Author response

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Dear Dr. Sander:

Here we provide responses to all of the comments made by the reviewer and specify the changes made to the manuscript. We have addressed all the comments and revised the manuscript accordingly.

Responses to reviewer comments

- An essential part of the original algorithm, the balancing of concentration changes and reaction rates, is missing in the implementation presented in the manuscript. The assumption that "the reader ensures that mass balance is achieved in their model output" (final author response and line 372) is unrealistic.

  Response:

  We updated the way we do our pathway analysis to balance the concentration changes and reaction rates including error pseudo-reactions that produce or destroy a species at the rate required to achieve balance. We included the following text in the manuscript to describe this way of balancing the concentration changes:

  "Before the construction of pathways, it is essential to ensure that the concentration changes of all species are balanced by the reaction's production and destruction (equation 1). The balance might not be fulfilled due to numerical errors. To quantify this problem, we assume that the difference between concentration changes and the total production by all reactions is due to the solver's numerical error, and we include error pseudo-reactions in the chemical system that produce or destroy a species at the rate required to fulfill the balance. We include the error pseudo-reactions in the construction of pathways. After the pathway construction finishes, we delete the pathways containing error pseudo-reactions, updating $\tilde{r_j}$, $\tilde{p_i}$ and $\tilde{d_i}$. We also include variables similar to $\tilde{r_j}$, $\tilde{p_i}$ and $\tilde{d_i}$ to track the rates of the pathways containing error pseudo-reactions. This approach gives the user information on how important the numerical error is in explaining the concentration changes. Ideally, the pathways containing error pseudo-reactions will not contribute significantly to the concentration change one is interested in understanding."

- In their model, the authors enforce the balance mentioned above by an "unphysical trick": They calculate the transport term as the difference of the concentration change and the reaction rates (including wet removal) (Eq. 47). As a consequence, the balance between concentration change, reaction rates (including wet removal) and transport is automatically guaranteed. However, this procedure implies that all numerical errors in the calculation of concentration changes and reaction rates are interpreted as transport effects. It is likely that this procedure leads to artificial pathways involving transport, e.g. D5. The reason for D5 given by the authors in the final response (incomplete representation of the chemistry) is less probable: The model contains the main O loss reaction $O + O_2 + M \longrightarrow O_3 + M$. This ensures a short chemical lifetime and a small mixing ratio of atomic oxygen, even if additional reactions are missing. As a consequence, transport fluxes of O should be small (compared to the O_3 loss rate to be explained).

Response:

We updated the way we do our pathway analysis in the *photochem* model to retrieve the transport rates directly from the model instead of using an inversion to calculate transport with equation 47. Figure 2 shows a comparison of transport rates calculated with equation 47 and transport rates directly retrieved from the model for different species. For some species, the inversion works very well, for example (CH_3O_2, CH_4, O_3), but for other species, the inversion does not perform well (for example O). This is likely due to the numerical error, as the reviewer argues.

Using the transport rates retrieved from the model results in an imbalance between the concentration changes and the reaction rates. To balance the concentration changes, we assume that the difference between concentration changes and the right-hand side of equation 47 is due to the numerical error, and we include error pseudo-reactions that produce or destroy a species at the rate required to balance the concentration changes. The numerical error is unavoidable, and this way of balancing the concentration changes can give the user an idea of how much the error contributes to explaining the concentration changes.

We revised our analysis with this updated method. Pathway $D5$ is no longer detected with this new approach. This result suggests that the reviewer was right, and this pathway was a consequence of interpreting numerical errors as transport. In our new analysis, the contribution of the pathways containing error pseudo-reactions to O_3 production or destruction was less than 1% (figure 2 shows an example of this). We updated the manuscript to describe the updated method and results.

We also update equation 47 to include a vertically distributed input flux (F_i) for some species (for example SO2)

- As Ox (= O3 + O + O(1D)) has a chemical lifetime of 1 year below 100 km (and much less in the middle atmosphere), it will be close to equilibrium in the million-year-long model run, i.e. the concentration is determined by the production rate (dependent on the changing [O2]) and the time scale of destruction. By determining production and destruction pathways of O_3 the authors show how this equilibrium is maintained at selected points in time. This is a valid analysis. However, it is not the answer to the problem that the authors announced to solve: “... know what are the chemical mechanisms that explain the O_3 concentration change ... as a consequence of the decrease in the O_2 surface input flux".

  In addition to the argument just mentioned, it can be noticed that the model has reached an equilibrium state and has thus forgotten the initial concentrations, corresponding to the unperturbed O_2 surface flux, at the times of the analysis (4.1 million years in Table 3 and 4.5 million years in Fig. 3) (cf. Fig. 4).

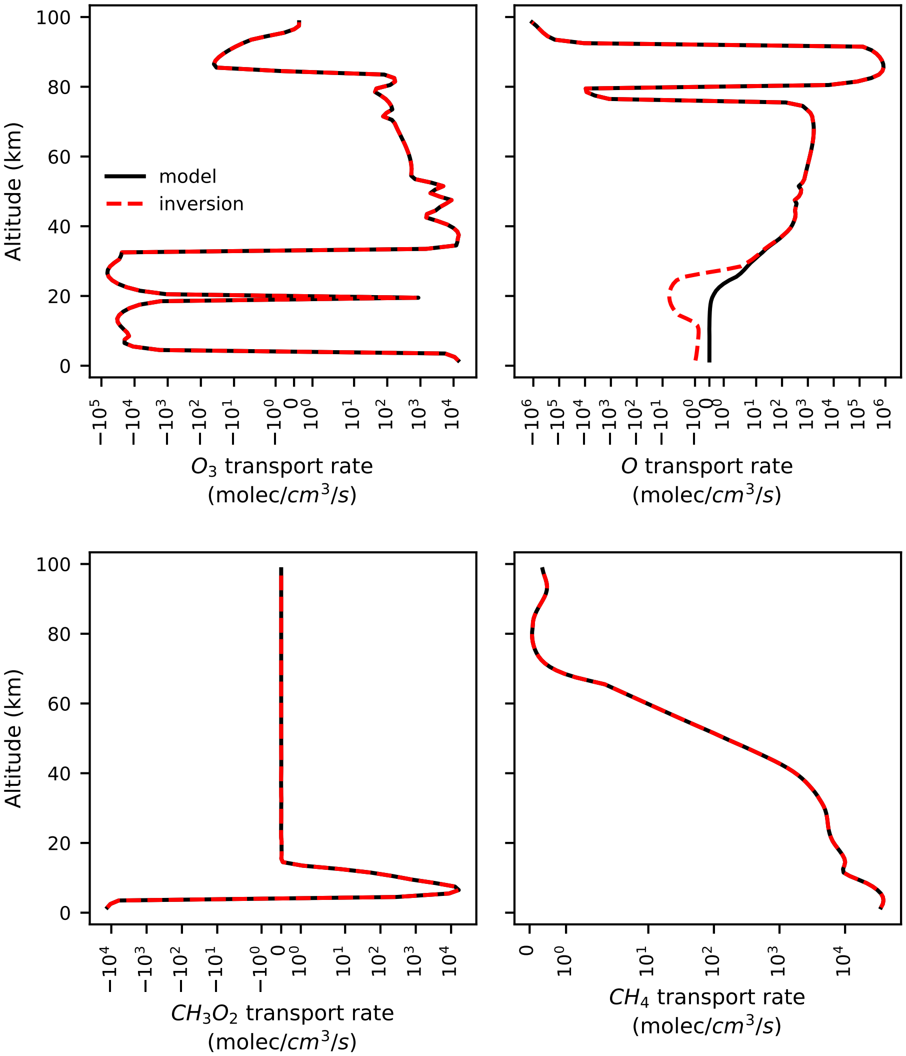

Figure 1: Comparison of transport rates calculated with equation 47 and transport rates directly retrieved from the model for different species at time=1.16 million years in our *photochem* model run.

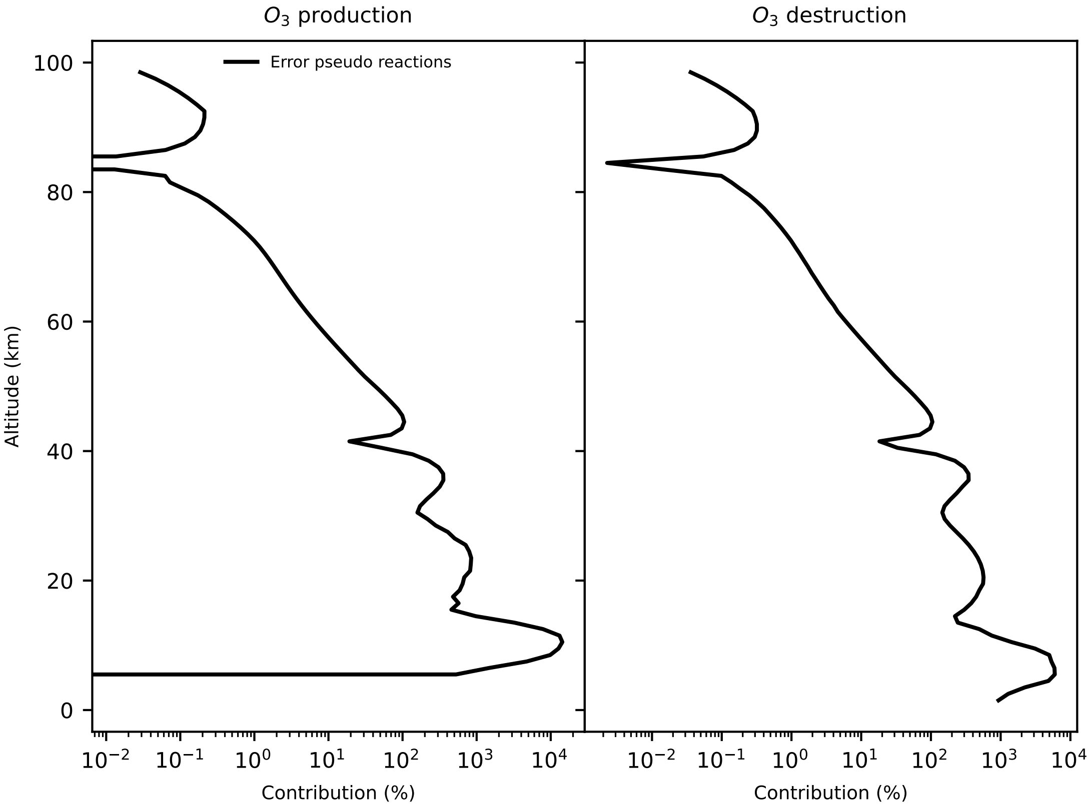

Figure 2: Contribution of error pseudo reactions to O_3 concentration change at time=1.16 million years in our *photochem* model run.

Response:

We updated the text in which we define the problem to focus more on finding pathways for O_3 production and destruction:

“We apply *Chempath* to the *photochem* model output to gain insight into the chemical reaction chains that produce and destroy O_3 in this model run."

We also updated our analysis to include points in time ranging from 1s to 1 million years. In all of the analyzed times the contribution profiles are similar. However, the rate of the pathways changes over time. We updated Figure 4 to show the rate profiles of the main pathways producing and destroying O_3 in the stratosphere at different points in time, ranging from 1s to 1 million years. we also include the following explanation of the O_3 concentration change over time:

“The decrease in O_3 concentration in our model run is likely the result of a decrease in O_3 production and destruction caused by the decrease in the O_2 input flux. For example, the rate of the main stratospheric O_3 producing and destroying pathways (P2.5 and D2.6) decreases over time (figure 5). This is likely the result of the decrease in the O_2 concentration leading to a decrease in O_3 production trough pathway P2.5. However, the contribution profiles shown in figure 4 have a similar structure in all the time steps we analyzed. Consequently, the pathways shown in figure 4 and listed in table 4 are a good representation of the pathways that produce and destroy O_3 across all times we analyzed in our model run."

- 72 concentration ⇒ mixing ratio. **Response**: We made the correction.
- enhance ⇒ reduce? **Response**: We made the correction.
- 90 and the model time in ⇒ at (to avoid mentioning “model time" twice)?

  Response: We repeat model time because we want to emphasize that the model time itself is an input.
- 93-94 These two sentences sound contradictory (must be ⇒ could also be).

  The length of the time interval of the pathway analysis can be chosen independently from the time step of the solver.

  Response: We find that when working with an adaptive solver the algorithm works better when applied to the model times where the solver finds a solution. We changed this sentence to reflect this:

  “We use the model times at which the solver obtains a solution for the system of equations."
- Equation (14): Does the multiplication mean a scalar product? The notations $[\mathrm{miq}] > 0$ and $[\mathrm{miq}] < 0$ are problematic: a vector is compared to a number.

  Response:

  We updated this equation to describe the deletion of a single pathway instead of multiple pathways. We also included a new notation to avoid using $[\mathrm{miq}] > 0$. We include the following text to describe the new notation:

  “We also use the notation $\mathrm{pos}([[x]])$ to refer to a function that makes the negative values of a vector or matrix zero, keeping only the positive values of $[[x]]$. Similarly, $\mathrm{neg}([[x]])$ is a function that makes the positive values of a vector or matrix zero, keeping only the negative values."

- 230 Equation (16): What kind of product (vector times matrix)?

  Response:

  We update the equation to:

  $$[x_{jc}] = \sum_{e=1}^{n_e} [[x'_{je}]]^T \cdot [w_e], \text{ where } j = 1 \dots n_r \text{ and } c = \text{ index of pathway to be split.} \tag{1}$$

  Equation 1 involves the matrix multiplication of $[[x'_{je}]]^T$ and the column vector $[w_e]$. In other words: the sum of the multiplicities of the sub-pathways multiplied by the weighs must be equal to the multiplicities of the split pathway.

- 244 section 5.2.2 ⇒section 5.5.2. **Response**: We made the correction.

- mik ⇒ [[mik]]. **Response**: We made the correction.

- Equation (33): [mi1] $>$ 0 and [mi1] $<$ 0: vector compared to number (cf. 206). Moreover, these expressions should not be placed within an equation.

  Response:

  We updated this equation to use our new notation to avoid comparing vectors and matrices to a number.

- The explanation “The expression 42 involves ... (44)" should appear directly after Equation (42).

  Response:

  We reorganized the text so that this explanation appears after equation 42.

- 444 updated ⇒ augmented? **Response**: We accepted the suggestion.

- Fig. 3 The abbreviation Ox (= Oxidation - of what?), standing near NOx and HOx, might be easily confused with Ox ($= O_3 + O^+ O(1\,D)$).

  Response:

  We changed this abbreviation to “Oxi" and included the species that is oxidized.

Responses to editor comments

- After reading your revised manuscript and the reviewer’s comments, I’ve come to the conclusion that major revisions are still necessary. The main problem is that the photochem application example produces unrealistic results. First, you announce in section 4:

  "We apply Chempath to the photochem model output to gain insight into the chemical reaction chains that produce and destroy O_3 in this model run."

However, instead of gaining insight into chemical reaction chains, you later admit that transport of CH3O2 and O is surprising. While it is true that Chempath can help model developers to find bugs in their code, I still think that it is necessary to provide an application example that produces correct results. Indeed, you conclude yourself:

"A proper evaluation of Chempath would require applying the algorithm in a fully validated model run..."

As far as I can see, there are two steps that may help you to achieve realistic results:

1. Try using only the difference between P_i and D_i (from your eqn 47) instead of $drho_i/dt$. This should give you a purely chemical system that is not affected by transport processes.

2. Balancing is very important. It is very good that Chempath produces a warning, but this doesn't solve the problem. Maybe implementing the method described by Lehmann (2002) helps.

Response:

We have updated our method of finding pathways in the *photochem* model, including transport rates directly retrieved form the model, and balancing the concentration changes including error pseudo-reactions in the reaction system.

Our revised method of finding pathways in the *photochem* model confirms that the CH_3O_2 transport pathways are correct given the reaction system we are using. We are gaining insight into the pathways that destroy and produce O_3 in the model we are using. This is exactly what Chempath is designed to do.

We include a new example of how to use Chempath in a simple box model that only involves chemical reactions (no transport). This example also shows that Chempath works correctly.

We update the text to delete this sentence: "A proper evaluation of Chempath would require applying the algorithm in a fully validated model run" and to emphasize that Chempath works correctly.