Atmos. Chem. Phys. Discuss., 14, C7508–C7513, 2014
www.atmos-chem-phys-discuss.net/14/C7508/2014/

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "First quasi-Lagrangian in-situ measurements of Antarctic Polar springtime ozone: observed ozone loss rates from the Concordiasi long-duration balloon campaign" *by* R. Schofield et al.

M. von Hobe (Referee)

m.von.hobe@fz-juelich.de

Received and published: 29 September 2014

The paper presents the first continuous ozone observations made on long duration balloons in the Antarctic polar vortex in winter. This innovative measurement generated an interesting and valuable dataset. The authors point out and analyze patterns in the data, opening the door to new scientific insights that can be gained. However, these scientific issues are often raised but not treated in enough detail to fully warrant the conclusions drawn, or to draw conclusions at all. Besides, I see a tendency for

overstatement, i.e. claims to be able to answer questions that cannot be answered by this particular dataset. Below, I make some comments and suggestions that, hopefully, will help to make the paper even more valuable than it already is.

Major issues

1. Description of "science value" of the dataset

I find the statement in the introduction "Despite these successes, important questions have remained unanswered because of the technological challenges of directly measuring stratospheric ozone losses in-situ" (page 22247, lines 21-23) somewhat hollow, although such sentences are often found in introductions of research papers. Please try to clearly formulate at least some of the "important questions" that remain unanswered (preferably those where you think your new data will make a significant contribution to answering them)! And please explain *how* the lack of high quality in-situ ozone loss measurements prevents them from being answered!

In the Arctic the combination of in-situ ozone loss measurements (i.e. Match sonde campaigns) and ozone observations by satellites in 2010 and 2011 have led to a rather good understanding of ozone loss in these winters. One concrete question is posed on page 22250 lines 12-13 about loss rates in cold Arctic Januaries. But I do not see how the present paper helps answer that question…in other words: why should better in-situ ozone loss observations in the Antarctic be any more helpful than previous aircraft campaigns (measuring many more parameters than just ozone loss) and Match observations in the Arctic in January?

With respect to the statement in the conclusions that the Concordiasi observations can be used to test the ability of chemistry climate models to capture the timing and spatial variations of ozone hole formation (page 22256, lines 18-21), I'm afraid that the Concordiasi measurements represent only a snapshot in time with insufficient statistics to pose a test case for chemistry climate models.

2. Potential use of the Concordiasi data to improve our understanding of the ClO dimer cycle kinetics

A large part of the introduction deals with uncertainties in the kinetics of the ClO dimer cycle. This chemical cycle is without doubt responsible for the largest part of catalytic ozone loss in polar winter, but it is not really investigated in any detail in the present manuscript. Conversely, it is explicitly transferred to another study by the statement in the conclusions on page 22256, lines 21-24 (I am not convinced that the Concordiasi ozone loss measurements will help to reduce these uncertainties, because they have indeed been greatly reduced recently; further reducing these uncertainties without actually using precise and highly resolved observations of the relevant chlorine species seems not very realistic). In that respect, the detailed discussion on this issue in the introduction seems a bit unnecessary. I suggest dropping much or all of the referrals to the ClO dimer kinetics from the present paper because it isn't really the main topic.

But if, for some reason, you decide to keep this discussion, then please

i) correct the statement starting at the very end of page 22248! The equilibrium constant from atmospheric observations is lower than the JPL recommendation, but it is not "consistently smaller than laboratory estimates". The study by Plenge et al. (2004) agrees quite well with observations, and the others are not necessarily in disagreement either, depending on how you do the analysis (see the extensive discussion in von Hobe et al., 2007).

ii) update the references for the laboratory and field studies on ClOOCl photolysis by Young et al. (2014) and Suminska-Ebersold et al. (2012) respectively. The latter study is the only one that derives the ClOOCl photolysis rate independent of the ClO recombination rate (the other studies all constrain the ratio J/k_{rec}).

3. Please provide more information on measurements and Match statistics

I can see how the post calibration demonstrates the long term stability of the ozone

sensors (Page 22251, lines 12 -23). However, the statement that the accuracy is better than 20 ppb would be much better supported by actually providing some information on the calibrations (standards, uncertainties) and showing the results of the comparisons with ozone sondes mentioned at the end of this paragraph.

It would also be nice to get a better feeling for the Match statistics. For example, the total number of matches (as defined by the constraints described in Section 2.1) obtained would be interesting to know. It would be great if you could label the symbols in Figures 3, 4, 5 and 6 with the number of matches used to compute the value plotted. If I understand correctly, this number should always be greater than 10, correct?

I would expect somewhat more natural variability than the error bars in the figures suggest. Do they show standard deviation or standard error of the regression slope? And I wonder how independent the matches making up the regressions are: how far apart (in time) do the start and end points of two match pairs have to be to treat them as two separate matches? In the context of Figure 6, I would find it interesting to know if there are any Match pairs with significant changes in PV between start and end point.

4. Discussion of exceptionally high ozone loss rates

Your results section ends with the statement that "Losses of up to 230 ppb/day are exceptional and dictate the speed at which the ozone hole forms in early September". I agree, and I note that your maximum loss rate is three times higher than the highest ozone loss rates observed during the 2003 Antarctic Match campaign (von der Gathen et al., 2004). That's why I would like to see more statistics, particularly on the regression line leading to this particular number (i.e. the 230 ppb/day), see my comment above.

And if you find something so exceptional, then you should at least try to find and provide an explanation! Looking at Figures 7 and 8, I see the high ClO and PSC occurrence extend well into the 0-90°E sector, and I see them being highest in the day 260-270 period and still high in the day 265-275 period. So why should the extremely high ozone loss rates occur only in the 0-90°W sector, only in the day 255-265 period (when sunlight is supposedly less than during the later 10-day-periods), and be observed only by the PSC 17 balloon? At the very least, I would expect a simple "standard chemistry" model run (I suggest to initialize with satellite data as shown in Figures 7 and 8) along the Match trajectories with > 200 ppb/day ozone loss to see how far off these ozone losses are from expected rates (I note that you calculate the trajectories with ATLAS, a Lagrangian CTM that should allow you to easily add box model chemistry onto the trajectories). If the difference is significantly beyond the combined measurement and model uncertainties, this would imply a new, yet unknown ozone removal process - an experimental artifact. Whatever it is, I would like to see more efforts to unravel this potential enigma.

5. Use of the technique to study mid-latitude ozone loss

The very last paragraph of the conclusions is highly speculative and should be removed. Mid-latitude ozone loss rates are much lower than the ones in the polar vortices, and the air is not isolated and confined to a very specific and regionally limited flow regime as in the Antarctic vortex. This will likely lead to i) significantly larger influence of missing processes, and ii) a reduced number of successful Matches.

Minor issues and technical corrections

Page 22248, line 2-3: the significant reduction of chlorine in the stratosphere has yet to come. Please rephrase the statement, e.g. "...significant CFC reductions brought about..." or "...significant chlorine reductions to be expected as a result of the Montreal protocol..."

Page 22251, lines 7-12: I suggest taking the last two sentences (or at least the last one) in this paragraph out. The particle data are not used in the present manuscript, and the NAT formation process is not discussed further.

Section 2.1: normally, you only have a numbering of subsections if there are at least

two: if there is a Section 2.1, I expect a Section 2.2 also.

Page 22252, line 5: the sentence "The balloons are not perfect tracers of air motion" sounds funny. I suggest rewording, e.g. "the balloons are not perfectly moving within an air mass".

Page 22254, line 5: do you mean longitude, as stated in the Figure caption?

Figures 3 to 6: please include the units in the y-axis titles!

References

Plenge, J., Kühl, S., Vogel, B., Müller, R., Stroh, F., von Hobe, M., Flesch, R., and Rühl, E.: Bond strength of chlorine peroxide, J. Phys. Chem., 109, 6730-6734, 2005.

Suminska-Ebersoldt, O., Lehmann, R., Wegner, T., Grooß, J. U., Hoesen, E., Weigel, R., Frey, W., Griessbach, S., Mitev, V., Emde, C., Volk, C. M., Borrmann, S., Rex, M., Stroh, F., and von Hobe, M.: ClOOCl photolysis at high solar zenith angles: analysis of the RECONCILE self-match flight, Atmos. Chem. Phys., 12, 1353-1365, 2012.

Von der Gathen et al., Quantitative Understanding of Ozone losses by Bipolar Investigations (QUOBI), final report, 2004, available at http://www.nilu.no/quobi/downloads.html .

Young, I. A. K., Jones, R. L., and Pope, F. D.: The UV and visible spectrum of ClOOCl, in preparation, Geophys. Res. Lett., 41, 1781-1788, 2014.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 22245, 2014.