We thank the two anonymous referees and Dr. Berresheim for their comments. We respond (in italics) to each point separately below. When appropriate, the responses also list all the relevant changes made in the revised manuscript.

Anonymous Referee #1:

This is a well structured paper which builds on previous radical measurements made in Polar regions, particularly at the South Pole, and highlights that the elevated oxidative capacity reported at the SP extends to other regions of Antarctica. The authors highlight the dominance of HONO as an OH source, but demonstrate inconsistencies in the HONO measurements and the observed radical concentrations. Using this approach, the authors conclude that the LOPAP technique, used to make the HONO observations, may suffer from an artefact under these conditions; similar conclusions are reached, using an alternative approach, in a companion paper. Inconsistencies in the NO:NO2 ratio and peroxy radical concentration observed are also highlighted. This paper is well suited for publication in Atmospheric, Chemistry and Physics and I only have some minor comments and clarifications listed below which should be addressed prior to publication:

1) Pg 15005, ln 25: Repetition of ln 11.

The note about local time in line 25 has been removed.

2) Pg 15006, ln 28: this manuscript would benefit from brief description of the role of the 'radical quencher (NO2)' here.

Added:

"NO_2 used as a scavenger removes not only the OH radicals, but also peroxy radicals converting them into HO_2NO_2 and RO_2NO_2 nitrates".

3) Pg 15007, ln 9: the manuscript would benefit from expanding briefly on the two OH measurements modes here – their purpose, did the two modes agree?

Added:

"Ratio of the signals with the short and the long conversion times may be used as an indicator of an artificial OH formation in the reactor [Kukui et al., 2008]."

Pg 15008, ln 12 – 15: Did the humidity change from point of humidification to end of the calibrator? Were any changes in [H2O] accounted for?

The [H2O] was controlled with the humidity sensor at the entrance into the photolysis reactor. We added on line 10:

"…the humidity measurements in the photolysis reactor"

Pg 15008, ln 20: The modelled HO2:RO2 ratio is dependent on the [CO] and [CH4] assumed. As neither CO nor CH4 were measured, what is the level of uncertainty in the radical ratio and overall [RO2] determined from estimating these values?

As discussed in Section 3.2 the uncertainty of about 10% (1σ) for the HO2/RO2 ratio was estimated using uncertainties of the measurements at Dome C. For the uncertainty of 10% was adopted for [CO] (Section 3.2). For [CH4] the uncertainty of 5% was used.

Pg 15009, ln 7: Why was the uncertainty greater during the night time?

During the night time the relative uncertainty was higher due to the lower measured signals.

Pg 15009, ln 9: Please provide the LOD for RO2 also.

Added:

"The lower limits of detection for OH and RO_2 radicals at signal-to-noise ratio of 3 and a 2 minute integration time were 5×10^5 molecule cm^{-3} and 2×10^6 molecule cm^{-3}, respectively."

Pg 15010, ln 26: this interference in the HONO measurements of 10 – 20 pptv needs to be followed by the [HO2NO2] assumed by Legrand et al. How does this estimated [HO2NO2] compare with the concentration calculated by the 0D model?

The corresponding paragraph is modified:

"Legrand et al. (this issue) report tests done both in the field and in the lab that tend to suggest an overestimation of HONO measurements in the range of 10 to 20 pptv due to the presence of HO_2NO_2 in the range of 50-100 pptv in the cold atmosphere at Dome C.. This range of HO_2NO_2 mixing ratios is in agreement with the median $[HO_2NO_2]$ of 80 pptv estimated from RO_2 and NO_2 levels measured at Dome C (see Section 3.2). Also, as discussed by Legrand et al. (this issue), similar levels of HO_2NO_2 were previously observed in Antarctica."

Pg 15011, ln 14: I believe 'Sect 2.2' should be 'Sect 3.2'

Corrected

Pg 15012: Following on from the description of the 1D model used to estimate the vertical distribution of HONO, I think it would be pertinent to state at this point the respective measurement heights of the radicals and HONO and, if different, the change in [HONO] estimated by the 1D model between the two heights.

The measurement heights for radicals (3m) and HONO (1m) are given in Sections 2.1 and 2.2, respectively. The 1D calculated HONO concentrations are presented in Figure 10.

Pg 15016, ln 16: '60%' should be '78%' according to fig 6.

Corrected:

"The variability of P_{HO2+NO} and P_{HONO} then explain ~80% of the variability of OH."

Pg 15016, ln 22: remove comma after 'etc.'

Corrected.

Pg 15019, ln 9: change to 'reduced by factors of 2, 4..'

Corrected.

Pg 15019, ln 18: change '0.25' to '4'

Corrected.

Section 3.5: Along with the comparison of HONO calculated with the 1D model and estimated from the radical budget, this section would benefit from a discussion on the expected HO2NO2 diurnal profile – what profile does the 0D model estimate for example? Does this profile suggest that the correction needing to be applied will vary diurnally?

The calculated 0D model diurnal profile of HO_2NO_2 (Figure A) does not exhibit any clear diurnal variation. We therefore think that, in absence of HO_2NO_2 measurements, further discussions based on these calculations would be too speculative.

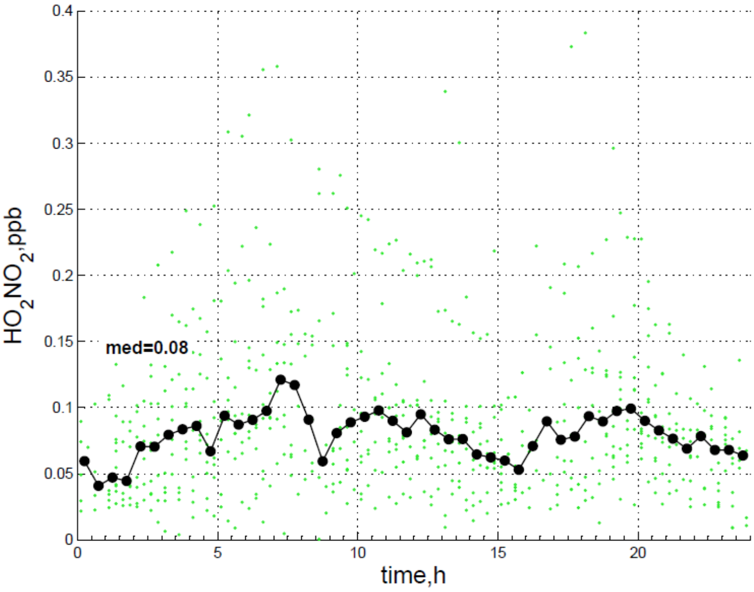

***Figure A**. Calculated diurnal profile of HO_2NO_2*

Pg 15022, ln 2: I can’t find a reference to the proposed gas-phase source of HONO from HO2.H2O + NO2 in Legrand et al. As highlighted by H Berresheim, the impact of this reaction as a sink for HO2 needs to be discussed in the manuscript given that the recycling of HO2 to OH is the second most important OH source.

This hypothetical HONO source would contribute for 10-20% of the HONO production from the reaction OH+NO and would result in less than 1% of the measured HONO. The discussion of HONO formation via reaction $HO_2(H_2O)+NO_2$ is added in the revised version of Legrand et al. (Section 5) For information we copy the corresponding text at the end of this document in the Appendix A.

Estimated with the rate constants presented in Legrand et al. (see Appenix A) the contribution of this reaction to the HO_2 losses is less than 1%.

We add the note about this reaction in Section 3.2:

“The contribution of the reaction of $HO_2(H_2O)$ with NO_2 (Li et al., 2014) to the RO_2 losses is estimated with the rate constants given in Legrand et al. (this issue) to be less than 1%.”

Pg 15022, ln 25: change to ‘the peak calculated..’

Corrected

Pg 15022, ln 26: How exactly was P(O3) calculated? Were losses of NO2 that did not result in ozone production (e.g. OH + NO2) considered? I think an equation that highlights the reactions considered needs to be added here.

In estimation of the ozone production rate the reactions of NO_2 *with OH and* RO_2 *were neglected compared to the photolysis of* NO_2*. We add appropriate note:*

"As seen in Figure 11, the peak calculated ozone production rate ($P(O_3)$*) is about 0.3 ppbv* h^{-1} *during daytime (using the measurements of* RO_2 *at 3 m, NO at 4 m above the snowpack and assuming* $P(O_3)$ *equal to* NO_2 *production rate in the reaction of* RO_2 *with NO)."*

Pg 15022, ln 28: It would be more appropriate to compare the P(O3) calculated with the diurnal O3 profile observed during the OPALE campaign rather than an earlier campaign at Dome C.

We agree but the detailed analysis of the ozone data gained at Dome C during the 2011-2012 campaign will be presented in a future publication (in preparation). At present, we can only compare our estimate with the value derived from ozone data gained over the 2007/08 summer season.

Table 2: Add a line after the reactions listed to separate from the summed radical budget section.

Corrected

Table 2: How was the 1σ uncertainty estimated?

Corrected

"1σ uncertainty estimated with accounting for measurement uncertainties"

Figure 7: A comment about the negative intercepts in the correlations between observations and model with zero HONO is needed.

The negative intercepts is the result of the difference in the modelled and measured diurnal profiles mentioned in Section 3.4 This difference is better visible on the Figure 8 from the diurnal profiles of the M/O ratios.

Dr. Berresheim

Overall, this is a very well written paper with strong enhancements in current knowledge of HOx/ROx/NOx chemistry in the Antarctic troposphere and thorough comparison with previous measurements by Mauldin et al. at South Pole. The crucial role of HONO (and/or HNO4) has been nicely confirmed.

1. However, the only major issue I have is that the paper is strongly entangled with the paper by Legrand et al. (same issue), and that in my opinion it needs to be somewhat "disentangled" to stand on its own. This pertains specifically to sub-chapter 3.5, the "Comparison with 1D model" where it seems that the reader has to flip-flop back and forth between the results of both papers in order to follow (and accept) the arguments made in the discussion (e.g., how much interference exactly due to HNO4? how crucial is snow temperature? how justified is a turbulent vs. molecular flux approach for HONO vertical transport?). I suggest that every time Kukui et al. use a result from Legrand et al. it should be clearly outlined, and indeed explained, in their discussion even if it means repeating some of the context from Legrand et al.

The following additions were made to provide more information from the work of Legrand et al.

Section 2.2 Last paragraph:

“*Legrand et al. (this issue) report tests done both in the field and in the lab that tend to suggest an overestimation of HONO measurements in the range of 10 to 20 pptv due to the presence of* HO_2NO_2 *in the range of 50-100 pptv in the cold atmosphere at Dome C.. This range of* HO_2NO_2 *mixing ratios is in agreement with the median* $[HO_2NO_2]$ *of 80 pptv estimated from* RO_2 *and* NO_2 *levels measured at Dome C (see Section 3.2). Also, as discussed by Legrand et al. (this issue), similar levels of* HO_2NO_2 *were previously observed in Antarctica.*”

Section 3.5 1st paragraph:

“According to Legrand et al. (this issue), about 100 pptv of HO_2NO_2 *may result in interference equivalent to about 15 pptv of HONO.”*

Section 3.5 Paragraph 2.

“*Under temperature conditions encountered at Dome C the HONO/*NO_x *ratio ranged from 0.57 during the day (at -25°C) and 0.3 at night (at -35°C).*”

2. Also, I cannot quite agree with the authors’ conclusions (p. 15022, line 20) that the model agrees well with night time HONO, as this seems to be not convincing for the 0-6 hours period shown in Fig. 10

The above statement about night-time agreement concerned the HONO estimated from the $OH+RO_2$ *budget (the blue line) which is in good agreement with 1D calculations for the period 0-6 hours. Note, however, that in accordance with suggestions of Referee 3 the Figure 10 has been modified to include the HONO derived from the budget with PSS estimated* NO_2*. The corresponding comments in the text have been modified as well.*

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3. A third point I would like to make is the authors' brief acknowledgement of the recent work by Li et al. (2014) of which they mention only in passing that the HO2(H2O) reaction with NO2 would be negligible at Antarctic temperatures as a source for HONO. However, they neglect to recognize that this reaction could - on the other hand - be a significant sink for HO2, and this should have implications for the model results.

Estimated with the rate constants presented in Legrand et al. (see Appenix A) the contribution of this reaction to the HO_2 losses is less than 1%.

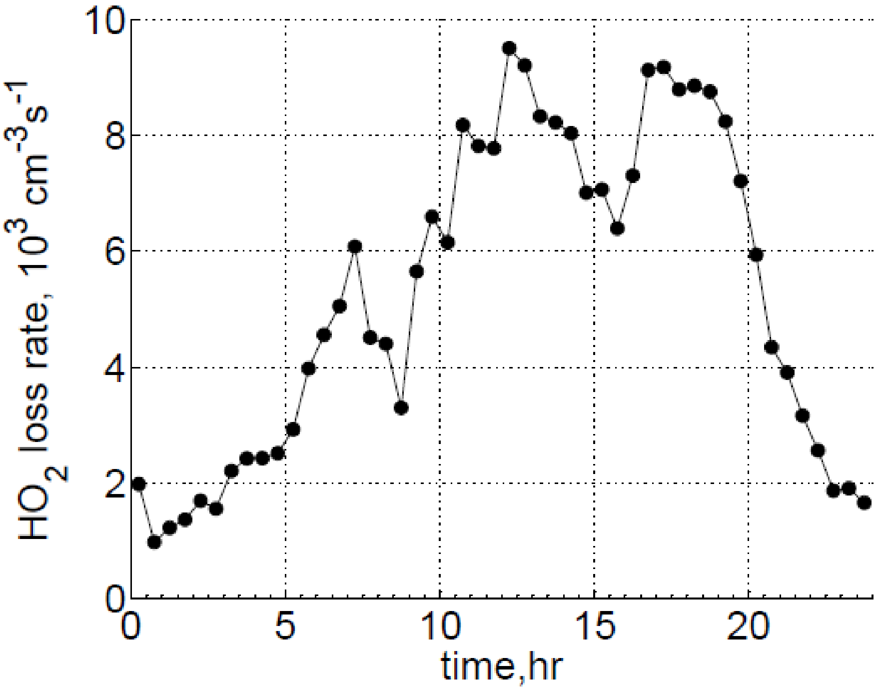

Figure B. Loss of HO_2 via $HO_2(H_2O)+NO_2$. (compare with Figure 5 of the manuscript)

We add the note about this reaction in Section 3.2:

"The contribution of the reaction of $HO_2(H_2O)$ with NO_2 (Li et al., 2014) to the RO_2 losses is estimated with the rate constants given in Legrand et al. (this issue) to be less than 1%."

Other than these three comments I have only some minor comments:

pp. 15007-8: With respect to instrument calibration please discuss

a) whether low ambient H2O concentrations presented any difficulties, and

At temperatures and humidity encountered at Dome C the time of conversion of SO_3 to H_2SO_4 in the conversion reactor was typically 0.5 ms during the day and at maximum of 1ms at night. This time is short enough compared with 4 ms and 20 ms used for two different OH measurements modes. According to the reactor model, the sensitivity varied less than 5% for the range of temperatures and humidity at Dome C. Absence of any artefact related to low H2O was also confirmed by an absence of variability of the ratio of the OH signals for the two different OH measurement modes.

b) Where and how far away the NO, NO2 exhaust flows were disposed and whether there could have been interferences with the measurements (also with respect to CO, CH4 for RO2) ?

The following text has been added at the end of Section 2.1:

"To avoid possible contamination of ambient air by the SO_2, NO and NO_2 reactants added to the chemical conversion reactor, a trap was set up at the pumps exhaust by using two 100 L cylinders containing zeolites. The cylinders were refilled several times during measurements. Flexible exhaust tube of 30 m length was always placed downwind from the container. When the exhaust tube was intentionally placed upwind and close to the radicals sampling point no effect on radical measurements was detected. Also, no influence of the exhaust on the measurements of NO_x and HONO could be noticed."

p. 15011, line 13: Where and how have these been "estimated in section 2.2" ? Please explain.

Corrected section 2.2 => Section 3.2

Anonymous Referee #3:

First-time measurements of OH and RO2 concentrations were reported for Dome C. High radical concentration measurements provide important evidence for a near surface oxidation layer over Antarctica due to snow emissions. Concurrent measurements of O3, HONO, NO, NO2, HCHO and H2O2 are used in a photochemical steady state model to analyze the radical budgets and the sources and sinks of OH and RO2. While the reported observations are valuable and the procedures of measurements and modeling results are described and analyzed well, I cannot say that I agree with the way that the conclusions of this paper is presented. The caveats for the conclusions are not apparent enough that a casual reader can easily misunderstand the results.

It will be better to clearly acknowledge the three problems in the analysis: (1) HONO measurement appears to have a (large) high bias; (2) NO2 measurement appears to have a (large) high bias; (3) The radical budget balance is off by a factor of 3 (comparing daily median net sources of OH and RO2 with net radical losses in Table 2).

Although the biases of (1) and (2) are described, most of the modeling analyses assume either (1) or (2) but not both. There lies a problem that needs to be rectified before publication.

The conclusions on how much HONO is "real" (line 16-22, P. 15001) is based on modelling analysis using observed NO2. If the high bias of NO2 measurement is removed, as in one model simulation (x0, NO2pss), the amount of HONO needed to explain observed OH and RO2 will be (much?) smaller than 25%. In fact, looking the modelling results, this is the simulation that has OH and RO2 concentrations in better agreement with the observations than most of the other simulations.

The discussion on the high bias of observed NO2 in P. 15017 and 15018 is very informative. I think the discussion should be presented before the discussion of radical budget analysis since NO and NO2 govern the cycling and loss of radicals. Either there is a large measurement bias or there is some significant unknown chemistry. If there is significant chemistry missing that can alter NO2/NO ratio by a factor of 3, the model simulated radical budgets without this chemistry cannot be correct. One has to question any conclusions drawn by the analysis. On the other hand, if it is measurement bias, which the authors seem to suggest being the case and I agree, the radical budget analysis should focus on the case not using the biased NO2 measurements (use NO2pss instead).

For problem (3), I think it's important to show if the radical budget is balanced for the x0-NO2pss case. Reducing HONO to 25% works (for the budget balance) because the radical loss estimate using observed NO is high. I think that a self-consistent balanced radical budget is a prerequisite before the modeling results can be used to draw useful conclusions.

The analysis based on Figure 10 is an excellent idea. However, the observed NO2 was used in the analysis. It would be more instructive to see how much HONO is required when calculated NO2pss is used.

While I support the publication of this paper, I think that the caveats for the analysis results need be clearly stated. I further suggest that substantial changes be made to restructure the paper to put more emphasis on the model results that account for both biases of (1) and (2).

We agree that possibility of NO_2 overestimation should be better introduced and emphasised in the manuscript. It may be noted, however, that in contrast to HONO measurements for which the interference from HNO_4 was identified, the reason for the observed large NO_2/NO ratio is not yet clear.

We have introduced the following changes:

- The budget calculations with PSS NO_2 *are presented in Table 2;*

- The Figure 10 shows two HONO profiles calculated with the measured and the PSS estimated NO_2*;*

***- The changes in the article text were made**:*

1) Abstract:

"To explain the observations of radicals in this case an additional source of OH equivalent to about (25-35)% of measured photolysis of HONO is required. Even with a factor of 5 reduction in the concentrations of HONO, the photolysis of HONO represents the major primary radical source at Dome C. To account for a possibility of an overestimation of NO_2 *observed at Dome C the calculations were also performed with* NO_2 *concentrations estimated by assuming steady state* NO_2*/NO ratios. In this case the net radical production from the photolysis of HONO should be reduced by a factor of 5 or completely neglected based on the photochemical budget of OH or 0D modelling, respectively."*

2) Section 2.2. In the description of the NOx measurements we emphasize the uncertainty related to the too large NO2/NO ratio.

"The NO_2 *and NO measurements are discussed in Frey et al. (this issue). The ratios of* NO_2 *to NO observed at Dome C during 2011-2012 campaign were up to 3 times larger than in 2009-2010 (Frey et al., 2013) and significantly larger, up to 7 times, than the ratios estimated assuming photochemical steady-state (PSS) conditions for NOx. It is suggested that some part of this inconsistency may be due to unknown interference leading to an overestimation of the* NO_2 *concentrations (Frey et al., this issue)."*

3) Section 3.2. In the discussion of the radical losses we discuss the results with PSS NO2 presented in Table 2.

"As the losses of OH and RO_2 *via the reactions with* NO_2 *may be overestimated due to unknown interference in the* NO_2 *measurements (Frey et al., this issue) we also present in the Table 2 (values in parenthesis) the radical losses for [*NO_2*] estimated assuming PSS conditions for NOx. In this case the net daytime radical losses are dominated by the radical cross reactions* RO_2+RO_2 *(25) and* $OH+RO_2$ *(20)."*

4) Section 3.3. In the discussion of the radical budget:

"As shown in Table 2 the assumption of steady-state NO_2 *concentrations lead to a significant overestimation of the net radical production for* RO_2 *and (*RO_2+OH*) even when neglecting net OH production by the photolysis of HONO. For OH budget, neglecting the net OH production by the HONO photolysis would lead to an underestimation of the OH production."*

5) Section 3.4 At the end of the section in the description of the 0D modelling:

"By assuming the PSS derived NO_2 *concentrations, the balance for the OH radical budget is achieved by reducing PHONO by a factor of 5, while for* RO_2 *and the sum of* RO_2 *and OH the radical production is overestimated even if the net source from HONO photolysis is neglected."*

6) Section 3.5 1D modelling. We have added to the Figure 10 the HONO derived from the OH budget with PSS NO2 and added the following comment to the text:

"The HONO mixing ratio-time profiles calculated with the 1D model are compared in Figure 10 with the HONO profiles resulting from analysis of the radical budgets. The levels of HONO derived from the OH budget with measured NO_2 *are about 10 pptv higher than the*

HONO values obtained using PSS NO_2 concentrations. In both cases the HONO mixing ratios derived from the OH budget are in reasonable agreement with [HONO] predicted by the 1D model (within 5 pptv)."

7) Section 4. We have modified the conclusion to better emphasise the possibility of NO2 bias. We have added the following text:

"The conclusions based on the radical budget analysis and 0D modelling using the measured concentrations of NO and NO_2 may be significantly biased because the chemical mechanism derived from the available field observations at Dome C is inconsistent with observed large ratios of [NO_2] to [NO]. Assuming that measured NO_2 mixing ratios were overestimated due to unknown interference and using instead [NO_2] estimated assuming steady-state results in lower radical losses and, hence, stronger overestimation of the radical production. In this case, based on the analysis of the radical budgets the observed concentrations of OH radicals are consistent with the levels of HONO corresponding to about (15-20)% of the measured values, while for the sum of the radicals the radical production is overestimated even neglecting the net OH source from the photolysis of HONO. Based on 0D modelling steady-state derived NO_2, the measured OH concentrations are in agreement with steady-state HONO mixing ratios (about 1-2 pptv), while the concentrations of RO_2 radicals are overestimated by about 50% even neglecting the net radical production by the photolysis of HONO.
Hence, in both cases corresponding to the measured or the PSS derived concentrations of NO_2 the calculations, 0D modelling or budget analysis, overestimate the OH and RO_2 concentrations. If this inconsistency is due to an overestimation of the concentrations of HONO, the degree of the overestimation depends on the concentrations of NO_2 used in the calculations. Using the measured NO_2 results in an overestimation of HONO by a factor of 3-4. If the concentrations of NO_2 are estimated assuming steady-state conditions the net radical production from the HONO photolysis should be reduced by a factor of 5 or completely neglected based on the budget of OH or 0D modelling, respectively. "

Other comments:

(1) Line 22-23, P15002, photolysis of H2O2 from snow emissions is a primary source. Photolysis of H2O2 formed from two HO2 is not a primary radical source.

"primary" is replaced by "net"

(2) Line 1-9, P15009, some estimates on how the measurement uncertainties affect the budget uncertainties would be useful.

The uncertainties presented in Table 2 or in Figure 9 were estimated from the measurement uncertainties (including OH and RO_2). The comment b) to the Table 2 was modified.

"b) 1σ uncertainty estimated with accounting for measurement uncertainties"

(3) Figure 1, please show the time series of NO, NO2, NO2pss. These species are critical for the discussion of radical budgets.

The NOx profiles are presented in the accompanying article of Frey et al. (this issue). Here we present only median values collected in Table 1. We added to the Table 1 the PSS estimated NO_2 median and range mixing ratios.

(4) Line 5-7, P15013, please show a figure of OH dependence on J(O1D). If J(O1D)+H2O is not a significant primary radical source (Table 2), why is there such a square-root dependence?

In this paper we present the dependence of OH on J(NO_2) which is found to be quasi-linear, but the correlation is weak. We show then that the correlation of OH is linear and strong with the production rates of OH from the photolysis of HONO and from the reaction HO2+NO. These dependences are in agreement with our conclusion about significance of these two sources at Dome C.

Concerning the dependence on J(O1D) we state in Section 3.1: "The relationship of [OH] with J(O(1D)) was close to a power-law dependence with an exponent of ~0.5 in agreement with a typical close to quadratic dependence of J(O(1D)) on J(NO2) observed at Dome C."

The dependence of OH on J(O1D) is shown below. As we do not see how this dependence with very large scattering can be helpful for the discussion of sources and sinks of the radicals we suggest that it should not be included in the article.

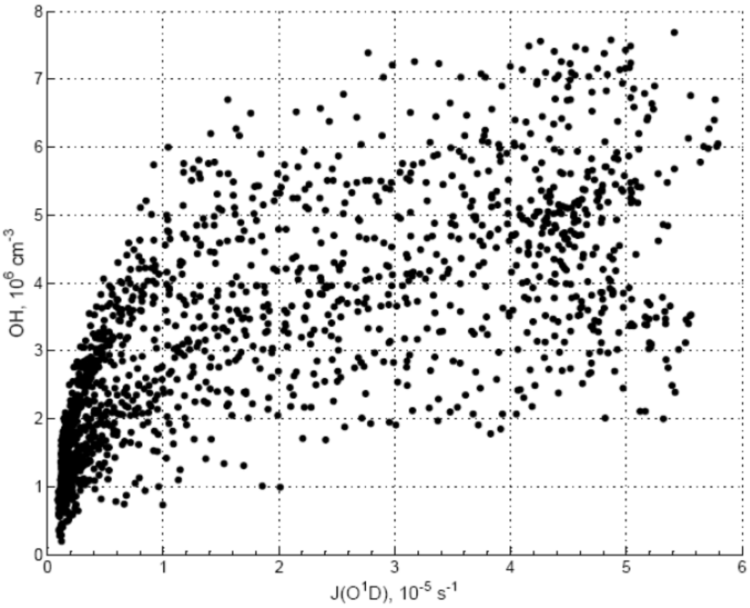

Figure C. Dependence of OH on J(O^1D).

(5) Figure 4, HONO produced from OH+NO+M -> HONO + M should be kept in the simulations of all x0 cases. Removing gas-phase produced HONO introduces an artificial radical sink, which can be large for high NO conditions and may explain some of the model bias, which seems to worsen with increasing NO.

In fact, the case x0 corresponds to the model with calculated PSS HONO not constrained with measured HONO. The corresponding correction is made in the figure captures for Figures 4,7,8 and in the text.

(6) Line 28, P. 15015, an average of 80 pptv HNO4 is much higher than 40-60 pptv observed at South Pole. It would be easy to see if HNO4 and the corresponding NO observations are compared between Dome C and South Pole.

"similar" is replaced by "somewhat higher than".

Note also that up to 150 pptv of HO_2NO_2 was observed between the ground and 50 m elevation over the Antarctic plateau (Slusher et al., J. Geophys. Res. Atmos., 115, D07304, doi:10.1029/2009JD012605, 2010)

(7) Line 16-17, P. 15016, the sum of two variabilities is > 100%. Please comment on what it means.

Corrected (please, see also the comment to this by referee 1):

"The variability of P_{HO2+NO} *or* P_{HONO} *then explain ~80% of the variability of OH."*

Appendix A:

About the reaction $HO_2(H_2O)+NO_2$ from Legrand et al. (this issue)

Another gas-phase source of HONO was recently proposed by Li et al. (2014) via reaction of $HO_2(H_2O)$ complex with NO_2:

$HO_2 + NO_2 \rightarrow HO_2NO_2$ (2)

$HO_2 + H_2O \leftrightarrow HO_2(H_2O)$ (3)

$HO_2(H_2O) + NO_2 \rightarrow$ HONO + other products (4)

Reaction of $HO_2(H_2O)$ complex with NO_2 was first suggested by Sander and Peterson (1984) to explain the observation of a linear dependence of the effective rate constant of the reaction of HO_2 with NO_2 on the concentration of water vapour in the temperature range 275-298 K. Assuming reaction mechanism (2-4) Sander and Peterson (1984) derived temperature dependence for the effective third-order rate constant of the reaction $HO_2+NO_2+H_2O$, $k^{III}_4(T)$, with $k^{III}_4(T)$ representing the product $k_4 \times K_3$, where k_4 is the bimolecular rate constant for reaction $HO_2(H_2O)$ with NO_2 and K_3 is equilibrium constant for reaction (3). The possible contribution of reaction (4) to form HONO at Concordia was evaluated by assuming a unity yield of HONO for the reaction (4). The rate constant $k_4(T)$ in the temperature range 275-298 K was estimated from the $k^{III}_4(T)$ data of Sander and Peterson (1984) using recent recommendations for $K_3(T)$ and $k_2(T)$ from Sander et al. (2011): $k_4(T)= k^{III}_4(T) / K_3(T) \times k_2(T) / k_2(T)^{Sander}$, where $k_2(T)^{Sander}$ are data from Sander and Peterson (1984). The values of $k_4(T)$ at low temperatures encountered at Concordia were obtained by extrapolating the $k_4(T)/k_2(T)$ data from Sander and Peterson (1984) and assuming a logarithmic dependence of $k_4(T)/k_2(T)$ on 1/T, similar to reaction of $HO_2(H_2O)$ with HO_2 (Sander et al., 2011). The resulting dependence ($k_4(T)/k_2(T) = 10^{-1505.3/T(K)+5.4}$) predicts significantly lower water enhancement effect at low temperature ($k_4/k_2=0.12$ at 240K compared to 2.2 at 298K). Using these k_4 values and observations of OH, NO, HO_2, NO_2 and H_2O, the low temperatures encountered at Concordia make negligible the formation of HONO from the reaction (4). This hypothetical HONO source would contribute for 10-20% of the HONO production from the reaction OH+NO and would result in less than 1% of the measured HONO.

Li, X., Rohrer, F., Hofzumahaus, A., Brauers, T., Häseler, R., Bohn, B., Broch, S., Fuchs, H., Gomm, S., Holland, F., Jäger, J., Kaiser, J., Keutsch, F. N., Lohse, I., Lu, K., Tillmann, R., Wegener, R., Wolfe, G. M., Mentel, T. F., Kiendler-Scharr, A., and Wahner, A.: Missing Gas-

Phase Source of HONO Inferred from Zeppelin Measurements in the Troposphere, Science, 344, 292-296, 2014.

Sander, S.P., and Peterson, A.E.: Kinetics of the reaction $HO_2+NO_2+M \rightarrow HO_2NO_2+M$, J. Phys. Chem., 88, 166-1571, 1984.

Sander, S.P., J. Abbatt, J.R. Barker, J.B. Burkholder, R.R. Friedl, D.M. Golden, R.E. Huie, C. E. Kolb, M.J. Kurylo, G.K. Moortgat, V.L. Orkin and P.H. Wine : "Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17," JPL Publication 10 June 2011, Jet Propulsion Laboratory, Pasadena, http://jpldataeval.jpl.nasa.gov, 2011.