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)
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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.
We thank Marc von Hobe for his constructive criticism of our paper that certainly has tightened and improved this paper. The inclusion of the Match statistics was a very valuable exercise.

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.
This sentence, and another later that are vague are made specific and removed respectively.
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!
Done – this dataset enables the longitudinal distribution of ozone loss to be studied, which is novel to this paper.
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.
This sentence has been removed – focussing only on the Antarctic situation.
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?
While we do see your point, that these Antarctic measurements cannot directly answer an Arctic question, the point we wished to make was that Balloon measurements such as made by this dataset do provide insight that aircraft measurements can not. We have modified the text accordingly to make this point more explicit. Balloon measurements enable the ozone loss to be measured over several days in vastly wider geographical sectors than would be accessible by aircraft in-situ measurements. The vertical resolution of satellite measurements (not being in-situ) limits the study of ozone loss rates within a single airmass. Aircraft campaigns studying ozone loss have

been extensively performed in the northern hemisphere. This is not true of the southern hemisphere.

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.
We disagree that these measurements would not be useful to test CCMs. To test a multi-year climate run this indeed would be true, but to test the ability to capture the temperature and corresponding rates of ozone loss in a chemistry climate model these balloon measurements are certainly useful (one such test would be to use the meteorological nudged version of the Unified Model to do this). Yes these measurements have time and altitude limitations to their usefulness, but the temperature data alone provides a useful test for the accuracy of gravity wave momentum flux within a mesoscale model simulations – as was done by [*Plougonven et al.*, 2013]. Similarly the ozone data could provide a test case for CCMs.

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.
We agree, this was too detailed and out of scope for the paper and this has been removed.

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/krec)

3. Please provide more information on measurements and Match statistics
Thank you for suggesting this improvement.

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.
The accuracy of the UCOz balloon borne ozone photometer is estimated to be 20ppb in flight with polar stratospheric ozone mixing ratios and environmental conditions. This estimate is based on pre-flight calibrations of all instruments, as well as in flight ozone sonde matches for the instrument aboard PSC16 and post flight calibrations for the instrument recovered from PSC16 and PSC17. Laboratory calibrations and pre-launch checks were carried out using a Thermo Environmental Instruments 49PS Ozone Primary Standard (Kalnajs and Avallone 2010). These tests indicated that all the UCOz instruments agreed with the Primary Standard to within the 1% stated accuracy of the Primary Standard. At the peak ozone mixing ratios observed during flight, this corresponds to an in flight uncertainty of less than 20ppbv.

The accuracy of the UCOz instrument aboard PSC16 was checked in flight by launching matched ozonesondes when PSC16 passed over participating research stations. Three ozonesondes were considered good matches, with horizontal displacements of less than 100km along isentropic surfaces from PSC16. These matches are shown in Figure R1 (here in response), and indicate agreement between the UCOz instrument and the ozonesondes to within the approximately 3% uncertainty of the ozonesondes.

Fortuitously, PSC16 and PSC17 were recovered at the end of their flights. This allowed unexpected post flight calibrations to be performed on these instruments. In both cases, the pre- and post- flight calibrations agreed with the TEI 49PS Primary Standard to within 1% of the full range, confirming that the UCOz instruments had not drifted over the duration of the flight.

We feel that this is too much detail to include in the paper, so have not altered the text.

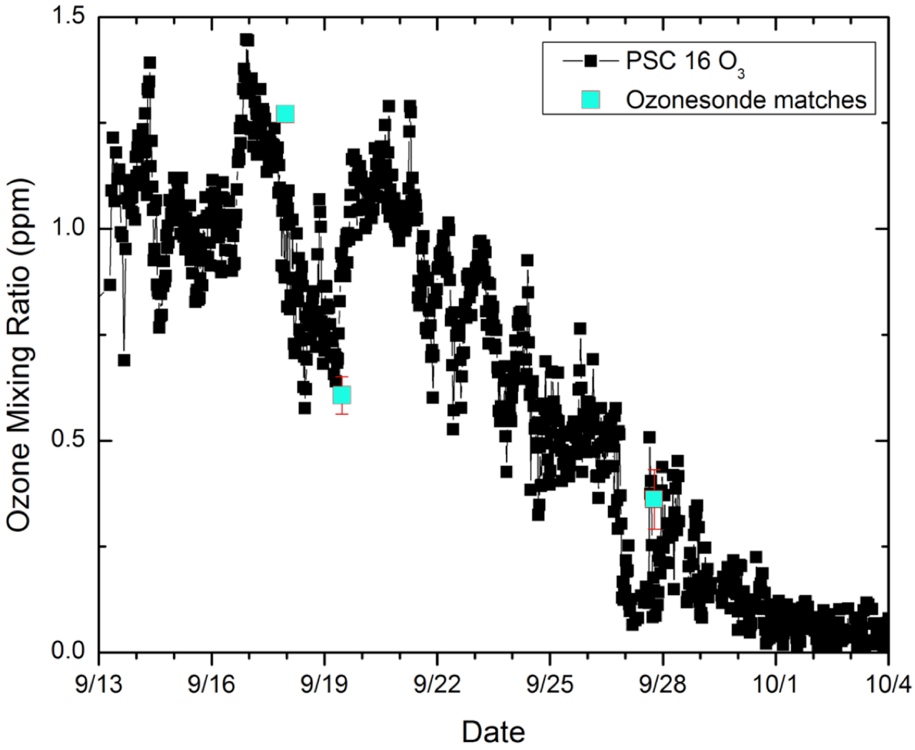


Figure R1: Comparison between coincident ozonesondes and Concordiasi balloon ozone measurements on PSC-16.

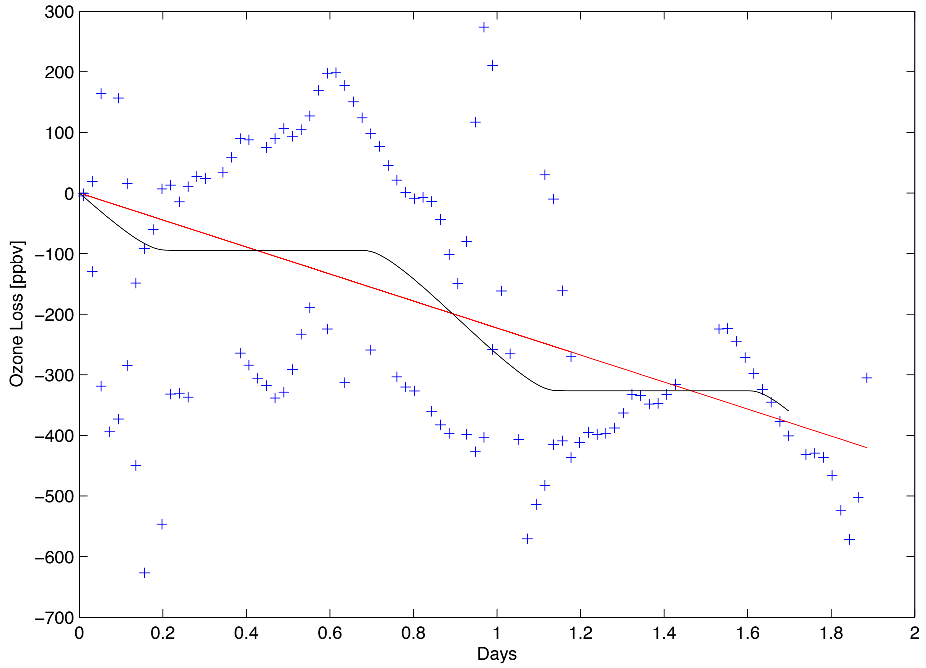
It would also be nice to get a better feeling for the Match statistics. For example, the total number of matches (as defined by the constraints described in Section 2.1) obtained would be interesting to know. It would be great if you could label the symbols in Figures 3, 4, 5 and 6 with the number of matches used to compute the value plotted.
This has been done, the number of matches involved in determining the loss rates are high, due to the balloons being almost isentropic.

If I understand correctly, this number should always be greater than 10, correct?
Yes.

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?
This is the standard error of the regression slope. This is now noted in the paper, in the caption to Figure 3.

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?
No constraint is made on the start and end points, except that they will be at least 15 mins apart as back trajectories are calculated with 15 minute timesteps. The start points are 7.5 hours apart to avoid matches being very close in time. The number of the matches included in each regression are large (included as suggested). I attach here the regression for the maximum ozone loss for the Peninsula end point, both as a

function of days and sunlit hour. It is interesting to note that some ozone loss is occurring in the dark – as seen by the nighttime portions of the sunlit hour plot.



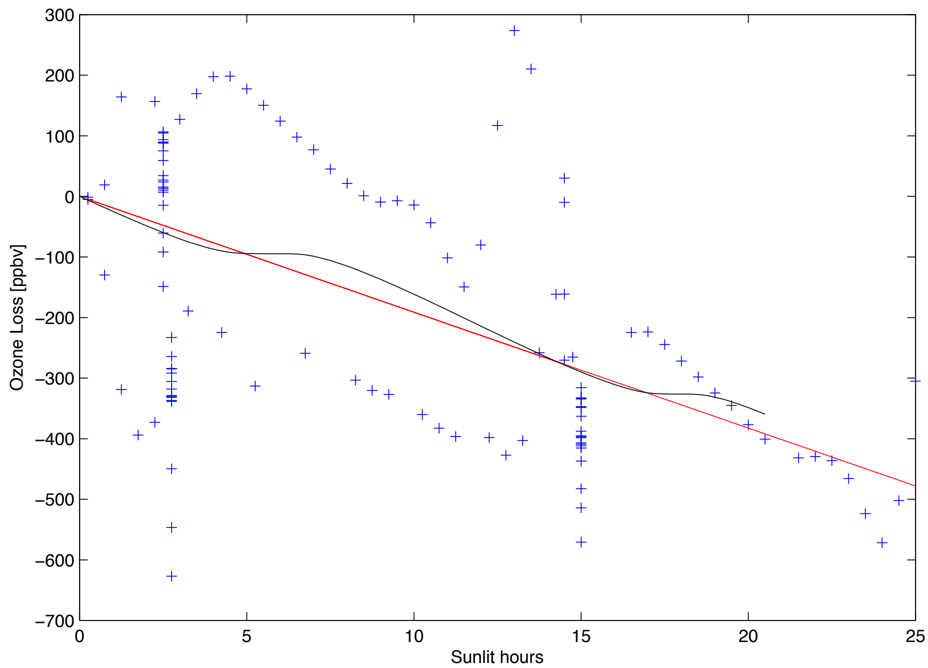


Figure 2: Ozone loss measurements from matches (blue crosses), regression of all matches for PSC-17 in the Peninsula sector (red line). In the black line is a box model run along one of the match trajectories.

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.
The absolute difference in PV for a match to be defined (one of the match criterion used) between the start and end points is 1 s^{-1} – so there will be no matches with a very large change in PV.

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.
The regression producing these high ozone loss rates is provided above. It is clear that it happens quickly (i.e. within 25 sunlight hours). The match statistics producing these fits are large due to the balloons being almost isentropic in their air mass trajectories.

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 0-90E 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?
We do believe that explaining the cause of this observation is important. We agree that testing against a chemical model would be ideal, and we intend to do so, but it is beyond the scope of this paper to perform a complete chemical model comparison; to do this justice would require exploring the very many matches provided here and that cannot be accomplished with current resources. We have explored this with some box model runs over 9 carefully chosen match trajectories (long duration).

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).
The box model chemistry requires initialization and significant spin up and is quite separate from the trajectory calculation. However as they share the underlying software architecture, we have been able to perform a simulation with ClOx=Cly along one long duration match trajectory for each 10 day time bin. This has allowed us to include a Cly ozone loss rate in figures 3 and 4. The results show that the 230 ppb/day loss rate requires full activation, but loss rates of up to 380 ppb/day would be possible for the PSC-16 if ClOx=Cly.

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.
No new ozone removal process is required.

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.
Yes this is a speculative outlook section about how ozone on the google-loon balloon platform could be useful, we have adjusted this to rather apply it to the upcoming Strateole 2 tropical experiment. However, I do not agree that the number of matches would necessarily be influenced. As the heat transport from the tropics is lower in the southern hemisphere relative to the northern hemisphere, exploration of cold stratospheric aerosol ozone loss may be possible. The sentences are cautionary and valid, we have chosen to leave this paragraph in the conclusions section largely unaltered – removing the Google loon reference however.

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"
Done.

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.
Done.

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.
Fixed have created a new section.

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".
This has been reworded to: 'The balloons do not perfectly follow the air parcels.'

Page 22254, line 5
do you mean longitude, as stated in the Figure caption?
Yes – thank you.

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

References

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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.
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Response references

Plougonven, R., A. Hertzog, and L. Guez (2013), Gravity waves over Antarctica and the Southern Ocean: consistent momentum fluxes in mesoscale simulations and stratospheric balloon observations, *Q.J.R. Meteorol. Soc.*, *139*(670), 101–118, doi:10.1002/qj.1965.