Review of

“Chempath 1.0: An open-source pathway analysis program for photochemical models”

(revised version of 3 December 2024)

by D. Garduño Ruiz et al.

(Numbers refer to line numbers in the manuscript version with tracked changes.)

Major comments

367 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.

438 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 $O + O_2 + M \rightarrow O_3 + M$. 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).

422-425 As O_x ($= O_3 + O + O(^1D)$) 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 $[O_2]$) and the time scale of destruction. By determinining 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).

Details

72 “concentration” ⇒ “mixing ratio”

81, 204 “enhance” ⇒ “reduce”?

90 “and the model time in” ⇒ “at” (to avoid mentioning “model time” twice)?

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 idependently from the time step of the solver.

206 Equation (14): Does the multiplication mean scalar product?
The notations “$[m_{iq}] > 0$” and “$[m_{iq}] < 0$” are problematic: a vector is compared to a number.

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

244 “section 5.2.2” ⇒ “section 5.5.2”

261 “m_{ik}” ⇒ “$[[m_{ik}]]$”

315 Equation (33): “$[m_{i1}] > 0$” and “$[m_{i1}] < 0$”: vector compared to number (cf. 206). Moreover, these expressions should not be placed **within** an equation.

347 The explanation “The expression 42 involves ... (44)” should appear directly after Equation (42).

444 “updated” ⇒ “augmented”?

Fig. 3 The abbreviation “Ox” ($\hat{=}$ “Oxidation” - of what?), standing near “NO_x” and “HO_x”, might be easily confused with “O_x” ($\hat{=}$ O_3 + O + $O(^1D)$).

500 “shows” ⇒ “show”