Atmos. Chem. Phys. Discuss., 11, C3770–C3780, 2011
www.atmos-chem-phys-discuss.net/11/C3770/2011/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Development of a simple unified volatility-based scheme (SUVS) for secondary organic aerosol formation using genetic algorithms" *by* A. G. Xia et al.

A. G. Xia et al.

airquality@gmail.com

Received and published: 22 May 2011

We are very grateful to Dr. Stockwell, Dr. Pankow, and our third anonymous referee for their insightful comments on this work. The discussion points from the three referees are dealt with in detail below. A revised manuscript reflecting some of the referees' suggestions will be submitted.

>Comment 1 from Dr. Stockwell: The main concern is that the validity of their scheme is limited by the validity of the Master Chemical Mechanism. While the MCM has considerable detail it is far ahead of the experimental data. Although the MCM is a very worthy effort, much of it is built from estimates, extrapolations and mechanistic

analogies based on the limited available laboratory data.

RESPONSE: Essentially, the validity of the new simple unified volatility-based scheme (SUVS) depends strongly on the "experimental data" used by genetic algorithms for data fitting.

In this work, the "experimental data" were obtained through simulating the chemistry in the MCM v3.1 under a wide range of conditions. As pointed out by Dr. Stockwell and our third referee, major uncertainties for the MCM v3.1 stem from the use of structure activity relationships for development and construction of this mechanism.

Here, we would like to emphasize that the focus of this paper is developing a methodology. If the benchmark mechanism of MCM v3.1 is revised, we can apply the same methodology to update the 412 parameters to reflect new changes. Meanwhile, the "experimental data" could also be generated by simulating other similar explicit chemical mechanisms, such as the self-generating mechanism (Aumont et al., 2005), or by using the real smog chamber experimental data.

>Comment 2 from Dr. Stockwell: Another concern is that the final result is a highly parameterized fit. Although the fit may be sufficient for modeling it does not appear to provide much insight into the real atmospheric processes that scientists what to understand. Maybe the authors would want to comment on this point.

RESPONSE: We agree with Dr. Stockwell that physical and chemical interpretation of the set of 412 parameters derived for the SUVS is important for understanding the real atmospheric process. Elliott et al. (2003) showed that incorporation of physical bounds on rate parameters ensures minimization of non-physical solutions using genetic algorithms. In this work, we investigated valid ranges of 100 reaction rate constants and 312 stoichiometric coefficients.

In the MCM, the reaction rate constants are different for different functional groups. Overall, they vary from 1.0e(-16) to 1.0e(-10), except for those in reactions (61-70). In

ACPD

11, C3770–C3780, 2011

the SUVS, for simplicity, 90 out of the 100 reaction rate constants were set in the same range outlined in Eq. (10). Similarly, the ranges of the stoichiometric coefficients are found to be reasonably lied between 0 and 1.0. In short, the physical bounds of the reaction rate constants and stoichiometric coefficients are within realistic constraints. Note that the reaction rate coefficient in the SUVS might be different from those in the MCM even for the same reaction type, because the species from the MCM are lumped in the SUVS. This is the reason why a wider range of the reaction rate constants are set for the SUVS.

Because all unknown parameters in the SUVS are bounded to certain valid ranges, they should give physical interpretation, but not a unique solution. This is because genetic algorithms, similar to neural network method, sometimes produce many different sets of parameters with good fit. One possible way to solve this issue to get an identical “best” solution is to use a hybrid optimization technique (Renders and Flasse, 1996;Rodriguez-Fernandez et al., 2006). This means other optimization methods are applied to post-process candidate solutions when no further improvement was found using the genetic algorithms. The uses of suitable optimization methods to post-process a large multi-dimensional system, such as the SUVS, merit further investigation.

Finally, some mechanism reduction techniques, such as those used in Xia et al. (2009), could be applied further to remove some reactions and/or some species from product list in some reactions, once contributions of those selected reactions to changes of species concentration are found to be always negligible.

>Comment 1 from Dr. Pankow: The use of the term "unified" here refers to the solid work of the authors to provide a "unification" of 1)kinetic models (as in the MCM), with 2) a simple representation of the volatility distribution for constituents of organic particulate matter. However, this reviewer finds it an overstatement to use "unified" to refer to the results of this work. In particular, "unified" would suggest that simultaneous consideration of all important parameters and modelling needs has been accomplished,

ACPD
11, C3770–C3780, 2011

and this is not the case. . . . consideration of activity coefficients must thus be included in any "unified" aerosol formation model.

RESPONSE: As summarized by Dr. Pankow, the term of “unified” in this manuscript refers to the unification of kinetic models under volatility-based framework (Donahue et al. 2006).

The inclusion of activity coefficients could potentially have a significant impact, relative to using unity. In this work, a value of unity for the activity coefficients was used here in order to simplify the calculations and avoid the need for group method estimation of activities. However, it should be noted that under conditions of high relative humidity non-unity activity coefficients may significantly perturb the partitioning. This effect should be examined in future research.

As we mentioned in our replies to Comment 1 from Dr. Stockwell, the “experimental data” used for optimization of the SUVS are not limited only to the explicit chemical mechanisms, such as the MCM. We could also use real smog chamber experimental data. In the later case, we believe that the unity and/or non-unity activity coefficients for all compounds are embedded into the term of “effective saturation coefficient” (Donahue et al. 2006) when using experimental data. In this sense, if we used laboratory data in fitting, we would be assuming that the laboratory generated particles behave as real ambient particles. Ultimately, the consideration of activity coefficients in the SUVS system is automatically included in the unification work for the kinetic model and the VBS set proposed in this SUVS framework.

>Comment 2 from Dr. Pankow: As a side note, on page 14 the activity coefficient zeta_i is incorrectly identiïňĄed as the "molality-based activity coefficient". In fact, zeta_i is the mole-fraction-scale-based activity coefficient.

RESPONSE: Thanks to the correction of the zeta_i to be mole-fraction-scale-based activity coefficient.

ACPD

11, C3770–C3780, 2011

>Comment 1 from Referee #3: How is the inorganic gas-phase chemistry handled? It would be helpful to include in the paper few sentences explaining how the SUVS is connected to the gas phase chemical scheme.

>Comment 2 from Referee #3:: Does the SUVS modify the Ox/NOx/HOx budget? On the other hand, if the SUVS scheme does not modify the budget of the inorganic species, then how is the HOx/NOx/Ox budget handled in the simulation including the SUVS?

RESPONSE: The two questions are related. We answer them together.

Theoretically, the inorganic gas-phase chemistry should be coupled with SUVS. This means reaction scheme should be revised to reflect HOx/NOX/Ox budget in the product list of these reactions.

Practically, in this work, our primary focus is to develop a simple scheme for organic aerosol formation. In order to derive unknown parameters for this scheme, we treat the HOx/NOx/Ox budget in a very simple way.

Specifically, by running MCM, we first obtain hourly profiles of all inorganic species and the starting organic species of alpha-pinene for a given scenario.

Next, the concentrations of these species are linearly interpolated within each one-hour period. These spline function interpolated concentrations are plugged into KPP generated Rosenbrock ODE solver to calculate the evolution of the SUVS 30 organic species during the 72-hour period.

As explained above, the inorganic gas phase chemistry was indirectly connected to the SUVS. The SUVS scheme does not modify the budget of any inorganic species. If one is interested to use the current version of SUVS, he has to provide the profiles of the inorganic species. Our future work would involve coupling of the inorganic and organic gas-phase chemistry. This means the inorganic species would appear in the product list in the SUVS, and the gas phase inorganic chemistry would be included. As

ACPD

11, C3770–C3780, 2011

suggested by our third referee, we will add a few sentences to explain the treatment of the inorganic chemistry and the Ox/NOx/Ox budget in our revised manuscript.

>Comment 3 from Referee #3: How reliable and useful is the SUVS scheme? The reliability of the SUVS scheme is directly linked to the accuracy of the MCM scheme.

RESPONSE: This question echoes the same MCM uncertainty issue raised by Dr. Stockwell. Please refer to the response to comment 1 from Dr. Stockwell in this reply.

>Comment 4 from Referee #3: The reliability of the final SUVS also depends on the accuracy of the method used to estimate these properties.

RESPONSE: If the MCM or other similar explicit chemical mechanism is used to generate the "experimental data" to describe evolution of the 10 lumped species (S), we agree that this work on the SUVS depends on the accuracy of the estimation methods for boiling points, vapor pressure, activity coefficients (if non-unity activity coefficients need to be calculated), and the lumping approach. This is the case for our study in this work.

On the other hand, if the real smog chamber experimental data were used to describe evolutions of volatility-based species required by the SUVS, the accuracy of the SUVS would depend on the accuracies of instruments to measure concentrations and volatilities.

>Comment 5 from Referee #3: The chemistry of most species produced after few oxidation steps is described in simplified way in the MCM. I don't think that the MCM (or any other detailed/explicit scheme) can be considered as a faithful representation of the actual atmospheric processes leading to SOA formation. It would therefore be useful that the paper includes a short discussion that put in perspective the reliability of the final SUVS.

RESPONSE: We agree that the MCM or other similar explicit scheme is only a simplified representation of the actual atmospheric process for SOA formation. To accurately

ACPD

11, C3770–C3780, 2011

describe ambient atmospheric oxidation system, the data used for the development of the SUVS should be based on real experimental data in both gas and aerosol phases. This paper represents the first step to study the SUVS only for alpha-pinene gas phase oxidation by using MCM v3.1 at a reference temperature. Our future research will investigate the single final SUVS system. This single system would be able to describe oxidation of different primary species, including multispecies system, for SOA formation. To acquire such a system, it requires compiling and integrating available smog chamber data into the SUVS by using the genetic algorithms.

As suggested by our third referee, we outlined the reliability of the final SUVS in the last part of the revised paper.

>Comment 6 from Referee #3: The optimization process seems to be too expensive to be performed systematically. I have the feeling that, at least for exploratory simulations, this computational cost could be used to directly solve the MCM in a 3D models (see for example Jacobson and Ginnebaugh, JGR, 2010, DOI:10.1029/2009JD013289 or Ying and Li, Atmos. Env., 2011, doi: 10.1016/j.atmosenv.2011.03.043).

RESPONSE: It is very interesting to see that the MCM has been implemented into 3D models in two recent works ((Jacobson and Ginnebaugh, 2010) and (Ying and Li, 2011)) without modification of gas-phase chemistry. Note that only gas phase chemistry for ozone formation is studied in both works. In order to study the organic aerosol formation by the complete MCM in the 3D model, the memory demand would be higher, because all condensable species from the MCM would exist in both gas and aerosol phases. The later part needs extra memory burden. In addition, our previous study (Xia et al, 2008) indicated that the computational cost for organic gas/particle partitioning process would be nine times higher than the gas phase chemistry at the given error threshold.

Most importantly, our objective is different from inclusion of detailed MCMs into the 3D models for three reasons. First, the SUVS is a very simple scheme with limited num-

ACPD

11, C3770–C3780, 2011

ber of species (30 species plus a number of starting primary organic species). When this scheme is finalized, it could be used in the regional and global model to study ozone and the SOA formation with little memory and computational cost. Second, as we mentioned early in our reply, SUVS is flexible and has the capacity to incorporate smog chamber data to study SOA formation. In contrast, simulating of the organic aerosols by using the MCM sometimes need to be adjusted by varied factors (Jenkin 2004, Johnson et al, 2006). Finally, this work was completed in the IBM power4 supercomputer with the use of 64 nodes. The total computational cost was acceptable at 5 days and 18 hours. Even when the MCM is revised, we could obtain the revised set of parameters for the SUVS within a week.

>Comment 7 from Referee #3: Is the SUVS approach sustainable? Furthemore, the authors claim that "the same SUVS with update parameters could be used to describe the SOA formation from different precursors". Does it mean that: a single SUVS can be tailored for various mixtures of primary species? In that case, is there good reason to believe that a reliable single set of parameters can be used to describe various mixtures of parent compounds?

RESPONSE: Similar to the original VBS proposed by Donahue et al. (2006), this SUVS approach is sustainable in terms of volatility-based species and chemical reactions.

This means a single SUVS would be used to describe various mixtures of primary species. For example, to develop a revised SUVS for alpha-pinene and beta-pinene mixture system, 30 additional unknown parameters for alpha-pinene initial oxidation with three oxidants (OH, O3, and NO3) would be integrated into the new SUVS system. These 30 new unknown parameters are assigned similar to those for alpha-pinene system shown in Part 1 in Figure 1.

We believe that a single set of parameters can be used to describe various mixtures of parent compounds, because genetic algorithms is a powerful tool to study up to billion-varibles optimization (Goldberg et al, 2007). The derived dataset for the final SUVS

ACPD
11, C3770–C3780, 2011

(most likely revised) would represent optimization of all atmospheric oxidation system for SOA formation within acceptable limit.

If future research indicated that one single SUVS is insufficient to describe the oxidation of all mixtures system, we could still group the oxidation systems into a few representative SUVS systems, say biogenic SUVS and anthropogenic SUVS. The bottom line is that, as suggested by our third referee, we would not use a separate set of parameters for each oxidation system.

>Comment 8 from Referee #3: Can we learn something from the optimization process? As described by the authors, the design of the SUVS is based on the key gas phase oxidation steps.

RESPONSE: The first thing we could learn from the optimization process is that we could compile all available data into the same single framework we propose beforehand. If the framework represents the ambient atmospheric process, the use of the optimization process would help to identify relationship between different organic compounds, especially when the gas and aerosol phase oxidation process are included in our future work. The second thing we could learn is that design of a suitable objective function is critical to the optimization process for a complex system. Finally, we would be able to ignore certain volatility-based pathway and even make further simplifications by using systematical mechanism reduction techniques, such as those outlined in Xia et al. (2009).

>Comment 9 from Referee #3: Can the optimized parameters be interpreted? Are they within the range of the “expected” values? It would be useful to publish the values of the parameters as supplementary material added to the paper.

RESPONSE: As we responded to comment 2 from Dr. Stockwell, the optimized parameters can be interpreted. All parameters lie within the expected range. For example, the reaction rate coefficients are physically bounded by the values we pre-investigated from the benchmark MCM v3.1. In addition, our sensitivity test indicated a valid range

ACPD

11, C3770–C3780, 2011

between 0 and 1.0 for all stoichiometric coefficients. If the bounds for each parameter could be further narrowed, the SUVS would be more accurate in describing the oxidation process. As suggested by the referee, we list the values of the 412 parameters as supplementary materials to this paper.

>Comment 10 from Referee #3: Can some properties be assigned to the set of lumped condensable species? The SUVS is here assessed on a molar basis. A final user will likely more be interested in SOA mass concentration. Can a molar mass be assigned to the 10 lumped condens able species? For later applications and comparisons with observations, the O/C and N/C ratio provide very useful constrain. Can a typical oxygen and nitrogen content be assigned to the SUVS?

RESPONSE: The conversion between mass-based and molar-based requires the values of mean molecular weights. In the alpha-pinene oxidation system, we derived the values for mean molecular weights of the 10 lumped species, and they are also listed in the supplemental materials. Thanks to the suggestion by the referee, we will investigate the use of O/C and N/C ratios for the data constrain. A typical oxygen and nitrogen content can be assigned to the SUVS based on the estimated or measured saturation concentrations.

References: Elliott, L., Ingham, D. B., Kyne, A. G., Mera, N. S., Pourkashanian, M., and Wilson, C. W.: Incorporation of physical bounds on rate parameters for reaction mechanism optimization using genetic algorithms, Combust Sci Technol, 175, 619-648, 10.1080/00102200390196377, 2003.

Renders, J. M., and Flasse, S. P.: Hybrid methods using genetic algorithms for global optimization, IEEE Trans. Syst. Man Cybern. Part B-Cybern., 26, 243-258, 1996.

Rodriguez-Fernandez, M., Mendes, P., and Banga, J. R.: A hybrid approach for efficient and robust parameter estimation in biochemical pathways, Biosystems,83, 248-265, 10.1016/j.biosystems.2005.06.016, 2006.

ACPD

11, C3770–C3780, 2011

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 3885, 2011.