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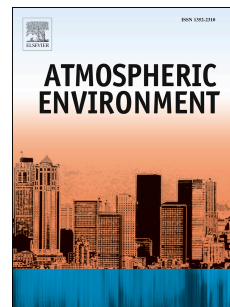
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# Accepted Manuscript

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## The CRI v2.2 reduced degradation scheme for isoprene

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### Abstract

The reduced representation of isoprene degradation in the Common Representative Intermediates (CRI) mechanism has been systematically updated, using the Master Chemical Mechanism (MCM v3.3.1) as a reference benchmark, with the updated mechanism being released as CRI v2.2. The complete isoprene degradation mechanism in CRI v2.2 consists of 186 reactions of 56 closed shell and free radical species, this being an order of magnitude reduction in size compared with MCM v3.3.1. The chemistry initiated by reaction with OH radicals, NO<sub>3</sub> radicals and ozone (O<sub>3</sub>) is treated. An overview of the updates is provided, within the context of reported kinetic and mechanistic information. The revisions mainly relate to the OH-initiated chemistry, which tends to dominate under atmospheric conditions, although these include updates to the chemistry of products that are also generated from the O<sub>3</sub>- and NO<sub>3</sub>-initiated oxidation. The revisions have impacts in a number of key areas, including recycling of HO<sub>x</sub> and NO<sub>x</sub>. The performance of the CRI v2.2 isoprene mechanism has been compared with those of the preceding version (CRI v2.1) and the reference MCM v3.3.1 over a range of relevant conditions, using a box model of the tropical forested boundary layer. In addition, tests are carried out to ensure that the performance of MCM v3.3.1 remains robust to more recently reported information. CRI v2.2 has also been implemented into the STOCHEM chemistry-transport model, with a customized close-variant of CRI v2.2 implemented into the EMEP MSC-W chemistry-transport model. The results of these studies are presented and used to illustrate the global-scale impacts of the mechanistic updates on HO<sub>x</sub> radical concentrations.

Keywords: Tropospheric chemistry; Biogenic hydrocarbons; Degradation mechanisms; HO<sub>x</sub> recycling; Mechanism reduction.

# 1    **1    Introduction**

2    The degradation of emitted volatile organic compounds (VOCs) has a major influence on the  
3    chemistry of the troposphere, contributing to the formation of ozone (O<sub>3</sub>), secondary organic  
4    aerosol (SOA) and other secondary pollutants (e.g. Haagen-Smit and Fox, 1954; Went, 1960;  
5    Andreae and Crutzen, 1997; Jenkin and Clemitshaw, 2000; Hallquist et al., 2009). Biogenic sources  
6    are reported to dominate emissions of organic material on a global scale (Guenther et al., 2012),  
7    with the reactive biogenic VOC isoprene (2-methyl-but-1,3-diene) making a major contribution. On  
8    a regional scale over Europe, isoprene is estimated to contribute more than 30 % of total biogenic  
9    VOC emissions, and 50 % of reactive biogenic VOC emissions (Simpson et al., 1999). Although there  
10    is a wide variation in both regional and global estimates (e.g. Arneth et al. 2008, Warneke et al.,  
11    2010, Langner et al., 2014), isoprene is believed to be the most abundantly emitted non-methane  
12    VOC in the atmosphere. Its emission rate may also be altered by future changes to climate and other  
13    environmental factors (e.g. Peñuelas and Staudt, 2010, Arneth et al, 2010, Simpson et al., 2014, and  
14    references therein). Reliable representations of the emissions and atmospheric oxidation chemistry  
15    of isoprene are therefore important components of chemistry-transport models (CTMs) applied to  
16    climate change and air quality assessments.

17    There have been some notable advances in the understanding of atmospheric isoprene chemistry  
18    over the past decade (e.g. Wennberg et al., 2018; and references therein), particularly in relation to  
19    recycling mechanisms for HO<sub>x</sub> radicals (i.e. OH and HO<sub>2</sub>), the chemistry of oxidized organic nitrogen  
20    species and the formation of species that contribute to SOA. This has been reflected in recent  
21    updates to detailed explicit gas-phase mechanisms, such as version 3.3.1 of the Master Chemical  
22    Mechanism, MCM v3.3.1 (Jenkin et al., 2015), which includes 1926 reactions of 602 species  
23    describing the complete gas phase oxidation of isoprene. Although such a mechanism cannot be  
24    used directly in applications requiring great computational efficiency, it provides a traceable link to  
25    elementary kinetic and mechanistic studies, and a reference benchmark mechanism against which

1 to develop, evaluate and optimize reduced chemical mechanisms. MCM v3.3.1 is thus used as the  
2 reference mechanism in the present work. Given its importance, new information on atmospheric  
3 isoprene chemistry is constantly emerging, and there have inevitably been some further advances  
4 since the release of MCM v3.3.1 in 2015. These have been reviewed recently by Wennberg et al.  
5 (2018), with a nearly complete gas-phase oxidation mechanism of isoprene and its major products  
6 also reported. As part of the present study, the impacts of some of the main mechanistic differences  
7 compared with MCM v3.3.1 have been examined for a range of relevant conditions, using a box  
8 model of the tropical forested boundary layer. The results of these comparisons are presented and  
9 discussed in Sect. 4 and in the Supplement (Sect. S2).

10 The Common Representative Intermediates (CRI v2) mechanism is a reduced (lumped chemistry)  
11 scheme of intermediate complexity (Jenkin et al., 2008). It was built up on a compound-by-  
12 compound basis for 115 non-methane VOCs, with the O<sub>3</sub>-forming ability of its chemistry optimised  
13 for each compound in turn by comparison with that of an earlier version of the Master Chemical  
14 Mechanism (MCM v3.1), using box model simulations (Jenkin et al., 2008). A key assumption in the  
15 construction method is that the potential for O<sub>3</sub> formation from a given VOC is related to the  
16 number of reactive (i.e. C-C and C-H) bonds it contains. This index allows generic intermediates to be  
17 defined, with each being used to represent a set of species possessing the same index, as formed in  
18 detailed mechanisms such as the MCM. A series of five progressively more reduced variants (CRI v2-  
19 R1 to CRI v2-R5) was also subsequently developed, using systematic and tested lumping of  
20 anthropogenic VOC emissions (Watson et al., 2008). The smallest of these (CRI v2-R5) has 609  
21 reactions of 220 species, with the suite of emitted non-methane VOCs represented by 22  
22 compounds. However, all these reduced v2 variants contain the same isoprene chemistry as CRI v2,  
23 consisting of 113 reactions of 43 species. Although still quite detailed, CRI v2-R5 has routinely been  
24 used in the 3-D global CTM, STOCHEM-CRI (e.g. Utembe et al., 2010; Khan et al., 2017), and both CRI  
25 v2 and CRI v2-R5 are among several mechanisms available to the 3-D European regional and global  
26 CTM, EMEP MSC-W (Simpson et al., 2012, 2018; McFiggans et al. 2019).

1 The CRI isoprene chemistry has been systematically revised and updated to reflect the recent  
2 advances in understanding (as represented in MCM v3.3.1), with the revised chemistry being  
3 released as part of CRI v2.2. These updates are described in Sect. 3. The performance of the CRI v2.2  
4 isoprene scheme has been examined for a range of relevant conditions, using the tropical forested  
5 boundary layer box model, and is compared with those of MCM v3.3.1 and the immediately  
6 preceding CRI v2.1<sup>1</sup> in Sect. 4. In addition, CRI v2.2 has been implemented into the STOCHEM-CRI  
7 model, with a customized close-variant of CRI v2.2 implemented into the EMEP MSC-W model. The  
8 results of these studies are presented and used to illustrate the global-scale impacts of the  
9 mechanistic updates on HO<sub>x</sub> radical concentrations.

## 10 **2 Model description**

### 11 **2.1 Zero-dimensional boundary layer box model**

12 The impact of recent mechanistic advances compared with MCM v3.3.1, and the performance of the  
13 CRI v2.2 isoprene mechanism, were examined in detail using simulations carried out with the box  
14 model of the tropical forested boundary layer applied previously by Jenkin et al. (2015), coded for  
15 application with the FACSIMILE kinetics integration package (MCPA Software). The aim of these  
16 studies was to test and compare the performance of the mechanisms for a range of idealised  
17 atmospheric conditions, with particular emphasis on the impacts of mechanistic differences on the  
18 partitioning and recycling of HO<sub>x</sub> and NO<sub>x</sub>.

19 The model was designed to simulate a well-mixed tropical forested boundary layer, 1000 m in  
20 depth. The boundary layer air parcel was continuously exchanged with the free troposphere on a  
21 timescale of 1 day, thus representing a loss process for longer-lived products. The free troposphere  
22 was assumed to contain the following limited series of trace species, which were mixed into the  
23 boundary layer on the same timescale: O<sub>3</sub> (20 ppb), CO (100 ppb), and HCHO (300 ppt). The model

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<sup>1</sup> Prior to the present work, the prevailing version of the mechanism was CRI v2.1. This contained the same reaction set as CRI v2, but with some generic rate coefficient revisions in parallel with those in the MCM v3.1 to v3.2 transition. The performance of the isoprene chemistry in v2 and v2.1 is therefore almost identical.

1 was initialised for seven days such that exchange processes reached steady state, and results from  
 2 the daylight portion of the eighth diurnal cycle were used in comparisons of mechanism  
 3 performance. The temperature followed a sinusoidal diurnal profile (average 298 K; amplitude 4 K),  
 4 leading to a peak temperature of 302 K in the early afternoon.

5 The diurnal variation of photolysis parameters was set for latitude 0° at equinox in all simulations.  
 6 Photolysis coefficients were calculated assuming clear sky conditions, using a parameterization  
 7 previously applied with the MCM (Saunders et al., 2003). For the present illustration, the loss of  
 8 product species via deposition or transfer to the condensed phase was not represented, the focus of  
 9 the simulations being chemical processing in the gas phase. The same inorganic reaction scheme  
 10 and parameters were used with each mechanism, so that the differences in performance result from  
 11 the differences in the organic chemistry, as summarised in Table 1.

13 **Table 1.** Isoprene mechanisms and mechanistic variants considered in the present work.

Mechanism	Description	Comment
MCM v3.3.1	Reference mechanism (Jenkin et al., 2015). Available at: <a href="http://mcm.york.ac.uk/">http://mcm.york.ac.uk/</a> .	-
CAL 1	MCM v3.3.1 with OH attack distribution, rate coefficients for reversible addition of O <sub>2</sub> to OH-isoprene adducts and for 1,6 H-shift reactions of Z- $\delta$ -hydroxy peroxy isomers based on Wennberg et al. (2018).	(a)
CAL 2	CAL 1 with products of 1,6 H-shift reactions of Z- $\delta$ -hydroxy peroxy isomers and of first-generation $\beta$ -hydroxy peroxy isomer + HO <sub>2</sub> reactions based on Wennberg et al. (2018).	(b)
CAL 3	CAL 2 with fates of first-generation oxy radicals based on Wennberg et al. (2018).	(c)
CAL 4	CAL 3 with product ratios for first-generation RO <sub>2</sub> + NO reactions based on Wennberg et al. (2018).	(d)
CRI v2.2	Reduced mechanism. Available at: <a href="http://cri.york.ac.uk/">http://cri.york.ac.uk/</a> .	-
CRI v2, v2.1	Preceding versions of the reduced mechanism.	(e)
<b>Comments</b> <sup>a</sup> The Z- $\delta$ -hydroxy peroxy isomers are denoted CISOPAO2 and CISOPCO2 in MCM v3.3.1 and Z- $\delta$ -1,4-ISOPOO and Z- $\delta$ -4,1-ISOPOO by Wennberg et al. (2018); <sup>b</sup> Wennberg et al. (2018) recommend partial formation of $\beta$ -hydroperoxy-aldehydes from 1,6 H-shift reactions. These species and their degradation chemistry were added to the mechanism according to Wennberg et al. (2018). Minor propagating channels included for reactions of HO <sub>2</sub> with $\beta$ -hydroxy peroxy radicals, denoted ISOPBO2 and ISOPDO2 in MCM v3.3.1 and $\beta$ -1,2-ISOPOO and $\beta$ -4,3-ISOPOO by Wennberg et al. (2018); <sup>c</sup> Adjusted fates incorporated for Z- $\delta$ -hydroxy oxy radicals, denoted CISOPAO and CISOPCO in MCM v3.3.1 and Z- $\delta$ -1,4-ISOPO and Z- $\delta$ -4,1-ISOPO by Wennberg et al. (2018); <sup>d</sup> The weighted average branching ratios for nitrate formation from first-generation RO <sub>2</sub> + NO reactions recommended by Wennberg et al. (2018) is about 33 % higher than that applied in MCM v3.3.1 at 298 K and 760 Torr; <sup>e</sup> These earlier versions (including the subset mechanism CRI v2-R5) contain identical sets of reactions describing isoprene degradation. CRI v2.1 is also available for download in FACSIMILE and KPP formats at <a href="http://cri.york.ac.uk/download.htm">http://cri.york.ac.uk/download.htm</a> .		

1 The boundary layer box received continuous emissions of isoprene and NO<sub>x</sub>, which were maintained  
2 throughout the model runs, and a fixed mixing ratio of 1.8 ppm methane was assumed. A constant  
3 base NO<sub>x</sub> emission rate of  $4.7 \times 10^9$  molecule cm<sup>-2</sup> s<sup>-1</sup> was applied, which is a globally averaged rate  
4 based on an annual total emission of 44.8 TgN, as applied by Derwent et al. (2003). This resulted in a  
5 daylight-averaged NO<sub>x</sub> mixing ratio of about 34 ppt in the MCM v3.3.1 simulation. To examine the  
6 NO<sub>x</sub> dependence of the chemistry, the NO<sub>x</sub> emission rate was scaled by factors of 3, 10, 30, 100 and  
7 200 which resulted in daylight-averaged NO<sub>x</sub> mixing ratios up to about 8 ppb.

8 The relative isoprene emission rate varied with temperature and photosynthetically active radiation  
9 (PAR) throughout the diurnal cycle, based on a standard algorithm (Guenther et al., 1995). The  
10 absolute magnitude of the emissions was set such that the daylight average emission rate was  $7.6 \times$   
11  $10^{11}$  molecule cm<sup>-2</sup> s<sup>-1</sup> ( $3.1 \mu\text{gm}^{-2} \text{h}^{-1}$ ), maximising at  $1.0 \times 10^{12}$  molecule cm<sup>-2</sup> s<sup>-1</sup> ( $4.2 \mu\text{gm}^{-2} \text{h}^{-1}$ ) in the  
12 early afternoon. These emissions fluxes are typical of those reported for tropical forested regions  
13 (e.g. Eerdeken et al., 2009).

14 Reaction with OH was the dominant fate of isoprene for the conditions of this illustration,  
15 accounting for between 89 and 93 % of isoprene removal in the MCM v3.3.1 simulations (depending  
16 on the NO<sub>x</sub> level). The contribution of the O<sub>3</sub>-initiated chemistry increases from about 4 % at the  
17 high end of the NO<sub>x</sub> range to about 11 % at the low end of the NO<sub>x</sub> range. The NO<sub>3</sub>-initiated  
18 chemistry is also simulated to contribute up to about 4 % to isoprene removal, with the maximum  
19 contribution towards the high end of the NO<sub>x</sub> range.

## 20 **2.2 3-D global modelling**

21 The impacts of the mechanistic updates on global scale HO<sub>x</sub> radical concentrations have been  
22 examined using the well-documented 3-D global CTMs, STOCHEM-CRI (Utembe et al., 2010; Khan et  
23 al., 2017), and EMEP MSC-W (Simpson et al., 2012, 2018; Stadtler et al., 2017, McFiggans et al.  
24 2019), which have been described in detail elsewhere. The implementation of CRI v2-R5 into the  
25 STOCHEM model has been reported previously by Utembe et al. (2010). In the present study, the

1 impacts of updating the isoprene chemistry to CRI v2.2 are presented. In the case of the EMEP MSC-  
2 W model, a closely-related bespoke version of the CRI v2.2 chemistry is applied, which performs  
3 consistently in relation to all the main criteria considered here (see Sects. 3.1 and S1 for further  
4 details). The performance of the isoprene mechanism relative to that of CRI v2.1 is illustrated.

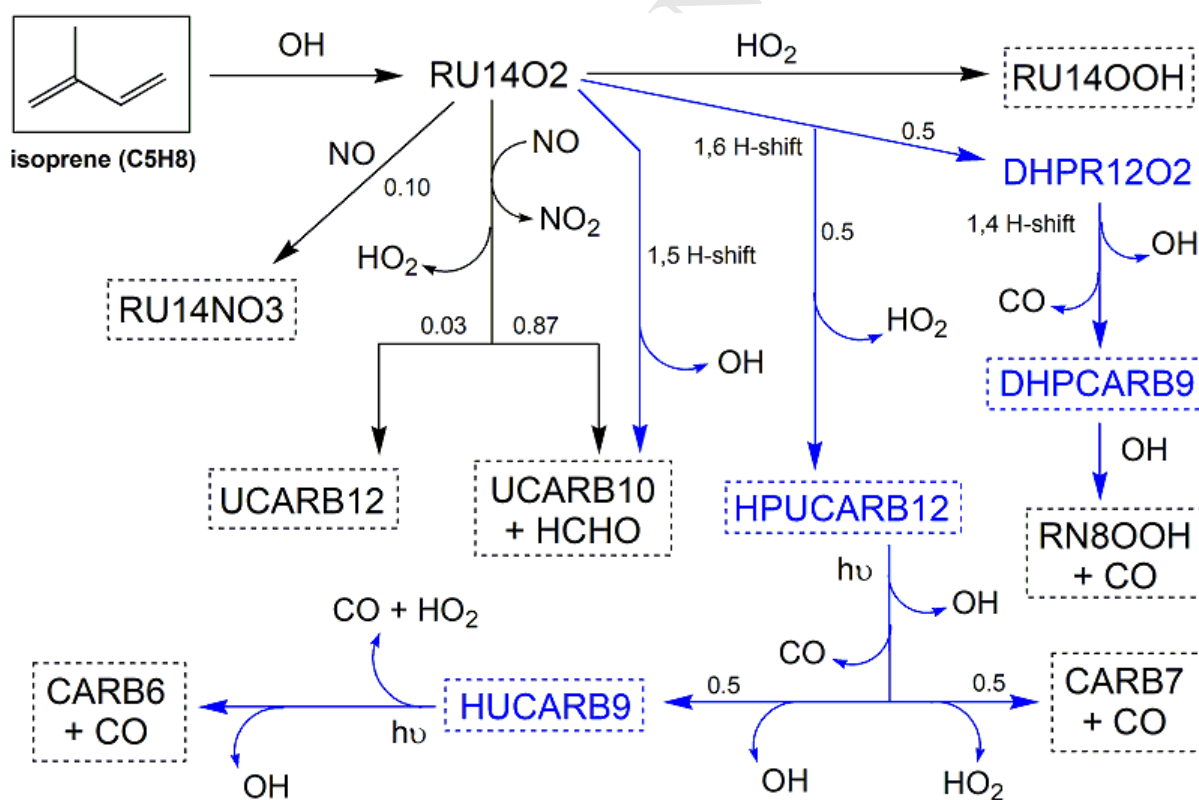
5 The emissions of biogenic VOCs differ slightly between the models. EMEP MSC-W applies isoprene  
6 emissions of 425 Tg/yr, and monoterpene emissions of 129 Tg/yr, all from terrestrial sources  
7 (Simpson et al., 2018). STOCHEM-CRI applies terrestrial isoprene emissions of 501 Tg/yr and  
8 monoterpene emissions of 127 Tg/yr (Utembe et al., 2010), with oceanic isoprene emissions of 1.9  
9 Tg/yr also recently included, based on Arnold et al. (2009). Although based upon entirely different  
10 land-cover maps and methodologies, the differences in the terrestrial isoprene and terpene  
11 emissions are therefore small compared to the range of values found in the literature (e.g. Arneth et  
12 al., 2008).

### 13 **3 Updates to isoprene chemistry in CRI v2.2**

14 The complete degradation chemistry of isoprene, as represented in CRI v2.2, consists of 186  
15 reactions of 56 species and includes chemistry initiated by reaction with OH, O<sub>3</sub> and NO<sub>3</sub>. It can be  
16 accessed via the new MCM website at the University of York (<http://mcm.york.ac.uk/>) or directly at  
17 <http://cri.york.ac.uk/>, where the mechanism can be viewed and downloaded using the subset  
18 mechanism assembling facility. As described previously by Jenkin et al. (2008) and Archibald et al.  
19 (2010a; 2010b), the isoprene chemistry included previously in CRI v2 and CRI v2.1 was developed  
20 and optimized so that its performance matched that of MCM v3.1. The updates described below  
21 therefore document the major changes to the mechanism since CRI v2.1. The revisions mainly relate  
22 to the OH-initiated chemistry, which tends to dominate under atmospheric conditions, although  
23 these include updates to the chemistry of some products that are also generated from the O<sub>3</sub>- and  
24 NO<sub>3</sub>-initiated oxidation.

### 1 3.1 Updates to the first-generation OH-initiated chemistry

2 The initial stages of the chemistry following addition of OH in the presence of O<sub>2</sub>, as represented in  
 3 CRI v2.2, are shown in Fig. 1. The reaction forms a single lumped peroxy radical (RU14O2), which is  
 4 representative of a set of six isomeric peroxy radicals formed following the (major) addition of OH to  
 5 the two terminal carbon atoms in isoprene. The minor addition to the two central carbon atoms is  
 6 not represented in CRI v2.2, this only accounting for about 8 % of the reaction in MCM v3.3.1.  
 7 Similarly to previous CRI versions, RU14O2 undergoes traditional bimolecular reactions with NO,  
 8 NO<sub>3</sub>, HO<sub>2</sub> and the pool of peroxy radicals (RO<sub>2</sub>) in CRI v2.2, but with rate coefficients and product  
 9 ratios revised (where necessary) based on those in MCM v3.3.1.



11  
12

13 **Figure 1:** Schematic of the main features of the OH-initiated oxidation of isoprene to first-generation closed-  
 14 shell products (shown in boxes), as represented in CRI v2.2. The main features of the chemistry following rapid  
 15 photolysis of HPUCARB12 and HUCARB9, and reaction of DHPCARB with OH, are also shown. Species and  
 16 routes shown in blue are new in CRI v2.2. For clarity, the scheme omits the reactions of RU14O2 with NO<sub>3</sub> and  
 17 the peroxy radical pool, and all bimolecular reactions of DHPR12O2, although these are included in the  
 18 mechanism. Further information on species class and identity is given in Table S3.

1 The most significant update to the first generation chemistry is the inclusion of 1,5 H-shift and 1,6 H-  
2 shift isomerization reactions for RU14O2 (and subsequent chemistry), characterized as part of the  
3 Leuven Isoprene Mechanism (LIM1) reaction framework developed by Peeters et al. (2009; 2014), as  
4 applied in MCM v3.3.1. As shown in Fig. 1, these provide additional routes that recycle and generate  
5 HO<sub>x</sub> radicals (i.e. OH and HO<sub>2</sub>), which are particularly significant under NO<sub>x</sub>-limited conditions. In  
6 practice, each type of isomerization is only available for a subset of the peroxy radicals represented  
7 by RU14O2, specifically two β-hydroxy isomers for the 1,5 H-shift reaction and two Z-δ-hydroxy  
8 isomers for the 1,6 H-shift reaction. As discussed previously (e.g. Peeters et al., 2014; Jenkin et al.,  
9 2015; Wennberg et al., 2018) the effective rate coefficients assigned to these reactions for a lumped  
10 peroxy radical therefore need to take account of the relative population of the component peroxy  
11 radical isomers under atmospheric conditions, and the prevailing total removal rate via the  
12 competing traditional bimolecular reactions ( $k_{tr}$ ). These were based on simulations of the effective  
13 bulk isomerization rates, using MCM v3.3.1. Because the peroxy radical population is dominated by  
14 the β-hydroxy isomers over the typical range of atmospheric conditions, the bulk 1,5 H-shift reaction  
15 could be represented acceptably by a single rate coefficient expression based on the weighted  
16 average of those applied to the β-hydroxy isomers in MCM v3.3.1 (see Sect. S1.1). However, the  
17 effective rate of the (more important) bulk 1,6 H-shift reaction ( $k_{bulk\ 1,6\ H}$ ) varies approximately  
18 linearly with  $k_{tr}$  over the typical tropospheric range of conditions, as first discussed by Peeters et al.  
19 (2014). It is therefore represented by an expression of the following form ( $k_0$  and  $A$  are fitted  
20 constants):

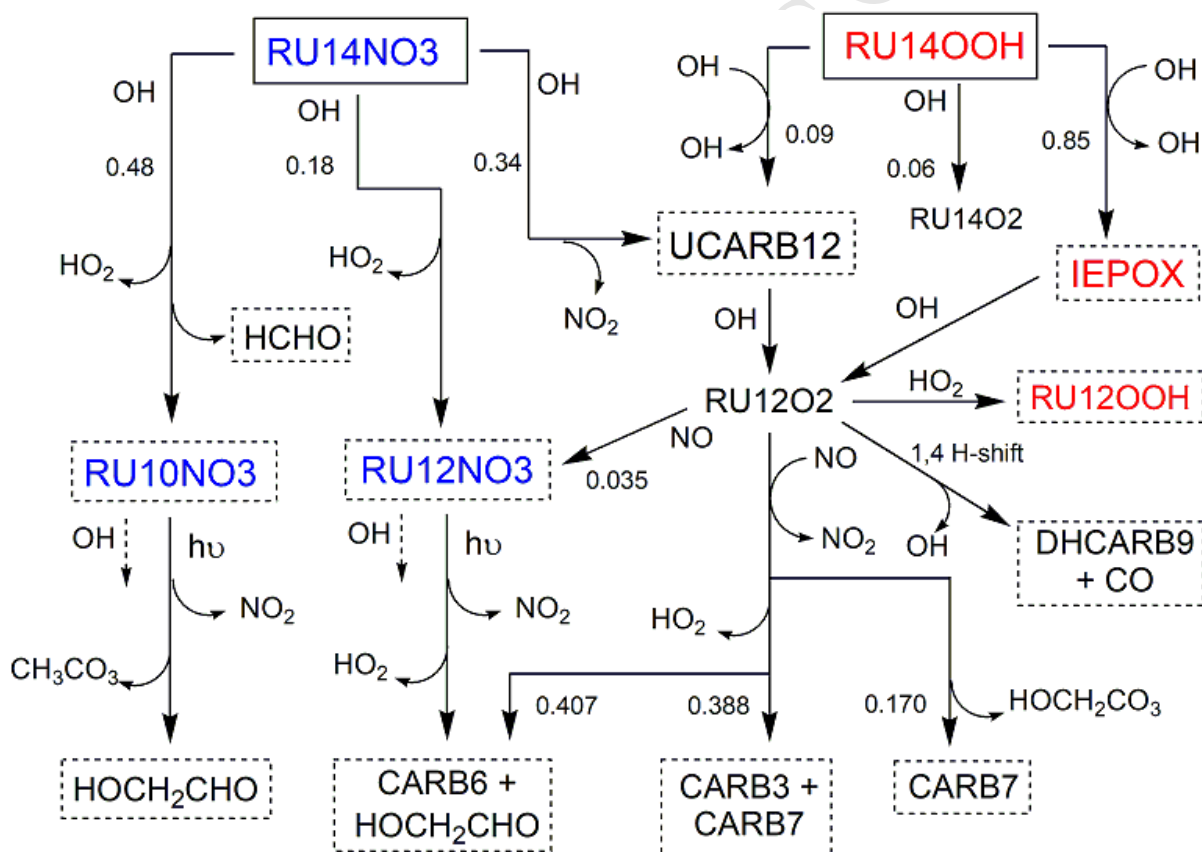
$$21 \quad k_{bulk\ 1,6\ H} = k_0 + (k_{tr} \times A) \quad (i)$$

22 This is discussed further in Sect. S1.1. However, to provide an alternative to the use of the  
23 conditions-dependent rate coefficient in Eq. (i), a more explicit reduced representation of the  
24 chemistry was also developed, using a set of three isomeric peroxy radicals to represent the six

1 formed in MCM v3.3.1. This alternative representation was applied in the EMEP MSC-W model, and  
 2 is described in more detail in Sect. S1.1.

3 Analogously to MCM v3.3.1, two product channels are represented for the 1,6 H-shift reaction (see  
 4 Fig. 1), leading either to the formation of HO<sub>2</sub> and a lumped unsaturated  $\delta$ -hydroperoxyaldehyde  
 5 product (HPUCARB12) or a lumped dihydroperoxy formyl peroxy radical (DHPR12O2), which reacts  
 6 significantly via a 1,4 H-shift isomerization reaction to form OH, CO and a dihydroperoxy carbonyl  
 7 product (DHPCARB9).

8



9

10 **Figure 2:** Schematic of the main features of the higher generation chemistry following oxidation of the lumped  
 11 first-generation nitrate (RU14NO<sub>3</sub>) and hydroperoxide (RU14OOH), as represented in CRI v2.2; also  
 12 incorporating the chemistry of the multi-generation product, UCARB12. Closed-shell organic products are  
 13 shown in boxes. Species containing nitrate groups are shown in blue, and species containing hydroperoxide or  
 14 epoxide groups are shown in red. For clarity, the scheme omits some minor initiation reactions and the  
 15 reactions of RU12O<sub>2</sub> with NO<sub>3</sub> and the peroxy radical pool, although these are included in the mechanism.  
 16 Further information on species class and identity is given in Table S3.

### 1 3.2 Updates to the higher-generation chemistry

2 The rate parameters applied to the further oxidation of the lumped first-generation products are  
3 generally weighted averages of those applied to the contributing species in MCM v3.3.1. These were  
4 based on the relative yields of the contributing species in the middle of the range of  $\text{NO}_x$  levels  
5 considered in the zero-dimensional boundary layer box model simulations (i.e. at  $\sim 0.5$  ppb  $\text{NO}_x$ ).

6 Selected features of the second- and higher-generation chemistry are illustrated in Figs. 1, 2 and S4.  
7 Figure 1 shows the main features of the chemistry following the rapid photolysis of the newly  
8 defined lumped  $\delta$ -hydroperoxyaldehyde product, HPUCARB12. This generates  $\text{HO}_x$  radicals, and  
9 leads significantly (50 %) to a lumped hydroxyvinyl carbonyl product (HUCARB9), which also  
10 photolyses rapidly to generate additional  $\text{HO}_x$ . This chemistry therefore substantially enhances the  
11  $\text{HO}_x$  regeneration and production that results from the preceding 1,6 H-shift reaction of RU14O2.

12 Figure 2 summarizes the main features of the chemistry of the lumped first-generation  
13 hydroxynitrate (RU14NO<sub>3</sub>) and hydroperoxide (RU14OOH), formed from the reactions of RU14O2  
14 with NO and HO<sub>2</sub>, respectively. RU14NO<sub>3</sub> is removed predominantly by reaction with OH radicals,  
15 with a lifetime of about 9 hours (for  $[\text{OH}] = 1 \times 10^6$  molecule  $\text{cm}^{-3}$ ). This represents a reduction in  
16 reactivity of almost a factor of two compared with CRI v2.1, reflecting that the distribution of the  
17 component species under atmospheric conditions contains a smaller contribution of the reactive  $\delta$ -  
18 hydroxynitrate isomers in MCM v3.3.1 than represented previously in MCM v3.1 (see discussion in  
19 Jenkin et al., 2015). As shown in Fig. 2, the reaction of RU14NO<sub>3</sub> with OH leads either to  $\text{HO}_x$   
20 propagation and formation of products that retain the nitrate group (RU12NO<sub>3</sub> and RU10NO<sub>3</sub>); or  
21 release of  $\text{NO}_x$  (as  $\text{NO}_2$ ) and formation of products not containing oxidized organic nitrogen,  
22 represented by UCARB12. The second-generation nitrates, RU12NO<sub>3</sub> and RU10NO<sub>3</sub>, are mainly  
23 representative of nitro-oxy carbonyl species in MCM v3.3.1, which have been reported to photolyse  
24 rapidly (Müller et al., 2014). Photolysis is therefore the dominant removal process assigned to  
25 RU10NO<sub>3</sub> and RU12NO<sub>3</sub>, such that  $\text{NO}_x$  is effectively exclusively regenerated at this oxidation step.

1 The lumped first-generation hydroperoxide, RU14OOH, is removed predominantly by reaction with  
2 OH radicals, with a lifetime of about 4 hours. This mainly results in the OH-neutral conversion to a  
3 lumped epoxydiol product (IEPOX), consistent with the observations of Paulot et al. (2009) and  
4 Bates et al. (2014). The further oxidation of IEPOX is dominated by reaction with OH radicals, with a  
5 lifetime of about a day. This forms the lumped peroxy radical, RU12O2, which represents a set of  
6 unsaturated peroxy radicals containing hydroxyl and carbonyl groups. This is consistent with the  
7 major routes applied in MCM v3.3.1, which are based on the mechanism presented by Bates et al.  
8 (2014).

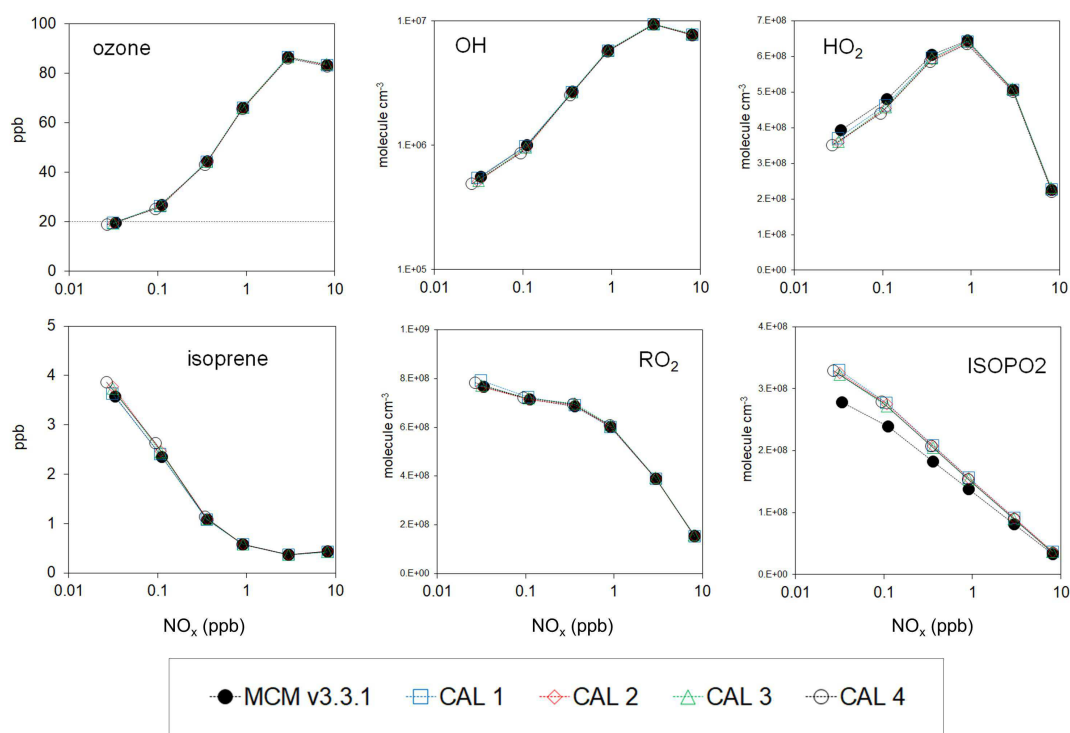
9 The major first generation products under the majority of atmospheric conditions are UCARB10 and  
10 formaldehyde, HCHO (see Fig. 1). UCARB10 is an unsaturated carbonyl species, which represents  
11 both methyl vinyl ketone (MVK) and methacrolein (MACR). The degradation of UCARB10 therefore  
12 incorporates the main features of the MVK and MACR chemistry as represented in MCM v3.3.1 with  
13 weighted average kinetic parameters and product ratios (see Fig. S4). Although much of this  
14 chemistry is unchanged from CRI v2.1, a 1,4 H-shift isomerization reaction is now incorporated for  
15 one of the product peroxy radicals, RU10AO2 (consistent with the study of Crouse et al., 2012), and  
16 the further OH-initiated oxidation of the second-generation product, methacryloyl peroxy nitrate  
17 (MPAN), now partially generates hydroxymethyl-methyl- $\alpha$ -lactone (HMML) in conjunction with  
18 release of NO<sub>3</sub> radicals. This represents the collective formation of the isomeric products, HMML  
19 and methacrylic acid epoxide (MAE), in MCM v3.3.1, which was based on the results of Kjaergaard et  
20 al. (2012) and Lin et al. (2013). In practice, the assumption applied in CRI v2.2 is more consistent  
21 with the more recent study of Nguyen et al. (2015), who report negligible formation of MAE.

## 1 **4 Boundary layer box modelling studies**

### 2 **4.1 MCM v3.3.1 reference simulations**

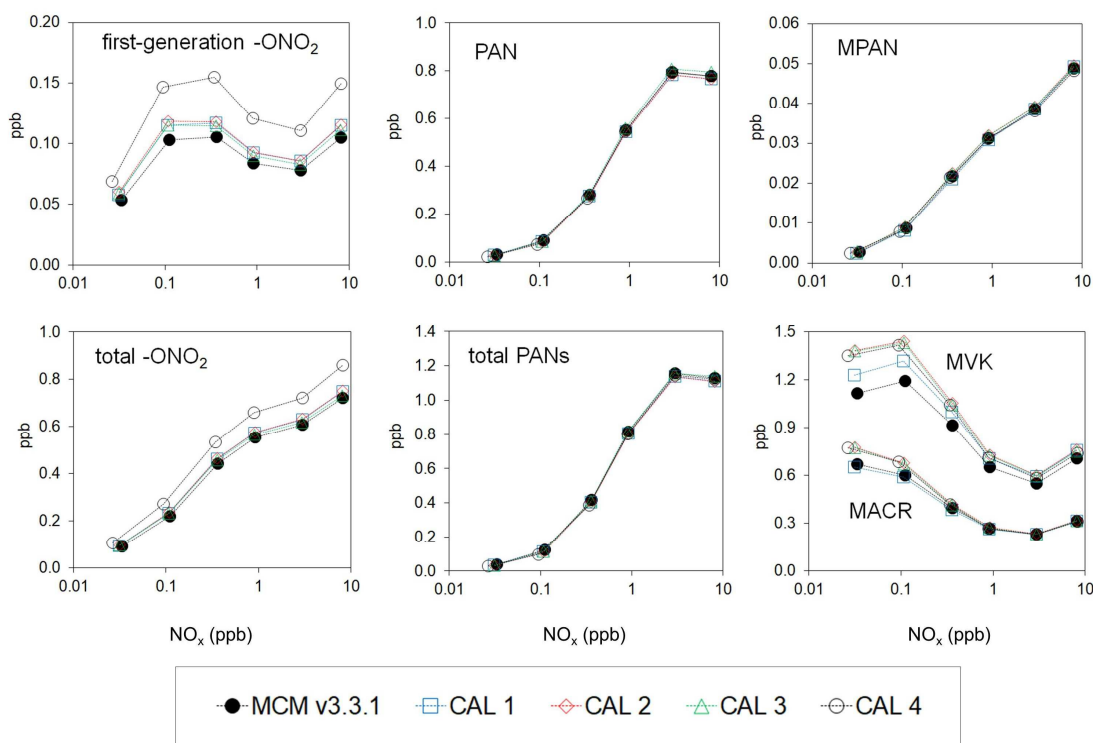
3 The MCM v3.3.1 simulations carried out using the zero-dimensional boundary layer box model have  
4 been reported and discussed in detail previously by Jenkin et al. (2015). These are used as the  
5 reference benchmark against which to compare the performance of CRI v2.2 and other mechanistic  
6 variants in the present work.

7 Wennberg et al. (2018) have reviewed recent laboratory and theoretical studies relevant to  
8 tropospheric isoprene degradation, and have compiled a detailed mechanism describing the gas-  
9 phase oxidation of isoprene and its major products. This takes account of information reported since  
10 the release of MCM v3.3.1, in particular a number of recent studies from the Caltech group of  
11 Wennberg and co-workers (e.g. Teng et al., 2017). Although the two mechanisms contain many  
12 common features, there are inevitably some mechanistic and parameter differences resulting from  
13 consideration of the more recent work by Wennberg et al. (2018), and from differing interpretations  
14 of the previously reported information. A series of the more important differences have therefore  
15 been implemented sequentially into MCM v3.3.1, resulting in the mechanistic variants denoted CAL  
16 1 to CAL 4 in Table 1. The performances of these variants are compared with that of MCM v3.3.1 in  
17 Figs. 3 – 5 (with additional information and an extended discussion provided in Sect. S2). These  
18 illustrate the simulated daytime-averaged levels of a number of key species formed during isoprene  
19 degradation, and their dependence on the level of  $\text{NO}_x$ . The changes implemented in the  
20 mechanistic variants generally have only relative minor effects on mechanistic performance, such  
21 that the performance of MCM v3.3.1 is considered to remain an acceptable benchmark for the CRI  
22 v2.2 evaluation reported below.



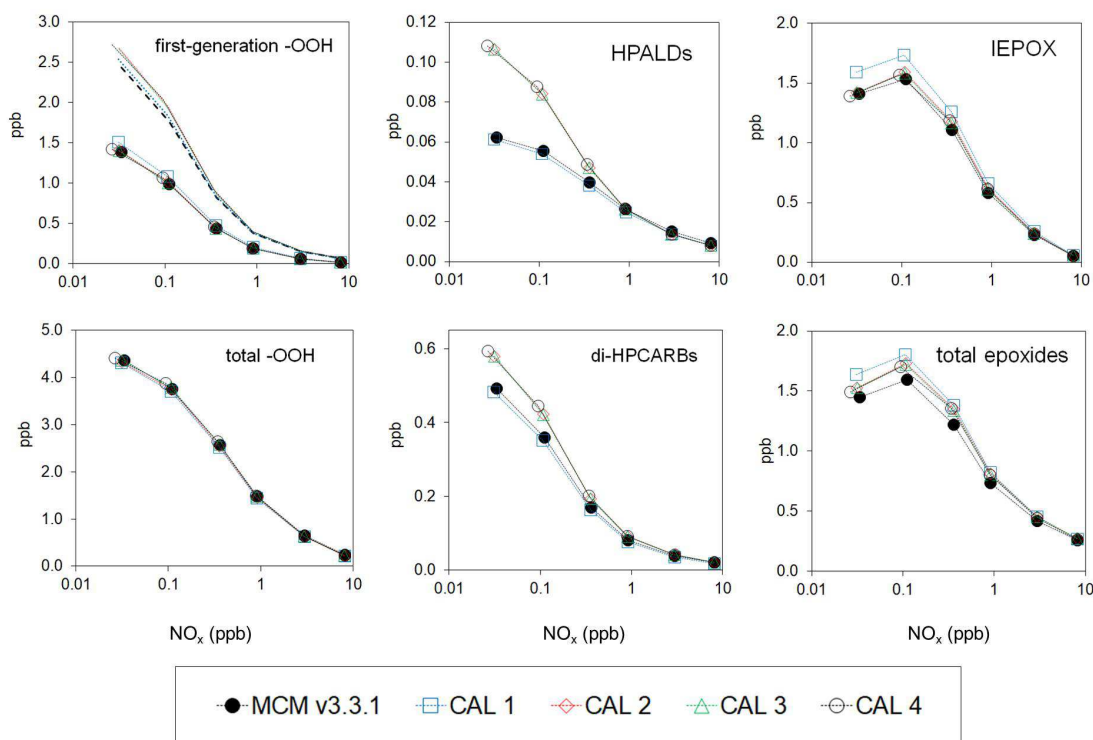
1

2 **Figure 3:** Comparison of performance of MCM v3.3.1 and the variants based on the Caltech scheme  
 3 (Wennberg et al., 2018), showing the  $\text{NO}_x$  dependence of the daylight-averaged mixing ratios or  
 4 concentrations of  $\text{O}_3$ , isoprene, OH,  $\text{HO}_2$ , total organic peroxy radicals (denoted  $\text{RO}_2$ ) and peroxy radicals  
 5 formed from the first-generation OH-initiated chemistry (denoted ISOP2). The broken line in the  $\text{O}_3$  panel  
 6 shows the background mixing ratio relative to which  $\text{O}_3$  is either produced or destroyed (see text).



7

8 **Figure 4:** As Fig. 3 for the organic oxidized nitrogen reservoirs, nitrates ( $-\text{ONO}_2$ ) and PANs; and methyl vinyl  
 9 ketone (MVK) and methacrolein (MACR). The first-generation nitrates are specifically those formed from the  
 10 reactions of NO with first-generation peroxy radicals (denoted "ISOP2" in Fig. 3).



1

2 **Figure 5:** As Fig. 3 for selected hydroperoxides and epoxides. The first-generation hydroperoxides are  
 3 specifically those formed from the reactions of HO<sub>2</sub> with first-generation peroxy radicals (denoted “ISOPO<sub>2</sub>” in  
 4 Fig. 3). The additional lines in the “first-generation -OOH” panel shows the effect of including HPALDs and di-  
 5 HPCARBs in the totals, with MCM v3.3.1 represented by the black heavy broken line and CAL 4 by the black  
 6 light broken line.

7

8 Comparing the results obtained with CAL 4 (in which all the mechanistic changes listed in Table 1

9 were implemented) with the MCM v3.3.1 results reveals two notable differences in performance.

10 First, the simulated collective levels of the unsaturated hydroperoxyaldehyde products (denoted

11 HPALDs) are generally higher in the CAL 4 simulation (Fig. 5). Wennberg et al. (2018) represent

12 partial formation of both  $\beta$ - and  $\delta$ -hydroperoxyaldehydes from the chemistry following the 1,6 H

13 shift isomerization reactions of the first-generation Z- $\delta$ -hydroxyperoxy radicals (tentatively based on

14 the results of Teng et al., 2017), whereas only  $\delta$ -hydroperoxyaldehydes are formed in MCM v3.3.1.

15 The photolysis rate assigned to the  $\beta$ - isomers is an order of magnitude lower than that of the  $\delta$ -

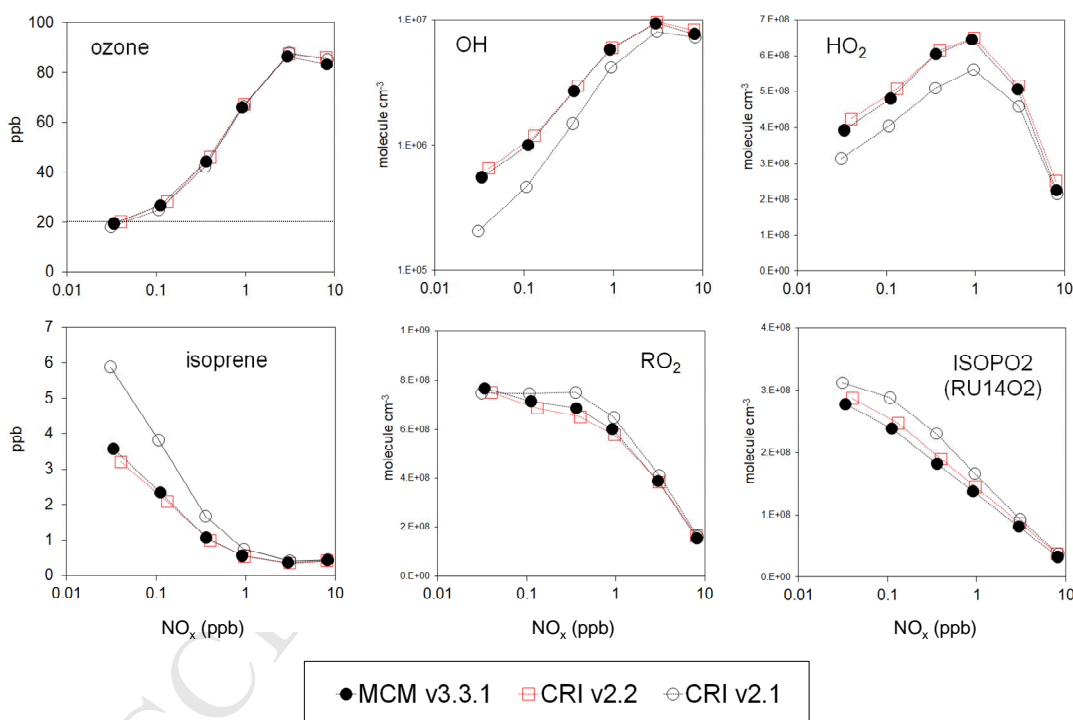
16 isomers, owing to the aldehyde and unsaturated C=C groups being conjugated in the latter, but not

17 in the former. This leads to the level of the  $\beta$ -hydroperoxyaldehydes being less suppressed, resulting

18 in higher total levels of HPALDs in the CAL2, CAL 3 and CAL4 simulations.

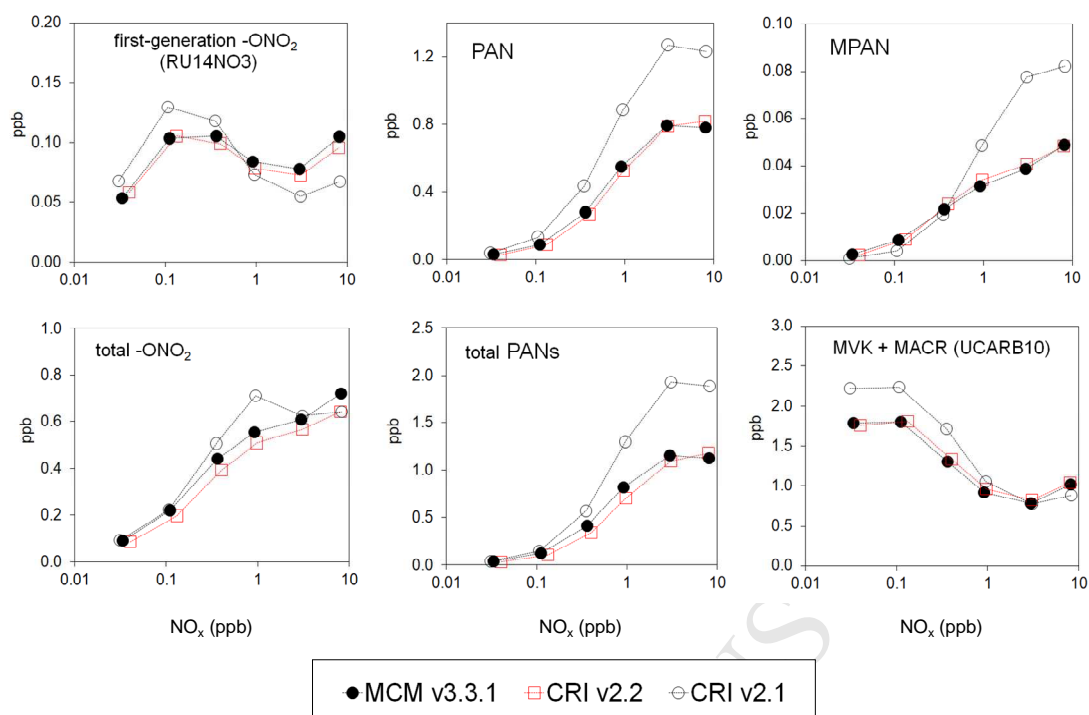
1 The second notable difference between the CAL 4 and MCM v3.3.1 simulations is an increasing  
 2 suppression of the  $\text{NO}_x$  level towards the low end of the considered  $\text{NO}_x$  emission range in the CAL 4  
 3 results. This is because the fractional formation of hydroxynitrate products from the first-generation  
 4  $\text{RO}_2 + \text{NO}$  reactions recommended by Wennberg et al. (2018) is about 33 % higher (at 298 K and 760  
 5 Torr) than that applied in MCM v3.3.1. This higher sequestration of oxidized nitrogen is also  
 6 apparent in the “first-generation  $-\text{ONO}_2$ ” and “total  $-\text{ONO}_2$ ” panels in Fig. 4. However, it is noted that  
 7 this difference in the applied hydroxynitrate yields is well within the reported uncertainties (e.g. see  
 8 discussion in Jenkin et al., 2015).

9



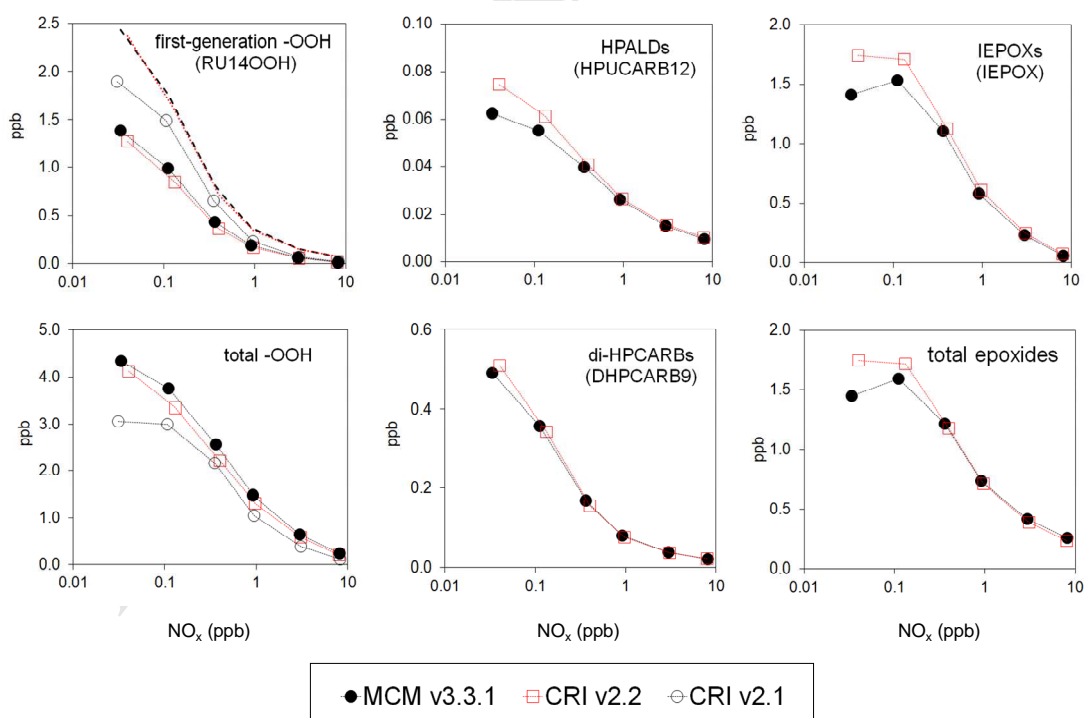
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11 **Figure 6:** Comparison of performance of MCM v3.3.1, CRI v2.2 and CRI v2.1, showing the  $\text{NO}_x$  dependence of  
 12 the daylight-averaged mixing ratios or concentrations of  $\text{O}_3$ , isoprene, OH,  $\text{HO}_2$ , total organic peroxy radicals  
 13 (denoted  $\text{RO}_2$ ) and peroxy radicals formed from the first-generation OH-initiated chemistry (denoted ISOP02).  
 14 The broken line in the  $\text{O}_3$  panel shows the background mixing ratio relative to which  $\text{O}_3$  is either produced or  
 15 destroyed (see text). Where applicable, the name of the corresponding lumped CRI species is given in brackets  
 16 (see also Table S3).



1

2 **Figure 7:** As Fig. 6 for the organic oxidized nitrogen reservoirs, nitrates ( $-\text{ONO}_2$ ) and PANs, and the collective  
 3 mixing ratio of MVK and MACR (in MCM v3.3.1) or UCARB10 (in CRI v2.2 and CRI v2.1). The first-generation  
 4 nitrates are specifically those formed from the reactions of NO with first-generation peroxy radicals (denoted  
 5 “ISOPO2” in Fig. 2). Where applicable, the name of the corresponding lumped CRI species is given in brackets  
 6 (see also Table S3).



7

8 **Figure 8:** As Fig. 6 for selected hydroperoxides and epoxides. The first-generation hydroperoxides are  
 9 specifically those formed from the reactions of  $\text{HO}_2$  with first-generation peroxy radicals (denoted “ISOPO2” in  
 10 Fig. 6). The additional lines in the “first-generation  $-\text{OOH}$ ” panel shows the effect of including HPALDs and di-  
 11 HPCARBs in the totals, with MCM v3.3.1 represented by the black heavy broken line and CRI v2.2 by the red  
 12 broken line. Where applicable, the name of the corresponding lumped CRI species is given in brackets (see  
 13 also Table S3).

## 1 4.2 CRI v2.2 simulations

2 The performances of CRI v2.2 and the preceding version, CRI v2.1, are compared with that of MCM  
3 v3.3.1 in Figs. 6 – 8. The results for the CRI v2.1 chemistry are comparable with those reported  
4 previously for MCM v3.1 (Jenkin et al., 2015), consistent with its performance being optimized to  
5 the earlier MCM version during development (Jenkin et al., 2008).

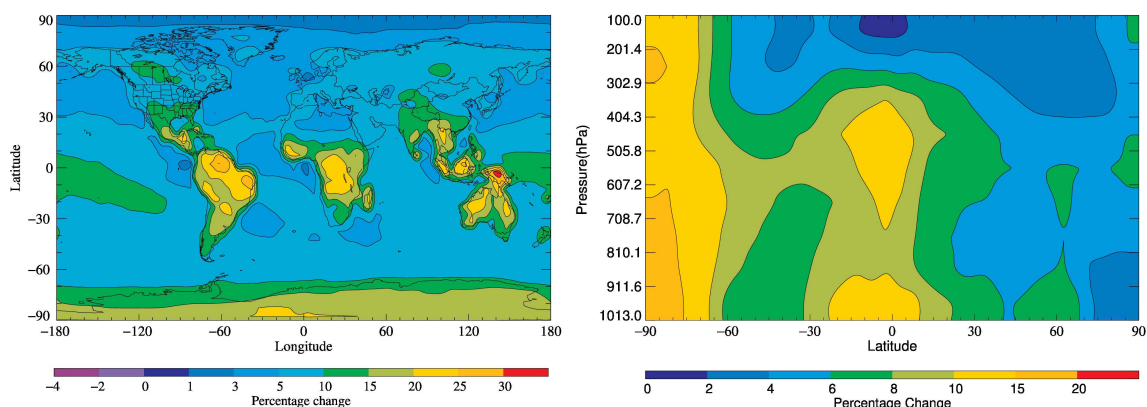
6 The results show that the changes implemented in CRI v2.2 bring its performance into generally  
7 good agreement with the current benchmark, MCM v3.3.1. Fig. 6 shows the impact of varying the  
8  $\text{NO}_x$  input on the simulated concentrations of  $\text{HO}_x$  radicals, illustrating the well-documented  
9 suppression in the calculated OH concentrations as the  $\text{NO}_x$  levels decrease (e.g. Jenkin et al., 1993;  
10 2015; Lelieveld et al., 2008). This results from the progressively decreasing efficiency of OH  
11 regeneration from the  $\text{NO}_x$ -catalysed free radical chemistry, and is particularly pronounced in the  
12 CRI v2.1 results, with the concentration of OH varying from a maximum of about  $8 \times 10^6$  molecule  
13  $\text{cm}^{-3}$  close to the high end of the  $\text{NO}_x$  range to about  $2 \times 10^5$  molecule  $\text{cm}^{-3}$  at the low end of the  
14 range. The updates implemented in CRI v2.2 have a significant impact on OH radical regeneration at  
15 lower  $\text{NO}_x$  levels. The simulated OH concentrations are a factor of 3 greater at the low end of the  
16  $\text{NO}_x$  range than those simulated with CRI v2.1, with this also suppressing the simulated isoprene  
17 mixing ratio. Fig. S5 confirms that the fluxes through the newly implemented OH regeneration  
18 routes are consistent with those simulated for the corresponding processes in MCM v3.3.1. These  
19 make a notable contribution at sub-ppb  $\text{NO}_x$  levels and collectively exceed that from the  $\text{NO}_x$ -  
20 catalysed free radical chemistry at  $\text{NO}_x$  levels below 100 ppt. Particularly important contributions  
21 are simulated to result from the chemistry initiated by the 1,6 H atom shift isomerization reaction of  
22 RU14O2 (including the subsequent rapid photolysis of HPUCARB12 and HUCARB9 and the 1,4 H shift  
23 reaction of DHPR12O2; see Sect. 3.1 and Fig. 1) and from the higher-generation 1,4 H atom shift  
24 isomerization reaction for RU10A02 (see Sect. 3.2 and Fig. S4).

1 Fig. 7 shows that the updates in CRI v2.2 result in simulated abundances of oxidized organic nitrogen  
2 species that are in acceptable agreement with MCM v3.3.1. The simplified representation of the  
3 multi-generation chemistry in CRI v2.2 leads to total abundances of organic nitrates (i.e. species  
4 containing  $-\text{ONO}_2$  groups) and PANs (i.e. species containing  $-\text{C}(\text{O})\text{OONO}_2$  groups) that are  
5 comparable to, although slightly lower than those simulated with MCM v3.3.1. This results in the  
6  $\text{NO}_x$  levels being slightly less suppressed in the CRI v2.2 simulations, with this being most apparent  
7 towards the low end of the considered  $\text{NO}_x$  emission range. The simulations of hydroperoxides and  
8 epoxides in Fig. 8 also show that the updates in CRI v2.2 (described in Sect. 3) bring its performance  
9 into agreement with that of MCM v3.3.1, with those for UCARB10 and MPAN in Fig. 7 illustrating  
10 that the lumped representation of MVK and MACR chemistry (Sects. 3 and S1.2) provides a  
11 consistent description.

## 12 **5 Global-scale modelling studies**

13 Illustrative global scale simulations have been carried out using both the STOCHEM-CRI and EMEP  
14 MSC-W models. Implementation of the CRI v2.2 isoprene chemistry into STOCHEM-CRI was found to  
15 result in respective increases in the simulated global tropospheric OH and  $\text{HO}_2$  burdens of 6.4 % and  
16 0.8 % relative to those simulated using CRI v2. However, the distribution plots of OH concentration  
17 changes (Fig. 9) show that the inclusion of the new chemistry increased OH levels significantly over  
18 low  $\text{NO}_x$  and high isoprene emission regions, i.e. the terrestrial tropical forests (typically 15 – 30 %) and the boreal regions over Russia and Canada (typically 5 – 10 %). The increase in OH  
19 concentrations has in turn shortened the lifetime of isoprene, leading to a decrease in its  
20 tropospheric burden of 16.6 %. The increase in modelled OH concentrations over regions of the  
21 Amazon and Borneo results in levels that are more consistent with the high atmospheric oxidizing  
22 capacity measured and discussed by Lelieveld et al. (2008), Pugh et al. (2010) and Taraborrelli et al.  
23 (2012).

25



1

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(a)

(b)

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**Figure 9:** The percentage changes of annual (a) surface [OH], (b) zonal [OH], simulated by STOCHEM-CRI following implementation of the CRI v2.2 isoprene chemistry. Simulations were carried out for 1998 and the results are mapped onto a Eulerian grid of dimensions  $5^\circ \times 5^\circ$  with nine equally vertically spaced pressure levels each  $\sim 100$  hPa in thickness. Isoprene emissions were 501 Tg/yr from terrestrial vegetation and 1.9 Tg/yr from oceanic sources (see Sect. 2.2). Base case [OH] plots are provided in Sect. S3.

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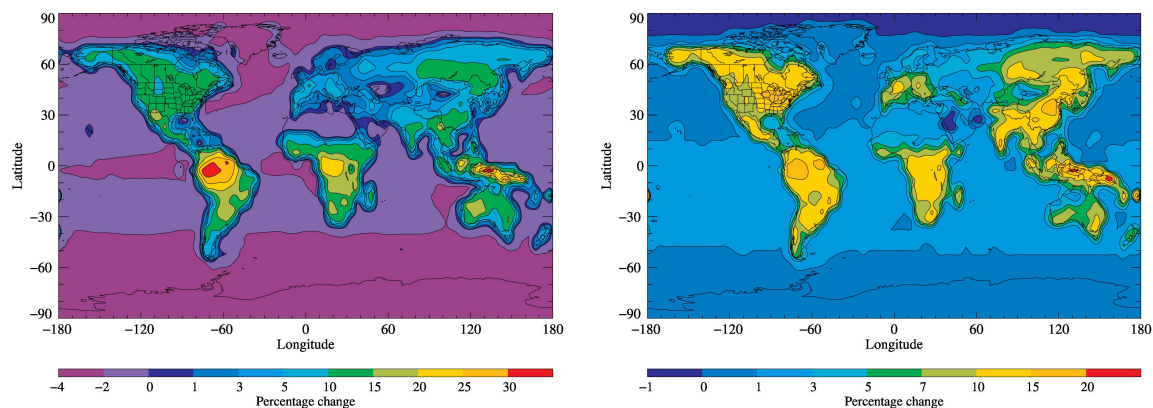
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Implementation of the EMEP variant CRI v2.2 isoprene chemistry into EMEP MSC-W model similarly resulted in notable increases in surface OH and HO<sub>2</sub> concentrations (Fig. 10) relative to the CRI v2.1 isoprene scheme, these being  $> 10\%$  in most of the Americas, sub-Saharan Africa, Southern and Eastern Asia, and Oceania. Once again, particular OH enhancements (20 – 50 %) were simulated in the equatorial forested regions characterized by elevated isoprene emissions and low NO<sub>x</sub>. The implementation of the updated isoprene chemistry in the two models therefore results in consistent impacts on the simulated terrestrial OH concentrations, given the differences in the applied meteorology, emissions and model resolution. However, the STOCHEM-CRI simulation also shows small enhancements in OH levels over the oceans which are not apparent in the EMEP MSC-W results. As will be discussed in more detail elsewhere, this mainly results from the recent inclusion of oceanic isoprene emissions in STOCHEM-CRI.



(a)

(b)

**Figure 10:** The relative changes in annual (a) surface [OH] and (b) surface [HO<sub>2</sub>], simulated by the EMEP MSC-W model following implementation of the EMEP variant CRI v2.2 isoprene chemistry. Simulations were carried out for 2010 with 1° × 1° grid resolution and are mapped at 5° × 5°. Isoprene emissions were 425 Tg/yr from terrestrial vegetation (see Sect. 2.2). Base case [OH] and [HO<sub>2</sub>] maps are provided in Sect. S3.

## 6 Summary and conclusions

9 The chemistry of isoprene degradation in the Common Representative Intermediates (CRI)  
10 mechanism has been systematically revised and updated to reflect recent advances in  
11 understanding (as represented in MCM v3.3.1), with the revised chemistry being released as part of  
12 CRI v2.2. The complete isoprene degradation mechanism in CRI v2.2 is represented by 186 reactions  
13 of 56 species, which treat the chemistry initiated by reaction with OH, O<sub>3</sub> and NO<sub>3</sub>. This is an order of  
14 magnitude reduction in size compared with MCM v3.3.1, in which isoprene degradation is  
15 represented by 1926 reactions of 602 species (Jenkin et al., 2015). A detailed overview of the  
16 updates has been provided, with reference to the reported kinetic and mechanistic information on  
17 which they are based. The revisions have impacts in a number of key areas, as illustrated by  
18 comparing the performance of the CRI v2.2 isoprene mechanism with that of the preceding version  
19 (CRI v2.1) over a range of relevant conditions in a box model of the tropical forested boundary layer.  
20 As a result, the revised representations of HO<sub>x</sub> and NO<sub>x</sub> recycling, and the production and removal of  
21 epoxide species, perform consistently with the corresponding processes in MCM v3.3.1. The revised

1 isoprene chemistry has been shown to have significant impacts on simulated HO<sub>x</sub> concentrations in  
2 global simulations using the STOCHEM-CRI and EMEP MSC-W chemistry-transport models.

3 The effects of recent advances in the understanding of isoprene degradation chemistry (as reviewed  
4 by Wennberg et al., 2018) have also been examined for a range of relevant conditions in the  
5 boundary layer box model, by implementing a series of the main mechanistic differences into the  
6 MCM v3.3.1 reference mechanism. Although there are some impacts on specific observables, the  
7 changes generally have only relative minor effects on overall mechanism performance. MCM v3.3.1  
8 is therefore considered to remain an acceptable benchmark for evaluation of reduced mechanisms,  
9 and a practical platform for testing the impacts of newly discovered mechanistic information  
10 relevant to isoprene degradation.

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15 UK Natural Environment Research Council (NERC) via grant NE/M013448/1 and the UK National  
16 Centre for Atmospheric Sciences (NCAS) Air Quality Science Programme. The EMEP modelling work  
17 was partially funded by EMEP under UNECE. Computer time for EMEP model runs was supported by  
18 the Research Council of Norway through the NOTUR project EMEP (NN2890K).

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## The CRI v2.2 reduced degradation scheme for isoprene

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### Highlights

- Isoprene chemistry in a reduced (lumped chemistry) scheme is updated.
- Detailed MCM v3.3.1 isoprene chemistry is used as a reference benchmark.
- An order of magnitude reduction in species and reaction numbers is achieved.
- Performance of MCM v3.3.1 is tested in relation to recently reported information.
- Impacts of updates on global-scale  $[\text{HO}_x]$  are illustrated using two global models.

**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: