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GECKO-A v1.0: Exploring VOC Oxidation Trajectories Through Comparison with the Master Chemical Mechanism

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Response to reviewers

Line and section numbers given in the responses refer to the original preprint. Manuscript changes are quoted as they appear in the revised manuscript.

Response to Reviewer 1 (William Carter)

Reviewer Comment 1 (RC1): *This paper is describes the first open-source release of the GECKO-A mechanism generation system and illustrates its capabilities by comparing its predictions for several representative compounds against those of the current version of the often-used Master Chemical Mechanism (MCM). This is classified as a model description paper, but actually does not do a very good job in this regard, for reasons discussed below. Its main contribution to the literature is that it shows that mechanisms must adequately represent multi-generation chemistry (i.e., reactions of products of products of products, etc.) in order to predict formation of organic aerosol (SOA) and water-soluble organic products. GECKO-A is capable of generating detailed mechanisms representing all generations of reactions leading to CO2 or nonvolatile products, while the MCM, though almost as detailed in its representation of first and second generation chemistry, only approximates the chemistry after the first two generations. This work shows that this causes gross underpredictions of SOA and soluble products, as well as affecting predictions of distributions of types of organic products formed.*

Authors' Answer (AA): We thank the reviewer for this summary opening the review. The reviewer's appreciation for the paper's main contribution is addressed in our response to RC2. The reviewer's concern that the paper falls short as a model description paper is developed in our responses to RC4 and RC5. The most significant omission raised on this point is the absence of results showing the effect of reduction parameters on the simulated trajectories. This omission is addressed in RC25.

RC2: *This demonstration of the unsuitability of mechanisms that do not treat 3+ generation reactions adequately for predicting SOA or condensable products is important and needs to be published. This inadequate treatment of multi-generation chemistry is not unique to MCM; it is a characteristic of every mechanism, however detailed, that is used in current atmospheric models that attempt to simulate realistic atmospheric mixtures. Although multi-generation mechanisms such as those derived using GECKO-A are much too large for practical atmospheric modeling applications, they are essential for evaluating the predictive capability of mechanisms used in such models, and for eventually developing more predictive mechanisms of a more practical size. This paper is important in clearly demonstrating the need for this work.*

AA: We appreciate the reviewer's positive note regarding the important contribution of this study to examining the role of multigenerational chemistry in the production of SOA and water-soluble species. Moreover, the development of explicit mechanisms is an area of shared interest for both the reviewer and the authors. This includes their use for evaluating the predictive capability of the simplified mechanisms used in air quality and climate models, as well as their use for guiding the development of such simplified mechanisms.

The main objective at the core of this paper, however, is to present the first open-source version of GECKO-A (v1.0) and to illustrate its capabilities through the exploration of oxidation trajectories for a

set of representative hydrocarbons. The comparison with the MCM is not intended to evaluate this specific mechanism, but rather to position GECKO-A relative to this recognized reference mechanism, widely used by the community. This objective is explicitly stated and reiterated several times throughout the manuscript (for example, lines 74–78, 367–370, 1057–1060). It is also reflected in the choice of the paper's title, which presents the comparison as a means rather than an end in itself. We return to the specific methodological aspects in our responses to RC5.

RC3: *GECKO-A is not a new model; its development and use was first published in 2005, and has been used in a number of published studies since then. Other than some updates to the chemistry and types of compounds that can be handled, it is unclear how its capabilities and scientific utility now is much different from the version described 20 years ago. However, the fact that it is now archived and is open source with presumably improved and more modular software will make this important model more sustainable for the future, and describing its capabilities in model description paper in GMD is entirely appropriate.*

AA: We thank the reviewer for this comment. His acknowledgment that archiving GECKO-A as sustainable open-source software constitutes a useful contribution, well suited to a model description paper published in GMD, is greatly appreciated.

The automatic generation of mechanisms from a prescribed chemical protocol has remained the founding principle of GECKO-A since 2005. This protocol has undergone substantial revision over the past twenty years. We would like to clarify, however, that the changes made since the original 2005 version go beyond incremental updates to the chemistry. The initial version was limited exclusively to the gas-phase chemistry of simple acyclic compounds (C<8). The current version extends the protocol to complex cyclic structures, including terpenes and aromatics (lines 106–124), and adds gas-particle and gas-wall partitioning (lines 82–86; detailed in Sect. 3.1). These developments considerably broaden the scope of application.

Code modernization is also an important point. Moving from Fortran 77 to a modular Fortran 90 codebase (line 68), testing across multiple compilers (line 71), and parallelizing the box model (lines 341–348) represent a substantial advance. This modernization enables the generation and integration of very large mechanisms, comprising several millions of species. These advances translate into concrete gains in computational efficiency: generating a mechanism of about 3 million species takes on the order of 500 minutes (Fig. 1d). In addition, parallelization of the companion box model provides a substantial speed-up (Fig. 2). For example, for the 5-day α-pinene simulation used in this study (2.7×10^6 species, 6.7×10^6 reactions), the simulation completes in about 200–300 minutes on 12 cores. This modernization also results in a more structured codebase. The modernized code significantly improves the sustainability of GECKO-A, making it easier for the community to use and contribute to, since it relies on widely available tools and formats, including Fortran, NetCDF output, and Git for version control.

The aim of this paper is precisely to bring these advances together into a citable, versioned release (v1.0), and to illustrate its capabilities through the exploration of oxidation trajectories for a representative set of hydrocarbons.

RC4: *Unfortunately, this manuscript has several deficiencies as a model description paper. It gives only a brief description of how GECKO-A operates and what it does, though it is probably sufficient because these have been well described in the literature already. It does describe the various user-configurable parameters that control the necessary reductions that affect the size of the mechanisms produced, but does not give enough examples of how the parameters affect the output other than the size of the mechanisms produced. Knowledge of the effects of these parameters on model predictions is necessary*

for users of the model to understand effects of the approximations each represent, and which parameter choices are appropriate for their applications. In addition, although the paper provides links where one can obtain the software, and there are links to run a limited version of the model online, there are no users manuals or instructions on how to install and use the software that can be found in this manuscript or any of its citations. Although the comparisons with MCM, which take up the bulk of the paper, are characterized as an evaluation of GECKO-A, in fact this is more of an evaluation of MCM.

AA: We agree with the reviewer that the description of GECKO-A provided is sufficient given the existing literature. The other points raised here are each taken up again later in the review: examples of parameter effects in RC25, installation and user-manual instructions in RC10 and RC18, and the MCM comparison in RC5 and RC20.

RC5: *It is up to the editors of GMD to decide whether this manuscript can be accepted in this form as a model description paper. If I were in their position, I would require at least a link to obtain instructions for use and installation, and much more information on how varying the parameters on affect model predictions. Failing that, this could be recast as an evaluation of MCM, and essentially all the results of the comparison be published in an appropriate journal on that basis. This would certainly be publishable and a substantial contribution to modeling science.*

AA: For model description papers, GMD guidelines state: "*Examples of model output should be provided, with evaluation against standard benchmarks, observations, and/or other model output included as appropriate. [...] Sufficient verification and evaluation must be included to show that the model is fit for purpose and works as expected.*" A comparison against another mechanism's output, used as a benchmark, is part of what GMD expects from a model description paper. It is not a departure from the category.

Concerning splitting the manuscript into two papers, as discussed above and in our response to RC2, the comparisons with the MCM are not intended as an “evaluation” of this specific mechanism, but rather to position GECKO-A relative to this recognized reference benchmark mechanism, which is in line with GMD guidelines. If we were to develop a stand-alone "model evaluation paper", GMD guidelines require that "*the model, model development, or model experiment has already been described in another paper.*" A stand-alone evaluation using GECKO-A mechanisms would therefore still need this description paper to exist first. Splitting the manuscript would not remove the need for it. It would only add a second paper downstream.

We think part of the confusion may come from the Results section itself. Every figure shows GECKO-A and MCM modeling results side by side, which can give the impression that the comparisons are the major outcomes of this work. However, each figure also documents the oxidative trajectory GECKO-A simulates for the parent hydrocarbon: carbon budget, volatility distribution, functionalization, OH reactivity, and so on. This is consistent with what GMD asks for from a model description paper: output from the model, evaluated against a benchmark. The comparison with MCM is the tool we use to present GECKO-A's output, not the end goal of the paper. We revise the section title to make this clearer (see Manuscript change below).

How the comparisons are designed is also relevant to this point. Comparing how two mechanisms treat organic chemistry is not straightforward, because organic chemistry feeds back on oxidant levels, which in turn affect the organic chemistry itself. To isolate the organic chemistry from this feedback, all simulations use a common, buffered chemical background (lines 442-484): fixed steady-state levels of NOx, O_3, and other species, held identical across GECKO-A and MCM runs through a shared inorganic mechanism and proxy species regulating Ox/NOx/HOx chemistry. Differences in the simulated

trajectories therefore come only from the organic chemistry itself. As stated in the manuscript, "*any differences observed between MCM and GECKO-A in mass balances stem solely from the oxidative pathways described by each mechanism, without feedback loops caused by changes in the simulated scenarios*" (lines 481-483). Several dedicated metrics were built around this buffered protocol: a normalized OH reactivity index (IOHR, line 641), a carbon-normalized Ox yield (YOx, line 750), a carbon-integrated abundance metric to rank species across mechanisms (CIA, line 810), a degree of functionalization (d_f, line 602), and a volatility-solubility framework for multiphase partitioning (Sect. 5.10). To our knowledge, this combination, a buffered comparison protocol paired with metrics spanning gas- and particle-phase organic composition, has not been used before to compare chemical mechanisms. This fits what GMD defines separately as "Methods for assessment of models": "*work on developing new metrics for assessing model performance*". We do not believe that this means the paper belongs in that category instead. GMD explicitly allows the overlap: papers built around this kind of methodology "*may be submitted as either methods for model assessment or model description papers.*" We note it here as an additional methodological contribution to the manuscript, alongside the description of GECKO-A itself.

We agree with the request for installation and user-manual instructions, and address it in RC10. We partly agree with the request for a parameter sensitivity analysis, and address it in RC25.

Manuscript change: Section 5 title revised from "Results" to "GECKO-A oxidative trajectories, benchmarked against MCM." A sentence is added at the start of Sect. 5: "Each result presented below illustrates the oxidative trajectory simulated by GECKO-A for a given hydrocarbon and scenario, with the MCM used throughout as a benchmark to assess this trajectory against an established reference mechanism."

RC6: *If changes are made to make this more suitable as a model description paper, my suggestion is that the MCM comparisons, which certainly stand alone, be made a separate paper, with the comparisons in the model description paper be restricted to comparing MCM with GECKO-A mechanisms restricted to the two generations of chemistry that the MCM is designed to represent (i.e., using "maxgen"=2). Otherwise, this is not really a fair comparison, and the multi-generation effects, which can be investigated more cleanly by comparing GECKO-A predictions with different generation limitations, dominate the results. Showing the effects of varying generation limitations and other user-modifiable parameters, with all else held the same, should be a part of the model description paper. The second paper, or the second part of a two-part paper, can then use the more comprehensive comparison with MCM to emphasize the importance of representing multi-generation effects in atmospheric models, and its implications for development of mechanisms in models in general.*
Given below is a discussion of various parts of the manuscript, with more detail given concerning some of my concerns, and some recommendations for improvements that the authors should consider.

AA: This comment raises several points. We answer each of them briefly here. Each answer points to the more detailed response elsewhere in this reply.

We do not adopt the split of this paper into two separate publications. This point is developed above, in our response to RC5.

We also do not restrict the main comparison to GECKO-A mechanisms limited to two generations (maxgen=2). This approach raises several methodological issues, developed in our responses to RC22 and RC23.

MCM serves as a benchmark in the comparison between GECKO-A and MCM, not as the mechanism under evaluation, as further discussed in responses to RC2 and RC5. This framework is detailed further in our response to RC20.

We agree with the reviewer on the need to show the effect of reduction parameters on the simulated trajectories, beyond their effect on mechanism size alone. A second mechanism, red-GECKO-A, is generated at lower chemical resolution. It is compared to GECKO-A in a new section of the manuscript. This point is developed in our response to RC25.

RC: ***Title, Abstract, and Introduction***

RC7: *I'm not sure that the title is optimum for this manuscript as written, though if it were split into two papers, or the model description aspects were de-emphasized and this submitted to another journal as an MCM comparison, then the title would change anyway. My comments below are based on assuming that the overall structure of the paper is retained.*

AA: As explained in our response to RC2 and RC5, we keep the paper's structure as a single paper, with the MCM used as a benchmark to position GECKO-A relative to an established reference mechanism. Under this structure, we think the title fits appropriately. GMD's own editorial policy requires a model name and version number in the title of a model description paper. "GECKO-A v1.0" leads the title for this reason. The rest, "Exploring VOC Oxidation Trajectories Through Comparison with the Master Chemical Mechanism," names GECKO-A's oxidation trajectories as the subject and the comparison with MCM as the method, consistent with the point made in our response to RC2.

RC8: *The abstract states that GECKO-A's performance is being evaluated against MCM, but the results and discussion sections are more like an evaluation of MCM. The abstract needs to state that the results indicate the importance of representing multi-generation reaction in predicting SOA and water solubility. This is a major result of this work, which dominated much of the discussion of results in the existing manuscript.*

AA: Concerning the first point, see our response to RC2 and RC5.

As for the abstract itself, we agree that it could better reflect this outcome. We add a sentence that explicitly mentions the importance of describing multigenerational oxidation to account for the production of water-soluble species.

Manuscript change: The abstract (lines 28-30) is extended as follows:
"[...] resulting in notable discrepancies in the predicted volatility of secondary organic carbon and, consequently, in secondary organic aerosol yields. These discrepancies stem from how each mechanism treats multigenerational oxidation. The two approaches remain similar for early-generation products, but diverge as later generations become predominant. This divergence also extends to the water solubility of secondary organic carbon, and to its partitioning into aqueous condensed phases."

RC9: *The introduction should have more discussion of history of GECKO-A-A since first publication in 2005 and give a timeline of major changes in types of compounds covered, chemical estimation methods (e.g. SARs), algorithms, and software. It would be useful for the introduction to include a summary of the major publications using results using GECKO-A, and indicate changes that have made since then and whether they may have affected results.*

AA: This is a reasonable suggestion, but we do not think it fits the scope of this paper. The intent here is to present what the v1.0 release contains and what it can do, not to trace its 20-year history. The manuscript is already substantial, and a proper historical account, with context for each change and its likely impact on past results, would be closer to a review article than to a model description paper.

That said, most of the elements the reviewer asks for are already in the text, distributed rather than presented as a single timeline. The introduction (lines 65-67) already traces the model's evolution: from small aliphatic and acyclic hydrocarbons to phase partitioning, mechanism reduction, and additional compound families. Section 2.1 (lines 107-108) dates these extensions through citations: cyclic species (Valorso et al., 2011) and monocyclic aromatics (Jenkin et al., 2018b). Lines 115-124 do the same for the SARs, with a dated reference for each family of reactions currently implemented. We add citations directly to the introduction's existing sentence, so this chronology is visible from the first mention (see Manuscript change below), without duplicating what is already detailed in Sect. 2.1.

On a summary of major publications using GECKO-A: lines 335-337 already list examples of box model applications, chamber studies and simulations of complex VOC mixtures in various environments. We recognize this list is not exhaustive, but do not think a fuller summary belongs in the introduction, for the same reason as above: with 20 years of use, this would require picking which studies to include and contextualizing each one, which is a different paper.

Manuscript change: Lines 65-67 revised to: "Initially designed to simulate the gas-phase oxidation of small (C<8) aliphatic and acyclic hydrocarbons (Aumont et al., 2005), GECKO-A has progressively evolved to include phase partitioning processes, mechanism reduction strategies, especially to deal with VOCs having a large carbon backbone, and the treatment of additional families of compounds such as monoterpenes and monocyclic aromatics (Valorso et al., 2011; Jenkin et al., 2018b). A chronology of updates to the structure-activity relationships (SARs) used in GECKO-A is given in Sect. 2.1."

RC: ***Model Description***

RC10: *As indicated above, there needs to be a user manual or at least information about user and installation instructions can be obtained. This information could be included in the SI.*

AA: Making this kind of documentation available and easy to find matters to us as much as it does to the reviewer, given the purpose of this release. User and installation instructions are provided in a wiki attached to the GitLab repository distributing the code, which is where a user would naturally look for them.

For context, the manuscript already points to this documentation in several places. Section 2.4 states that the GECKO-A GitLab repository comes "*together with a wiki for technical documentation*" (line 246). Section 3.3 states that the box model's GitLab repository includes "*a dedicated wiki for user guidance*" (lines 354-355), and points to a Python script for output post-processing hosted and documented there (lines 362-364). The Code availability section states that "*dedicated wiki pages provide technical documentation and usage instructions*" (line 1119). The wiki documentation for both GECKO-A and the box model is also explicitly linked in README files in both repositories.

That said, we recognize a live wiki does not fully meet what GMD expects here. It evolves over time and is not tied to the specific code version archived and described in this paper. We therefore archive a snapshot of the current wiki content, corresponding specifically to GECKO-A v1.0.

Manuscript change: The Code availability and Data availability sections are revised as follows.

Code availability: "The source codes of GECKO-A v1.0 and its companion box model v1.0 are permanently archived on Zenodo at https://doi.org/10.5281/zenodo.15309905 (Aumont et al., 2025a) and https://doi.org/10.5281/zenodo.15310153 (Aumont et al., 2025b), respectively. Both codes are also publicly available on GitLab (https://gitlab.in2p3.fr/ipsl/lisa/geckoa/public). Dedicated wiki pages there provide technical documentation and usage instructions. A frozen snapshot of this documentation, corresponding specifically to GECKO-A v1.0 and its box model, is included in the archive referenced in the Data availability section."
Data availability: "The data supporting this study are permanently archived on Zenodo: https://doi.org/10.5281/zenodo.23034925, 2026 (Aumont et al., 2026). This archive includes the chemical mechanisms generated with GECKO-A v1.0 for this study, using both the GECKO-A and red-GECKO-A parameter sets (Table 1). It also includes the MCM v3.3.1 mechanism reformatted to comply with the file standards adopted by the GECKO-A tools, and all model outputs in NetCDF format. Finally, it includes a frozen snapshot of the user documentation of GECKO-A v1.0 and its box model."
In addition, references to the user documentation in Sect. 2.1, 2.4 and 3.3 now point to this archived snapshot (Aumont et al., 2026).

RC11: *The manuscript has a relatively large section describing the box model that can be used to carry out simulations using the large mechanisms that are generated. This is useful for those who may consider using the box model and is needed so results presented concerning phase changes can be duplicated, but is not central to the scientific issues being studied, and I wonder if much of the detail here could be moved to the SI.*

AA: Any mechanism needs to be integrated to produce results, and that is what Sect. 3 describes. The box model is introduced as GECKO-A's "companion" tool from the start of the paper (lines 63-64, 74), not as a secondary add-on. A description of the tool's capabilities is not complete without it.

We also note that Sect. 3.1 includes formalism, such as gas-wall partitioning, that is not used in the results presented here (see our response to RC5, and to comment 5 from the second reviewer, on the same topic). This is consistent with the section's purpose: describing what the box model tool can do, not only what this particular study uses.

RC: ***Mechanism Construction***

RC12: *It might be appropriate to more information about the sources of manually assigned rate constants and mechanisms in GECKO-A as well as the SARs used in the estimates. There is some short discussion of this, but is restricted to summarizing the major SARs, but not all of the types of reactions that are considered where SARs are not employed.*

AA: We agree. Indeed, the paper lists the SARs used (lines 115-125) but does not specifically state where to find the rate constants taken directly from experimental data. We add a short clarification on this point. However, we do not think it is necessary to include the complete list of these data in the SI. They are directly available in GECKO-A as simple, human-readable ASCII files. These files are organized one per reaction type, and their names are self-explanatory. The full set of files is available in the DATA directory of the archived GECKO-A v1.0 repository (see Code availability, line 1115).

Manuscript change: We add the following sentences after line 103, just before Sect. 2.1:
"Similarly, whenever experimental kinetic or product data are available for larger organic species, they are given priority over SAR-based estimates during mechanism generation. These data are compiled in dedicated files within the DATA directory of the distributed version, organized by reaction type (e.g.,

VOC+OH, VOC+NO3, …). As for the C1 and inorganic chemistry files described above, each of these files also includes the corresponding literature references."

RC13: *The mechanism construction section should also give a reference documenting the current inorganic and C1 mechanism used by GECKO-A (and for MCM in the comparisons). The reference should include a complete listing of the mechanism so people can duplicate the results presented here and if it is not available in a published paper it should be in the SI.*

AA: We agree. Moreover, reproducibility is a GMD requirement. This is already the case here. All chemical mechanisms generated with GECKO-A v1.0 for this study, including the inorganic and C_1 chemistry, are archived on Zenodo, together with the reformatted MCM mechanism and all model outputs (Data availability, line 1121). More specifically, the origin of the predefined chemistry for inorganic and C_1 species is documented in two dedicated files (mch_inorg.dat and mch_singlec.dat) located in the DATA directory of the GECKO-A v1.0 repository. This point is already mentioned at lines 97–99. All the information needed to reproduce the simulations presented here should therefore already be available.

RC: ***Mechanism Configuration***

RC14: *Table 1 is an important summary of parameters controlling use of GECKO-A that needs to be understood by users of the model and also by readers to interpret some of the results discussed in this paper. Even though they are discussed in the text, the table should include a few words to briefly indicate what each is for so it can serve as convenient reference for the reader or user. It would also be helpful if they were listed in the same order as discussed in the text (or vise-versa).*

AA: We thank the reviewer for this practical suggestion. We agree and will revise Table 1 accordingly.

Manuscript change: Table 1 will be reordered to follow the sequence used in Sect. 2.2, and a short description column will be added for each parameter, as follows:

- maxgen: Maximum number of oxidation generations
- critvp: p_{sat} cutoff ($\log_{10}$ atm) for gas-phase reactivity
- TK: Reference temperature (K)
- brcut: Minimum branching ratio to retain a product
- rxloss: Minimum yield to assign explicit products
- yldcut: Minimum branching ratio × yield to retain a reaction
- isomerfg: Enable surrogate (isomer) lumping
- highnoxfg: Restrict RO2 reactions to RO2+NO only
- rx_ro2_multiclass: RO2+RO2 treated as 9 vs. 1 classes
- g2pfg: Enable gas–particle mass transfer
- g2wfg: Enable gas–wall mass transfer

A footnote also indicates the namelist section in which each parameter is set.

RC15: *This section, or the SI, should clarify about how Ymax is calculated when yields of intermediates leading to the subject product are affected by bimolecular reactions of the intermediates (e.g., peroxy + NO, HO2, RO2), whose relative importance depends on atmospheric conditions. Are the competing bimolecular reactions all assumed to be equally important for calculation of Ymax? I presume that the parameters "highnoxfg" and "rx_ro2_multiclass") are relevant to this. If so, they should be discussed at the same time Ymax is first discussed. If not, the discussions of all these parameters need to be clarified. If extensive discussions are required to clarify this, it could be given in the SI.*

AA: Y_{max} is computed during mechanism generation, independently of atmospheric conditions. This choice reflects a design principle of GECKO-A: mechanisms are intended to be generated once and applied across a wide range of conditions, rather than tailored to a specific environment. Y_{max} does not represent the true, environment-dependent yield, which can only be assessed once the mechanism is resolved in the box model under a specific scenario. Y_{max} is instead propagated along the mechanism as the branching ratio (or product stoichiometric coefficient) of each reaction channel, multiplied by the Y_{max} of the parent species. When a species can be formed through several pathways, the highest contribution is retained.

The competing bimolecular reactions of peroxy radicals are not all assumed to be equally important. RO_2+NO and RO_2+HO_2 are significant pathways under most atmospheric conditions. Reactions with NO and HO_2 are therefore each assigned the full branching ratio of the parent species (100%). On the other hand, RO_2+RO_2 reactions are significant only under specific conditions, such as very low NOx levels. Reactions with other RO_2 are thus assigned a fixed *a priori* fraction of that branching ratio (2%). Treating all these pathways as equally important would make species formed only through RO_2+RO_2 reactions look as significant as those formed under most conditions. This matters for two reasons. First, Y_{max} is used to select surrogate species during isomer substitution (Sect. 2.2). Species of little real-world significance could therefore be kept in the mechanism instead of more significant ones. Second, Y_{max} is also used, through the rxloss and yldcut thresholds, to decide whether a species or reaction is pruned from the mechanism. If RO_2+RO_2 reactions were instead assigned the full branching ratio of the parent species, like RO_2+NO and RO_2+HO_2, their contribution would appear to be much larger than it typically is. This would keep species and reactions in the mechanism that are unnecessary under most conditions.

highnoxfg and rx_ro2_multiclass are not directly involved in the Y_{max} calculation. highnoxfg restricts the chemistry of the RO_2 radical to the RO_2+NO channel during mechanism generation. The other bimolecular RO_2 reactions are then absent from the mechanism entirely. This does not change how Y_{max} is calculated for the reactions that remain. highnoxfg simply removes some reactions from the mechanism before that calculation applies. rx_ro2_multiclass controls whether RO_2+RO_2 reactions are distinguished into nine classes or treated as a single class. Either way, the same 2% weighting factor is used for Y_{max}.

Manuscript change: The following sentences are added in Sect. 2.2, after lines 171-172: "This choice reflects a design principle of GECKO-A. Mechanisms are intended to be generated once and applied across a wide range of conditions, rather than tailored to a specific environment. For peroxy radical reactions with NO or HO_2, the calculation assumes 100% conversion of the parent radical through the considered pathway. Reactions with other peroxy radicals are instead assumed to convert only a small, fixed a priori fraction of the parent radical. This avoids biasing mechanism generation toward pathways that are significant only under specific conditions. Such pathways would otherwise appear more important than they typically are. This affects both the selection of species for isomer substitution and the decision to keep species and reactions in the mechanism (see below)."

RC16: *More information about priority scheme for using surrogate species if "isomerfg" is selected should be given, at least in the SI. It seems to me that some efficiency might be gained if this were applied to peroxy radicals as well as stable products.*

AA: We acknowledge that this priority scheme has not been properly documented. We are adding a description in the SI (see the manuscript change below), along with a reference in the main text at line 187.

Regarding the extension of this scheme to peroxy radicals: the expected efficiency gain is real, but so is the difficulty. RO2 chemistry depends on the position of functional groups relative to the peroxy group itself, as reflected in the structure-activity relationships (SARs) used (Jenkin et al., 2019). None of the current criteria account for this. The autoxidation chemistry planned for the next version of GECKO-A (see Conclusions) adds a further complication, as H-shift rates depend on the position of the labile H-atom relative to the RO2 group. That structural feature is absent from the present scheme. Given these upcoming developments, it now seems premature to set up a dedicated substitution protocol for RO2 radicals. It seems more appropriate to develop such a protocol once autoxidation has been implemented. This remains a key direction for future development. On a side note, a recent comparison between GECKO-A and chemical mechanisms derived using the SAPRC MechGen generator provides direct support for this priority (MechGen includes autoxidation). This gap was identified as a major source of discrepancy between the two mechanism generation systems (Lee-Taylor et al., 2026). This point is now discussed in the Conclusions.

Manuscript change: The following new SI subsection will be added, with a pointer at line 187:
Priority scheme for surrogate (isomer) selection
When the "isomerfg" option is enabled, a newly generated species can be replaced by a positional isomer already present in the mechanism. The two species must share the same molecular formula and the same set of functional groups. Substitution is restricted to non-radical species with more than four carbon atoms, beyond the second generation only. The newly generated species must also have a formation yield below 3%. If several matching isomers exist, the following structural criteria are applied in order. At each step, only isomers meeting the criterion are retained. If no isomer meets it, the current list remains unchanged, and the next criterion is applied:
1. Carbon skeleton branching pattern (relative numbers of primary, secondary, tertiary, and quaternary carbon nodes)
2. Number of –CO–CO– conjugated pairs
3. Number of 1,2-interactions between functional groups
4. Number of terminal CH3 groups
5. Presence of long terminal alkyl chains, checked from longest (four-carbon) to shortest (two-carbon)
6. Number of –CO–CO– pairs located at a chain terminus
7. Number of 1,4-interactions, followed by 1,3-interactions between functional groups
8. Number of specific –CO–CHO, –CO–C(O)OONO$_2$, –CO–C(O)OH, and –CO–C(O)OOH conjugated pairs
9. Number of CH_2, CH, and C carbon types, in that order
If, after all criteria have been applied, more than one isomer still matches, the isomer already present in the mechanism with the highest Y_{max} is selected.

RC17: *It would also be helpful to indicate which of these parameters are new to this version or significantly changed, and which were used in the 2005 version, and what were used in most of the previous published papers that used GECKO-A.*

AA: Among the parameters listed in Table 1, only "brcut" and "maxgen" were part of the original 2005 version. The other parameters were introduced progressively as the capabilities of GECKO-A expanded. A detailed history of when each parameter was introduced, or how it was configured in each previous study, would only be meaningful if these studies were revisited in their own context. This falls outside the scope of the present paper. In addition, the model configuration used in the previous studies is described in the corresponding publications, even though parameter values are not necessarily listed explicitly.

RC: ***Website and Documentation***

RC18: *As indicated above, there is no mention or reference to a users manual or instructions on how to install and use this model. There is an online version of GECKO-A that is relatively easy to use, but its capability is limited to only one generation and uses other restrictive options, which is necessary because this is very computer resource intensive software. A Google search for a manual or instructions was unsuccessful, suggesting that such manuals do not exist, at least not online. The journal description of model description papers given online as guide to authors states that they "should" include a user manual. Is this not a strict requirement for model description papers in GSM?*

AA: As already noted in RC10, installation and usage instructions are not missing: they are on a wiki attached to the GitLab repository distributing the code, https://gitlab.in2p3.fr/ipsl/lisa/geckoa/public, and on the box model's own wiki, linked from the same repository. We agree a live wiki is not an adequate substitute for a version-specific manual, and this is why we archive a frozen snapshot of it, as described in RC10.

Concerning whether this is a strict requirement, we note that GMD's guidelines distinguish "should" (encouraged) from "must" (required), and the user manual falls under "should" in the relevant text. Either way, we are providing a version-specific manual, as described above.

RC19: *The link given on Line 255, "(www.GECKO-Aa.lisa.u-pec.fr, last access January 2026)", did not work. I found "GECKO-Aa.lisa.u-pec.fr/" (no "www") using Google, and it looks like this is presumably what they meant.*

AA: Thank you for pointing out the typo.
Manuscript change: Line 255 corrected to: geckoa.lisa.u-pec.fr

RC: ***MCM Description and Comparison with GECKO-A***

RC20: *The description of MCM should summarize which of the chemical estimates or SARs used when MCM 3.3.1 was constructed are different from those now used by GECKO-A, especially those that were found to affect the results of the comparison.*

AA: A direct comparison of the SARs feeding the construction protocols of MCM and GECKO-A is not straightforward. Updates to a specific SAR do not propagate automatically through MCM. These updates are carried out on a compound by compound basis, generally documented in a dedicated paper. The isoprene scheme, for instance, was revised in a standalone update (Jenkin et al., 2015), separate from updates to other compound classes or other reaction types. MCM v3.3.1 is therefore not built on a single, internally consistent set of SARs that could be listed and compared against GECKO-A's. It is a patchwork of chemistry from different periods, with updates varying by compound family. A SAR-by-SAR comparison is therefore not carried out exhaustively and a priori in this study. Fine-grained mechanistic analysis is only considered a posteriori, when a salient divergence emerges from the comparison of simulation results. This is the case, for example, for methylcatechol chemistry (Sect. 5.6a), or for benzaldehyde and maleic anhydride chemistry (Sect. 5.8). These three cases involve aromatic chemistry, whose representation in MCM v3.3.1 is largely based on the MCMv3.1 update (Bloss et al., 2005a).

This brings us back to the recurring point in this review, that comparing simulation results amounts to "evaluating" the MCM. We have already addressed this in our responses to RC2 and RC5. The MCM was built at a resolution suited to its original purpose, primarily to simulate gas-phase HOx/NOx/Ox chemistry with respect to multi-day ozone formation (line 1085). The mechanisms generated here with

GECKO-A, by contrast, are built at a deliberately higher resolution. This difference in resolution is a design choice, driven above all by the aim of exploring GECKO-A's ability to describe oxidative trajectories. The MCM retains its status here as a benchmark, a reference widely adopted by the community, used to determine whether the simulated discrepancies reflect the contribution of higher chemical resolution, or instead point to significant differences owing to the protocol implemented in GECKO-A v1.0. The MCM's value as a benchmark also comes from how it was built. The MCM does not always strictly follow its own development protocol and SARs. In places, reactions or rate coefficients were adjusted to reproduce chamber observations (e.g., Bloss et al., 2005a, b; Jenkin et al., 2012; Jenkin et al., 2015). The MCM therefore also reflects observational knowledge beyond its construction rules. We show here that the higher chemical resolution of GECKO-A has a limited effect on ozone formation in NOx-rich environments (Sect. 5.6b), but a considerable effect on SOA production through multigenerational chemistry (Sect. 5.1-5.2). We also show one example where the comparison reveals a flaw in GECKO-A rather than in the MCM: maleic anhydride chemistry, whose formation protocol requires revision (lines 885-905).

However, this interpretive framework is not stated explicitly in the paper. We propose to make it explicit in the introduction.

Manuscript change:
The following paragraph is added after line 416 (Sect. 4.2): "Incorporating updates into a manually built mechanism is also difficult, as already noted in the introduction (Sect. 1). In practice, updates are not applied as a single, mechanism-wide revision each time a new SAR becomes available. They are instead introduced on a compound-by-compound basis, documented in dedicated publications (e.g., Jenkin et al., 2015, for isoprene). As a result, MCM v3.3.1 combines chemistry from different periods, with updates varying by compound family. In addition, some reactions or rate coefficients were adjusted to reproduce chamber observations (e.g., Bloss et al., 2005a, b; Jenkin et al., 2012; Jenkin et al., 2015). The MCM therefore reflects observational knowledge beyond its construction rules, which reinforces its value as a benchmark."

The following sentences are added after line 78 (Introduction), where the comparison with MCM is first introduced: "In this comparison, the MCM is used as a benchmark. When the simulated trajectories diverge, the aim is to determine the origin of the discrepancy. It may reflect the added value of GECKO-A's higher-resolution explicit treatment relative to the MCM's necessary simplifications. It may instead point to limitations specific to GECKO-A. This distinction guides the interpretation of results throughout the paper."

RC21: *The most important difference between MCM and GECKO-A is that MCM only attempts to represent chemical detail for the first two generations of reactions, and uses highly approximate methods to represent reactions of subsequent generations. This is necessary since otherwise it would be impossible to derive the mechanism manually. Because of this, the section describing MCM should give more detail on the approximate methods MCM uses to represent higher generation processes. There is some discussion of this when it affected the results, but it is better that this discussion be in this section, which can be referred to in cases where it affects the results.*

AA: The MCM does not treat the first two generations in detail and then switches to approximation. The simplification rules (yield threshold, isomer lumping, treatment of minor products; see Sect. 4.2) apply continuously, generation after generation, and their effect grows stronger as the number of generations increases. This is the progressive divergence we describe in our own Conclusions (lines 1065-1076): GECKO-A/MCM trajectories are similar while first-generation species dominate, then diverge as later generations become predominant.

The main simplification rules applied by MCM beyond the first generations are already listed in Sect. 4.2 (lines 409-413), with a pointer to Jenkin et al. (1997) and Saunders et al. (2003) for the full detail (line 416).

As with the SARs (RC20), fine-grained analysis of these reduction choices is only carried out where it clarifies a salient divergence between the two mechanisms. This is the logic followed throughout Sect. 5.

RC22: *The comparison with MCM is appropriate because this is a well-used mechanism that is also intended to incorporate near-explicit chemical detail that employs similar if not the same estimation methods in most cases, while being developed using a totally different approach. However, to be useful as a fair comparison, the parameters used when deriving the GECKO-A mechanisms for comparison with MCM should be consistent with those used (or considered in a qualitative sense) when MCM was developed. The effects of the reduction parameters on the GECKO-A simulations should be demonstrated separately, so the comparison with MCM should employ comparable parameters. The limitation of generations in MCM makes it most directly comparable to GECKO-A mechanisms derived for no more than two generations, i.e., using "maxgen=2". Comparisons using 2-generation GECKO-A mechanisms would allow differences between MCM and GECKO-A on representation of the detailed chemistry to be more unambiguously studied. Since GECKO-A uses similar estimation methods and chemical assignments in many (but not all) cases, the comparison can also provide evidence that the GECKO-A software is implementing the chemistry as intended. As it is, the results of the comparison, which uses GECKO-A mechanisms derived for multiple generations and least reduction, are dominated by the fact that MCM was not designed to represent the higher generation reactions with chemical detail.*

AA: We share the reviewer's view that the MCM is an appropriate reference for comparison. The question of fairness would only arise if the aim were to evaluate MCM itself, which we have already clarified (RC5, RC20). The choice of a deliberately high resolution for GECKO-A, with no generation limit and no isomer lumping, follows an objective already discussed in RC4: documenting the oxidative trajectories produced by GECKO-A in detail (Sect. 4.1, lines 385-390).

As noted in our response to RC21, oxidation in MCM does not stop after two generations. Limiting GECKO-A mechanisms to 2 generations would therefore not make the comparison fairer. It would introduce its own bias instead, particularly for gas-phase metrics (SOG, IOHR, YOx), which depend on the progress of oxidation beyond the second generation in both mechanisms. It would also rule out discussing one of the most informative cases in our own analysis: CO3C85OOH (Sect. 5.6a) is a third-generation product responsible for the anomalous accumulation observed during octane oxidation in MCM (line 674). A GECKO-A mechanism limited to two generations would not go far enough to represent the corresponding oxidation step, making the comparison impossible for this case.

What the reviewer proposes is really a different study: systematically quantifying the effect of GECKO-A's reduction parameters on the simulated mass balance. This is explicitly mentioned as beyond the scope of the present paper (lines 973-974). This point is in fact the subject of ongoing work with the GENOA tool (Conclusions, lines 1090-1094), though in a different context from a comparison with the MCM.

RC23: *If MCM is compared with 2-generation GECKO-A mechanisms, then the method GECKO-A uses to represent higher generation products becomes important, so its difference compared to the MCM approach should also be discussed. It looks to me like the GECKO-A method is biased towards underestimating the effects of gas-phase reactivities and yields of higher generation products, while the*

MCM method is biased towards overestimating these because many of these products are not ultimately consumed. This should be pointed out and discussed if so.

AA: We understand this comment as addressing the maxgen=2 setting discussed in RC22, not the full mechanism used in this study.

Under that setting, the bias described for GECKO-A is correct, and mechanical. Beyond maxgen, a species X is transcribed as X + Ox → n XCLOSS (lines 152-156), where XCLOSS is a carbon sink with no real product. Setting maxgen=2 would therefore remove the entire contribution of any third-generation and later species.

The impact of this loss varies strongly by parent compound. Fig. S3 (updated to Fig. 17 in the revised manuscript, Sect. 6, added in response to RC25) shows that the carbon budget of butane is almost entirely carried by generation 1 and 2 species, while that of dodecane carries a growing contribution from generations 3 and 4 over time. A uniform truncation at maxgen=2 would therefore disproportionately affect the five compounds studied here. We also note that the accumulation of low-generation products, such as acetone in α-pinene chemistry (Sect. 5.8), does not reflect a truncation artifact, but the species' own low reactivity.

The bias described for the MCM is of a different nature. Unlike the GECKO-A bias, which would be specific to the maxgen=2 setting, the MCM one is an intrinsic property of its construction, independent of the generational depth chosen for GECKO-A. It is therefore already visible in the full mechanism used in this study, as shown in our Sect. 5.6a, with one caveat on "*ultimately*". The four cases discussed (CO3C85OOH, C121OOH, APINAOOH, MCATEC1OOH) are not permanent sinks: each has an effective loss pathway, but this pathway becomes very slow under low-NOx conditions. For CO3C85OOH, for instance, effective loss occurs through photolysis (83 h) and through reaction with NO (27 h) (lines 686-689). It is this slowness, not a complete absence of consumption, that artificially inflates cumulative reactivity over the simulated timescale.

These two biases, though different in nature, would combine if a comparison at maxgen=2 were attempted. Quantifying each of these effects precisely is, as noted in our response to RC22, a separate study, beyond the scope of this paper.

Manuscript change: The following sentences are added after line 971 (Sect. 5.9): "This contribution, however, varies by parent compound. For butane, the carbon budget is almost entirely carried by first- and second-generation species. For dodecane, species from generations three and four make an increasing contribution to this budget as oxidation proceeds (Fig. 17)."

RC24: *The other parameter that affect the comparison with MCM is "brcut", whose effective value varies with compound in MCM but I don't think is ever lower than 5%, and is often much higher. On the other hand, Table 1 indicates that the GECKO-A mechanisms derived here used cutoff that was an order of magnitude lower. For best comparison with MCM, they should use "brcut"=5% and select the "isomerfg" option, which allows lumping of isomers that is often used in MCM. The other reduction parameters are mainly important in multi-generation derivations, so would not be important in this comparison of limited generation mechanisms.*

AA: This follows the same logic as RC22: isolating the contribution of each reduction parameter (brcut, isomerfg, maxgen) from the others. The last sentence of this comment is set within the maxgen=2 setting discussed throughout RC22-24; our response to RC23 already addresses why we do not adopt this setting for the comparison presented here.

This point really connects to everything we have discussed since RC20. Our goal in this comparison is not to treat the two mechanisms as equals, since they differ fundamentally in resolution. It is instead to understand which assumptions or protocol choices drive the discrepancies observed between them. Deconvolving these effects rigorously, between two independently built mechanisms, is far from trivial. It requires a dedicated methodology, of the kind we introduced in RC5 to isolate organic chemistry from oxidant feedbacks. We take this up together with the sensitivity analysis discussed in RC25. This has been the point of this comparison from the start: to position GECKO-A relative to an established reference, not to evaluate the MCM.

RC: ***Effects of Choices of GECKO-A Parameters***

RC25: *As indicated above, a major omission of this paper is lack of sufficient information showing how the GECKO-A-derived mechanisms are affected by the choice of user-modifiable parameters listed in Table 1. The only information regarding this given in Figure 1, which has plots showing the effects of using different selections for the maximum number of generations, whether isomers with the same substituents are lumped, and the choice of the low volatility vapor pressure cutoff, affect the numbers of species in the mechanisms. There is no information on the effects of these and other parameters on the actual predictions of the mechanism, such as SOA and soluble product formation, reactivity metrics, or organic product distributions. This is at least as important as effects of the parameters on mechanism size, if not more so.*

AA: We agree with the reviewer. As indicated in our response to RC22, the primary objective of this study was to generate a high-resolution mechanism, in order to examine the oxidative trajectories in detail. The absence of any results obtained with a mechanism generated at a lower resolution is an important omission in a paper dedicated to presenting the capabilities offered by GECKO-A.

To address this omission, a second mechanism, denoted red-GECKO-A, was generated for each of the five parent compounds. This mechanism relies on more stringent reduction parameters. The aim is to examine the effect of the chemical resolution of the mechanism on the simulated trajectories (Introduction). The parameters retained are based on the default values of the open-source version of GECKO-A, except for two parameters (Table 1). This choice is justified in Sect. 4.1. The effect of this configuration on the size of the generated mechanism is presented in Sect. 2.3, complementing Fig. 1 already cited by the reviewer.

GECKO-A and red-GECKO-A are compared in a new section (Sect. 6), titled "red-GECKO-A versus GECKO-A". This comparison covers a single configuration, chosen to illustrate the reduction capabilities offered by GECKO-A. As indicated in our response to RC22, a systematic quantification of the effect of each reduction parameter taken separately remains to be done but lies beyond the scope of this paper.

The same protocol used for the GECKO-A/MCM comparison in Section 5 is followed in Sect. 6, with red-GECKO-A simply substituted for the MCM. The two main results of this comparison are discussed in the main text: the gas- and particle-phase carbon budget (Fig. 16), and carbon budget breakdown by oxidation generation (Fig. 17). The remaining comparisons are provided in the SI (Fig. S6 to S14), with discussion limited to their main points. These elements cover, in the order cited by the reviewer: SOA and soluble product formation (Fig. 16 and Fig. S14); bulk reactivity metrics I_{OHR} and YOx (Fig. S10); and organic product distributions, through several complementary descriptors (distribution by

generation, Fig. 17; by functional group, Fig. S8; degree of functionalization, Fig. S9; isomer group diversity, Fig. S11; dominant isomer groups, Fig. S12).

This comparison shows that red-GECKO-A faithfully reproduces the trajectories simulated with GECKO-A for three of the five parent compounds (butane, toluene, α-pinene), across all descriptors examined. Substantial discrepancies appear for octane and dodecane, under NOx-poor conditions. These discrepancies mainly concern the partitioning of organic carbon between the gas and particulate phases, and its distribution across oxidation generations. In contrast, the nature of the functional groups produced, as well as the dominant isomer groups, remain nearly unchanged.

Manuscript change: Given the extent of these changes, they are summarized here rather than reproduced in full. A complete new section, "6 red-GECKO-A versus GECKO-A", was added to the manuscript, presenting this comparison in full. Corresponding additions were made in the Abstract, the Introduction, to introduce this comparison, in Sect. 2 and Sect. 4, to define the red-GECKO-A configuration and its effect on mechanism size, and in the Conclusion, to summarize the main results and their implications for mechanism reduction.

RC: ***Results***

RC26: *The results section is dominated by comparing predictions of MCM with the GECKO-A mechanisms produced with very low levels of reduction and no effective limitation on generations. Although not optimum for documenting GECKO-A for reasons discussed above, these results are important and need to be published, since they clearly show the that mechanisms, however detailed, that do not represent the higher generations are totally unsuitable for predicting SOA or soluble products. Overall I think present manuscript presents the comparisons results reasonably well, and use a reasonably comprehensive set of metrics for this purpose. The main omission, besides not showing the effects of how varying the GECKO-A parameters affect model predictions, is not showing how much SOA, solubility, and groups of various kinds can be attributed to each generation.*

AA: We thank the reviewer for this positive assessment of the Results section. This concerns both the presentation of the results and the choice of metrics used to compare GECKO-A and the MCM.

The reviewer raises the same omission as RC25: results showing the effect of reduction parameters on GECKO-A's simulated trajectories. We refer to our response to RC25 on this point.

The contribution of carbon by oxidation generation is given in Fig. 17, for GECKO-A and red-GECKO-A. The discrepancy between the two mechanisms is largest for dodecane. Sect. 6 shows that this discrepancy peaks at the third generation, where SOA and SOG are further broken down.

This addresses the SOA part of the reviewer's comment. Solubility and functional-group composition, however, are given in Fig. S14 and Fig. S8-S9, but not resolved by generation. As the reviewer notes, the set of metrics already provided in this study is “reasonably comprehensive”. Extending these two descriptors to a per-generation resolution would therefore lie beyond the scope of this paper. We leave this finer decomposition to dedicated future work.

Manuscript change: See the manuscript change provided in response to RC25.

RC: ***Conclusions***

RC27: *The conclusion section is useful in pointing out areas where the chemistry in GECKO-A needs to be improved, and the need for work on reduction approaches so computer generated mechanisms can be used to improve mechanisms in models. Although not presently usable in practical models, multi-generation mechanisms produced by systems such as GECKO-A are necessary to improve and evaluate such models.*

AA: Thank you for this observation.

RC28: *As discussed above, I think the greatest contribution of this paper is the demonstration of the importance of representing higher generation reactions when predicting SOA or water soluble products. This has implications for the predictive capabilities of all mechanisms currently used in atmospheric models. Because it is not practical to use million-reaction mechanisms in such models, other approaches are needed to predict SOA and soluble products based on the actual chemistry involved. I do not think these conclusions are adequately pointed out in this section.*

AA: We agree and add two sentences to the Conclusions section.

Manuscript change: The following is added after line 1094: "More broadly, explicit multigenerational mechanisms such as GECKO-A or MechGen (Carter et al., 2025a) are essential to our fundamental understanding of the chemistry driving SOA and water-soluble organic carbon formation. Other, necessarily simplified approaches remain essential for predictive modeling, but explicit mechanisms currently provide a benchmark for this purpose. This benchmark is traceable to current chemical understanding (Ervens et al., 2024)."

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Response to Reviewer 2 (anonymous)

Reviewer Comment (RC): *General Comments*
In this manuscript the authors describe a comparison of two computational methods for simulating the gas-phase oxidation of selected volatile organic compounds (VOCs) under atmospheric conditions ranging from polluted to clean air. The Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A) and the Master Chemical Mechanism (MCM) have both been widely used for many years to model complex atmospheric chemistry. Unlike the MCM, for which VOC oxidation mechanisms have been developed on more of a case-by-case basis, GECKO-A can create a mechanism for almost any compound structure using a set of fundamental reaction pathways and rate constants based on experimental data in the literature and structure-activity relationships. Mechanisms for the oxidation of butane, octane, dodecane, toluene, and alpha-pinene generated with a new open- source version of GECKO-A and the latest version of the MCM were incorporated into box models that treat processes such as inorganic species chemistry, gas-particle and gas-wall partitioning, and photolysis to compare the performance for a variety of outputs including gas- and particle-phase carbon budgets, volatility and functional group distributions, water solubility, OH reactivity, Ox production, and product molecular composition.
This is an excellent paper. The background information about the different approaches used in GECKO-A and the MCM is very useful for readers not familiar with the details of these models, and the comparisons yield valuable insights into their relative strengths and weaknesses for a wide range of calculated quantities of atmospheric interest. The paper is well-organized, the results are clearly explained and interpreted, and the authors discuss the limitations and planned future improvements. I recommend publication in GMD after the following minor comments are addressed.

Authors' Answer (AA): We thank the reviewer for this positive assessment of the work.

RC: *Specific Comments*
1. Page 4, line 128: Does GECKO-A include ring-closing reactions for alkoxy radicals?

AA: No, ring-closure (cyclization) reactions of alkoxy radicals onto a double bond are not included in the current version of GECKO-A. The alkoxy radical chemistry implemented in GECKO-A v1.0 follows the structure-activity relationships (SARs) of Vereecken and Peeters (2009, 2010) (as indicated on lines 115-117), which address decomposition, isomerization, and reaction with O_2 for alkoxy radicals, but not intramolecular addition onto unsaturated bonds.

Unlike the case of RO_2 radicals, for which a structure-activity relationship is available (Vereecken et al., 2021a), a systematic and validated structure-activity relationship for ring closure from an unsaturated alkoxy radical does not currently exist. This pathway has been characterized for specific systems, such as the NO_3-initiated oxidation of isoprene (Carlsson et al., 2023; Vereecken et al., 2021b) and the OH-initiated oxidation of isoprene and monoterpenes (Vereecken and Peeters, 2004, 2012). Extending the current protocol for alkoxy radicals to account for this pathway would require developing a dedicated structure-activity relationship, which is beyond the scope of the present version.

The original text (line 128) explicitly states that GECKO-A does not account for ring closure for unsaturated RO_2 radicals, but it does not mention the case of alkoxy radicals. This is a separate limitation that had not been explicitly mentioned. We have revised the text accordingly (see the change made to the manuscript below).

Manuscript change: We have revised the sentence originally at lines 127-129 as follows:

"Major limitations include the absence of H-shift isomerization reactions involving RO2 radicals and ring-closure (cyclization) reactions for unsaturated RO2 radicals (e.g., Bianchi et al., 2019; Crounse et al., 2013; Vereecken and Nozière, 2020; Vereecken and Peeters, 2004; Vereecken et al., 2021a), as well as ring-closure reactions of unsaturated alkoxy radicals (e.g., Carlsson et al., 2023; Vereecken and Peeters, 2004, 2012; Vereecken et al., 2021b). […] Ring-closure reactions of unsaturated alkoxy radicals would first require a dedicated structure-activity relationship, which is not currently available."

RC: *2. Page 4, line 140 and Conclusions: Are there any plans to include multiphase reactions that form oligomers?*

AA: The Conclusions section mentions dimer formation via RO_2 + RO_2 reactions in the gas phase (line 1101). It also indicates that preliminary work is underway to incorporate this process into a future version of GECKO-A (lines 1111-1113).

Regarding multiphase oligomerization more specifically, there are no plans to include this process in the short or medium term. A simple parameterization to represent the effect of condensed-phase dimerization is conceptually straightforward to design (for example, a bimolecular reaction between species already present in the condensed phase). However, such a parameterization requires at minimum a structure-activity relationship (SAR) to estimate the associated rate constants. To our knowledge, no such SAR is currently available with the level of generality required for implementation in GECKO-A.

RC: *3. Page 4, line 158: Can partitioning of radicals also be important and included in the mechanism?*

AA: The timescale of gas-particle equilibrium in our simulations is on the order of a few minutes (line 549). The gas-phase lifetime of most organic radicals is short compared to the characteristic timescale of mass transfer from the gas phase to the particle phase. This is particularly true for alkoxy radicals, whose gas-phase lifetime is typically several orders of magnitude shorter than the gas-particle transfer timescale.

Peroxy radicals, on the other hand, can have gas-phase lifetimes close to this order of magnitude, particularly under low-NOx conditions where bimolecular loss is slower. GECKO-A does not yet incorporate RO_2 autoxidation reactions, which are often very fast. Incorporating these reactions would reduce the effective gas-phase lifetime of RO_2, which would likely reinforce the assumption that gas-particle partitioning of RO_2 remains a relatively minor process under most conditions for most RO_2.

The development of a phase-transfer treatment for radicals in GECKO-A is also limited by the lack of vapor pressure estimates for radicals. The approach in the current model relies on an estimate of the saturation vapor pressure of each species. To our knowledge, no appropriate structure-activity relationship currently exists for estimating vapor pressures for radical species. Existing estimation methods (for example, those used in GECKO-A and listed at lines 119-120) were developed and parameterized exclusively for stable closed-shell compounds. This currently prevents representing radical partitioning with the current configuration of the model, independently of the kinetic argument raised above.

Even setting aside the question of vapor pressure, the dynamic gas-particle partitioning treatment currently implemented in GECKO-A for closed-shell species would likely not be sufficient for radicals. Radical reactivity in the condensed phase is expected to be fast, potentially faster than in the gas phase (e.g., Renbaum and Smith, 2009). Under such conditions, condensed-phase chemistry, rather than simple phase transfer, is likely what controls the net exchange of radicals between the gas and particle phases. Recent work has also shown that peroxy radicals can be efficiently taken up by certain solid surfaces

through reactive (redox) uptake rather than simple dissolution (Durif et al., 2024), and that their condensed-phase reactivity can differ from their gas-phase chemistry (for example, enhanced formation of organic nitrates from RO_2 + NO in the condensed phase; Barber et al., 2024).

Modeling radical mass transfer would therefore require a description of condensed-phase radical chemistry, in addition to the mass-transfer parameterization itself. Neither of these elements is currently available at the level of generality required for implementation in GECKO-A.

RC: *4. Page 6, Table 1: One of the impressive features of GECKO-A is its ability to simulate multigeneration chemistry. But how necessary and important is this? In their comprehensive lab study of a-pinene oxidation Isaacman-VanWertz et al. (Nat Chem, 10, 462, 2018) conclude that within about one day of atmospheric oxidation most carbon is sequestered into two long-lived reservoirs: volatile oxidized gases and low-volatility particles.*

AA: Our GECKO-A simulations are consistent with two features of the oxidation sequence described by Isaacman-VanWertz et al. (2018) for α-pinene. The first is the progressive shift from functionalization to fragmentation. Both processes compete throughout oxidation, but their balance changes as oxidation proceeds. In our simulations, early-generation species are primarily mono- and bifunctional. More heavily functionalized species only form later (lines 586-587), while fragmentation becomes progressively dominant, ultimately producing CO and CO_2 (lines 565-568). The second feature is the sequestration of low-volatility carbon in a relatively unreactive particle reservoir. Figure 3 shows that SOA concentrations reach a plateau for all hydrocarbons, including α-pinene, after approximately 1-2 days of simulated time. Isaacman-VanWertz et al. (2018) also identified a second long-lived reservoir, made of volatile oxidized organic gases. Our simulations do not reproduce such a reservoir, except marginally (e.g., through acetone formation). Non-sequestered gas-phase carbon continues to be converted to CO and CO_2 over the simulated period (Fig. 5) and does not reach a fully unreactive state within the duration of our simulation.

Although maxgen was set to 20 to minimize the impact of mechanism reduction on the simulated trajectories (line 387), this limit is never reached in practice. Figure 1b shows that the number of species generated reaches a plateau after approximately 6-8 generations (line 229). Furthermore, Figure S3 (updated to Fig. 17 in the revised manuscript, Sect. 6, added in response to RC25 from the first reviewer) shows that species from generations beyond the fourth contribute only marginally to the mass balance. The manuscript states that "most of the SOC mass is accounted for by species up to the fourth generation, regardless of the parent hydrocarbon or scenario considered " (lines 969-971). This corroborates the reviewer's point and suggests "significant potential for mechanism simplification in GECKO-A without major loss of chemical information" (line 971). This potential is illustrated by red-GECKO-A, a reduced configuration (maxgen=5). It is compared to GECKO-A in a new section added to the manuscript, in response to comments from the first reviewer (RC25 and RC26).

As indicated in the Conclusions (lines 1096-1113), the next version of GECKO-A will incorporate RO_2 autoxidation. This process is expected to generate multifunctional, low-volatility species as early as the first generations, whereas the current protocol requires several generations of sequential functionalization. Although this effect remains to be quantified, this process is expected to substantially increase the sequestration of organic carbon into the particle phase from the earliest stages of the simulation, likely reducing the number of generations needed to reach a given SOA yield. This point is developed further in the Conclusions, in connection with the reduced mechanism red-GECKO-A (see RC25 in review 1).

RC: *5; Page 10, line 321: Is there a reason the parameterization for gas-wall partitioning developed by Krechmer et al. (EST, 50, 5757, 2016), which is used in GECKO-A in the study by Peng et al. (ACP, 21, 14649, 2021) is not implemented?*

AA: We thank the reviewer for this comment. We would like to clarify that gas-wall partitioning was not activated in the simulations presented in this study (g2wfg = False, Table 1). The description given at lines 305-321 simply documents this feature of GECKO-A, as the paper aims to present the range of options offered by the tool.

The default treatment currently documented in GECKO-A (lines 311-321) follows Matsunaga and Ziemann (2010), as implemented by La et al. (2016). This implementation uses a fixed uptake rate constant common to all species, with a default characteristic timescale of 15 minutes for wall uptake. The effective wall sorption capacity is represented by the empirical parameter ($C_w/M_w\gamma_w$), expressed as a molar concentration. For simplicity, GECKO-A uses two default values covering broad classes of compounds (hydrocarbons and oxygenated compounds, line 320). Matsunaga and Ziemann (2010) and Yeh and Ziemann (2015) reported values for several distinct compound families, however, not just two. These two values constitute a simple default parameter that users can adjust for specific applications.

In the parameterization of Krechmer et al. (2016), as used by Peng et al. (2021) in a GECKO-A-based study, the effective wall sorption capacity (C_w) itself decreases as species volatility decreases. This parameterization further links the characteristic uptake timescale to the surface-to-volume ratio of the specific chamber considered (for example, about 1000 s for the CU chamber used by Peng et al., 2021, versus the fixed, chamber-independent default value of 900 s currently used in GECKO-A).

Both parameterizations describe gas-wall partitioning as a reversible first-order process governed by an uptake rate and an equilibrium constant. Adopting the formulation of Krechmer et al. (2016) would mainly require updating the numerical values used for the uptake rate constant and the equilibrium relationship, rather than a fundamental structural change to the box model. Peng et al. (2021) show that such a substitution is feasible within the existing GECKO-A framework. More generally, the box model provides a generic framework for gas-wall mass transfer rather than a chamber-specific parameterization. Users can replace the default values with those suited to their chamber and application, as Peng et al. (2021) did.

Manuscript change: We have added the following sentences (originally after line 321):
"The values provided here define a generic framework for gas-wall mass transfer within the GECKO-A code structure. These default parameterizations are intended as a practical starting point and should be adjusted by the user to the specific chamber and compounds under consideration, for example by substituting alternative published parameterizations such as that of Krechmer et al. (2016), as illustrated by Peng et al. (2021)."

RC: *6. Page 23, Figure 7 and page 32, Figure 11: It appears that the reactions of butane, octane, and dodecane do not form ether groups at any oxidation timescale. Are the authors aware of recent computational chemistry results from Arathala et al. (JPCA, 125, 5963, 2021) that indicate that the timescale for cyclization of 1,4-hydroxycarbonyls in the gas phase to form cyclic hemiacetals can be on the order of seconds to minutes due to catalysis by HO2 or HNO3, respectively. For example, the calculated timescale is ~30 min under the range of HO2 concentrations used here and ~10 s for 2 ppb of HNO3. For alkanes this can have a major impact on the chemistry, since 1,4-hydroxycarbonyls are ~60% of the first-generation products and the corresponding cyclic hemiacetals have a tertiary H atom with an alpha-ether group that will greatly enhance (~10x) the rate of abstraction by OH and drive much of the subsequent secondary reactions through this pathway. The authors could comment on how*

this might impact the results presented here and could also consider adding this rather simple feature as an option to their alkane models.

AA: We thank the reviewer for pointing us to Arathala et al. (2021), which we were not aware of. GECKO-A can include a pathway forming cyclic hemiacetals (and subsequently dihydrofurans, DHFs) from 1,4-hydroxycarbonyls, but this pathway is currently implemented only as a heterogeneous, condensed-phase process as described in La et al. (2016). This process was not included in the mechanisms generated for this study, as only gas-phase chemistry was considered here (line 400), and for consistency with the MCM, which does not include this chemistry either. This option (dhffg) is not among the parameters listed in Table 1, but can be activated by adding it to the "process" section of the mechanism-generation namelist.

Arathala et al. (2021) present ab initio calculations showing that cyclization of 1,4-hydroxycarbonyls to form the corresponding hemiacetal may also occur in the gas phase via catalysis by species such as HO_2 or HNO_3, becoming atmospherically relevant. As noted by the reviewer, 1,4-hydroxycarbonyls account for a major fraction of first-generation alkane oxidation products. Their gas-phase cyclization could therefore affect the subsequent oxidation of alkanes, independently of particle or wall partitioning.

GECKO-A's mechanism-generation architecture is well suited to test this kind of sensitivity, as it allows alternative reaction protocols to be activated selectively and compared systematically. However, since the rate constants reported by Arathala et al. (2021) currently rest on theoretical (ab initio) calculations for a single prototype compound, without experimental kinetic validation or a generalized SAR applicable across 1,4-hydroxycarbonyl structures, we prefer to await further development before incorporating this pathway into GECKO-A's default protocol.

Manuscript change: We have added the following sentences after line 249 (Sect. 2.4):
"In addition to the parameters summarized in Table 1, the namelist can include further options, allowing users to activate additional, optional reaction pathways that are not enabled by default. This includes, for example, the heterogeneous formation of cyclic hemiacetals and dihydrofurans (DHFs) from 1,4-hydroxycarbonyls (Lim and Ziemann, 2009). This option is activated with the dhffg flag, to be added in the "process" section of the namelist (see the user documentation of GECKO-A v1.0 in Aumont et al., 2026)."

RC: *7. I understand that this paper describes a model-model comparison, but it would be useful to include some comments about how well they have been shown to simulate experimental results.*

AA: The primary objective of this study is to present the newly released open-source version of GECKO-A (v1.0) and to explore in detail the oxidative trajectories, chemical budgets, and volatility distributions it produces under a range of environmental conditions. The comparison with MCM is used here as a benchmark to position GECKO-A relative to an established reference mechanism (see also the detailed responses to Reviewer 1).

Earlier versions of GECKO-A have been evaluated against experimental observations in several dedicated studies. As noted at lines 335-337, the GECKO-A box model has previously been evaluated against laboratory chamber data (La et al., 2016; McVay et al., 2016; Peng et al., 2021) as well as against complex, realistic VOC mixtures representative of urban, forested, and outflow environments (Lee-Taylor et al., 2011, 2015; Mouchel-Vallon et al., 2020). Valorso et al. (2011), cited at line 110 of this manuscript, similarly evaluated GECKO-A-simulated SOA formation from α-pinene photooxidation against chamber measurements.

A systematic evaluation of GECKO-A would require a benchmark dataset for routinely testing successive versions of the model. Developing and maintaining such a dataset would be valuable but is beyond the scope of the present paper.

Manuscript change: We have revised the sentence at lines 335-337 to explicitly note that these applications included evaluation against experimental data: "Examples of box model applications include evaluation against laboratory chamber data (e.g., La et al., 2016; McVay et al., 2016; Peng et al., 2021; Valorso et al., 2011) as well as simulations of realistic, complex VOC mixtures in urban and forested environments and outflow plumes (e.g., Lee-Taylor et al., 2011, 2015; Mouchel-Vallon et al., 2020)."

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