

We would like to thank the reviewers for their time and valuable comments that have helped to improve our paper. To guide the review process, comments from reviewers are in black, responses in blue, and *new text added to the paper in green*. Links are provided below for easy navigation in the document.

[Anonymous Referee #2 \(RC1\)](#)

[Anonymous Referee #3 \(RC2\)](#)

Anonymous Referee #2 (RC1)

This paper describes an enlargement of the organic mechanism within the MOZART suite of models. It updates some aspects of the propane chemistry and then develops the butane, pentane and larger chemistry. In general this paper is a good description of the updates made. I think there should be some clarifications and additions before the paper is published but these should be minor.

Larger issues:

1.1) The authors could do a better job of justifying the additional of a more complex chemistry scheme. There are still outstanding significant science questions where a more complicated chemistry could help to answer these questions. The authors could try and do more to justify the need for additional chemistry.

We thank the reviewer for suggesting that we clarify the scientific motivation for the additional chemistry. We have expanded the Introduction to identify two questions that a more explicit alkane mechanism can help address: how lumping affects the inferred production and lifetimes of individual oxygenated products, and whether discrepancies between modeled and observed OVOCs arise from underestimated precursor abundances or from their chemical formation and loss.

The revised manuscript provides a specific example through the MEK-to-n-butane comparison in Sect. 5. By representing n-butane separately, T3 allows this precursor-product relationship to be evaluated against observations, which is not directly possible with the lumped BIGALK representation. The agreement in this ratio, despite underestimated concentrations of both species, helps assess the role of precursor abundance in the MEK bias. Similarly, the comparison of individual butanes and pentanes and their isomer ratios helps distinguish errors in emission magnitudes from errors in relative isomer composition.

We have also strengthened the Conclusions to explain why these capabilities matter even though the effects of T3 on global ozone and OH are small. The additional chemistry changes the production, lifetimes, and distributions of individual oxidation products and enables their evaluation using speciated observations. The revisions are provided below.

Lines 75–80

These limitations raise questions about both the budgets of alkane oxidation products and the interpretation of model–observation differences. How does representing chemically distinct products with a single surrogate affect their inferred production and atmospheric lifetimes? To what extent can underestimated precursor abundances explain biases in oxygenated products, and to what extent do their formation and loss pathways contribute? Addressing these questions requires separate representation of the relevant precursors and products. Comparisons of their concentrations and ratios can then help assess the contributions of emissions and chemistry.

Lines 740–746

Evaluation against ATom observations shows broadly similar performance across mechanisms for major air pollutants and oxidants, with biases remaining for individual species. T3 additionally enables evaluation of individual C4–C5 alkanes, propanal, and PPN. Agreement in the branched-to-total butane and pentane ratios supports the relative isomer composition of emissions, while the persistent underestimation of their absolute concentrations suggests that emission magnitudes are too low. The MEK-to-n-butane ratio provides a further diagnostic: T3 reproduces the observed ratio despite underestimating both species, suggesting that insufficient precursor abundance contributes to the remaining MEK bias. Agreement in absolute MEK concentrations nevertheless varies by region and season.

Lines 747–752

The small effects of T3 alkane chemistry on global ozone and OH are accompanied by substantial changes in individual oxygenated products. Separating MEK from higher ketones and using compound-specific oxidation pathways changes the simulated production and lifetimes of these products, even when total alkane burdens remain similar. Explicit precursor and product tracers also allow observations to constrain relationships that are obscured by lumping. T3 therefore provides a useful tool to investigate alkane-derived OVOC budgets and to assess the contributions of precursor emissions and oxidation chemistry to model–observation discrepancies, at a level of complexity that remains tractable for global simulations.

1.2) Presumably some of the potential impacts could be to global oxidation. It would be useful in the abstract and text to discuss how much the O₃ budget, OH concentration etc are changed by these updates. Even if they are very small it would be useful to discuss this.

We agree that the effects of the chemistry updates on global oxidant levels should be quantified more directly. We separately evaluated the two sets of updates introduced in this study: the common kinetic and photolysis updates represented by T1.3 and the subsequent addition of T3 alkane chemistry. Because the whole-atmosphere ozone burden is dominated by stratospheric ozone, we focus on the globally integrated ozone burden at pressures greater than 100 hPa, the volume-weighted mean OH concentration over the same pressure range, and the global area-weighted mean surface OH concentration.

Relative to T1.2 using the same anthropogenic emission inventory, the T1.3 updates increase the ozone burden by 0.72–0.81%, the volume-weighted mean OH concentration by 2.28–2.36%, and the surface OH concentration by 2.03–2.08%. Adding T3 alkane chemistry to the corresponding T1.3 or T2.3 parent mechanism produces smaller changes: the ozone burden changes by –0.06 to +0.07%, the volume-weighted mean OH concentration by –0.05 to +0.05%, and the surface OH concentration decreases by 0.21–0.35%.

For comparison, across the four updated mechanism configurations, the CEDS simulations produce values higher than the corresponding CAMS simulations by 1.36–1.43% for the ozone burden, 2.90–3.03% for the volume-weighted mean OH concentration, and 11.0–11.2% for the surface OH concentration. The inventory effect therefore exceeds the effect of the chemistry updates in each comparison. The contrast is largest at the surface, consistent with a stronger influence of emission differences near the surface, whereas the inventory effect on volume-weighted mean OH is only slightly larger than the effect of the T1.3 updates.

Thus, the common T1.3 updates produce modest but measurable changes in global OH, whereas the further addition of T3 alkane chemistry has only a minor effect on global ozone and OH.

We considered adding these results to the Abstract, as suggested by the reviewer. However, the Abstract is already at the journal's word limit, and the diagnosed changes in global ozone and OH are small. We therefore retained the Abstract's focus on the principal findings concerning mechanism development and OVOC budgets. Instead, we have addressed this point in detail in the new Sect. 4.6 by separately quantifying how the T1.3 updates, T3 alkane chemistry, and emission inventory choice affect the ozone burden and OH concentrations.

4.6 Effects on global ozone and OH

Beyond reactive nitrogen, we also assess whether the chemistry updates affect broader atmospheric oxidation. We examine the globally integrated ozone burden at pressures greater than 100 hPa, the volume-weighted mean OH concentration over the same pressure range, and the global area-weighted mean surface OH concentration. We use the pressure-limited ozone burden because the whole-atmosphere burden is dominated by stratospheric ozone, which is not directly affected by the tropospheric chemistry updates examined here.

Relative to T1.2 using the same anthropogenic emission inventory, the common kinetic and photolysis updates represented by T1.3 increase the ozone burden by 0.72–0.81%, the volume-weighted mean OH concentration by 2.28–2.36%, and the surface OH concentration by 2.03–2.08%. Adding T3 alkane chemistry to the corresponding T1.3 or T2.3 parent mechanism produces smaller changes: the ozone burden changes by –0.06 to +0.07%, the volume-weighted mean OH concentration by –0.05 to +0.05%, and the surface OH concentration decreases by 0.21–0.35%. Thus, the explicit T3 alkane chemistry has little influence on global ozone and OH, despite its substantial effects on the budgets and distributions of individual alkane-derived products.

For comparison, across the four updated mechanism configurations, the CEDS simulations produce values higher than the corresponding CAMS simulations by 1.36–1.43% for the ozone burden, 2.90–3.03% for the volume-weighted mean OH concentration, and 11.0–11.2% for the surface OH concentration. The differences associated with the emission inventories therefore exceed those caused by the chemistry updates for all three quantities. The contrast is largest at the surface, consistent with the stronger influence of emission differences near the surface, whereas the inventory-related difference in volume-weighted mean OH is only slightly larger than the effect of the T1.3 updates. Overall, the common T1.3 updates produce modest but

measurable changes in global OH, whereas the subsequent addition of T3 alkane chemistry primarily affects individual alkane-derived products rather than broader oxidant levels.

1.3) There are no isomer of propane. There are 2 of butane. There are 3 of pentane (n-pentane, isopentane (methyl-butane), neopentane (di-methyl-propane)) but only 2 of the pentane isomers are discussed. Why is this? Is there some justification? It might be obvious but it would be good to state this obvious.

We thank the reviewer for pointing this out. We agree that the omission of neopentane was not sufficiently explained in the original manuscript. Neopentane was not explicitly represented in T3 because of its low atmospheric abundance, its relatively slow reaction with OH, and the lack of corresponding ATom measurements. For example, Swarthout et al. (2013) reported a mean neopentane mixing ratio of 17 pptv, approximately two orders of magnitude lower than those of n-pentane (2,010 pptv) and i-pentane (1,980 pptv). The IUPAC-recommended OH reaction rate coefficient at 298 K is also lower for neopentane ($9.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) than for n-pentane ($3.76 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and i-pentane ($3.74 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Furthermore, neopentane was not measured by TOGA during ATom. Given its expected minor contribution to C5 alkane chemistry and the absence of a direct observational constraint in ATom, we did not introduce a separate neopentane tracer and oxidation mechanism. We also note that neopentane emissions are not discarded. Because neither CEDS nor CAMS resolves pentane isomers (Sect. 3.2), neopentane is contained within the reported pentane totals and is apportioned to NPENTANE and IPENTANE by the i/n ratios of Tables S7 and S8. We have revised the text for clarity, as follows:

Lines 100-102: The third pentane isomer, neopentane (2,2-dimethylpropane), is not resolved separately. It is much less abundant than n-pentane and i-pentane and also reacts more slowly with OH, so its contribution to pentane oxidation is expected to be more than an order of magnitude smaller than that of either of the other two isomers (Atkinson et al., 2006; Swarthout et al., 2013).

1.4) There are a lot of simulations discussed here. It would be useful to keep some consistent description of there. Table 1 contains some of these detail but I think it would be useful to have a section which give some more description of these even if it repeat information that has already been given. Can it be repeated what the difference is between T1.3_T3 vs T2.3_T3. This is quite confusing. It would be useful to repeat some information to clarify.

We thank the reviewer for pointing out that the simulation configurations were difficult to follow. We have clarified their descriptions in three places. First, we have rewritten the opening of Sect. 2.8 to explain the sequence of T1 updates and explicitly define T2.3. Second, we have added a footnote to Table 1 to explain the version labels and the "_T3" suffix. Third, we have expanded Sect. 3.3 to describe the five mechanism configurations and state explicitly how T1.3_T3 and T2.3_T3 differ.

Both configurations use the same T3 alkane chemistry, but they retain the other chemistry of their respective parent mechanisms. Thus, T2.3_T3 includes the more detailed isoprene and terpene chemistry of T2, whereas T1.3_T3 retains the corresponding T1 chemistry. The revised Sect. 3.3 also distinguishes the ten core simulations from the additional ketone photolysis sensitivity simulation. The revisions to Sect. 2.8 and Table 1 also address Comment 1.13.

Lines 367-372

In this study, we examine changes in global VOCs and OVOCs due to chemical mechanism updates and compare them with the effects of anthropogenic emission inventory selection. We use five mechanism configurations: T1.2, T1.3, T2.3, T1.3_T3, and T2.3_T3 (Table 1). T1.2 represents the T1 configuration used before this study, while T1.3 incorporates the common kinetic and photolysis updates described in Sect. 2.8. T2.3 includes the corresponding updates applied to T2, which contains more detailed isoprene and terpene chemistry. T1.3_T3 and T2.3_T3 add the same T3 alkane chemistry to T1.3 and T2.3, respectively, while retaining the other chemistry of each parent mechanism.

Each configuration is run with both CEDS and CAMS anthropogenic emissions, giving ten core simulations. For a given emission inventory, comparisons between T1.2 and T1.3 assess the effects of the common kinetic and photolysis updates. Comparisons of T1.3_T3 with T1.3 and T2.3_T3 with T2.3 isolate the effects of adding T3 alkane chemistry. Comparisons between T1.3 and T2.3, or between T1.3_T3 and T2.3_T3, assess the effects of the more detailed isoprene and

terpene chemistry in T2. Comparisons between CEDS and CAMS for the same mechanism assess the influence of emission inventory selection. An additional simulation, CEDS_T2.3_T3_jKET10x, tests the sensitivity to doubled C4–C6 ketone photolysis rates relative to the standard configuration, with acetone photolysis unchanged (Sect. 2.8; Table 1), bringing the total to eleven simulations.

Minor comments.

1.5) Line 34. I don't think speculation about the potential use of the scheme in urban air quality is worth commenting upon unless there is some evidence in the paper to support it.

We agree that our approximately 1° global simulations, evaluated primarily against ATom observations in the remote atmosphere, do not provide evidence regarding the effects of T3 on urban air quality. We have therefore removed the speculative statement from the Abstract that T3 is expected to be more important for urban air-quality applications. We have replaced it with conclusions directly supported by this study: across the ATom-sampled profiles, differences among mechanism cases are small for major pollutants, while T3 enables species-specific budgets and evaluation of individual alkanes and their oxidation products. We have revised the Abstract as follows:

Lines 30–34: Against ATom observations, all mechanisms perform similarly for major pollutants, whereas T3 enables evaluation of previously unrepresented species including propanal and peroxypropionyl nitrate, with generally improved simulation of oxygenated compounds, although performance varies temporally and spatially. Lumped approaches therefore remain adequate for global-scale major pollutants, but explicit treatment is needed to evaluate individual alkanes and their oxygenated products.

We have also revised the corresponding text in the Conclusions section to frame the effects in polluted environments as an open question requiring future evaluation rather than as an expected outcome:

Lines 753–757: This study focuses on the global-scale evaluation of the T3 mechanism as a first step in assessing its performance. The effects of detailed alkane chemistry in polluted urban environments and biomass-burning hot spots remain to be evaluated. Future work should assess

T3 in such environments using higher-resolution regional simulations such as MUSICA to determine whether, and under what conditions, the explicit representation of individual alkane species and their oxidation products affects ozone and secondary pollutant formation and improves air-quality predictions.

1.6) Line 45. Compared to the millions of potential species, its not that "most" of the species are unmeasured, the overwhelming number are not measured.

We agree and have replaced "Most" with "The vast majority" to better reflect the extent of unmeasured species and reactions.

Lines 45-46: The vast majority of these species and reactions are not directly measured but are instead predicted by automated chemical mechanisms using structure-activity relationships (SARs) (Aumont et al., 2005; Mouchel-Vallon et al., 2020).

1.7) Line 57. It would be useful to say what the authors mean by "better" model performance.

By "better model performance," we meant closer agreement between simulated and observed concentrations. We have revised the sentence to make this explicit.

Lines 57-59: While detailed chemistry with more compounds does not necessarily guarantee closer agreement between simulated and observed concentrations, it provides valuable insights into atmospheric processes and enables comprehensive evaluation of chemical reaction sets.

1.8) Figures 1 and 2. I might move this to after the description of the chemistry rather than having them first.

We have moved Figs. 1 and 2 to follow Sect. 2.6, after the description of the reaction pathways illustrated in these figures.

1.9) Line 99. It would be useful to indicate that molecule names in capital without subscripts (C3H6) refers specifically to the model tracer, whereas if they are indicated by subscripts (C₃H₆) this indicates the molecule in general. Same with other model species.

We thank the reviewer for this helpful suggestion. We have added a notation statement at the beginning of Sect. 2 that distinguishes model tracer names from molecular formulas, and we have applied this convention consistently throughout the text, figures, tables, and the Supplement. We have also noted that several tracers are lumped surrogates that do not correspond to a single compound, and pointed readers to Table S3 for the complete list of model species with their chemical formulas and descriptions. We have also updated the chemical formula column in Table S3 to use subscripted numbers consistently.

Lines 105-109: Throughout this paper, model species names are written without subscripts (e.g., C3H8, CH3COCH3, NBUTANE, and MEK) and denote CAM-chem tracers, whereas chemical formulas with subscripted numbers (e.g., C₃H₈ and CH₃COCH₃) refer to molecular species in general. Note that several tracers are lumped surrogates that do not correspond to a single compound (e.g., BIGALK, C6ALKANES, and ALKNIT). Table S3 lists all model species together with their chemical formulas and descriptions.

Table S3. C₃-C₆ alkanes and their oxidation products used in this study. Species newly added in T3 are shown in bold. Species used only in T1/T2 are shown in italic. Species used across all mechanisms (T1/T2/T3) are shown in normal font.

Species name	Chemical Formula	Description
C₃		
C3H8	C ₃ H ₈	propane
<i>C3H7O2</i>	<i>C₃H₇O₂</i>	<i>propyl peroxy radical</i>
NC3H7O2	C₃H₇O₂	n-propyl peroxy radical
IC3H7O2	C₃H₇O₂	isopropyl peroxy radical
CH3COCH3	CH ₃ COCH ₃	acetone
PROPANAL	C₂H₅CHO	propanal
PROPANOL	C₃H₈O	n-propanol
IPROPANOL	C₃H₈O	isopropanol
C2H5CO3	C₂H₅CO₃	propionyl peroxy radical
<i>C3H7OOH</i>	<i>C₃H₇OOH</i>	<i>propyl hydroperoxide</i>
NC3H7OOH	C₃H₇OOH	n-propyl hydroperoxide
IC3H7OOH	C₃H₇OOH	isopropyl hydroperoxide

CH ₃ COOOH CH ₃ OOH PPN	CH ₃ COOOH CH ₃ OOH C ₂ H ₅ CO ₃ NO ₂	peracetic acid methyl hydroperoxide peroxy propionyl nitrate
C ₄		
NBUTANE	C ₄ H ₁₀	n-butane
ISOBUTANE	C ₄ H ₁₀	isobutane
NBUPO2	C ₄ H ₉ O ₂	1-butyl peroxy radical
NBUO2	C ₄ H ₉ O ₂	2-butyl peroxy radical
TBUO2	C ₄ H ₉ O ₂	t-butyl peroxy radical
NBUPOOH	C ₄ H ₁₀ O ₂	n-butyl hydroperoxide
NBUOOH	C ₄ H ₁₀ O ₂	s-butyl hydroperoxide
TBUOOH	C ₄ H ₁₀ O ₂	t-butyl hydroperoxide
NBUPO	C ₄ H ₉ O	n-butoxy radical
NBUO	C ₄ H ₉ O	s-butoxy radical
BUTANAL	C ₄ H ₈ O	butanal
MEK	C ₄ H ₈ O	methyl ethyl ketone
BUTOL2	C ₄ H ₁₀ O	2-butanol
TBUOH	C ₄ H ₁₀ O	t-butanol
NBUPOHO2	C ₄ H ₉ O ₃	4-hydroxy butyl peroxy radical
OHBUTANAL	C ₄ H ₈ O ₂	4-hydroxy butanal
C ₅		
BIGALK	C ₅ H ₁₂	lumped alkanes (≥C ₄)
NPENTANE	C ₅ H ₁₂	n-pentane
IPENTANE	C ₅ H ₁₂	isopentane
ALKO2	C ₅ H ₁₁ O ₂	lumped alkane peroxy radical from BIGALK
NPENTO2A	C ₅ H ₁₁ O ₂	3-pentyl peroxy radical
NPENTO2B	C ₅ H ₁₁ O ₂	2-pentyl peroxy radical
IPENTO2A	C ₅ H ₁₁ O ₂	t-pentyl peroxy radical
IPENTO2B	C ₅ H ₁₁ O ₂	3-methyl-2-butyl peroxy radical
ALKOOH	C ₅ H ₁₂ O ₂	lumped alkane hydroperoxide
NPENTOOHA	C ₅ H ₁₂ O ₂	3-hydroperoxy pentane
NPENTOOHB	C ₅ H ₁₂ O ₂	2-hydroperoxy pentane
IPENTOOHA	C ₅ H ₁₂ O ₂	1,1-dimethylpropyl hydroperoxide
IPENTOOHB	C ₅ H ₁₂ O ₂	2-hydroperoxy-3-methyl butane
NPENTOA	C ₅ H ₁₁ O	3-pentoxy radical
NPENTOB	C ₅ H ₁₁ O	2-pentoxy radical
IPENTOB	C ₅ H ₁₁ O	3-methyl 2-butyl alkoxy radical
PENTANONE3	C ₅ H ₁₀ O	3-pentanone
PENTANONE2	C ₅ H ₁₀ O	2-pentanone
NELSON	C ₅ H ₁₀ O	methyl isopropyl ketone
PENTANOL3	C ₅ H ₁₂ O	3-pentanol
PENTANOL2	C ₅ H ₁₂ O	2-pentanol
IPENTOL	C ₅ H ₁₂ O	t-pentyl alcohol
M2BUTOL	C ₅ H ₁₂ O	2-methyl-3-butanol
ALKNIT	C ₅ H ₁₁ ONO ₂ ^a	lumped alkyl nitrates
C ₆		
C6ALKANES	C ₆ H ₁₄ ^a	lumped alkanes (≥C ₆)
C6ALKO2	C ₆ H ₁₃ O ₂	peroxy radical from C6ALKANES
C6ALKOOH	C ₆ H ₁₄ O ₂	lumped hydroperoxide from C6ALKO2 + HO2
C6KETOOH	C ₆ H ₁₂ O ₃	2-hydroperoxy-5-hexanone

C6ALKOHO2 HYDROXYKETONE	C6H13O3 C6H12O2	peroxy radical from C6ALKANES after H-shift lumped hydroxyketones (2-hydroxy 5-hexanone)
C6DIKETONE	C6H10O2	lumped diketones (2,5-hexanedione)

^a For lumped model species, the chemical formula shown represents the surrogate and does not necessarily describe every compound mapped to that species.

1.10) Line 115. There are other potential initiation reactions of these molecule. They react with halogens, and IUPAC contains rate constants for NO₃+n-C₄H₁₀. Perhaps some words about why other oxidants have been ignored.

We agree that the original text did not explain why initiation reactions with oxidants other than OH were excluded. For n-butane, the IUPAC-recommended rate coefficient for reaction with NO₃ at 298 K is $4.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, approximately five orders of magnitude smaller than the OH reaction rate coefficient used in T3 ($2.35 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Assuming an illustrative nighttime NO₃ mixing ratio of 10 pptv for 12 h d⁻¹ at 1 atm and a 24 h mean OH concentration of $1 \times 10^6 \text{ molecules cm}^{-3}$, the daily integrated NO₃-initiated loss is approximately 0.25% of the OH-initiated loss of n-butane. We therefore expect NO₃-initiated oxidation to make only a minor contribution to its global loss. In contrast, Cl reacts rapidly with n-butane, with a rate coefficient of $2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The model chemistry used here includes stratospheric ClO_x and halocarbon chemistry and a limited set of Cl-initiated hydrocarbon reactions, but it does not comprehensively represent tropospheric chlorine activation, multiphase chemistry, and VOC oxidation pathways required to evaluate Cl-initiated oxidation in marine, coastal, and polluted environments. Adding isolated Cl reactions for the new alkane tracers would therefore not provide an internally consistent representation of tropospheric chlorine chemistry. We have clarified this scope and limitation in Sect. 2.2 as follows:

Lines 119-125: In T3, oxidation of the parent alkane tracers considered here is initiated by bimolecular reactions with OH, followed by O₂ addition to form alkyl peroxy radicals. Initiation by NO₃ is not included because the rate coefficients for its reactions with these saturated alkanes are several orders of magnitude smaller than the corresponding OH reaction rate coefficients. Under representative remote tropospheric conditions, the NO₃-initiated loss of n-butane is estimated to be less than 1% of its OH-initiated loss. Although halogen atoms, particularly Cl,

react rapidly with alkanes and may be regionally important, consistent treatment of these pathways would require a more comprehensive representation of tropospheric halogen activation and cycling than is included in the present model chemistry. Such an extension is beyond the scope of this study.

1.11) Line 120. When talking about the primary, secondary and tertiary channel it might be useful to describe what is meant exactly. Is this the first, second and third generation products, or it is peroxy radicals which are formed from attacking the different carbon atoms in the carbon chain?

We have clarified in Sect. 2.2 that "primary," "secondary," and "tertiary" describe the carbon site from which OH abstracts H and, consequently, the structure of the alkyl peroxy radical formed after O₂ addition. Specifically, the relevant carbon atom is bonded to one, two, or three other carbon atoms, respectively. These terms do not denote the first, second, or third generation of oxidation products.

Lines 125-129: Here, "primary," "secondary," and "tertiary" describe the carbon site from which OH abstracts H: the carbon atom is bonded to one, two, or three other carbon atoms, respectively. Subsequent O₂ addition forms the corresponding primary, secondary, or tertiary alkyl peroxy radical. These terms refer to the degree of carbon substitution and the resulting peroxy radical structure, not to the generation number of oxidation products.

1.12) Line 130. By assuming that ALKNIT is C₅ I think this conserve nitrogen but leads to a lack of conservation of Carbon. This isn't a problem but it should be stated that this could lead to an imbalance in the carbon budget.

We thank the reviewer for identifying this limitation of the ALKNIT surrogate. ALKNIT is parameterized as a C₅ alkyl nitrate, whereas the nitrate-forming reactions involve C₂-C₆ alkyl peroxy radicals. Thus, nitrogen is conserved on a one-to-one basis in each reaction, but carbon number is not. We note, however, that the C₅ assignment is close to the production-weighted mean for the CEDS simulation. Using the contributions given in Sect. 2.3 (C₂ 9%, C₃ 8%, C₄ 12%, C₅ 17%, and C₆ 54%) and assigning six carbon atoms to the C₆ category, the production-weighted mean carbon number of

the precursor peroxy radicals is 4.99. Thus, the reaction-level carbon-number discrepancies nearly cancel in globally integrated ALKNIT production in this simulation. Because C6ALKANES represents alkanes with six or more carbon atoms, however, this calculation is based on the assigned surrogate carbon numbers and does not determine the exact carbon content of the actual alkyl-nitrate mixture. We have added a statement of this limitation to Sect. 2.3, as follows:

Lines 150-151: In T3, all alkane-derived organic nitrates are represented by a single surrogate species (ALKNIT), which is parameterized as a C5 alkyl nitrate surrogate but is formed from C2–C6 alkyl peroxy radicals.

Lines 155-159: Nitrogen is conserved in each nitrate-forming reaction, but carbon number is not, so the surrogate mapping can introduce an imbalance in the carbon budget. As shown by the production contributions given above, this imbalance is small in the global aggregate because the production-weighted mean carbon number of the precursor peroxy radicals is close to five. Nonetheless, carbon- or mass-budget quantities based on the ALKNIT representation should be interpreted as surrogate-equivalent quantities rather than as an exact elemental carbon budget.

1.13) Line 215. I found this quite confusing. The original publication is said to be Emmons et al., 2020 so how can there be a prior version to this? This section should be rewritten to increase its clarity. Perhaps Table 1 could be extended to provide more information and detail about what is different between all of these versions?

We thank the reviewer for identifying that the version chronology was unclear. In the original manuscript, we had inadvertently combined two distinct internal versions under a single label. T1 refers to the mechanism published by Emmons et al. (2020), whereas the decimal labels denote successive internal development states of the respective base mechanisms in the CESM/CAM-chem development repository and do not correspond to separate formal releases. T1.1 introduced the NO_x-dependent SOA yield parameterization of Jo et al. (2021), as documented in Schwantes et al. (2022), whereas T1.2 subsequently updated reaction rate constants based on JPL Publication 19 and is not associated with a separate publication. The original text attributed both changes to T1.2, making the version history unclear. We have corrected and rewritten

the opening of Sect. 2.8, explicitly defined T2.3, which was previously used in Table 1 without definition, and added a footnote to Table 1 summarizing the naming convention. These revisions also address Comment 1.4.

We have revised the text in Sect. 2.8 as follows:

Lines 250-256: The T1 mechanism was originally documented (Emmons et al., 2020). Following that publication, the version that introduced the NO_x-dependent SOA yield parameterization (Jo et al., 2021) is referred to as T1.1, as documented by Schwantes et al. (2022). The subsequent version, referred to as T1.2, updated reaction rate constants based on JPL Publication 19 (Burkholder et al., 2019); this update is not associated with a separate publication. T1.2 therefore represents the state of the mechanism in use before the present study. The additional common updates described in this section produce T1.3. The same set of updates is applied to the T2 mechanism of Schwantes et al. (2020) to produce T2.3. T1.3 and T2.3 are used directly and also serve as the parent mechanisms for the corresponding T3 configurations listed in Table 1.

We have also added the following footnote to Table 1:

Table 1. Model configurations and chemical mechanism complexity for different MOZART mechanism versions (T1, T2, T3) with two anthropogenic emission inventories (CEDS and CAMS). The number of chemical species, photolysis reactions, and kinetic reactions for each mechanism configuration are shown for each case. Note that the numbers include stratospheric chemistry reactions.

<i>Case name^a</i>	<i>Mechanism^a</i>	<i>Anthropogenic Emission</i>	<i>Number of species</i>	<i>Number of photolysis reactions</i>	<i>Number of kinetic reactions</i>
<i>CEDS_T1.2</i>	<i>T1.2</i>	<i>CEDSv2021_04_21</i>	<i>231</i>	<i>123</i>	<i>418</i>
<i>CEDS_T1.3</i>	<i>T1.3</i>	<i>CEDSv2021_04_21</i>	<i>232</i>	<i>124</i>	<i>424</i>
<i>CEDS_T2.3</i>	<i>T2.3</i>	<i>CEDSv2021_04_21</i>	<i>320</i>	<i>168</i>	<i>743</i>
<i>CEDS_T1.3_T3</i>	<i>T3 based on T1.3</i>	<i>CEDSv2021_04_21</i>	<i>278</i>	<i>142</i>	<i>557</i>
<i>CEDS_T2.3_T3</i>	<i>T3 based on T2.3</i>	<i>CEDSv2021_04_21</i>	<i>366</i>	<i>186</i>	<i>876</i>
<i>CAMS_T1.2</i>	<i>T1.2</i>	<i>CAMSv5.3</i>	<i>231</i>	<i>123</i>	<i>418</i>
<i>CAMS_T1.3</i>	<i>T1.3</i>	<i>CAMSv5.3</i>	<i>232</i>	<i>124</i>	<i>424</i>
<i>CAMS_T2.3</i>	<i>T2.3</i>	<i>CAMSv5.3</i>	<i>320</i>	<i>168</i>	<i>743</i>
<i>CAMS_T1.3_T3</i>	<i>T3 based on T1.3</i>	<i>CAMSv5.3</i>	<i>278</i>	<i>142</i>	<i>557</i>
<i>CAMS_T2.3_T3</i>	<i>T3 based on T2.3</i>	<i>CAMSv5.3</i>	<i>366</i>	<i>186</i>	<i>876</i>

^a *Version labels follow the internal numbering sequence used in the CESM/CAM-chem development repository and do not denote separate formal releases. T1 denotes the mechanism documented by Emmons et al. (2020). T1.1 adds the NO_x-dependent SOA yield parameterization of Jo et al. (2021), as documented by Schwantes et al. (2022), and T1.2 further updates reaction rate constants based on JPL Publication 19 (Burkholder et al., 2019). The version number ".3" denotes the common updates described in Sect. 2.8, applied to the T1 and T2 bases to produce*

T1.3 and T2.3, respectively. The configuration suffix "_T3" denotes the further addition of the T3 alkane chemistry developed in this work to the indicated parent mechanism.

1.14) Line 270. I'm confused about how the species have been mapped here. Is there no mapping to the butane isomers? Could this be given as a table? With more of an explanation about what is being emitted by the biosphere?

We thank the reviewer for pointing out that the emission mapping was difficult to follow. We have added Table S6 listing the MEGAN compounds previously assigned to BIGALK and their mapping in T3, and expanded the explanation in Sect. 3.2. Pentane and pentanal are mapped to NPENTANE, oxopentanal to C6DIKETONE, and the remaining 19 compounds to C6ALKANES. We also clarify that this residual group contains oxygenated and terpenoid compounds as well as alkanes. Regarding the butane isomers, neither n-butane nor isobutane is included in the MEGAN2.1 compound list reported in Table 1 of Guenther et al. (2012). Consequently, there is no direct biogenic emission mapping to NBUTANE or ISOBUTANE in our simulations. Emissions of both butane isomers are, however, included from anthropogenic sources and biomass burning: anthropogenic butanes are split into NBUTANE and ISOBUTANE using the sector-specific i/n ratios derived in Tables S7 and S8, and FINNv2.5 BIGALK is partitioned among all five T3 alkane tracers using the emission-factor fractions in Table S10. We have revised Sect. 3.2 and added Table S6 as follows:

Lines 316-324

For T3, the MEGAN compounds previously assigned to BIGALK are remapped as follows: pentane and pentanal to NPENTANE, oxopentanal to C6DIKETONE, and the remaining 19 compounds to C6ALKANES (Table S6). This residual group spans carbon numbers from six to fifteen and includes oxygenated and terpenoid compounds as well as alkanes. Its combined mapped source is 2.68 Tg yr^{-1} for 2016–2018, expressed using the C6ALKANES molecular weight with the number of molecules conserved during mapping. This represents approximately 8.7% and 10.3% of total direct C6ALKANES emissions in the CEDS and CAMS simulations, respectively. Approximately 70% of the mapped biogenic source comes from 1,8-cineole, camphor, hexanal, and 1-hexanol. This contribution therefore represents a surrogate-mapped biogenic VOC source rather than emissions composed entirely of $\geq C6$ alkanes.

Table S6. Mapping of MEGAN emission species previously assigned to BIGALK in T1 and T2 to the corresponding model species in T3. Compounds are listed in order of increasing carbon number. The T3 mapping is identical for the T1.3_T3 and T2.3_T3 configurations. MEGAN species identifiers are reproduced as used in the model configuration.

<i>MEGAN emission species</i>	<i>Molecular formula</i>	<i>T1/T2 species</i>	<i>T3 species</i>
<i>pentane</i>	<i>C5H12</i>	<i>BIGALK</i>	<i>NPENTANE</i>
<i>pentanal</i>	<i>C5H10O</i>	<i>BIGALK</i>	<i>NPENTANE</i>
<i>oxopentanal</i>	<i>C5H8O2</i>	<i>BIGALK</i>	<i>C6DIKETONE</i>
<i>hexane</i>	<i>C6H14</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>hexanal</i>	<i>C6H12O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>hexanol_1</i>	<i>C6H14O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>heptane</i>	<i>C7H16</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>heptanal</i>	<i>C7H14O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>heptanone</i>	<i>C7H14O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>octanal</i>	<i>C8H16O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>octanol</i>	<i>C8H18O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>nonanal</i>	<i>C9H18O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>decanal</i>	<i>C10H20O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>tricyclene</i>	<i>C10H16</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>camphor</i>	<i>C10H16O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>fenchone</i>	<i>C10H16O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>thujone_a</i>	<i>C10H16O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>thujone_b</i>	<i>C10H16O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>cineole_1_8</i>	<i>C10H18O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>borneol</i>	<i>C10H18O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>bornyl_ACT</i>	<i>C12H20O2</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>cedrol</i>	<i>C15H26O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>

1.15) Line 333. Why does the propane concentration change at all? Presumably this is due to changes in the OH between the simulations rather than differences in the propane oxidation rate?

The reviewer is correct. For a given emission inventory, propane emissions are identical across mechanisms, and the total C₃H₈ + OH rate coefficient is unchanged. Therefore, the small inter-mechanism differences in propane burden reflect differences in the simulated OH field rather than changes in propane oxidation kinetics. These OH differences arise mainly from the updated isoprene and terpene chemistry in T2, as already noted for BIGALK in Sect. 4.2. We have made this explicit in the text.

Lines 399-404: The global burden of propane shows minimal sensitivity to mechanism choice (<5% variation between cases), while emission inventory selection drives much larger differences (~20% variation: 231–241 Gg for CEDS versus 285–297 Gg for CAMS). For a given emission inventory, propane emissions and the total C₃H₈ + OH rate coefficient are identical across mechanisms. Thus, the small differences in propane burden reflect differences in the simulated OH field, arising mainly from the updated isoprene and terpene chemistry in T2 (Sect. 4.2), rather than changes in propane oxidation kinetics.

1.16) Line 343. It should explain that the BIGALK for T3 is the sum of a set of species. Its not a real specie.s

We agree with the reviewer. Although the individual tracers were listed in the section heading and text, we did not explicitly state that BIGALK is not a species in T3 and that the T3 values shown are post-processing aggregates. We have now made this explicit in the text and in the caption of Fig. 3.

Lines 412-415: Note that BIGALK is a transported model species only in T1 and T2. In T3, BIGALK refers to a post-processing diagnostic constructed from the five alkane tracers NBUTANE, ISOBUTANE, NPENTANE, IPENTANE, and C6ALKANES, rather than to a transported species. For the burden diagnostics in Fig. 3a and b, the masses of these five tracers are summed, allowing direct comparison with the BIGALK burden simulated in T1 and T2.

Fig. 3 caption: In T3, BIGALK is not a transported species: the values shown are post-processing sums of NBUTANE, ISOBUTANE, NPENTANE, IPENTANE, and C6ALKANES, computed in the units of each panel for direct comparison with T1 and T2.

1.17) Line 367. I'm not sure what the (0.31-3.06 Tg yr⁻¹) means. Is that it increases by 0.31 from 3.06 or is this a range of changes?

We thank the reviewer for pointing out this ambiguity. The parenthetical values indicated a range of increases in global acetone chemical production across cases, not a change from one value to another. We have clarified the comparison and updated the numerical range using the revised simulation results. The increases are larger for the CEDS simulations (3.04 and 3.54 Tg yr⁻¹ relative to T1.3 and T2.3, respectively) than for the CAMS simulations (0.17 and 1.28 Tg yr⁻¹, respectively).

Lines 442-445: Adding T3 alkane chemistry increases global acetone chemical production by 0.17–3.54 Tg yr⁻¹ relative to the corresponding T1.3 or T2.3 parent mechanism using the same emission inventory, with larger increases for CEDS than for CAMS (Table S11). However, the T2 terpene updates dominate the overall acetone budget changes.

1.18) Line 386. "decrease significant in T2" Compared to what simulation? T1?

We thank the reviewer for pointing this out. The comparison is between T2.3 and T1.3 using the same anthropogenic emission inventory. We have made this explicit and separated the changes in chemical production and burden, which differ in magnitude: acetone chemical production is lower in T2.3 than in T1.3 by 39–40%, and the burden by about 25%. We have also updated the corresponding statement earlier in Sect. 4.3, which previously reported the burden reduction as approximately 23%.

Lines 478-480: First, acetone chemical production and burden are lower in T2.3 than in T1.3 by 39–40% and about 25%, respectively, using the same anthropogenic emission inventory. These reductions represent the dominant change in total ketone budgets.

1.19) Line 423. It would be useful to show whether NO_y changes from these different simulations. Overall does NO_y change?

We have calculated both whole-atmosphere and global tropospheric NO_y burdens. We report the tropospheric burden in the revised text because approximately two-thirds of the whole-atmosphere NO_y burden lies above the model tropopause, where NO_y is not directly affected by the tropospheric alkane chemistry developed here. Across the ten core simulations, the whole-atmosphere NO_y burden ranges from 3.408 to 3.460 Tg N, whereas the tropospheric burden ranges from 1.084 to 1.129 Tg N. More specifically, adding T3 alkane chemistry decreases the whole-atmosphere NO_y burden by 0.5–0.7% and the tropospheric NO_y burden by 1.3–1.6% relative to the corresponding parent mechanisms using the same anthropogenic emission inventory. Thus, the changes in individual reactive-nitrogen reservoir species discussed in Sect. 4.5 primarily represent redistribution within NO_y, while the effect on the total NO_y burden remains minor. We have added the tropospheric result to Sect. 4.5 as follows.

Lines 556–561: Although T3 alters the burdens and distributions of individual reactive-nitrogen reservoir species, its effect on total NO_y is small. Relative to the corresponding parent mechanisms using the same anthropogenic emission inventory, the globally integrated tropospheric NO_y burden decreases by 1.3–1.6% when T3 alkane chemistry is added, with PPN included in this calculation for the T3 simulations. These results indicate that the changes described above primarily reflect a redistribution of reactive nitrogen among reservoir species and across altitudes, rather than a substantial change in the total tropospheric NO_y burden.

1.20) ATOM figures. It's clear that the model significantly underestimates the alkane concentrations under all simulations. It would be useful to make some comments about what this means. This seems to suggest that the emissions are likely significantly underestimated. It would be useful to explicitly say this

We agree that the implications of the alkane underestimation should be stated more explicitly. We have strengthened the discussion in Sect. 5 to explain that the persistent underestimation of propane and C4–C5 alkanes across mechanisms using both CEDS

and CAMS suggests that their emissions are likely underestimated. The agreement in the branched-to-total alkane ratios further supports the relative isomer composition used in the simulations, despite the underestimated absolute concentrations.

Lines 653-658: The agreement in the branched-to-total alkane ratios supports the relative isomer composition prescribed using the emission ratios in Tables S7 and S8. However, propane and individual C4-C5 alkane concentrations remain underestimated across the chemical mechanisms using both CEDS and CAMS emissions. These results suggest that underestimated emission magnitudes in both inventories are an important contributor to the model-observation discrepancies. For butanes and pentanes, the agreement in the isomer ratios points to emission magnitudes rather than isomeric speciation as the more likely source of error.

This paper presents MOZART-T3, a new version of the MOZART/CAM-chem mechanism. It replaces the single lumped $\geq C_4$ alkane species (BIGALK) with explicit butanes, pentanes, and a $\geq C_6$ lump. The authors run T1, T2, and T3 with two emission inventories and compare the results to ATom aircraft data. The work is careful and clearly documented, and the result that lumping is fine for major pollutants but not for individual OVOCs is useful. I give general comments first, then minor and technical ones. I would suggest a minor revision.

General Comments:

2.1) The MEK improvement in T3 is convincing. My one caution is the absolute bias, which is still about -30%. Because n-butane is also too low, I cannot tell whether the mechanism yield is right (and MEK is low only because n-butane is low) or whether the mechanism itself is off. The MEK-to-n-butane ratio would separate these. If n-butane emissions are too low, both n-butane and the MEK made from it drop together, so the ratio barely changes. Comparing the modeled and observed MEK/n-butane ratio therefore tests the chemistry without the emission bias, in the same way you already did for propane products in Fig. S7.

We thank the reviewer for this helpful suggestion. We have added the vertical profile of the MEK-to-n-butane ratio to Fig. S9. The standard T3 simulations lie within the observed interquartile range throughout the sampled profile and closely reproduce the observed median ratio and its vertical variation, despite underestimating the absolute concentrations of both species. This agreement supports the representation of MEK formation and loss relative to n-butane in T3 and suggests that the remaining MEK underestimation is largely associated with insufficient n-butane abundance. This comparison also illustrates an additional benefit of T3: explicitly representing n-butane enables evaluation of the relationship between a specific precursor and its oxidation product, which is not directly possible with the lumped BIGALK representation in T1

and T2. One caveat is that the ratio reflects additional MEK sources and differences in the photochemical histories of the two species, so it does not independently determine the MEK yield from n-butane oxidation. We have also included this discussion in the main text.

This diagnostic also informs the ketone photolysis sensitivity analysis discussed in our response to Comment 2.3. Doubling the photolysis rates of MEK and the C5–C6 ketones produces systematically lower MEK-to-n-butane ratios and poorer agreement with the observed medians. This comparison provides additional observational support for retaining the standard photolysis scaling.

We have also clarified the treatment of measurements below detection limits and the matching of model samples for the aircraft concentration and ratio comparisons. The revised text and caption are provided below.

Lines 602-608

For concentration comparisons, when measurements are below their detection limits, we assign a value of zero rather than excluding those data points, to avoid sampling biases toward higher concentrations. For ratio comparisons, however, we exclude samples in which either species is below its detection limit, because assigning zero would produce an artificial zero ratio or an undefined ratio. Model values are sampled at the same retained points, so the ratio comparisons represent the subset of observations in which both species are above their respective detection limits.

Lines 685-694

The standard T3 simulations lie within the observed interquartile range of the MEK-to-n-butane ratio throughout the sampled profile and closely reproduce the observed median ratio and its vertical variation (Fig. S9), despite underestimating the absolute concentrations of both species. This agreement supports the representation of MEK formation and loss relative to n-butane in T3 and suggests that the remaining MEK underestimation is largely associated with insufficient n-butane abundance. By explicitly representing n-butane, T3 enables this evaluation of a specific precursor-product relationship, which is not directly possible with the lumped BIGALK representation in T1 and T2. Although the ratio also reflects additional MEK sources, photochemical age, and mixing, it provides a complementary constraint beyond absolute concentrations alone. Doubling the photolysis rates of MEK and the C5–C6 ketones produces systematically lower ratios and poorer agreement with the observed medians, providing

additional observational support for the standard MEK photolysis rate of five times that of acetone (Sect. 2.8).

Addition to the caption of Fig. S9

Ratio comparisons exclude observations in which either species is below its detection limit, and model values are sampled at the same retained points (Sect. 5).

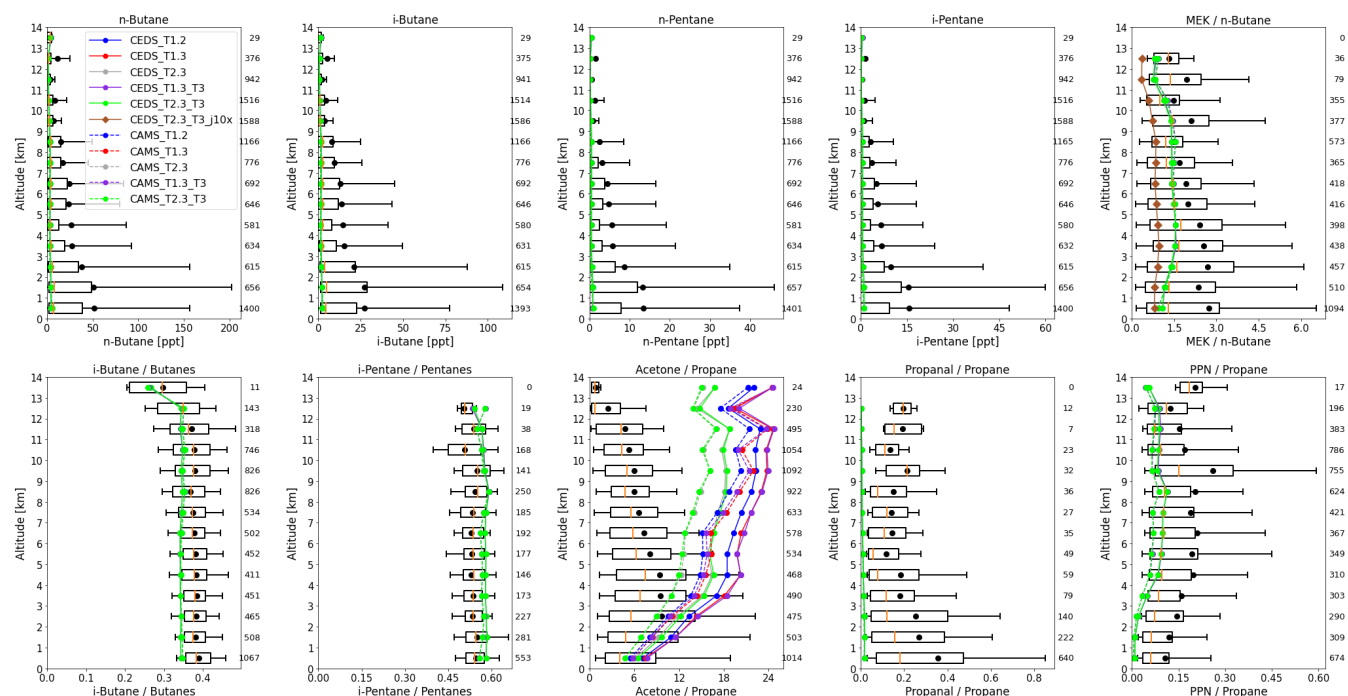


Figure S9. Same as Figure S8 but for explicit C4–C5 alkane species (*n*-butane, *i*-butane, *n*-pentane, *i*-pentane), ratios of branched isomers to total alkanes (*i*-butane/butanes, *i*-pentane/pentanes), and OVOCs to parent hydrocarbons (MEK/*n*-butane, acetone/propane, propanal/propane, PPN/propane). Brown diamonds additionally show the ketone photolysis sensitivity simulation, CEDS_T2.3_T3_jKET10x (Table 1), abbreviated as CEDS_T2.3_T3_j10x in the legend for compactness. Ratio comparisons exclude observations in which either species is below its detection limit, and model values are sampled at the same retained points (Sect. 5).

2.2) The new $\geq C6$ chemistry is not constrained by data. The 60% H-shift branching is a rough estimate, and the Praske et al. (2018) rate is uncertain by a factor of ten and applied to the whole $\geq C6$ group from a single species. Its products are lumped surrogates, so there is nothing to measure them against. The authors should say which new species are tested against data (alkanes, acetone, MEK, PPN, propanal) and which are predictions only. Also, please justify mapping all remaining biogenic BIGALK onto C6ALKANES — this may be why $\geq C6$ alkanes are too high versus ATom.

We thank the reviewer for highlighting the need to distinguish the observational evaluation from the less constrained aspects of the $\geq C6$ chemistry. Our ATom comparisons include individual C4–C5 alkanes, the measured $\geq C6$ alkane aggregate, acetone, MEK, PPN, and propanal. However, these comparisons do not independently constrain the assumed 60% branching fraction or the peroxy radical H-shift rate applied to the $\geq C6$ group. The rate expression used in T3 is taken from the structure–activity relationship (SAR) of Vereecken and Nozière (2020), rather than directly from the measurements reported by Praske et al. (2018); we have corrected this attribution in Sect. 2.5, where the uncertainties associated with this rate and its extrapolation to the $\geq C6$ group are discussed. We have also stated explicitly in Sect. 2.6 that the C6 intermediates and multifunctional product surrogates are not directly evaluated against observations in this study.

Regarding biogenic emissions, T3 retains the residual MEGAN source grouping previously assigned to BIGALK in T1 and T2, while separating pentane and pentanal into NPENTANE and oxopentanal into C6DIKETONE. The remaining 19 compounds are assigned to C6ALKANES. This group spans carbon numbers from six to fifteen and includes oxygenated and terpenoid compounds as well as alkanes. This treatment carries forward the existing surrogate approach; it does not imply that all contributing compounds are $\geq C6$ alkanes. We have added Table S6 to document the molecular formulas and mapping of all 22 compounds.

For 2016–2018, the global mean anthropogenic C6ALKANES sources are 26.0 and 21.3 Tg yr⁻¹ from CEDS and CAMS inventories, respectively, 2.11 Tg yr⁻¹ from FINNV2.5

biomass burning, and 2.68 Tg yr⁻¹ from the mapped MEGAN compounds. The biogenic contribution is expressed using the C6ALKANES molecular weight, with the number of molecules conserved during mapping. It is dominated by oxygenated and terpenoid compounds: 1,8-cineole, camphor, hexanal, and 1-hexanol together account for approximately 70% of the mapped biogenic source.

We agree that this mapping may contribute to the overestimate of $\geq$ C6 alkanes relative to ATom observations, and its contribution along the flight tracks has not been quantified separately. However, the mapped biogenic source accounts for only approximately 8.7% and 10.3% of global direct C6ALKANES emissions in the CEDS and CAMS simulations, respectively, with anthropogenic emissions accounting for 84.5% and 81.7%. Furthermore, the apparent overestimate is also strongly sensitive to the treatment of below-detection-limit measurements: as discussed in Sect. 5, the normalized mean bias decreases from 132–170% to 22–41% when these observations are assigned their detection limits rather than zero. In addition, TOGA reports only five individual $\geq$ C6 alkanes, whereas the model tracer represents the full class. These differences in measurement treatment and species coverage complicate attribution of the apparent overestimate to the biogenic mapping. We have clarified the mapping and its magnitude in Sect. 3.2 and noted this limitation of the observational comparison in Sect. 5.

Lines 218-223

The assumed 60% branching fraction and the application of a SAR-based peroxy radical H-shift rate to the $\geq$ C6 group remain uncertain. Although the parent alkane aggregate and several oxidation products are evaluated against ATom observations in Sect. 5, these comparisons do not independently constrain the individual pathways within the $\geq$ C6 scheme. The C6 intermediates and multifunctional product surrogates, including C6ALKOHO2, C6ALKOOH, HYDROXYKETONE, C6KETOOH, and C6DIKETONE, remain model predictions without direct observational evaluation in this study.

Lines 316-324

For T3, the MEGAN compounds previously assigned to BIGALK are remapped as follows: pentane and pentanal to NPENTANE, oxopentanal to C6DIKETONE, and the remaining 19 compounds to C6ALKANES (Table S6). This residual group spans carbon numbers from six to

fifteen and includes oxygenated and terpenoid compounds as well as alkanes. Its combined mapped source is 2.68 Tg yr⁻¹ for 2016–2018, expressed using the C6ALKANES molecular weight with the number of molecules conserved during mapping. This represents approximately 8.7% and 10.3% of total direct C6ALKANES emissions in the CEDS and CAMS simulations, respectively. Approximately 70% of the mapped biogenic source comes from 1,8-cineole, camphor, hexanal, and 1-hexanol. This contribution therefore represents a surrogate-mapped biogenic VOC source rather than emissions composed entirely of ≥C6 alkanes.

Lines 646-649

The biogenic emission mapping may also contribute to the overestimate of ≥C6 alkanes, because C6ALKANES receives emissions of oxygenated and terpenoid compounds in addition to alkanes (Sect. 3.2; Table S6). These mapped biogenic emissions account for approximately 9–10% of the global direct C6ALKANES source, which is dominated by anthropogenic emissions, and their contribution to the discrepancy along the ATom flight tracks has not been quantified.

Table S6. Mapping of MEGAN emission species previously assigned to BIGALK in T1 and T2 to the corresponding model species in T3. Compounds are listed in order of increasing carbon number. The T3 mapping is identical for the T1.3_T3 and T2.3_T3 configurations. MEGAN species identifiers are reproduced as used in the model configuration.

MEGAN emission species	Molecular formula	T1/T2 species	T3 species
pentane	C5H12	BIGALK	NPENTANE
pentanal	C5H10O	BIGALK	NPENTANE
oxopentanal	C5H8O2	BIGALK	C6DIKETONE
hexane	C6H14	BIGALK	C6ALKANES
hexanal	C6H12O	BIGALK	C6ALKANES
hexanol_1	C6H14O	BIGALK	C6ALKANES
heptane	C7H16	BIGALK	C6ALKANES
heptanal	C7H14O	BIGALK	C6ALKANES
heptanone	C7H14O	BIGALK	C6ALKANES
octanal	C8H16O	BIGALK	C6ALKANES
octanol	C8H18O	BIGALK	C6ALKANES
nonanal	C9H18O	BIGALK	C6ALKANES
decanal	C10H20O	BIGALK	C6ALKANES
tricyclene	C10H16	BIGALK	C6ALKANES
camphor	C10H16O	BIGALK	C6ALKANES
fenchone	C10H16O	BIGALK	C6ALKANES
thujone_a	C10H16O	BIGALK	C6ALKANES
thujone_b	C10H16O	BIGALK	C6ALKANES

<i>MEGAN emission species</i>	<i>Molecular formula</i>	<i>T1/T2 species</i>	<i>T3 species</i>
<i>cineole_1_8</i>	<i>C10H18O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>borneol</i>	<i>C10H18O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>bornyl_ACT</i>	<i>C12H20O2</i>	<i>BIGALK</i>	<i>C6ALKANES</i>
<i>cedrol</i>	<i>C15H26O</i>	<i>BIGALK</i>	<i>C6ALKANES</i>

2.3) The MEK photolysis rate should be tested. You set it to 5× acetone. But the quantum yield in the literature spans a factor of two (~0.15–0.17 versus ~0.34–0.38), which allows anywhere from about 5× to 10× acetone. So 5× is the low end. A higher, equally valid value would lower MEK further and make the –30% bias worse. Please report the MEK photolysis rate and lifetime before and after the change, and show how the MEK bias and vertical profile respond across the 5–10× range.

We thank the reviewer for suggesting this sensitivity test. We have performed an additional simulation, CEDS_T2.3_T3_jKET10x, to evaluate the effect of increasing the MEK photolysis rate from five to ten times that of acetone. The label “jKET10x” refers to this tenfold MEK-to-acetone photolysis ratio. Acetone photolysis is unchanged, and the simulation otherwise follows CEDS_T2.3_T3. For consistency, the photolysis rates of the C5–C6 ketones are also doubled: their scaling relative to acetone increases from five to ten, except for C6DIKETONE, for which it increases from ten to twenty. This sensitivity simulation is now included in Table 1 and Table S11. Its MEK concentration profiles are shown in Figs. 8 and S10, and its MEK-to-n-butane ratio profile is shown in Fig. S9.

Increasing the scaling from five to ten raises the mean MEK photolysis rate sampled along the ATom flight tracks from 3.29×10^{-6} to $6.59 \times 10^{-6} \text{ s}^{-1}$. The global lifetime against photolysis, calculated as the global MEK burden divided by its globally integrated photolysis loss, decreases from 8.41 to 4.47 days. The total atmospheric lifetime, accounting for chemical loss and deposition, decreases by 26.6%, from 2.63

to 1.93 days, and the global MEK burden decreases by 26.6%, from 0.152 to 0.112 Tg. Global MEK chemical production remains approximately 9.49 Tg yr⁻¹, indicating that the photolysis changes have little effect on its globally integrated chemical production.

As anticipated by the reviewer, increasing photolysis worsens the overall MEK underestimation. Across the 11,548 model-observation pairs, the modeled mean MEK concentration decreases from 9.28 to 6.29 ppt, compared with the observed mean of 12.99 ppt, and the NMB changes from -28.6% to -51.6%. Figure 8 and Fig. S10 show the corresponding changes in the aggregated and campaign- and region-specific vertical profiles.

The MEK-to-n-butane comparison introduced in response to Comment 2.1 provides an additional constraint. For the 5,516 samples in which both species are above their detection limits, the observed median ratio is 1.352. The modeled median decreases from 1.328 in the standard simulation to 0.811 in the sensitivity simulation (Fig. S9).

These results demonstrate that MEK remains sensitive to the assumed photolysis rate. The overall MEK abundance and the median precursor-product ratio provide additional observational support for retaining the standard factor of five within the present model configuration. They do not uniquely determine the photolysis rate, because uncertainties in MEK sources and other loss processes remain. We have described the sensitivity experiment in Sect. 2.8 and added its budget and observational consequences to Sects. 4.3 and 5.

Lines 277-281

To assess sensitivity to the assumed ketone photolysis rates, we perform an additional simulation based on CEDS_T2.3_T3 in which the MEK photolysis rate is increased from five to ten times that of acetone (CEDS_T2.3_T3_jKET10x; Table 1); the label “jKET10x” refers to this tenfold MEK-to-acetone photolysis ratio. The C5–C6 ketone photolysis rates are also doubled consistently: their scaling relative to acetone increases from five to ten, except for C6DIKETONE, for which it increases from ten to twenty. Acetone photolysis and all other model settings are unchanged.

Lines 465-468

Doubling the photolysis rates of MEK and the C5–C6 ketones in CEDS_T2.3_T3_jKET10x decreases the global MEK burden by 26.6%, from 0.152 to 0.112 Tg, while chemical production remains approximately 9.49 Tg yr⁻¹ (Table S11). The global lifetime against photolysis, calculated as burden divided by photolysis loss, decreases from 8.41 to 4.47 days, and the total atmospheric lifetime, including chemical loss and deposition, decreases from 2.63 to 1.93 days.

Lines 695-701

Increasing the MEK photolysis scaling from five to ten times that of acetone increases the overall negative bias in MEK relative to ATom observations (Fig. 8 and Fig. S10). For the collocated samples, the mean modeled MEK concentration decreases from 9.28 to 6.29 ppt, compared with the observed mean of 12.99 ppt, and the NMB changes from -28.6% to -51.6%. The mean MEK photolysis rate along the sampled flight tracks increases from 3.29×10^{-6} to $6.59 \times 10^{-6} \text{ s}^{-1}$. For samples with both MEK and n-butane above their detection limits, the modeled median MEK-to-n-butane ratio decreases from 1.328 to 0.811, compared with the observed median of 1.352 (Fig. S9). The standard scaling of five times the acetone photolysis rate gives better agreement with the observed MEK abundance and median MEK-to-n-butane ratio than the higher scaling of ten.

Table S11. Annual global budgets for ketone species including emissions (anthropogenic, biomass burning, and biogenic), chemical production and loss rates, dry and wet depositions, source totals (emission + chemical production) and loss totals (chemical loss + deposition), atmospheric burden, and atmospheric lifetime across different simulation cases. All emission, production, loss, and deposition values are in Tg yr⁻¹, burden in Tg, and lifetime in days.

Species	Case	Emission (Anth.)	Emission (BB)	Emission (Biog.)	Chem. Prod.	Chem. Loss.	Dry Dep.	Wet Dep.	Emission (All)	Source (All)	Loss (All)	Burden	Lifetime
KETONE	CEDS_T1.2	3.50	16.17	42.31	128.88	131.86	57.68	1.43	61.98	190.86	190.97	5.40	10.32
	CEDS_T1.3	3.08	16.17	42.26	129.41	132.18	56.77	1.40	61.51	190.92	190.35	5.09	9.77
	CEDS_T2.3	3.08	16.17	42.29	95.24	108.75	47.41	1.09	61.54	156.78	157.25	3.93	9.12
	CEDS_T1.3_T3	3.08	16.17	42.66	163.93	158.12	57.25	9.85	61.90	225.84	225.22	4.98	8.07
	CEDS_T2.3_T3	3.08	16.17	42.66	127.09	132.52	47.87	8.83	61.90	188.99	189.22	3.83	7.38
	CEDS_T2.3_T3_jKET10x	3.08	16.17	42.67	126.59	133.05	47.40	8.28	61.91	188.50	188.73	3.77	7.30
	CAMS_T1.2	7.60	16.17	42.34	116.02	123.04	57.87	1.41	66.11	182.13	182.32	5.26	10.53
	CAMS_T1.3	6.68	16.17	42.33	117.05	122.74	57.15	1.40	65.18	182.23	181.29	5.04	10.15
	CAMS_T2.3	6.68	16.17	42.34	82.42	99.21	47.77	1.09	65.18	147.60	148.08	3.86	9.51
	CAMS_T1.3_T3	6.68	16.17	42.72	148.99	147.13	57.71	9.39	65.57	214.56	214.22	4.88	8.32
	CAMS_T2.3_T3	6.68	16.17	42.73	112.30	121.45	48.32	8.36	65.57	177.88	178.13	3.72	7.62
CH3COCH3	CEDS_T1.2	0.59	5.63	42.31	83.57	84.38	46.04	1.27	48.53	132.10	131.69	4.59	12.73
	CEDS_T1.3	2.35	5.63	42.26	84.67	85.32	47.19	1.28	50.24	134.91	133.80	4.59	12.52
	CEDS_T2.3	2.35	5.63	42.29	51.88	63.20	37.90	0.98	50.27	102.15	102.07	3.44	12.29
	CEDS_T1.3_T3	2.35	5.63	42.27	87.71	87.46	48.35	1.32	50.26	137.96	137.13	4.73	12.58
	CEDS_T2.3_T3	2.35	5.63	42.27	55.42	65.50	39.07	1.02	50.26	105.68	105.58	3.58	12.38
	CEDS_T2.3_T3_jKET10x	2.35	5.63	42.28	55.43	65.51	39.07	1.02	50.26	105.69	105.60	3.58	12.37
	CAMS_T1.2	1.27	5.63	42.34	81.74	83.09	46.22	1.27	49.25	130.99	130.58	4.57	12.77

Species	Case	Emission (Anth.)	Emission (BB)	Emission (Biog.)	Chem. Prod.	Chem. Loss.	Dry Dep.	Wet Dep.	Emission (All)	Source (All)	Loss (All)	Burden	Lifetime
	CAMS_T1.3	5.10	5.63	42.33	83.18	85.19	48.30	1.30	53.06	136.24	134.80	4.63	12.53
	CAMS_T2.3	5.10	5.63	42.34	49.95	62.97	38.99	0.99	53.07	103.01	102.95	3.46	12.26
	CAMS_T1.3_T3	5.10	5.63	42.34	83.35	85.62	48.90	1.32	53.07	136.42	135.84	4.67	12.54
	CAMS_T2.3_T3	5.10	5.63	42.34	51.23	63.62	39.60	1.01	53.07	104.31	104.23	3.51	12.29
MEK	CEDS_T1.2	2.92	10.54		45.31	47.48	11.64	0.16	13.45	58.76	59.28	0.80	4.94
	CEDS_T1.3	0.73	10.54		44.75	46.85	9.58	0.12	11.26	56.01	56.55	0.50	3.25
	CEDS_T2.3	0.73	10.54		43.36	45.55	9.51	0.11	11.26	54.63	55.18	0.49	3.26
	CEDS_T1.3_T3	0.73	10.54		9.50	15.39	5.71	0.04	11.26	20.76	21.13	0.15	2.64
	CEDS_T2.3_T3	0.73	10.54		9.49	15.39	5.70	0.04	11.26	20.75	21.12	0.15	2.63
	CEDS_T2.3_T3_jKET10x	0.73	10.54		9.49	15.70	5.40	0.03	11.26	20.76	21.13	0.11	1.93
	CAMS_T1.2	6.33	10.54		34.28	39.95	11.65	0.14	16.86	51.14	51.74	0.69	4.86
	CAMS_T1.3	1.58	10.54		33.87	37.54	8.85	0.10	12.12	45.99	46.49	0.41	3.25
	CAMS_T2.3	1.58	10.54		32.48	36.25	8.79	0.10	12.12	44.59	45.13	0.40	3.26
	CAMS_T1.3_T3	1.58	10.54		7.49	14.06	5.89	0.04	12.12	19.61	19.99	0.14	2.63
	CAMS_T2.3_T3	1.58	10.54		7.49	14.06	5.89	0.04	12.12	19.60	19.98	0.14	2.63
PENTANONE2	CEDS_T1.3_T3				2.38	2.33	0.05	0.002		2.38	2.38	0.01	1.41
	CEDS_T2.3_T3				2.38	2.32	0.05	0.002		2.38	2.38	0.01	1.41
	CEDS_T2.3_T3_jKET10x				2.38	2.33	0.05	0.002		2.38	2.38	0.01	1.25
	CAMS_T1.3_T3				0.89	0.86	0.02	0.001		0.89	0.89	0.00	1.68
	CAMS_T2.3_T3				0.89	0.86	0.02	0.001		0.89	0.89	0.00	1.69
PENTANONE3	CEDS_T1.3_T3				2.59	2.47	0.11	0.005		2.59	2.58	0.02	2.98
	CEDS_T2.3_T3				2.58	2.47	0.11	0.005		2.58	2.58	0.02	2.99
	CEDS_T2.3_T3_jKET10x				2.58	2.48	0.09	0.004		2.58	2.58	0.02	2.38
	CAMS_T1.3_T3				0.98	0.93	0.05	0.002		0.98	0.98	0.01	3.46
	CAMS_T2.3_T3				0.98	0.93	0.05	0.002		0.98	0.98	0.01	3.47
NELSON	CEDS_T1.3_T3				1.71	1.67	0.04	0.001		1.71	1.71	0.01	1.97
	CEDS_T2.3_T3				1.69	1.65	0.04	0.001		1.69	1.69	0.01	1.98
	CEDS_T2.3_T3_jKET10x				1.69	1.66	0.03	0.001		1.69	1.69	0.01	1.66
	CAMS_T1.3_T3				0.71	0.69	0.02	0.001		0.71	0.71	0.00	2.36
	CAMS_T2.3_T3				0.69	0.67	0.02	0.001		0.69	0.69	0.00	2.39
HYDROXYKETONE	CEDS_T1.3_T3				25.09	20.82	0.98	3.28		25.09	25.07	0.02	0.27
	CEDS_T2.3_T3				22.86	18.98	0.94	2.91		22.86	22.84	0.02	0.26
	CEDS_T2.3_T3_jKET10x				22.88	19.10	0.92	2.84		22.88	22.86	0.02	0.25
	CAMS_T1.3_T3				23.10	19.00	0.89	3.19		23.10	23.08	0.02	0.27
	CAMS_T2.3_T3				20.85	17.15	0.86	2.82		20.85	20.83	0.02	0.27
C6KETOOH	CEDS_T1.3_T3				9.03	7.95	0.38	0.70		9.03	9.02	0.003	0.12
	CEDS_T2.3_T3				8.70	7.68	0.36	0.65		8.70	8.69	0.003	0.12
	CEDS_T2.3_T3_jKET10x				8.70	7.68	0.36	0.65		8.70	8.69	0.003	0.12
	CAMS_T1.3_T3				8.60	7.57	0.36	0.66		8.60	8.59	0.003	0.12
	CAMS_T2.3_T3				8.27	7.31	0.34	0.61		8.27	8.26	0.003	0.12
C6DIKETONE	CEDS_T1.3_T3			0.38	25.93	20.05	1.65	4.51	0.38	26.31	26.20	0.04	0.52
	CEDS_T2.3_T3			0.38	23.97	18.53	1.61	4.20	0.38	24.35	24.34	0.03	0.52
	CEDS_T2.3_T3_jKET10x			0.38	23.43	18.60	1.47	3.73	0.38	23.82	23.80	0.03	0.45
	CAMS_T1.3_T3			0.38	23.87	18.38	1.59	4.18	0.38	24.25	24.15	0.03	0.52
	CAMS_T2.3_T3			0.38	21.91	16.86	1.55	3.87	0.38	22.29	22.28	0.03	0.52

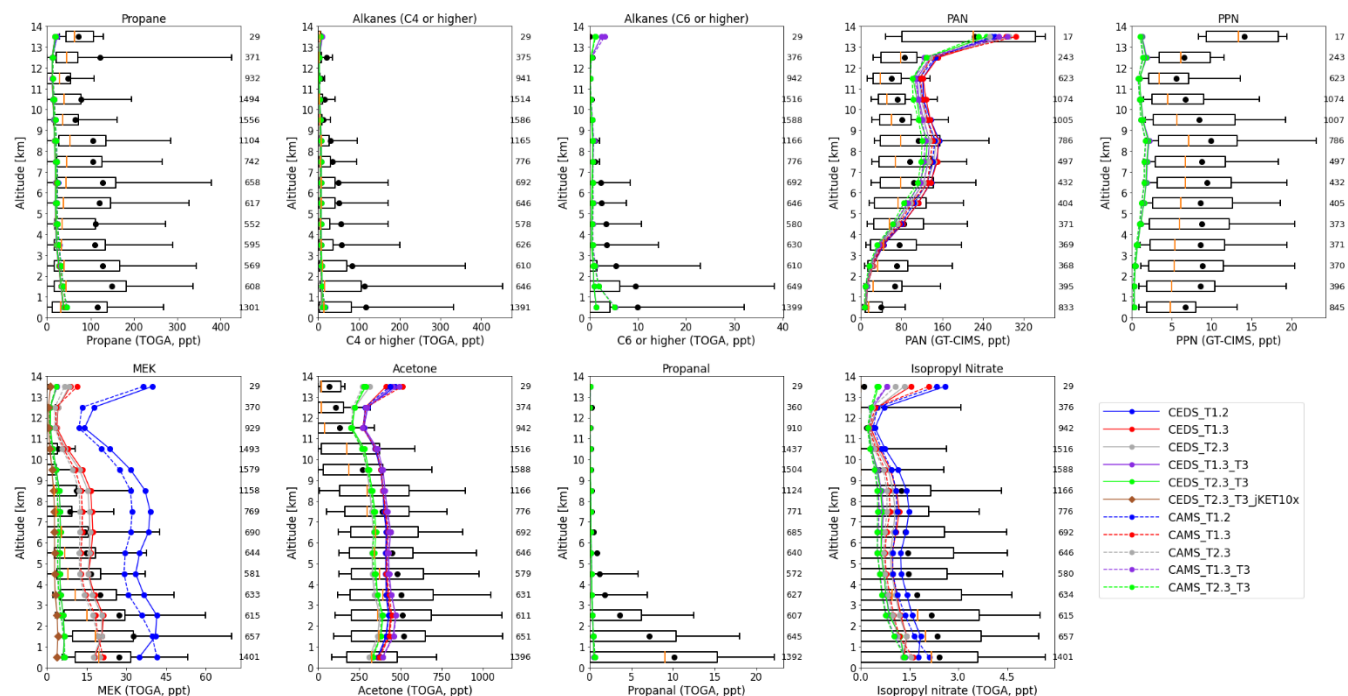


Figure 8. Vertical profiles of alkanes (propane, C4 or higher, C6 or higher), PANs (PAN, PPN), and OVOCs (MEK, acetone, propanal, isopropyl nitrate) compared with ATom observations. Box-and-whisker plots show the distribution of ATom measurements at each altitude bin, with the box representing the interquartile range, the orange line indicating the median, and whiskers extending to the 10th and 90th percentiles. Black dots represent the mean of observations. Model median values from different mechanism and emission inventory combinations are shown as colored lines and symbols. Numbers on the right y-axis indicate the number of observations in each altitude bin. Note that PPN and propanal are represented only in T3 mechanism, and the model results for isopropyl nitrate represent total lumped alkyl nitrates (ALKNIT) for approximate comparison with observations. Measurements below their detection limits are assigned a value of zero (Sect. 5), so lower whiskers extend to zero where the 10th percentile is zero and are not visible where both the 10th and 25th percentiles are zero.

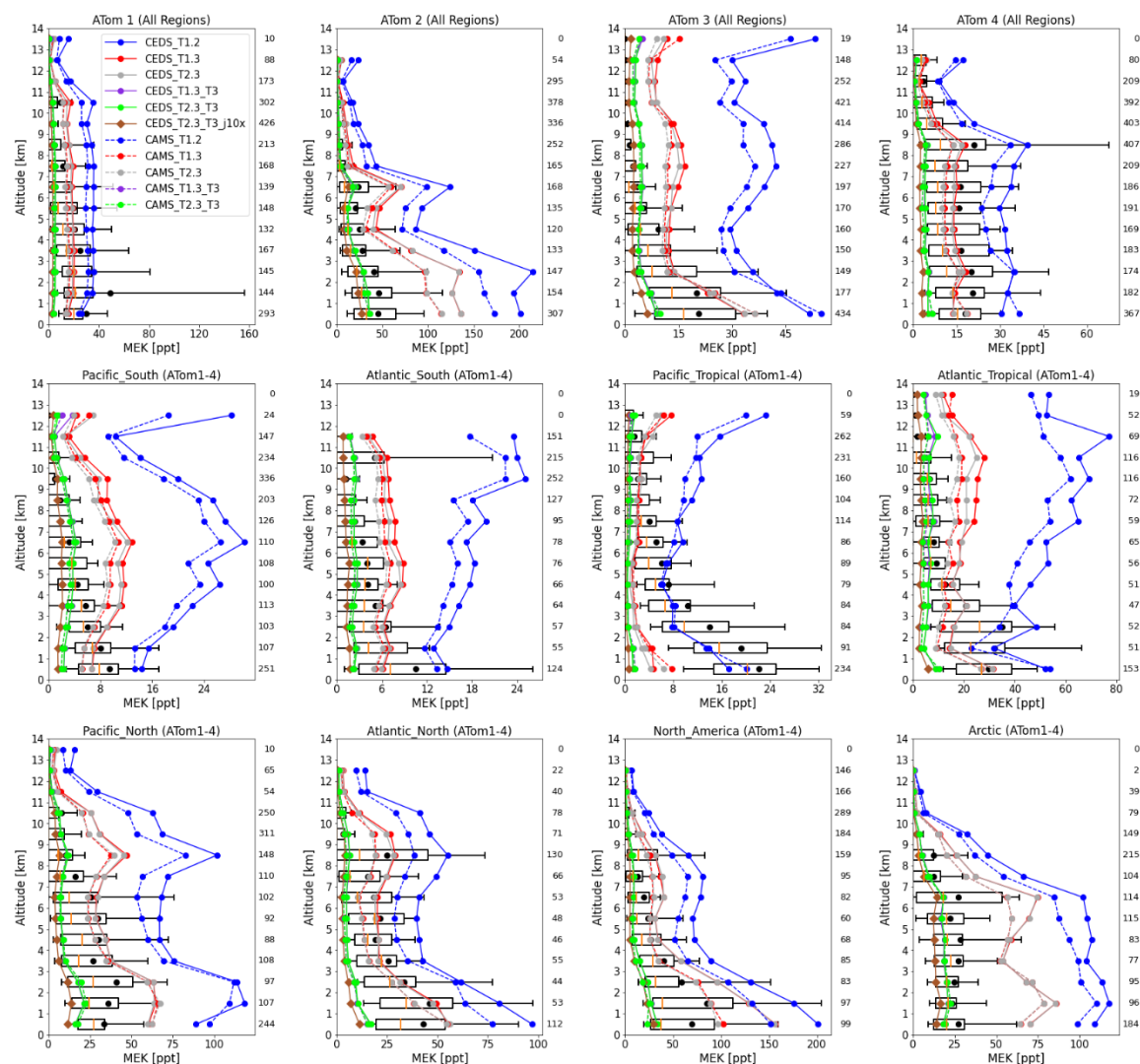


Figure S10. Vertical profiles of MEK for individual ATom campaigns (ATom-1 through ATom-4) and by region. Regional definitions are shown in Figure S11. Box-and-whisker plots show the distribution of ATom measurements at each altitude bin, with the box representing the interquartile range, the orange line indicating the median, and whiskers extending to the 10th and 90th percentiles. Black dots represent the mean of observations. Model median values from different mechanism and emission inventory combinations are shown as colored lines and symbols. Brown diamonds additionally show the ketone photolysis sensitivity simulation, CEDS_T2.3_T3_jKET10x (Table 1), abbreviated as CEDS_T2.3_T3_j10x in the legend for compactness. Numbers on the right y-axis indicate the number of observations in each altitude bin.

Minor and Technical Comments:

2.4) Figure 4: For the alkanes (Fig. 3), you show maps of the differences between mechanisms at the surface and at 500 hPa. These are helpful. The ketone section only has global totals and time series. Could you add the same kind of difference maps for the ketones, especially MEK? The mechanism differences are largest for MEK, and the change comes mostly from certain regions. A map would show where the MEK drop happens.

We thank the reviewer for this suggestion. We have added global maps of MEK to the main manuscript as Fig. 5 and acetone maps to the Supplement as Fig. S3. Both figures show mixing ratios and relative changes at the surface and 500 hPa, averaged over 2016–2018 using CEDS anthropogenic emissions. The maps distinguish the common updates from T1.2 to T1.3, the differences between T1.3 and T2.3, and the subsequent addition of T3 alkane chemistry.

For MEK, the T1.3 updates decrease mixing ratios over broad regions, whereas differences between T1.3 and T2.3 are relatively small. Adding T3 alkane chemistry to T1.3 produces a further widespread decrease, with larger percentage decreases at 500 hPa. At the surface, elevated MEK mixing ratios persist over tropical South America and Africa, where the relative reductions are smaller than over many remote regions.

Acetone shows a different response. The changes from T1.2 to T1.3 are relatively small, while the transition from T1.3 to T2.3 produces widespread decreases at both the surface and 500 hPa. Adding T3 alkane chemistry to T2.3 increases acetone mainly in the Northern Hemisphere. These maps complement the global budgets by showing where the mechanism-dependent changes occur. We have added descriptions of these spatial patterns to Sect. 4.3.

Lines 445-449

The spatial distributions of acetone and its relative changes between mechanisms are shown in Fig. S3 for simulations using CEDS anthropogenic emissions. The changes from T1.2 to T1.3 are

relatively small (Fig. S3b, d), while the transition from T1.3 to T2.3 produces widespread decreases at both the surface and 500 hPa (Fig. S3f, h). The relative reductions extend across remote ocean regions and are particularly evident at 500 hPa. Adding T3 alkane chemistry to T2.3 increases acetone mainly in the Northern Hemisphere (Fig. S3j, l).

Lines 459-464

The spatial patterns of the MEK changes are shown in Fig. 5 for simulations using CEDS anthropogenic emissions. The common updates from T1.2 to T1.3 decrease MEK mixing ratios over broad regions at both the surface and 500 hPa (Fig. 5b, d), whereas differences between T1.3 and T2.3 are comparatively small (Fig. 5f, h). Adding T3 alkane chemistry to T1.3 produces a further widespread decrease, with larger percentage decreases at 500 hPa (Fig. 5j, l). At the surface, elevated MEK mixing ratios persist over tropical South America and Africa, where the relative reductions are smaller than over many remote regions (Fig. 5i, j).

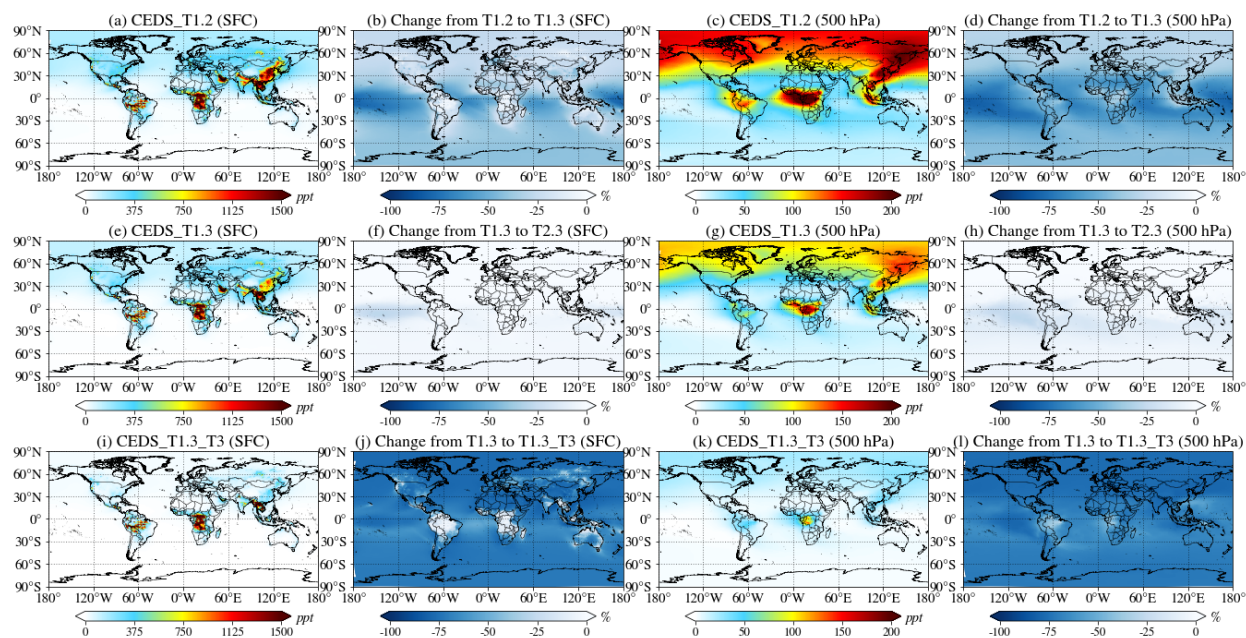


Figure 5. Global distributions of MEK mixing ratios and their relative changes between chemical mechanisms, averaged over 2016–2018 using CEDS anthropogenic emissions. Mixing ratios are shown for T1.2 (a, c), T1.3 (e, g), and T1.3_T3 (i, k) at the surface and 500 hPa. Relative changes show the effects of the common kinetic and photolysis updates from T1.2 to T1.3 (b, d), the transition from T1.3 to T2.3 (f, h), and the addition of T3 alkane chemistry to T1.3 (j, l). Percentage changes are calculated as $100 \times (\text{updated} - \text{reference})/\text{reference}$, where the reference is the first configuration named in each comparison. Note the different mixing-ratio color scales at the surface and 500 hPa.

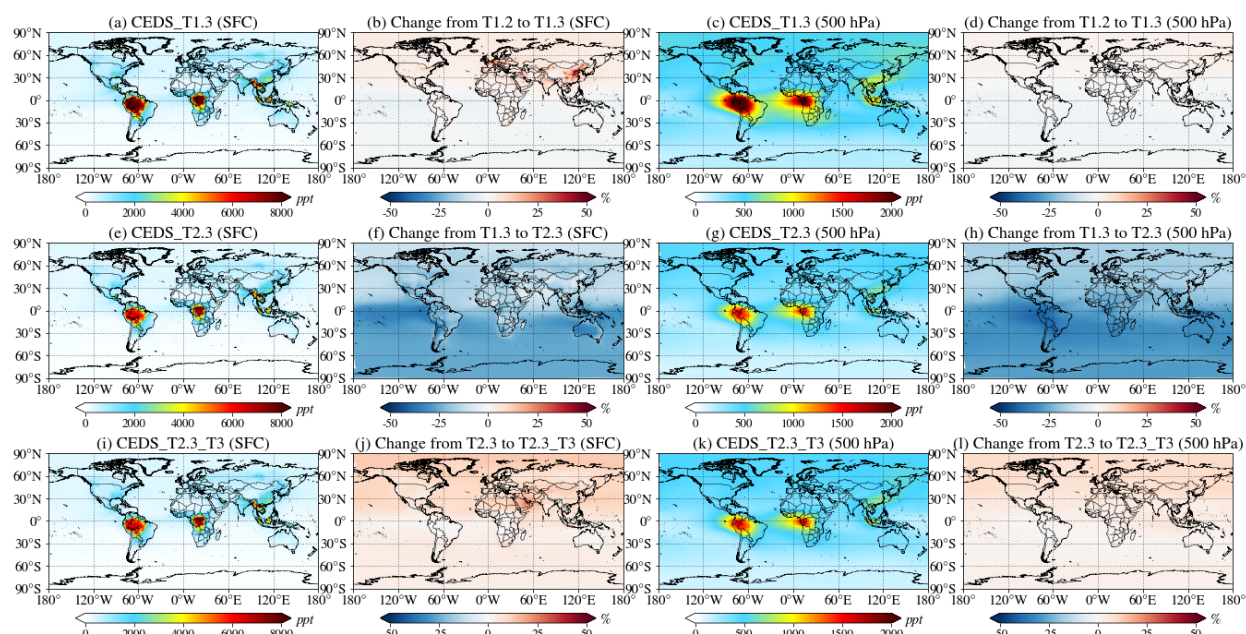


Figure S3. Global distributions of acetone mixing ratios and their relative changes between chemical mechanisms, averaged over 2016–2018 using CEDS anthropogenic emissions. Mixing ratios are shown for T1.3 (a, c), T2.3 (e, g), and T2.3_T3 (i, k) at the surface and 500 hPa. Relative changes show the effects of the common kinetic and photolysis updates from T1.2 to T1.3 (b, d), the transition from T1.3 to T2.3 (f, h), and the addition of T3 alkane chemistry to T2.3 (j, l). Percentage changes are calculated as $100 \times (\text{updated} - \text{reference})/\text{reference}$, where the reference is the first configuration named in each comparison. Note the different mixing-ratio color scales at the surface and 500 hPa.

2.5) Sect. 4.5 (p. 20, "NH"): Please write out "NH" (Northern Hemisphere) the first time it is used. It appears in the ALKNIT section without being defined.

We have defined "Northern Hemisphere (NH)" at its first occurrence in Sect. 4.3.

The relative reductions extend across remote ocean regions and are particularly evident at 500 hPa. Adding T3 alkane chemistry to T2.3 increases acetone mainly in the Northern Hemisphere (NH) (Fig. S3j, l).

2.6) Sect. 5 (p. 22, “meteorological fields”): The text says CAM-chem “reproduces the meteorological fields” during ATom. This is misleading. The winds and temperature are nudged to MERRA-2. So the meteorology is set by the nudging, not reproduced by the model. Please change this to talk about oxidants (OH, HO₂, O₃) instead of meteorology. Or, if you did compare the nudged meteorology to ATom, please show it.

We thank the reviewer for this suggestion. CAM-chem calculates meteorology using its own dynamics and physics, with horizontal winds and temperature nudged toward MERRA-2. We have now added a direct comparison of the simulated meteorological fields with ATom observations in Fig. S7.

Temperature and winds agree well with the observed vertical profiles, consistent with the nudging. Specific humidity and relative humidity, neither of which is nudged, capture the main vertical variations but show positive biases, with NMBs of 7.6–8.0% and 11.0–11.7%, respectively. The meteorological profiles are nearly identical across the simulations, suggesting that differences in meteorology are unlikely to explain the chemical differences among the mechanism and emission inventory configurations.

We have added this evaluation to Sect. 5 and revised the original statement to distinguish the meteorological comparison from the evaluation of chemical species.

Lines 609–614

We first compare the simulated meteorological fields with ATom observations (Fig. S7). Temperature and winds agree well with the observed vertical profiles, consistent with their nudging toward MERRA-2 (Sect. 3.1). Specific humidity and relative humidity, neither of which is nudged, capture the main vertical variations but show positive biases, with NMBs of 7.6–8.0% for specific humidity and 11.0–11.7% for relative humidity across the simulations. The meteorological profiles are nearly identical across the simulations, suggesting that differences in meteorology are unlikely to explain the chemical differences among the mechanism and emission inventory configurations.

Lines 615–617

We then evaluate the simulated distributions of major air pollutants and oxidants, including ozone, NO, NO₂, CO, OH, HO₂, formaldehyde, and acetaldehyde (Fig. S8). Overall, the model captures the broad features of the observed vertical distributions during ATom, although biases remain for individual species, as discussed below.

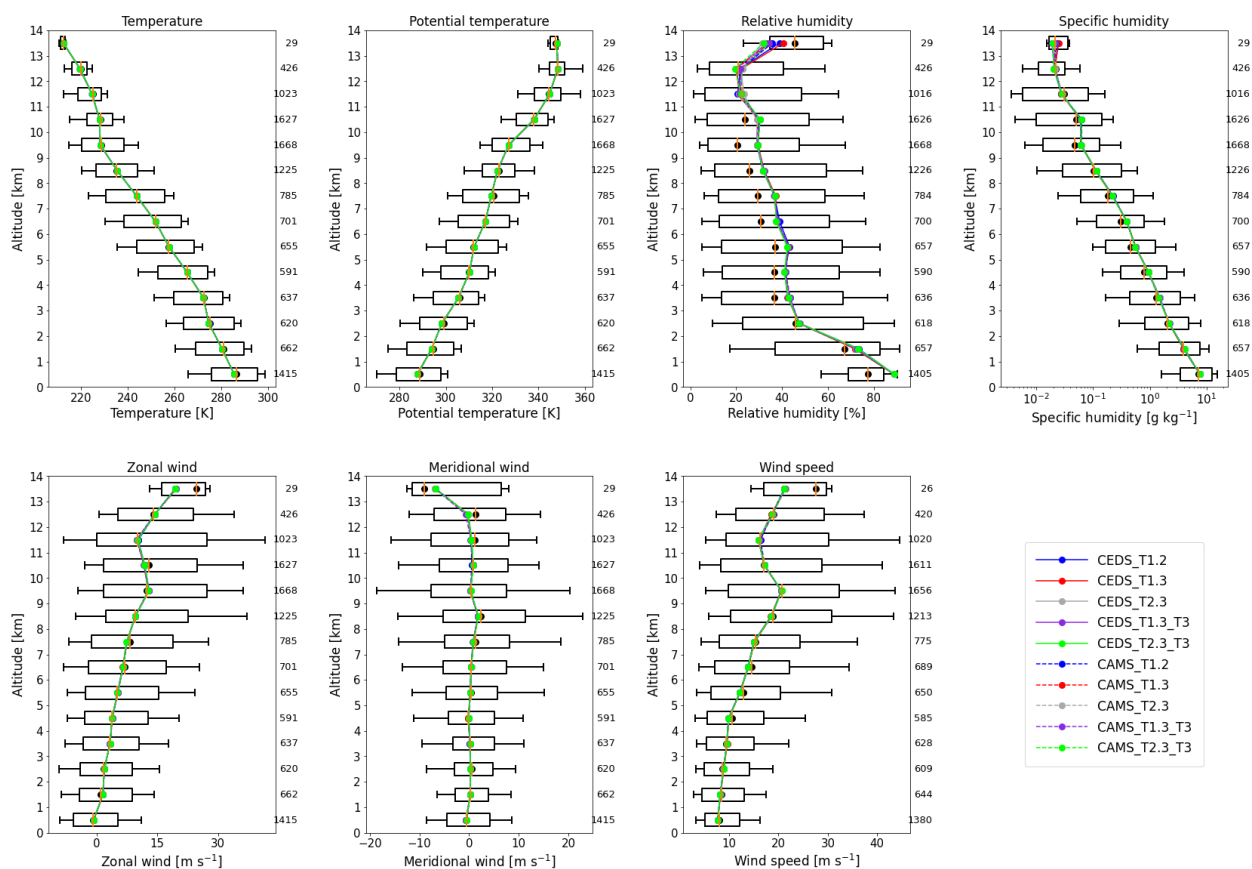


Figure S7. Vertical profiles of temperature, potential temperature, relative humidity, specific humidity, zonal wind, meridional wind, and wind speed for ATom-1 through ATom-4. Box-and-whisker plots show the distribution of ATom measurements in each altitude bin, with boxes representing the interquartile range, orange lines indicating the median, and whiskers extending to the 10th and 90th percentiles. Black dots represent observed means. Colored lines and symbols show model medians for the different chemical mechanism and emission inventory configurations, sampled at the aircraft locations and times. Numbers on the right-hand side of each panel indicate the number of observations in each altitude bin. Horizontal winds and temperature are nudged toward MERRA-2 (Sect. 3.1). Note the logarithmic scale for specific humidity.

2.7) Figure 7 (p. 25): Some panels have no lower whisker. Is this because the 10th percentile is zero, since below-detection-limit values are set to zero (Sect. 5)? If so, please say this in the caption. Otherwise it looks like a plotting error.

The lower whiskers are not visible in some altitude bins because measurements below their detection limits are assigned a value of zero, as described in Sect. 5. Where the 10th percentile is zero, the lower whisker extends to zero; where both the 10th and 25th percentiles are zero, the lower whisker collapses onto the lower edge of the box and is not visible. We have clarified this in Sect. 5 and in the caption of Fig. 8 (Fig. 7 in the submitted version).

Lines 604–605

As a result, lower whiskers in the concentration comparisons extend to zero where the 10th percentile is zero and are not visible where both the 10th and 25th percentiles are zero.

Addition to the caption of Fig. 8

Measurements below their detection limits are assigned a value of zero (Sect. 5), so lower whiskers extend to zero where the 10th percentile is zero and are not visible where both the 10th and 25th percentiles are zero.

2.8) Typographical: Table S7: “Taifei” → “Taipei.”). Figures 1 and 2 have almost the same caption. Please state clearly that Fig. 1 shows RO₂ + NO chemistry and Fig. 2 shows RO₂ + HO₂ chemistry, so the two are easier to tell apart.

We have corrected “Taifei” to “Taipei” in Table S8 (Table S7 in the submitted version). We have also revised the opening sentences of the captions of Figs. 1 and 2 to distinguish RO₂ + NO and RO₂ + HO₂ chemistry immediately. The Fig. 1 caption retains the clarification that the C6ALKANES pathway includes the complete oxidation scheme, covering RO₂ + NO, RO₂ + HO₂, and hydrogen shift reactions. The Fig. 2 caption refers readers to Fig. 1 for this scheme.

Figure 1. Simplified comparison of alkane oxidation schemes in MOZART-T1 versus MOZART-T3 mechanisms for RO₂ + NO chemistry. Branching ratios are shown where applicable. The C6ALKANES pathway illustrates the complete oxidation scheme, including RO₂ + NO, RO₂ + HO₂, and hydrogen shift reactions. MOZART-T2 chemistry is identical to T1 for alkanes.

Figure 2. Simplified comparison of alkane oxidation schemes in MOZART-T1 versus MOZART-T3 mechanisms for RO₂ + HO₂ chemistry. Branching ratios are shown where applicable. The C6ALKANES pathway is shown in Fig. 1. MOZART-T2 chemistry is identical to T1 for alkanes.

2.9) Table S1 (IC₃H₇O₂ + CH₃O₂ rate): The rate for IC₃H₇O₂ + CH₃O₂ is written as "100E-13 exp(-293/T)". This looks like a typo. The n-propyl version (NC₃H₇O₂ + CH₃O₂) is "1.00E-13 exp(+557/T)". Please check the number (100E-13 = 1.0×10⁻¹¹, about 100 times faster) and the sign in the exponent.

We thank the reviewer for identifying the typographical error in the prefactor, which we have corrected from "100E-13" to "1.00E-13" in Table S1. On checking this entry against the model mechanism file, we also found and corrected an error in the listed products. The correct products and rate expression were used in all simulations; these errors were confined to the table and did not affect the simulation results.

The signs in the exponents are both correct. Following Eq. (22) of Jenkin et al. (2019), the 298 K rate coefficient is calculated as twice the geometric mean of the self-reaction rate coefficients of IC₃H₇O₂ (1.0 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹) and CH₃O₂ (3.5 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹), giving k(298 K) = 3.74 × 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹. Applying Eq. (24) of Jenkin et al. (2019), with a prefactor of 1.00 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹, gives E/R = +293 K and hence exp(-293/T). The same procedure for NC₃H₇O₂, whose self-reaction rate coefficient at 298 K is 3.0 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹, gives k(298 K) = 6.48 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ and exp(+557/T). The opposite signs therefore follow from the different self-reaction rate coefficients of the two isomers when applying this parameterization.

Corrected entry in Table S1

IC₃H₇O₂ + CH₃O₂ → 0.80 CH₂O + 0.80 CH₃COCH₃ + 0.20 IPROPANOL + 1.20 HO₂ + 0.20 CH₃OH

Rate coefficient: 1.00E-13 exp(-293/T)

2.10) Table S4 (pentane $\Delta H/R$): IPENTANE uses $\Delta H/R = 6014$ K (the default value), while NPENTANE uses 3400 K. The two isomers have almost the same volatility, so this is inconsistent. Please explain the difference.

We thank the reviewer for pointing out this inconsistency. When the simulations were originally configured, the temperature-dependence parameter for isopentane was not available in the compilation of Sander (2015), so the model default of 6014 K was used. The updated compilation of Sander (2023) includes a value of 3000 K from Plyasunov and Shock (2000). We have replaced the default with this value in the model, updated Table S4 and its reference, and added Sander (2023) to the corresponding discussion in the main text.

We reran the four T3 simulations that were affected, which are the previously completed simulations containing explicit IPENTANE, and updated the corresponding results throughout the manuscript and Supplement. The additional ketone photolysis sensitivity simulation was performed after this correction and already used the updated value.

Across the four paired simulations, the correction reduces IPENTANE wet deposition by 43.7–48.3%. However, wet deposition accounted for only about 1×10^{-7} of the total IPENTANE sink in the original simulations, indicating a negligible direct effect through this removal pathway. Comparing the original and revised simulations, IPENTANE burden and lifetime differ by at most 0.014%, and total diagnosed IPENTANE loss differs by at most 0.0006%. These small differences do not affect the conclusions concerning the IPENTANE and overall C5 budgets.

Lines 286–287

For species not covered by JPL19, we adopt values from the comprehensive compilations by Sander (2015, 2023).

Updated entry in Table S4

IPENTANE temperature-dependence parameter: 3000 K.

Reference: Sander (2023), based on Plyasunov and Shock (2000).

2.11) Table S2 (diketone/hydroxyketone photolysis): C6DIKETONE photolysis is set to 10× acetone, and HYDROXYKETONE to 5× acetone. These are large factors, and they mostly set the very short lifetimes of these species (Table S10). Please add a short reason or reference, since these species are not otherwise checked.

We thank the reviewer for requesting clarification. HYDROXYKETONE is assigned the same photolysis rate as MEK, which is five times that of acetone in our mechanism, as discussed in Sect. 2.8. For C6DIKETONE, represented by 2,5-hexanedione, we apply an additional factor of two to account for its two carbonyl groups, giving a rate ten times that of acetone. This treatment is consistent with MCM v3.3.1, which assigns $J_{<22>}$ to 2-hexanone (HEX2ONE) and $2 \times J_{<22>}$ to 2,5-hexanedione (CO25C6), where $J_{<22>}$ is the MEK photolysis rate.

We have clarified this rationale in Sect. 2.7 and added a note to Table S2. The sensitivity simulation described in our response to Comment 2.3 also doubles these rates, increasing the scaling relative to acetone from five to ten for HYDROXYKETONE and from ten to twenty for C6DIKETONE.

Lines 244–248 (Sect. 2.7, replacing the final sentence)

For $\geq C_5$ ketones, including HYDROXYKETONE, we use the MEK photolysis rate, set to five times that of acetone (Sect. 2.8). For C6DIKETONE, represented by 2,5-hexanedione, we assume additive contributions from its two carbonyl groups and use twice the MEK photolysis rate, or ten times that of acetone. This treatment is consistent with MCM v3.3.1, which assigns $J_{<22>}$ to 2-hexanone and $2 \times J_{<22>}$ to 2,5-hexanedione, with $J_{<22>}$ representing MEK photolysis.

Footnote added to Table S2

^aHYDROXYKETONE uses the MEK photolysis rate, equal to five times that of acetone. C6DIKETONE uses twice this rate to account for its two carbonyl groups, consistent with the treatment of 2,5-hexanedione in MCM v3.3.1 (Sect. 2.7).