

Anonymous Referee #1

This paper documents a boxmodeling system for the Master Chemical Mechanism (MCM). The MCM is a very large, near explicit mechanism describing the degradation of 143 primary compounds into CO₂ and H₂O. As such, the MCM is too computationally expensive to be run in global chemistry models or even air quality models. However the MCM is often used to benchmark smaller ‘lumped’ chemistry schemes by comparison using a zero-dimensional boxmodel, or by comparison with results from controlled chamber experiments. Much of the boxmodeling work in the past used expensive commercial software, and this new open source system was developed in part to avoid these costs, but also to provide potential additional capability beyond commercial ‘black-box’ systems. The paper is generally well written, with examples provided on how the model works and performs. However, AtChem is presented as being a new and novel free system (line 52) without acknowledging any of the recent efforts to produce similar open source boxmodels, some if not all are also designed to run the MCM. These models are missing from the literature review. The literature cited between lines 23-29 are studies using boxmodels, some were commercial like FACSIMILE, some not. The review does not cover the models themselves. I have scored ‘fair’ for scientific significance (substantial new concepts, ideas, or methods) and scientific quality (consideration of related work, including appropriate references) based on this and the decision not to upgrade the representation of photolysis, which many of the other open source boxmodels have done (see major questions). If the paper is to be published, acknowledgement of previous work towards production of open source boxmodels should be included in the literature review. I also would suggest the authors look into (at least comparing) other photolysis schemes.

We thank the referee for their comments and suggestions. Please find below our replies and the related modifications to the manuscript. The line numbers refer to the version of the manuscript published on GMDD.

Major questions

More than 10 years ago, the MCM website moved to output the entire mechanism (or a chosen subset) in a variety of formats. One of those formats was KPP (kinetic PreProcessor software) which is the basis for some of these recent open source codes – Knote et al’s (2015) boxmodel extensions to KPP (BOXMOX, <https://www2.acom.ucar.edu/modeling/boxmox-box-model-extensions-kpp>), Sander et al’s (2011) Chemistry As A Box Model Application (CAABA), and the Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC, http://wiki.seas.harvard.edu/geos-chem/index.php/DSMACC_chemical_box_model) (Emmerson and Evans, 2009). There is a wiki page listing 10 of these models: https://en.wikipedia.org/wiki/Kinetic_PreProcessor I am also aware of boxmodels which do not use these KPP format codes – FOAM (Wolfe et al., 2016) uses Matlab. So I’m missing why the authors developed their own model from scratch rather than building on another system which is freely available?

References to other open source modelling frameworks have been added to the manuscript. With regard to the question of why AtChem was developed from scratch instead of building on other work, it should be noted that AtChem-online has been available for some time. The first version of the model was released in 2010, although there was not an accompanying publication at the time.

Although this has changed in the past few years (as the referee points out), at the time the choice of modelling tools was rather limited and the available ones were expensive and/or not very easy to use for novice modellers. As explained in the introduction (lines 50-60) and at the beginning of Section 2 (lines 75-76), AtChem-online was created as a free community modelling toolkit to facilitate the use of the MCM within the EUROCHAMP atmospheric

chamber community, by providing a tool that could be used by researchers without an experienced modelling background.

The offline version, Atchem2, was released more recently (in 2017) and is based on the same code as AtChem-online. Therefore, Atchem2 is not a new model, but a development and an improvement of a pre-existing model. Given the fact that a paper about AtChem-online had not been published, it just makes sense that the older online version of the model is presented together with the newer offline version. This has the added benefit of documenting the model developments within the formal literature.

The final paragraph of the Introduction has been modified as follow:

“AtChem was conceived with the above principles and objectives in mind: the code is free, open source and publicly available. It was released online in 2010, introduced to the EUROCHAMP community via a two day workshop, and briefly described in the annual EUROCHAMP report in late 2010. In recent years, a number of other open source modelling tools and frameworks have been released: some include their own chemical mechanism (e.g., CAABA, Sander et al. (2011)), while others are designed to use primarily the MCM (e.g., PyBox, Topping et al. (2018)). Most these tools – such as DSMACC (Emmerson and Evans, 2009), BOXMOX (Knote et al., 2015), and FOAM (Wolfe et al., 2016) – give the user the flexibility to run different chemical mechanisms. Although AtChem was designed mainly to encourage the use of the MCM in atmospheric chemistry studies (and hence to facilitate its evaluation by the community), it can be easily adapted to model other chemical systems and to use other chemical mechanisms, as long as they are provided in the correct format.”

The method for calculating photolysis rates in AtChem is a shortcoming. AtChem uses (quite an old) 2-stream method for calculating photolysis rates, and looking at figure 4, consistently underpredicts the measured rates. This photolysis scheme has been used with MCM modeling for ~20 years or so. Yes, it is important to adjust for cloudy conditions using measured photolysis rates. However not all investigators (and particularly students using AtChem in the classroom) have the luxury of being able to measure photolysis rates to perform the correction in equation 4, or to use directly as a constraint. If equation 3 can only be relied upon to produce good results at 500 m altitude, 45 degrees N on July 1st, then why was the photolysis method not updated given the opportunity for designing this new system? If AtChem had used one of the other open source systems as a basis, photolysis could be calculated on-line, where such parameters can be changed. CAABA gives users a range of options for calculating photolysis – JVAL, RADJIMT, DISSOC, (Sander et al., 2019). There's also FAST-JX (Wild et al., 2000) which users of GEOSChem and the UK chemistry and aerosol (UKCA) community prefer (https://www.ess.uci.edu/researchgrp/prather/scholar_software/fast-jx). BOXMOX and DSMACC use the Tropospheric Ultraviolet and Visible radiation (TUV, (Madronich and Flocke, 1997)), now at version 5.3.2 <https://www2.acom.ucar.edu/modeling/tuv-download>. i.e., there are plenty of other systems available. Given that photolysis is so important to OH production, correcting the underestimation produced by the 2-stream method is crucial for AtChem to be of use to other researchers, and should be considered.

There is a misunderstanding here about the calculation of the photolysis rates.

First, it is important to distinguish between what is in the MCM and what is in AtChem. The MCM uses a 2-stream scattering model to calculate the photolysis rates of the relevant species; a fitting procedure to the 2-stream scattering model results is then used to derive the empirical parameters I , m , n , which are used in Equation 3 to calculate the photolysis rates as a function of the solar zenith angle in a computationally efficient manner. This methodology is explained in the MCM protocol papers (Jenkin et al, 1997, Saunders et al., 2003). AtChem does not use the 2-stream scattering model, but simply implements Equation 3.

Second, the values of the empirical parameters I , m , n are not prescribed in AtChem, which takes the values of the version of the MCM that is being used. The reason for this approach is that AtChem is designed to use the MCM as is. We think it is not up to the AtChem developers to correct or fix the MCM; this is a task better left to the MCM developers and documented within the MCM protocol. Moreover, nothing prevents the users from providing their own set of empirical parameters based on their preferred photolysis scheme (as stated on lines 229-230). Alternatively, the photolysis rates can be constrained to measurements or to offline-calculated values, as is frequently done by MCM modellers (see line 232). It is left to the users to decide how they wish to parametrise/constrain the photolysis rates, based on their specific needs.

Finally, we do agree with the referee that the 2-stream scattering model is no longer up to date. Indeed, the next version of the MCM will use an updated version of the TUV model to calculate the photolysis rates. But this does not mean that equation 3 will no longer be used. It simply means that the output of TUV will be used to derive a new set of I , m , n parameters. We have no evidence that equation 3 is not reliable and therefore we see no reason to design a new method to calculate the photolysis rates in AtChem. It is however true that the set of I , m , n used in the current version of the MCM (3.3.1) would benefit from an update.

To make this point clearer the following modifications have been made to the manuscript:

Lines 225-227: sentence changed to “The empirical parameters I , m , n are calculated, for each version of the MCM, as explained by Jenkin et al. (1997) and Saunders et al. (2003): in the MCM v3.3.1 (and previous versions), the empirical parameters are obtained by fitting Eq. 3 to the output of a two-stream isotropic scattering model, which incorporates the appropriate photolysis cross-sections and quantum yields.”

Line 230: “to replace the default values of I , m , n and τ .” changed to “to replace the values of I , m , n and τ provided by the MCM”

Line 232: changed to “The photolysis rates can also be set to constant values, constrained to measured data or constrained to values calculated offline using a suitable radiative transfer model”

Line 250: “in Eq. 3” changed to “in the MCM”

As this is a model description paper, please explain how the dilution factor is calculated. In a number of places in the text constraining the boundary layer height is mentioned which would impact the chemical concentrations, but it is not explained. This also applies to the chamber open roof experiments. Please also mention whether the model has a capability for entrainment of stratospheric air into the troposphere (which is a feature of BOXMOX), or exchange of air with air masses outside the box (a feature of CAABA).

A complete explanation of each environment variable can be found in the AtChem manual, which is included with the AtChem code. To clarify the (optional) usage of the variables used to parametrise the emission, dilution and deposition of chemical species, the following paragraph has been added to Section 2.2:

“Chemical reactions can also be written without reactants or products, which is useful to parametrise non-chemical processes in the model, if required. For example, emission of species P1 can be parametrised as:

% Er : = P1 ;

where E_r is the emission rate in s^{-1} . Likewise, dry deposition and dilution of species R1 can be parametrised, respectively, as:

% Vd/BLHEIGHT : R1 = ;
% DILUTE : R1 = ;

where Vd is the deposition velocity in cm s^{-1} , BLHEIGHT is the boundary layer height in cm and DILUTE is the dilution rate in s^{-1} . BLHEIGHT and DILUTE are environment variables (Sect. 2.3), and therefore can be set to a value chosen by the user or constrained to prescribed values.”

AtChem does not explicitly include entrainment of stratospheric air into the troposphere, although this process can be easily parametrised in the same way as the emissions can be parametrised. Note that the description of non-chemical processes outlined above is rather simplistic, although it is good enough for several applications. Implementation of more sophisticated approaches to model non-chemical processes is left to the users, according to their specific needs.

The choice of examples shown to demonstrate the AtChem system are at odds with the description of why it was developed. For example line 345 “AtChem2 was developed specifically for the long and complex simulations need for field studies”. AtChem2 is then demonstrated using only 2 days from a ~ 40 day TEXAQs campaign. Were these two days chosen because they provided the best model-observation comparison? Why not show the whole TEXAQs time series, which would show that AtChem has been rigorously tested?

We chose to show only 3 days of the TexAQs model simulation mainly for reasons of clarity and simplicity. The entire model run, and associated analysis, is shown in Sommariva et al., (2011) and, although it was performed with an older version of AtChem, the agreement between the two versions is good (see line 359 and the modified Figure 7). We don't think that showing the whole time series would add much to this paper, which is a technical manuscript within the “Model description papers” remit of GMD.

It is true that the example in Section 3.2 is meant to show how AtChem2 can be used to carry out long simulations. However, please keep in mind that a fully constrained model, such as the one used for the TexAQs campaign, runs almost in real time. Depending on the computer system, a 3 days simulation takes between 2 and 4 days to complete. This is much longer than the chamber simulation shown in Section 3.1, which was completed in a couple of hours. Therefore we feel that the example shown in Section 3.2 provides an adequate demonstration of the enhanced capabilities of AtChem2.

Editorial comments

Title. I think GMD prefers a version number to be assigned to the model being described.

The version number has been added to the title (see also reply to the Editor's comments).

line 174 represents the start of a new paragraph but mentions ‘this’ modeling technique, which is not defined, or must relate to the paragraph above. I assume the latter, in which case it isn't a new paragraph.

The line break has been removed.

Line 204. ‘study’ not studies

Corrected.

Line 268. “since the model...” This and the following sentence are both very long, and could be broken up.

The paragraph has been rewritten as:

“The model configuration and constraints are read by the executable at runtime: there is no need to compile the model more than once, unless the chemical mechanism or parts of the source code are modified by the user (Fig. 5). This approach makes it quick and easy to set up batch model runs. With AtChem-online batch model runs are not possible because compilation is automatically performed on the web server when the model run is started: the chemical mechanism, the configuration files and the model constraints have to be uploaded via the Web Interface before every run and the model has to be recompiled every time it is executed, regardless of the changes that the user has made.”

Line 350. Why is the latest version of the MCM not being used here?

The reason is that we wanted to be consistent with the model results published in Sommariva et al. (2011). See also the reply to a similar comment by referee #2.

Line 371. The reader needs to know what compounds were being constrained here – for example I’m assuming NO was constrained because of the statement about NO being the main destruction term. Earlier in this section reference is given to the model set-up in Sommariva et al (Sommariva et al., 2011), but as the results here rely upon the constraints they should be stated.

The sentence at line 353 has been rewritten as:

“The model constraints – CO, CH₄, H₂, NO, NO₂, O₃, SO₂, H₂O, 65 VOC, j(O₁D), j(NO₂), j(NO₃), aerosol surface area, temperature, pressure, latitude and longitude – and configuration were the same as in the model described by Sommariva et al. (2011).”

Figure 2. the plots are too small to be seen properly.

The size of the figure has been increased.

Figure 6, top right panel. A legend is missing for the three colors.

The legend has been corrected.