Geosci. Model Dev. Discuss.,
https://doi.org/10.5194/gmd-2018-106-SC1, 2018

Geoscientific
Model Development
Discussions
Open Access

Interactive comment on "Accelerating simulations using Direct Relation Graphs for atmospheric chemistry mechanism reduction" *by* Zacharias M. Nikolaou et al.

A. Kerkweg

kerkweg@uni-bonn.de

Received and published: 2 May 2018

Dear authors,

in my role as Executive editor of GMD, I would like to bring to your attention our Editorial version 1.1: http://www.geosci-model-dev.net/8/3487/2015/gmd-8-3487-2015.html This highlights some requirements of papers published in GMD, which is also available on the GMD website in the 'Manuscript Types' section: http://www.geoscientific-model-development.net/submission/manuscript_types.html In particular, please note that for your paper, the following requirement has not been met in the Discussions paper:

Printer-friendly version

Discussion paper

- "The main paper must give the model name and version number (or other unique identifier) in the title."

Please provide a name and a version number for the (software producing the) sceleton mechanism in the title of your revised manuscript. Note, that a name and a version number are important to identify your specific developments.

As explained in
https://www.geoscientific-model-development.net/about/manuscript_types.html. GMD is encouraging authors to upload the program code of models (including relevant data sets) as supplement or make the code and data of the exact model version described in the paper accessible through a DOI (digital object identifier). In case your institution does not provide the possibility to make electronic data accessible through a DOI you may consider other providers (eg. zenodo.org of CERN) to create a DOI. Please note that in the code accessibility section you can still point the reader to how to obtain the newest version. If for some reason the code and/or data cannot be made available in this form (e.g. only via e-mail contact) the “Code Availability” section need to clearly state the reasons for why access is restricted (e.g. licensing reasons).
Especially, please note, that it is not enough, that the code will be available in the future. It must be available now and the exact version of the code published in this article needs to be made available.

Yours, Astrid Kerkweg

Interactive comment on Geosci. Model Dev. Discuss., https://doi.org/10.5194/gmd-2018-106, 2018.

Response to reviewer Astrid Kerkweg

We thank the reviewer for her comments.

We have attached as supplementary material the code used for the reduction, and we have included the name of the code in the manuscript title as per the reviewer comments.

Geosci. Model Dev. Discuss.,
https://doi.org/10.5194/gmd-2018-106-RC1, 2018

Geoscientific
Model Development
Discussions

Interactive comment on "Accelerating simulations using Direct Relation Graphs for atmospheric chemistry mechanism reduction" *by* Zacharias M. Nikolaou et al.

M. Krol (Referee)

m.c.krol@uu.nl

Received and published: 6 May 2018

This is an interesting piece of work. Reduction of chemical mechanisms in chemistry transport models received relatively little attention, while there is a lot of computational effort to win. The paper is well written, and clearly organized. A solid introduction which sets the theory, and a short method section (some questions in the annotated pdf document). The results are spit in two parts (1) box model evaluation (2) full 3D model evaluation.

I have some problems with both approaches. The mechanisms are tested in a box model under relatively polluted conditions only, and at surface temperatures and pres-

Printer-friendly version

Discussion paper

sure. In a real setting, the scheme will also be applied to the upper atmosphere, where completely different conditions will prevail. I argue that the choice of scenarios is not balanced for a true atmospheric simulation. The same holds for the 3D validation, which uses unclearly formulated conditions for the initial and boundary conditions, and does not apply emissions. Furthermore, only the lowest 9 layers are analysed, which reinforces my point above.

An important point is made at the end of the result section. By removing species (i.e. reduced hydrocarbons), biases may be introduced that propagate through e.g. HO and CO. This is undesirable since these biases may accumulate in global models (not so much in regional models that apply boundary conditions). This is exactly the reason that lumped species have been introduced. This would involve the merger of species, instead of removal of species (and assumptions about similar effects on overall chemistry).

When the authors manage to address these main points, I think the paper is a valuable contribution to GMD. I guess it would also be good to provide the community with the tools the authors developed on top of the KPP code, but I guess this is mandatory in GMD.

Further comments can be found in the annotated manuscript.

Please also note the supplement to this comment:
https://www.geosci-model-dev-discuss.net/gmd-2018-106/gmd-2018-106-RC1-supplement.pdf

---

Interactive comment on Geosci. Model Dev. Discuss., https://doi.org/10.5194/gmd-2018-106, 2018.

Response to reviewer Maarten Crol

We thank the reviewer for his comments on our manuscript, and also for proof-reading the paper. We have carefully considered all of the reviewer's comments and revised the manuscript accordingly. These revisions have been highlighted using red-coloured fonts and are referred to appropriately in our specific response below.

We would like to note that the aim of this study is to introduce a general framework for developing skeletal chemistry. Our interest here, is in the lower levels of the troposphere in regions of heavy pollution which lead to ozone formation, hence the choice of the high VOC/NOx conditions for developing the skeletal chemistry. At the same time, such conditions activate a large number of VOC-relevant reactions which are of interest to us. Furthermore, additional validation in the revised manuscript indicates that the reduction process is not particularly sensitive to the VOC/NOx ratio as the reviewer suggests. The methodology/tools described in this study are general, and are expected to be applied by different groups on a case-specific basis. Furthermore, we would like to note that care has to be taken when using atmospheric chemical mechanisms. As indicated by Stockwell et al. [1], RACM is intended to be valid for the troposphere and not for the higher levels of the atmosphere. Thus, care has to be taken when interpreting results for the stratosphere, which in most regional models is not even being adequately resolved or modelled.

1. The reviewer raised concerns regarding the validation process, which is comprised of both box-model runs and air-quality forecast simulations using WRF-Chem. The reviewer also argues that "the choice of scenarios is not balanced for a true atmospheric simulation".

It is important to note, that atmospheric chemical mechanisms were developed/validated against limited sets of experimental smog-chamber data and box-model simulations only [2-9]. This good point was also stressed in the comments of this work by W. Stockwell (16/05/2018). Nevertheless, these mechanisms are used in air-quality forecast and climate simulations where substantially different conditions prevail. Chemical mechanisms are not typically validated using forecast/climate simulations, since it is extremely difficult to obtain accurate, real-time, satellite (or otherwise) measurements of all species present in a chemical mechanism throughout the entire atmosphere and compare with simulation results. Furthermore, validation of these mechanisms is typically conducted at atmospheric conditions only since varying solar radiation is the dominant factor driving and affecting atmospheric chemical reactions [2-9]. It is also important to note that, to the knowledge of the authors, this is the first study of its kind where both box-model and forecast simulations are used in tandem for validation purposes. From a validation point of view, doing forecast simulations covers a much larger sample space than what is traditionally covered in box-model simulations, examining the effects of both pressure and temperature variations.

2. The reviewer argues that only the lower nine levels were used for validation which is not representative of conditions in the upper atmosphere.

We would like to note that our interest in this study is in the lower levels of the troposphere where heavy pollution leads to ozone production, hence why the analysis was conducted for the lower levels in the atmosphere which covers the planetary boundary where most mixing processes occur. It is also important to note that regional air-quality forecasting codes such as WRF-Chem, are not usually tuned for the upper levels of the atmosphere. However, in the revised version of the manuscript, we have included additional error calculations using the upper levels of the troposphere where substantially different conditions (pressure, temperature, species mixing ratios) are found. The errors are shown in Figs. 13-18 for O_3, CO and HCHO. These errors are of the same order of magnitude as for the lower levels of the troposphere. For ozone, which is the target species, the errors are also found to be small (Figs.13 and 14) indicating the strength of the method. These results indicate that the skeletal mechanisms work even at these conditions, which are substantially different from the conditions used to develop the skeletal mechanism in the first place. Again, we stress the point that the most important parameter is variation in solar radiation (night-day).

3. The reviewer further mentions that emissions should be included for a "true validation".

When validating a model one must first limit to the extent possible any external influences/uncertainties which would otherwise bias the model's predictions, thus over-shadowing the actual performance of the model. Emissions inventories for atmospheric chemistry, contain many uncertainties. Modelling emissions is a challenge alone, and emissions inventories as used in forecasting codes have many inter-dependencies (mesh resolution, chemical mechanism, appropriate speciation profiling of chemical compounds etc.). Ground-based stations are finite, and global models run on much coarser meshes than forecast codes hence dynamical downscaling is also an issue. In such a case, one would not be able to deduce whether the errors are due to the reduction process, or due to the uncertainties/errors in the emissions inventories used. For this reason, we chose to turn emissions off, in order to clearly evaluate the performance of the reduced mechanism i.e. free from emissions' modelling uncertainties, in a first step. This is now discussed in the revised version of the manuscript on page 9.

4. The reviewer mentions that the mechanisms were developed for polluted conditions only, and it is unclear whether they would work equally well for other conditions.

The set of conditions used, were taken from the study of Heard et al. [3] who used the same conditions for developing reduced chemistry for CBM-EX with overall good results. The reason we use such high VOC/NOx conditions is because we are interested in near-surface ozone production where such conditions are typical of polluted environments. The method described in this study is general and can be applied for developing skeletal chemistry for specific conditions of interest. Furthermore, we have conducted box-model runs for low VOC/NOx conditions and these are included as a new figure (Fig. 5) in the revised manuscript. Even though the skeletal mechanism was developed for high VOC/NOx, the results in Fig. 5 show that it performs reasonable well even for lower VOC/NOx conditions. We have additionally conducted validation as per point 2 above where substantially different conditions prevail.

5. The reviewer argues that initial and boundary conditions are unclear.

Initial and boundary conditions for the metereological fields are discussed in the manuscript. For the chemistry, the model is using idealised climatological-based conditions details of which can be found in the WRF-Chem manual. We are unsure of what the reviewer means by "standard value everywhere" in the supplement. The initial conditions are fixed to a constant value for some species (e.g. CO), while for other species they vary with spatial position. On the boundaries, zero-gradient (to match values inside domain) or fixed value conditions are used depending on the local flow direction (open system). It is also important to note that the analysis is conducted after a 5-day spin-up time. By this time, the fields have reached a mature state. In the study of Ritter et al [9], the effect of using the hard-coded chemical boundary conditions and user-specified ones were compared, by running WRF-Chem simulations. Although some differences were found in ozone concentration profiles between the two simulations, the profiles obtained were clearly in correlation with each other, of the same order of magnitude, and the differences were well within experimental/measurement errors for the species mixing ratios.

Further comments:

P4, L5:

Acronyms are used to avoid using the full sentence, otherwise the text would be full of the repeating sentences.

P4, L5:

As explained in the text, this is the net rate of a species from a given reaction. The net rate of a species from a reaction, can be positive or negative, depending on the difference between the stoichiometric coefficients of the species, and the rate of the reaction. Note that the general case may involve reactions with reverse rates. We refer the reviewer to published studies on the matter in the literature e.g. Pepiot-Desjardins and Pitsch. Combust. Flame 154 (2008) 67-81, K. Niemeyer, C. Sung, M. Raju. Combust. Flame 157 (2010) 17601770, T. Lu, C. Law. Proc. Combust. Inst. 30 (2005) 13331341.

P4, L25:

The max function is needed because the net rate can be positive or negative. The function in Eq. 3 ensures that positive net rates are identified as production terms, while negative net rates are identified as destruction terms, as per the DRGEP method. We refer the reviewer to published studies on the matter in the literature e.g. Pepiot-Desjardins and Pitsch. Combust. Flame 154 (2008) 67-81, K. Niemeyer, C. Sung, M. Raju. Combust. Flame 157 (2010) 17601770, T. Lu, C. Law. Proc. Combust. Inst. 30 (2005) 13331341.

P5, L14:

The example in Fig. 1 is a simple illustration of how the search algorithm works. The algorithm takes as input the overall interaction coefficients, which are calculated using Eq. 6. All that matters for the search are the overall interaction coefficients.

P7, L27:

In this study, the box-model runs were validated for a 48-hour period. However, in a forecast simulation, time-steps are of the order of minutes. E.g. after the operator split scheme, the mixing ratio values are updated and a new initial-value problem is solved, operator-splitting again and so on. So in essence, the reduced mechanism actually needs to be accurate over this smaller time range only, before the next initial-value problem is solved. This is now rephrased in the revised version of the manuscript.

References

[1] R.W. Stockwell, F. Kirchner, M. Kuhn, S. Seefeld. J. Geoph. Res. 102, (1997) 2584725879. A new mechanism for regional atmospheric chemistry modeling.

[2] K.M. Emmerson and M.J. Evans. Atm. Chem. Phys. 9 (2009) 1831-1845. Comparison of tropospheric gas-phase chemistry schemes for use within global models.

[3] A.C. Heard, M.J. Pilling, A.S. Tomlin. Atm. Chem. Phys. 32 (1998) 1059-1073. Mechanism reduction techniques applied to tropospheric chemistry.

[4] J. Liang, M.Z. Jacobson. Atm. Env. 34 (2000) 3015-3026. Comparison of a 4000-reaction chemical mechanism with the carbon bond IV and an adjusted carbon bond IV-EX mechanism using SMVGEAR

II.

[5] L.E. Whitehouse, A.S. Tomlin, M.J. Pilling. Atm. Chem. Phys. 4 (2004) 2025-2056. Systematic reduction of complex tropospheric chemical mechanisms, Part I: sensitivity and time-scale analyses.

[6] M.K. Neophytou, D.A. Goussis, M. van Loon, E. Mastorakos. Atm. Env. 38 (2004) 36613673. Reduced chemical mechanisms for atmospheric pollution using Computational Singular Perturbation analysis

[7] M. Gerry, G. Whitten, J. Killus, M. Dodge. J. Geoph. Res. 94, (1989) 1292512956. A photochemical kinetics mechanism for urban and regional scale computer modelling.

[8] M.E. Jenkin, L.A. Watson, S.R. Utembe, D.E. Shallcross. Atm. Env. 42 (2008) 7185-7195. A Common Representative Intermediates (CRI) mechanism for VOC degradation. Part 1: Gas phase mechanism development.

[9] M. Ritter, M.D. Muller, O. Jorba, E. Parlow, L.J. Sally Liu. Metereol. Atmos. Phys. 119 (2013) 59-70. Impact of chemical and meteorological boundary and initial conditions on air quality modeling: WRF-Chem sensitivity evaluation for a European domain

Geosci. Model Dev. Discuss.,
https://doi.org/10.5194/gmd-2018-106-RC2, 2018

Geoscientific
Model Development
Discussions

Interactive comment on "Accelerating simulations using Direct Relation Graphs for atmospheric chemistry mechanism reduction" *by* Zacharias M. Nikolaou et al.

WRS Stockwell (Referee)

william.r.stockwell@gmail.com

Received and published: 16 May 2018

This paper presents an interesting approach to chemical mechanism reduction. The series of mechanisms used for air quality modeling include the Regional Atmospheric Chemistry Mechanism (RACM), the Carbon Bond Mechanism and the Statewide Air Pollution Research Center Mechanism (SAPRC) and these are reduced mechanisms. The reduction process used by the mechanism developers has not been a formal process like the one discussed by the authors. Mechanism developers have used a process based on chemical knowledge and the simulation of many environmental chamber experiments to develop their reduced mechanisms. Sometimes mechanism developers used their mechanisms to simulate results of simulations made with highly detailed, very explicit mechanisms or to make simulations of field observations. Most often box models are used in these simulations to eliminate (or ignore) the impact of meteorology on the chemistry. Developers add and subtract species, reactions and entire chemical reactions schemes from their reduced mechanisms until the simulations adequately fit the results of environmental chamber experiments, simulations made by very explicit mechanisms or field observations. The aggregated species used in the reduced mechanisms, such as those in RADM, are used to simplify the representation of atmospheric chemistry. The selection of the model species and their corresponding reactions can affect the mechanism's ability to simulate particular domains. For example, early versions of Carbon Bond and SAPRC were designed to simulate highly polluted urban regions and they would not have been accurate for regional or global atmospheric simulations. The design goals of the developers could be considered to be a source of bias in the reduced mechanisms. However, possible design bias is not limited to the developers of RACM, Carbon Bond or SAPEC. The authors should point out clearly that there is no single skeletal mechanism. There are in fact, many possible skeletal mechanisms that may be generated from a larger atmospheric chemistry mechanism. A skeletal mechanism for ozone simulation will be very different than one for the modeling of acid deposition. A skeletal mechanism for acid deposition would be based on the mechanism's ability to simulate sulfate, nitric acid, organic acids and aqueous phase oxidants (H2O2 and organic peroxides). The two skeletal mechanisms would be expected to be very different even if the two skeletal mechanisms were derived from the same source mechanism. The same could be said about a skeletal mechanism for the simulation of secondary particulate matter formation. A potential user must realize the dangers in using a skeletal mechanism for ozone as a general propose atmospheric mechanism in a global or regional model. I believe that the authors' overall approach is valid to produce an ozone skeletal mechanism. But I recommend that a wider variety of conditions that range from relatively clean to the highly polluted be used for the box modeling. Also, in the WRF-Chem modeling, a range of altitudes (layers) from the surface to the upper troposphere should be considered in the authors analysis and evaluation because RACM was designed to be valid over this range too. The authors might write something about applying their methods to highly explicit chemical mechanisms. A. Kaduwela, D. Luecken, W. Carter and R. Derwent. New Directions: Atmospheric Chemical Mechanisms for the Future. Atmospheric Environment, 122, 609-610, (2015), propose that very explicit chemical mechanisms be developed first and then objectively reduced to develop new reduced mechanisms for regulatory modeling. The authors approach could be useful in providing a suite of skeletal mechanisms for ozone, PM and other pollutants. I must note that there has been much research from combustion that has been applied to the reduction of atmospheric chemical mechanisms. For example, Michael J. Pilling and his colleagues have been particularly active. For example, see the paper: A.C. Heard, M.J. Pilling and A. S. Tomlin, Mechanism Reduction Techniques Applied to Tropospheric Chemistry, Atmospheric Environment, 32, 1059-1073 (1998). The authors should improve their discussion of prior research. Finally, J is not a photolysis rate rather it is a photolysis rate coefficient (or photolysis frequency and its units are reciprocal time). A photolysis rate is the product of J and the chemical species that photolyzes. Please correct this in the paper.

Interactive comment on Geosci. Model Dev. Discuss., https://doi.org/10.5194/gmd-2018-106, 2018.

Response to reviewer William Stockwell

We thank the reviewer for his very useful and constructive comments. We have carefully considered all of the reviewer's comments and revised the manuscript accordingly. These revisions have been highlighted using green-coloured fonts and are referred to appropriately in our specific response below.

1. Indeed, we perfectly agree with the reviewer in that skeletal mechanisms have traditionally been developed not through a formal procedure such as the one proposed in this study. Starting from a detailed set of reactions one can (in principle) develop a number of different subset skeletal mechanisms for the specific application in mind. This is now made clear on page 11 of the revised manuscript.

2. As per the comments by M. Crol, we have now added additional validation for low VOC/NOx ratios and for the higher levels of the troposphere, where RACM is expected to be valid according to [1].

3. We thank the reviewer for the reference of Kaduwela et al. Indeed, there should be a formal and coordinated process of developing atmospheric chemical mechanisms. This is now discussed on page 11 of the revised manuscript.

4. We thank the reviewer for the reference of Heard et al. This work is discussed in the original manuscript on page 2. Indeed, most reduction methods were developed from the need to simulate efficiently combustion processes, however most reduction applications for atmospheric chemistry employ lumping and not methods such as DRGEP. We have tried to improve upon the discussion of previous work and we welcome any additional references from the reviewer for further improving this section.

5. J is now corrected on page 6 of the revised manuscript-we thank the reviewer for spotting this.

References:

[1] R.W. Stockwell, F. Kirchner, M. Kuhn, S. Seefeld. J. Geoph. Res. 102, (1997) 25847-25879. A new mechanism for regional atmospheric chemistry modeling.