

We thank **Referee #3** 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 #3:**

First-time measurements of OH and RO<sub>2</sub> 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 O<sub>3</sub>, HONO, NO, NO<sub>2</sub>, HCHO and H<sub>2</sub>O<sub>2</sub> are used in a photochemical steady state model to analyze the radical budgets and the sources and sinks of OH and RO<sub>2</sub>. 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) NO<sub>2</sub> 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 RO<sub>2</sub> 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 NO<sub>2</sub>. If the high bias of NO<sub>2</sub> measurement is removed, as in one model simulation (x0, NO<sub>2</sub>pss), the amount of HONO needed to explain observed OH and RO<sub>2</sub> will be (much?) smaller than 25%. In fact, looking the modelling results, this is the simulation that has OH and RO<sub>2</sub> concentrations in better agreement with the observations than most of the other simulations.

The discussion on the high bias of observed NO<sub>2</sub> 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 NO<sub>2</sub> 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 NO<sub>2</sub>/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 NO<sub>2</sub> measurements (use NO<sub>2</sub>pss instead).

For problem (3), I think it's important to show if the radical budget is balanced for the x0-NO<sub>2</sub>pss 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 NO<sub>2</sub> was used in the analysis. It would be more instructive to see how much HONO is required when calculated NO<sub>2</sub>pss 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<sub>2</sub> 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<sub>4</sub> was identified, the reason for the observed large NO<sub>2</sub>/NO ratio is not yet clear.*

***We have introduced the following changes:***

- *The budget calculations with PSS NO<sub>2</sub> are presented in Table 2;*
- *The Figure 10 shows two HONO profiles calculated with the measured and the PSS estimated NO<sub>2</sub>;*

***- 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<sub>2</sub> observed at Dome C the calculations were also performed with NO<sub>2</sub> concentrations estimated by assuming steady state NO<sub>2</sub>/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 OD modelling, respectively.”*

*2) Section 2.2. In the description of the NO<sub>x</sub> measurements we emphasize the uncertainty related to the too large NO<sub>2</sub>/NO ratio.*

*“The NO<sub>2</sub> and NO measurements are discussed in Frey et al. (this issue). The ratios of NO<sub>2</sub> 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 NO<sub>x</sub>. It is suggested that some part of this inconsistency may be due to unknown interference leading to an overestimation of the NO<sub>2</sub> concentrations (Frey et al., this issue).”*

*3) Section 3.2. In the discussion of the radical losses we discuss the results with PSS NO<sub>2</sub> presented in Table 2.*

*“As the losses of OH and RO<sub>2</sub> via the reactions with NO<sub>2</sub> may be overestimated due to unknown interference in the NO<sub>2</sub> measurements (Frey et al., this issue) we also present in the Table 2 (values in parenthesis) the radical losses for [NO<sub>2</sub>] estimated assuming PSS conditions for NO<sub>x</sub>. In this case the net daytime radical losses are dominated by the radical cross reactions RO<sub>2</sub>+RO<sub>2</sub> (25) and OH+RO<sub>2</sub> (20).”*

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

*“As shown in Table 2 the assumption of steady-state NO<sub>2</sub> concentrations lead to a significant overestimation of the net radical production for RO<sub>2</sub> and (RO<sub>2</sub>+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 OD modelling:*

*“By assuming the PSS derived NO<sub>2</sub> concentrations, the balance for the OH radical budget is achieved by reducing PHONO by a factor of 5, while for RO<sub>2</sub> and the sum of RO<sub>2</sub> 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 NO<sub>2</sub> 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<sub>2</sub> are about 10 pptv higher than the HONO values obtained using PSS NO<sub>2</sub> 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 NO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>] to [NO]. Assuming that measured NO<sub>2</sub> mixing ratios were overestimated due to unknown interference and using instead [NO<sub>2</sub>] 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<sub>2</sub>, the measured OH concentrations are in agreement with steady-state HONO mixing ratios (about 1-2 pptv), while the concentrations of RO<sub>2</sub> 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<sub>2</sub> the calculations, 0D modelling or budget analysis, overestimate the OH and RO<sub>2</sub> 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<sub>2</sub> used in the calculations. Using the measured NO<sub>2</sub> results in an overestimation of HONO by a factor of 3-4. If the concentrations of NO<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> from snow emissions is a primary source. Photolysis of H<sub>2</sub>O<sub>2</sub> formed from two HO<sub>2</sub> 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<sub>2</sub>). 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, NO<sub>2</sub>, NO<sub>2</sub>pss. These species are critical for the discussion of radical budgets.

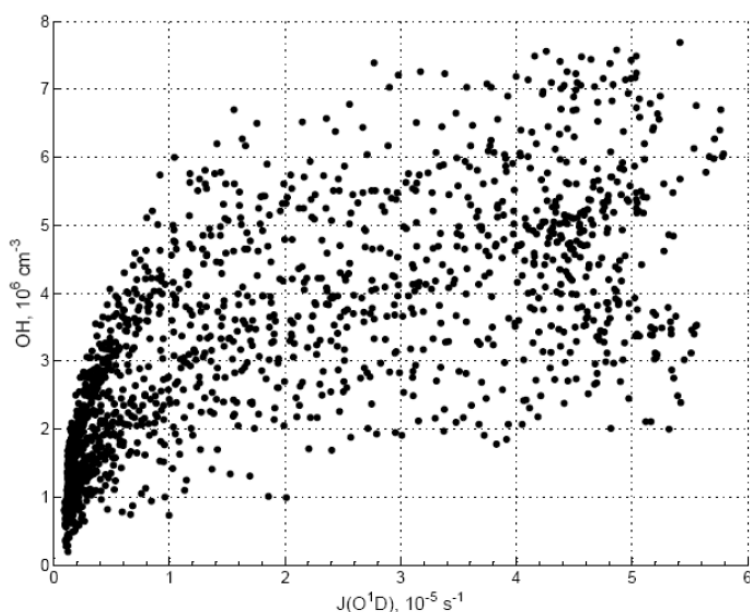
*The NO<sub>x</sub> profiles are presented in the accompanying article of Frey et al. (this issue). Here we present only median values collected in Table 1. We added to the Table 1 the PSS estimated NO<sub>2</sub> median and range mixing ratios.*

(4) Line 5-7, P15013, please show a figure of OH dependence on J(O<sup>1</sup>D). If J(O<sup>1</sup>D)+H<sub>2</sub>O 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<sub>2</sub>) 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 HO<sub>2</sub>+NO. These dependences are in agreement with our conclusion about significance of these two sources at Dome C.*

*Concerning the dependence on J(O<sup>1</sup>D) we state in Section 3.1: “The relationship of [OH] with J(O<sup>1</sup>D)) 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<sup>1</sup>D)) on J(NO<sub>2</sub>) observed at Dome C.”*

*The dependence of OH on J(O<sup>1</sup>D) 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<sup>1</sup>D).*

(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 HNO<sub>4</sub> is much higher than 40-60 pptv observed at South Pole. It would be easy to see if HNO<sub>4</sub> 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<sub>2</sub>NO<sub>2</sub> 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  $P_{HO_2+NO}$  or  $P_{HONO}$  then explain ~80% of the variability of OH.”*