Authors' Response to Reviews of

GENerator of reduced Organic Aerosol mechanism (GENOA v1.0): An automatic generation tool of semi-explicit mechanisms

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EC: *Editors' Comment*,   RC: *Reviewers' Comment*,   AR: Authors' Response,   ☐ Manuscript Text

1. Uploaded files validated on 05 Oct 2022

Notification to the authors:

Please ensure that the colour schemes used in your maps and charts allow readers with colour vision deficiencies to correctly interpret your findings. Please check your figures using the Coblis – Color Blindness Simulator (https://www.color-blindness.com/coblis-color-blindness-simulator/) and revise the colour schemes accordingly.

AR: All figures have been checked. As a result, we have revised figures 3, 5, 7, 11 in the main paper and figures A1, B1 in the Appendix.

2. Topical Editor decision: Publish subject to minor revisions (review by editor) on 28 Oct 2022

EC: *Dear Authors,*

I am pleased to inform you that your revised manuscript is accepted for publication after some minor/technical revisions. Please find below a list of final reviewer comments. Please revise your manuscripts accordingly or write a reply in case you consider the comments as not appropriate.

Best regards,
Andrea Stenke

AR: Thank you editor and reviewers for the positive comments. We have carefully considered the following comments and revised the manuscript accordingly. Please note that the line and section numbers mentioned in the response correspond to the version of the manuscript before revision.

RC: *My most substantive concern involves the fact that they apparently did not consider (or did not state that they considered) differences in volatility among their acceptance criteria for lumping. It seem to me that this should be the most important criterion given that this work is focused on SOA modeling. The first additional example given in Section C1 involves lumping a compound with an aldehyde group with one with a carboxylic acid group. I would think that these groups would have substantially different effects on vapor pressures and therefore SOA formation impacts.*

AR: In BCARY reduction, the difference in saturation vapor pressure was indeed not explicitly considered when lumping condensables. However, when searching for a lumpable target for one condensable, GENOA ranks all other condensables according to their difference in saturation vapor pressure. In other words, species with similar saturation vapor pressures are lumped together first. Meanwhile, saturation vapor pressures, which result from molecular structures, may also be constrained by restricting some key molecular structures of lumpable species. Therefore, the lumping of condensables may take into consideration the difference in vapor pressure to some extent.

The lumping examples presented in Appendix C1 are intended to demonstrate the possibility of lumping dissimilar compounds (with real examples from BCARY reduction). For this reason, we have selected examples of lumped species with distinct molecular structures. Despite the first example in Appendix C1 having different functional groups, the difference in their saturation vapor pressure is only around two orders of magnitude: 1.5×10^{-12} atm for C1313NO3 and 2.8×10^{-14} atm for C152NO3.

Additionally, GENOA offers a user-chosen option to lump condensables based on their saturation vapor pressure, allowing lumping only if their saturation vapor pressures are within the user-specified log-scale range. The BCARY reduction was tested with this option, however, a more effective reduction was obtained without it (which is the "Rdc." mechanism described in the paper). The result could indicate that BCARY, which typically derives low volatile organic compounds, may not need a stringent restriction on saturation vapor pressure for lumping (i.e., current limitations may be sufficient).

Nevertheless, we totally agree with the reviewer that saturation vapor pressure plays a crucial role in SOA formation, and this lumping option could be beneficial for other SOA precursors. In order to inform the user, we have included this lumping option (although not used in BCARY reduction) in the supplementary Excel file titled "User-chosen reduction options and parameters". We have also added the explanation to the paper:

> *Section 2.2.3, line 221:*
>
> The difference in saturation vapor pressure between lumpable condensables is not explicitly restricted in BCARY reduction. However, it is implicitly considered, as GENOA searches and attempts to lump species with similar saturation vapor pressures first. Nonetheless, the user can activate the option to limit the range of saturated vapor pressure differentials between lumpable condensables, along with other user-chosen reduction options listed in the supplementary material.

RC: *On line 130 they define "extremely fast reaction" suitable for pre-reduction as one with a reaction rate grater than 10^6 sec^{-1}. However, rates have units of concentrations per unit time, not $time^{-1}$. They should state that this is a unimolecular or pseudo-unimolecular rate constant.*

AR: Sorry for the misleading. We have corrected it in the paper:

> *Section 2.1, line 130:*
>
> This process skips extremely fast unimolecular reactions (i.e., the reaction rate constant of 10^6 s^{-1} corresponding to a lifetime of 1 μs) to avoid numerical problems.

RC: *On line 183 they call the MCM species BCALOO an alkoxy radical. It actually is supposed to represent a Criegee intermediate.*

AR: Thank you for pointing out the mistake. We have corrected it in the paper:

> *Section 2.2.2, line 182:*
>
> As shown in Table 2, the ~~alkoxy radicals~~ <u>Criegee intermediate</u> BCALOO formed ~~from~~<u>during the</u> ozonolysis of BCAL (reaction No. 11 in Table 1) is jumped over to its only destruction product BCLKET.

RC: *Couldn't the "jumping" example on Table 2 have been done at the "pre-reduction" step since it involves no change in predicted organic species? It does involve changes in inorganics, but as pointed out their reduced mechanisms are only used for SOA, which depends only on organic product predictions.*

AR: Although both pre-reduction and reduction via jumping are capable of jumping reactions without altering organics, they serve different purposes and act on different reaction pathways.

This pre-reduction is not intended to reduce the mechanism, but rather to provide a reliable reference mechanism. Therefore, it only involves very fast degraded species that undergo a single unimolecular reaction with a constant kinetic rate coefficient (e.g., no temperature effect). As these reactions are extremely fast (i.e., rate constant of 10^6 s^{-1}) and independent of environmental conditions, they only cause numerical issues in simulation and should be removed from the reference mechanism.

In contrast to pre-reduction, jumping is used to search for all possible reductions, which may involve reactions that are relatively slow or affected by environmental conditions. It is necessary to validate the reduction with an evaluation. As shown in Table 2, even though BCALOO degrades into a single species BCLKET, the process involves five bimolecular reactions that may vary depending on the environment (i.e., BCLKET-derived SOA may be affected by variations in inorganic concentrations and relative humidity). As a result, the example in Table 2 may be more appropriate for jumping than pre-reduction and requires further evaluation.

A few sentences have been added to the paper to clarify the difference between jumping and pre-reduction:

> *Section 2.2.2, line 188:*
>
> There are similarities between reduction by jumping and pre-reduction in the sense that both can jump reactions without affecting organic compounds. However, the two processes serve different purposes, as pre-reduction is intended to provide a reliable reference mechanism for training, whereas jumping is used in training to search for possible reductions. On the one hand, the current pre-reduction only reduces very fast degraded species that undergo a single unimolecular reaction with a constant kinetic rate coefficient (e.g., no temperature effect). In this case, one species may lead to several degradation products. As these reactions are extremely fast and independent of atmospheric conditions, they only cause numerical issues in simulation and should be removed from the reference mechanism. On the other hand, jumping may be relatively slow or affected by environmental conditions, and therefore, an evaluation is necessary. Jumping is currently limited from one species to another at a time. As shown in Table 2, the degradation of BCALOO into BCLKET involves five bimolecular reactions, which may affect SOA formation under different atmospheric conditions (e.g., with different inorganic concentrations and relative humidity (RH)).

RC: *Section C1 says figure C1 has the structures of the nitrates in the first lumping example, but I could not find them in this figure. I also could not find the structure of the species mentioned in the second example there.*

AR: Sorry for the mistake. We have added the molecular structures of C1313NO3, C152NO3, C1310OH, and BCALBOC to Fig. 1 (Fig. C1 in the appendix).
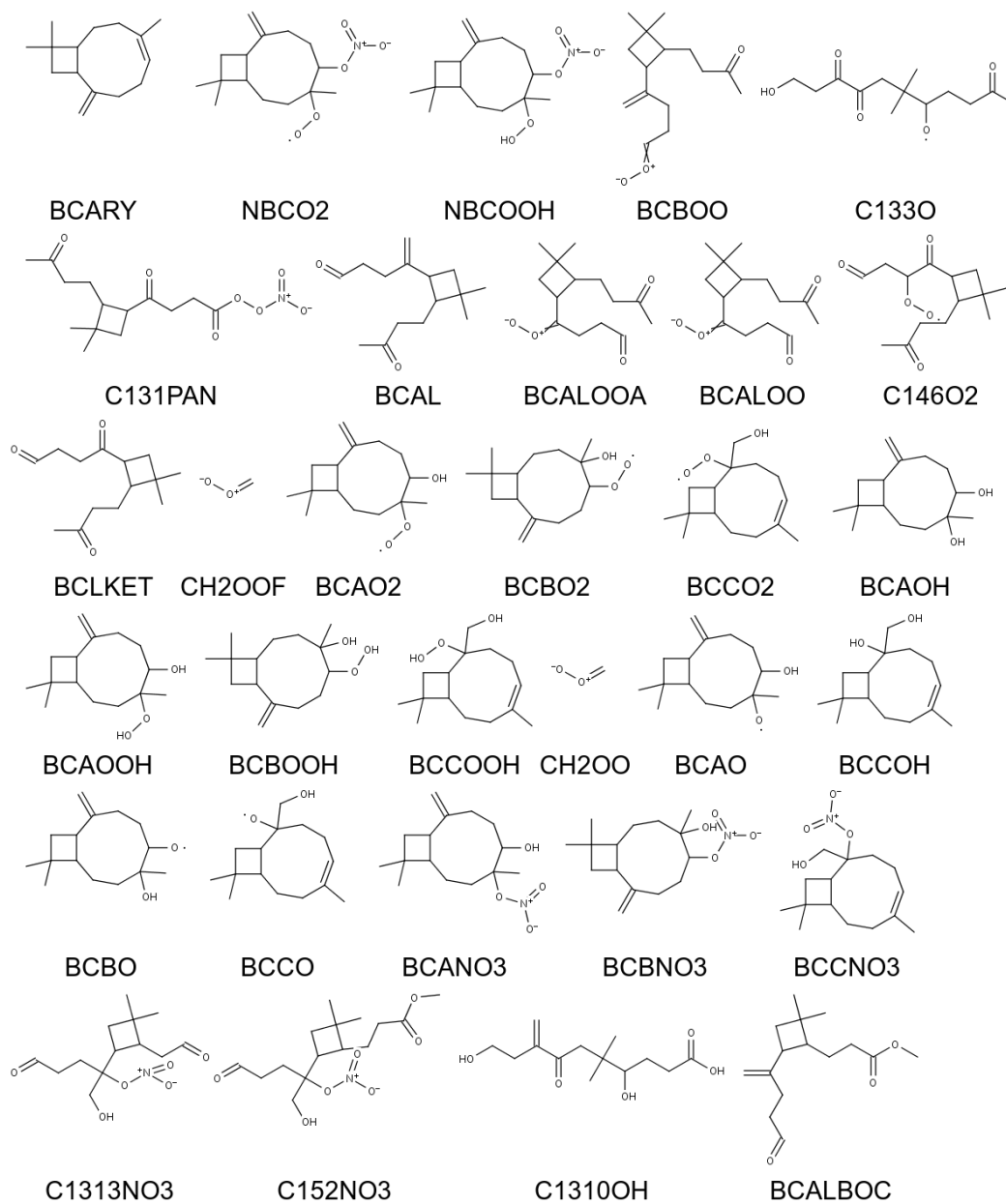
Figure 1: Molecular structures of the MCM species that are mentioned in the paper. For more information, please visit the MCM website.

RC: *The example shown on Tables 3 and 4 could be applied without conducting model simulations if the chemical lifetimes of all the species are the same, since the weighting ratios would then just be the branching ratios for formations of the 3 radicals. They are close to the same because the RO2+RO2 reaction is the only one where rate constants are different, and this is usually a very minor process compared to the competing reactions (see Figure 2), and the "removal" process should have removed these reactions before going to the "lumping" step. Maybe having an additional step between "removal" and "lumping" should be done to see what lumping can be done independent of environmental conditions."*

AR: Tables 4 and 5 demonstrate lumping and replacing (Original reactions in Table 3), which are not the real cases in the BCARY reduction, but were chosen for ease of explanation. Currently, all reduction strategies, including lumping, allow only a reduction of up to two species at a time. During the actual BCARY training, BCAO2, BCBO2, and BCCO2 were merged into one surrogate with two reductions: first, BCAO2 and BCBO2 were lumped together into mBCAO2 in a reduction via lumping, then BCCO2 was replaced by mBCAO2 in a reduction via replacing.

As the reviewer pointed out, it is logical to lump the MCM species BCAO2, BCBO2, and BCCO2 together due to their similar structures and reactions. Their weighting ratios for lumping can be derived directly from their branching ratios in the OH reaction of BCARY (Reaction No.17). In fact, we have tested this reduction, and it only introduced an average error of less than 0.1% (max error of 0.64%) on the testing dataset, indicating that it is a highly effective reduction.

Although the current training can lead to a similar result with two reductions, extra errors might be introduced due to the computation of the weighting ratios. Therefore, we agree with the reviewer that this type of lumping, which is solely based on species' theoretical similarity, can be an effective extension of the current lumping strategy. It may allow the lumping of multiple species at the same time and not compute weighting ratios based on the selection of the training dataset. Investigations are required to determine the general criteria for this new type of lumping.

We have added the explanation to the paper:

Section 2.2.3, line 209:

~~In~~ Chemical lifetimes and reference concentrations may be close for species that share similar structures and undergo analogous reactions. In cases where these species originate from the same reaction, they can be lumped directly, with the branching ratios of the formation reaction serving as weighting ratios. As an example, BCAO2, BCBO2, and BCCO2 undergo equivalent reactions, with the exception of the RO_2 reaction of BCBO2. Since the BCARY degradation is not much sensitive to RO_2, BCAO2, BCBO2, and BCCO2 can be lumped together with $f_{w,a}$, $f_{w,b}$ and $f_{w,c}$ equal to the branching ratios of reaction No.17, i.e., 0.408, 0.222, and 0.37, respectively.

Most lumping involves species that are not isomers and undergo different reactions, which makes lumping multiple species at the same time highly uncertain. Therefore, in practice, GENOA attempts to lump only two species in a single reduction in order to ensure ~~accuracy and effectiveness~~ the effectiveness of computation. A lumping of multiple species can be achieved by combining several reductions (e.g., first lumping BCAO2 with BCCO2 to form mBCAO2, and then lumping BCBO2 into mBCAO2).