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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Stratospheric ozone loss in the Arctic winters between 2005 and 2013 derived with ACE-FTS measurements" *by* Debora Griffin et al.

Anonymous Referee #2

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General remarks

Let me start by saying that this is a very good paper. It has many strengths and using a high quality data set such as ACE-FTS to perform a consistent analysis of Arctic ozone loss constitutes a very valuable scientific study. Using six different methods (and comparing the results) and employing the information from a 'simulation only' analysis is an achievement.

Nonetheless, I have reservations about the paper which concern the conclusions drawn from the paper and the discussion of the different methods. I also think that that the

existing literature on the subject should be discussed in a more balanced way. Further, some additional references (of course not necessarily every single paper mentioned in this review) should be taken into account.

My first general point is that I suggest improving the discussion of the various methods. In the paper it is stated that the tracer-tracer method "neglects descent from high altitudes". This is a bit vague, what means "high altitudes" in this case? Perhaps "above the ozone maximum", where ozone is no longer chemically inert? This should be clarified. And there are a number of studies that address the point of descent from high altitudes in the tracer-tracer method (see below) that should not be neglected. The same is true for the issue of "mixing across the vortex edge" which is discussed for the tracer-tracer method. The basis for the discussion in the manuscript so far is the important work by Michelsen et al. (1998) and Plumb et al. (2000), but there is also a discussion of the arguments presented in these papers in the literature which should not be neglected (e.g., Müller et al., 2005, cited in the manuscript, but not in this context) and (Salawitch et al., 2002, not discussed in the manuscript so far, see also below).

Further, it seems to be tacitly assumed in the manuscript that these issues (high altitude descent and mixing across the edge) do not affect the other methods used in this study. (See for example the discussion on the artificial tracer method below). I strongly suggest to describe the impact of these issues on all considered methods.

Perhaps most importantly, if I accept the conclusion from the paper that the 'descent' method is the most reliable one (at least it seems to be a method with very small error estimates), there appear to be significant differences between the SLIMCAT simulations (SLIMCAT only) and the estimated ozone loss. In the sense that SLIMCAT overestimates the chemical ozone loss. For example for 2009/2010 the simulated loss is 51 ± 7 DU and the descent deduced loss is 13 ± 3 DU, for the winter 2004/2005, the comparison is 67 ± 3 and 47 ± 4 DU. (Are these error estimates for ozone loss really comparable). Perhaps I am misreading this conclusion on the reliability of the methods,

but the manuscript should provide a clear guidance to what the message of the paper is in this respect. Thus, I think the paper should discuss these questions in more detail and make a clearer statement on simulated versus observed ozone loss.

In summary, I suggest a more extensive and a more balanced discussion of both the employed methods and the obtained results in a revised version of the manuscript.

Discussion

Artificial tracer method

The authors use the artificial tracer method by Esler and Waugh (2002), who have developed the method for NO_y in midlatitudes: they report that they construct an "artificial 'reference tracer' from a linear combination of other long-lived tracers. The reference tracer is designed so that, as far as possible, it has a linear canonical relationship with NO_y in midlatitudes".

The further development of the technique for analysing ozone loss was done by Jin et al. (2006). They state: "The decrease of O_3 with respect to this artificial long-lived tracer can be regarded as the chemical O_3 loss. However, because the correlations inside and outside the vortex are different, this method cannot correct for the mixing across the vortex edge. This kind of mixing can only increase O_3 for an artificial tracer value, which suggests that neglecting mixing across the edge gives a conservative O_3 loss estimate for this method". This concept is also illustrated in Fig. 1 of this review.

Thus it is an oversimplification to say that the artificial tracer method compensates for 'mixing'. If mixing occurs across the vortex edge, this will be mixing between two different ozone-tracer relations, even though both could be linear (Fig. 1). And then mixing would have an effect in tracer-tracer space. The authors might not agree with

this concept, but I think a discussion is necessary.

Tracer-tracer method

In the manuscript it is stated that the tracer-tracer method (e.g., p. 7, l. 11) "neglects descent from high altitudes". This is a bit vague, what means "high altitudes" in this case? Perhaps "above the ozone maximum", where ozone is no longer chemically inert? However, e.g. Salawitch et al. (2002) (in a study using tracer-tracer relations) consider data up to 8.9 hPa, which is a relatively high altitude in the stratosphere. They also discuss the question of ozone at higher altitudes (Salawitch et al., 2002, see paragraphs [43] and [44]).

In particular, Salawitch et al. (2002) state that the "*Plumb et al.* [2000] model results for χ_2 versus χ_1 are driven primarily by supply of air at the top of the vortex with near zero mixing ratios of both species. Our observations exhibit a critical difference with respect to these heuristic model calculations. The OMS measurements show that the top of the Arctic vortex is supplied with air having mixing ratios of O_3 between 3 and 4 ppm, considerably higher than the final value of [O_3] in the inner vortex".

Moreover, there could be intrusions of mesospheric air to lower altitudes, which are discussed by Müller et al. (2007), in a case study. They conclude that "measurements influenced by mesospheric air show ozone mixing ratios ranging between 3.6 and 5.6 ppm, which are clearly greater than those found in the "early vortex" reference relation employed to deduce chemical ozone loss".

Rex et al. (2002) is cited (p. 7., l. 8) in support of the criticism of the tracer-tracer method. And indeed, Rex et al. (2002) mention that "*Michelsen et al.* [1998] and *Plumb et al.* [2000] have suggested that before chemical loss of ozone occurred, mixing between subsided inner vortex air with extravortex air may lead to a flattening out of the curved O_3/N_2O relation and thus may be mistaken as chemical loss of ozone.

However, . . . " But the overall conclusion of Rex et al. (2002) on this issue reads: "Thus the overall changes in the O_3 versus N_2O relation observed during the course of winter could not have been caused by transport, and rather represent a lower limit for the true chemical loss of ozone". Therefore, I suggest rethinking of how to use this citation in the paper.

Further, especially for the winter of 1999/2000 there are a number of studies (not taken into account in the manuscript so far) that argue that transport alone could not have led to the observed changes in the O_3 versus N_2O relation (tracer-tracer method).

Richard et al. (2001) report that "there is relatively little change in the ER-2 O_3:N_2O [. . .] relationships over the two week period between 20 January and 3 February 2000. Additionally, the O_3:N_2O profiles are found to be similar to the early winter vortex balloon profiles which allow extension of the relationships to regions above the ER-2 flight altitudes thus defining the chemical composition of air that later descends to ER-2 sampling altitudes (18-21 km). [. . .] Therefore, these relationships allow for the establishment of a winter vortex reference to quantify O_3 chemical loss occurring during late February/early March2000."

Another piece of evidence on these issues is provided by Ray et al. (2002) who find that "mixing of midlatitude air into the winter vortex is not a significant contributor to the observed ozone changes in the 1999/2000 season".

Of course, the authors do not need to follow/accept these arguments but I think a more balanced discussion in the manuscript is necessary rather than relying mainly on the arguments of Michelsen et al. (1998) and Plumb et al. (2000) here.

Comments

- p. 2., l. 7: "Here we show" – I think it is not really new that these tracers are suitable.
- p.2, l. 20: This is true for the time period of elevated stratospheric chlorine and bromine.
- p. 3., l. 1: Suggest citing here also the early theoretical study by Carslaw et al. (1994).
- p. 3., l. 1, 2: Perhaps helpful: information on observed PSCs is now also available from MIPAS (Spang et al., 2017).
- P. 3., l. 6: The paper by Solomon et al. (1986) is mostly about heterogeneous chlorine activation, less on the relevant catalytic ozone loss cycles.
- p. 3., l. 8: the point is that low temperatures are required but they need to last long enough into the period when sufficient sunlight is available to drive the ozone loss (as it is the case regularly in the Antarctic).
- p.3., l. 28: This statement is also true for the Antarctic. Perhaps look at ozone loss estimates for the Antarctic.
- p. 4., l. 2: I do not think this statement is correct as written here, see the detailed discussion.
- p. 7., l. 8: Rex et al. (2002) is cited here in support of the criticism of the tracer-tracer method. However Rex et al. (2002) state that "Thus the overall changes in the O_3 versus N_2O relation observed during the course of winter could not have been caused by transport, and rather represent a lower limit for the true chemical loss of ozone". I think some of the citations used in l. 12 of this page are more appropriate here.

- p.7., l. 12: I cannot see what the contribution of the citation to Michelsen et al. (1998, GRL) is here. This paper does not discuss ozone. Either explain why the citation is needed or drop the citation.
- p. 7., l. 15: add 'over a polar season'; of course tracers like methane or CFC-12 *are* influenced by chemical processes, otherwise there would be no vertical profile.
- p. 7., l. 28: "neglecting mixing processes from the edge [. . .] over estimation of chemical ozone loss. . . ". I do not think that the papers cited here make this point. See statement from Rex et al. (2002) above. Also, Müller et al. (2005) state in the abstract that "mixing across the polar vortex edge impacts ozone-tracer relations in a way that may solely lead to an 'underestimation' of chemical ozone loss and not to an overestimation"; this discussion needs to be revised.
- p. 10., l. 9: If there is descent from higher altitudes, as discussed in the paper elsewhere; would the 'passive ozone assumption' hold? If ozone is not in complete darkness, it is not passive at higher altitudes.
- p.10., l. 18: what about Wohltmann et al. (2017) here?
- p. 10., l. 32: Why HISPLIT? Would it not be more consistent to calculate the trajectories with the (diabatic) trajectory scheme of ATLAS. And likewise not change the meteorological analysis?
- p. 12., l. 1: Is there a comparison (or comments along this line) between the polar chemistry of SLIMCAT and ATLAS?
- p. 13, l. 14: It is true that it is worrying that tracer profiles do not agree well for March 2005 (which is not shown directly in Fig. 6a). However, I do not understand why this is only a problem for the tracer-tracer method. I suggest that you also discuss the impact of this finding on other ozone loss estimates considered here.

Also the column ozone loss estimates do not seem to differ too much (perhaps with the exception of OCS) for the different tracers in 2005 (Fig. 6).

- p. 13., l. 23: explain why this is likely.
- p. 13., l. 33, 34: it seems obvious to me that average decent profiles will have a small standard deviation, but perhaps I misunderstand. In any event it would be good to give a citation for the smaller uncertainties and how they are calculated.
- p. 18., l. 24: There also could be more comparison here with results in the literature based on the methods used in this study. For example, Tilmes et al. (2006) and Rösevall et al. (2008) report chemical ozone loss for the Arctic winter 2004/2005.

Details

- p. 2, l. 32: drop 'ice' here this discussion is about NAT and STS
- p. 3., l. 13: *an* Arctic...
- p. 5., l. 6: trace *gases*
- p. 6., l. 21: I would formulate: . . . "not a sufficient number of measurements" . . .
- p. 8, 9: Eqs. (1) – (4): do not use italics for ppb and ppt
- p. 9., l. 26: here and elsewhere, use proper minus signs; i.e. -25 rather than -25
- p. 10., l 10: *is* applied
- p. 11., l. 27: citation for SLIMCAT chemistry scheme?

- p. 19, l. 24: "... ACE, also known as SCISAT" – is this really true?
- p. 19., l. 4: citation for loss in 2010? Also same line 'larger' than what?
- References: there are still a few typos, missing spaces, additional spaces, etc.

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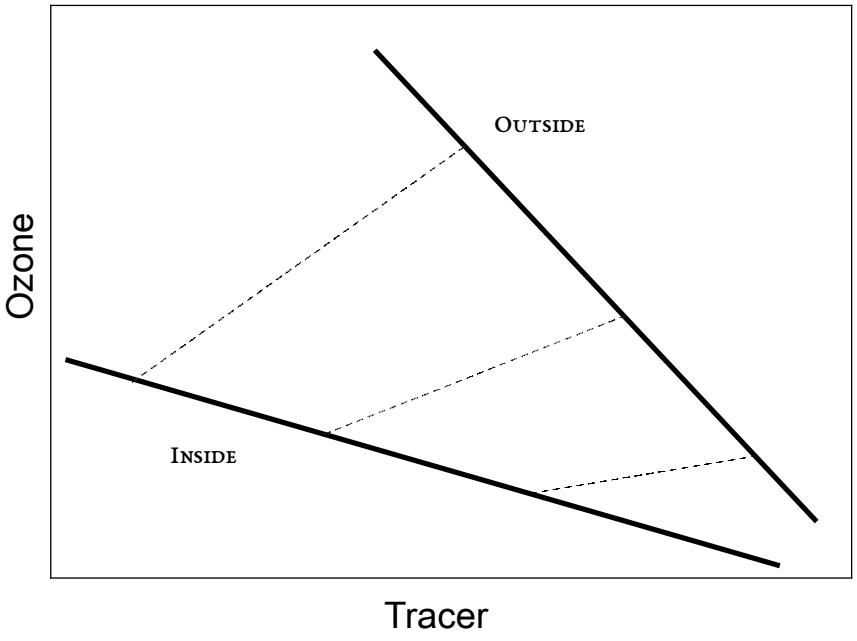

Fig. 1. Schematic view of mixing across the vortex edge for linear ozone tracer relations; see also Fig. 5 in Jin et al. (2006).