₁
	GLYOX + hv = HCHO + CO	J ₃₂
	GLYOX + hv = CO + CO + HO2 + HO2	J ₃₃
CRI v2	CARB3 + hv = CO + CO + HO2 + HO2	J ₃₃

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

92 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
94 produced from aromatic degradation whilst GLYOX is a degradation product of many
other non-aromatic NMVOCs in MCM v3.2.

96 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
98 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.
100 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
102 to less HO_{2x} production.

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

106 S4 Extra Plots

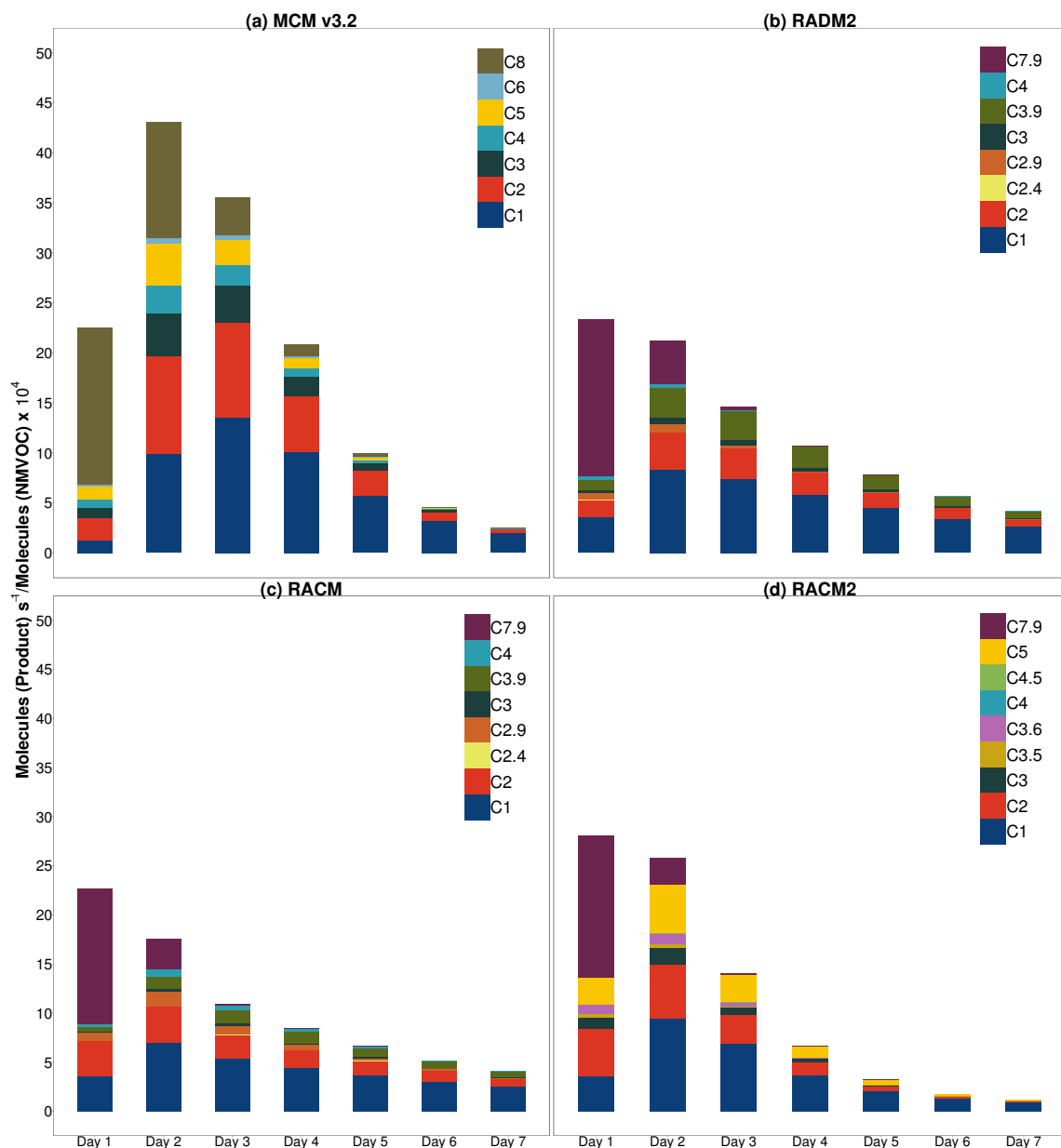


Figure S2: The O_x production budgets from octane degradation attributed to the number of carbon atoms in (a) MCM v3.2, (b) RADM2, (c) RACM and (d) RACM2.

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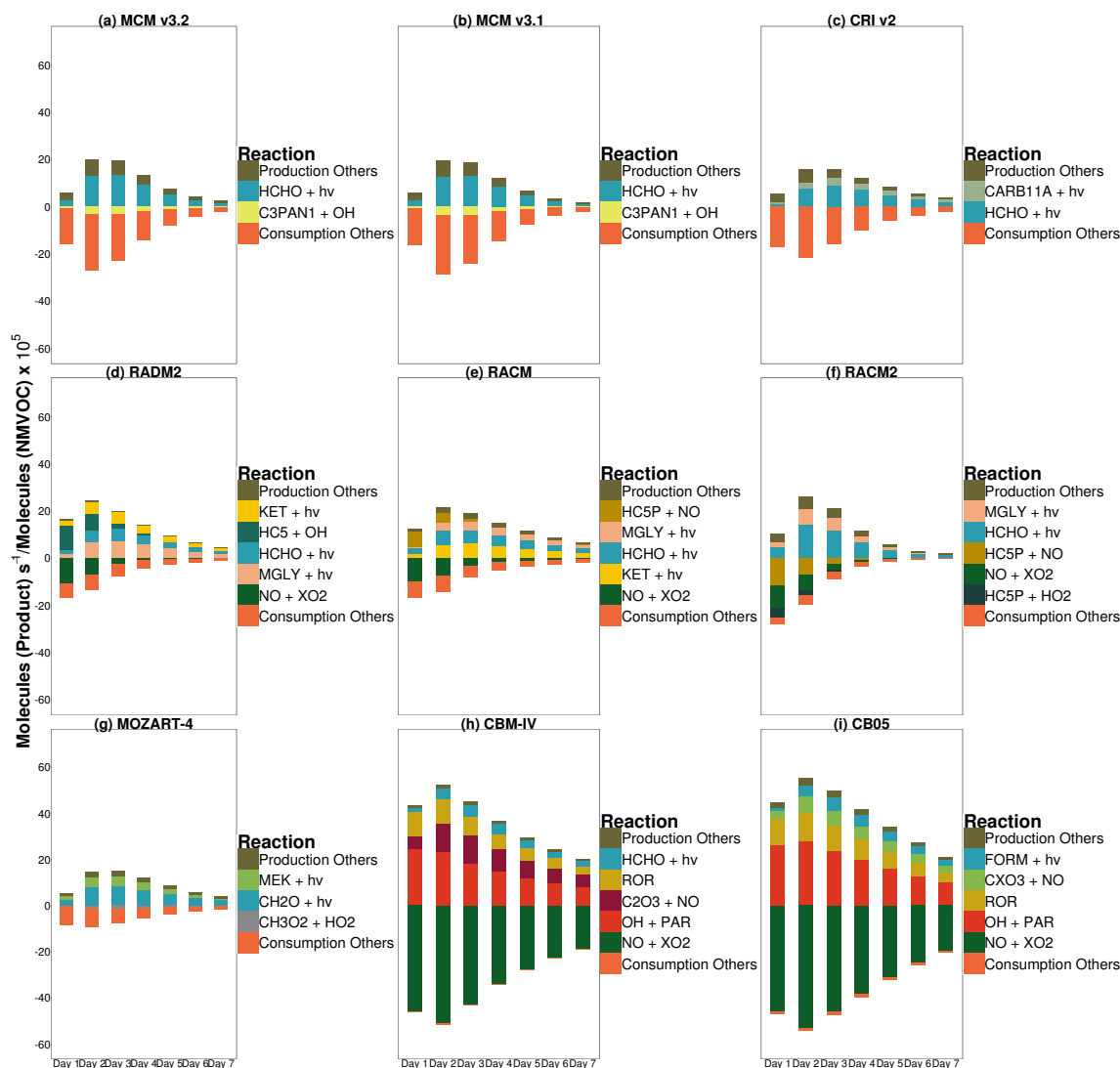


Figure S3: The radical family production and loss budgets from pentane degradation attributed to the responsible reactions in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

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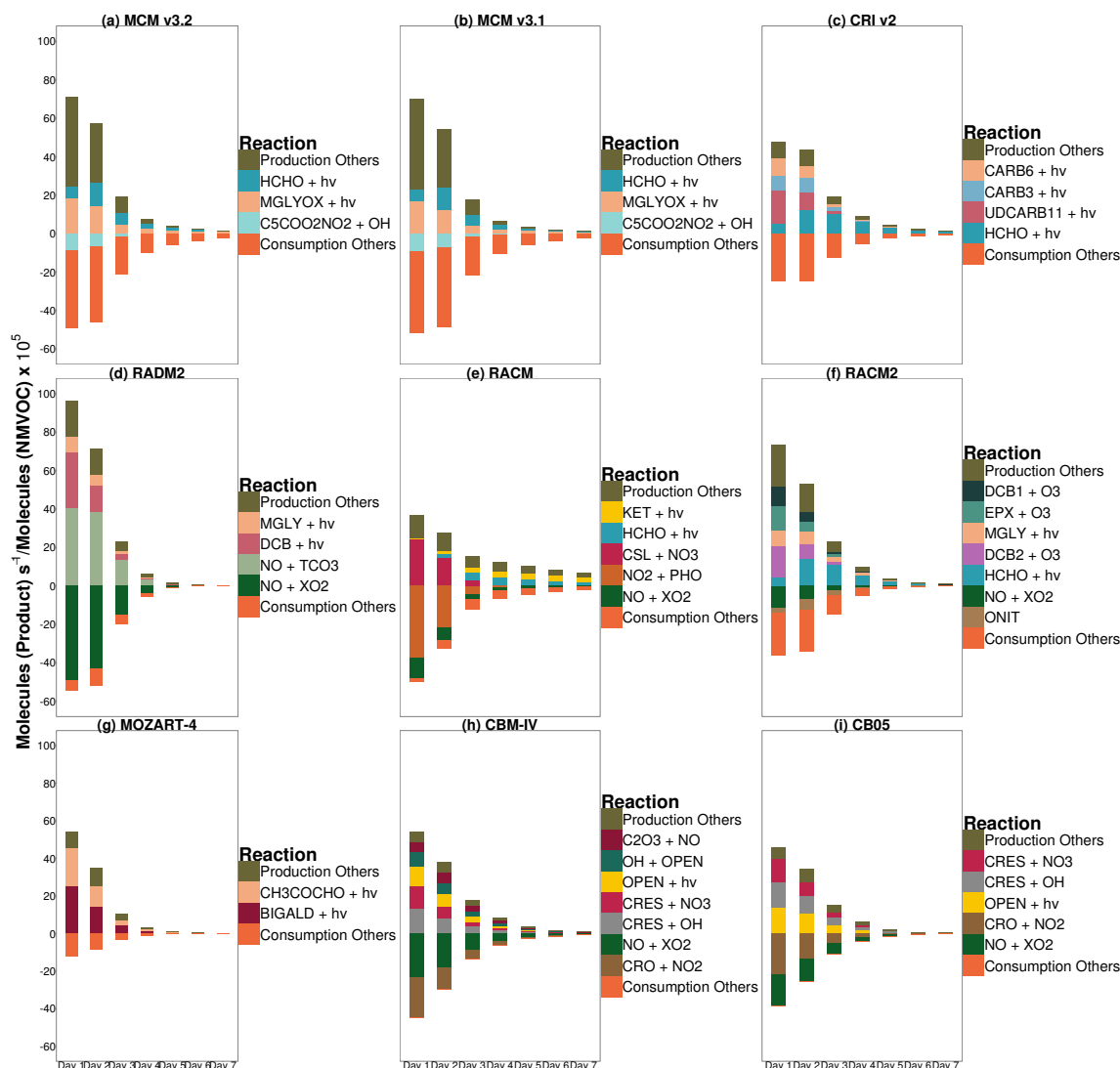


Figure S4: The radical family production and loss budgets from toluene degradation attributed to the responsible reactions in (a) MCM v3.2, (b) MCM v3.1, (c) CRI v2, (d) RADM2, (e) RACM, (f) RACM2, (g) MOZART-4, (h) CBM-IV and (i) CB05.

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