

Review of

“Beyond self-healing: Stabilizing and destabilizing photochemical adjustment of the ozone layer ”

by A. Match et al.

General

I like the general idea of the paper, namely a focus on the issue of “self-healing” and to look into the detailed chemical mechanisms involved. And these mechanisms are indeed discussed in detail.

But I also have reservations about the study. First, I think that the paper is not well formulated in many respects; I suggest a “methods” section where the employed models are better described and introduced. And the available literature at this point is rather old. Second, the paper sounds almost like a global study (e.g. abstract), but throughout the paper the tropics are mentioned. (But not the mid-latitudes). So is this a paper on tropical ozone? The neglect of transport seems to limit the range of applicability. Third, I do not agree that the Chapman cycle constitutes a good approximation of the state of the ozone layer; the loss term of ozone in the atmosphere is at no altitude dominated by the Chapman reaction R4 (Fig. 2). Finally, the assumptions on stratospheric cooling and ozone depletion are likely to be crude (no time period given, no altitude dependence assumed) so that the question arises what can be learned about the real atmosphere based on such assumptions.

In summary, I think the paper needs work and improvement. The assumptions (and range of applicability) should be clear and there should be a clear message.

Comments

Neglecting stratospheric transport of ozone

Clearly stratospheric ozone is strongly influenced by transport (Fig. 1 of this review); this is acknowledged by the authors of the paper. However, in the main body of the paper this is only noted in passing (and not at all in the introduction)

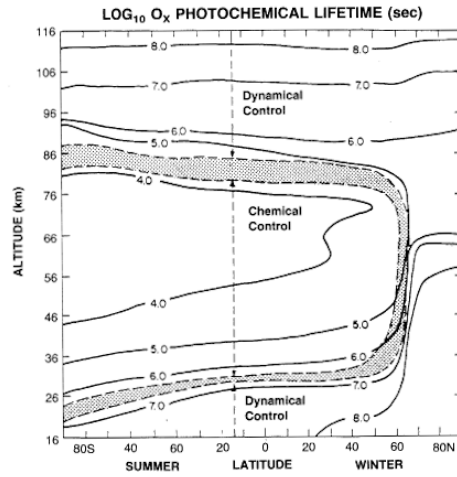


Figure 1.1.2-1 Logarithm of the computed lifetime of the odd oxygen family in Northern Hemisphere winter versus latitude and height, from the Garcia-Solomon two-dimensional model (from Garcia and Solomon, 1985). Regions dominated by chemical and dynamical processes are indicated.

Figure 1: Chemical and dynamical control of ozone in the stratosphere. (from WMO, 1990).

and not really employed in the text. I have noted that there is section 8.1. But in my opinion, the study needs to be clear about in which regions (due to transport) the employed analysis is not applicable. At the moment the study reads like a “photochemistry only” study, where transport is inserted as an ‘add on’.

Chapman cycle

The paper makes the point that the “Chapman model” explains the gross features of the ozone layer. I am sorry, but I cannot agree. The “Chapman model” is known to be incorrect since decades. At no altitude, the Chapman reaction R4 dominates ozone loss (Fig. 2 of this review; see also Portmann et al. (2012) and the textbooks cited in the manuscript). The total column ozone (referred to in this paper) globally (and seasonally resolved) would look very different than observed, if there was only the “Chapman model”. The problem is already visible in Fig. 5C (of the paper), but how would look a comparison of ozone “(Chapman vs. observations)” in mid-latitudes in winter? Or in the polar regions.

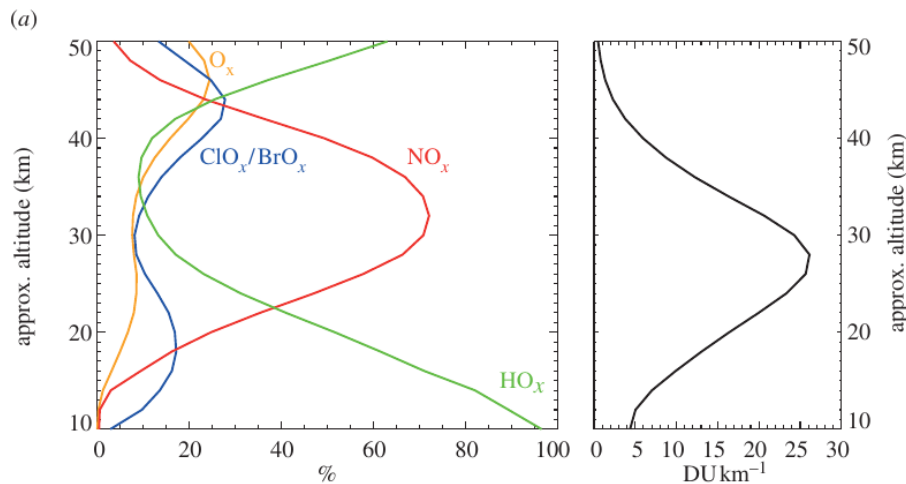


Figure 2: The left panel shows the relative global mean ozone loss rates by chemical family computed for 2000 levels of source gases by the NOCAR two-dimensional model. The right panel shows the global mean ozone profile, which highlights the ozone layer maximum in the middle stratosphere. (from Portmann et al., 2012).

The authors have a good point in emphasising the wave length resolved variation of penetration of radiation throughout the stratosphere.

I understand the idea of the study is to quantify the response of the (tropical?) ozone layer to ozone depletion aloft, but in my understanding this requires to get the ozone loss terms (and their dependency on photolysis) right – the “Chapman model” cannot do this.

Finally, I cannot see a conceptual advantage of using the “Chapman model” – the catalytic cycles that impact ozone loss essentially speed up reaction R4 (compared to a pure “Chapman model”) so why is it not possible to go this route?

Range of validity of the results

The paper should be clear about the range of validity of the results presented here. If I read the abstract (and the title) it looks like a global analysis. But it is not. Clearly, heterogeneous chemistry (and thus polar ozone loss) is neglected (which would be available in the linear scheme Cariolle and Teyssèdre, 2007), this is

okay. But nonetheless, Fig. 1 extends to the poles.

Clearly tropospheric ozone chemistry is not the point here, this paper is on stratospheric processes. And certainly there is no 10 K cooling in the troposphere. In spite of this, Figs. 1, 6 and 7 extend to the ground.

Moreover, I am not convinced that the processes discussed here are valid for the entire stratosphere. Sometimes, the tropics are mentioned (e.g., Fig. 5c is only for the tropics) and particular effects are only discussed for the tropics (e.g., line 456). Does this mean that the analysis presented here is only for the tropics? If yes it should be stated. And how are the tropics defined here? If both the tropics and the extra-tropics are discussed here, there are likely different processes relevant for these altitudes – do you disagree?

Finally, in the tropics, the mean reaction rate between ≈ 20 -40 km increases by more than an order of magnitude – I think this process is relevant for the arguments on chemical processes put forward here and should not be ignored.

The employed assumptions on ozone loss and stratospheric cooling

This study uses assumptions on ozone loss and stratospheric cooling. These assumptions are supposed to be somewhat realistic to be useful and applicable to the real atmosphere. First, suggesting a change in ozone or temperature without giving a time period is not very useful. If you are looking for numbers of changes that are realistic for particular time periods, WMO (2022) might be helpful. The strongest ozone change is at the poles (not treated here) and in the upper stratosphere.

Second, assuming a uniform (altitude independent) change of ozone throughout the atmosphere is not realistic (WMO, 2022) and this assumption is even worse for temperature (sorry, but you seem to assume 10 degree *reduction* of temperature at ground level ...).

Ozone (O₃), O and the O_x family

The analysis in the submitted manuscript does not involve a discussion of the O_x = O₃ + O family. The textbook knowledge (conventional wisdom) states that it does not matter whether O or O₃ is lost through chemistry, but only if a member of the family O_x = O₃ + O is lost. That is, reaction R4 (in the manuscript) is an O_x loss,

but not R3. But in contrast, R3 is stated in the manuscript as a *loss of ozone*. The reason for using the concept of an O_x family is of course that reactions R2 and R3 are very fast (at least by more than an order of magnitude) compared to all other reactions of importance in the stratosphere. This point seems to be worked out again at the bottom of page 15 in the manuscript, i.e. the null cycle from R3 to R2. It is of course okay to disagree with the textbook knowledge on the O_x family but I do not recommend to ignore it. If you do something else here I suggest justifying it against the O_x family concept. As I read the paper, R3 is considered as a *loss of ozone* – I do not think this is true, with consequences for the arguments put forward in the manuscript. But I am happy to be convinced otherwise.

However, I think that all the other catalytic cycles impacting stratospheric ozone (and their dependence of the actinic flux at particular wavelengths) should not be ignored.

Model description and documentation

The paper uses the MOBIDIC model; I would not call this model a “chemistry-climate model” – it is a two-dimensional model; (“chemistry-climate model” sounds a bit like CMIP, which is misleading). As far as I understand the paper, the chemistry scheme used in MOBIDIC is the Cariolle scheme (Eq. 1) – so I suggest to make this very clear in the paper. (Or the other way around, if I am not correct here). Further, the cited documentation on MOBIDIC is decades old (1985) and what is cited is not an extensive description of the model (but rather a conference contribution). (Is there a more recent description of the model?) It is also not clear from the paper, why for such two dimensional model calculations one needs to use the linear Cariolle scheme, rather than performing a full chemistry simulation. Regarding two-dimensional models, there were other options (e.g. Fleming et al., 2011, 2015, but of course there are other alternatives); I do not think that computational issues are an argument today (for such studies). Did the authors consider testing the performance of the Cariolle scheme against a full chemistry simulation?

I was indeed shown (Meraner et al., cited in the paper) that the annual mean total ozone column and the tropical ozone profile of MOBIDIC agree well for linear and the explicit chemistry schemes. However, other issues remain. For the purpose of the present study, I think that in particular the partial ozone column *above* some altitude is important. Further, is the performance outside of the tropics relevant here? If not, this needs to be explicitly discussed. If I understand correctly,

MOBIDIC has issues with HNO₃, especially in high latitudes in summer – is this correct?

Also, MOBIDIC and the Cariolle scheme have certainly evolved over time during the decades since the cited reference in 1985. I would be good to have at least some information on the new parameters of the Cariolle scheme (see also below). Further, in the paper there is a discussion of a “fully interactive” calculation (see also below); there is some description of the calculation in the paper, but I suggest to make it very clear right from the start, which calculations and which models are used here (and which are not used, no tropospheric chemistry, no heterogeneous chemistry). Perhaps there could be a methods section in the paper, where such things are discussed?

Abstract and title

ACP suggests that titles should be concise and consistent with the content and purpose of the article. For research articles, ACP prefers titles that highlight the scientific results/findings or implications of the study. I am not sure if this is the case here. I like the idea of mentioning “self healing” in the title (as this is a commonly known concept), but ideas like ‘stabilising the ozone layer’ are not well known and would not tell the reader much (before reading the paper).

There are general guidelines for ACP papers:

https://www.atmospheric-chemistry-and-physics.net/policies/guidelines_for_authors.html

I think the abstract is currently about 270 words which is longer than suggested by ACP. Consider shortening the abstract.

Some minor issues

- l. 21: explain what is “dangerous”.
- l. 22: here you could mention transport of ozone.
- Fig. 1: What is the reason for the ‘blue’ areas in Fig. 1. b towards the polar regions?
- l 32.: citation for “generally”

- l. 33: the processes with an impact on O₃ should be discussed.
- l. 52: absorption of what?
- l. 104: I am not sure, but are you arguing about the HO_x production from O here? This discussion could be more explicit.
- l. 107: “might contribute” – how can we (e.g. looking at model results) determine whether there is a contribution or not?
- l. 113: “some of the O” – this is a major point (see the discussion on O_x above). Can you quantify “some”? Below (page 15) you say that “some” is practically all. That implies that R3 is not really a sink of O₃. More discussion?
- l. 115: “leakage of O” – I agree. But this is dominated by the catalytic cycles that are ignored in the Chapman theory.
- l. 116: stratospheric versus tropospheric ozone: “grows with altitude towards the surface” is unclear.
- l. 125: can you better quantify “some amount”
- l. 127: you emphasise the *magnitude* here – but doesn’t this involve the magnitude of the catalytic O_x loss terms?
- l. 128: regarding the “magnitude”, it would be good to have a good estimate of the chemical loss rates appropriate here.
- l. 131: transport would be helpful here.
- l. 131: here and elsewhere: does “column ozone” mean total column ozone’ or the ‘partial column ozone above the altitude in question’
- l. 138: this is true only if transport of ozone can be neglected.
- l. 142: citations for “previous studies”
- l. 148: (Eq. 1) how are the *P* and *L* terms that are used here calculated?
- l. 150: how is this “basic state” calculated/determined?
- l. 160: Fig. 1 shows the polar latitudes nonetheless.

- l. 161: are there recent citations?
- l. 171: the “deep tropics” are mentioned here: is this the suggested range of validity of the present analysis? Is there any other reason for discussing a particular atmospheric region?
- l. 176: I do not agree that the “overall shape of the ozone layer” is described by the Chapman theory (see Fig. 5c in this paper and Fig. 2 in this review).
- Fig. 3: panels a) and b) look similar but I am not convinced that they are. I suggest a difference plot. And what about summer/winter conditions? They should be considered as well. And there is a substantial increase in reaction rates with altitude.
- l. 191: citations for “is attributed”?
- l. 195: I like the idea behind Eq. (2), but I am afraid it is not clear how the “fully interactive” used here is calculated. Below it looks like a calculation based on the Cariolle scheme, but this should be clear when the term is introduced.
- l. 204: convert from mixing ratios to number density – but why? What is the reason for making this step?
- l. 207: “quasi-steady state” – is this assumption justified?
- l. 217: does this mean that you investigate only tropical ozone here?
- l. “uniform reduction” is not what is observed in the real atmosphere regarding tropical ozone depletion (WMO, 2022).
- l. 229: How is G_0 defined? How is this quantity derived? Also what altitude is z_1 ? Why has a value of 60 km been chosen?
- l. 251: G_0 could be defined as a perturbation in mixing ratio – would this not be better? At least it should be considered, what a constant value of $G_0 = 10^8 \text{ molec cm}^{-3}$ in ozone density means for mixing ratio.
- l. 268: why only half? Photochemical adjustment gives you the sign of the change, but why is it half?
- l. 273: “entire stratosphere” – also when transport is important?

- l. 89: is there a latitude range for the validity of the “40 km” statements?
- l. 297: I do not agree with this assessment of the Chapman cycle. See for example Fig. 5c in this manuscript. How does the comparison (Chapman vs. real world) look for ozone at other latitudes and seasons?
- l. 333: argument for “photochemical equilibrium”?
- l. 334: the atmosphere is not isothermal – why is this assumption necessary? It only affects the chemical rate constants – is this correct?
- l. 343: You could use a compilation of photochemical parameters (Burkholder et al., 2019) instead of a textbook. No major impact for the questions treated in the manuscript.
- l. 355: photolysis of ozone (R3) is seen here (and elsewhere in the manuscript) as a sink of ozone. This is not the case, if the $O_x = O + O_3$ family is considered (independent of Chapman). This is explained below in terms of a null cycle for ozone (l. 356, l. 371), which reiterates many of the ideas of O_x ; the loss of O_x is through R4. It is not clear to me why the O_x is not used, but then reintroduced (it seems) through the ozone null cycle.
- l. 385: try $\left($ for larger brackets
- l. 387: an equation can not be negative (only a term in an equation)
- l. 396: how is the situation for other months?
- Eqs. 14 and 15: are these equations valid at the pole?
- l. 426: is “above 40 km” valid for all altitudes?
- l. 429: why is it not possible to calculate P and L in a chemical model?
- l. 451: suggest separating transport and catalytic chemistry – these two processes can be rather different.
- l. 456: you say “tropics” here – is the analysis also valid outside the tropics.
- l. 458: photolysis of ozone mostly drives the null cycle; see above.

- l. 465: here (and elsewhere in the manuscript): what is meant by “column ozone”? I assume, partial column ozone above the level in question. And not total column ozone. I suggest being a bit more precise here.
- l. 482: “terminates” – coming from above or from below?
- l. 493: “approximating”. Is this true for all conditions discussed here? E.g. at all seasons? I am also not sure that the approximation is needed.
- l. 554/555: this text is similar to the text in lns. 498/499.
- l. 581: “all the way to the surface” – isn’t this extrapolation a bit dangerous given the fact that tropospheric chemistry is neglected?
- l. 586: Do you have a citation for “surprising”?
- l. 595: I am confused here. What is the major difference between the chemistry of MOBIDIC and the Cariolle scheme? Is there a chemical difference? Or is it mainly transport?
- l. 639: incomplete citation
- l. 614: You say “tropics” here: is the paper on tropical ozone?
- l. 619: “down to the surface”: this sounds very speculative; the analysis presented here is not for tropospheric altitudes in many respects.
- l. 620: The MOBIDIC code and the employed coefficients of the Cariolle scheme (Eq. 1) should also be available.
- l. 645: which journal?
- l. 705: citation should contain pages or an electronic id.
- l. 709: is this citation correct? Do you mean WMO (2018)?

References

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