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Interactive comment on “Summertime NO_x measurements during the CHABLIS campaign: can source and sink estimates unravel observed diurnal cycles?” *by* S. J.-B. Bauguitte et al.

Anonymous Referee #2

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Review of acp-2009-445

The paper by Bauguitte et al. has set out having the goal of improving our understanding of NOx chemistry at the polar site Halley Bay, Antarctica. The data set recorded was a component of a larger field program, CHABLIS. The time period over which NOx data were collected was 1 Jan to 10 Feb 2005. A major characteristic of the NOx data was its exhibiting a clear diurnal cycle (reflecting the low latitude of the site, 75° S) with an average peak value of 24 pptv. The peak value typically appeared between the hours of 19:00 and 20:00 GMT, approximately 5 hrs after high noon. Specific objectives of this effort were: to understand the maximum levels reached; the detailed

trends in the NOx cycle in terms of snow emissions rates (photochemically driven); the in-situ chemistry as a controller of NOx loss (especially the role of halogen species); and finally, to a lesser extent, assessing the impact of local meteorology.

I believe the authors have put together a scientifically interesting paper and that the NOx data as well as the associated chemical and physical parameters collected during the CHABLIS field experiment will represent an important contribution to the scientific literature. The overall chemical picture emerging from the study also has merit; and thus, I believe the paper should be published at some point. This said, I also find that the text in some cases presents what appears to be misleading information, in other cases it is simply unclear as stated (at least to this reviewer), and still in other places it appears to be incomplete in some key aspects. Thus, I believe the manuscript really needs further serious attention before finally being considered for publication.

Detailed Comments: 1) –section 2.1. Methods Although this reviewer will state at the start that the concerns expressed in the text that follows will not significantly alter the scientific conclusions of this paper, it still remains critical that field scientist not misrepresent the quality of their data by making sensitivity statements and listing detection limits that are more representative of some ideal laboratory world. In this specific case, it seems incredulous to the reviewer that the authors are claiming to have a chemiluminescence sensor having a field proven detection limit of 1 pptv for NO and 4 pptv for NO2. For starters, most credible analytical chemists use a signal-to-noise ratio of 2:1 to define a field detection limit for a species, not 1:1. Second, the total uncertainty should be arrived at from a propagation of error analyses of all errors. Although the authors did this to some degree, it is important to recognize that more often than not, systematic errors are variable in nature and shift in their value with changes in environmental conditions. Typically, therefore, they can not simply be subtracted away. Most importantly are those errors that one strongly suspects are present in the system but there may be no simple way to quantify them, again partly due to their variability in time. In this context, the authors note that both HONO and HO2NO2 were possible interferents in their system, but they were not successful in quantifying either of these and then seeming assumed they were insignificant. That HO2NO2 was present is clearly indicated, however, in the text where it is listed as a significant loss pathway for NOx. That HONO was present, although not discussed, is suggested by the HONO measurements reported by Clemitshaw et al., at scientific meetings. Although I understand that these measurements are still quite suspect, even so it suggests at a minimum that some other NOy species was present at the multi-pptv level that gave rise to what was believed to be a HONO signal and thus represents still another interference source. The long and short of this discussion is that although there is little doubt that signal levels as low as 1 pptv were observed in this study (and subsequently attributed to NO or NO2), this is not convincing evidence for a detection limit of 1 pptv for NO and 4 pptv for NO2. The fact that several NO2 signals ranged from "negative" 5 to 7 pptv is just one more indication of the limitations of the system.

2) Section 2.2 -2.3. Flux measurements and photolysis rates. Although these sections were reasonably well written it would be quite helpful to many readers if the authors would clearly distinguish what differences are involved in this papers assessment of the in-snow nitrate photolysis rates versus those previously published by other team members (e.g., Wolff et al., 2002 and Jones et al., 2007). Specifically, what parameters or assumptions have been altered if any?

3) Section 2.4. Ancillary data sets. It is somewhat confusing to the reviewer that the IO and BrO mean noontime mixing ratios are given as 4.3 and 3.8 pptv and yet a non-zero mixing ratios for SZA > 90° were listed respectively as 0.5 and 1.4 pptv. For example, Jones et al (2008) give the detection limit for both species as 1-2 pptv. Does this not suggest that the latter values may, in fact, represent a possible interference level for these species?

4) section 3.1. Time series. "NO2 hourly means appear negative —- resulting from poor artifact correction and hence increased systematic uncertainty". This to some extent highlights the concerns this Reviewer attempted to express earlier under statement

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Section 3.2. Several other investigators work are cited here as also showing a diurnal cycle in NOx. It would be helpful to the reader if the authors would make a more quantitative comparison between their diurnal profile for NOx and that of other investigators and then later on in the discussion section note how any differences might be related to possible differences in the respective chemistries at the different sites.

5) Section 4.1 -4.2. Modeling/Results a) It is not obvious how equation 2, even as guided by the minimization equation 3, enfolds the BL assumption of 100m in the calculation. There also must be an uncertainty in the results for both α and τ. Both E(nitrate) and NOx must have uncertainties (e.g., ±1 σ of the mean). This discussion needs to be expanded on. b) It would appear that the major assumption in these model calculations is that involving the boundary layer depth. It was taken to be 100m, referencing Jones et al., 2008. However, Jones makes clear that no direct observations of this height were made during the CHABLIS study until Dec 2004 and that an older data base was used in lieu of real-time measurements. The older study provided a range of values from < 40m to 110m with an overall mean value of 70m. This information leads to at least two questions: 1) why was 100m selected when the average value was 70m? 2) How sensitive is the model output to shifts in the BL depth value? It seems at a minimum the authors should carry out a set of sensitivity calculations which would show the reader how values of α or τ might change as a function of BL depth, e.g., over the range of 40 to 110m. Reflecting on the study by Anderson and Bauguitte (2007), it also is a major disappointment (e.g., big questions about the validity of the proposed chemistry) that considering Anderson and Bauguitte succeeded in reproducing the diurnal profile for NOx with minimal chemistry by changing BL depth and other meteorological parameters. It appears that no effort was made by the authors to explore a modeling approach that might combined key aspects of the two approaches. c) The stated snow emission flux of 1.7 to 3.4 x 108 molec/cm-2 s-1 measured over the time period of 1-4 Feb is never discussed in terms of what factors (e.g., meteorological) may have been

responsible for this spread. Thus, the reader is left guessing as to the possible reasons for this. Is it simply a reflection of the general uncertainty in the technique employed?

6) Section 5.1 -5.4 . NOx lifetime calculations a) In the calculation of the NOx lifetime based on the halogens IO and BrO (the most critical species according to the authors for removal of NOx), an assumed 3 pptv value was used for each species. However, the stated detection limit by Jones et al., (2008) for each of these species is 1-2 pptv. If, as in the case of NO and NO2, this detection limit for the halogens is also based on a signal to noise ratio of 1:1 it would suggest that there is considerable uncertainty in the actual value of the halogen concentrations, possibly as high as factors of 1.5 to 2. Since these species are believed to be the most critical ones in the removal of NOx it seems that this fact should be noted somewhere in their discussion of this chemistry. b) In addition to halogen nitrate formation and its subsequent removal via aerosol, the conversion of NOx into HO2NO2 is also listed as a removal pathway. For any of these species to be effective sinks, however, they must be removed by aerosol and hydrolyzed but this process is in competition with photolysis. Thus, it is stated that this loss occurs only as high solar zenith angles are reached. In the case of HO2NO2, though the authors mention thermal decomposition, they fail to present any calculations of lifetime based on this. In fact, this reviewer's estimates of this lifetime at the temperatures at Halley Bay suggests that the lifetime for this species is significantly less than 1 hr at all times of day. Thus, it should probably be removed as a significant sink species for NOx. c) Is there a reason why there has not been an effort by the authors to compare their estimated NOx lifetime with those estimated by other investigators at other polar sites. This would be helpful. Any significant differences could then be discussed in terms of possible differences in the chemistry at the different sites. This would seemingly give the authors estimate more credibility.

7) Section 6.1. NO/NO2 ratios. " the inclusion of all NO2 data (i.e., close to/below detection limit), is affecting the shape of our diurnal cycle." Based on the reviewer's comment # 1, even a larger amount of the NO and NO2 data should be removed in

defining the shape and value of ratio as presented in the diurnal profile.

8) Section 7.0. Dicussion a) "We showed that our observed mean NOx diurnal cycle can be reproduced using a simple chemical steady state NOx analysis with a realistic quantified NOx emission rates from snow ". What is the meaning of a "realistic quantified" emission rate? b) "Our NOx lifetime study identified —— pernitric acid and halogen nitrates and their aerosol uptake." The reviewers comment # 6b would strongly suggest that pernitric should not be listed here. c) Comparison discussion starting with: "Evans et al. (2003) modeled the Arctic —- HNO4 formation, aerosol uptake and hydrolysis as the dominant NOx loss —- in spring". The thermal decomposition of pernitric is a very strongly function of temperature and the spring average temperature in the Arctic is probably much lower than that experienced in late summer at Halley Bay. Thus, I'm not convinced that we are comparing apples to apples. d) "Under halogen free conditions, this study finds that HNO4 loss channel — 50% of the NOx loss at noon". As discussed above this needs to be reassessed. I think it may be way high if thermal decomposition is considered. e) "in coastal regions the halogens tend to mitigate this effect due to the reduced NOx lifetime and reduction in the NO/NO2 ratio". This is a misleading statement in that implicit in it is the idea that a reduction of the NO/NO2 ratio and a shortening of the NOx lifetime necessarily lead to the absence of photochemical O3 production. It is more involved than this. For example, in the typical atmospheric chemical system when peroxide radicals are in abundance, the ratio of NO/NO2 also drops relative to that predicted when only O3 is present. But in the latter case this decrease in the NO/NO2 ratio still leads to the subsequent production of photochemical O3. Thus, the authors should consider making this point more clear in that the decrease in this ratio is a result of the halogens (IO and BrO) converting NO to NO2 (thus competing with HO2 plus NO) but in the process they destroys O3 just as NO plus O3 when it converts to NO2 destroys O3. Peroxides, as noted above, also reduce the ratio by producing NO2 but don't consume an O3 in the process.

Shortening the lifetime of NOx is also tricky. HOx radicals can also shorten the NOx lifetime (complex chemistry) but the net effect can still be O3 production. Thus, the . important thing that halogens do is set up a competitive chemical system of NO2 photolysis versus NO2 reaction with IO or BrO, thereby decreasing the rate of production of O atoms. This of course leads to a lower rate of production of O3 per molecule of NO2 formed from NO.

9) Section 8. Conclusions. a) “with some contribution from HNO4”. As before, this needs to be re-examined. b)”will affect the isotopic signature of archived nitrate impurities held in snow”. Not to be nit-picking here but to call “nitrate” (a natural constituent of the polar atmosphere) in Antarctica an “impurity” in snow seems to be going overboard. It is simply a minor/ trace constituent in snow.

Other Comments: Generally speaking, the text as written flows nicely and the author are to be congratulated. However, the referencing is another matter. For starters the reference Evans et al. 2003 is missing in the reference section. There may be others. More importantly, the authors have been very generous in citing all of their own work and that of individuals they frequently work with but they seem to be out of touch with regards to other major efforts that recently have been published. As but a few examples of this: regarding O3 production at polar sites, there is the recent work by Legrand et al., 2009, Helmig et al., 2008a, Helmig2008b, Oltmans et al., 2008: regarding BL depths, Helmig et al., 2002, Neff et al., 2008. A significant effort should be made to re-examine the referencing in the text as related to others efforts directed toward understanding polar chemistry.

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