

Review of

“Protection without poison: Why tropical ozone maximizes in the interior of the atmosphere ”

by A. Match et al.

General

I think it is good that this paper addresses issues of catalytic cycles of ozone loss and ozone production in the tropical stratosphere. The study goes back to textbooks and examines what can be learned from the ‘classic’ explanations and in how far they should perhaps be modified.

However, the paper needs to have a clearer message. I do not think that the fact that tropical ozone has a peak (in concentration) at about 26 km is the new finding that this papers wants to report. And also not the concentration of ozone at this altitude. As I read the paper, what is new here is the advance in understanding of several issues that is gained through the different simplified models. I do not think this aspect is coming across very well.

The analysis in the paper also based on certain assumptions, which are important for the presented derivations. I suggest mentioning these assumptions clearer and upfront (rather than in the course of particular derivations). There are also questions about the “real world” ozone representation (i.e., MERRA-2, see also below).

Overall I suggest improvements to the manuscript. The message of the paper should come across more clearly.

Comments

Applicability of the analysis

Clearly, the maximum (in concentration) of ozone is not the same everywhere, in particular it depends on latitude. It is not clear which region the paper is addressing, looking at section 2 it seems the entire atmosphere (but the the maximum is more than one value); however the title says ‘tropical’. Further, the maximum of

ozone concentration at a particular altitude (even for a given latitude) can only be considered a fixed number for some kind of climatology (i.e., for some averaging; see also below). This aspect should be addressed in the paper, e.g., there should be more information in the caption of Fig. 2 (which latitude range, which period? etc., see also comments on Fig. 3). Transport is represented rather crudely (l. 120-127) and the analysis is restricted to the tropical lower stratosphere. So is the tropical (lower) stratosphere the regime to which this analysis should be applied? I think the answer is ‘yes’, but this should be clearly stated throughout the paper.

Another aspect is tropospheric ozone. At some instances in the paper it is clearly stated that this analysis is not about tropospheric ozone chemistry (l. 468). This is correct and I agree. But this is not clearly and upfront stated in the paper. And some of the figures (e.g. 2, 4, 5) extend to the ground, leaving the impression that the discussion in the paper is relevant also for tropospheric altitudes (for which is it not). Looking at Figs. like Fig. 5, it is clear that the real atmosphere (here MERRA-2, see also below) does not look like anything in the ‘non-photolytic sink regime’ below the tropopause. Moreover, given the fact that the tropical tropopause is at about 18 km (Hoffmann and Spang, 2022); most of the the ‘non-photolytic sink regime’ in Fig. 5 is irrelevant.

Damping

Throughout the paper, the concept of “damping” is used. It is mainly applied to ozone (O_3) or to O (where $O_x = O + O_3$). To me “damping” is the energy loss of an oscillating system through dissipation. Here this concept seems to be used as a synonym for change of O_3 or O at a particular location through chemical (catalytic) loss and advection of O_3 (e.g., advection of low ozone from below in the tropical lower stratosphere).

The concepts of chemical change and advection of stratospheric ozone are well known (see e.g. the textbooks cited in this manuscript), so I do not really see the advantage of redefining these concepts in terms of “damping”. At least, I suggest that the wording used here is related to the well established concepts of catalytic loss and advection of stratospheric ozone. Furthermore, these concepts apply to ozone in photochemical equilibrium, where $\partial O_3/\partial t = \partial O/\partial t = 0$ – correct?

Twenty six kilometres

Throughout this paper (starting with the abstract, ls. 2, 10) the altitude of the peak of the ozone layer (in terms of concentration) is a key point here. And the transition between two photochemical regimes. Twenty six kilometres is the number that is reported. However, how certain is this number; no error estimate is given, what is the uncertainty for the 26 km? Also, is there a variability of the 26 km with other atmospheric parameters (e.g. QBO, Nivano et al., 2003; Diallo et al., 2018).

Perhaps more importantly, any successful simulation of the tropical ozone layer should not only reproduce the location of the peak in altitude but also the vertical distribution in ozone concentration with altitude (including the ozone concentrations at the peak); I think this aspect could be treated more thoroughly in this paper.

Assumptions

There are a number of assumptions on ozone made in this study that are mentioned; however I suggest to state these assumptions more clearly ad upfront. For example, photochemical equilibrium of ozone is assumed ($\partial[\text{O}_3]/\partial t = 0$; l. 138), which is a strong assumption. This assumption is not valid for a large part to the stratosphere. (Which seems to be the reason why this analysis is restricted to the tropics). Further there are assumptions like an isothermal atmosphere (also not realistic) and other assumptions (l. 293) that should be clear.

Catalytic cycles destroying ozone

The Chapman (1930) model is known to be incorrect insofar as it neglects the most relevant catalytic ozone loss cycles (e.g., Portmann et al., 2012). Thus to investigate tropical ozone (which seems to be the target here) one needs to look at the tropical profiles for the relevant species driving ozone loss in the tropics. I do not think this is the case here and I recommend changing it. Global estimates are not helpful here, the atmosphere is very different in the tropics and in the mid-latitudes. Already decades ago, researchers (including the editor of the present manuscript) have invested substantial effort into deriving ozone loss cycles in the tropics (e.g., Crutzen et al., 1995).

Formation and destruction of ozone

In the introduction, there is a discussion of the ozone sources and sinks in the atmosphere. While I like the idea to go back to the textbooks, it should be clear that much more is known today than what is discussed in Fig. 1. Some modern textbooks are cited, but another example is Portmann et al. (2012). Regarding the history of the debate on the relevant sinks of ozone in the atmosphere I also recommend the book by Brasseur (2019).

Odd oxygen

Commonly, odd oxygen O_x is defined as $O_x = O + O_3$. This is also done here. This is a well established concept (see e.g. the textbooks cited in this manuscript). However, O_x is used here first (l. 132) before being defined (l. 136). But more importantly, the concept needs to be introduced briefly before being used (even if the reviewer has learned about O_x before). Further, below (l. 163) O_y is mentioned – but without knowing what this is, any discussion below on O_y is not very useful. Define in this paper what O_y is.

Ozone in the real world

As a reference for ozone in the real atmosphere, MERRA-2 (Gelaro et al., 2017) is used. Always one particular profile is presented, but it is not clear what the profile shows. In the caption of Fig. 3, one reads that this is a tropical ozone profile (30°S to 30°N), but this is not the most conservative estimate of the tropics; perhaps 20°-20° would be more appropriate? Has this sensitivity been explored? The profile is for 2018. I could not find another place in the manuscript where the profile is explained (which should be changed). I assume that it is a zonal mean profile and that the profile is annually averaged (of course, I am not sure). But this should be clearly stated in the manuscript. Another question is, which vertical resolution was used for MERRA-2 ozone.

Further, how was 2018 chosen? As pointed out in the manuscript tropical ozone depends on the solar UV-flux, which is changing with the 11-year solar cycle (albeit not by a factor of two). Tropical ozone might also be influenced by the QBO (see above); could this point be of interest here? If only one single year is considered, why was a reanalysis chosen rather than direct measurements (e.g. MLS, Waters et al., 2006; Han et al., 2019). A climatology based on (ozone)

observations could be an alternative (e.g., SWOOSH, Davis et al., 2016).

Technical issues

The paper could be easier to read. There are a few issues where a clearer language would help. The paper talks about a “gray ozone layer” – to me this is jargon. This term (gray ozone) is not familiar to the readers of ACP; it is rather a shorthand for assumptions about the lack of a spectral dependence of σ_{O_3} and σ_{O_2} .

In Eq. 7 (l. 160) a_5 (and similar coefficients) are used. I cannot see that these coefficients have been defined before (did I overlook anything?). It would be good to explain here what the atmospheric meaning of a_5 (etc.) is.

Also, O_y , is used in the paper, but this is not an established notation (see also the comments on odd oxygen above). I also suggest a better introduction to the concept of ‘damping’ to make the paper more easily accessible (again see discussion above). Further, there is ‘appendix B’ two times in the paper – this is confusing.

There are recommendations by ACP; the abstract is likely too long. Also, it would be good if the coefficients for the Cariolle 2.9 scheme used here were available – in this way the results of this paper could be reproduced and the coefficients be used for other purposes.

Minor issues

- l. 17: This is a matter of opinion, but I suggest not attributing the discovery of the ozone layer to Hartley alone; see the discussion by Brasseur (2019).
- l. 35: I suggest also to have a look at the classic textbook by Dobson (1963). While the textbooks want to give a simple message to the reader, it is clear that production of ozone alone, without a loss mechanism for ozone would simply convert O_2 to ozone. This is why Dobson (1963), on page 105 of his book, calls the chapter “FORMATION AND DESTRUCTION OF OZONE”.
- l. 50: The quoted MERRA-2 ozone profile is for the tropics (information only in the caption). But how are the tropics defined here? For which period is the ozone profile valid? Likely the MERRA-2 ozone is the same as the

one in Fig. 3 – correct? Does MERRA-2 assimilate ozone observations? Perhaps add a reference for MERRA-2 (see above).

- l. 64: Is it clear here what passive and active sinks are?
- l. 83: ‘gray radiative transfer’ is not clear to me here (see also above).
- l. 83: ‘endogenously’ sounds like a medical term to me – is it really helpful here?
- eq. 3: larger brackets for the exponential function (also elsewhere)
- l. 122: ‘damping ozone’ could be better explained
- l. 128: is this ‘augmentation’ meant to be globally or tropical?
- l. 130: I think the coefficients z_O and z_{O_3} are important for this paper, but they are not reported (did I miss anything?)
- Fig. 3: I would not call MOBIDIC a chemistry climate model; I think nowadays something else is understood by the term chemistry climate model.
- l. 157: how is this vertical scale determined?
- l. 167: I do not understand, why ‘globally averaged’ profiles of chemical constituents are used. The paper is on tropical ozone.
- l. 176 ‘eff’ should not be in italics
- l. 182: more need to be explained here that ‘average’ – see also above.
- l. 187: I do not think that it is necessary to use globally averaged profiles here. (Also the profile is probably not ‘catalytic’.)
- l. 197: Does the Chapman cycle sink ever dominate in the atmosphere?
- l. 216: adding the reactions that lead to the ‘domination’ would be helpful here.
- Fig. 4: It should be clear that this figure is for the tropics. Second, the figure extends to the ground, but the tropospheric chemistry prevailing below ≈ 18 km is not discussed here.

- l. 241: It is not clear here where the 26 km value comes from.
- l. 270: solutions are only for equations, not for a ‘layer’. (Also l. 294).
- l. 298: is it clear here *why* the transition altitude is the altitude of the ozone maximum?
- l. 314: the surface is not a region where these theories should be applied.
- l. 430, 431: I am confused here: the red line in Fig. 5 is discussed (source/sink paradigm) – it does not provide a good estimate for the ozone maximum. However the Chapman+2 model (magenta line) does. So why are we concerned about the red line if the Chapman+2 model seems appropriate?
- l. 436: ‘generalized destruction’ is not clear.
- l. 473: change * to \cdot
- l. 476: why are the absorption coefficients not taken from the most recent kinetic recommendation (Burkholder et al., 2020)?
- l. 477: Why is it not possible to approximately take the atmospheric temperature profile into account when calculating temperature dependent kinetic parameters?
- Fig. C1: I cannot see the magenta line mentioned in the caption in this figure.
- l. 614: ‘The atmospheric environment’ is listed here twice.

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