

***Interactive comment on* “Mechanism reduction for the formation of secondary organic aerosol for integration into a 3-dimensional regional Air Quality Model: α -pinene oxidation system” by A. G. Xia et al.**

A. G. Xia et al.

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We are grateful to the referees for their insightful comments on this work. The discussion points from the two referees are dealt with in detail below. A revised manuscript reflecting some of the referees' suggestions will be submitted.

> Referee 1, comment 1: the application of the "Principal component analysis" method, particularly with regard to eigenvalues and eigenvectors and how the threshold criteria are applied to them. It is not clear what these mean and how these are derived. Also, how do you apply a scalar threshold quantity to a vector?

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The part (section 2.4.2) of introducing "principal component analysis" has been revised. In particular, the derivation of the PCA method via an objective function and the interpretation of the eigenvalues and eigenvectors are given to indicate how the method is used to find important reactions. In addition, the threshold criteria are included in this revised part.

> Referee 1, comment 2: the utility and general applicability of the "linear lumping method"

The referee questioned the application of the "linear lumping method" for a real world model which must cover many emitted VOCs. He also made recommendations to lump "many of the different ketone, PAN, hydroperoxide, or acid isomers that are formed in this mechanism" by using reactivity-based lumping approach.

Lumping based on the chemical structure and reactivity is referred as chemical lumping method. It is a widely used method for developing and/or reducing a chemical mechanism. Many directly emitted VOC species have been lumped in this way to describe the formation of ozone. In addition, many products with similar chemical structures, such as the ketones, PAN, hydroperoxide could have been lumped.

Another lumping approach is mathematically based. Based on rigorous or relaxed mathematic transformation, the number of species could be reduced. Many techniques (Li and Rabitz, 1989; Li and Rabitz, 1990; Li et al., 1994a; Li et al., 1994b; Huang et al., 2005) have been developed to describe the exact and/or approximate lumping since the original mathematically based lumping approaches were proposed (Kuo and Wei, 1969; Wei and Kuo, 1969). The simple linear lumping method developed in this paper is a method that belongs to this class of mathematically based lumping approach.

A key component of the mathematical approaches is that the test sets of initial concentrations span the range of realistically possible species concentrations: if the VOC ratios do not change over the range of reasonable atmospheric conditions, the mathematics show that the lumping is reasonable in that the impact on the remainder of

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the mechanism is below the error criterion. If the VOC ratios do vary over different test cases, then the VOCs would not be selected for lumping. For a mechanism with many precursor VOCs, it is thus more likely that the product VOCs from a given precursor may be lumped, rather than the initial precursor VOCs themselves. An exception would be a case in which a pair of precursor VOCs with similar reactivities are emitted in similar ratios by a relative small number of emitting processes.

The linear lumping method can be applied complementarily to chemical-based lumping method. Linear lumping is unlikely to lump products from different emitted species, but it could lump the products and/or intermediate products from one single source as demonstrated in this paper.

> Referee 1, comment 3: The reduction methods, such as the DRG or DRGEP methods, simply eliminate species, without replacing them by something to make up for the loss. This results in biases and radicals unconserved in the mechanism's simulations. If the "unimportant" species were not simply removed, but replaced by some "major" species that is closest to it in reactivity, then at least you would not be biasing the mechanism, and if done properly the resulting errors may tend to cancel out. Some cases it may be appropriate to increase the rate constant for competing reactions or somehow lump it with competing processes rather than just removal.

The performance of the reduced mechanism based on the DRG or DRGEP method depends strongly on the chosen threshold. The 20% bias found in the tests performed here could be reduced through using a more restrictive threshold criteria in the selection process. The selection of the optimum threshold value is a balance between mechanism accuracy and reduction intensity. A smaller threshold value would lead to a better model performance for ozone and the SOA formation. In the future, a constraint of an upper limit error (say 5% or 10%) for ozone and the SOA should be applied in mechanism reduction procedure.

According to the definition of the DRG and DRGEP methods, if a radical is removed

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by either method at a chosen threshold, it means the radical is not important to the production and loss of any important species.

DRG and DRGEP methods are very efficient to reduce large chemical mechanisms. The computational cost to reduce a chemical mechanism is linear to the number of the chemical species. Both methods require a minimum system-dependent knowledge to reduce chemical mechanisms.

However, we used two different computer systems to perform the mechanism reduction: (1) running a box model for all different scenarios in a Linux machine; and (2) performing data-analysis by using MATLAB on a Window XP machine. So a trial-and-error method was used to find an optimum. In the future, reducing chemical mechanism via DRG or DRGEP method can be performed automatically in one machine when a constraint for maximum error is applied.

We agree with the referee that DRG and DRGEP methods need to be improved with further examination of the removed species and reactions. The referee recommends some practical methods to improve the methods, such as replacing the "unimportant species" with chemically related "major species" and modifying reaction rate coefficient to compensate on the removal of completing reactions. All the recommendations merit further investigation.

> Referee 1, technical correction 1: The meaning of the "stoichiometric coefficient" for reactants and products in Equation (1).

As suggested by the referee, the characteristics of the positive and the negative features for the "stoichiometric coefficient" are explicitly explained immediately after the introduction of Equation (1) in the revised manuscript.

> Referee 1, technical correction 2: it appears that Equation (6) and Equation (10) are inconsistent with regard to the sign of these coefficients. If positive coefficients are used for products shouldn't the "-" in Equation (6) be removed since if a compound is

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the product in a reaction?

A typo of the negative sign "-" in Equation (6) was removed in the revised manuscript.

> Referee 1, technical correction 3: On page 13326 line 7 they refer to "reduced mechanism from stage 4 #2". But to be consistent with Table 1 shouldn't it be #3?

There is a typo on page 13326 line 7. It should be referring to "reduced mechanism from stage 4 #3"

> Referee 1, technical correction 4: Some of the url's given in the reference list for obtaining reports by Carter are given as pah.cert.ucr.edu. Those addresses are no longer valid, and need to be changed to www.cert.ucr.edu.

The URLs for Carter's reports have been changed from pah.cert.ucr.edu to www.cert.ucr.edu in the revised manuscript

> Referee 2, comment 1: The broader applicability of the linear lumping approach to atmospheric organic chemistry mechanisms: the approach as described can yield practical reductions only in relatively simple systems (e.g., chamber experiments with a single VOC). In full atmospheric mechanisms there are many more emitted VOCs (from different sources with different speciations and temporal profiles), and many products can be formed from more than one precursor and at more than one generation of oxidation.

The linear lumping method can be applied complementarily the chemical-based lumping method. It is unlikely to lump products from different emitted species, but it could lump the products and/or intermediate products from one single source as demonstrated in this paper. Note that this would come out of the error analysis; the products of the same precursor VOC would have a greater tendency to be "lump-able"; the method would tend to not recommend lumping of species with different precursor VOCs, since the latter would be less likely to maintain a constant relative ratio over different test cases and over time.

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> Referee 2, comment 2: how the work described fits into the larger programme of work implied by the title, perhaps some indication should be given on what level of simplicity is required for the target 3-D modelling activities, and on how the current works fits into the broader work programme implied by the title of the paper.

Within a much larger framework for the SOA formation, alpha-pinene and isoprene are served as two surrogates for the SOA formation from biogenic sources. In addition, another two aromatic compounds, toluene and m-xylene, represent anthropogenic sources for SOA formation. The total number of species of the full chemical system for the four species is 814. If a reduction ratio of 2.5-3.0 is applied to the full mechanism using the reduction methods described in this paper, it is estimated that the total number of organic species and radicals is about 270-300. Finally, a reactivity-based lumping approach would be applied to reduce the number of the chemical species to around 200 for use in a 3D air quality model.

Note that one reference has been changed in our paper; we replaced the old reference of

Huang, H., Fairweather, M., Tomlin, A. S., Griffiths, J. F., and Brad, R. B.: A dynamic approach to the dimension reduction of chemical kinetic schemes, *Computer-Aided Chemical Engineering*, 20A, 229-234, 2005

with the new reference of

Huang, H., Fairweather, M., Griffiths, J. F., Tomlin, A. S., and Brad, R. B.: A systematic lumping approach for the reduction of comprehensive kinetic models, *P Combust Inst*, 30, 1309-1316, 2005

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 8, 13301, 2008.

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