We thank Dr. Berresheim 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.

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%.
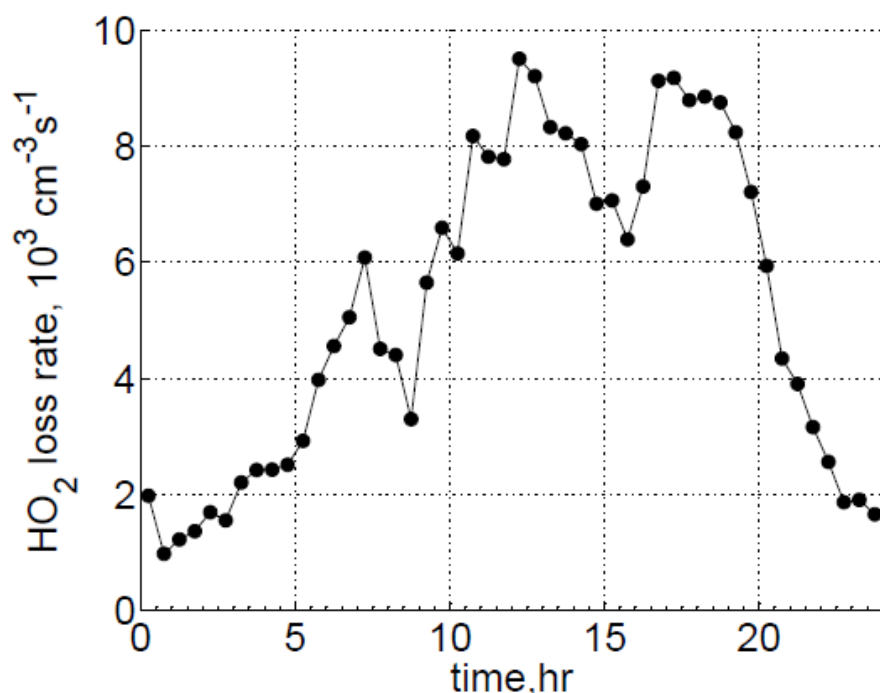

Figure B. Loss of HO_2 via $HO_2(H_2O)+NO_2$. (compare with Figure 5 of the manuscript)

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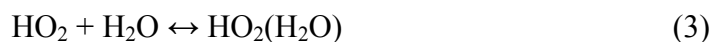
p. 15011, line 13: Where and how have these been "estimated in section 2.2" ? Please explain.

Corrected section 2.2 => Section 3.2

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:

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

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

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

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.