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Comment

Interactive comment on “Large mixing ratios of atmospheric nitrous acid (HONO) at Concordia (East Antarctic plateau) in summer: a strong source from surface snow?” by M. Legrand et al.

M. Legrand et al.

Michel.LEGRAND@lgge.obs.ujf-grenoble.fr

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Author responses to referee comments

Please note that in the following our responses and comments are marked with “AU”.

Response to anonymous Referee #2

This is a nice piece of work discussing the abundance of nitrous acid during the austral summer 2011/2012 at the Concordia site, located on the East Antarctic plateau. HONO was measured by means a long path absorption photometer (LOPAP).

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These measurements led to hourly mixing ratios of HONO measured in December 2011/January 2012 of 35 ± 5.0 pptv, similar to those measured in December 2010/January 2011.

While these large concentrations suggest a local source of HONO, in addition to weak production from the oxidation of NO by the OH radical, they also point toward a possible interference from HNO₄.

This paper nicely combines field data, with laboratory based measurements and modelling. All conclusions are reasonable to me and certainly discussed in detail.

However, as one of the main outcome of this study arises from the two laboratory investigations performed at BAS and PSI, I was wondering if some more information could be added.

On the photochemical experiments performed on collected ice, which was used to derive somehow the yield of HONO (at least compared to NO_x), I'm surprised by the use of a quite powerful lamp (1000 W) in a quite small reactor. While the wavelength dependence is clear, what about the energy dependence? The gas flow in this system is quite high, lowering certainly the residence time in the reactor and also the photolysis of HONO. But it is difficult to really assess that from the information provided. Did you assess how much HONO was photolyzed in your system? As NO₂ and HONO would get degraded at different rates, this may have affected your HONO to NO_x ratio. Any comment on that ?

AU: OK right and in the revised version we report more details showing that under our working conditions we can neglect the photolysis of NO₂ in the snow chamber. This is also true for HONO whose the photolysis rate is some 6 times slower than the one of NO₂. The text has been updated as follows: "The short residence time of NO₂ (around 4 s) in our small chamber prevents significant photolysis of NO₂ to occur during the experiments. Indeed, the JNO₂ of $2 \cdot 10^{-2} \text{ s}^{-1}$ measured by Cotter et al. (2003) for a 1000 W Xenon-arc lamp, as also used in the present study, leads to a lifetime of NO₂

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with respect to photolysis of 50 s at the front of the snow block.”

The production of HONO via organic matter is disregarded because of the low amount of complex organic acids measured. But is this the right metric for that? Indeed, low amount of such organic material but well located in the snow pack could potentially have a big impact through some catalytic reactions (where big quantities are not required but rather the availability of the catalytic material).

AU: Thank you for this comment: We agree and we reworded the text: “If HULIS are located at the surface of snow grains, much more than 2 ppbC of HULIS would be available there to react with NO₂ present in interstitial air of the snowpack to produce HONO.”

The interference of HNO₄ seems to be clear. However HNO₄ has been discussed to be a source of HONO in the marine boundary layer via cloud chemistry (see Williams et al, Atmos. Chem. Phys., 2, 39-54, 2002). Could the same type of chemistry occur in the specifically cold environment of the Antarctic? Would it then be a significant source of HONO?

AU: Williams et al. (2002) report that HONO accumulates in the presence of cloud chemistry (due to the decomposition of NO₄⁻ into NO₂⁻). The simulation of this cloud chemistry suggests that in mid-latitude marine boundary layer the mixing ratio of HONO would be enhanced by 2 to 10 pptv at night. Even though the level of NO₂ of 100 pptv assumed in their study (moderately polluted marine atmosphere) is rather similar (within a factor of 2) to those observed at Concordia, the relatively warm temperatures encountered at mid latitudes leads to a fast thermal HNO₄ decomposition and does not permit HNO₄ to reach the high mixing ratios seen in Antarctica. On the other hand, the liquid water content in the marine atmosphere (0.4 g cm⁻³ assumed in their study) is several orders of magnitude larger than what we can expect at -30°C at Concordia. The expected weakness of this liquid water chemistry of HNO₄ at Concordia is supported by the fact that during overcast conditions (see grey background area in Figure 1) no

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systematic enhancement of measured HONO is detectable.

Response to J. Pinto (Referee 1)

Legrand et al report measurements HONO at the Concordia field site in Antarctica, a model calculation of HONO concentrations in surface air with gas phase production from the reaction of NO with OH. They also performed experiments in the laboratory to demonstrate the potential for HONO to be generated in the snowpack. Measured HONO concentrations were found to be substantially than those inferred from their estimated flux from the snow pack and gas phase production. They performed tests in the lab to determine the potential interference caused by HNO₄ in measurements of HONO made using LOPAP. However, since they did not measure HNO₄ during this field campaign they could not quantify the extent of this interference. Because of thermal decomposition, HNO₄ might not be as important as a potential source of interference at lower latitudes, but this begs the issue of what other atmospheric components behave in a manner similar to HONO in the sampling solution in the LOPAP instruments. This is a very nice study integrating information obtained in the field and the laboratory. I only have few minor comments and requests for clarification:

What HNO₄ levels are supported by atmospheric modelling ?

AU: Slusher et al. (2002) (GRL, 29 (21)) discussed their HNO₄ observations (mean value of 25 pptv) from the South Pole with model simulations. They pointed out several uncertainties related to (1) the equilibrium constant of the reaction of NO₂ and HO₂ (mainly the thermal decomposition rate at -30°C) and (2) the dry deposition velocity. It has also to be emphasized that in the absence of NO₂ measurements at the South Pole, in their calculations Slusher et al. (2002) used calculated steady-state NO₂ from observed NO levels.

HNO₄ was not measured at Concordia but a mean value of 64 pptv (up to 150 pptv) (i.e. higher than the South Pole one) was observed between the ground and 50 m elevation over the Antarctic plateau (Slusher et al. 2010). Applying parameters (kinetic

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rates and dry deposition velocity) used by Slusher et al. (2002) we calculate a mean mixing ratio of 80 pptv for Concordia conditions (on the basis of observed RO₂ and NO₂ levels).

HONO might be produced by heterogeneous reactions on soot surfaces. Could the reaction of NO₂ with soot (either airborne or in the snow pack) perhaps emitted by the station or by vehicles be a source of HONO?

AU: In the remote atmosphere of the South Pole Bodhaine et al. (1995) (JGR, 100, 8967-8975) reported very BC values, with a mean summer concentrations of 1 ng m⁻³. Certainly station activities would enhance such a very low atmospheric level (and possibly contaminate the snow). However as stated in section 2.2 “During the measurement campaign, the main wind direction was from the southeast to southwest and very rare were episodes with wind blowing from North (i.e. from the direction of the station).” Data corresponding to these events were removed from the data set.

If there was substantial interference by HNO₄, what effect would it have on the diel (24-h) variability of HONO shown in Fig.3? Would interference be uniform throughout the day?

AU: Figure 3 suggests a slightly larger interference at night than at noon. That would suggest a maximum of HNO₄ at that time, possibly due to the accumulation of NO₂, the residual presence of HO₂ and the decreasing thermal decomposition. As discussed above, applying parameters used by Slusher et al. (2002) we simulate rather unchanged values from 70 pptv at night and 90 pptv during the day. Given the uncertainties of these simulations and in the absence of HNO₄ observations (including its diurnal cycle) we can only say that we don't expect a strong change of the interference from day to night, which is consistent what we see in Figure 3.

p. 11767 l. 29 – please use a few words to describe “E-e” scheme.

AU: OK this sentence has been reworded as follows: “Parametrization of turbulence

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in the lowest model layer of MAR is based on the Monin-Obukhov Similarity theory (MOST). Above the surface boundary layer, turbulence is parametrized using the $E - \varepsilon$ model that includes two prognostic equations for turbulent kinetic energy and its dissipation.”

Some mention of the extent of interference by NO_z or other species in the PC/ chemi luminescence method for NO₂ would be nice. I know they were mentioned in other publications but to save the reader time it might be better to say something here.

AU: Ok in the revised version we report more details on this point: “The chemiluminescence detector measured NO in one channel and the sum of NO and NO originating from the photolytic conversion of NO₂ in the other channel. As discussed by Frey et al. (2013), among various nitrogen oxides able to interfere on the photolytic conversion channel only HONO has to be considered leading to an overestimation of NO₂ levels by less than 5%.”

. . .and a few line edits.

p. 11752, l. 2 -“recycling of HOX into OH”, sounds a little odd as OH is a member of the HOX family. May be, “HO₂” instead of HOX?

AU: OK we replace HO_x by HO₂.

p. 11758, l. 5 – “too weak”

AU: OK done

p. 11760, l.7 – “thermal decomposition”

AU: OK done

p.11761, l. 9-11 – sentence is not clear as written, please reword. Did you mean to say there is strong static stability, inhibiting vertical mixing? ,

AU: OK this sentence has been reworded as follows: “In polar region, the strong static

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stability of the atmosphere often inhibits vertical mixing of surface emissions between the surface boundary layer and the rest of the atmosphere.”

l. 17 – collapse, rather than abrupt thinning?

AU: Yes done

p. 11764, l. 24 – “doped”,

AU: OK done

l. 27 – “act”

AU: OK done

p. 11769, l. 9 – “sole”

AU: OK done

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 11749, 2014.

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