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

Reviewer # 3

RC: *This paper presented a reduction strategy and developed a software package to reduce the mechanism of SOA formation. The paper is reasonably well written. The method described is innovative and effective. However, there are some information misleading and inappropriate. The current manuscripts needs to be modified before it is accepted for publication.*

AR: We would like to thank reviewer # 3 for the positive comments and constructive suggestions, which helped us to substantially improve our manuscript. We have carefully considered all of these 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.

1. General comments

RC: *The authors chose sesquiterpenes as an example to show the methods to reduce SOA formation mechanism.*

AR: Sesquiterpene was selected because it is a well-known source of SOA, and its formation mechanism is well documented. Sesquiterpene is also an ideal candidate for model development and demonstration of the reduction methodology, as the oxidation products of sesquiterpene are less volatile and tend to condense more readily than those of lighter molecules such as monoterpene and isoprene.

We have added the reason why we selected sesquiterpene to the main paper:

> *Section 1, line 72:*
>
> The application of GENOA to the MCM degradation scheme of β-caryophyllene (BCARY) (Jenkin et al., 2012) is described in Sect. 3. ~~The~~ β-caryophyllene ~~species is selected because it widely serves as a benchmark for modeling the tropospheric chemistry and SOA formation relevant to~~ is selected for investigation and demonstration of the GENOA algorithm, because it is one of the most abundant and representative sesquiterpene (SQT)~~(e.g., Li et al., 2015; Xavier et al., 2019), and its degradation has been evaluated in chamber simulations (Jenkin et al., 2012). The BCARY scheme in the STOCHEM-CRI mechanism (Khan er al., 2017) and~~ Sesquiterpenes are well-known source of SOA (Hellén et al., 2020; Tasoglou and Pandis, 2015 and the formation mechanism of BCARY is well documented in the ~~experiment data of Tasoglou and Pandis (2015) are also used for evaluation of~~

near-explicit MCM mechanism (Jenkin et al., 2012). Studies have also compared BCARY SOA yields simulated using the MCM mechanism to chamber data (e.g., Xavier et al., 2019). BCARY is therefore an ideal candidate for model development and demonstration of the reduction methodology. In this paper, the near-explicit MCM BCARY degradation scheme serve as a reliable benchmark for GENOA. The experiment data from Tasoglou and Pandis (2015); Chen et al. (2012) are also compared to the newly developed reduced mechanism in Appendix A.

RC: *One obvious question is that most of the reactions listed are linear and therefore analytical solutions can be achieved. In such case, the reduction may be of less significance.*

The formation of SOA from VOC degradation involves many processes, including gas-phase multi-generation oxidation and gas-to-particle mass transfer. These processes are highly non-linear. For example, the gas-to-particle mass transfer depends on the concentration and composition of both the gas and the particle phases. As the particle composition depends on the environmental conditions and on the formation of other organic compounds (i.e., non-ideality), it is not possible to define an analytical solution. The process of SOA formation from sesquiterpene is, therefore, complex and non-linear.

RC: *Moreover, the authors did not show the impact of reduction on the concentration of short-lifetime oxidants, such as OH, HO2 and NO3, which have an important influence on SOA yields. How are the coupling between VOC species and oxidants resolved? Reasonable explanations should be highlighted.*

AR: The reduced SOA mechanism focuses solely on reproducing the SOA concentration of those simulated with explicit mechanisms, with fewer species and reactions. Thus, the oxidant concentrations are simulated using implicit gas-phase chemical mechanisms. Current reduced mechanisms do not affect the concentrations of O_3 and major radicals (OH, NO_3, NO, HO_2) produced by the implicit gas-phase mechanism.

In air quality modeling, implicit SOA mechanisms are often based on the surrogate approach (e.g., Odum's two-product) or the Volatility Basis Set. They are added to implicit gas-phase mechanisms without altering the pathways of oxidants. The same approach is adopted for our semi-explicit SOA mechanisms. Our reduced SOA mechanisms, which include gas-phase chemical mechanisms and aerosol properties for condensable gas-phase species derived from certain SOA precursors, can be added to the implicit gas-phase mechanism in the 3-D model. For example, the 3-D CHIMERE model can simulate SOA using the implicit gas-phase mechanism MELCHIOR2 and SOA mechanism H^2O [Couvidat et al., 2018]. With our reduced SOA mechanisms, SOAs in CHIMERE are simulated by MELCHIOR2, the reduced SOA mechanisms generated by GENOA, and H^2O for other SOA precursors not covered by our mechanisms.

For the paper, We have added the explanation of how the coupling is generally resolved between VOC species and oxidants in 3-D models:

Section 1, line 36:

~~Along with~~ To complete implicit gas-phase mechanisms, implicit SOA mechanisms have been developed to model specifically the SOA formation without modifying the concentrations of ozone and major radicals (Kim et al., 2011) . In 3-D modeling, implicit SOA mechanisms or parameterizations are usually added to implicit gas-phase mechanisms, conserving the oxidant chemistry of the implicit gas-phase mechanism.

Implicit SOA mechanisms are often established based on experimental data from smog chamber experiments to represent the formation and evolution of SOA, such as the two-product empirical SOA

> model (Odum et al., 1996) and the volatility basis set (VBS) that splits VOC oxidation products into a uniform set of volatility "bins" Donahue et al., 2006).

We have also added the following statements about our semi-explicit mechanisms:

> *Section 2, line 80:*
>
> The generated semi-explicit mechanisms are designed to preserve the accuracy of explicit mechanisms for SOA formation, while keeping the number of reactions/species low enough to be suitable for large-scale modeling, particularly ~~3D~~ in 3-D AQMs. The focus of the semi-explicit mechanism is solely on the accurate modelling of SOA. Because ozone, major radicals, and other inorganics are also affected by inorganic and other VOC chemistry, their concentrations are not tracked with the semi-explicit mechanism. Instead, they are simulated using existing implicit gas-phase chemical mechanisms.

Additionally, details about implicit gas-phase mechanisms of the 3-D CHIMERE model and how 3-D CHIMERE results are used for 0-D simulations have been added to the paper:

> *Section 2.2, line 193:*
>
> The version of CHIMERE and its configuration is described in Lanzafame et al. (2022). The ~~monthly average~~ 3-D CHIMERE simulations were conducted with the implicit gas-phase MELCHIOR2 mechanism (Derognat et al., 2003), which contains 120 reactions and less than 80 lumped species. The MELCHIOR2 mechanism describes the degradation of sesquiterpenes by three oxidant initiated reactions (HUMULE reacts with OH, O3, and NO3, respectively), where the the species HUMULE represents the lumped class of all sesquiterpenes.
>
> The monthly diurnal profiles of hourly meteorological data (e.g., temperature, relative humidity), and hourly concentrations of ~~oxidants and~~ oxidant, radical, and other inorganic species were extracted from each location. That information is required in the 0-D simulations with SSH-aerosol (see section 2.4) to reproduce SOA concentrations and compositions under near-realistic conditions. Since the reduced SOA mechanism focuses only on SOA formation, the meteorological data and the concentrations of oxidants, radicals and inorganics are assumed to remain intact during the 0-D SOA simulation. The coordinates and time of each condition are also provided to calculate the solar zenith angle. Because the reduction focuses on the impact on SOA variation, and because no inorganic reactions are considered in the reduced chemical mechanism, the oxidant, radical and inorganic concentrations ~~are fixed as the hourly background~~, as well as the environmental parameters, are fixed to the diurnal profiles obtained from the CHIMERE data in 0-D SOA simulations. The concentration of HUMULE (denoted C_{SQT} as the CHIMERE surrogate for sesquiterpene ~~(denoted C_{SQT})~~ is used to estimate the SQT concentration.

Moreover, the GENOA methodology would preserve both SOA and oxidant concentrations in the reduced SOA mechanism if relevant criteria were included in the training process. This may be a potential direction for future development of the GENOA algorithm.

RC: *Since GENOA is a semi-explicit mechanism and designed to be used in 3-D models, how can the species in GENOA be matched with the species in 3-D models. One problem that arises is whether GENOA is scale adaptive so that the transport of organic species is well resolved depending on the problem of concern. If not, the package may be useful in optimizing mechanisms for specific urban scenarios and then used in regulatory modeling rather than stated "multi-scale AQM" by the authors.*

AR: As we mentioned in the previous comment, semi-explicit SOA mechanisms are added to the implicit mechanisms of the 3-D model. The additional species from semi-explicit SOA mechanisms are then transported by the 3-D model. In the case of sesquiterpene-SOA, only 14 gas-phase species within six condensable species need to be added to the 3-D model, which is a computational scale that is fully acceptable for transport in 3-D modelling. When applied to nested simulation domains (for example over an European domain, a domain over a country and over a city), the user need to use the same semi-explicit SOA mechanisms across all domains, so that the species are the same for transport. In that case, the SOA mechanism has to be trained under all conditions that might be encountered in each domain. As such, GENOA is not "scale adaptive", since the size of the mechanisms does not change with the domain size. Therefore, transport of those additional VOC species is not a problem. To avoid confusion, we have removed the word "multi-scale" from the paper.

RC: *It would be more useful if the manuscript can include some information on memory optimization and computational efficiency.*

AR: Thanks for the suggestion. We have included the reduced CPU time for the testing process in the paper:

> *Section 3.2.1, line 380:*
>
> During the testing procedure, the "Rdc." mechanism is evaluated at 12 159 locations, with two different starting times (0 h and 12 h). The 0-D testing for "Rdc." took approximately 2% of the CPU time consumed by MCM.

In addition, we have tested the memory usage of the MCM and RDC mechanisms with the box model SSH-aerosol. As shown in Fig.1, the peak memory consumption is reduced by 96% (from 11.8 MiB to 577.1 KiB) after the reduction. It should be noted that the result of 0-D testing may not be linear to the computational efficiency of 3-D modeling since 3-D simulations include other processes (e.g., transport, deposition). However, the results confirm that the semi-explicit SOA mechanism is conducive to large-scale modeling.

Generally speaking, in 3-D modelling, the most time-consuming process is solving the gas-particle partitioning in SOA modelling. The number of condensable species has a significant impact on CPU performance. As for memory consumption, it varies with the number of species transported especially in the condensed phase, as those are often considered for different particle sizes. Therefore, decreasing the number of compounds that may partition to the condensed phase is a priority for semi-explicit mechanisms. For sesquiterpene, the number of condensables increases only by six, which is acceptable for most large-scale simulations.

2. Specific comments

RC: *L26: three-dimensional models -> three-dimensional (3-D) models*

AR: Revised.

RC: *L27: 3D -> 3-D*

AR: Changed.

RC: *L32: carbon-bound -> carbon-bond*

AR: Changed.

Figure 1: Memory maps for MCM (top panel) and "Rdc." (bottom panel) mechanisms simulated with SSH-aerosol under the same conditions. The graphs are generated with massif-visualizer.

RC: *L34: The expression "These mechanisms were primarily developed for ozone simulation" may be NOT appropriate.*

AR: Sorry for the ambiguity. This phrase has been revised as follows:

> *Section 1, line 34:*
>
> ~~These mechanisms were primarily developed for ozone simulation and reflect only the most significant chemical phenomena occurring in the atmosphere, where VOCs are represented by~~ Implicit gas-phase mechanisms were developed and validated to simulate the concentrations of oxidants and other conventional air pollutants such as ozone and NO_2. In these mechanisms, VOCs have been grouped into a limited number of model species because of computational considerations, and the SOA formation is usually not considered.

RC: *Table 1: As the authors stated "using surrogates assigned to molecular structures", listing the information of molecular structure of major species in another table would be better for other researchers to understand the reduction strategy.*

AR: Thanks for the helpful comment. An Excel file containing molecular structures of condensable species in the "Rdc" mechanism (Fig. 2) will be added as a new supplementary material.

RC: *Table2: please check the expressions of reactions and coefficients.*

AR: Sorry for the misleading. The wrong coefficient has been corrected in Table 2 of the paper (0.8 BCBO to 0.6 BCBO). We have also checked that the RO2 reaction of BCBO2 indeed produces species BCAOH, not BCBOH (which does not exist in the MCM mechanism).

RC: *L425-428: Some quantitative explanations associated with the results in L415-418 is necessary.*

AR: Thanks for the suggestion. We have added the explanation as follows:

> *Section 3.2.2, line 425:*
>
> The N/C ratio, however, is underestimated by the "Rdc." mechanism by 37 % on average (ratio equal to 0.019 in MCM and to 0.012 in "Rdc.")~~. The N/C ratio is consistent with the nitrogen-containing SOA mass distribution discussed previously, as a result of~~, indicating the over reducing organic nitrites in ~~the building process of~~ "Rdc.". A total of three nitrogen-containing organics (NBCO2, NBCOOH, and C131PAN) are preserved in "Rdc.", of which two (NBCO2, NBCOOH) are first-generation products. Therefore, during the first 10 hours, the N/C ratio curve simulated by "Rdc." drops, whereas in MCM it increases as higher-generation nitrates are produced.

References

[Couvidat et al., 2018] Couvidat, F., Bessagnet, B., Garcia-Vivanco, M., Real, E., Menut, L., and Colette, A. (2018). Development of an inorganic and organic aerosol model (chimere 2017β v1. 0): seasonal and spatial evaluation over europe. *Geosci. Model Dev*, 11(1):165–194.

Name of the UNIFAC groups	Index	NBCOOH	C141CO2H	BCKSOZ	C133CO	C132OOH	C131PAN
alkane CH3	0	3.00E+00	1.89E+00	2.90E+00	8.20E-01	2.97E-02	2.00E+00
alkane CH2	1	5.00E+00	4.69E+00	3.10E+00	1.64E+00	5.73E-02	4.00E+00
alkane CH	2	2.00E+00	1.89E+00	2.00E+00	8.19E-01	1.70E-02	2.00E+00
alkane C	3	1.00E+00	9.45E-01	9.99E-01	4.10E-01	1.49E-02	1.00E+00
methanol CH2OH	5		5.53E-02	5.24E-04	5.85E-01	9.85E-01	
methanol CH2OH	6		6.90E-04	9.27E-07	3.09E-04		
methanol COH	7		1.42E-04	5.30E-04	6.96E-05	3.02E-04	
calcohol between two alcohols OHCH2OH	9		4.09E-04	2.04E-05	1.22E-04	1.21E-03	
calcohol between two alcohols OHCHOH	10		2.72E-04	1.30E-05	1.22E-04	6.05E-04	
calcohol between two alcohols OHCOH	11		6.90E-04	6.48E-06	6.10E-05	3.02E-04	
calcohol in tails of alcohol OHCH3OH	12		1.11E-01	1.34E-03	1.18E+00	2.27E+00	
calcohol in tails of alcohol OHCH2OH	13		1.11E-01	2.34E-03	6.06E-01	3.47E+00	
calcohol in tails of alcohol OHCHOH	14		1.05E-05	1.05E-03	1.00E-02	1.32E+00	
calcohol in tails of alcohol OHCOH	15		5.47E-02	5.24E-04	5.90E-01	9.85E-01	
alkene CH2=C	18	1.00E+00	1.00E+00				
alkene CH=C	19		5.27E-06				
alcohol OH	26		5.61E-02	1.05E-03	5.90E-01	9.85E-01	
ketone CH3CHO	29		9.92E-01	1.01E-01	9.95E-01	6.96E-01	1.00E+00
ketone CH2CHO	30		1.24E-01	9.99E-01	2.17E+00	6.69E-01	1.00E+00
aldehyde CHO	31		1.42E-02	1.01E-01	5.42E-03	1.88E-01	
ester CH3COO	32				5.30E-03	3.75E-03	
ether CHO	36			8.99E-01		2.96E-01	
carboxylic acid COOH	37		9.39E-01		4.10E-01	1.89E-02	
nitrate CHONO2	40	1.00E+00					
hydroxyperoxide CH2O-OH	42					2.59E-04	
hydroxyperoxide CHO-OH	43					1.68E-01	
hydroxyperoxide CO-OH	44	1.00E+00				8.32E-01	
hydroxyperoxide CHO-OC	52			8.99E-01		2.96E-01	
peroxyacyl nitrates PAN	54						1.00E+00

Figure 2: UNIFAC functional group decomposition for the condensable species in the "Rdc." mechanism.