

Interactive comment on “Measurements of OH and RO₂ radicals at Dome C, East Antarctica” by A. Kukui et al.

Anonymous Referee #3

Received and published: 2 July 2014

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

C4367

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 modeling 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 modeling 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

C4368

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).

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.
- (2) Line 1-9, P15009, some estimates on how the measurement uncertainties affect the budget uncertainties would be useful.
- (3) Figure 1, please show the time series of NO, NO₂, NO2pss. These species are critical for the discussion of radical budgets.
- (4) Line 5-7, P15013, please show a figure of OH dependence on J(O_{1D}). If J(O_{1D})+H₂O is not a significant primary radical source (Table 2), why is there such a square-root dependence?
- (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.
- (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.
- (7) Line 16-17, P. 15016, the sum of two variabilities is > 100%. Please comment on what it means.

C4369

- (8) Line 20-25, P. 15019, these are the type of results that are more robust than the simulations with measured NO₂.
- (9) Line 20-22, P. 15022, if the measurement of HONO has a large high bias, there is no reason to state that this model result is an underestimation.
- (10) Line 17-18, P. 15023. A near-surface oxidation layer over Antarctica was proposed and simulated by Wang et al. (2007) (Atmos. Environ., 41, 3944-3958, 2007). It should be acknowledged and referenced.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 14, 14999, 2014.

C4370