Anonymous Referee #2: Submitted on 23 Jan 2011

Re-review of: "Summertime NOx measurements during the CHABLIS campaign: can source and sink estimates unravel observed diurnal cycles?"

General Comments:

This is the second review of the Bauguitte et al., manuscript. This updated version is clearly an improvement over the original version. That said, the Reviewer is still troubled by what he believes are at least two major shortfalls in the paper. He is also of the opinion that these are in need of being corrected before the manuscript can be accepted for publication.

Major points

A) HONO snow emissions now have been reported by several investigators in the Arctic and to a more limited extent in the Antarctic. Though the authors have finally agreed that HONO is the major source of potential error in their study, they still appear reluctant to look into this issue in any great detail. Their attitude still appears to be that it can be dismissed as they have brushed off any further testing of their instrument with the statement: "HONO is too difficult to make in pure form in the lab." However, this species, if indeed emitted from the snow-pack, has the potential for impacting nearly every aspect of the science being discussed in the current paper (e.g., see comments latter in this text). Information now circulating within the polar chemistry community suggests that HONO measurements, in fact, may have been carried out during the CHABLIS field study. This Reviewer has no first hand information regarding this possibility. If CHABLIS HONO data exist, however, he would encourage the authors to reveal these in the current manuscript along with a brief discussion of the reasons why they were rejected. There are several reasons for my taking this position, but the only one that needs to be presented here is the fact that as stated above the potential impact from HONO as an interferant in the measurement of NO2 in the Halley Bay experiments is sufficiently high that the overall setting represents one that could be an important learning experience for the larger polar chemistry community. He understands that whether HONO emissions actually produced a measurable interference during the CHABLIS study may not be known with absolute certainty until much later when new field studies are carried out at coastal Antarctic sites using instruments that are both HONO and NO2 specific. But the role of HONO in polar chemistry is an issue that most likely will be with us for many years to come and exploring the CHABLIS data set in greater detail could provide an important starting point. In the current paper, confidence in the NO2 observations would appear to be pivotal to accepting the proposed chemistry in this paper. Thus, among other things it would prudent for the authors to note in an appropriate place in the paper that the conclusions drawn in this paper are very much based on the assumption that there have been no significant contributions to the measured NO2 signal level from snow emissions of HONO. In addition, they need to modified Table 1 to read, "This accuracy statement is based on estimated known systematic errors only"

In the current paper, this Reviewer also recommends that, in addition to the possibility of presenting measured but rejected CHABLIS HONO data, a further effort be made

by the authors to clarify for the average reader the detailed nature of this systematic error. For example, though the magnitude of the HONO error may currently be unknown; its direction is not. It will always lead to a measured value for NO2 that is too high. Furthermore, based on the results of Zhou et al.(2001), because of HONO's very short lifetime the magnitude of this systematic error will likely be a strong function of both the height at which sampling takes place as well as the degree of atmospheric turbulence, e.g., vertical mixing. The closer the measurement point is to the snow's surface the larger will be the impact; and, on average, the greater the vertical mixing the greater the variability seen in the measured value of HONO.

Because the authors have expressed some reluctance to quantify their NOx (NO2) instruments sensitivity to HONO via chemical tests, the Reviewer would suggest their thinking in terms of an alternative (albeit less accurate) approach. From a simple inspection of the Ryerson instrument paper cited by the authors (their instrument is stated to be a near clone of the Ryerson instrument.), one can get a rough estimate of the interference from an inspection of the absorption cross-section data for each species over the optical bandwidth of the filter used to reduced unwanted light reaching the PMT. A first cut at this by the Reviewer gave a ratio of 1: 2.5. That is, in the chemiluminescence detection of NO2, HONO would be ~ 2.5 times less sensitive than NO2 itself. This approximate value immediately tells us that for very large values of NO2 (e.g., hundreds of pptv) the likelihood of a significant interference from HONO is quite small. However, during CHABLIS, 30% of the NO2 data is at 5 pptv or less; and the max value reported is 11 pptv. Thus, a value of HONO even at the 10 pptv level potentially represents a significant perturbation to the NO2 profile. This fact strongly suggests that further exploration of this interference is merited, particularly in the context of better understanding the types of conditions in the field that might have provided the highest probability of interference, and thus, might have influenced one or more of the conclusions drawn.

B) It is suggested that any new text addressing the HONO interference issue be located in the front sections of the paper, e.g., the "experimental section". Similarly, this Reviewer would recommend that such "bombshell" text as appears near the end of this paper, starting on line 639 (e.g., that the chemical processes used in the current paper to explain the trends in NOx could just as easily be explained in terms of atmospheric dynamics, Anderson and Bauguitte, 2007) should also be moved to the beginning of the paper. This move will provide the reader with a much clearer idea of what the real purpose of this paper is; and, at the same time, make them more aware of the possible limitations of the data set being used. Note, it is still a very important data set!

C) The second area of the paper still in need of significant adjustment is that involving estimates of the NOx flux at Halley Bay and their comparison with values reported at other polar sites. NOx flux values reported for Halley Bay were the result of three different approaches: 1) a steady state NOx analysis of field data, 2) one calculated using a snow-pack radiative-transfer model, and 3) one based on direct measurements of NOx on a tower involving establishing the NOx vertical gradient in combination with tower estimates of the surface diffusivity. The respective values reported for each approach were: 3.5 x 108 molec/cm2/s for noontime conditions, 1.9 x 108 molec/cm2/s daily average, and 12.6x 108 molec/cm2/s, noontime conditions or 7.8x 108 molec/cm2/s daily GMT mean. Regarding the latter two values (the highest

values), the author's state: "These flux measurements are much higher than the flux derived from our steady state NOx analysis, or the noon-time flux maxima reported for Neumayer." They then continue with the statement: "Using Table 2 allows us to put our measurement in context with other polar NOx flux measurements, though it is impossible to provide a quantitative comparison due to the varying parameters that may affect the NOx flux (time of year/day, latitude, altitude, nitrate ion snow content). "

For this Reviewer, the second statement appears to be quite appropriate, particularly when the comparison being made might involve an NOx flux measurement at some distant location involving a different technique and/or quite different environmental conditions. Falling into this category would be the many studies reported in the Arctic and the more limited ones reported at South Pole. What does not make sense to the Reviewer is the author's lack of initiative in discussing the possible reasons for the large differences between the three approaches used in evaluating the Halley Bay flux. Nor does it make sense not to critically compare their results with those at Neumayer, a site studied by two of the co-authors on this paper. The authors noted in the current text that their four day direct flux measurement effort (approach #3) resulted in only one day's worth of data due to problems related to measuring the NOx gradient on the tower. Nowhere in this discussion, however, do they give the reader a clue as to which flux determination provided the most reliable value, that is, the one they have the highest confidence in. If the two indirect approaches provided the best flux value, why bore the reader with two pages of text which describes all the details of the more direct tower measurement technique. On the other hand, if the tower experiment delivered the most reliable flux value, why avoided any discussion of the fact that this approach gives a value that is 4 to 5 times higher than the two indirect methods cited as well as 4 times higher than the earlier measurement at Neumayer. This issue is not resolved either by the results they have entered into Table 2 (A Table that compares NOx flux measurements at different global sites). Of the three approaches used in assessing the Halley Bay flux, only that involving the tower measurement technique (the highest value) is presented in the Table 2.

The Reviewer request, therefore, that Table 2 and the associated text be sorted out so that the reader has some idea what flux determination the authors place the highest confidence in; and, equally important, they need to provide text that may explain the very large disagreement between the direct and indirect methods.

Interestingly, as regards to the high flux value generated from the tower observations of NOx, this Reviewer might hypothesize that this represents an example of the impact from snow emissions of HONO. These emissions would have been more efficiently measured during this study due to the fact that the lower sampling height chosen for the study was only 1.5 m above the snow's surface. This can be compared to the typical sampling height that used during most of their study which was 6m. As noted in the study reported by Zhou et al., due to HONO's short lifetime, the 1.5 m sampling height could have easily had 2 -3 times higher HONO levels than at 6 m, depending on the vertical mixing at the time. This would have led to a bias in the recorded measurement of NOx since their measurement would then have consisted of a combination of NO, NO2, and HONO.

D) In their section dealing with lifetimes for NOx and the ratio of NO/NO2, the authors rather quickly come to focus on the chemical roles played by the halogen oxides BrO and IO. Within the last year there has been new data reported from Arctic coastal sites which make the case that chlorine chemistry will emerge as the most important controlling halogen rather than bromine and/or iodine. Assuming further studies demonstrate this to be true, it is highly likely that coastal sites in Antarctic will also soon reveal a similar chemical picture. Considering the importance that the authors have placed on bromine and iodine chemistry in this paper, an interesting addition to this paper might be for them to comment/speculate what they believe would be the influence of this new chlorine chemistry on their current conclusions.

E) Final Question: An interesting point made by the authors starting on line 652 was the observation that the diurnal profile as well as the magnitude of the peak values for NO and NO2 did not appreciably change as a result of sampling under blizzard conditions. Though they cite several possible reasons how one might rationalize this finding recognizing the presence of low light conditions during a blizzard, this Reviewer must ask whether HONO emissions (detected as NO2) might also have played a key role in this unusual chemical environment?

Referencing

Referencing has been improved but in at least two locations additions should be considered: On pg 84 should add Zhou et al., 2001, and Chen et al., 2004.
On line 668 should consider adding: Helmig et al., 2008, and Oltmans et al., 2008

Author's response to reviewer #2 comments that were submitted 23 Jan 2011

Major point A)

An attempt was indeed made to measure HONO during the CHABLIS campaign, and the data have been referred to in publications. A short synopsis might go like this: Clemitshaw (2006) presented 1 days data as being a representative diurnal cycle; Bloss et al. (2010) tried to use the HONO measurements, but couldn't reconcile them with their modelled NOx or HOx values; Jones et al (2011), a paper on which Clemitshaw was also an author, basically laid the data to rest given the subsequent evidence that the measurement technique suffered from an artefact, so did not give a true representation of HONO. Indeed, there is growing evidence within the scientific community that there is a general problem with wet chemical methods used to measure HONO via a single channel (Kleffmann and Wiesen, 2008), which is particularly significant for studies at high latitudes (Liao et al., 2006; Chen et al, 2004; Sjostedt et al., 2007).

Probably the best assessment of HONO during the CHABLIS campaign comes from the paper by Bloss et al. (2010), where modelling calculations, constrained by CHABLIS data, can only reconcile observations when HONO is less than 0.22 pptv. However, the reviewer is correct that this is an important issue and should be clearly addressed in the manuscript. In response, we have calculated the potential HONO interferent for our system, and included the following text in the instrument description (section 2.1): "Using the Oriel filters transmittance data, the USHIO lamp

intensity, and NO2 and HONO absorption cross sections from JPL evaluation 14, Frey et al. (2011) estimate a HONO interference in the NO2 PLC of our system of ~22%. While an attempt to measure HONO was made during CHABLIS (Clemitshaw, 2006), subsequent assessments showed that the derived values were not consistent with observed NOx or HOx (Bloss et al., 2007; 2010). Indeed, data could only be reconciled when HONO was less than 0.22 pptv. Even with a potential interferent of 22%, at such low mixing ratios, it would seem that HONO is not likely to be a major interferent to the NO2 measurements reported here. Conclusions drawn in this paper are therefore based on the assumption that there have been no significant contributions to the measured NO2 signal from ambient HONO."

The caption for Table 1 has been modified as suggested by the reviewer.

Major point B)

As described above, the text exploring the potential for HONO interferent, and the basis for the paper's conclusions, is now placed up front in section 2.1. Further, we have included text in the introduction referring to the Anderson and Bauguitte study: "This approach contrasts with an earlier study (Anderson and Bauguitte, 2007) using a subset of the data presented here. In that study, a simple boundary layer tracer diffusion model was successfully used to reproduce the observed NOx diurnal cycle, the timing being critically dependent on τ, a tracer decay rate."

Major point C)

Derivations of fluxes are extremely difficult and the uncertainties in the results are large. It is therefore highly appropriate to explore flux derivations at a single location using a variety of methods. However, the different methods as described by the reviewer cannot be directly compared: the indirect method described by Bauguitte et al derives an average noon flux for measurements from 1st Jan to 10th Feb, with the caveat that the derived flux is strongly dependent on the assumed boundary layer height, which is known to be highly variable in Antarctica; the direct method derives a flux only for a single day, reporting both the noon maximum and the daytime average. The flux derived using the radiative transfer model is reported in a different paper, and as a 24-hour average (and note that the number was slightly revised during the review stage of this paper). To address the reviewers concerns, we have - slightly rearranged section 4.2 to make the flow more logical - included the noon maximum flux derived by Jones et al (2011) as unpublished data as a means of comparing the indirect methods - emphasised the influence of boundary layer height, which is both highly variable and uncertain - added text to emphasise that a direct comparison of all these results cannot be made, but also to suggest that a long-duration flux study to properly assess the different methodologies would be an extremely useful exercise.

Note, Table 2 reports results from direct measurements only. This fact is made clear from changes to the text (line 413 "Snow pack NOx fluxes derived from direct measurements in previous polar studies are summarised in Table 2") and the figure caption ("Summary of NOx fluxes derived through direct measurements in Arctic and Antarctic studies."

We note that the reviewer considers HONO as a potential source of error for the flux measurements, but point out that such an interferent would (presumably) have also affected the Neumayer measurements.

Major point D)

In response to the reviewers suggestion about chlorine chemistry, we have added the following text to the Discussion: "Our assessment did not include chlorine chemistry, which may play a role, but which we are unable to examine in a constrained way due to lack of observations. We note, however, that gamma for chlorine nitrate hydrolysis is small ~ 0.002 compared to the 0.3 value for bromine nitrate. It would therefore be a less significant NOx sink event if ClNO3 was at the same concentration as BrNO3. The rate constant for ClO+NO is half that of BrO+NO so is less likely to impact the NO/NO2 ratio."

Major point E)

During a blowing snow event, light levels would be suppressed at ground level, but at the top of the blowing snow layer, they would be much the same as on any other cloudy day. Blowing snow has nitrate impurities, much as snow on the ground. Further, air above and within the blowing snow layer is extremely well mixed. For these reasons, the system is not so dissimilar to when snow is lying on the ground. We therefore do not see any particular reasons why HONO should be more important than on other, more quiescent, days.

Minor comments:

The referencing has been updated as suggested.

Anonymous Referee #2: Submitted on 10 Jan 2012

The Paper "Summertime NOx measurements during the CHABLIS campaign: can source and sink estimates unravel observed diurnal cycles?" by Bauguitte et al., has been substantially improved over the last version, and can now be considered for publication after their consideration of the following important points:
1) I strongly recommend as I have on previous occasions that under the authors "Methods" section where they begin the discussion of HONO that they not only give the reference to Clemitshaw, 2006) who made the HONO measurements, but that they also give the reader a break (e.g.,not having to look up another paper) and actually cite at that point in the paper both the range of measured HONO values reported as well as the median value estimated. I would also hasten to add that they further reflect on the following fact. Their modeling calculations from which you estimate the amount of HONO that would be compatible with other measured parameters has been initiated with the assumption that all measured input data to their model are correct and furthermore that the model is "complete" in its representation of all the major chemical and physical processes that ultimately control the concentration level of HONO. In other words, there has to be a considerable uncertainty in their estimate of the HONO level that could be compatible with other measurements and they have not acknowledged this uncertainty!

2) In regards to their new discussion which attempts to downplay the possible role of chlorine chemistry (as oppose to bromine and iodine) during the CHABLIS experiments, they present the argument that the rate of hydrolysis of chlorine nitrate is much slower than that for bromine and also that the reaction rate for ClO + NO is half the rate of that involving bromine. Whereas, I would not quibble about these differences that they have presented, what they have overlooked is the fact the most recent studies in the Arctic (OASIS) have shown that chlorine is likely to be the most important halogen that affects fast chemistry and that the conditions during summer in the coastal arctic are not dramatically different than summertime coastal conditions in Antarctica. This suggests that there are likely chemical channels for moving chlorine into its active form other than that cited by the authors in their revised manuscript. Thus, I again suggest to the authors that they modify their text to leave open the real possibility that new studies in Antarctica may reveal further surprises, such as chlorine chemistry. Please note that the possibility that chlorine driven chemical processes might be quite significant under CHABLIS conditions would potentially define an area where modeling uncertainties, as cited above under (1), could be quite significant.

Editor response to Authors on 11 January 2012

Dear Authors:

The referee makes a few additional comments that require some minor commenting and corrections by you to address. Once this is complete then I will be delighted to be able to accept your manuscript for publication. It will not be necessary to conduct any further review.

Yours sincerely,

Bill Sturges