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Atmospheric Chemistry and Physics Discussions

Interactive comment on “The multi-seasonal NO_y budget in coastal Antarctica and its link with surface snow and ice core nitrate: results from the CHABLIS campaign” *by* A. E. Jones et al.

Anonymous Referee #2

Received and published: 22 April 2007

Jones et al. present a NOy budget during the CHABLIS campaign (Halley Bay, Antarctica), starting in fall and ending in summer. The manuscript is well organized, clear and well written. The title, figures and tables are appropriated and cover nicely a concise text. Their manuscript follows a logical presentation with data presentation, validation, interpretation and discussion. They first present the species measured, establish a NOy budget, validate it by comparing with another location, compare this budget with snow recorded to establish which NOy species is responsible for the nitrate snow and use a simple production rate approach to determine the main source of NOx in this coastal station.

The main results are 1/ the organo-nitrate dominates the NOy budget in winter and the inorganic nitrate in summer 2/ the increase of nitrate snow during seasons is best explained by inorganic nitrate 3/ the NOx source is probably dominated by snow emission in summer and spring

The main issue with this paper is the haste with which it seems to have been written, not in its form but more in its content. I wonder why this paper comes first and why the authors did not wait the publication of other CHABLIS manuscripts first. It makes no sense to publish monthly-averages from full resolution data sets without the latter been validated by the community. In particular they are using average PAN values obtained with a new instrument. Should not this new instrument been validated and reviewed first? Same for HONO, even if they are using apparently a technique that is now quite common for HONO. Considering the importance of this species for future evaluation of HOx and NOx families and the possible interferences when measuring HONO (for instance ISCAT as noted by the authors), should not the HONO concentrations been validated first, with the HOx budget (Bloss et al 2007)? My feeling is that the authors are puting the cart before the horse with 6 manuscripts in preparation cited and many references to personal communication. Should these works be published first in support of this MS?

A discussion is lacking on the possible sources of the organo-nitrate at Halley bay. Where MeONO2 and PAN are coming from (continental, local formation in winter, ocean)? With such long record, why meteo data were not used to constrain the orign of this species, using wind direction, temperature profile, structure of the troposphere? Jones et al. suggested in a previous work a possible oceanic source for alkyl nitrate? Why was this not discussed with the current data sets? May be, it will be in the upcoming papers but again this highlight the necessity to publish first the high resolution data sets in first place.

No discussion of the possible role of HNO4 is given beside the fact that they did not measure it. Using only GEOS-Chem model to dismiss this species is not enough.

Arguments developped by Slusher et al. 2002 should be used.

Regarding the co evolution of inorganic nitrate and snow nitrate. As demonstrated in the study case, the high concentration of nitrate snow observed at the end of august seems to be related to the scavenging of atmospheric nitrate by snowfall. During the following months, Sept-Oct the p-NO3- concentration is still high while the snow does not reflect this behaviour. Why? Wasn't there any snowfall during this period? Their p-NO3- seasonal profile is odd in comparison with other coastal antarctic records (DDU, Neumayer, Mawson) which usually display a double peak (late winter and late srping); Why p-NO3 doesn't peak in december as observed by Rankin and Wolff (2003) at the same location? Is 2004/2005 a unusual year? Halogens are very efficient to convert NOx to NOy via the hydrolysis of XONO2. Is this process active in spring?

The conclusion that nitrate photolysis in snow is an important local source of NOx relies greatly on the radiation transfer model they're using. This section needs better and more detailed descriptions of the Grenfell's model. Progress have been made since the Grenfell work. How their JNO3- compare for instance with Qiu et al. (2002), Simpson et al. (2002) or their actinic flux with Phillips and Simpson (2005)? More generally, the authors lack to integrate the work of other colleagues on this issue.

Specific comments:

Page 4131 line3: "but some higher resolution data" Should it not be lower resolution. Daily is at a lower resolution than 6-hour sampling rate?

Same page line 8: Is the standard error the right uncertainty to report? Std error is used when the same sample is measured many times. Here it is a monthly average so standard deviation should be reported instead. Should we expect a constant monthly value? This make no sense.

Same page line 22: why not using Weller et al, 2002 reference instead of Minikin, personal communication? Weller et al. 2002 reported the seasonality of nitrate at

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Interactive Comment

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Neumayer.

Page 4133 line 4: Change savarino et al. 2006 to Savarino et al., 2007 (the paper is now published in acp)

Same page line8: S. Bauguitte is co author of the paper, personal communication is inappropriate here. At least used unpublished data or even better nothing.

Page 4135 line 13: NO2 is not reported in table 2 for South Pole. Also in table 2 LIF definition should be given. The references cited in this table caption are not all reported in bibliography (Huey, Arimoto)

Page 4136 line 2: Since both techniques are not absolute in measuring total NOy, none of them can be used as an absolute reference. It is therefore not correct to say that Halley data capture the dominant NOy component just on the fact that they both agree on. There are consistent, yes but this doesn't preclude a bias in both techniques. Rewording is needed here.

Page 4138 line 13 and 18: change ppb to ppt;

Page 4140 line 8: Please don't forget your colleague's works. Add Ridley 2000, Honrath 2002 Davis 2001 in the reference citation.

Page 4141 line 15: Jones et al, 1999 do not present their 6-hourly resolution data for HNO3 in this paper, so used unpublished data.

Section 4.3: Well a 50% uncertainty for the NOx flux out of the snow seems to be too optimistic. All TUV models assume a flat surface snow, is it the case at Halley bay? Also the calculation assumes that all nitrates in snow are available for dissociation. If some of the nitrate is located in the bulk ice, the cage effect will prevent the escape of photo-products. Can those uncertainties be better evaluated? Is the Halley snow acidic or alkaline? As stated by the authors, p-NO3- is partially driven by sea salt aerosols. Will NaNO3 in snow be so easily photodissociated? Beine et al 2005, 2006 showed that snow alkalinity can radically change the behaviour of photochemical product yields.

Such issue needs to be discussed, especially with coastal sites and the proximity of the ocean.

Page 4146 line 11: It doesn't seem to me that savarino et al report measurement of TIN but rather p-NO3- even if they agreed that part of HNO3 may have been collected on their filters

Page 4146 line 26: Well, before moving to a 3D global transport chemistry model which is time consuming to change, adapt and run, I will advise the author to use a two-box model with snow and BL. Such models are perfectly adapted to their needs. Only if complex transports and/or global evaluation of the snow emission are required, a 3D model should be used. A 3D model is like a tanker, to change its direction it takes a lot of time. Considering the number of assumptions to be solved and the number of sensitivity runs needed before establishing the right parameterizations, a 3D model is definitely not the right way to go. The strength of this paper will greatly improve if a box model work is associated with the measurements.

The community is impatient to see the outcome of the Chablis experiments. After the ISCAT experiments, this is a long awaited campaign that will nicely document the seasonality of the Antarctic BL at a coastal site. However, I don't think this paper is the best way to start. If there was a new discovery changing the way we see this environment I will have no problem with this approach, but this is not the case. The present MS is a good summary of the NOy family at Halley, as such it should be published after the core papers. I also encourage the authors to fill out their manuscript with a model before publication.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 4127, 2007.