

The MCM v3.3.1 degradation scheme for isoprene

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Abstract

The chemistry of isoprene degradation in the Master Chemical Mechanism (MCM) has been systematically refined and updated to reflect recent advances in understanding, with these updates appearing in the latest version, MCM v3.3.1. The complete isoprene degradation mechanism in MCM v3.3.1 consists of 1927 reactions of 603 closed shell and free radical species, which treat the chemistry initiated by reaction with OH radicals, NO₃ radicals and ozone (O₃). A detailed 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 some products that are also generated from the O₃- and NO₃-initiated oxidation. The revisions have impacts in a number of key areas, including HO_x recycling, NO_x recycling and the formation of species reported to play a role in SOA-formation mechanisms. The performance of the MCM v3.3.1 isoprene mechanism has been compared with those of earlier versions (MCM v3.1 and MCM v3.2) over a range of relevant conditions, using a box model of the tropical forested boundary layer. The results of these calculations are presented and discussed, and are used to illustrate the impacts of the mechanistic updates in MCM v3.3.1.

1 Introduction

The degradation of emitted volatile organic compounds (VOCs) has a major influence on the chemistry of the troposphere, contributing to the formation of ozone (O₃), secondary organic aerosol (SOA) and other secondary pollutants (e.g. Haagen-Smit and Fox, 1954; Went, 1960; Andreae and Crutzen, 1997; Jenkin and Clemitshaw, 2000; Hallquist et al., 2009). Approximately 90 % of organic material emitted globally is estimated to originate from biogenic sources (Guenther et al., 1995), with a major contribution from the reactive biogenic VOC, isoprene (2-methyl-buta-1,3-diene). In Europe, isoprene is estimated to contribute more than 30 % of total biogenic VOC emissions, and 50% of reactive biogenic VOC emissions. Such estimates vary widely on a regional if not a global scale (e.g. Arneth et al. 2008, Warneke et al., 2010, Langner et al., 2014), but isoprene is believed to be the most abundantly emitted non-methane VOC in the atmosphere. The emission rate may also be altered by future changes to climate and other environmental factors (e.g. Peñuelas and Staudt, 2010, Arneth et al, 2010, Simpson et al., 2014, and references therein). Reliable representations of isoprene emissions and atmospheric oxidation are therefore essential components of chemistry-transport models (CTMs) applied to climate change and air quality assessments.

The potential impact of isoprene emission and oxidation on the composition of the global atmosphere has stimulated extensive study of its atmospheric chemistry, and there have been some notable advances in understanding over the past decade. These developments include numerous laboratory and theoretical studies of the kinetics and products of key elementary reactions, and elucidation and evaluation of mechanisms using chamber data (see references in Sect. 2), with additional information also resulting from the evaluation and intercomparison of mechanisms used in models (e.g. Archibald et al., 2010a; 2010b; Stavrou et al., 2010; Stone et al., 2011). The results of field studies have been used to test understanding of isoprene chemistry, and to identify potential gaps in that understanding under atmospheric conditions. Such studies have stimulated or informed many of the recent laboratory, chamber and theoretical investigations; particularly in relation to missing recycling mechanisms for HO_x radicals (e.g. Tan et al., 2001; Thornton et al., 2002; Martinez et al., 2003; Ren et al., 2008; Lelieveld et al., 2008; Butler et al., 2008; Karl et al., 2009; Taraborrelli et al., 2012), the chemistry of oxidized organic nitrogen species (e.g. Horowitz et al., 2007; Perring et al., 2009) and the formation of species that contribute to SOA (e.g. Claeys et al., 2004; Chan et al., 2010; Froyd et al., 2010; Lin et al., 2013).

The Master Chemical Mechanism (MCM) provides a detailed description of atmospheric gas-phase organic chemistry, that has been widely used by the atmospheric science community both directly, and as a benchmark representation against which to develop and optimise reduced chemical mechanisms for use in CTMs. The MCM isoprene chemistry has been systematically revised and updated to reflect recent advances in understanding, with the updated mechanism provisionally released in March 2015 as MCM v3.3, as described in the “discussion” version of this paper (Jenkin et al., 2015). This has been further refined on the basis of a series of review comments, leading to the current finalised version, MCM v3.3.1. In this paper, a detailed overview of the updates is provided, within the context of reported kinetic and mechanistic information. The performance of the MCM v3.3.1 isoprene scheme has been examined for a range of relevant conditions, using a box model of the tropical forested boundary layer. The results of this study are presented, and are used to illustrate the impacts of the mechanistic updates in MCM v3.3.1.

2 Updates to isoprene chemistry in MCM v3.3.1

The complete degradation chemistry of isoprene, as represented in MCM v3.3.1, consists of 1927 reactions of 603 species, and includes chemistry initiated by reaction with OH, O₃ and NO₃. It can be viewed and downloaded using the subset mechanism assembling facility, available as part of the MCM website (<http://mcm.leeds.ac.uk/MCM>). The isoprene chemistry included previously in v3.1 (consisting of 605 reactions of 201 species) has been described in some detail by Pinho et al. (2005) and Archibald et al. (2010a), and the updates described below therefore document the major changes to the mechanism since MCM v3.1. These were partially implemented in MCM v3.2 (released in 2011), which contained 1428 reactions of 447 species. All those updates have been retained or further refined, with substantial additional revisions in the latest update to MCM v3.3.1. The revisions mainly relate to the OH-initiated chemistry, which tends to dominate under atmospheric conditions, although these include updates to the chemistry of some products that are also generated from the O₃- and NO₃-initiated oxidation. The revisions have impacts in a number of key areas, including HO_x recycling, NO_x recycling and the formation of species reported to play a role in SOA-formation mechanisms. The following subsections provide a detailed overview of the updates.

2.1 Updates to the first-generation OH-initiated chemistry

2.1.1 OH addition ratios and reactions of OH-isoprene adducts with O₂

The initial stages of the chemistry following addition of OH to isoprene in the presence of O₂, as represented in MCM v3.3.1, are shown in Fig. 1. In contrast to previous versions of the mechanism, the minor addition of OH to the central carbon atoms (i.e. at positions 2 and 3) is now represented, with respective addition ratios of 57.6 %, 4.2 %, 4.2 % and 34.0 % at positions 1, 2, 3 and 4. As described in more detail in Sect. 2.1.4 below (and in Sect. S1.1 of the Supplement), these were defined using a combination of structure-activity relationships (SARs) and optimisation of the first-generation mechanism to reported product yields. However, these addition ratios are fully consistent with those that have been reported in a number of theoretical studies (e.g. McGivern et al., 2000; Lei et al., 2000; Greenwald et al., 2007; Peeters et al., 2009).

The chemistry of the minor adducts formed from addition of OH to the central carbon atoms is based on the mechanism postulated in the theoretical study of Park et al. (2003). This involves isomerisation of the OH-isoprene adducts to form α -hydroxyalkenyl radicals, which each react with O₂ to form HO₂ and an unsaturated C₅ carbonyl product. Addition of OH at position 2 thus leads to the exclusive formation of pent-4-en-2-one (PE4E2CO) and HO₂ by this mechanism (see Fig. 1). Based on information reported in Park et al. (2003), addition of OH at position 3 is assumed to lead to competitive formation of both the isomeric unsaturated C₅ carbonyl, 3-methyl-but-3-enal (ME3BU3ECHO), and HO₂ via the isomerisation mechanism, and direct addition of O₂ to the initial OH-isoprene adduct to form a β -hydroxy peroxy radical (denoted ISOP34O2). As represented in MCM v3.3.1, this results in a total yield of unsaturated C₅ carbonyls of 6.2 %, which is consistent with that reported by Zhao et al. (2004).

The chemistry following the major addition of OH to the terminal carbon atoms (i.e. at positions 1 and 4) has been substantially revised in MCM v3.3.1, and is based on the Leuven Isoprene Mechanism (LIM1) reaction framework reported in the theoretical studies of Peeters et al. (2009; 2014), as also shown in Fig. 1. In each case, OH addition leads to the formation of *E*- and *Z*- isomers of a hydroxyalkenyl radical possessing an allyl resonance. Reversible addition of O₂ occurs at two possible sites in each resonant hydroxyalkenyl radical isomer, resulting in the formation of a β -hydroxy peroxy radical and *E*- and *Z*- isomers of a δ -hydroxy

peroxy radical (i.e. ISOPBO₂, CISOPAO₂ and ISOPAO₂ from OH addition at carbon 1; and ISOPDO₂, CISOPCO₂ and ISOPCO₂ from OH addition at carbon 4). The reversibility of O₂ addition allows the peroxy radical population to be redistributed between the various isomers in each subset, such that the relative population of the peroxy radicals also depends on the prevailing rates of other removal processes for the peroxy radicals. As recommended in the review comment of Peeters (2015), the kinetic parameters applied to the O₂ addition and peroxy radical back decomposition reactions are based on those calculated by Peeters et al. (2014), but with each increased by a factor of five on the basis of the experimental characterisation of the equilibration of peroxy radicals in each subset, as recently reported in preliminary form by Crounse et al. (2014). The resultant kinetic parameters are given in Table S1.

2.1.2 Peroxy radical reactions

As with previous versions of the MCM (Jenkin et al., 1997; Saunders et al., 2003), the β - and δ -hydroxy peroxy radicals undergo bimolecular reactions with NO, NO₃ and HO₂; and are also removed via reaction with the peroxy radical “pool” to represent the collective effect of peroxy radical self- and cross-reactions. Small revisions to the generic rate coefficients for the NO and NO₃ reactions were implemented in MCM v3.2, and these are retained in MCM v3.3.1 (see Sect. 2.3). The rate coefficients for the other reactions remain based on the rules presented previously by Saunders et al. (2003).

Fig. 2 shows the mechanisms following the (major) propagating channels of the reactions of the peroxy radicals with NO, involving the formation of the corresponding oxy radicals and their subsequent reactions to form first-generation oxygenated end products, which are discussed further in Sect. 2.1.3. Fig. 2 also shows competing unimolecular isomerisation reactions that are newly implemented in MCM v3.3.1 for specific peroxy radical structures. As originally postulated by Peeters et al. (2009) and da Silva et al. (2010), 1,5 H atom shift isomerisation reactions are now represented for the β -hydroxy peroxy radicals, ISOPBO₂ and ISOPDO₂, leading to the respective formation of methylvinyl ketone (MVK) and methacrolein (MACR), in conjunction with HCHO and OH. The applied isomerisation rates are the LIM1 values calculated recently by Peeters et al. (2014), as presented in Table S1, with these also being generally consistent with those reported by da Silva et al. (2010).

Also based on the mechanism originally proposed by Peeters et al. (2009), the newly defined Z- isomers of the δ -hydroxy peroxy radicals, CISOPAO2 and CISOPCO2, each undergoes a 1,6 H atom shift isomerisation reaction to produce a resonant C₅ hydroxy hydroperoxyalkenyl radical. As shown in Fig. 3, these are represented to react with O₂ partially (50 %) via α -hydroxy H atom abstraction to yield HO₂ and the unsaturated hydroperoxyaldehyde products C5HPALD1 and C5HPALD2; with experimental evidence for the production of these products being reported by Crounse et al. (2011) and Berndt (2012). Based on the recent study of Peeters et al. (2014), the reactions of O₂ with the hydroxy hydroperoxyalkenyl radicals are also represented to proceed equally via addition γ - to the OH group, leading to the production of the complex dihydroperoxy α -formyl peroxy radicals, C536O2 and C537O2 (see Fig. 3), these species being referred to as “di-HPCARPs” by Peeters et al. (2014). Under “low NO_x” conditions, C536O2 and C537O2 are represented to react significantly via 1,4 H atom shift isomerisation reactions, for consistency with newly implemented chemistry for the methacrolein-derived α -formyl peroxy radical, MACRO2 (see Sect. 2.2.1). This leads to significant formation of the dihydroperoxycarbonyl products (DHPMEK and DHPMPAL) in conjunction with OH and CO. The temperature-dependent rate expressions applied to the 1,6 H atom shift isomerisation reactions are based on those reported recently for LIM1 by Peeters et al. (2014) for CISOPAO2 and CISOPCO2, but scaled to recreate the phenomenological bulk isomerisation rate (k_{bulk}) to form the unsaturated hydroperoxyaldehyde products (C5HPALD1 and C5HPALD2) for the conditions of the experiments reported by Crounse et al. (2011) (see Sect. S1.4 for further details). It is noted that further support for operation of the LIM reaction framework, optimised to the observations of Crounse et al. (2011), has been reported by Fuchs et al. (2013), based on measurements of OH and peroxy radicals during the chamber oxidation of isoprene.

The branching ratios applied to the propagating and terminating channels of the reactions of the β - and δ -hydroxy peroxy radicals with NO have been revised in MCM v3.3.1. The branching ratios to nitrate product formation from the terminating channels are assumed to be equivalent for the secondary peroxy radical (ISOPDO2) and the tertiary peroxy radical (ISOPBO2), but the remaining (primary) peroxy radicals are assigned terminating channel ratios that are 20 % lower. This reflects the well-established lower propensities of primary peroxy radicals to form nitrates (e.g. Carter and Atkinson, 1989; Lightfoot et al., 1992), which is also supported by the recent study of Teng et al. (2015) for hydroxyperoxy radicals formed

from the reactions of OH with alkenes. The absolute values applied to the branching ratios were adjusted to result in an optimised total first-generation yield of nitrate products of 10 % at the high [NO] limit (see Sect. 2.1.4). As discussed by Archibald et al. (2010a), this value was previously assigned on the basis of a chamber evaluation of reported yields, and is in agreement with the current recommendation of the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation (<http://iupac.pole-ether.fr/>).

As with previous versions of the MCM, the reactions of the β - and δ -hydroxy peroxy radicals with HO₂ each proceeds by a single channel producing a hydroxy-hydroperoxide product and O₂. It is noted that some evidence for minor channels for the β -hydroxy peroxy radicals producing MVK (from ISOPBO₂) and MACR (from ISOPDO₂) has been reported (Paulot et al., 2009a; Liu et al., 2013; Navarro et al., 2013), with the implication that this results from a propagating channel also producing OH radicals. However, no direct evidence for OH formation from the reactions of HO₂ with β -hydroxy peroxy radicals has been reported to date (e.g. Dillon et al., 2008), such that implementation of propagating channels awaits further experimental confirmation.

2.1.3 Oxy radical reactions

Fig. 2 illustrates the reactions of the β - and δ -hydroxy oxy radicals, formed from propagating channels of the peroxy radical reactions, which lead to the formation of a number of first-generation oxygenated end products.

The well-established chemistry of the β -hydroxy oxy radicals, ISOPBO and ISOPDO, is essentially unchanged from previous versions of the MCM. These oxy radicals are thus represented to decompose by C-C bond scission, leading to respective formation of MVK and MACR in conjunction with the CH₂OH radical, which reacts with O₂ to produce HCHO and HO₂. The newly represented minor oxy radical, ISOP34O, also decomposes to produce HCHO and a C₄ α -hydroxyalkenyl radical, which reacts with O₂ to form MACR and HO₂ (see Fig. 2). The (relatively minor) δ -hydroxy oxy radicals, ISOPAO and ISOPCO, react via processes that were initially implemented in MCM v3.2, although these are now limited to those reactions that are available for the *E*- isomers of these structures. ISOPCO thus reacts exclusively with O₂ to produce the unsaturated hydroxyaldehyde, HC4CCHO (see Fig. 2). ISOPAO reacts via a 1,5 H shift isomerisation reaction, leading to the ultimate formation of hydroxymethacrolein (HMACR), HCHO and HO₂ via a multi-step mechanism involving a

further C₅ peroxy radical, as postulated by Dibble (2002) and Zhao et al. (2003) (see Fig. S3 and Sect. S1.3 for further details). Evidence for unsaturated C₄ hydroxycarbonyl formation was subsequently reported by Zhao et al. (2004), consistent with formation of HMA CR and/or isomeric products. It is noted that these fates for ISOPAO and ISOPCO are not supported by the very recent study of Nguyen and Peeters (2015), who theoretically characterised their rapid conversion into the corresponding Z- isomers (CISOPAO and CISOPCO), the chemistry of which is discussed below. However, the above reactions of ISOPAO and ISOPCO are currently retained, so that a route to the formation of HMA CR as a minor product remains in MCM v3.3.1.

As shown in Fig. 2, a number of fates are included for the newly defined Z- isomers of the δ -hydroxy oxy radicals, CISOPAO and CISOPCO. These are all initiated by a 1,5 H atom shift isomerisation, to produce a resonant C₅ dihydroxy alkenyl radical in each case, which is represented to react three ways (see Figs. S1 and S2 and Sect. S1.2 for further details):

(i) α -hydroxy H atom abstraction, to yield HO₂ and a C₅ unsaturated hydroxyaldehyde product (i.e. HC₄CCHO or HC₄ACHO). These reactions are required to account for the reported yields of C₅ unsaturated hydroxyaldehydes (Zhao et al., 2004; Baker et al., 2005; Paulot et al., 2009b).

(ii) Addition of O₂ γ - to the OH group, as postulated by Dibble (2004). This initiates sequences of reactions, involving C₅ α -formyl peroxy radicals (C526O₂ and C527O₂), leading to the ultimate formation of either methyl glyoxal (MGLYOX), glycolaldehyde (HOCH₂CHO) and OH from CISOPAO, or glyoxal (GLYOX), hydroxyacetone (ACETOL) and OH from CISOPCO. The mechanism is based on that reported by Peeters and Nguyen (2012) (see Figs. S1 and S2). Evidence for minor formation of glyoxal, glycolaldehyde and hydroxyacetone (or subsets of these) as first-generation products has been reported in the chamber studies of Volkamer et al. (2006), Galloway et al. (2011) and Paulot et al. (2009b).

(iii) Dehydration/cyclisation and subsequent reaction with O₂, leading to the formation of 3-methylfuran (M3F) and HO₂ by the mechanism postulated by Francisco-Márquez et al. (2003). These reactions are included to account for the reported minor formation of 3-methylfuran in a number of studies (e.g. Atkinson et al., 1989; Paulson et al., 1992; Ruppert and Becker, 2000; Brégonzio-Rozier et al., 2015). The agreement of the yields of 3-methylfuran in those “NO_x present” studies, in conjunction with the reported time dependence of its production (e.g. Benkelberg et al., 2000; Lee et al., 2005), appear to indicate that it is

formed (at least partially) as a first-generation product in the gas phase. However, it is noted that it is also likely formed by heterogeneous reactions of the C₅ unsaturated hydroxyaldehyde products, HC₄CCHO and HC₄ACHO (Dibble, 2007), such that there are uncertainties in the contribution of its gas phase formation.

2.1.4 Optimisation of first-generation OH-initiated chemistry

As described in greater detail in Sect. S1 of the Supplement, the first generation OH-initiated chemistry was optimised using reported product yields, with a number of constraints that have been described above in Sects. 2.1.1-2.1.3. Fig. 4 shows the resultant calculated molar yields of the main products as a function of NO mixing ratio at 298 K. These tend towards limiting values at the high end of the [NO] range shown, with little change at mixing ratios greater than about 500 ppb. This corresponds to conditions where reaction with NO is the dominant fate for all peroxy radicals in the system.

At lower [NO], the back decomposition reactions of the β - and δ -hydroxy peroxy radicals formed from OH addition at positions 1 and 4 (see Fig. 1) become increasingly competitive with the NO reactions, leading to a systematic variation in the relative peroxy radical population and a resultant impact on the product yields, as described in detail by Peeters et al. (2009; 2014). In addition to this, unimolecular isomerisation reactions also compete more effectively for specific peroxy radical structures. Under many atmospheric and chamber conditions, the reactions of peroxy radicals with HO₂ and with the peroxy radical pool would also likely start to compete towards the low end of the displayed [NO] range in Fig. 3; although the extent of this competition depends on the absolute radical concentration. The impact of these reactions therefore requires simulation of specific atmospheric or chamber conditions, and is not included in the illustration in Fig. 4.

The optimisation procedure primarily considered data from chamber studies performed with sufficient NO_x to correspond to the high [NO] limit in Fig. 4, which is the majority of reported “NO_x-present” studies. A number of parameters were varied to optimise the agreement in the calculated and reported product yields. These were the relative importance of OH attack at positions 1 and 4 in isoprene (which mainly influences the relative yields of MVK and MACR), and the relative importance of the three fates of the Z- isomers of the δ -hydroxy peroxy radicals, CISOPAO and CISOPCO, as described in Sect. 2.1.3 (which influences the formation of a number of the more minor first-generation products). This procedure

1 resulted in generally good agreement between the reported yields and those calculated with
2 MCM v3.3.1 at the high [NO] limit (see Sect. S1 and Table S2 for full details).

3 The yields calculated for the major products HCHO (61.0 %), MVK (34.1 %) and MACR
4 (23.6 %) at the high [NO] limit are therefore consistent with the respective reported yields of
5 (60.8 ± 4.5 %), (35.1 ± 5.2 %) and (23.6 ± 2.8 %) in “high NO_x” studies (see Table S2). As
6 shown in Fig. 4, the mechanism predicts an increase in the yields of these products at lower
7 [NO], with maximum respective values of about 77 %, 49 % and 27 % at about 1–2 ppb NO.
8 The relative yield of MVK and MACR generally increases with decreasing [NO], with the
9 rapid increase at the low end of the scale being consistent with the preliminary results of
10 Crounse et al. (2014), as discussed by Peeters (2015). However, it is noted that both the
11 absolute yields of MVK (approaching 50 %) and MVK/MACR ratios (≈ 1.8) are not fully
12 consistent with those reported by Karl et al. (2006) and Liu et al. (2013), based on
13 experiments carried out with NO mixing ratios of about 0.2 and 9 ppb, respectively. These
14 studies both report MVK yields of about 41 % and MVK/MACR ratios in the range 1.4–1.5
15 (i.e. similar to those at the high [NO] limit).

16 The yields of a number of minor products formed wholly or partially from the reactions of
17 CISOPAO and CISOPCO were also optimised to be consistent with reported studies at the
18 high [NO] limit (see Table S2). These are the C₅ hydroxycarbonyls (HC4ACHO and
19 HC4CCHO), 3-methylfuran, glyoxal/hydroxyacetone and methyl glyoxal/glycolaldehyde. As
20 shown in Fig. 4, the yields of all these products are predicted to decrease as [NO] is lowered.
21 In the cases of the C₅ hydroxycarbonyls and 3-methylfuran, this is due to the decreased
22 production of CISOPAO and CISOPCO that results from a combination of the increased
23 operation of the isomerisation reactions for the precursor peroxy radicals (CISOPAO₂ and
24 CISOPCO₂) and the general redistribution of the peroxy radical population (Peeters et al.,
25 2014). For glyoxal/hydroxyacetone and methyl glyoxal/glycolaldehyde, however, the yields
26 are predicted to be particularly sensitive to [NO], with complete inhibition of their formation
27 from CISOPAO and CISOPCO at the low end of the [NO] range. In addition to the decreased
28 production of CISOPAO and CISOPCO, their formation is also influenced by the chemistry
29 of the α -formyl peroxy radicals (C526O₂ and C527O₂), as formed in the mechanism
30 theoretically characterised by Peeters and Nguyen (2012) and applied here (see Figs. S1 and
31 S2). As discussed further below (Sects. 2.2.1 and 2.2.3), 1,4 H atom shift isomerisation
32 reactions are included for C526O₂ and C527O₂, for consistency with newly implemented

chemistry for the methacrolein-derived α -formyl peroxy radical, MACRO2, as also suggested by Peeters and Nguyen (2012). These isomerisation reactions compete more effectively as [NO] is lowered, thereby inhibiting formation of glyoxal/hydroxyacetone and methyl glyoxal/glycolaldehyde.

As indicated above in Sect. 2.1.2, the total yield of first-generation organic nitrates was assigned a value of 10 % at the high [NO] limit, based on the results of a previous chamber evaluation (Pinho et al., 2005) and the IUPAC Task Group recommendation, with this also being consistent with the range of the reported values (see Table S2). This total includes contributions from five isomeric hydroxynitrates (ISOPANO3, ISOPBNO3, ISOPCNO3, ISOPDNO3 and ISOP34NO3), and additional minor contributions from a further three species formed in the mechanisms generating hydroxymethacrolein (C524NO3), glyoxal/hydroxyacetone (C527NO3) and methyl glyoxal/glycolaldehyde (C526NO3) (see Fig. 5a). Compared with MCM v3.2, the main consequence of the revised branching ratios applied to the individual peroxy radical isomers in MCM v3.3.1 (described in Sect. 2.1.2) is an increased contribution of the tertiary β -hydroxynitrate (ISOPBNO3) and a decreased contribution of the secondary β -hydroxynitrate (ISOPDNO3). The resultant relative contributions of these β -hydroxy isomers, and the fractional contribution of the δ -hydroxy isomers (ISOPANO3 and ISOPCNO3) at the high [NO] limit (shown in Fig. 5b) are consistent with the preliminary results of Crounse et al. (2014). However, the distribution does not appear to match the results of any of the previously reported studies (Giacopelli et al., 2005; Paulot et al., 2009b; Lockwood et al., 2010), which display some variability (Fig. 5a). The mechanism predicts a slight decrease in the total first-generation nitrate yield as [NO] is lowered, falling to about 8 % at the low end of the considered range (see Fig. 4). This results mainly from the impact of competing isomerisation reactions for selected peroxy radicals. The associated [NO]-dependences of the β -hydroxy isomer ratio, and the δ -hydroxy isomer contribution, are consistent with the preliminary results of Crounse et al. (2014) (see Fig. 5b).

Fig. 4 also illustrates the increasing formation of the unsaturated hydroperoxyaldehydes (C5HPALD1 and C5HPALD2) and the dihydroperoxycarbonyls (DHPMEK and DHPMPAL) as [NO] decreases, these species being formed from the chemistry initiated by the 1,6 H atom shift isomerisation reactions of CISOPAO2 and CISOPCO2 (see Fig. 3), within the LIM1 reaction framework (Peeters et al., 2014). As indicated above (Sect. 2.1.2), the formation of

the unsaturated hydroperoxyaldehydes was optimised to recreate the phenomenological bulk isomerisation rate (k_{bulk}) reported by Crounse et al. (2011), which was about 0.002 s^{-1} at 295 K, under conditions when the peroxy radical loss rate through bimolecular reactions (k_{tr}) was $\approx 0.021 \text{ s}^{-1}$ (see section S1.4 and Fig. S4 for further details). As shown in Fig. 3, the chemistry initiated by the 1,6 H atom shift isomerisation reactions also provides additional first generation routes to methyl glyoxal and (particularly) glyoxal, which are most effective at intermediate [NO], when the reactions of NO with the α -formyl peroxy radicals C536O2 and C537O2 can compete with their 1,4 H atom shift isomerisation reactions. Evidence for operation of these routes has been reported by Crounse et al. (2012a), through detection of the hydroperoxycarbonyl co-products, HCOCH2OOH and HYPERACET (see Fig. 3).

Although not specifically optimised, the mechanism predicts a yield of hydroxymethacrolein (HMACR) of 3.3 % at the high [NO] limit, which is consistent with the yield of C₄ hydroxycarbonyls of $(3.3 \pm 1.6) \%$ reported by Zhao et al. (2004). This shows a modest variation with [NO], resulting mainly from the redistribution of the peroxy radical population (see Fig. 4). As indicated above (Sect. 2.1.1), the yield of unsaturated C₅ carbonyls (6.2 %) also agrees well with the yield of $(8.4 \pm 2.4) \%$ reported by Zhao et al. (2004). This shows no variation with [NO] because the unsaturated C₅ carbonyls are formed following prompt isomerisation of the minor OH-isoprene adducts, formed from OH addition at positions 2 and 3 in isoprene (see Fig. 1).

2.2 Updates to the higher-generation chemistry

2.2.1 Methacrolein (MACR)

Fig. 6 shows the main features of the chemistry following the reaction of OH with MACR, with the newly implemented updates in MCM v3.3.1 highlighted. These are as follows:

(i) A competitive 1,4 H atom shift isomerisation reaction is now included for the α -formyl peroxy radical, MACRO2, formed from the major OH addition channel, resulting in the direct formation of hydroxyacetone, CO and OH. This reaction was proposed and characterised by Crounse et al. (2012b), and the applied temperature-dependent rate coefficient is based on their reported value (see Table S3); with additional support deriving from the recent chamber study of Fuchs et al. (2014). For consistency, 1,4 H atom shift isomerisation reactions have also been included for a number of other α -formyl peroxy radicals. These include HMACRO2

(formed analogously from the reaction of OH with hydroxymethacrolein, HMA CR); and the C₅ peroxy radicals C₅7O₂ and C₅8AO₂, which have a number of sources in the isoprene mechanism, including the analogous reactions of OH with unsaturated C₅ hydroxy carbonyls (HC₄CCHO and HC₄ACHO, respectively), and the reaction of OH with the major isoprene epoxydiol (IEPOXB), as described further in Sect. 2.2.3. They also include the complex α -formyl peroxy radicals, C₅26O₂ and C₅27O₂ (formed in the newly implemented first-generation chemistry forming glyoxal/hydroxyacetone and methylglyoxal/glycolaldehyde, as discussed above in Sects. 2.1.3 and 2.1.4 and shown in Figs. S1 and S2); and the “di-HPCARPs”, C₅36O₂ and C₅37O₂ (formed following the 1,6 H atom shift isomerisation reactions of CISOPAO₂ and CISOPCO₂, as discussed in Sect. 2.1.2 and shown in Fig. 3).

(ii) The products of the reaction of OH with methacryloyl peroxy nitrate (MPAN) have been updated on the basis of the studies of Kjaergaard et al. (2012) and Lin et al. (2013). As shown in Fig. 6, the reaction now has significant channels forming hydroxymethyl-methyl- α -lactone (HMML) and methacrylic acid epoxide (MAE), in conjunction with release of NO₃ radicals. HMML and MAE have been postulated by the above authors to play a role in SOA-formation mechanisms, through efficient reactive uptake on acidic aerosol particles to form condensed phase 2-methylglyceric acid. The representation of heterogeneous chemistry is outside the scope of MCM v3.3.1, but their gas phase removal via reactions with OH is represented (see Sect. 2.2.7).

(iii) The products of the reaction of OH with methacrylic peroxy acid (MACO₃H) have been updated on the basis of the study of Kjaergaard et al. (2012). As shown in Fig. 6, the reaction now has a major channel forming hydroxyacetone and CO, and a minor channel forming hydroxymethyl methyl- α -lactone (HMML), in conjunction with release of OH radicals in each case. The products of the reactions of OH with a number of structurally similar peroxy acids have also been updated to include major OH-forming channels. These include HMA CO₃H, formed from hydroxymethacrolein (HMA CR) oxidation; and HC₄ACO₃H and HC₄CCO₃H, formed from the oxidation of the unsaturated C₅ hydroxycarbonyls, HC₄ACHO and HC₄CCHO. In these cases, however, OH formation is represented to occur exclusively in conjunction with CO and the corresponding dihydroxycarbonyl product, such that the minor channels forming products analogous to HMML are not currently represented.

2.2.2 Nitrates

Substantial revisions to the further degradation chemistry of the first-generation nitrate products were previously implemented in MCM v3.2, which included the chemistry initiated by reactions with both OH and O₃, and photolysis. These generally followed the rules in the MCM scheme-writing protocol (Jenkin et al., 1997; Saunders et al., 2003), but without the major simplifications previously applied to oxidised organic nitrogen species. The treatment also made use of the structure-activity relationship (SAR) method of Vereecken and Peeters (2009) to estimate the impacts of the nitrate groups (-ONO₂) on the reactions of the intermediate oxy radicals, and took account of information in a number of experimental studies (e.g. Paulot et al., 2009b; Lockwood et al., 2010) in defining parameters for specific reactions. The update added about 400 reactions of over 100 species to the mechanism. The majority of this chemistry has been retained unchanged in MCM v3.3.1, although selected important updates have been implemented, based on the results of more recent studies (e.g. Suarez-Bertoa et al., 2012; Lee et al., 2014; Müller et al., 2014).

The rate coefficients for the initiation reactions with OH and O₃ have been revised to take account of the recent study of Lee et al. (2014), leading to a notable reduction in the importance of the O₃-initiated chemistry compared with MCM v3.2. Representative average atmospheric lifetimes for the first-generation nitrates with respect to these reactions are estimated to be about 8.5 hours (for [OH] = 10⁶ molecule cm⁻³) and 9.4 days (for 20 ppb O₃), based on the nitrate distribution calculated at 1 ppb NO. Because of the [NO]-dependence of the first-generation chemistry discussed above, it should be noted that the distribution of nitrates varies with conditions, such that the corresponding average lifetimes are about 5 hours and 2 days for the distribution calculated at the high [NO] limit, which contains a greater proportion of the more reactive 1,4- and 4,1-substituted species, ISOPANO₃ and ISOPCNO₃.

A general overview of the OH-initiated chemistry over several generations is illustrated in Fig. 7. An important feature of the degradation chemistry is the extent to which the organic products retain the nitrate group, whether NO_x is released, or whether additional NO_x is sequestered to form dinitrate products. Fig. 7 shows that about 40 % of the second-generation products formed from the OH-initiated chemistry retain the nitrate group (in conjunction with HO_x propagation), with about 50 % leading to the release of NO_x in the form of NO₂ (in conjunction with HO_x loss). A small fraction (10 %) is estimated to generate dinitrate

1 products, with these processes leading to loss of both NO_x and HO_x . These proportions are
2 broadly consistent with the product yields reported by Lee et al. (2014) for the OH-initiated
3 oxidation of selected first-generation nitrate isomers, and also with constraints on the
4 lifetimes and the extent of nitrate group recycling derived from atmospheric observations in
5 the continental USA (Perring et al., 2009). Fig. 7 also demonstrates that the subsequent
6 generations of product have generally longer lifetimes with respect to reaction with OH than
7 the first-generation nitrates, but with progressively greater proportions of NO_x being released
8 at each oxidation step. For simplicity, the illustration in Fig. 7 assumes that the level of NO is
9 sufficiently high that the reactions of intermediate peroxy radicals with HO_2 and the peroxy
10 radical pool are of minor importance. The participation of these reactions tends to increase the
11 proportion of nitrate-retaining products, owing to the greater importance of terminating
12 reaction channels that preclude release of NO_x , e.g. the formation of multifunctional
13 hydroperoxynitrates from the reactions with HO_2 .

14 The representation of the O_3 -initiated chemistry also results in only partial release of NO_x in
15 the initial oxidation step, with about 65 % formation of second-generation products that retain
16 the nitrate group. Once again, this is consistent with the product yields reported by Lee et al.
17 (2014) for the O_3 -initiated oxidation of selected first-generation nitrate isomers. The identities
18 of the major nitrate-containing products overlap substantially with those generated from the
19 OH-initiated chemistry, such that the subsequent OH-initiated oxidation and NO_x release
20 follows a similar pattern to that shown in Fig. 7. By analogy with the ozonolysis of simple
21 alkenes, the O_3 -initiated chemistry is also currently estimated to generate OH radicals with an
22 average yield of about 50 %, although this is somewhat higher than reported by Lee et al.
23 (2014) for selected isomers.

24 The mechanism also includes photolysis reactions for the first-generation nitrates, and for
25 many of the multifunctional nitrate products formed from the OH- and O_3 -initiated chemistry.
26 The majority of these higher generation nitrate products contain α - or β -carbonyl groups (e.g.
27 all the mono-nitrate species shown in Fig. 7), and the representation of their photolysis in
28 MCM v3.3.1 has been updated on the basis of the recent study of Müller et al. (2014) and the
29 discussion comment of Müller (2015), leading to associated clear sky lifetimes in the range
30 1–10 hours (for solar zenith angle = 30°). As a result, photolysis is now the major fate in most
31 cases, leading to quantitative release of NO_x in the form of NO_2 , in conjunction with HO_x
32 formation. This tends to inhibit formation of the third- and fourth-generation mono-nitrate

products shown in Fig. 7, and results in substantial NO_x regeneration from the second-generation species. The third-generation di-nitrate species also generally contain carbonyl groups α - to at least one nitrate group, and therefore photolyse efficiently. This leads about equally to the formation of either NO_2 , HO_x and mono-nitrate products, or the release of two molecules of NO_2 in conjunction with organic products not containing a nitrate group.

2.2.3 Hydroperoxides and epoxydiols

The chemistry of the first-generation hydroxy-hydroperoxides was also substantially revised in MCM v3.2 to represent dominant formation of isomeric epoxydiol products, with associated prompt regeneration of OH, as characterised by Paulot et al. (2009a). The epoxydiols are believed to play an important role in the formation of SOA from isoprene (Paulot et al., 2009a; Lin et al., 2011), and have been detected in ambient samples (e.g. Chan et al., 2010; Froyd et al., 2010). A provisional representation of the gas-phase degradation of the epoxydiols was also included in MCM v3.2. This chemistry has been updated in MCM v3.3.1, mainly based on the results of the recent study of Bates et al. (2014).

Fig. 8 shows an overview of the degradation mechanism following reaction of OH with the five isomeric isoprene hydroxy-hydroperoxides included in MCM v3.3.1. They are estimated to react rapidly with OH, leading to atmospheric lifetimes in the approximate range 2–6 hours, for $[\text{OH}] = 10^6 \text{ molecule cm}^{-3}$. Under representative “low NO_x ” conditions (based on the peroxy radical distribution at the low end of the $[\text{NO}]$ range in Fig. 4), the MCM v3.3.1 representation results in the formation of the isomeric epoxydiols (IEPOXA, IEPOXB and IEPOXC) with a collective yield of about 85 %, which is consistent with that reported by Paulot et al. (2009a). This is dominated by IEPOXB (accounting for about 95 % of the total), this isomer being formed from the two most abundant hydroxy-hydroperoxides, ISOPBOOH and ISOPDOOH (see Fig. 8). This is also consistent with the distribution of the epoxydiol isomers reported by Bates et al. (2014).

The epoxydiols are removed by reaction with OH, with rate coefficients based on those reported by Bates et al. (2014) for IEPOXC and *cis*- and *trans*- isomers of IEPOXB, leading to associated atmospheric lifetimes of about 1 day. It is noted that Jacobs et al. (2013) reported somewhat higher rate coefficients for the reactions of OH with IEPOXA and the *trans*- isomer of IEPOXB, consistent with atmospheric lifetimes of about 8 hours. The rate coefficients of Bates et al. (2014) are currently adopted in MCM v3.3.1, because they allow a broadly

consistent representation of the sequential formation and removal kinetics of the hydroperoxide and epoxydiol isomers reported by Paulot et al. (2009a). However, there is clearly some uncertainty in the lifetimes of these species.

The main features of the subsequent degradation chemistry of IEPOXB are shown in Fig. 8. These are also largely based on the mechanism presented by Bates et al. (2014), which can potentially account for the formation of a number of end products reported and quantified in that study. The mechanism thus produces a low yield (11 %) of products retaining the epoxide group (i.e. IEB1CHO and IEB4CHO). The remainder of the chemistry forms three ring-opened isomeric peroxy radicals, C57O2 (37 %), C58AO2 (37 %) and C59O2 (15 %), which all also have a number of other sources in the MCM v3.3.1 isoprene chemistry. As indicated above in Sects. 2.1.4 and 2.2.1, the more abundant α -formyl peroxy radical isomers (C57O2 and C58AO2) are also generated from the degradation of the C₅ hydroxy carbonyls (HC4ACHO and HC4CCHO). The newly implemented 1,4 H atom shift isomerisation reactions are likely to be the dominant fates for C57O2 and C58AO2 under most atmospheric conditions (see Sect. 2.2.1), leading to the formation of OH, CO and the dihydroxycarbonyl products, MACROH and HO12CO3C4 (see Fig. 8). The significant formation of these species is also consistent with the product study of Bates et al. (2014).

2.2.4 Unsaturated C₅ hydroperoxyaldehydes (HPALDs)

Fig. 9 shows the main features of the degradation chemistry for the newly implemented unsaturated C₅ hydroperoxyaldehydes, C5HPALD1 and C5HPALD2, which is based on information provided in the appraisals of Peeters and co-workers (Peeters et al., 2009; Peeters and Müller, 2010; Peeters et al., 2014).

The dominant fate of the hydroperoxyaldehydes is photolysis, which results from absorption into the α,β -enal chromophore, followed by dissociation of the weak O-O bond in the hydroperoxide group, to form OH and an energy-rich C₅ oxy radical in each case (see Fig. 8). Efficient photolysis was originally proposed by Peeters et al. (2009), with subsequent experimental confirmation reported by Wolfe et al. (2012) for the structurally-similar species, *E*-4-hydroxyperoxy-hex-2-enal. The assigned photolysis rate is thus based on the UV absorption cross sections of the well-studied α,β -enal, methacrolein (MACR), with an assumed unity quantum yield, leading to an associated clear sky lifetime of about 30 minutes (for solar zenith angle = 30°). As discussed by Peeters et al. (2014), the subsequent chemistry

of the C₅ oxy radical products is subject to some uncertainty, but is provisionally based on information provided in that study for the Z- conformer of C5HPALD1, supplemented by rules as defined in the previous MCM protocol (Saunders et al., 2003). This leads to the formation of two new unsaturated C₄ hydroxycarbonyl products (HVMK and HMAc in Fig. 9).

As shown in Fig. 9, the reactions with OH with C5HPALD1 and C5HPALD2 are also represented, with these reactions typically making a minor contribution to the removal of the hydroperoxyaldehydes. The rate coefficients and product channels for these reactions are based on the appraisal of Peeters and Müller (2010), leading to associated atmospheric lifetimes of about 5 hours (for [OH] = 10⁶ molecule cm⁻³). The reactions of the hydroperoxyaldehyde species with O₃ and NO₃ are also included in MCM v3.3.1, with representations that are consistent with the rules in the MCM protocol (Saunders et al., 2003).

2.2.5 Glyoxal

The chemistry of the HCOCO radical, formed most significantly from the OH-initiated oxidation of glyoxal (GLYOX), has been updated in MCM v3.3.1. This has taken particular account of information reported in the studies of Orlando and Tyndall (2001), da Silva (2010) and Lockhart et al. (2013). As a result, the mechanism now includes a temperature and [O₂] dependence for the relative formation of CO and CO₂, a route to direct OH recycling, and no longer sequesters NO_x in the form of the PAN species, HC(O)C(O)O₂NO₂ (see Sect. S2.1 for further details).

2.2.6 3-Methylfuran

The rate coefficient for the reaction of OH with 3-methylfuran is based on the studies of Atkinson et al. (1989) and Aschmann et al. (2011), leading to an associated atmospheric lifetime of about 3 hours (for [OH] = 10⁶ molecule cm⁻³). The subsequent mechanism currently leads to quantitative formation of HO₂ and 2-methylbutenedial (C4MDIAL), which is consistent with the yield of (83 ± 33) % reported by Gómez Alvarez et al. (2009), and informed by the theoretical study of Zhang et al. (2008). However, it is noted that Aschmann et al. (2014) have recently reported a lower yield of (38 ± 2) % from experiments with much higher levels of NO (about 5 ppm), indicating that the mechanism is probably [NO]-dependent. The chemistry initiated by the reactions with O₃ and NO₃ is also represented, with

the rate coefficients taken from the study of Alvarado et al. (1996) and subsequent mechanisms based on rules presented previously (Saunders et al., 2003).

2.2.7 Other products

The updates to the chemistry described above lead to the formation of a number of other new products. These include the unsaturated C₅ carbonyls (PE4E2CO and ME3BU3ECHO) (Fig. 1), the unsaturated C₄ hydroxycarbonyls (HVMK and HMAc) (Fig. 9), the C₄ dihydroperoxycarbonyls (DHPMEK and DHPMPAL) (Fig. 3), hydroxymethyl-methyl- α -lactone (HMML) (Fig. 6), methacrylic acid epoxide (MAE) (Fig. 6), and other (usually minor) multifunctional products containing combinations of functional groups. These compounds are all degraded using the rules presented previously by Jenkin et al. (1997) and Saunders et al. (2003). The degradation chemistry of HMML is augmented to take account of chemistry reported more recently for the epoxydiol, IEPOXB (Bates et al., 2014), and results in partial formation of HCOOH (see Sect. S2.2 for further details).

In the cases of HVMK and HMAc, removal via rapid photolysis (initially forming OH and a stabilised hydroxyvinyl radical) is also represented, as recommended by Peeters et al. (2014), and in the discussion comment of Müller (2015). This leads to clear sky photolysis lifetimes of about an hour for HVMK and HMAc (for solar zenith angle = 30°).

2.3 Generic updates

Small revisions were made to a number of generic rate coefficients for peroxy radical reactions in MCM v3.2, and these are retained in MCM v3.3.1. These include those for the reactions of acyl peroxy radicals (of generic formula RC(O)O₂) with NO and HO₂, and the reference rate coefficient for the reactions of other peroxy radicals with NO and NO₃ (see Sect. S2 and Table S3 for further details).

The reactions of acyl peroxy radicals with HO₂ were also previously revised to include major radical propagating channels, as follows:



This has relevance to the reactions of 47 complex acyl peroxy radicals formed during isoprene degradation in MCM v3.3.1 (e.g. the methacryloyl peroxy radical, MACO₃, formed from methacrolein), in addition to CH₃C(O)O₂ itself. The branching ratios are based on the current IUPAC recommendations for the reaction of CH₃C(O)O₂ with HO₂ (<http://iupac.pole->

ether.fr/), such that 44 % of the reaction proceeds via the propagating channel (R1) in each case; this being based on the experimental determinations of Hasson et al. (2004), Jenkin et al. (2007) and Dillon and Crowley (2008). It is noted that the recent results of Groß et al. (2014), based on direct OH detection, suggest an even higher branching ratio, $(62 \pm 9) \%$, and this may therefore influence future recommendations.

The rate coefficients for the formation and back decomposition of peroxyacetyl nitrate (PAN, $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$) have been updated in MCM v3.3.1, on the basis of the recent recommendations of the IUPAC Task Group (<http://iupac.pole-ether.fr/>). These rate coefficients are also applied to the analogous reactions forming and removing peroxyacetyl nitrates in general, with the exception of MPAN decomposition, for which the rate coefficient remains based on the IUPAC recommendation for that specific reaction.

3 Examination of the performance of MCM v3.3.1

The performance of the MCM v3.3.1 isoprene mechanism was compared with those of MCM v3.1 and MCM v3.2 using simulations carried out with a boundary layer box model, coded for application with the FACSIMILE kinetics integration package (MCPA Software). The aim of these studies was to examine and illustrate the effects of the updates described in Sect. 2 for a range of idealised atmospheric conditions, with particular emphasis on the impacts on HO_x and NO_x partitioning and recycling.

3.1 Model description

The model was designed to simulate a well-mixed tropical forested boundary layer, 1000 m in depth. The boundary layer air parcel was continuously exchanged with the free troposphere on a timescale of 1 day, thus representing a loss process for longer-lived products. The free troposphere was assumed to contain the following limited series of trace species, which were mixed into the boundary layer on the same timescale: O_3 (20 ppb), CO (100 ppb), HCHO (300 ppt). The model was initialised for 7 days such that exchange processes reached steady state, and results from the daylight portion of the 8th diurnal cycle were used in comparisons of mechanism performance. The temperature followed a sinusoidal diurnal profile (average 298 K; amplitude 4 K), leading to a peak temperature of 302 K in the early afternoon. The diurnal variation of photolysis parameters was set for a latitude of 0° at equinox in all simulations. Photolysis coefficients were calculated assuming clear sky conditions, using a parameterization

1 previously applied with the MCM (Saunders et al., 2003). For the present illustration, the loss of
2 product species via deposition or transfer to the condensed phase was not represented, the focus
3 of the simulations being chemical processing in the gas phase. The same inorganic reaction
4 scheme and parameters were used with each MCM version, so that the differences in
5 performance result from the changes to the organic chemistry, as summarised above.

6 The boundary layer box received continuous emissions of isoprene and NO_x , which were
7 maintained throughout the model runs, and a fixed mixing ratio of 1.8 ppm methane was
8 assumed. A base NO_x emission rate of $4.7 \times 10^9 \text{ molecule cm}^{-2} \text{ s}^{-1}$ was applied, which is a
9 globally-averaged rate based on an annual total emission of 44.8 TgN, as applied by Derwent et
10 al. (2003). This resulted in daylight-averaged NO_x mixing ratios of about 30 ppt (with small
11 variations between mechanisms). To examine the NO_x -dependence of the chemistry, the NO_x
12 emission rate was scaled by factors of 3, 10, 30, 100 and 200 which resulted in daylight-
13 averaged NO_x mixing ratios up to about 8 ppb (again with small variations between
14 mechanisms). The relative isoprene emission rate varied with temperature and
15 photosynthetically active radiation (PAR) throughout the diurnal cycle, based on a standard
16 algorithm (Guenther et al., 1995). The absolute magnitude of the emissions was set such that the
17 daylight average emission rate was $7.6 \times 10^{11} \text{ molecule cm}^{-2} \text{ s}^{-1}$ ($3.1 \text{ mg m}^{-2} \text{ h}^{-1}$), maximising at
18 $1.0 \times 10^{12} \text{ molecule cm}^{-2} \text{ s}^{-1}$ ($4.2 \text{ mg m}^{-2} \text{ h}^{-1}$) in the early afternoon. These emissions fluxes are
19 typical of those reported for tropical forested regions (e.g. Eerdeken et al., 2009).

20 Reaction with OH was the dominant fate of isoprene for the conditions of this illustration,
21 accounting for between 89 % and 93 % of isoprene removal in the MCM v3.3.1 simulations
22 (depending on the NO_x level). The contribution of the O_3 -initiated chemistry increases from
23 about 4 % at the high end of the NO_x range to about 11 % at the low end of the NO_x range. The
24 NO_3 -initiated chemistry is also simulated to contribute up to about 4 % to isoprene removal,
25 with the maximum contribution towards the high end of the NO_x range.

26 **3.2 Results**

27 Selected results of the series of simulations using the MCM v3.3.1 isoprene chemistry are
28 shown in Figs. 10–15, along with the corresponding results of simulations using MCM v3.1
29 and MCM v3.2, where applicable. These illustrate the simulated daytime-averaged levels of a
30 number of key species formed during isoprene degradation, or fluxes through key reactions,
31 and their dependence on the level of NO_x .

3.2.1 Ozone

As shown in Fig. 10, the simulated levels of O₃ are relatively insensitive to the mechanistic updates implemented in MCM v3.2 and MCM v3.3.1. Consistent with conventional understanding of VOC degradation (e.g. Jenkin and Clemitshaw, 2000), the simulated formation of O₃ with all the mechanisms progressively increases with the availability of NO_x, leading to maximum mixing ratios of between 86 and 91 ppb close to the high end of the range of NO_x inputs considered (see Fig. 10), corresponding to average O₃ production rates of almost 3 ppb h⁻¹. At the low end of the NO_x input range, the chemistry leads to very slight net O₃ removal, at rates between -0.02 and -0.07 ppb h⁻¹. This is because its removal via direct photolysis and reaction with isoprene, and its reactions with HO₂ and OH, slightly outweigh its formation from the NO_x-catalysed free radical chemistry and other minor sources (i.e. the minor channels of the reactions of HO₂ with acyl peroxy radicals).

3.2.2 HO_x radicals

Fig. 10 also shows the impact of varying the NO_x input on the simulated concentrations of HO_x radicals. This shows the well-documented suppression of calculated OH concentrations as the NO_x levels decrease (e.g. Jenkin et al., 1993; Lelieveld et al., 2008), which results from the progressively decreasing efficiency of OH regeneration from the NO_x-catalysed free radical chemistry. This is particularly pronounced in the MCM v3.1 results, with the concentration of OH varying from a maximum of about 8×10^6 molecule cm⁻³ close to the high end of the NO_x range, to below 2×10^5 molecule cm⁻³ at the low end of the range. As described above in Sect. 2, the updates implemented in MCM v3.2 and MCM v3.3.1 are expected to have a collectively significant impact on OH radical regeneration at lower NO_x levels. This is clearly apparent in the MCM v3.3.1 results presented in Fig. 10, for which the OH concentrations are a factor of three greater at the low end of the NO_x range than those simulated with MCM v3.1, with this also suppressing the simulated isoprene mixing ratio. To illustrate this further, Fig. 11 compares the fluxes through the newly implemented OH regeneration routes with that through the reaction of HO₂ with NO (i.e. that resulting from the NO_x-catalysed free radical chemistry). This confirms that the collective flux through the new routes makes a notable contribution at sub ppb NO_x levels, and exceeds that from the NO_x-catalysed free radical chemistry at NO_x levels below 100 ppt. Particularly important contributions are simulated to result from the chemistry initiated by the 1,6 H atom shift isomerisation reactions of CISOPAO2 and CISOPCO2 (including the 1,4 H shift reactions of

C536O2 and C537O2 and the photolysis of C5HPALD1 and C5HPALD2; see Sects. 2.1.2 and 2.2.4), and from the higher generation 1,4 H atom shift isomerisation reactions for MACRO2, C57O2 and C58AO2 (see Sect. 2.2.1).

The newly implemented updates also lead to (more modest) increases in the HO₂ radical concentrations, with those simulated with MCM v3.3.1 being about 30 % greater at the low end of the NO_x range than those simulated with MCM v3.1 (see Fig. 10). The simulated total concentration of organic peroxy radicals (RO₂) is insensitive to the mechanistic changes, although the first-generation peroxy radicals (denoted “ISOPO2” in Fig. 10) make a reduced contribution to the total in the MCM v3.3.1 simulation, particularly at lower NO_x levels. This results mainly from the significant operation the newly implemented peroxy radical isomerisation reactions in MCM v3.3.1.

3.2.3 Oxidised organic nitrogen

Fig. 12 shows the simulated levels of organic nitrates (i.e. species containing -ONO₂ groups) and PANs (i.e. species containing -C(O)OONO₂ groups), and subsets of these totals. The results for the organic nitrates show that the updates implemented in MCM v3.2 and MCM v3.3.1 have a considerable impact on the simulated abundance of those formed from the first-generation OH-initiated chemistry (denoted “first-generation -ONO₂” in Fig. 12). The suppression in the simulated levels in MCM v3.2 relative to MCM v3.1 results mainly from the inclusion of the O₃-initiated removal chemistry. As discussed in Sect. 2.2.2, revisions to the rate coefficients for the O₃ reactions in MCM v3.3.1 result in a notable reduction in the importance of the O₃-initiated chemistry compared with MCM v3.2, leading to an increase in the abundance of the first-generation nitrates. The distribution of first generation nitrates also has a reduced OH reactivity in MCM v3.3.1, resulting from both the changes to the nitrate-forming branching ratios for the β-hydroxy peroxy radicals (Sect. 2.1.2) and from the reduction in the fractional contribution of the more reactive δ-hydroxy species (ISOPANO3 and ISOPDNO3) under atmospheric conditions (see Fig. 5b). Despite this, the first-generation nitrate levels at low NO_x remain substantially suppressed relative to the MCM v3.1 simulation. This is partly because of the greater abundance of OH radicals, leading to enhanced removal rates, and partly because the significant operation of the newly implemented peroxy radical isomerisation reactions in MCM v3.3.1 reduces the yield of first-generation nitrates at lower NO_x levels.

1 The simulated abundance of total organic nitrates also shows differences that result from the
2 substantial updates made to the chemistry in MCM v3.2 and MCM v3.3.1 (see Sect. 2.2.2). The
3 more rigorous representation of the formation of higher-generation nitrates in MCM v3.2 leads
4 to a notable increase in the total organic nitrate abundance. However, the levels simulated with
5 MCM v3.3.1 are reduced relative those with MCM v3.2. This is mainly because of the
6 implementation of rapid photolysis for α - and β -carbonyl nitrates (which make a large
7 contribution to the higher generation species) leading to NO_x regeneration; and also because of
8 the greater abundance of OH radicals at low NO_x .

9 To illustrate the details of the nitrate chemistry further, Fig. 13 shows the relative
10 contributions of the initiation reactions contributing to the removal of first- and second-
11 generation organic nitrates in the MCM v3.3.1 simulations, and the associated regeneration of
12 NO_x . The oxidation of the first-generation nitrates is mainly initiated by reaction with OH,
13 accounting for between 76 % and 97 % of the removal depending on the level of NO_x . At the
14 high end of the NO_x range, the OH-initiated oxidation results in 47 % regeneration of NO_x
15 (along with 43 % formation of mononitrate products and 10 % formation of dinitrate
16 products), consistent with the appraisal in Sect. 2.2.2 and Fig. 7. As shown in Fig. 13, the
17 extent of NO_x regeneration from the OH-initiated chemistry progressively decreases with the
18 level of NO_x , to just over 20 % at the low end of the NO_x range. This is because of the
19 increasing operation of termination reactions for the intermediate nitro-oxy peroxy radicals,
20 and the associated formation of nitrate-retaining products (e.g. hydroperoxynitrates from the
21 termination reactions with HO_2). However, the increasing contribution of photolysis to first-
22 generation nitrate removal at low NO_x levels (with associated quantitative NO_x formation)
23 supplements NO_x regeneration, such that the total extent of NO_x regeneration from the first-
24 generation nitrates is close to 40 % for most of the NO_x range, for the conditions of the
25 present simulations.

26 As also shown in Fig. 13, the oxidation of the second-generation nitrates is initiated
27 significantly by both photolysis and reaction with OH, with photolysis generally making the
28 major contribution (60–70 %). As indicated above, this is mainly because of the
29 implementation of rapid photolysis for α - and β -carbonyl nitrates, which make a large
30 contribution to the second-generation species. At the high end of the NO_x range, these species
31 dominate the distribution, with their photolysis resulting in essentially quantitative NO_x
32 formation (see Sect. 2.2.2). The increasing contribution of other nitrate species at lower NO_x

(e.g. hydroperoxynitrates) leads to a decrease the associated NO_x regeneration to just below 90% at the low end of the range. The OH-initiated oxidation results in about 50% NO_x regeneration at the high end of the NO_x range (consistent with the appraisal in Sect. 2.2.2 and Fig. 7), but with this steadily decreasing with NO_x level, as the speciation of the second-generation nitrates changes. The resultant total extent of NO_x regeneration from the second-generation nitrates is between about 60 % and 85 % over the entire NO_x range (see Fig. 13). These results therefore suggest that between about 75 % and 90 % of NO_x is regenerated during the oxidation of the first- and second-generation nitrates, for the conditions of the present simulations.

Fig. 12 also shows the simulated levels of PAN and total PANs, which are notably reduced in the MCM v3.3.1 simulation, mainly as a result of the update to the generic parameter applied to PAN decomposition (see Sect. 2.3). PAN consistently accounts for about 70 % of the abundance of total PANs in all simulations, and therefore makes the dominant contribution. The simulated levels of MPAN show a reduction in the MCM v3.2 simulation as a result of updates to the chemistry of MACR made at that time (e.g. including changes to the branching ratios of the initiation reaction with OH), with further slight reductions resulting from those implemented in MCM v3.3.1. The PAN/MPAN ratio has typically been reported to lie in the approximate range 4–10 in isoprene dominated environments (e.g. Williams et al., 1997; Roberts et al., 2002, 2007). The ratios calculated using MCM v3.3.1 lie close to the upper bound of this range at the lower end of the considered NO_x range, although they reach values up to about 20 towards the high end of the range. However, because PAN sources persist over several generations of isoprene oxidation, the PAN/MPAN ratio is expected to be sensitive to air mass age, with lower values at shorter extents of chemical processing that may not be fully captured by the idealised model used here, particularly at the high end of the NO_x range.

3.2.4 Organic hydroperoxides and epoxides

Fig. 14 shows the simulated levels of organic hydroperoxides (i.e. species containing -OOH groups) and epoxides, and subsets of these totals. The results for the organic hydroperoxides show that the updates implemented in MCM v3.3.1 lead to a notable reduction in the simulated abundance of those formed from the traditional first-generation OH-initiated chemistry (denoted “first-generation -OOH” in Fig. 14). To allow direct comparison with the MCM v3.1 and MCM v3.2 results, this category specifically includes only those hydroperoxides formed from the reactions of HO_2 with the first-generation peroxy radicals (denoted “ISOP O_2 ” in

Fig. 10). The reduced abundance results partly from the enhanced removal of the hydroperoxides by reaction with OH, and partly because of the significant operation of the newly implemented peroxy radical isomerisation reactions in MCM v3.3.1, which compete directly with the HO₂ reactions that form the hydroperoxides. However, it should be noted that the 1,6 H atom shift isomerisation reactions of CISOPAO₂ and CISOPCO₂ result in the formation of a suite of species that contain (one or more) hydroperoxide groups, with these also contributing to the first-generation hydroperoxide abundance via non-traditional mechanisms (see Fig. 3). These include the unsaturated hydroperoxyaldehydes (C5HPALD1 and C5HPALD2) and the dihydroperoxycarbonyls (DHPMEK and DHPMPAL), the abundances of which are also shown in Fig. 14. Inclusion of these species in the first-generation total leads to approximately a factor of two increase, as illustrated by the broken line in the “first-generation -OOH” panel. The significant operation of the 1,6 H atom shift isomerisation chemistry also generally increases the abundance of higher-generation species containing hydroperoxide groups, as shown in the “total -OOH” panel of Fig. 14.

As described in Sect. 2.2.3, the epoxydiols (collectively denoted “IEPOX” in Fig. 14) are formed from the OH-initiated chemistry of the traditional first-generation hydroxy-hydroperoxides, with this chemistry represented in MCM v3.2 and MCM v3.3.1. The updates to the chemistry in MCM v3.3.1 result in a general lowering of their abundance, because of the inhibition of the formation of the precursor hydroxy-hydroperoxides (as indicated above). The epoxydiols also make the dominant contribution to the total epoxide abundance in both the MCM v3.2 and MCM v3.3.1 simulations, but with additional notable contributions from the formation of HMML and MAE from the OH-initiated chemistry of MPAN at the high end of the NO_x range in the MCM v3.3.1 results (see Sect. 2.2.1). The reaction of OH with HMML partially forms HCOOH, as represented in MCM v3.3.1 (see Sects. 2.2.7 and S2.2). This source is simulated to make a notable contribution (about 30 %) to HCOOH formation towards the high end of the NO_x range for the conditions of these simulations, although its major source remains the reaction of water vapour with the stabilised Criegee intermediate CH₂OO, formed from isoprene ozonolysis (40–50% relative humidity). However, representation of reactive uptake of HMML on aerosol particles (e.g. Kjaergaard et al., 2012) would reduce the importance of its gas phase degradation as a source of HCOOH.

3.2.5 Carbonyl product ratios

Fig. 15 shows the simulated levels of the well-established C₄ unsaturated carbonyls (MVK and MACR), formed from the first-generation chemistry, and the α -dicarbonyls (GLYOX and MGLYOX), which are formed over several generations of isoprene oxidation. In isoprene-dominated environments, observed ratios of these pairs of species have typically been reported to lie in the approximate ranges 0.8–2 for MVK/MACR (e.g., Spaulding et al., 2003; Kuhn et al., 2007; Karl et al., 2009) and 0.2–0.7 for glyoxal/methyl glyoxal (e.g., Lee et al., 1995, 1998; Spaulding et al., 2003). Fig. 15 also shows the corresponding simulated daylight-averaged ratios in comparison to these observed ranges.

The updates to the first-generation chemistry in MCM v3.2 resulted in a reduction in the first-generation yield of MVK relative to that in MCM v3.1, leading to MVK/MACR ratios over the complete simulated NO_x range that are consistent with the reported range of observed values. As discussed in Sect. 2.1.4, the substantial changes to the first-generation chemistry in MCM v3.3.1 have tended to increase the first-generation yield of MVK relative to that of MACR at NO levels characteristic of the atmospheric range, leading to MVK/MACR ratios in the range 1.7–2.4, i.e. close to the upper bound of the reported range of observed values (Fig. 15).

The simulated levels of GLYOX and MGLYOX show some systematic differences resulting from the updates implemented in MCM v3.2 and MCM v3.3.1. These have resulted in a progressive suppression of the simulated GLYOX/MGLYOX ratios. Those simulated with MCM v3.3.1 (in the range 0.14–0.33) are close to the lower bound of the observed ratios over the complete NO_x range (Fig. 15).

4 Summary and conclusions

The chemistry of isoprene degradation in the Master Chemical Mechanism (MCM) has been systematically refined and updated to reflect recent advances in understanding, with these updates appearing in the latest version, MCM v3.3.1. The complete isoprene degradation mechanism in MCM v3.3.1 consists of 1927 reactions of 603 closed shell and free radical species, which treat the chemistry initiated by reaction with OH radicals, NO₃ radicals and ozone (O₃). A detailed overview of the updates has been provided, with reference to the reported kinetic and mechanistic information on which they are based. The revisions mainly relate to the OH-initiated chemistry, which generally dominates under atmospheric conditions, although these include updates to the chemistry of some products that are also

1 generated from the O_3 - and NO_3 -initiated oxidation. The revisions have impacts in a number
2 of key areas, as illustrated by comparing the performance of the MCM v3.3.1 isoprene
3 mechanism with those of earlier versions (MCM v3.1 and MCM v3.2) over a range of
4 relevant conditions in a box model of the tropical forested boundary layer.

5 The updates have a collectively significant impact on OH radical regeneration at lower NO_x
6 levels, with particularly important simulated contributions resulting from the chemistry
7 initiated by the 1,6 H atom shift isomerisation reactions of the (Z-) δ -hydroxy peroxy radicals,
8 CISOPAO2 and CISOPCO2, and from the higher generation 1,4 H atom shift isomerisation
9 reactions of the α -formyl peroxy radicals (e.g. MACRO2, C57O2 and C58AO2).

10 The simulated recycling of NO_x from the degradation of oxidised organic nitrogen species has
11 also been modified considerably by the updates. The degradation of organic nitrates formed
12 from the first-generation OH-initiated chemistry results in about 40 % regeneration of NO_x ,
13 owing to the dominance of their OH-initiated removal, which leads significantly to products
14 that retain the nitrate group. The degradation of the second-generation nitrates leads to much
15 greater NO_x regeneration (60–85 %), owing to a major contribution from their rapid photolysis,
16 with associated near-quantitative NO_x regeneration.

17 The updates also include the formation of a number of species that have been reported to play a
18 role in SOA-formation mechanisms, including epoxydiols (initially implemented in MCM
19 v3.2), hydroxymethyl-methyl- α -lactone (HMML) and methacrylic acid epoxide (MAE).
20 Although the chemistry in MCM v3.3.1 is limited to gas-phase processes, the explicit
21 formation of such species provides the basis for coupling with condensed-phase transfer
22 mechanisms in simulations of detailed SOA composition, e.g. as described recently by Li et
23 al. (2015).

24 The MCM v3.3.1 isoprene mechanism is believed to provide a valid description of current
25 detailed understanding of the atmospheric degradation of isoprene, and a benchmark
26 representation against which to develop and optimise reduced isoprene mechanisms. In
27 addition, it also provides an ideal platform for testing the impacts of newly discovered
28 mechanistic information relevant to isoprene degradation that is constantly emerging.

5 Mechanism access and availability

MCM v3.3.1 is available via the MCM website (<http://mcm.leeds.ac.uk/MCM>). A number of tools are provided which allow the mechanism to be downloaded or navigated online. The whole mechanism, or specified subsets, can be extracted in a variety of formats (including FACSIMILE, KPP, FORTRAN and XML), facilitating the construction of bespoke mechanisms which can be incorporated directly into atmospheric or chamber models. The complete mechanism treats the degradation of 143 emitted VOCs.

The isoprene subset mechanism described in the present paper can be downloaded by adding isoprene (C₅H₈) to the “Mark List” and using the “Extract” facility. The mechanism in FACSIMILE input format is also provided in the Supplement.

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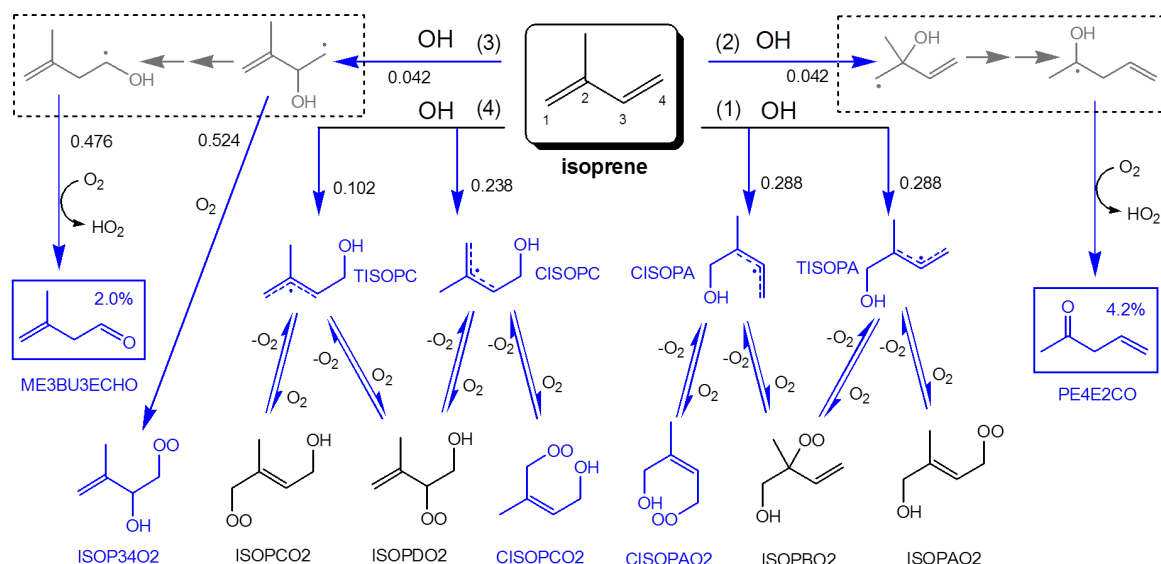


Fig. 1. Schematic of the addition of OH to isoprene and the reactions of OH-isoprene adducts with O₂, as represented in MCM v3.3.1. Species in solid boxes are first-generation oxygenated end products, with their molar yields at 298 K. Species and routes shown in blue are new in MCM v3.3.1. The chemistry in broken boxes is not included explicitly in the mechanism, but is shown to clarify the routes to the corresponding products (see Park et al., 2003).

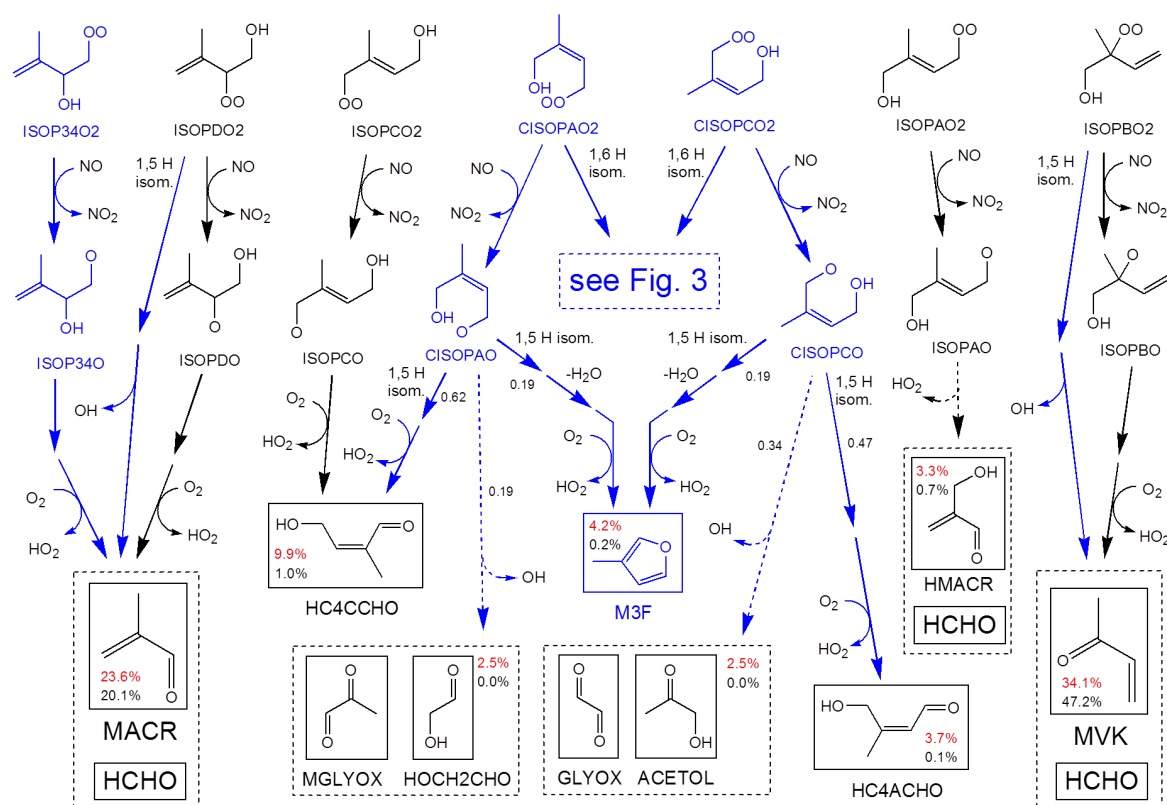


Fig. 2. Schematic of the mechanisms following the propagating channels of the reactions of the first-generation β - and δ -hydroxy peroxy radicals with NO, and competing unimolecular isomerisation reactions (see also Fig. 3). Species in solid boxes are the resultant first-generation oxygenated end products, with their associated molar yields at 10 ppm NO (in red) and 100 ppt NO (in black) at 298 K (see text and Fig. 4 for further details). HCHO has multiple sources, such that its total yield is 61.0 % at 10 ppm NO and 68.0 % at 100 ppt NO. Species and routes shown in blue are new in MCM v3.3.1. Broken arrows indicate multistep mechanisms, involving the reactions of additional peroxy and oxy radicals (see Sect. 2.1.3 and Figs. S1–S3).

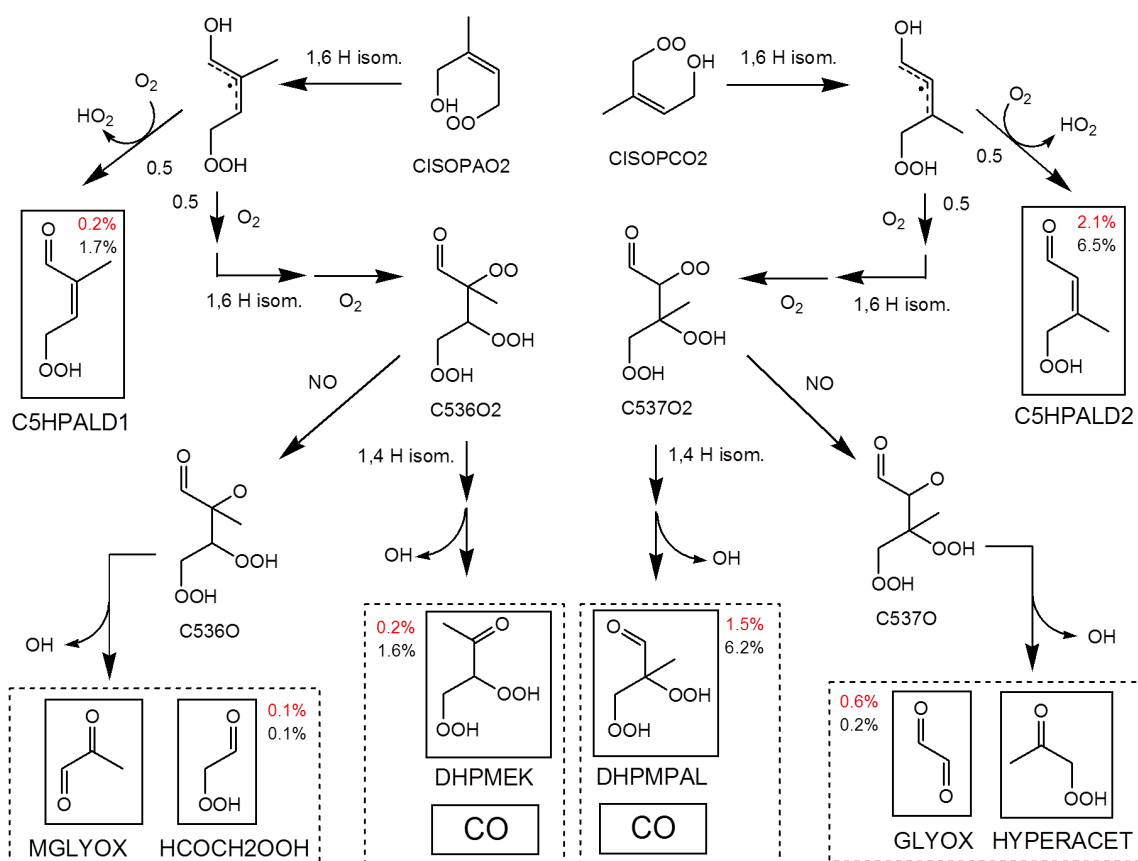
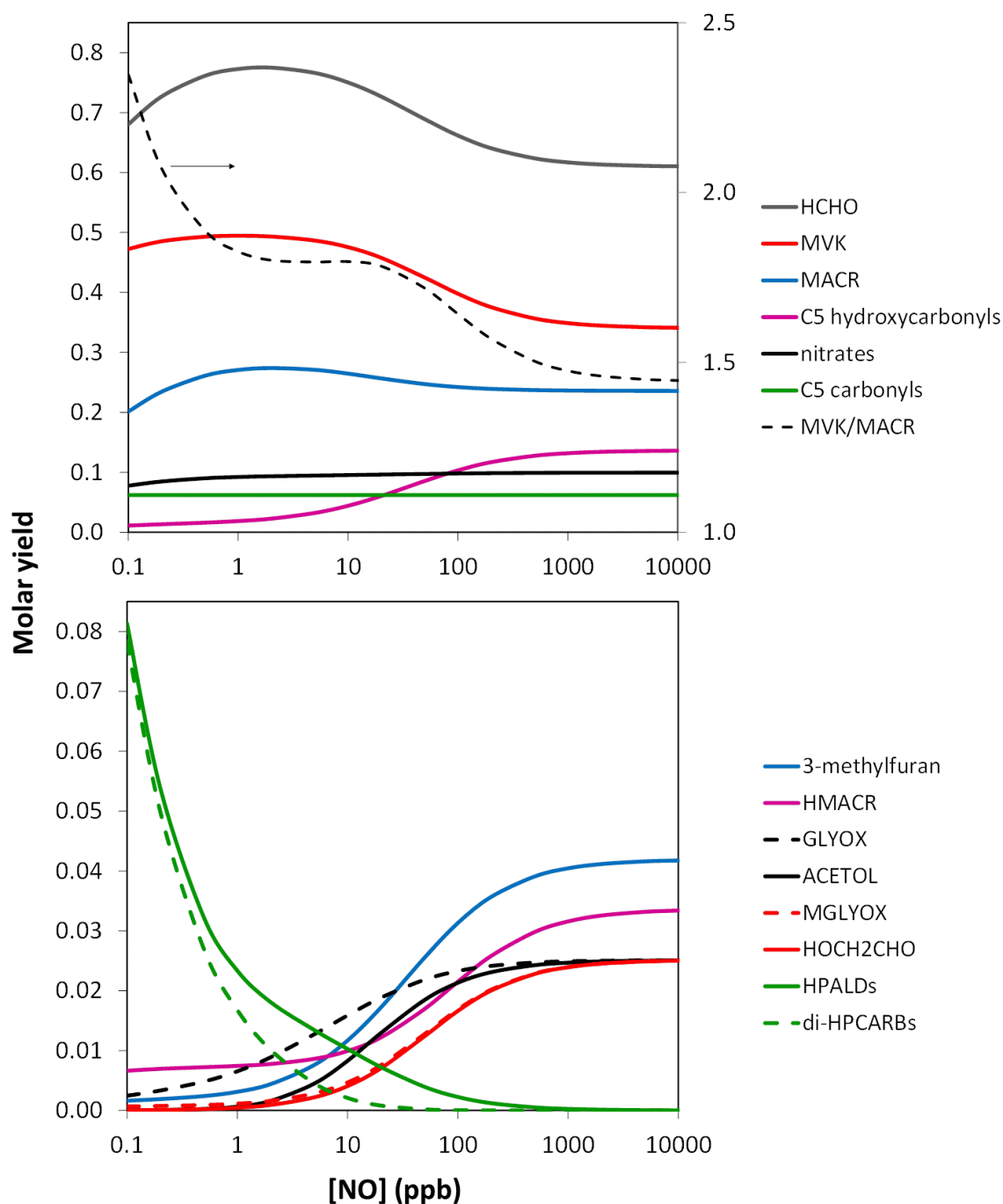


Fig. 3. Schematic of the mechanisms following the 1,6 H atom shift isomerisation reactions of CISOPAO2 and CISOPCO2, as represented in MCM v3.3.1 (see also Fig. 2). As in Fig. 2, propagating channels of the reactions of NO with the intermediate peroxy radicals (C536O2 and C537O2), and competing unimolecular isomerisation reactions, are shown. Species in solid boxes are the resultant first-generation oxygenated end products, with their associated molar yields at 1 ppb NO (in red) and 100 ppt NO (in black) at 298 K (see text and Fig. 4 for further details). Note that GLYOX and MGLYOX are also formed via alternative routes, shown in Fig. 2.



1
 2 Fig. 4. Molar yields of main first-generation products of the OH-initiated oxidation of
 3 isoprene as a function of NO mixing ratio, at 298 K, as represented in MCM v3.3.1 (see
 4 discussion in Sect. 2.1.4). C₅ hydroxycarbonyls are HC₄ACHO and HC₄CCHO; C₅ carbonyls
 5 are PE₄E₂CO and ME₃BU₃ECHO; HPALDs are C₅HPALD1 and C₅HPALD2; di-
 6 HPCARBs are DHPMEK and DHPMPAL; and nitrates are as shown in Fig.5. The broken
 7 line in the upper panel is the MVK/MACR yield ratio, as quantified on the right-hand scale.

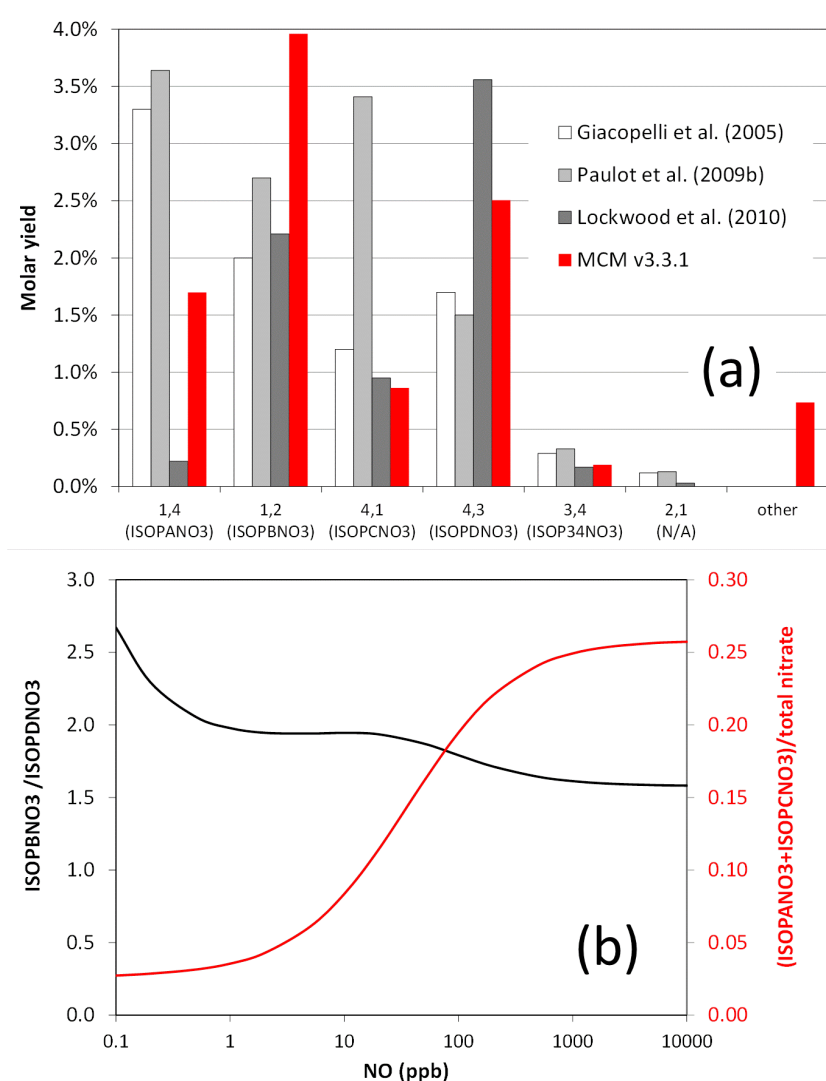
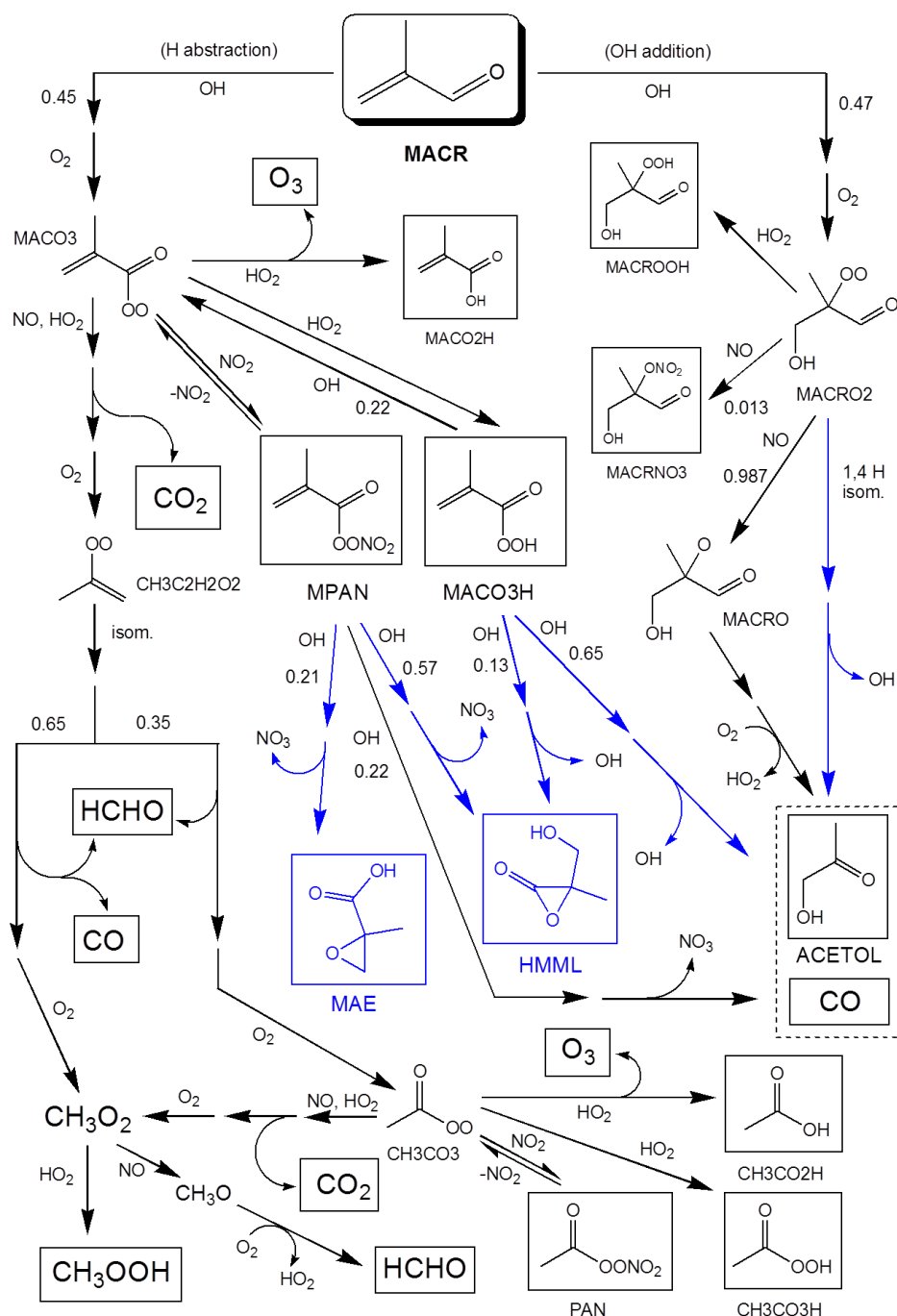
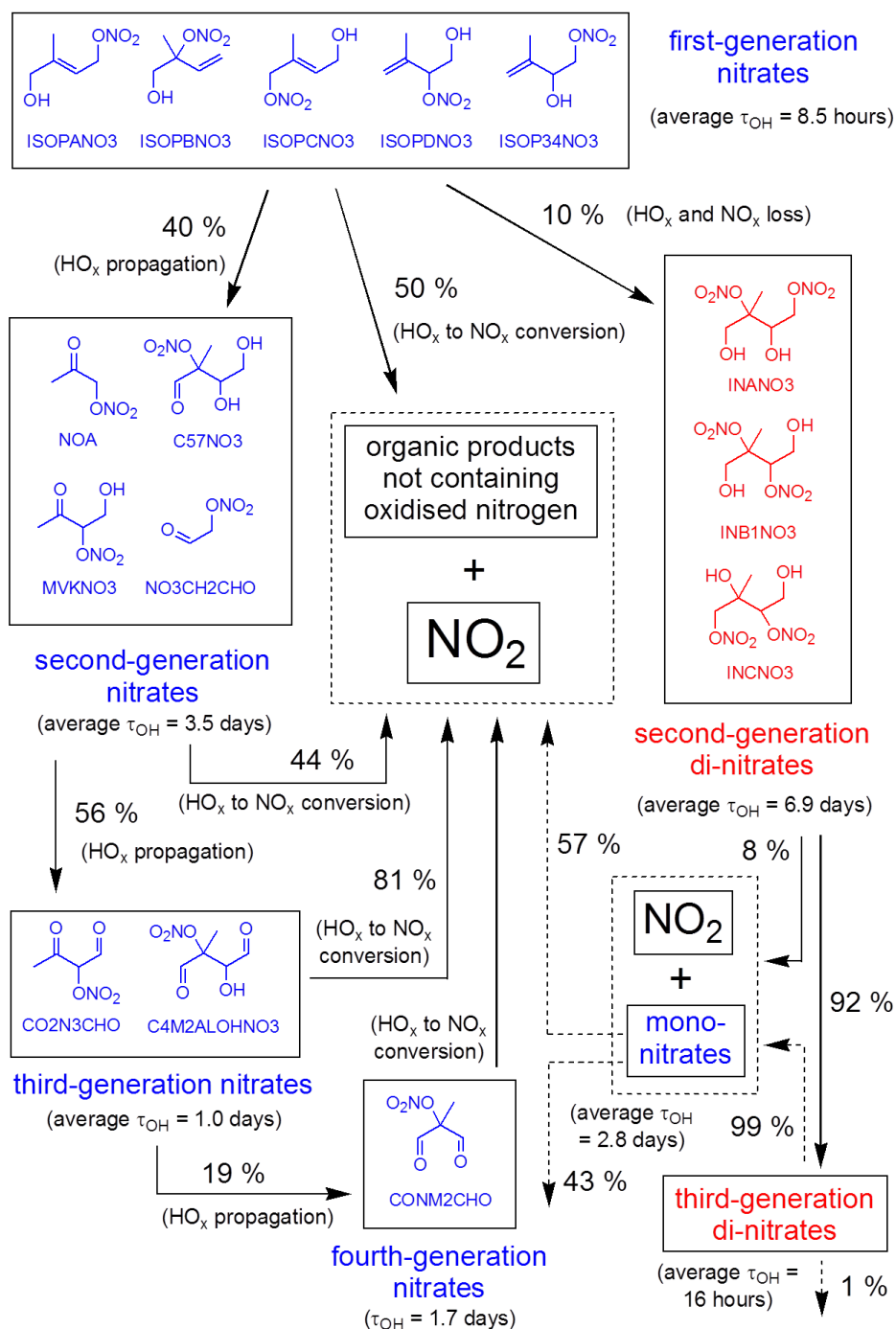


Fig. 5. (a) Reported molar yields of speciated nitrate products formed from the first-generation OH-initiated oxidation of isoprene (see Fig. 7 for structures). The “1,4” and “4,1” categories include contributions from both *E*- and *Z*- isomers, where reported. The MCM v3.3.1 values correspond to 298 K at the high [NO] limit (see Fig. 3), with the total yield being 10 %. The “other” category includes C524NO₃ (formed in the mechanism to HMA CR formation), C526NO₃ (formed in the mechanism to methyl glyoxal/glycolaldehyde formation) and C527NO₃ (formed in the mechanism to glyoxal/hydroxyacetone formation). The “2,1” isomer is not formed in MCM v3.3.1; (b) [NO]-dependences of the ratio of the β-hydroxy isomers (ISOPBNO₃/ISOPDNO₃) and the fractional contribution of the δ-hydroxy isomers (ISOPANO₃ and ISOPCNO₃). The displayed [NO] range corresponds to values of k_{tr} in the approximate range 0.022 – 2200 s⁻¹.



1
2 Fig. 6. Schematic of the main features of the mechanism following reaction of OH with
3 methacrolein (MACR), as represented in MCM v3.3.1. For clarity, the chemistry of the minor
4 (8%) OH addition channel, and the reactions of the intermediate peroxy radicals with NO₃
5 and the peroxy radical pool are not shown. Species in solid boxes are oxygenated end
6 products. Species and routes shown in blue are new in MCM v3.3.1. The further chemistry of
7 MPAN and MACO3H is also shown, to illustrate newly implemented updates.



1

2 Fig. 7. Overview of the OH initiated degradation of the first-generation nitrates in MCM

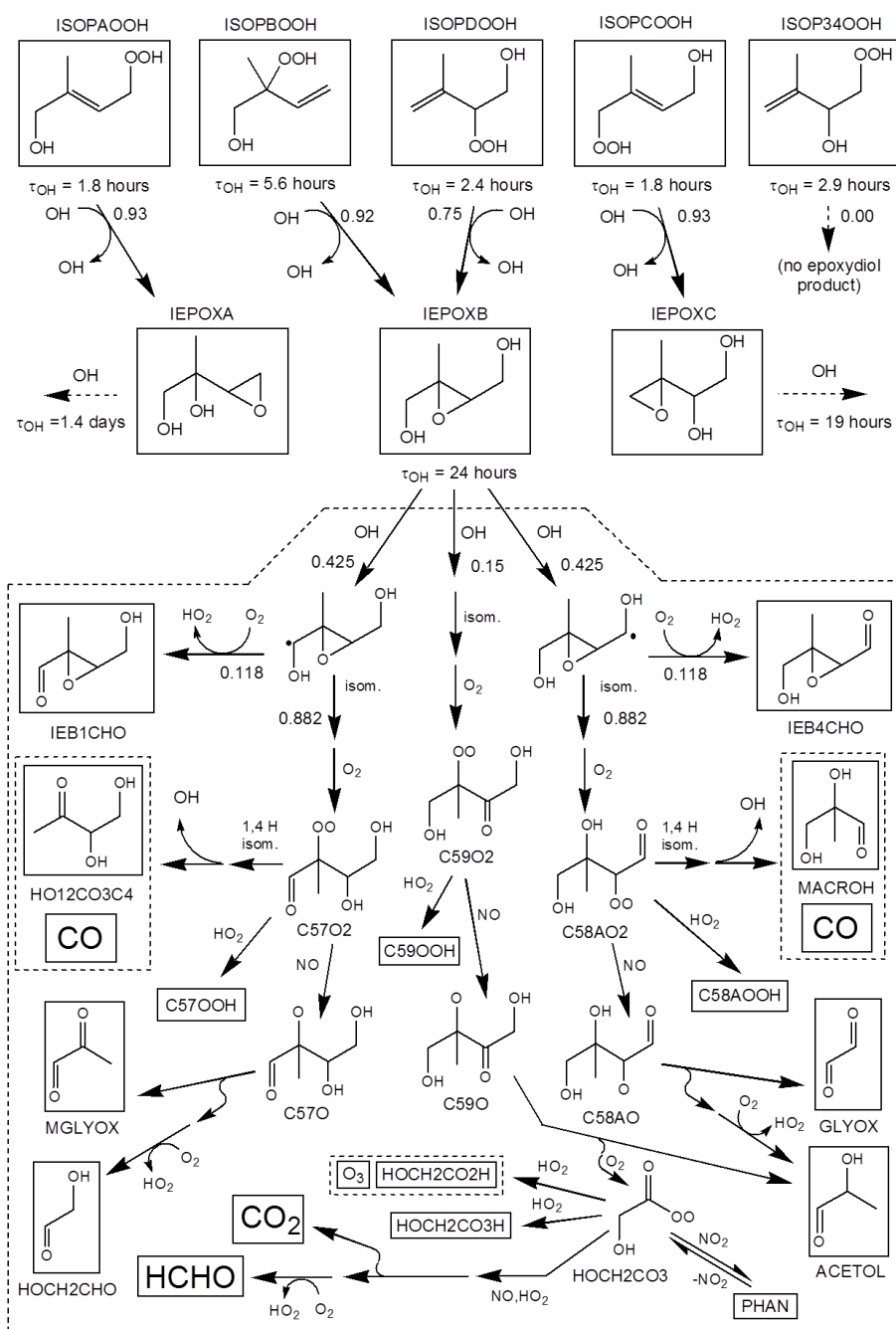
3 v3.3.1, based on the calculated distribution at 1 ppb NO. Products with one nitrate group are

4 shown in blue, and those with two nitrate groups are shown in red. Where sets of species are

5 shown, these collectively account for $\geq 90\%$ of the nitrate yield in the given category.

6 Representative average lifetimes (τ_{OH}) for reactions of the groups of products with OH are

7 shown, based on $[OH] = 10^6 \text{ molecule cm}^{-3}$.



1
2 Fig. 8. Overview of the OH initiated degradation of isoprene hydroxy-hydroperoxides, as
3 represented in MCM v3.3.1. The dominant formation of the isomeric epoxydiol products is
4 shown, with the further degradation of the most abundant isomer, IEPOXB. For clarity, the
5 terminating reactions of peroxy radicals with NO and the reactions of peroxy radicals with
6 NO₃ and the peroxy pool are not shown. Representative lifetimes (τ_{OH}) for reactions with OH
7 are shown, based on $[\text{OH}] = 10^6 \text{ molecule cm}^{-3}$.

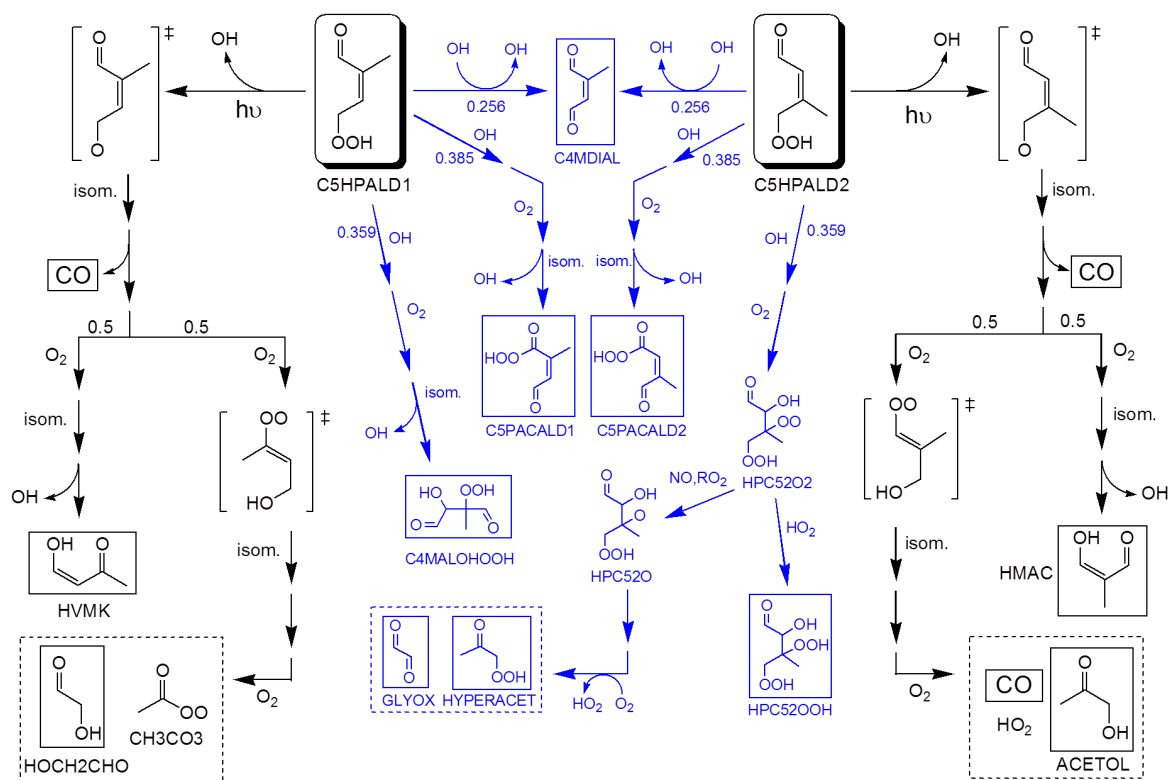
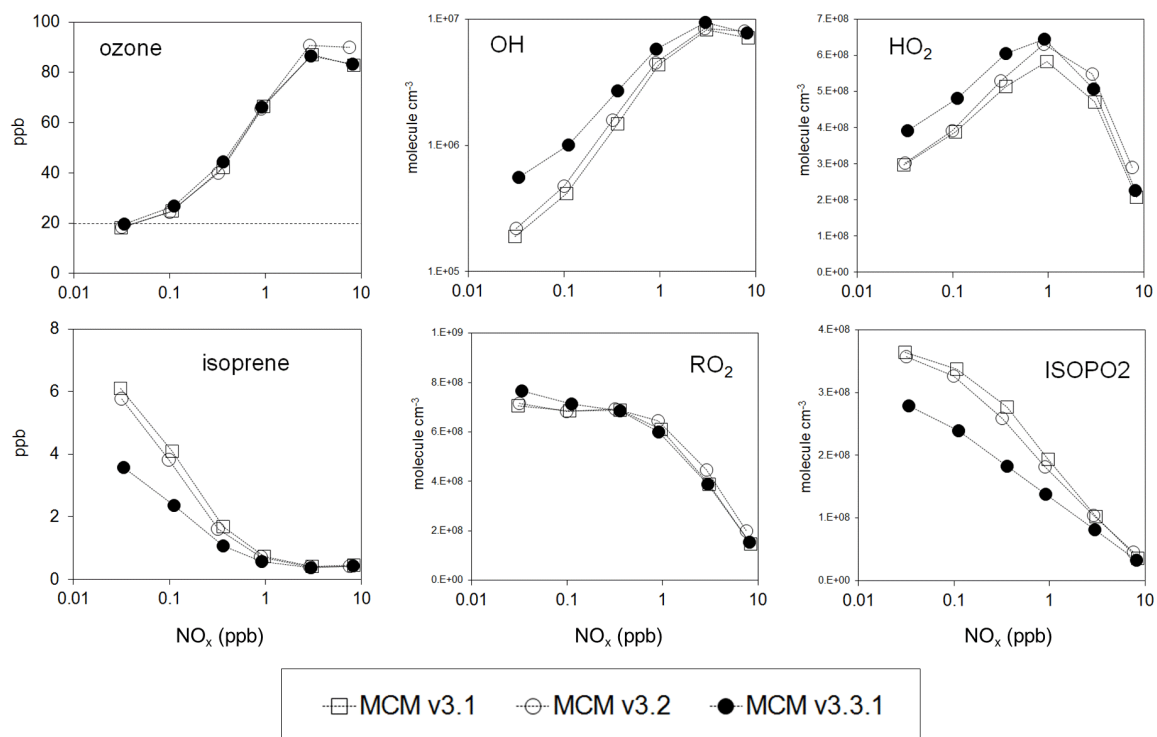


Fig. 9. Overview of the degradation mechanisms for the unsaturated C₅ hydroperoxyaldehydes, C5HPALD1 and C5HPALD2, as currently represented in MCM v3.3.1. The (major) chemistry initiated by photolysis is shown in black; and the (minor) OH initiated chemistry is shown in blue. For clarity, the reactions of the peroxy radicals with NO₃ are not shown.



1
2 Fig. 10. Comparison of performances of MCM v3.1, MCM v3.2 and MCM v3.3.1, showing
3 the NO_x-dependence of the daylight-averaged mixing ratios or concentrations of O₃, isoprene,
4 OH, HO₂, total organic peroxy radicals (RO₂) and peroxy radicals formed from the first-
5 generation OH-initiated chemistry (ISOP2). The broken line in the O₃ panel shows the
6 background mixing ratio relative to which O₃ is either produced or destroyed (see text).

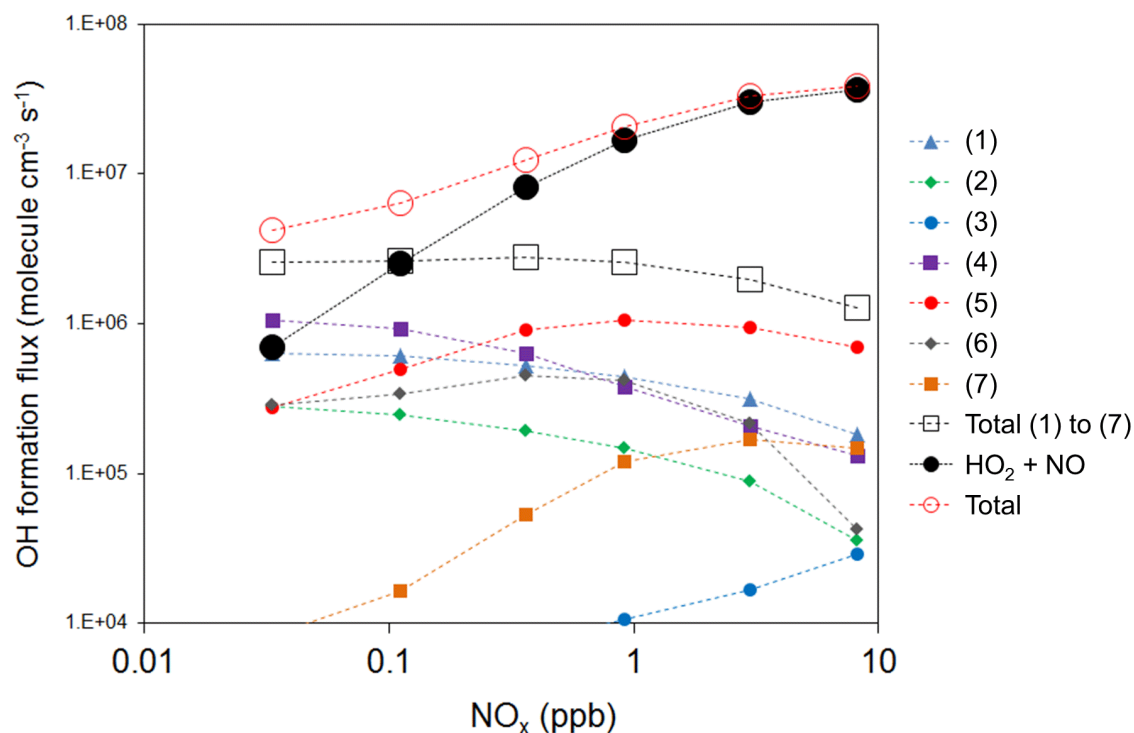
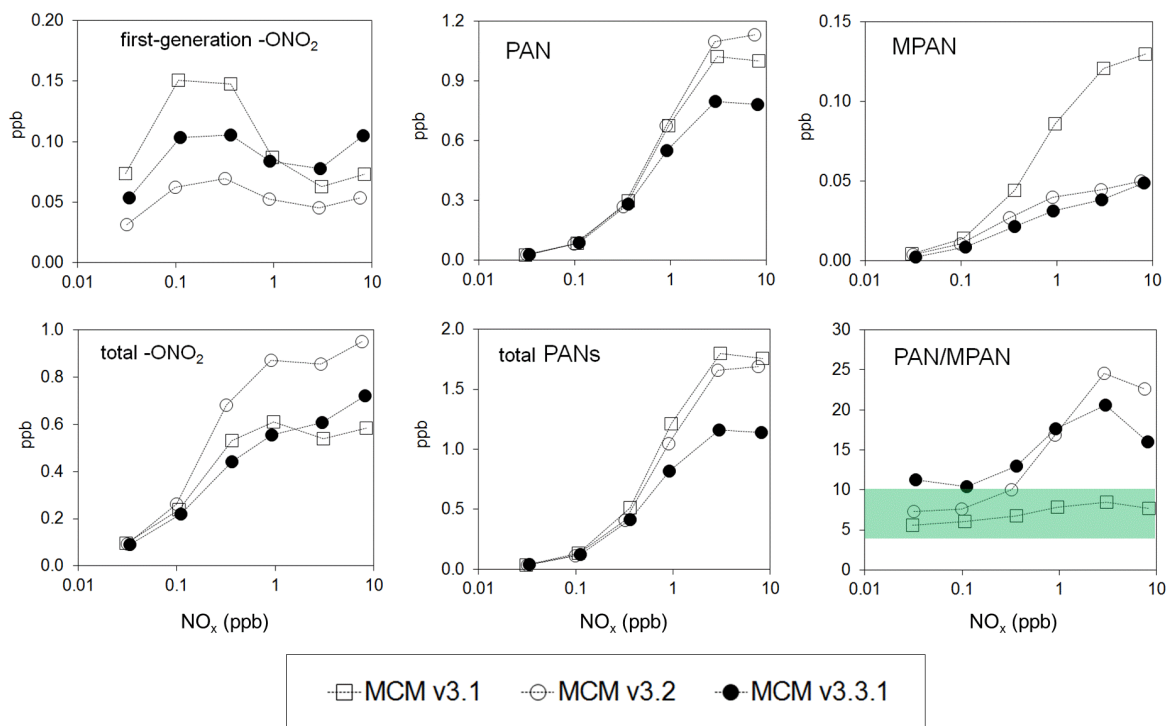


Fig. 11. Comparison of daylight averaged fluxes through the newly implemented OH regeneration routes with that through the reaction of HO₂ with NO. (1) First generation chemistry of C536O₂ and C537O₂ (Fig. 3), dominated by their 1,4 H shift reactions; (2) First generation 1,5 H shift reactions (i.e from ISOPBO₂, ISOPDO₂ and C524O₂) (Figs. 2 and S3); (3) First generation chemistry of C526O₂ and C527O₂ (Figs. S1 and S2), dominated by their 1,4 H shift reactions; (4) Reaction sequence following the rapid photolysis of C5HPALD1 and C5HPALD2 (Fig. 9), including subsequent rapid photolysis of HMAc and HVMK (Sect. 2.2.7); (5) Higher generation 1,4 H shift isomerisation reactions (e.g. from MACRO₂, C57O₂ and C58AO₂) (Figs. 6 and 8); (6) RC(O)O₂ + HO₂ reactions (Sect. 2.3); (7) HCOCO + O₂ (i.e. included in the update to glyoxal chemistry, Sect 2.2.5).



1
 2 Fig. 12. Comparison of the performances of MCM v3.1, MCM v3.2 and MCM v3.3.1,
 3 showing the NO_x-dependence of the daylight-averaged mixing ratios of the organic oxidised
 4 nitrogen reservoirs, nitrates (-ONO₂) and PANs, and the daylight-averaged PAN/MPAN ratio.
 5 The first-generation nitrates are specifically those formed from the reactions of NO with first-
 6 generation peroxy radicals (denoted “ISOPO₂” in Fig. 10). The shaded band in the
 7 PAN/MPAN panel represents the typical range of reported observed values in isoprene-
 8 dominated environments (see text).

9

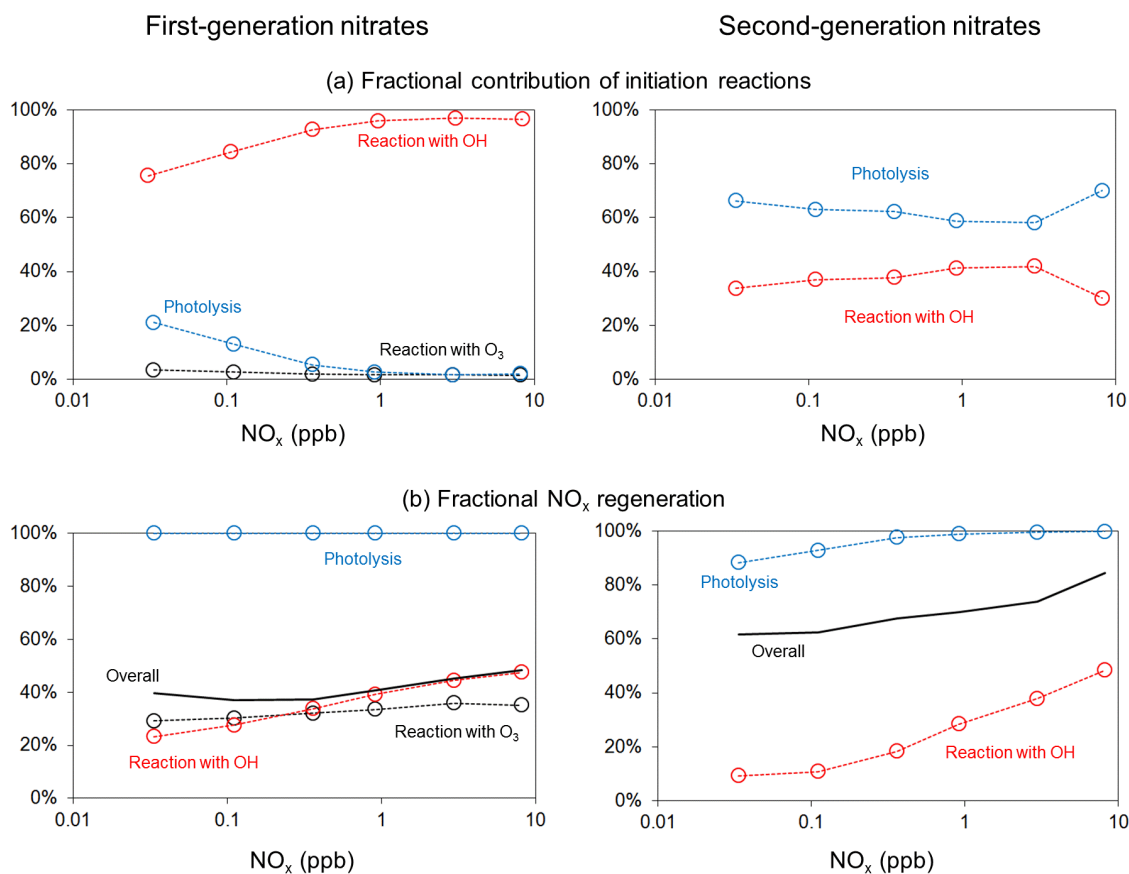
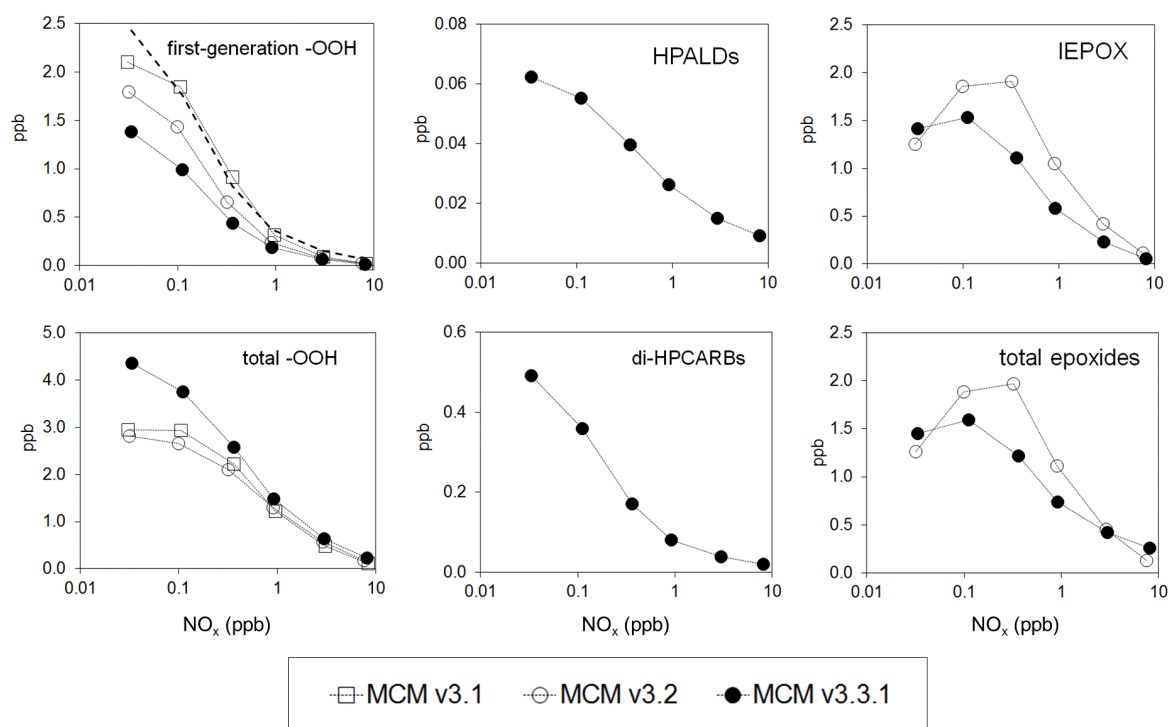


Fig. 13. (a) Comparison of the fractional contributions of the initiation reactions contributing to the removal of first- and second generation organic nitrates in the MCM v3.3.1 simulations; (b) The fractional regeneration of NO_x resulting from each of the initiation reactions for first- and second-generation organic nitrates, and the overall fractional NO_x regeneration in each case.



1
2 Fig. 14. Comparison of the performances of MCM v3.1, MCM v3.2 and MCM v3.3.1,
3 showing the NO_x-dependence of the daylight-averaged mixing ratios of selected
4 hydroperoxides and epoxides. The first-generation hydroperoxides are specifically those
5 formed from the reactions of HO₂ with first-generation peroxy radicals (denoted “ISOPO₂” in
6 Fig. 10). HPALDs are C5HPALD1 and C5HPALD2; di-HPCARBs are DHPMEK and
7 DHPMPAL; and IEPOX includes the epoxydiols, IEPOXA, IEPOXB and IEPOXC. The
8 heavy broken line in the “first-generation -OOH” panel shows the effect of including
9 HPALDs and di-HPCARBs in the MCM v3.3.1 total.

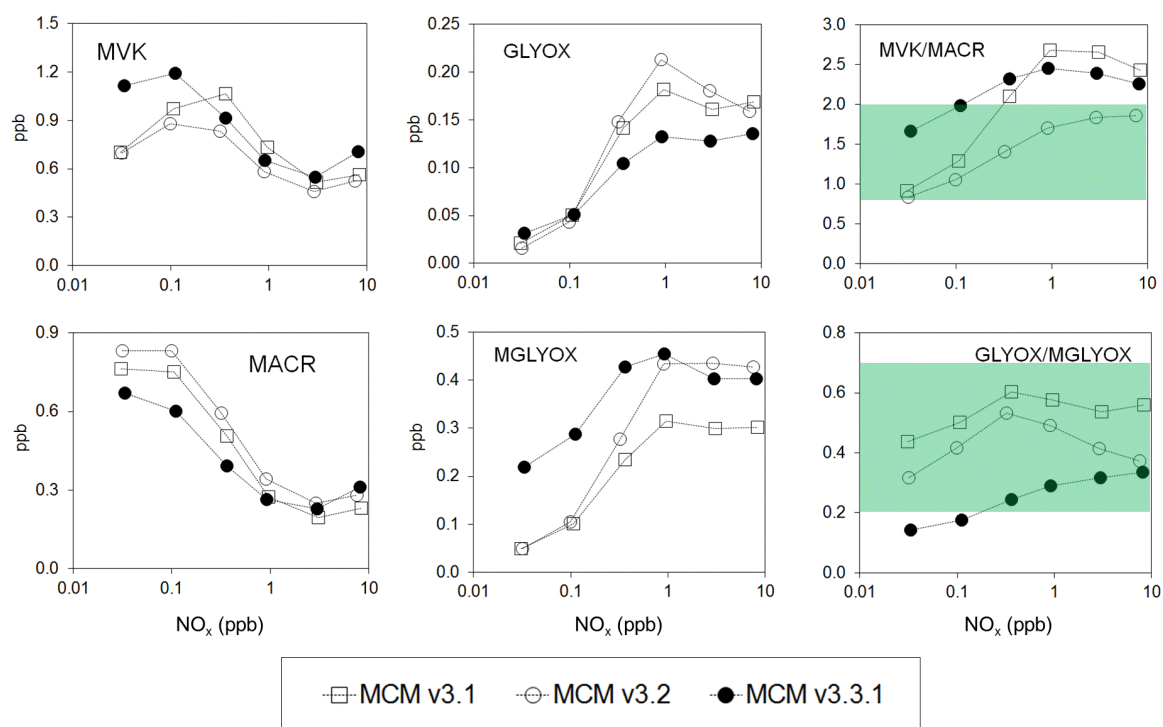


Fig. 15. Comparison of the performances of MCM v3.1, MCM v3.2 and MCM v3.3.1, showing the NO_x-dependence of the daylight-averaged mixing ratios of MVK, MACR, glyoxal (GLYOX) and methylglyoxal (MGLYOX); and the daylight-averaged ratios, MVK/MACR and GLYOX/MGLYOX. The shaded bands in the MVK/MACR and GLYOX/MGLYOX panels represent the typical ranges of reported observed values in isoprene-dominated environments (see text).