

Responses to questions in Review

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Thank you so much for a thorough and detailed review. We will address all the comments in our final response, which will be submitted after the open discussion ends (after the 6th of November). Here we respond to major questions in the review:

1. Before the actual determination of pathways, the original algorithm checks the balance of the input data (= output of a chemical model) (Lehmann, 2002, Section 3.1): Are the reaction rates consistent with the concentration changes calculated by the model? This is an essential step to detect (and possibly correct) imbalances, which may arise from numerical inaccuracies (e.g., because of a large time step in the chemical model). Balanced input data are indispensable for the actual pathway formation. The authors do not mention how they solve this problem in their implementation.

Response: We assume that the user ensures mass balance is fulfilled in their model output. Our implementation does not try to correct imbalances. However, in response to this comment we updated the code to include a function that displays a warning if any of the species are not balanced by the reactions. The warning is displayed if balance is not fulfilled to a relative tolerance of 1×10^{-3} if the concentration change is greater or equal to 1 molecule/cm³, and to an absolute tolerance of 1×10^{-3} if the concentration change is lower than 1 molecule/cm³. We use an absolute tolerance for concentration changes lower than 1 molecule/cm³ because we consider that concentration changes lower than 1×10^{-3} molecules/cm³ are unimportant. We will update the text to clarify the necessity of mass balance in the chemical model to be analyzed.

In the example presented in section 4 of the manuscript, the application of equation 46 ensures that the concentration changes are balanced by the reaction, transport, and rainout rates. In our analysis, the function described above does not display a warning. For many species the balance has a better precision than a relative tolerance of 10^{-3} , but for some species like O the precision is not better than 10^{-4} . That is why we chose a relative tolerance of 10^{-3} for our warning function.

2. How does the algorithm choose a splitting of a pathway into subpathways if this splitting is not unique? Does the formulation "we choose the solution that minimizes the most equation 19" mean that a solution of equation 19 is chosen? Although it is true that the optimization problem (19) has a global minimum (line 221), it is not guaranteed that there is a unique solution. In fact, if Equation (17) has multiple solutions, this will also be the case for the related optimization problem (19).

Response: We chose the first solution that minimizes equation 19 found by Scipy’s `lsq_linear` algorithm. As a response to this comment, we updated the code to include the option to solve equation 17 of the manuscript with the procedure described in section 5.5.1 of Lehmann (2004). We show a comparison of O_3 destruction pathways using these two different methods of solving equation 17 in figure 1 and table 1. Our results are very similar using the two methods of solving equation 17. We will update the text to describe this new option.

| ID | Pathway | Contribution lsq_linear % | Contribution Lehmann (2004) % | Alt km |
|-----------|---|---------------------------------|-------------------------------------|-----------|
| $D_{2.1}$ | $2(\text{CH}_4 + \text{OH} \longrightarrow \text{CH}_3 + \text{H}_2\text{O})$ $\text{O}(^1\text{D}) + \text{H}_2\text{O} \longrightarrow \text{OH} + \text{OH}$ $2(\text{CH}_3 + \text{O}_2 + \text{M} \longrightarrow \text{CH}_3\text{O}_2 + \text{M})$ $\text{O}_3 + \text{h}\nu \longrightarrow \text{O}(^1\text{D}) + \text{O}_2$ $2(\text{CH}_3\text{O}_2 \longrightarrow \text{CH}_3\text{O}_{2\text{trpt}})$ Net: $\text{O}_2 + 2\text{CH}_4 + \text{O}_3 \longrightarrow \text{H}_2\text{O} + 2\text{CH}_3\text{O}_{2\text{trpt}}$ | 33.608 | 33.611 | 0.5 |
| $D_{2.2}$ | $2(\text{CH}_4 + \text{OH} \longrightarrow \text{CH}_3 + \text{H}_2\text{O})$ $2(\text{CH}_3\text{O} + \text{O}_2 \longrightarrow \text{H}_2\text{CO} + \text{HO}_2)$ $\text{HO}_2 + \text{HO}_2 \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2$ $2(\text{CH}_3 + \text{O}_2 + \text{M} \longrightarrow \text{CH}_3\text{O}_2 + \text{M})$ $2(\text{CH}_3\text{O}_2 + \text{O} \longrightarrow \text{CH}_3\text{O} + \text{O}_2)$ $2(\text{H}_2\text{CO} + \text{h}\nu \longrightarrow \text{CO} + \text{H}_2)$ $2(\text{O}_3 + \text{h}\nu \longrightarrow \text{O} + \text{O}_2)$ $\text{H}_2\text{O}_2 + \text{h}\nu \longrightarrow \text{OH} + \text{OH}$ Net: $2\text{CH}_4 + 2\text{O}_3 \longrightarrow 2\text{H}_2 + 2\text{H}_2\text{O} + \text{O}_2 + 2\text{CO}$ | 13.697 | 14.51 | 5.5 |
| $D_{2.3}$ | $\text{HO}_2 + \text{HO}_2 \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2$ $2(\text{OH} + \text{O}_3 \longrightarrow \text{HO}_2 + \text{O}_2)$ $\text{H}_2\text{O}_2 + \text{h}\nu \longrightarrow \text{OH} + \text{OH}$ Net: $2\text{O}_3 \longrightarrow 3\text{O}_2$ | 22.404 | 22.442 | 7.5 |
| $D_{2.4}$ | $\text{O}_3 \longrightarrow \text{O}_{3\text{trpt}}$ Net: $\text{O}_3 \longrightarrow \text{O}_{3\text{trpt}}$ | 83.208 | 83.195 | 10.5 |
| $D_{2.5}$ | $\text{O}_3 + \text{h}\nu \longrightarrow \text{O} + \text{O}_2$ $\text{O} \longrightarrow \text{O}_{\text{trpt}}$ Net: $\text{O}_3 \longrightarrow \text{O}_2 + \text{O}_{\text{trpt}}$ | 33.453 | 33.333 | 15.5 |
| $D_{2.6}$ | $\text{O}(^1\text{D}) + \text{H}_2\text{O} \longrightarrow \text{OH} + \text{OH}$ $\text{OH} + \text{HO}_2 \longrightarrow \text{H}_2\text{O} + \text{O}_2$ $\text{OH} + \text{O}_3 \longrightarrow \text{HO}_2 + \text{O}_2$ $\text{O}_3 + \text{h}\nu \longrightarrow \text{O}(^1\text{D}) + \text{O}_2$ Net: $2\text{O}_3 \longrightarrow 3\text{O}_2$ | 27.694 | 28.375 | 16.5 |
| $D_{2.7}$ | $\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$ $\text{NO}_2 + \text{O} \longrightarrow \text{NO} + \text{O}_2$ $\text{O}_3 + \text{h}\nu \longrightarrow \text{O} + \text{O}_2$ Net: $2\text{O}_3 \longrightarrow 3\text{O}_2$ | 49.204 | 49.202 | 28.5 |

| | | | | |
|------------|--|--------|--------|------|
| $D_{2.8}$ | $\text{HO}_2 + \text{O} \longrightarrow \text{OH} + \text{O}_2$ $\text{OH} + \text{O}_3 \longrightarrow \text{HO}_2 + \text{O}_2$ $\text{O}_3 + h\nu \longrightarrow \text{O} + \text{O}_2$ $\text{Net: } 2 \text{O}_3 \longrightarrow 3 \text{O}_2$ | 12.92 | 12.891 | 23.5 |
| $D_{2.9}$ | $\text{O}(^1\text{D}) + \text{N}_2 \longrightarrow \text{O} + \text{N}_2$ $\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$ $\text{NO}_2 + \text{O} \longrightarrow \text{NO} + \text{O}_2$ $\text{O}_3 + h\nu \longrightarrow \text{O}(^1\text{D}) + \text{O}_2$ $\text{Net: } 2 \text{O}_3 \longrightarrow 3 \text{O}_2$ | 39.97 | 39.973 | 38.5 |
| $D_{2.10}$ | $\text{O}(^1\text{D}) + \text{N}_2 \longrightarrow \text{O} + \text{N}_2$ $\text{HO}_2 + \text{O} \longrightarrow \text{OH} + \text{O}_2$ $\text{OH} + \text{O}_3 \longrightarrow \text{HO}_2 + \text{O}_2$ $\text{O}_3 + h\nu \longrightarrow \text{O}(^1\text{D}) + \text{O}_2$ $\text{Net: } 2 \text{O}_3 \longrightarrow 3 \text{O}_2$ | 10.943 | 10.946 | 42.5 |

Table 1: Comparison of O_3 destruction pathways for two different methods of solving equation 17 in the main manuscript: Using the first solution found by Scipy’s `lsq_linear` and using the procedure described in Lehmann(2004). We only show the first 10 destruction pathways shown in figure 1.

3. Table 3: Pathways D2,1, P2,3, P2,4, P2,5: In the troposphere CH_3O_2 has a short chemical lifetime (usually < 1 min). Therefore we would expect that its fate is controlled by local chemistry, not by transport. Nevertheless, the pathways mentioned above involve transport of CH_3O_2 . Is it possible that this transport of CH_3O_2 is a numerical artifact, resulting from its calculation according to Eq. (46)? There the (possibly small) contribution of transport T_i is calculated as the difference of (possibly larger) chemical terms. Pathway D2,5: The same type of question applies to D2,5: This pathway involves transport of atomic oxygen, which has a short chemical lifetime in the altitude region indicated (around 15.5 km).

Response: In the model we used CH_3O_2 has a tropospheric number density that ranges between 10^6 and 10^{11} molecules/ cm^3 , and a lifetime against chemical destruction that ranges between 1 and 170 days (figure 2, first row). That is why CH_3O_2 transport rates are important in our results. Figure 2 (first row) presents the different terms of equation 46 for CH_3O_2 between 0 and 20km. The chemical production and destruction do not balance the CH_3O_2 rate of concentration change, so we assume that transport contributes to the remaining molecules to achieve balance. As a consequence, we do not think the presence of CH_3O_2 transport in some pathways is a numerical artifact. This might be the result of an incomplete representation of the CH_3O_2 chemistry in the *photochem* model. We did not find references with observational CH_3O_2 concentrations to compare to the model we are using. Are you aware of any?

We show the different terms of equation 46 for O between 0 and 35km in figure 2 (second row). The chemical production and destruction do not balance the O rate of concentration change between 12 and 35 km. As a consequence, O transport shows as important in these altitudes in our results using the *photochem* model.

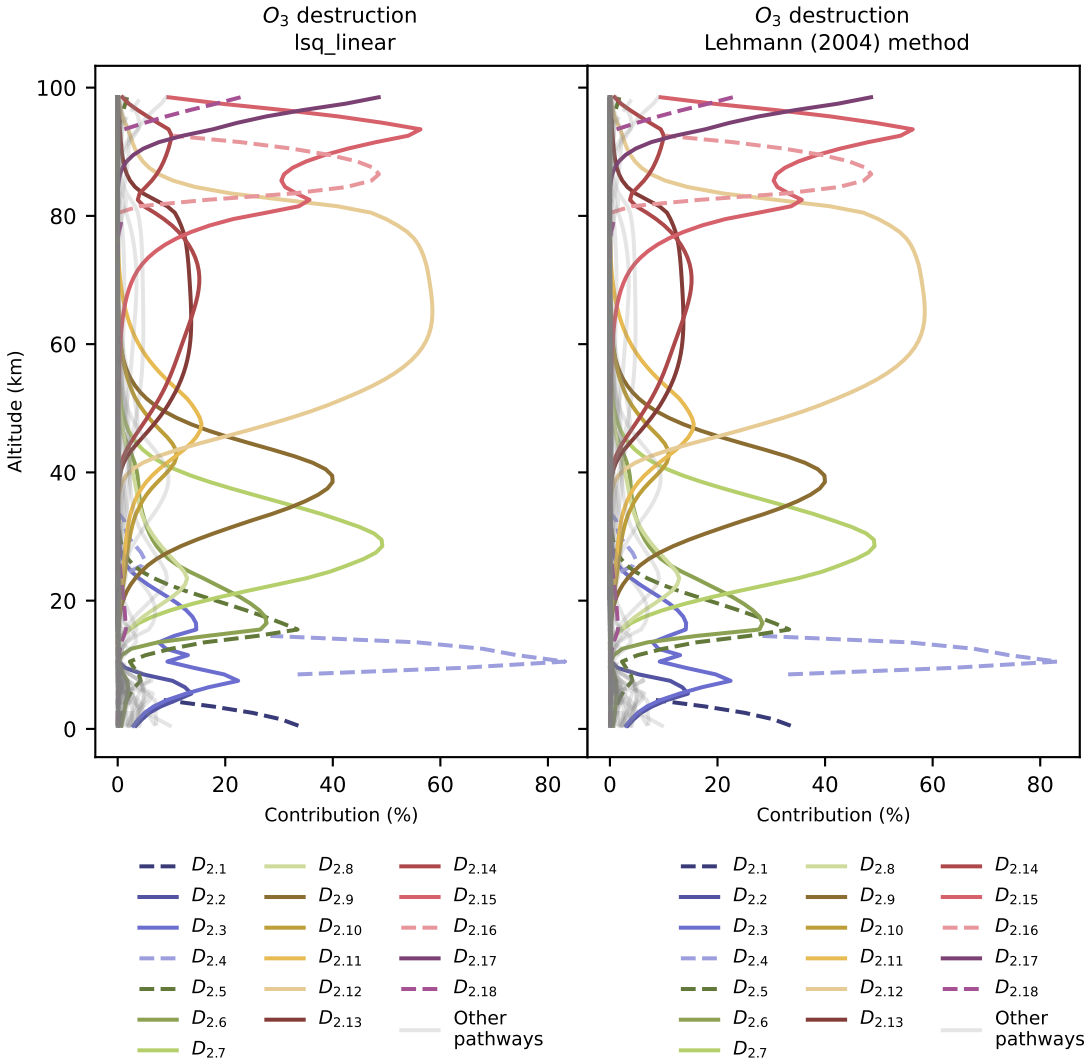


Figure 1: Comparison of O_3 destruction pathways for two different methods of solving equation 17 in the main manuscript: Using the first solution found by Scipy's lsq_linear (left column) and using the procedure described in Lehmann(2004) (right column).

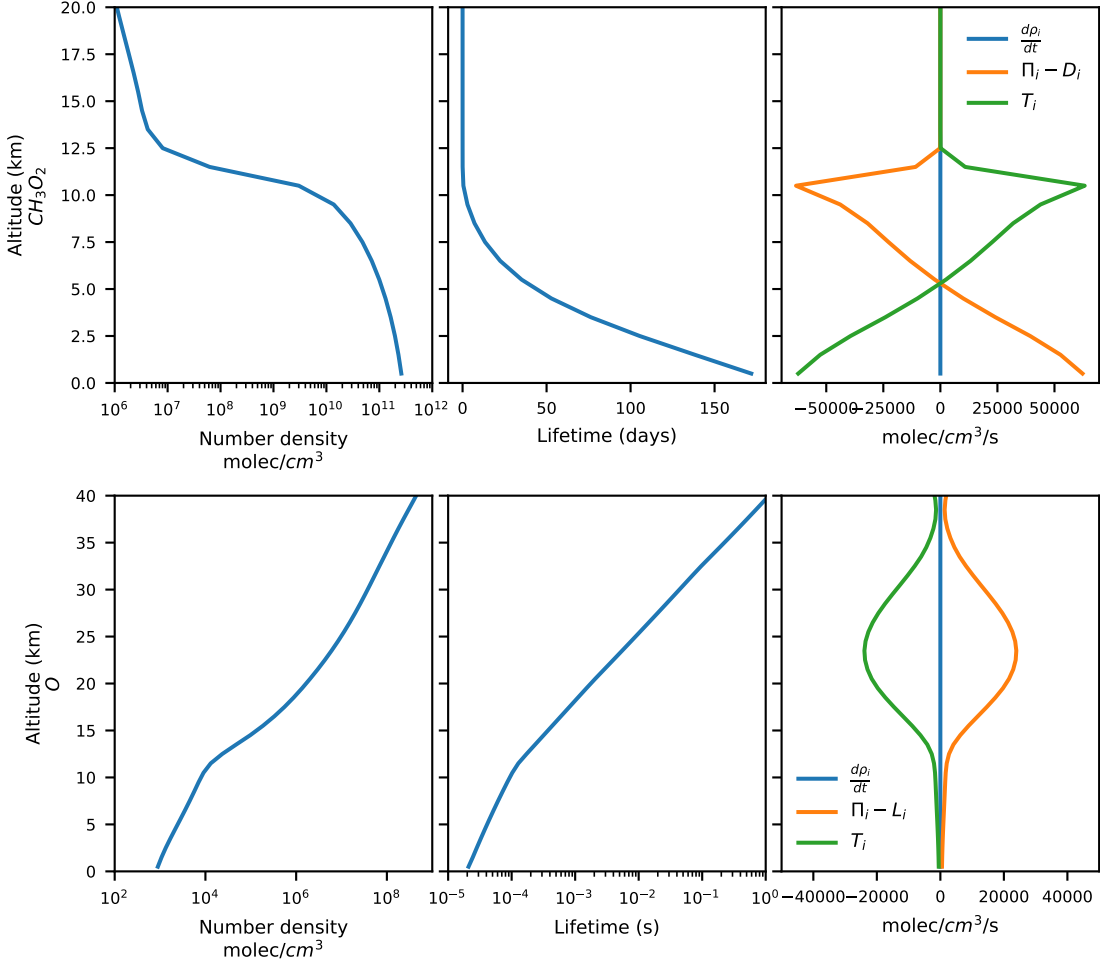


Figure 2: Number density (first column), lifetime against chemical destruction (second column) and terms of equation 46 in the main manuscript (third column) for CH_3O_2 (first row) and O (second row). The label definitions in the third row are $\frac{d\rho_i}{dt}$ (rate of concentration change), $\Pi_i - L_i$ (chemical production minus destruction), T_i (transport rates). We do not show rainout rates because they are zero or very close to zero.

4. How many of the 1281 reactions have a rate $> f_{min}$, so that they actually take part in the formation of pathways?

Response: The number of reactions with rate $> f_{min}$ varies with altitude, and ranges from 78 to 132. We will update the text to mention this.

5. CH₄ is not photochemically produced in Earth's atmosphere (G. Brasseur and S. Solomon: *Aeronomy of the Middle Atmosphere*, Springer, Dordrecht, 2005: p. 296). If this is true also in your model, then f_{min} as defined in lines 388-389 will be zero.

Response: Our reaction system also includes a pseudo-reaction for CH₄ supply from transport. For this reason, f_{min} is different from zero. We will clarify this in the manuscript.

6. How long is one time step? **Response:** The *photochem* model uses a solver that uses a variable timestep (CVODE BDF method created by Sundials Computing). In our simulation the timestep varies from 10^{-5} s to 10^{12} s. In our analysis we only output the model results when the simulation time is greater than 10^{11} s. We will clarify this in the manuscript.