Second response to Reviewers: "Beyond self-healing: Stabilizing and destabilizing photochemical adjustment of the ozone layer" (EGUSPHERE-2024-147)

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August 1, 2024

We are pleased to hear that the reviewer supports our revisions to accommodate their thoughtful comments from the first round, and we are pleased to revise the paper to address their thoughtful minor recommendations on the second submitted version of the manuscript. Throughout this Response to Reviewers, reviewer comments will be in black and our author comments will be in blue.

General

I see that the second version of the paper has seen a lot of work by the authors. I like in particular the change in the discussion in the paper throughout from the classical Chapman model to the Chapman+2 model. However, rereading the paper, I still feel that there are changes to the paper that did improve the readability and accuracy of the manuscript.

Therefore, I suggest that the authors consider the comments below and try to improve the paper further. I consider these changes 'minor'. If considered necessary, I would read the revised version of the paper again, but this should be the decision of the editor.

We are pleased to hear that the reviewer approves of the Chapman+2 model for the development of a theory of photochemical adjustment. We thank them again for their comments that helped move us in this direction.

Comments

Range of applicability

I still think the paper could be clearer to where the ideas put forward here could be applied. For example, looking at Fig. 4 (and reading the caption) the proposed concept looks like a global (albeit 1D) result. However, in l. 176 it is stated that the calculation (and thus Fig. 4) is for tropical ozone. Furthermore, in the caption of Fig. 4 (and elsewhere in the

paper) the 40 km demarcation is mentioned. From the explanation (which starts on page 8) I understand that 40 km is valid for the tropics (l. 176). If I am incorrect then the discussion following Fig. 4 should explain why the 40 km can be considered a global value (possibly one could repeat the calculation shown in Fig. 4 for a mid-latitude ozone profile). If on the other hand 40 km is more a tropical value, this should be clear throughout the paper (in particular in the conclusions).

Good point about the opportunity for more clarity in the caption about the geographic location of Figure 4. Given that this figure is for the tropics, in particular using the coefficients from the equator, we now label the caption as the "*Equatorial* ozone response to..." using the "*equatorial* coefficients from the Cariolle v2.9 linear ozone model" [italics added here for emphasis]. Note that the coefficients reasonable coherent throughout the tropics, so the equatorial column can be thought of as representing the entire tropical atmosphere.

We have further specified the location of applicability for our Chapman calculation, where overhead solar zenith angle is used to specify a tropical column as: "photochemical adjustment is destabilizing above 40 km *in the tropical atmosphere*" [emphasis added]

At line 455, we now state: "The bottom of the destabilization layer occurs robustly around 40 km *in the tropics*" [emphasis added]

In our Conclusions (line 595): "We have also characterized a new and unconventional region of photochemical destabilization above 40 km in the tropical stratosphere and even farther aloft at high latitudes."

Equations 4 and 5

I suggest formulating the assumptions used for deriving equations 4 and 5 more clearly. You assume

$$\frac{d\mathrm{O}}{dt} = \frac{d\mathrm{O}_3}{dt} = 0 \tag{1}$$

i.e., steady state between O and O3 (I would not call this "typical equilibria"). Then you use reactions (R1) to (R6) to derive algebraic equations and then you replace the O2 concentration by a constant value. Correct? Assuming constant O2 concentration in (R1) would not give the desired result, would it?

We have clarified this derivation in several ways. We now say: "For steady state solutions to the Chapman Cycle, the molar fraction of O_2 is several orders of magnitude larger than that of O and O_3, and will be treated as constant ($C_{O_2} = 0.21$). Then, setting $\partial \mathrm{O}/\partial t = \partial[\mathrm{O}_3]/\partial t = 0$, these reactions can be algebraically solved to yield a quadratic equation for O_3 at a given altitude:" We refer the curious reader to more details about this photochemical system to a related paper: "This photochemical system has been described in more detail in Match et al. (2024), which explains why the number density of ozone has an interior maximum in the tropical atmosphere." Note that we do in fact assume constant

[O_2] concentrations in R1, as is standard for solving the Chapman system, such that the amount of O_2 is prescribed as fully external to the Chapman system.

Model description and documentation

I said in my first review: " . . . MOBIDIC and the Cariolle scheme have certainly evolved over time during the decades since the cited reference in 1985. It would be good to have at least some information on the new parameters of the Cariolle scheme . . . ".

I appreciate the statement by the authors that the communication of the parameters of the scheme are a private communication and that this is a reason for not publishing these parameters. However, I suggest that the authors obtain the permission from D. Cariolle to make the parameters available to the public (in an appendix or in a table). I believe this would be of advantage to everybody considering to use the Cariolle scheme (and it would also be good for the paper).

We are sympathetic to the idea that all data should be available for others. We have reached out to Dr. Cariolle to share with him that there is broad community interest in his dataset and to encourage him to consider sharing the data more broadly and systematically through a long-term public repository. We believe this could be a valuable resource for the community, but given that the data is not our intellectual property, this is ultimately not our decision. We hope that in the meantime, interested readers will be able to follow our footsteps and request the coefficients through personal communication.

Some minor issues

- l. 7: "that" → "the enhanced" Revised.
- l. 13: "if" → "when" Revised.
- l. 14: "where" → "when" Revised.
- l. 20: "continual" → "continuous" but perhaps this is not the best way of describing the balance by P and L in the ozone layer Continual → continuous.
- 23: "reduce ozone at a particular altitude" We believe the reviewer wants to help us forestall confusion about why the ODS can strictly reduce ozone while also leading to increases. We emphasize that our statement about strict reductions is for the *local* response, as we have stated: "As was perhaps first noted by Johnston (1972), emitting an ozone-depleting substance whose local chemical effects strictly reduce ozone can nonetheless cause ozone to increase at certain locations (subsequent treatments include Dütsch, 1979; WMO, 1985; Solomon et al., 1985; Fomichev et al., 2007; Meul et al., 2014)." Our statement is correct.
- l. 24: replace "locations" by "altitudes"? Revised.

- l. 24: do you also want to include Hartmann (1978) in this list of references? Added.
- l. 26: you mention ODSs here, while Fig. 1 says CFCs. Perhaps make clear in the text that the same thing is meant. We now emphasize that the model experiment imposes halocarbons which includes the more-familiar CFCs.
- l. 37: "because" → "from" Revised.
- l. 37: "allows" → "allowing" Revised.
- l. 193: The top of the atmosphere (considered here) is 60 km ? this is how I read these lines. Could you explicitly state this? And the numbering is from the top downwards ? so the top of the atmosphere is z0. Is this correct? I think the paper could be a bit clearer here. The top of our model atmosphere is above 60 km, and 60 km is the fifth model level down from the top, at which we begin imposing our perturbation. We further clarify a point that benefits clarification following discussions of our method by noting at the end of that paragraph: "In this way, our calculation is locally linear in the overhead column ozone perturbation, but the dependence on overhead column ozone means that the ozone response at any given altitude depends nonlocally on the changes aloft."
- l. 193: Do you mean "zi, where i = 0,1?N"? Or "i = 1,N"? Suggest to be accurate here. Also why not state what N is? Revised. We now state, "Both of these offline calculations have been performed on the discrete grid of the Cariolle v2.9 linear ozone model, with levels z_i, i = 1, 2, ..., N (where N = 91) numbered from the top of the atmosphere downwards, each with a thickness of Δz_i ranging from >3 km above 55 km to less than 1 km below the ozone maximum around 26 km."
- l. 194: It would be good to give the value of the thickness employed here. Revised in previous comment.
- l. 268: What is meant with "foundational" here? Drop this word here? We would like to retain the word foundational meaning to reflect that the Chapman Cycle provides the foundation for subsequent ozone science. As noted in Brasseur (2020), the puzzle of higher ozone at high latitudes compared to low latitudes led some analysts to seek to explain the ozone layer as a consequence of the high-energy particles that lead to the auroras over the poles. Chapman was the first scientist to explain ozone formation in terms of UV photochemistry, a foundational advance for all subsequent work on the topic. (Only later was the puzzle of high latitude ozone resolved by the work Brewer and Dobson.)
- l. 270: "rich theories" is not really clear here Removed "rich".

- l. 285: "This assumption" is "CO2 = 0.21" ? correct?. But I think the central assumption is the equilibrium between O and O3 (see also above). As noted previously in this response, we have revised the reflect this central assumption more clearly: "For steady state solutions to the Chapman Cycle, the molar fraction of O_2 is several orders of magnitude larger than that of O and O_3, and will be treated as constant ($C_{O_2} = 0.21$). Then, setting $\partial O/\partial t = \partial[O_3]/\partial t = 0$, these reactions can be algebraically solved to yield a quadratic equation for O_3 at a given altitude:"

- Eq. 17: try "\left" and "\right)" instead of the brackets in the LaTeX equation. Revised.

- l. 583: lower than what? Reworded for clarity: "Ozone-depleting substances can lead to increases in ozone at some altitudes, known as self-healing, which have been argued to result from ultraviolet fluxes reaching deeper into the atmosphere."

As a minor note, we have identified a missing factor of 2 to both terms on the r.h.s of Equation 15, which has been corrected in the Equation and in our calculation of Figure 3c. Our main emphasis using Equation 15 was on its sign, which was strictly unaffected by the omitted factor, so our conclusions are unaffected.

References

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