Review of

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

(revised version of 7 April 2025)

by D. Garduño Ruiz et al.

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

Major comment

The authors introduce a way of tracking the consequences of imbalances in the input data. However, they do **not** provide a remedy for such imbalances.

379 As the authors only provide a tracking of imbalances, the headline of Section 3.2 "Balancing of concentration changes" is misleading and should therefore be changed.

382-383 "... we assume that the difference between concentration changes and the total production by all reactions is due to the solvers numerical error...": In most applications the concentration change is calculated by the solver (with high accuracy), whereas the reaction rates are calculated separately after the main model run (from data with less temporal resolution than the internal calculations by solver), which introduces larger errors (and justifies a subsequent modification of the rates).

395 As stated correctly by the authors, they request that the user ensures the balance of the input data. As explained above, this may be problematic for some users. Therefore a corresponding information ("warning") should be included in the abstract and introduction together with a notice that a part of the original algorithm of Lehmann (2004) was not implemented.

Details

76-371 Please check carefully throughout the whole manuscript whether the square brackets really denote matrices or vectors as defined in line 76 or just single elements of a matrix or vector (contrary to their definition in line 76), **for instance**:

- Table 1: $[dc_i]$ should be explained as "**vector** of the concentration changes..." (or the square brackets would have to be removed).
- Table 1 (last line): If $[\tilde{c}_i]$ and $[d_i]$ denote vectors, then $[\tau_i]$ must be calculated by element-wise division.

- Eq. (1): This looks like a product of a matrix and a vector, but then the summation would not be correct (and there is one closing bracket too much).
- 200: "where $i = 1, ..., n_s$" seems to denote n_s individual equations, which contradicts the vector notation in Eq. (14).
- 218: You mention **one** vector $[w_e]$, but calculate the sum over n_e such vectors in Eq. (16). (Is the transpose symbol in Eq. (16) correct?)

77-79 "keeping only the positive values" ⇒ "keeping only the positive values and zero"? (analogously for negative values)

366 I suggest to keep the deleted "as branching points" for clarity.

412-413 "constant rates" or "constant rate constants"? "these rates" or "these rate constants"?

426 "We run Chempath ... in all the model times...": This sounds like points in time. What is the length of the time intervals analysed, corresponding to dt in Table 1?

472 "We run Chempath ... at 32 time points...": cf. previous question.

473 Does this sentence mean that the model run was 1 million years long (cf. also line 439)? If so, why do Table 4 and Figs. 3, 4, and 5 show results for "time = 1.16 million years"?

505 Probably the sequence of causes and effects is: decrease of the O_2 input flux ⇒ decrease of the O_3 production rate ⇒ decrease of the O_3 concentration ⇒ decrease of the O_3 loss rate

520-521 Under conditions of present Earth (troposphere), the reaction CH_3O_2 + NO → ..., which is included in your model, would ensure a short lifetime of CH_3O_2. However, the mixing ratio of NO in your model seems to be extremely small: From the lowest points in Figure 3 (red line) we can obtain the following rough estimate of the NO mixing ratio r_{NO}:

$$\begin{aligned} r_{NO} &= [NO]/[M] \\ &\leq [NO]/(5 \cdot [O_2]) \\ &\approx 4 \cdot 10^4/(5 \cdot 2 \cdot 10^{18}) \\ &= 4 \cdot 10^{-15} \\ &= 4 \cdot 10^{-6} \text{ ppb} \end{aligned}$$

521 "these species": which species (or why plural)?

Table 4 The unit of the rates (molec/(cm^2·s)) seems to imply vertically integrated rates. However, the figure caption says "... rates ... correspond to the height at which the pathways contribute the most..."

Typos

219 "weighs" ⇒ "weights"

425 "figure 2e" ⇒ "figure 2f"

503 "$P_{2.9}$ to $P_{2.18}$" ⇒ "$D_{2.9}$ to $D_{2.18}$"