

Interactive comment on “Chemical ozone loss in the Arctic winter 1991–1992” by S. Tilmes et al.

Anonymous Referee #2

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General comments

In this paper chemical ozone loss is recalculated in the Arctic polar vortex in winter 1991-1992 based on HALOE, ER-2 and Kiruna balloon data. In particular the authors claim to have calculated the ozone losses below 400 K during the high aerosol loading due to the eruption of Mt. Pinatubo which leads to the main new conclusions of this study. Such a calculation would be an important contribution to the polar ozone loss discussion. Therefore in addition, great emphasis is placed on an attempt to validate HALOE data in altitudes where the retrieval is significantly influenced by the aerosols in particular below 400 K. Unfortunately, the attempt to validate those HALOE measurements cannot be regarded as successful and even more a thorough error analysis in general is lacking. Any reference to this issue is not comprehensible. As long as those HALOE measurements cannot be trusted in the needed accuracy and a conclusive error analysis is missing I cannot recommend publishing the paper in ACP.

Specific comments

1. The authors cite Hervig et al. (1995) (hereafter H95) twice (page 10099/line 15, P10103/L15) with respect to the HALOE ozone measurements: "After a correction of the data, the uncertainty of O3 mixing ratios in the peak aerosol layer is 25%." A similar statement can indeed be found in H95 as last sentence of the section "Error Analysis", but more vague and it cannot be used as an argument in this case: "We feel that representative correction uncertainties in the peak aerosol layer under normal conditions are 15%, 25%, and 60% in H2O, O3, and NO2 mixing ratios, respectively." I can only guess what H95 consider as normal conditions, e.g. background aerosol conditions. However, one can be sure that they don't refer to the Arctic condition in the winter 1991/1992 with heavy aerosol loading as normal conditions. In their "Error Analysis" section H95 give an ozone example of a heavy aerosol loading case: "The correction uncertainty increases with increasing pressure, reaching 25% by 45 mbar and 50% by 70 mbar." (cf. figure 19 therein). In fact, assuming that HALOE version 19 data is used it can be stated that all used ozone profiles comprise uncertainties of at least 50% below 400 K. In most cases the uncertainty at 400 K is much higher. In all cases the uncertainty increases strongly with decreasing altitude.

2. Even with the wrongly assumed maximum ozone uncertainty of 25% the authors see the need to validate those data. This is tried in section 5. For this effort seven balloon profiles, the data of three ER-2 flights, one HALOE profile in January, one HALOE profile in February and a bunch of HALOE profiles starting from 21 March 1992 were available. From these profiles one has to exclude the January HALOE profile due to its location near the vortex border (cf. minor specific comments below). The February HALOE profile has minimum temporal distances of 8 days to the nearest balloon measurement (not used) and 5 days to the nearest ER-2 measurement. The late winter HALOE profiles have at least a temporal distance of 9 days to the nearest balloon measurement. In this scanty data situation the profiles are compared and discussed.

I see two problems with this kind of effort. First, any agreement of profiles is attributed as a validation of HALOE profiles. A case of disagreement is attributed to meanwhile occurring ozone loss (P10108/L11). One cannot validate ozone profiles and simultaneously determine ozone loss with this data set. The system is clearly under-determined for such an approach. In addition some statements are just wrong: "The balloon profile taken over Kiruna on 5 March ... (Fig, panel c, ...) ... does not show significant deviations from the reference profile." (P10107/L28-P10108/L1). Below 470 K this statement is correct. However above 470 K some deviations exist in the order of 20% with one deviation of about 100% at 625 K. "Ozone mixing ratios of balloon and satellite observations are in agreement, see panel d" (P10108/L1-2). In fact, they differ below 470 K by about 0.4 ppm which accounts to about 100% at 400 K and below.

Second, even if this under-determination would not exist this is not a state-of-the-art validation. I recommend to study some recent validation papers e.g. of satellite data. There, a great deal is undertaken to satisfy collocation conditions and to yield a sufficient statistic of data. Deviations are clearly arranged in plots e.g. in terms of relative differences. Nothing of those efforts can be found in this HALOE study. Instead, lots of speculations are presented (P10106/L26, P10107/L5/L12/L14, P10108/L11) and profiles are compared in plots with steep gradients, where possible differences can practically not be identified.

I therefore disagree with the statement "It is shown that HALOE O3 and CH4 observations are reliable between 350 and 700 K" (P10108/L16). It would be an indication whether such a statement would be correct if one would be able to convince the HALOE PI to create a version 20 data set with strongly reduced uncertainties during the times and locations of heavy aerosol loading as a result of this study.

3. A thorough error analysis is virtually missing. Here, I discuss the reference function only. For me it seems to be quite courageous to place a fit with six degrees of freedom through a data set with 14 data points. The outcome has a constant uncertainty of 0.29 ppm. How is this uncertainty calculated? I cannot believe in the constancy. I would

expect that a proper calculated covariance matrix - leading to individual uncertainties of the fit parameters - would yield uncertainties which are smallest somewhere in the middle and which increase to the borders. What are the uncertainties of the individual measurements? What are the uncertainties of the CH₄/N₂O conversion relation? Are those uncertainties addressed in the given determination of the uncertainty?

In general I am unsure about the presented reference data in Fig. 5, upper panel. It seems that the whole profile of 12 December 1991 is shown but only part of the 5 December 1991 data. However, in section 5 it is mentioned that the measurements of 5 December were well inside the vortex whereas the measurements of 12 December were partly outside of the vortex. In case both data sets have not been mixed up, why are those values selected? In case both data sets have been mixed up, why are four values with CH₄ around 1.4 ppm missing?

In fact, the main new conclusions of this study are based on two measurements below 400 K. The fit deviates in the lower most point by about 50% to 70% more ozone from the measurement. Is the calculated ozone loss below 400 K due to such a technical artefact? Presumably not, but it shows the fragility of the whole approach.

It should be clear that in such a scanty data situation a thorough error analysis is mandatory starting with the measurement errors which propagate in several stages into the final results, the ozone loss values! A last comment: The uncertainty of the final results is not only influenced by the uncertainty of the reference profile but of the uncertainty of the late measurements, too of course (P10110/L24-26).

Minor specific comments

P10100/L19-22: This might be true for CH₄ measurements. There are a lot more in-situ ozone measurements available, i.e. additional ozone sonde data.

P10104/L5-7: Which profiles are originally N₂O profiles, which CH₄ profiles?

P10105/L4-5: "Descent results in larger ozone and lower CH₄ mixing ratios within the

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polar vortex than outside the vortex." c.f. also P10108/L14-16. True is that descent results in increasing ozone and decreasing CH₄ mixing ratios at a constant altitude due to the gradients. This leads in general to the given statement below about 500 to 550 K. Above that transition region ozone mixing ratios within the vortex are smaller than outside the vortex. The descent only shifts the transition region upwards. This is due to the fact that ozone is depleted on the way from the tropics to the poles.

P10107/L3: The authors speculate that the HALOE profile, taken on 14 January within the vortex boundary region, was possibly influenced by air from outside the vortex. Taken into account the boundary location, the line of sight of the instrument and the retrieval mechanism of those measurements one can be sure that the measurement was influenced by air from outside the vortex. Here, a plot like those in Figs. 3 and 4 would be appropriate including the line of sight.

Technical corrections

P10104/L7: Mention version number of HALOE data.

P10098/L10: "In spite" instead of "In stipe".

Fig. 2b: Some symbols for the 5 December 1991 flight are missing.

Fig. 4: Why is Kiruna highlighted on 8 February? Caption mentions 15 February but 17 February is shown. Why are HALOE profile locations shown which are not used in the study? The plot for 18 March is unnecessary. It is unnecessary to show the ER-2 locations on 22 March.

Fig. 8: "partial" instead of "partical".

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