We thank **Referee #1** for the 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.

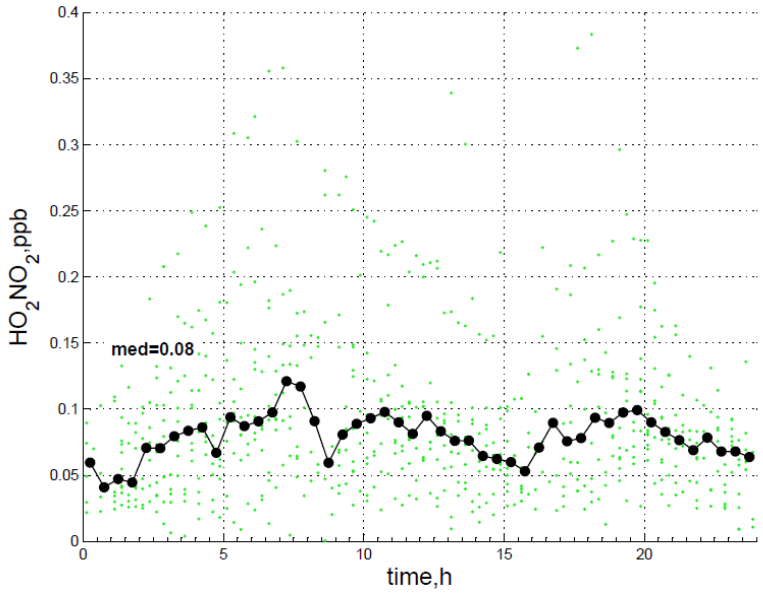

***Figure A**. Calculated diurnal profile of HO_2NO_2*

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.

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:

$$HO_2 + NO_2 \rightarrow HO_2NO_2 \quad (2)$$

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

$$HO_2(H_2O) + NO_2 \rightarrow HONO + \text{other products} \quad (4)$$

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→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.