

## 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).

These measurements led to hourly mixing ratios of HONO measured in December 2011/January 2012 of  $35 \pm 5.0$  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 HNO<sub>4</sub>.

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<sub>x</sub>), 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 NO<sub>2</sub> and HONO would get degraded at different rates, this may have affected your HONO to NO<sub>x</sub> 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 NO<sub>2</sub> in the snow chamber. This is also true for HONO whose the photolysis rate is some 6 times slower than the one of NO<sub>2</sub>. The text has been updated as follows: "The short residence time of NO<sub>2</sub> (~ 4 s) in our small chamber prevents significant photolysis of NO<sub>2</sub> to occur during the experiments. Indeed, the  $J_{\text{NO}_2}$  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 NO<sub>2</sub> 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 NO<sub>2</sub> present in interstitial air of the snowpack to produce HONO."

The interference of HNO<sub>4</sub> seems to be clear. However HNO<sub>4</sub> 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 NO<sub>4</sub><sup>-</sup> into NO<sub>2</sub><sup>-</sup>). 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 NO<sub>2</sub> 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 HNO<sub>4</sub> decomposition and does not permit HNO<sub>4</sub> to reach the high mixing ratios seen in Antarctica. On the other hand, the liquid water content in the marine atmosphere ( $0.4 \text{ g cm}^{-3}$  assumed in their

study) is several orders of magnitude larger than what we can expect at  $-30^{\circ}\text{C}$  at Concordia. The expected weakness of this liquid water chemistry of  $\text{HNO}_4$  at Concordia is supported by the fact that during overcast conditions (see grey background area in Figure 1) no 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  $\text{HNO}_4$  in measurements of HONO made using LOPAP. However, since they did not measure  $\text{HNO}_4$  during this field campaign they could not quantify the extent of this interference. Because of thermal decomposition,  $\text{HNO}_4$  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  $\text{HNO}_4$  levels are supported by atmospheric modelling ?

**AU:** Slusher et al. (2002) (GRL, 29 (21)) discussed their  $\text{HNO}_4$  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  $\text{NO}_2$  and  $\text{HO}_2$  (mainly the thermal decomposition rate at  $-30^{\circ}\text{C}$ ) and (2) the dry deposition velocity. It has also to be emphasized that in the absence of  $\text{NO}_2$  measurements at the South Pole, in their calculations Slusher et al. (2002) used calculated steady-state  $\text{NO}_2$  from observed NO levels.

$\text{HNO}_4$  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 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  $\text{RO}_2$  and  $\text{NO}_2$  levels).

HONO might be produced by heterogeneous reactions on soot surfaces. Could the reaction of  $\text{NO}_2$  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  $1 \text{ ng m}^{-3}$ . 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  $\text{HNO}_4$ , 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  $\text{HNO}_4$  at that time, possibly due to the accumulation of  $\text{NO}_2$ , the residual presence of  $\text{HO}_2$  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  $\text{HNO}_4$  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 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 -  $\epsilon$  model that includes two prognostic equations for turbulent kinetic energy and its dissipation.”

Some mention of the extent of interference by NO<sub>z</sub> or other species in the PC/ chemi luminescence method for NO<sub>2</sub> 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 NO<sub>2</sub> 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 NO<sub>2</sub> 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, “HO<sub>2</sub>” instead of HOX?

**AU:** OK we replace HO<sub>x</sub> by HO<sub>2</sub>.

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 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

On following pages, the revised manuscript text is given with major changes highlighted:

1  
2 **Large mixing ratios of atmospheric nitrous acid (HONO) at Concordia (East Antarctic**  
3 **plateau) in summer: A strong source from surface snow?**

4  
5 Michel Legrand<sup>1,2</sup>, Susanne Preunkert<sup>1,2</sup>, Markus Frey<sup>3</sup>, Thorsten Bartels-Rausch<sup>4</sup>, Alexandre  
6 Kukui<sup>5,6</sup>, Martin D. King<sup>7</sup>, Joel Savarino<sup>1,2</sup>, Michael Kerbrat<sup>1,2</sup>, and Bruno Jourdain<sup>1,2</sup>

7  
8 <sup>1</sup> Univ. Grenoble Alpes, LGGE, F-38000 Grenoble, France

9 <sup>2</sup> CNRS, LGGE, F-38000 Grenoble, France

10 CNRS/Univ. Grenoble Alpes, Laboratoire de Glaciologie et Géophysique de l'Environnement  
11 (LGGE) UMR 5183, Grenoble, F-38041, France

12 <sup>3</sup> British Antarctic Survey (BAS), Natural Environment Research Council, Cambridge, UK

13 <sup>4</sup> Laboratory of Radio and Environmental Chemistry, Paul Scherrer Institute (PSI), 5232  
14 Villigen, Switzerland

15 <sup>5</sup> Laboratoire des Atmosphères, Milieux, Observations Spatiales (LATMOS), Paris, France

16 <sup>6</sup> Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E) UMR-  
17 CNRS, Orléans, France

18 <sup>7</sup> Department of Earth Sciences, Royal Holloway University of London, Egham, Surrey,  
19 TW20 0EX, UK

20  
21 Correspondence email: [Legrand@lgge.obs.ujf-grenoble.fr](mailto:Legrand@lgge.obs.ujf-grenoble.fr)

22  
23  
24  
25 **Abstract**

26 During the austral summer 2011/2012 atmospheric nitrous acid was investigated for the  
27 second time at the Concordia site (75°06'S, 123°33'E) located on the East Antarctic plateau  
28 by deploying a long path absorption photometer (LOPAP). Hourly mixing ratios of HONO  
29 measured in December 2011/January 2012 ( $35 \pm 5.0$  pptv) were similar to those measured in  
30 December 2010/January 2011 ( $30.4 \pm 3.5$  pptv). The large value of the HONO mixing ratio at  
31 the remote Concordia site suggests a local source of HONO in addition to weak production  
32 from oxidation of NO by the OH radical. Laboratory experiments demonstrate that surface  
33 snow removed from Concordia can produce gas phase HONO at mixing ratios half that of  
34 NO<sub>x</sub> mixing ratio produced in the same experiment at typical temperatures encountered at

1 Concordia in summer. Using these lab data and the emission flux of  $\text{NO}_x$  from snow  
2 estimated from the vertical gradient of atmospheric concentrations measured during the  
3 campaign, a mean diurnal HONO snow emission ranging between 0.5 and  $0.8 \times 10^9$  molecules  
4  $\text{cm}^{-2} \text{ s}^{-1}$  is calculated. Model calculations indicate that, in addition to around 1.2 pptv of  
5 HONO produced by the NO oxidation, these HONO snow emissions can only explain 6.5 to  
6 10.5 pptv of HONO in the atmosphere at Concordia. To explain the difference between  
7 observed and simulated HONO mixing ratios, tests were done both in the field and at lab to  
8 explore the possibility that the presence of  $\text{HNO}_4$  had biased the measurements of HONO.

## 10 **1. Introduction**

11 The existence of an oxidizing boundary layer over the Antarctic continent was first  
12 highlighted by measurements carried out at the South Pole, where a mean concentration of  
13  $2.5 \times 10^6$  OH radicals  $\text{cm}^{-3}$  was observed (Mauldin et al., 2001a), making the South Pole  
14 atmospheric boundary layer as oxidative as the remote tropical marine boundary layer  
15 (Mauldin et al., 2001b). Chen et al. (2001) and Davis et al. (2001) showed that the presence of  
16 high concentrations of  $\text{NO}_x$  produced by the photolysis of nitrate present in surface snow  
17 permits the required efficient recycling of  $\text{HO}_2$  into OH. Aside from snow photochemical  
18 emission of  $\text{NO}_x$  that acts as a secondary source of OH, the role of HONO as a primary source  
19 of OH remains unclear. Using a mist chamber followed by ion chromatography analysis of  
20 nitrite, Dibb et al. (2004) reported a median HONO mixing ratio close to 30 pptv at the South  
21 Pole. However, follow-up measurements by laser-induced fluorescence (LIF) indicated lower  
22 mixing ratios (6 pptv on average) and an interference with  $\text{HNO}_4$  has been suspected (Liao et  
23 al., 2006). Furthermore, as discussed by Chen et al. (2004) the consideration of 30 pptv of  
24 HONO in the lower atmosphere over the South Pole leads to an OH over-prediction by gas-  
25 phase photochemical models by a factor of 3 to 5. The authors questioned whether the  
26 discrepancy between observed and simulated concentrations of OH at the South Pole was due  
27 to measurements of HONO suffering from overestimation due to chemical interferences or if  
28 the mechanisms of the model missed  $\text{HO}_x$  and  $\text{NO}_x$  losses.

29 Even at the level of a few pptv, the presence of HONO requires a source other than the  
30 gas-phase reaction of NO with OH and many studies measuring HONO in atmospheres  
31 overlying snow covered regions suspected HONO to be emitted from the surface snow in  
32 addition to  $\text{NO}_x$  (see Grannas et al. (2007) for a review). It has to be emphasized that most of  
33 the studies of HONO have concerned high (Arctic, Greenland) and mid (Colorado and Alps)  
34 northern latitudes where, in relation to the chemical composition of snow, the involved

1 HONO production processes would be very different compared to the case of Antarctica.  
2 Concerning Antarctic snow, following the pioneering shading experiment done by Jones et al.  
3 (2000) on snow from the coastal Antarctic site of Neumayer, numerous studies investigated  
4 the release of NO<sub>x</sub> from the snow (see references in Frey et al., this issue), but only two  
5 studies reported on HONO snow emissions and none of them examined together HONO and  
6 NO<sub>x</sub> emissions. Beine et al. (2006) reported small HONO fluxes ( $3 \times 10^7$  molecule cm<sup>-2</sup> s<sup>-1</sup>)  
7 above the Browning Pass (coastal Antarctic) snowpack. However, the snow chemical  
8 composition at that site is very atypical with a large presence of calcium (up to 4 ppm)  
9 attributed to the presence of a lot of rock out-crops at the site. As a consequence, even if  
10 nitrate is abundant (typically 200 ppb in fresh snow and more than 1 ppm in aged snow), the  
11 snow from that site appears to be weakly acidic and sometimes alkaline. Finally a few  
12 investigations of the vertical distribution of HONO were made at the South Pole (Dibb et al.,  
13 2004) but no fluxes were calculated. These previous Antarctic studies of HONO were using  
14 either mist chambers (Dibb et al., 2002) or high-performance liquid chromatography  
15 techniques (Beine et al., 2006). These “wet chemical instruments” sample HONO on humid  
16 or aqueous surfaces followed by analysis of the nitrite ion. However, it is well known that  
17 many heterogeneous reactions lead to the formation of nitrite on similar surfaces (Gutzwiller  
18 et al., 2002, Liao et al., 2006). In addition to these chemical interferences, it is also known  
19 that HONO can decompose or be formed on various surfaces (Chan et al., 1976). That may  
20 affect data when sampling lines of up to 30 m length were used for polar measurements (see,  
21 e.g., Beine et al., 2006).

22 Motivated by a strong need to extend investigations of the oxidation capacity of the  
23 lower atmosphere at the scale of the whole Antarctic continent, the OPALE (Oxidant  
24 Production over Antarctic Land and its Export) project was initiated at the end of 2010 in East  
25 Antarctica. The first OPALE campaign was conducted during austral summer 2010/2011 at  
26 the coastal site of Dumont D’Urville (Preunkert et al., 2012) and focused on OH and RO<sub>2</sub>  
27 measurements (Kukui et al., 2012). During this first campaign, preliminary investigations of  
28 HONO were performed at the continental site of Concordia (also denoted DC, 3233 m above  
29 sea level). In spite of the use of a long path absorption photometer (LOPAP), thought to avoid  
30 all known artefacts, high mixing ratios of HONO were observed (from 5 to 59 pptv, Kerbrat  
31 et al., 2012). In the framework of the OPALE project, a second summer campaign (2011-  
32 2012) was conducted at DC with simultaneous measurements of HONO, NO, NO<sub>2</sub>, OH and  
33 RO<sub>2</sub> that are discussed in a set of companion papers of which this is one.

1           The paper presented here focuses on HONO data gained during the second campaign at  
2 DC. It also reports on snow irradiation experiments conducted in the laboratory at British  
3 Antarctic Survey (BAS) on surface snow samples collected at Concordia in view to quantify a  
4 possible photochemical snow source of HONO. This was done by measuring simultaneously  
5 HONO with the LOPAP, NO and NO<sub>2</sub> with a 2-channel chemiluminescence detector. From  
6 these data we crudely estimate the amount of HONO released from snow within the lower  
7 atmosphere at Concordia on the basis of the NO<sub>x</sub> snow emissions derived from the vertical  
8 gradient of atmospheric concentrations measured during the campaign by Frey et al. (this  
9 issue). The derived values of the HONO flux were used in 1D modeling calculations to  
10 evaluate the contribution of this snow source to the large HONO mixing ratios observed at  
11 DC. Finally, to evaluate a suspected possible interference of HNO<sub>4</sub> on the HONO mixing  
12 ratio measured by the LOPAP, field experiments were conducted by heating sampled air prior  
13 to its introduction in the LOPAP device, heating being a convenient way to destroy HNO<sub>4</sub>.  
14 The selectivity to HNO<sub>4</sub> and the response of the LOPAP during the heating events was also  
15 investigated in laboratory by mass spectrometry at Paul Scherrer Institute (PSI).

16

## 17 **2. Methods and Site**

### 18 **2.1 HONO measurement method**

19           HONO was measured using a long path absorption photometer (LOPAP) which has  
20 been described in detail elsewhere (Heland et al., 2001; Kleffmann et al., 2002). In brief, after  
21 being sampled into a temperature controlled stripping coil containing a mixture of  
22 sulfanilamide in a 1N HCl solution, HONO is derivatized into a coloured azo dye. The light  
23 absorption by the azo dye is measured in a long path absorption tube by a spectrometer at 550  
24 nm using an optical path length of 5 m. The LOPAP did not have long sampling lines or inlet.  
25 The stripping coil was placed directly in the atmosphere being sampled. The LOPAP has two  
26 stripping coils connected in series to correct interferences. In the first coil (channel 1), HONO  
27 is trapped quantitatively together with a small amount of the interfering substances. Assuming  
28 that these interfering species are trapped in a similar amount in the second coil (channel 2),  
29 the difference between the signals resulting from stripping in each coil provides an  
30 interference-free HONO signal (Heland et al., 2001) Air was sampled at a flow rate of 1 L  
31 min<sup>-1</sup> and the flow rate of the stripping solution was of 0.17 mL min<sup>-1</sup>. Calibrations were  
32 performed every five days. Relative deviations of the calibration signal were of 3% and 9% at  
33 3σ for channel 1 and 2, respectively. The quantification limit of the LOPAP instrument used  
34 in this study was as low as 1.5 pptv (taken as 10 σ of all zero measurements done by sampling

1 pure N<sub>2</sub>) with a time resolution of 9 min. More details on the set up of the LOPAP device in  
2 the fields can be found in Kerbrat et al. (2012). Similarly to the first campaign, the amount of  
3 interferences in the second coil was on average  $9 \pm 7$  % of total signal (instead of  $10 \pm 5$  %  
4 found by Kerbrat et al. (2012) in 2010/2011). The LOPAP was tested for numerous possible  
5 interfering NO<sub>x</sub> and NO<sub>y</sub> species including alkylnitrates. It was concluded that when  
6 significant the two channels approach was able to well correct the HONO data (Kleffmann  
7 and Wiesen, 2008). It has, however, to be emphasized that no tests have been conducted for  
8 HNO<sub>4</sub>.

9 During the field campaign, HONO was occasionally sampled in the snow interstitial air  
10 by pumping air through a PFA tube (5 m long, 4 mm internal diameter) at a flow rate of 1 L  
11 min<sup>-1</sup>. In addition, to evaluate a possible influence of HNO<sub>4</sub> on HONO measurements, field  
12 experiments were undertaken by heating air sampled through a 9 m long PFA tube. Tests  
13 were performed to evaluate potential loss or formation of HONO in the PFA tubes by running  
14 the LOPAP for 30 min with and without a tube connected to the inlet of the LOPAP,  
15 sampling air at the same height. In order to account for possible fast natural change of HONO  
16 mixing ratios the test was repeated three times successively. The tests were carried out with  
17 ambient mixing ratios of 20 pptv as encountered at mid-day December 23<sup>rd</sup> and 40 pptv in the  
18 morning December 28<sup>th</sup>. In the two cases losses of around 4 pptv and 7 pptv were observed  
19 when using the 5 m and 9 m long PFA tube, respectively. These losses will be considered in  
20 discussing HONO mixing ratios in interstitial air (see Sect. 3) or the interference of HNO<sub>4</sub>  
21 (see Sect. 6).

22

## 23 **2.2 Field atmospheric measurements and snow samplings**

24 The second OPALE field campaign took place at DC located over the high East  
25 Antarctic plateau from late November 2011 to mid-January 2012. Nitrous acid was measured  
26 1 m above ground level, about 900 m south-southwest from the main Concordia station.  
27 Measurements that started December 4<sup>th</sup> were interrupted from December 9<sup>th</sup> to 15<sup>th</sup>,  
28 December 16<sup>th</sup> to 18<sup>th</sup>, and December 28<sup>th</sup> to 30<sup>th</sup> afternoon due to problems on the LOPAP  
29 device. January 1<sup>st</sup>, 2<sup>nd</sup>, and from January 10<sup>th</sup> to 13<sup>th</sup> air measurements were stopped to  
30 measure HONO in snow interstitial air. During the measurement campaign, the main wind  
31 direction was from the southeast to southwest. Several episodes with wind blowing from  
32 North (from 10°W to 60°E sector), i.e. from the direction of the station, were encountered  
33 (see the red points in Fig. 1). During some of these pollution events (December 31<sup>st</sup> around  
34 22:00 for instance), sharp peaks of HONO mixing ratios exceeding 100 pptv were observed.



1 These events were also detected in the  $\text{NO}_x$  time series (Frey et al., this issue) with sharp  
2 peaks in the range of 100 ppbv or more (120 ppbv December 31<sup>st</sup> around 22:00 for instance).  
3 The ratio of excess of HONO to excess of  $\text{NO}_x$  during these events is close to  $10^{-3}$ . The ratios  
4 of  $\text{HONO}/\text{NO}_x$  reported by measurements made in traffic tunnels range from  $3 \times 10^{-3}$   
5 (Kirchstetter et al., 1996) to  $8 \times 10^{-3}$  (Kurtenbach et al., 2001). When compared to ratios  
6 observed in tunnels, the lower ratio seen in the plume of the DC station when it reaches the  
7 sampling line is likely due the rapid photolytic destruction of HONO whose the lifetime is  
8 still as short as 20 min at the high solar zenith angles prevailing at DC around 22:00 in  
9 summer. In the following the data corresponding to red points reported in Fig. 1 were  
10 removed from the HONO data set.

11 Concurrent measurements of chemical species that are relevant for discussion include  
12 ozone, NO,  $\text{NO}_2$ , OH, and  $\text{RO}_2$ . Surface ozone was monitored simultaneously to HONO using  
13 UV absorption monitors (Thermo electron Corporation model 49I) deployed at DC since  
14 2007 (Legrand et al., 2009). Nitrogen oxides were determined by deploying a 2 channel  
15 chemiluminescence detector (Bauguitte et al., 2012; Frey et al., 2013; Frey et al., this issue).  
16 The chemiluminescence detector measured NO in one channel and the sum of NO and  $\text{NO}_2$   
17 originating from the photolytic conversion of  $\text{NO}_2$  in the other channel. As discussed by Frey  
18 et al. (2013), among various nitrogen oxides able to interfere on the photolytic conversion  
19 channel only HONO has to be considered leading to an overestimation of  $\text{NO}_2$  levels by less  
20 than 5%. The radicals (OH and  $\text{RO}_2$ ) were measured using chemical ionisation mass  
21 spectrometry (Kukui et al., 2012; Kukui et al., this issue). During the campaign the photolysis  
22 rate of HONO was documented using a Met-Con  $2\pi$  spectral radiometer equipped with a  
23 CCD detector and a spectral range from 285 to 700 nm (see details in Kukui et al., this issue).

24 Different surface snow samples were collected at DC and returned to the UK to be used  
25 in irradiation experiments (see Sect. 2.3 and Sect. 4). First, the upper 12 cm of snow were  
26 collected in December 2010. Second, the upper centimetre of snow corresponding to freshly  
27 drifted snow was collected December 6<sup>th</sup> 2011. The samples were characterized by their  
28 specific surface area (SSA). Measurements were performed using an Alpine Snowpack  
29 Specific Surface Area Profiler, an instrument similar to that one described by Arnaud et al.  
30 (2011) based on the infrared reflectance technique. Briefly, a laser diode at 1310 nm  
31 illuminates the snow sample at nadir incidence angle and the reflected hemispherical radiance  
32 is measured. The hemispherical reflectance at 1310 nm is related to the SSA using the  
33 analytical relationship proposed by Khokanovsky and Zege (2004). The SSA of the drifting  
34 snow is close to  $26 \text{ m}^2 \text{ kg}^{-1}$ , and the upper 12 cm is  $17 \text{ m}^2 \text{ kg}^{-1}$ . Such values appears to be

1 close to typical Dome C values reported in the literature (Gallet et al., 2011), suggesting that  
2 lab experiments conducted on these snow samples (see Sect. 4) may be relevant to discuss at  
3 least qualitatively natural processes occurring at DC.

4 The upper surface snow (from 0 to 1 cm, and from 0 to 12 cm) at DC were also sampled  
5 and analysed for major anions and cations following working conditions reported in Legrand  
6 et al. (2013). For cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{NH}_4^+$ ), a Dionex 500 chromatograph  
7 equipped with a CS12 separator column was used. For anions, a Dionex 600 equipped with an  
8 AS11 separator column was run with a quaternary gradient of eluents ( $\text{H}_2\text{O}$ ,  $\text{NaOH}$  at 2.5 and  
9 100 mM, and  $\text{CH}_3\text{OH}$ ) allowing the determination of inorganic species ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ )  
10 as well as methanesulfonate ( $\text{CH}_3\text{SO}_3^-$ ). The acidity of samples can be evaluated by the ionic  
11 balance between anions and cations with concentrations expressed in micro-equivalents per  
12 liter ( $\mu\text{Eq L}^{-1}$ ):

$$13 \quad [\text{H}^+] = [\text{Cl}^-] + [\text{NO}_3^-] + [\text{SO}_4^{2-}] + [\text{CH}_3\text{SO}_3^-] - [\text{Na}^+] - [\text{K}^+] - [\text{Mg}^{2+}] - [\text{Ca}^{2+}] - [\text{NH}_4^+] \quad (1)$$

14

### 15 **2.3 Snow irradiation experiments conducted at BAS**

16 As discussed in Sect. 5, model simulations indicate that the production of HONO from  
17 the reaction of OH with NO is far **too** weak to explain observations at Dome C and that an  
18 additional light driven HONO source is needed. To quantify a possible photochemical snow  
19 source of HONO, lab experiments were conducted at BAS by irradiating snow collected at  
20 DC and measuring gas-phase evolution of NO and  $\text{NO}_2$  with a 2-channel chemiluminescence  
21 detector (Bauguitte et al., 2012) as deployed at DC (Frey et al. 2013, Frey et al. this issue) and  
22 HONO with the LOPAP that ran at DC during the 2010/2011 and 2011/2012 campaigns. A  
23 20 cm long cylinder (6 cm inner diameter) was filled with  $\sim 120$  g of snow inside an airtight  
24 glass reaction chamber (total length of 40 cm, 6 cm inner diameter) and put in a freezer of  
25 which the temperature was varied between  $-5$  to  $-35^\circ\text{C}$ . Further details on the characteristics  
26 of the reaction chamber can be found in Meusinger et al. (2014). The reaction chamber is  
27 maintained vertically in a freezer and a 1000 W Xenon-arc lamp was put above the freezer.  
28 The snow was irradiated by directing the light axially along the tube through a quartz  
29 window, which makes up the top surface of the chamber. Chemically pure air was supplied to  
30 the chamber from a pure air generator (Ecophysics, PAG003) in which air is dried at  $-15^\circ\text{C}$ .  
31 To match the relative humidity of the snow under investigation and limit metamorphism the  
32 chemically pure (humid) air dry was passed through a cold trap at the temperature of the  
33 experiment. Note that with this system and for temperatures above  $-30^\circ\text{C}$ , no condensation  
34 trace was observed in the tubes outflow of the chamber. The flow rate of zero air was 4.3 L

1 min<sup>-1</sup> while the detection systems sampled processed air at a rate of 2.0 L min<sup>-1</sup> for NO<sub>x</sub> and  
2 1.0 L min<sup>-1</sup> for HONO. The overflow of 1.3 L min<sup>-1</sup> was diverted through a flow metre to  
3 check for potential leaks. While the inlet line between the reaction chamber and the NO<sub>x</sub>  
4 analyser was several m long, the length between the outlet of the reaction chamber and the  
5 LOPAP inlet was kept as short as possible (i.e. 25 cm). To do so the inlet of the LOPAP was  
6 arranged in the freezer. The wavelength range of the 1000 W Xenon-arc lamp (Oriel  
7 Instruments) was 200-2500 nm, modulated using filters with various cut-on points. **The short**  
8 **residence time of NO<sub>2</sub> (~ 4 s) in our small chamber prevents significant photolysis of NO<sub>2</sub> to**  
9 **occur during the experiments. Indeed, the J<sub>NO<sub>2</sub></sub> of 2 10<sup>-2</sup> s<sup>-1</sup> measured by Cotter et al. (2003)**  
10 **for a 1000 W Xenon-arc lamp, as also used in the present study, leads to a lifetime of NO<sub>2</sub>**  
11 **with respect to photolysis of 50 s at the front of the snow block.**  
12

#### 13 **2.4 Experiments performed at PSI to investigate a possible HNO<sub>4</sub> interference on** 14 **HONO measurements**

15 As will be discussed in Sect. 6, it may be difficult to reconcile typical mixing ratios of  
16 HONO measured 1 m above surface snow at Concordia with a reasonable estimate of the  
17 mixing ratio of HONO owing to emissions from snow due to snowpack photochemistry. It  
18 was suspected that HNO<sub>4</sub> was detected and measured as HONO by the LOPAP instrument.  
19 As briefly reported below, a few experiments conducted at PSI indicate that the LOPAP  
20 instrument does have an interference for HNO<sub>4</sub>. Mixing ratios of HNO<sub>4</sub> were not measured at  
21 DC, so the aim of the experiments described below was not to quantify the interference to  
22 enable correction of the Concordia HONO data, but to demonstrate that such an interference  
23 exists. The result of an experiment conducted under specific conditions is reported. A full  
24 characterization of the interference on HONO at various mixing ratios of HNO<sub>4</sub> in the  
25 presence or not of other trace gases present at DC is beyond the scope of this paper.

26 The interference of the LOPAP device was examined at the PSI where a gas-phase  
27 synthesis of HNO<sub>4</sub> has been developed by irradiating a mixture of NO<sub>2</sub>/H<sub>2</sub>O/CO/O<sub>2</sub>/N<sub>2</sub> at 172  
28 nm (Bartels-Rausch et al., 2011). By-products of the synthesis are HONO, HNO<sub>3</sub>, and H<sub>2</sub>O<sub>2</sub>.  
29 The synthesis gas was fed into the sampling unit of the LOPAP and the resulting LOPAP  
30 signals in presence and absence of HNO<sub>4</sub> were compared. Heating the synthesis gas to a  
31 temperature of 100°C prior to sampling by the LOPAP allowed selective removal of HNO<sub>4</sub>  
32 from the gas mixture. The mixing ratios of HONO, NO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> that are present in the  
33 synthesis gas were independently monitored with a chemical ionisation mass spectrometer  
34 (CIMS), which was calibrated by using several analysers as detailed in Ulrich et al. (2012).

1 An example of the mixing ratios of HNO<sub>4</sub> and HONO measured by CIMS and of the  
2 corresponding LOPAP signals in channel 1 and 2 is shown in Fig. 2. The relative amount of  
3 HONO (780 pptv) and HNO<sub>4</sub> (1000 pptv) observed in the synthesized mixture (prior heating)  
4 is typical for this synthesis (Bartels-Rausch et al., 2011). The experiment shows the response  
5 of the signals when the heating trap used to decompose HNO<sub>4</sub> is applied. As seen in Fig. 2,  
6 the mixing ratios of HONO, NO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> or O<sub>3</sub> that may influence the response of the LOPAP  
7 instrument did not change upon the **thermal** decomposition of HNO<sub>4</sub>. A decrease of the  
8 LOPAP signal in channel 1 is observed during the heating event, indicating that 1 ppbv of  
9 HNO<sub>4</sub> corresponds to a signal in the LOPAP of 150 pptv. Examination of the signals of the  
10 two LOPAP channels (Fig. 2) suggests that HNO<sub>4</sub> has been efficiently sampled in the first  
11 channel. It is well known that HNO<sub>4</sub> efficiently decomposes to NO<sub>2</sub><sup>-</sup> in acidic solutions  
12 (Regimbal and Mozurkewich, 1997), just like HONO does in the LOPAP sample unit. Based  
13 on the identical hydrolysis products, one might thus expect a rather large interference. The  
14 high sampling efficiency of HONO and potentially HNO<sub>4</sub>, both of which have similar  
15 partitioning coefficients to acidic solutions, is driven by the fast reaction of their hydrolysis  
16 product (NO<sub>2</sub><sup>-</sup>) with the reagents in the sampling solution of the LOPAP instrument. A full  
17 characterization of the interference by HNO<sub>4</sub> (its behaviour and quantification over a large  
18 range of concentrations, in the presence or absence of other gases) is needed to improve the  
19 use of the LOPAP in very cold atmospheres. We suggest a detailed investigation of LOPAP  
20 instrument response to different compositions of test gas mixture (i.e. with larger mixing  
21 ratios of H<sub>2</sub>O<sub>2</sub>), and with an investigation of the potentially complex (non-linear) chemistry of  
22 sampled gases. At this stage we can only exclude an oxidation of the dye used in the LOPAP  
23 instrument by HNO<sub>4</sub>, as careful inspection of the absorption spectrum of the LOPAP dye  
24 reveals no significant change during heating. Assuming the interference of HONO signal by  
25 HNO<sub>4</sub> to be linear, one would expect an interference of ~15 pptv in the HONO signal due to a  
26 mixing ratio of 100 pptv of HNO<sub>4</sub>. Given the absence of measurements of the mixing ratio of  
27 HNO<sub>4</sub> at Concordia, further experiments were conducted in the field at Concordia to directly  
28 estimate this interference as detailed in Sect. 6.

29

### 30 **3. HONO observations at Concordia**

31 Removing data suspected to have been impacted by pollution from station activities (see  
32 Sect. 2.2), one-minute average mixing ratio of  $35 \pm 14$  pptv is observed in December  
33 2011/January 2012 compared to  $28 \pm 12$  pptv measured by Kerbrat et al. (2012) for December  
34 2010/ January 2011/2012.

1 The mean diurnal cycles of surface ozone, HONO, air temperature and the PBL height  
2 simulated by MAR are reported and compared for the two summers in Fig. 3. In polar region,  
3 the strong static stability of the atmosphere often inhibits vertical mixing of surface emissions  
4 between the surface boundary layer and the rest of the atmosphere. At DC, the surface  
5 absorbs solar radiations during the day, heats the lower atmosphere and generates positive  
6 buoyancy that is responsible for an increase of turbulent kinetic energy and the subsequent  
7 increase of the boundary layer height seen in Fig. 3. This boundary layer is referred to as the  
8 "daytime boundary layer". The surface cooling after 17:00 generates negative buoyancy near  
9 the surface. A new boundary layer referred as the "night-time boundary layer" develops but  
10 remains less active than the previous daytime boundary layer. The collapse of the boundary  
11 layer after 17:00 seen in Fig. 3 is in fact the representation of the transition between the  
12 daytime and nighttime boundary layer.

13 The two mean summer ozone records indicate a drop of 1 to 2 ppbv around mid-day  
14 compared to early morning and evening values (Fig. 3). This small surface ozone change over  
15 the course of the day at DC has already been observed by Legrand et al. (2009) who attributed  
16 it to the increase of the PBL height in the afternoon that counteracts a local photochemical  
17 production of O<sub>3</sub> in the range of 0.2 ppbv hr<sup>-1</sup> during day-time.

18 Consistently with the previous 2010/2011 measurements from Kerbrat et al. (2012), the  
19 HONO mixing ratios exhibit a well-marked diurnal variation characterized by morning  
20 (around 5:00-7:00) and evening (around 20:00) maxima exceeding mid-day values by some  
21 10 pptv. Therefore, in addition to an expected more efficient photolysis of HONO during the  
22 day, the increase of the daytime boundary layer may also accounts for the observed decreased  
23 HONO mixing ratios during the day in spite of a more active snow source (see discussions in  
24 Sect. 5). Such a diurnal variability characterized by noon minimum was also observed for  
25 NO<sub>x</sub> by Frey et al. (2013) and attributed to the interplay between photochemical snow source  
26 and boundary layer dynamics.

27 As shown in Fig. 3, the larger HONO mixing ratios calculated for 2011/2012 (diurnal  
28 mean of 35 ± 5.0 pptv) with respect to the 2010/2011 ones (diurnal mean of 30.5 ± 3.5 pptv)  
29 concern both the mid-day minimum and the morning/evening maxima. The difference  
30 between the two summers is however reduced when the first week of measurements  
31 undertaken December in 2011 is removed with a lower diurnal mean (31.7 ± 4.3 pptv instead  
32 of 35 ± 5 pptv over the entire measurement period, see the blue points in Fig. 3). The case of  
33 beginning of December 2011 with respect to the rest of the summer 2011/2012 is highlighted  
34 in Fig. 3. It can be seen that the far thinner PBL height of early December (maximum of 145

1 m instead of 350 m over the entire period) may have lead to a more confined HONO  
2 production (see violet points in Fig. 3). Note also the relatively high ozone mixing ratios at  
3 that time ( $33 \pm 4$  ppbv in early December instead of  $26 \pm 1$  ppbv over the entire period).  
4 Conversely, at the end of the period the PBL became thicker (maximum of 570 m) and the  
5 mixing ratios of ozone ( $24 \pm 1$  ppbv) and nitrous acid ( $31 \pm 4$  pptv) were lower than on  
6 average (see red points in Fig. 3). Finally, early December 2011 the highest daily average  
7 mixing ratio of HONO was observed December 7<sup>th</sup> and 8<sup>th</sup> (56 pptv, Fig. 1) correspond not  
8 only to a thin PBL but also to lowest value of total ozone column (260 DU instead of  $296 \pm$   
9  $20$  DDU average) measured by the SAOZ at DC. Similarly, during the 2010/2011  
10 campaign the highest values reported at the end of the campaign (44 pptv from 15<sup>th</sup> to 18<sup>th</sup>  
11 January) by Kerbrat et al. (2012) correspond to the lowest value of total ozone column (270  
12 DU instead of  $303 \pm 17$  DDU on average). It therefore seems that HONO mixing ratios  
13 measured at 1 m at DC are also sensitive to the UV actinic flux reaching the surface. This link  
14 between stratospheric ozone and photochemistry of snow at the ground is discussed in more  
15 detail by Frey et al. (this issue).

16 It therefore seems that one of the main causes for the difference between the 2011/2012  
17 and 2010/2011 mean summer values is mainly related to slightly different atmospheric  
18 vertical stability conditions experienced over the different sampling times of the two  
19 summers, with an earlier HONO sampling in December 2011 than in December 2010 leading  
20 to higher HONO mixing ratios in a very thin and stable boundary layer. In conclusion, this  
21 second study of HONO confirms the abundance of this species in the lower atmosphere at DC  
22 with a typical mean mixing ratio of 30 pptv from mid-December to mid-January.

23 As already discussed by Kerbrat et al. (2012) (see also Sect. 5), the existence of a large  
24 photochemical source of HONO in the snow-pack is needed to explain these large mixing  
25 ratios of HONO measured above the snowpack. Measurements of the mixing ratio of HONO  
26 were therefore performed in snow interstitial air at different depths. From the top few cm of  
27 the snowpack down to 75 cm depth, mixing ratios of HONO in snowpack interstitial air  
28 tended to exceed those in the air above the snowpack, supporting the existence of a snow  
29 source of HONO (Fig. 4). However, given the interference of HNO<sub>4</sub> on HONO mixing ratio  
30 data as discussed in Sect. 6, it is difficult to use the observed vertical gradient of HONO  
31 mixing ratio to derive an estimate of emission of HONO from the snowpack. Indeed, typical  
32 values of HNO<sub>4</sub> mixing ratios are available in lower atmosphere of the Antarctic plateau  
33 (Sect. 6) but not yet in snow interstitial air. Also it remains difficult to accurately estimate the

1 production rate of HNO<sub>4</sub> in snow interstitial air from the reaction of NO<sub>2</sub> with HO<sub>2</sub> versus its  
2 uptake on natural ice surface.

3 To confirm the snowpack as a source of HONO (and as detailed in the following  
4 section) we carried out a laboratory experiment to evaluate the ratio of HONO to NO<sub>x</sub>  
5 released from natural surface snows collected at DC under controlled laboratory conditions  
6 (i.e. wavelength of light, temperature, snow specific area) to estimate the HONO snow  
7 emission flux relative to the snow emission flux of NO<sub>x</sub> for the same snowpack as derived  
8 from atmospheric concentration vertical gradient measured during the campaign by Frey et al.  
9 (this issue).

10

#### 11 4. Lab experiments on natural snow collected at DC

12 Table 1 summarized the results of experiments conducted at BAS by irradiating surface  
13 snows collected at Dome C (see Sect. 2.3). NO<sub>x</sub> and HONO are produced when snow is  
14 irradiated. Several laboratory experiments were conducted to investigate the wavelength,  
15 temperature and snow chemical composition dependence of HONO release from snow.  
16 Similar to previous laboratory experiments conducted by Cotter et al. (2003) on surface  
17 snows collected in coastal Antarctica, the NO<sub>x</sub> release is found to halve when the optical filter  
18 in the front of the irradiation lamp (cut off for < 295 nm) is replaced by a cut off filter for  
19 illumination wavelength smaller than 320 nm (Table 1). Cotter et al. (2003) demonstrated no  
20 measurable emission of NO<sub>x</sub> from the snow when illuminated with a lamp with wavelengths  
21 shaded below 345 nm, being consistent with NO<sub>3</sub><sup>-</sup> photolysis. Fig. 5 illustrates the wavelength  
22 dependence of HONO release showing the effect of insertion of a filter with different cut-on  
23 points. Similarly to the NO<sub>x</sub>, the HONO release is decreased by a factor two when inserting  
24 the filter at 320 nm and become insignificant at 385 nm (Table 1).

25 While the observed wavelength dependency of the NO<sub>x</sub> release supports the hypothesis  
26 that the photolysis of nitrate present in snow is the major source of released NO<sub>x</sub> (via its  
27 major channel: NO<sub>3</sub><sup>-</sup> + hv → NO<sub>2</sub> + O<sup>-</sup>), for HONO it is still unclear if either the nitrate  
28 photolysis efficiently produces directly HONO from hydrolysis of NO<sub>2</sub><sup>-</sup> produced by the  
29 second channel of the nitrate photolysis (NO<sub>3</sub><sup>-</sup> + hv → NO<sub>2</sub><sup>-</sup> + O) or HONO is  
30 produced from NO<sub>2</sub> (Villena et al., 2011). Indeed, lab experiments conducted on nitrate doped  
31 ice suggest that the first channel is a factor of 8-9 more efficient than the second one. It is  
32 suspected that the HONO production may be significantly higher than it is when considering  
33 this second channel since the NO<sub>2</sub> produced by the first channel may subsequently act as a  
34 precursor of HONO. The wavelength dependency of HONO release observed during previous

1 experiments does not however help to separate the primary and secondary source of HONO  
2 during irradiation since they were done with chemically pure air and when placing the cut off  
3 filter at 385 nm we suppress the primary source of HONO as well as NO<sub>2</sub> that is needed for  
4 secondary HONO production.

5 Among possible secondary productions it is generally accepted that the reduction of  
6 NO<sub>2</sub> on photo-sensitized organic material like humic acid (George et al., 2005; Bartels-  
7 Rausch et al., 2010) would proceed more efficiently than the disproportionation reaction of  
8 NO<sub>2</sub> ( $2 \text{ NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3$ ) (Finlayson-Pitts et al., 2003). As discussed by  
9 Grannas et al. (2007), the relevance of this secondary production was supported even for  
10 Antarctica by the significant presence of dissolved fulvic acid reported for Antarctic snow  
11 (26-46 ppbC) by Calace et al. (2005). However, the previously assumed ubiquitous presence  
12 of organics in polar snow that is needed to reduce NO<sub>2</sub> into HONO was recently reviewed by  
13 Legrand et al. (2013) who found that organics (and humic acids) are far less abundant in  
14 Antarctica compared to Greenland or mid-latitude glaciers like the Alps. For instance, the  
15 typical dissolved organic content of summer surface snow is only 10-27 ppbC at Concordia  
16 (Legrand et al., 2013) against  $110 \pm 45$  ppbC at Summit and 300 ppbC in the Alps.  
17 Furthermore, recent HULIS measurements of surface snows collected at DC do not confirm  
18 the previously observed abundance (2 ppbC instead of 26-46 ppbC). From lab experiments  
19 conducted by irradiating ice films containing humic acid in the presence of NO<sub>2</sub>, Bartels-  
20 Rausch et al. (2010) derived production rates of HONO from NO<sub>2</sub>. From that the authors  
21 roughly estimated light driven HONO fluxes of  $10^{13}$  molecule m<sup>-2</sup> s<sup>-1</sup> from snow covered  
22 surface area assuming the presence of 100 pptv NO<sub>2</sub> in the snow interstitial air and a  
23 concentration of 10 ppbC of humic acid in snow. Keeping in mind uncertainties in  
24 extrapolating lab experiments to conditions relevant to the lower atmosphere at Dome C, with  
25 typical NO<sub>2</sub> mixing ratios of 1 to 10 ppbv in interstitial air at 10 cm below the surface at  
26 Dome C (Frey et al., this issue), the presence of 2 ppbC of HULIS in snow may still lead to a  
27 significant HONO production from NO<sub>2</sub> at the site. **If HULIS are located at the surface of  
28 snow grains, much more than 2 ppbC of HULIS would be available to react with NO<sub>2</sub> present  
29 in interstitial air of the snowpack to produce HONO.**

30 Irradiation experiments with insertion of the filter at 295 nm were conducted at  
31 temperatures ranging from 240 to 260 K. As seen in Table 1, whereas the NO<sub>x</sub> release was  
32 found to be temperature independent (as previously shown by Cotter et al., 2003), a large  
33 dependence is found for HONO with an increase by a factor of 2.2 when the temperature of  
34 snow is increased from 240 to 260 K. A temperature dependence of the HONO emissions is



1 expected since the partition coefficient of HONO between ice and air increases by a factor of  
2 5.8 between 240 K and 260 K (Crowley et al., 2010). As a consequence the HONO to NO<sub>x</sub>  
3 release is smaller at 240K than at 260K. For the example of the surface snow reported in  
4 Table 1, this ratio steadily increases from 0.3 at 240 K, 0.5 at 250 K to 0.8 at 260 K.

5 As reported in Table 1, experiments were made with DC snow containing from to  
6 1400 ppb of nitrate. As expected higher nitrate content leads to higher snow release of NO<sub>x</sub>  
7 and HONO but the increase of HONO is larger than the one of NO<sub>x</sub>. For instance, at a  
8 temperature close to -20°C, the first upper cm of surface snow releases almost twice more  
9 HONO compared NO<sub>x</sub> than the snow collected from the surface to 12 cm depth. The more  
10 acidic character of the snow collected in the upper first centimetre compared to the one  
11 collected down to 12 cm below the surface (see Table 1) may favour the release of a weak  
12 acid species like HONO.

## 14 5. Model calculations

15  
16 Observed atmospheric mixing ratios were compared with steady-state calculations  
17 made by considering major gas-phase sources and sinks of HONO. The major sink of HONO  
18 is its photolysis. The photolysis rate constant ( $J_{\text{HONO}}$ ) were measured with a  $2\pi$   
19 spectroradiometer (see Sect. 2.2). The value of  $J_{\text{HONO}}$  was calculated for light from  $4\pi$   
20 steradians from the downwelling value of  $J_{\text{HONO}}$  measured over  $2\pi$  steradians by assuming a  
21 surface albedo of 0.95, a typical value for regions covered by dry snow and wavelength  
22 shorter than 400 nm (Hudson et al., 2006; France et al., 2011). The main gas-phase  
23 production of HONO is the reaction of NO with OH radicals. Steady-state calculations  
24 indicate that under noon conditions encountered at DC (a  $J_{\text{HONO}}$  value of  $3.7 \times 10^{-3} \text{ s}^{-1}$ ,  $5 \times 10^6$   
25 OH rad.  $\text{cm}^{-3}$  (Kukui et al., this issue), and 50 pptv of NO (Frey et al., this issue)), a HONO  
26 mixing ratio of 1 pptv is expected. Steady-state calculated diurnal HONO profile (Fig. 6)  
27 suggests a HONO maximum of 2.5 pptv at 19:00 due to the presence of a maximum of 120  
28 pptv of NO (Frey et al., this issue).

29 Another gas-phase source of HONO was recently proposed by Li et al. (2014) via  
30 reaction of HO<sub>2</sub>(H<sub>2</sub>O) complex with NO<sub>2</sub>:




1 Reaction of  $\text{HO}_2(\text{H}_2\text{O})$  complex with  $\text{NO}_2$  was first suggested by Sander and Peterson  
2 (1984) to explain the observation of a linear dependence of the effective rate constant of the  
3 reaction of  $\text{HO}_2$  with  $\text{NO}_2$  on the concentration of water vapour in the temperature range 275-  
4 298 K. Assuming reaction mechanism (2-4) Sander and Peterson (1984) derived temperature  
5 dependence for the effective third-order rate constant of the reaction  $\text{HO}_2+\text{NO}_2+\text{H}_2\text{O}$ ,  $k^{\text{III}}_4(\text{T})$ ,  
6 with  $k^{\text{III}}_4(\text{T})$  representing the product  $k_4 \times K_3$ , where  $k_4$  is the bimolecular rate constant for  
7 reaction  $\text{HO}_2(\text{H}_2\text{O})$  with  $\text{NO}_2$  and  $K_3$  is equilibrium constant for reaction (3). The possible  
8 contribution of reaction (4) to form HONO at Concordia was evaluated by assuming a unity  
9 yield of HONO for the reaction (4). The rate constant  $k_4(\text{T})$  in the temperature range 275-298  
10 K was estimated from the  $k^{\text{III}}_4(\text{T})$  data of Sander and Peterson (1984) using recent  
11 recommendations for  $K_3(\text{T})$  and  $k_2(\text{T})$  from Sander et al. (2011):  $k_4(\text{T}) = k^{\text{III}}_4(\text{T}) / K_3(\text{T}) \times$   
12  $k_2(\text{T}) / k_2(\text{T})^{\text{Sander}}$ , where  $k_2(\text{T})^{\text{Sander}}$  are data from Sander and Peterson (1984). The values of  
13  $k_4(\text{T})$  at low temperatures encountered at Concordia were obtained by extrapolating the  
14  $k_4(\text{T})/k_2(\text{T})$  data from Sander and Peterson (1984) and assuming a logarithmic dependence of  
15  $k_4(\text{T})/k_2(\text{T})$  on  $1/\text{T}$ , similar to reaction of  $\text{HO}_2(\text{H}_2\text{O})$  with  $\text{HO}_2$  (Sanders et al., 2011). The  
16 resulting dependence ( $k_4(\text{T})/k_2(\text{T}) = 10^{-1505.3/\text{T}(\text{K})+5.4}$ ) predicts significantly lower water  
17 enhancement effect at low temperature ( $k_4/k_2=0.12$  at 240K compared to 2.2 at 298K). Using  
18 these  $k_4$  values and observations of  $\text{OH}+\text{NO}$ ,  $\text{HO}_2$ ,  $\text{NO}_2$  and  $\text{H}_2\text{O}$ , the low temperatures  
19 encountered at Concordia make negligible the formation of HONO from the reaction (4). This  
20 hypothetical HONO source would contribute for 10-20% of the HONO production from the  
21 reaction  $\text{OH}+\text{NO}$  and would result in less than 1% of the measured HONO.

22 An additional source of HONO is obviously required to account for observed mixing  
23 ratios of a few tens of pptv. On the basis of laboratory experiments presented in Sect. 4, we  
24 examine to what extent the snow photochemical source of HONO accounts for atmospheric  
25 observations of HONO at Concordia. Simulations were made with a numerical 1-D box  
26 model that considers, in addition to the above-mentioned gas-phase sources and sinks of  
27 HONO, a flux from the snow and its diffusive vertical transport. The turbulent diffusion  
28 coefficients ( $K_z$ ) were calculated by the regional atmospheric MAR model (Modèle  
29 Atmosphérique Régional). Since cloud cover is responsible for an increase of around 50% of  
30 the down-welling long-wave radiations in summer at DC, when the cloud cover is  
31 underestimated, the surface heat budget is not well simulated and this strongly impacts the  
32 turbulence simulated by the model. We therefore performed calculations only for days with  
33 clear sky conditions (see Fig. 1).

1 We used the MAR model with a horizontal resolution of 20 km centred at Concordia;  
2 a top level is at 1 hPa with 100 vertical levels. The vertical resolution is 0.9 m up to 23 m  
3 above the surface, and decreases upward. MAR  $K_z$  values are linearly interpolated to the  
4 vertical grid used in our 1D simulation, spacing 0.1 m from the ground to 5 m, 0.2 m from 5  
5 to 7 m, 0.5 m from 7 to 10 m, around 1 m from 10 to 20 m and then increases up to 120 m at  
6 1200 m height, respectively. MAR data above a height of 1200 m were not used here since  
7 during investigated period the top of the PBL remained below this value. The MAR model  
8 uses primitive equations with the hydrostatic assumption. A description of the model that has  
9 been validated with respect to observations from Automatic Weather Station at DC, is given  
10 by *Gallée and Gorodetskaya* [2008] and references therein. **Parametrization of turbulence in**  
11 **the lowest model layer of MAR is based on the Monin-Obukhov Similarity theory (MOST).**  
12 **Above the surface boundary layer, turbulence is parametrized using the E -  $\epsilon$  model that**  
13 **includes two prognostic equations for turbulent kinetic energy and its dissipation.** MAR  
14 simulations have been recently validated for winter with respect to observations **from**  
15 Automatic Weather Station at Concordia (*Gallée and Gorodetskaya*, 2008) and for **summ**  
16 (*Gallée et al.*, this issue). The boundary layer (PBL) height was computed from MAR  
17 simulations by taking the height where the turbulent kinetic energy decreases below 5 % of  
18 the value of the lowest layer of the model.

19 In Fig. 6 we report the simulated diurnal cycle of HONO mixing ratio at 1 m above the  
20 ground at Concordia when a photochemical snow release of HONO is applied. The HONO  
21 flux used in these calculations was obtained by multiplying the values of the  $\text{NO}_x$  snow  
22 emission flux derived from field observations at Concordia (*Frey et al.*, this issue) by the  
23 temperature dependent factor reported for surface snow in Table 1. Since, as discussed in  
24 section 4, lab experiments indicate no significant change of the ratio of HONO/ $\text{NO}_x$  release  
25 when replacing the filter with a 295 nm **cut-on** point by the one at 320 nm (Table 1), and  
26 given a maximum of the aqueous absorption cross section for nitrate centered at 300 nm  
27 (*Gaffney et al.*, 1992), we have assumed that the ratio is similar under the two wavelength  
28 conditions and used the temperature dependency found when the filter with a cut-off point at  
29 295 nm was inserted (Table 1). In this way under temperature conditions encountered at  
30 Dome C we have assumed a HONO/ $\text{NO}_x$  ratio ranging from 0.57 during the day (at  $-25^\circ\text{C}$ )  
31 and 0.3 at night (at  $-35^\circ\text{C}$ ). The derived HONO snow emission flux estimate would represent  
32 an upper limit since, as seen in Sect. 4, the upper 12 cm of snow emits less HONO than  $\text{NO}_x$   
33 compared to the surface snow. As seen in Fig. 6, using this upper estimate of the HONO snow  
34 emission (mean diurnal value of  $0.8 \times 10^9$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ ) simulations show that, in

1 addition to around 1.2 pptv of HONO produced by the NO oxidation, the HONO snow  
2 emissions can account for 10.5 pptv of HONO in the atmosphere at Concordia. Assuming a  
3 lower HONO to NO<sub>x</sub> ratio of snow emissions as suggested by the experiment conducted with  
4 the upper 12 cm of snow collected at Concordia (Table 1), mean diurnal HONO emission of  
5  $0.5 \times 10^9$  molecules cm<sup>-2</sup> s<sup>-1</sup> is estimated leading to a related HONO mixing ratio of 6.5 pptv  
6 (total of 8 pptv together with NO oxidation). It has also  be emphasized that these estimated  
7 HONO snow emission fluxes were derived from values of the HONO/NO<sub>x</sub> photochemical  
8 production ratio observed in laboratory experiments carried out by flowing zero air through  
9 the snow instead of natural interstitial air of which the chemical composition may be very  
10 different.

11 An upper value of the ratio of HONO to NO<sub>x</sub> mixing ratios often serves as a reference  
12 value to discuss the consistency of HONO mixing ratios (Kleffmann and Wiesen, 2008;  
13 Villena et al., 2011). Steady-state calculations indicate that the HONO/NO<sub>x</sub> ratio reaches a  
14 maximum value equal to the ratio of HONO to NO<sub>x</sub> lifetimes ( $\tau_{\text{HONO}}/\tau_{\text{NO}_x}$ ), when it is  
15 assumed that HONO is the sole source of NO<sub>x</sub>. The measured HONO photolysis rate  
16 constants (see Sect. 2.2) indicate an atmospheric lifetime of HONO at Concordia ranging  
17 from 4.5 min to 24 min at 12:00 and 0:00, respectively. Using OH and HO<sub>2</sub> concentrations  
18 observed by Kukui et al. (this issue), an atmospheric lifetime of NO<sub>x</sub> ranging from 3 hours at  
19 12:00 to 7 hours at 0:00 can be estimated. From that, the upper limit of the HONO/NO<sub>x</sub> ratio  
20 at Concordia would be close to 0.03 and 0.06 at 12:00 and 0:00, respectively. Using the  
21 HONO mixing ratios simulated when a mean diurnal HONO snow emission of  $0.8 \times 10^9$   
22 molecules cm<sup>-2</sup> s<sup>-1</sup> is considered (Fig. 6) and NO<sub>x</sub> mixing ratios observed at Concordia  
23 (around 200 pptv, Frey et al., this issue), we calculate a mean diurnal HONO/NO<sub>x</sub> ratio of  
24 0.06. This value slightly exceeds the maximum steady state HONO/NO<sub>x</sub> ratio estimated from  
25 HONO and NO<sub>x</sub> photochemical lifetimes. Note, however, that more accurate estimation of the  
26 upper limit of the HONO/NO<sub>x</sub> ratio should take into account also HONO and NO<sub>x</sub> vertical  
27 distributions determined by the vertical diffusivity and the conversion of HONO to NO<sub>x</sub>, as  
28 well as by a possibility of non steady state conditions. As the consideration of these factors  
29 may lead to a higher HONO/NO<sub>x</sub> ratio, the higher HONO/NO<sub>x</sub> ratio of about 0.06 cannot be  
30 considered as a strong indication of an error in the simulated HONO mixing ratios derived  
31 with an assumed HONO snow emission of  $0.8 \times 10^9$  molecules cm<sup>-2</sup> s<sup>-1</sup>.

32

33 **6. A possible HNO<sub>4</sub> interference on HONO measurements made with a LOPAP ?**

1 As discussed in the previous section, field measurements of boundary layer HONO  
2 mixing ratios at DC in summer (30 pptv) significantly exceed values calculated by  
3 considering a HONO snow source estimated from the observed NO<sub>x</sub> snow source and the  
4 relative abundance of HONO and NO<sub>x</sub> releases observed during snow irradiation BAS  
5 experiments (8 to 12 pptv). As reported in Sect. 2.4, lab experiments conducted with the  
6 LOPAP have shown a possible overestimation of HONO by ~15 pptv due to the presence of  
7 100 pptv of HNO<sub>4</sub>.

8 Although HNO<sub>4</sub> data are not available at Dome C, its presence is very likely since its  
9 atmospheric lifetime with respect to thermal decomposition becomes significant at low  
10 temperatures (lifetime close to 2 h at -20°C, Sanders et al., 2011). Whereas the first  
11 measurements of HNO<sub>4</sub> in Antarctica reported moderate mixing ratios (mean of 25 pptv  
12 observed over a few days in December 2000 at the South Pole, Slusher et al., 2002),  
13 following investigations revealed higher values. First, from 40 pptv in December to 60 pptv  
14 during the second half of November were observed in 2003 at the South Pole (Eisele et al.,  
15 2008). Second, a mean value of 64 pptv (up to 150 pptv) was observed between the ground  
16 and 50 m elevation over the Antarctic plateau (Slusher et al. 2010). These latter values of  
17 HNO<sub>4</sub> mixing ratio together with the above-discussed inconsistencies between simulations  
18 and observations stimulate efforts to investigate a possible interference of HNO<sub>4</sub> on the  
19 LOPAP instrument. Note that given the HNO<sub>4</sub> lifetime with respect to thermal decomposition  
20 of a few hours at -20°C, we don't expect interference during snow experiments conducted at  
21 BAS since HNO<sub>4</sub> initially present in snow collected at DC would have been destroyed during  
22 its storage of a few months at -20°C. Furthermore, production of HNO<sub>4</sub> during the BAS  
23 experiments (Sect. 4) following the release of NO<sub>2</sub> under irradiation of snow is far too slow to  
24 have significantly impacted HONO measurements.

25 Even though laboratory experiences conducted at <sup>PSI</sup> under certain conditions clearly  
26 showed that the LOPAP instrument has interference for HNO<sub>4</sub> (see Sect. 2.4), the absence of  
27 HNO<sub>4</sub> atmospheric data at Dome C hampers any accurate attempt to correct HONO data from  
28 the presence of HNO<sub>4</sub>. Instead, field experiments were conducted at Concordia heating the air  
29 sampled by the LOPAP to thermally decompose HNO<sub>4</sub>. This air was heated by sucking air  
30 through a 8 m long PFA tube covered with a temperature controlled heating tape and placed  
31 in an insulated box. When heating the tube, the air temperature in the PFA tube was of 37°C  
32 leading to a lifetime of HNO<sub>4</sub> with respect to its thermal decomposition of 3.2 s (Sanders et  
33 al., 2011). The experiment was performed by running the LOPAP for ~ 20 min with and  
34 without heating the tube connected to the inlet of the LOPAP. In order to account for possible

1 fast natural change of HONO mixing ratios the test was repeated three times successively. A  
2 systematic drop of HONO values was observed. Given the applied air sampling flow rate of  
3  $1.78 \text{ L min}^{-1}$  ( $1 \text{ L STP min}^{-1}$ ), the residence time of the air in the tube is 3.3 s. If attributed to  
4 the thermal decomposition of  $\text{HNO}_4$  during the heating (64% under these working  
5 conditions), the mean observed drop of 5.5 pptv of HONO would correspond to an  $\text{HNO}_4$   
6 artefact of around 9 pptv.

7 This indirect estimation of an overestimation of HONO measurements due to the  
8 presence of  $\text{HNO}_4$  is consistent with experiences conducted at PSI if the presence of 50-100  
9 pptv of  $\text{HNO}_4$  is assumed at Dome C. On the other hand, the difference between observed and  
10 simulated HONO mixing ratios presented in Sect. 5 suggests a mean diurnal overestimation  
11 close to 20 pptv (ranging from 17 pptv around noon to 22 pptv during the night). In their  
12 discussions of the observed levels of  $\text{HO}_x$  radicals, Kukui et al., (this issue) found that the  
13 consideration of 30 pptv of HONO is inconsistent with radical observations leading to about 2  
14 times overestimation of  $\text{RO}_2$  and OH concentrations. Conversely, neglecting the OH  
15 production from HONO leads to an underestimation of radical levels by a factor of 2. Kukui  
16 et al. (this issue) showed that a quite fair agreement with OH measurements is achieved with  
17 HONO mixing ratios derived from the 1D modelling with a HONO snow emission flux equal  
18 to about 30% of that of  $\text{NO}_x$ . Finally, though being slightly higher, the best guess of HONO  
19 mixing ratios derived in Sect. 5 for Concordia (8 to 12 pptv) are in the range of mixing ratios  
20 measurements made at the South Pole using laser-induced fluorescence (6 pptv, Liao et al.,  
21 2006).

## 22

## 23 7. Conclusions

24 This second study of HONO conducted in the atmosphere of the East Antarctic plateau  
25 by deploying a LOPAP confirms unexpectedly high mixing ratios close to 30 pptv. A mixing  
26 ratio of 8-12 pptv can be rationalized based on emissions of HONO from snow of  $0.5\text{-}0.8 \times 10^9$   
27 molecules  $\text{cm}^{-2} \text{ s}^{-1}$  derived from studies of the irradiation experiments surface snow collected  
28 from Concordia and scaled down to the  $\text{NO}_x$  emissions derived from observations made at  
29 DC by Frey et al. (this issue). Experiments conducted in the field and in the lab to identify the  
30 cause of such a discrepancy point to a possible overestimation of HONO in the range of 10 to  
31 20 pptv due to the important presence of  $\text{HNO}_4$  in this cold atmosphere. An accurate  
32 correction of the HONO data from the presence of  $\text{HNO}_4$  is not yet possible. Further work,  
33 both in the lab to quantify the interference at different levels of  $\text{HNO}_4$  and in the presence of

1 various other species and in the field at Concordia to obtain mixing ratios of HONO and  
2 HNO<sub>4</sub> at the same time are needed.

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5

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**References:**

Arnaud, L., Picard, G., Champollion, N., Dominé, F., Gallet, J.C., Lefebvre, E., Fily, M., and Barnola, J.M.: Measurement of vertical profiles of snow specific surface area with a 1 cm resolution using infrared reflectance: instrument description and validation, *J. of Glaciol.*, 57 (201), 17–29, 2011.

Bartels-Rausch, T., Brigante, M., Elshorbany, Y.F., Ammann, M., D’Anna, B., George, C., Stemmler, K., Ndour, M., and Kleffmann, J. : Humic acid in ice: Photo-enhanced conversion of nitrogen dioxide into nitrous acid, *Atmos. Environ.*, 44, 5443–5450, doi:10.1016/j.atmosenv.2009.12.025, 2010.

Bartels-Rausch, T., Ulrich, T., Huthwelker, T., and Ammann, M.: A novel synthesis of the radiactively labelled atmospheric trace gas peroxyxynitric acid, *Radiochim. Acta*, 99, 1–8, doi:10.1524/ract.2011.1830, 2011.

Bauguitte, S.J.-B., Bloss, W.J., Evans, M.J., Salmon, R.A., Anderson, P.S., Jones, A.E., Lee, J.D., Saiz-Lopez, A., Roscoe, H.K., Wolff, E.W., and Plane, J.M.C.: Summertime NO<sub>x</sub> measurements during the CHABLIS campaign: can source and sink estimates unravel observed diurnal cycles?, *Atmos. Chem. Phys.*, 12(2), 989–1002, doi:10.5194/acp-12-989-2012, 2012.

Beine, H.J., Amoroso, A., Dominé, F., King, M., Nardino, M., Ianniello, A., and France, J. L.: Surprisingly small HONO emissions from snow surfaces at Browning Pass, Antarctica, *Atmos. Chem. Phys.*, 6, 2569–2580, <http://www.atmos-chem-phys.net/6/2569/2006/>, 2006.

Calace, N., Cantafora, E., Mirante, S., Petronio, B. M., and Pietroletti, M.: Transport and modification of humic substances present in Antarctic snow and ancient ice, *J. Environ. Monit.*, 7, 1320-1325, 2005.

Chan, W.H., Nordstrom, R.J., Galvert, J.G., and Shaw, J.H.: An IRFTS spectroscopic study of the kinetics and the mechanism of the reactions in the gaseous system, HONO, NO, NO<sub>2</sub>, H<sub>2</sub>O, *Chem. Phys. Lett.*, 37(3), 441–446, doi:10.1016/0009-2614(76)85010-5, 1976.



1  
2 Chen, G., Davis, D., Crawford, J., Nowak, J.B., Eisele, F., Mauldin, R.L., Tanner, D., Buhr,  
3 M., Shetter, R., Lefer, B., Arimoto, R., Hogan, A., Blake, D.: An investigation of South Pole  
4 HOx chemistry: comparison of model results with ISCAT observations, *Geophys. Res. Lett.*,  
5 28 (19), 3633-3636, 2001.  
6  
7 Chen, G., Davis, D., Crawford, J., Mauldin III, R., Eisele, F., Huey, G., Slusher, D., Tanner,  
8 D., Dibb, J., Buhr, M., Hutterli, M., McConnell, J., Lefer, B., Shetter, R., Blake, D.,  
9 Lombardi, K., and Arnoldy, J. : A reassessment of HOx South Pole chemistry based on  
10 observations recorded during ISCAT 2000, *Atmos. Environ.*, 38(32), 5451–5461,  
11 doi:10.1016/j.atmosenv.2003.07.018, 2004.  
12  
13 Cotter, E.S.N., Jones, A.E., Wolff, E.W., and Bauguutte, S.J.-B.: What controls photochemical  
14 NO and NO<sub>2</sub> production from Antarctic snow? Laboratory investigation assessing the  
15 wavelength and temperature dependence, *J. Geophys. Res.*, 108(D4), 4147,  
16 doi:10.1029/2002JD002602, 2003.  
17  
18 Crowley, J.N., Ammann, M., Cox, R.A., Hynes, R.G., Jenkin, M.E., Mellouki, A., Rossi,  
19 M.J., Troe, J., and Wallington, T.J.: Evaluated kinetic and photochemical data for  
20 atmospheric chemistry: Volume V – heterogeneous reactions on solid substrates, *Atmos.*  
21 *Chem. Phys.*, 10(18), 9059–9223. doi:10.5194/acp-10-9059-2010, 2010.  
22  
23 Davis, D., Nowak, J.B., Chen, G., Buhr, M., Arimoto, R., Hogan, A., Eisele, F., Mauldin, L.,  
24 Tanner, D., Shetter, R., Lefer, B., and McMurry, P. : Unexpected high levels of NO observed  
25 at South Pole, *Geophys. Res. Lett.*, 28(19), 3625–3628, doi:10.1029/ 2000GL012584, 2001.  
26  
27 Dibb, J.E., Arsenault, M., Peterson, M.C., and Honrath, R.E. : Fast nitrogen oxide  
28 photochemistry in Summit, Greenland snow, *Atmos. Environ.*, 36, 2501-2511,  
29 doi:10.1016/S1352-2310(02)00130-9, 2002.  
30  
31 Dibb, J.E., Huey, L.G., Slusher, D.L., and Tanner, D. J.: Soluble reactive nitrogen oxides at  
32 South Pole during ISCAT 2000, *Atmos. Environ.*, 38, 5399–5409, 2004.  
33

1 Eisele, F., Davis, D.D., Helmig, D., Oltmans, S.J., Neff, W., Huey, G., Tanner, Chen, G.,  
2 Crawford, J., Arimoto, R., Buhr, M., J., Mauldin, L., Hutterli, M., Dibb, J., Blake, D.,  
3 Brooks, S.B., Johnson, B., Roberts, J.M., Wang, Y., Tan, D., and Flocke, F. : Antarctic  
4 tropospheric chemistry investigation (ANTCI) 2003 overview, *Atmos. Environ.*, 42(12),  
5 2749–2761, doi:10.1016/j.atmosenv.2007.04.013, 2008.

6

7 Finlayson-Pitts, B.J., Wingen, L.M., Sumner, A.L., Syomin, D., and Ramazan, K.A.: The  
8 heterogeneous hydrolysis of NO<sub>2</sub> in laboratory systems and in outdoor and indoor  
9 atmospheres: An integrated mechanism, *Phys. Chem. Chem. Phys.*, 5, 223–242,  
10 doi:10.1039/b208564j, 2003.

11

12 France, J.L., King, M.D., Frey, M.M., Erbland, J., Picard, G., Preunkert, S., MacArthur, A.,  
13 and Savarino, J.: Snow optical properties at Dome C, Antarctica; implications for snow  
14 emissions and snow chemistry of reactive nitrogen, *Atmos. Chem. Phys.*, 11, 9787-9801,  
15 2011.

16

17 Frey, M.M., Brough, N., France, J.L., Anderson, P.S., Traulle, O., King, M.D., Jones, A.E.,  
18 Wolff, E.W., and Savarino, J.: The diurnal variability of atmospheric nitrogen oxides (NO and  
19 NO<sub>2</sub>) above the Antarctic Plateau driven by atmospheric stability and snow emissions, *Atmos.*  
20 *Chem. Phys.*, 13, 3045–3062, doi:10.5194/acp-13-3045-2013, 2013.

21

22 Frey, M.M., Roscoe, H.K., Kukui, S., Savarino, J., France, J.L., King, M.D., Legrand, M., and  
23 Preunkert, S.: Atmospheric nitrogen oxides (NO and NO<sub>2</sub>) at Dome C, East Antarctica, during  
24 the OPALE campaign, this issue.

25

26 Gaffney, J.S., Marley, N.A., and Cunningham, M.M.: Measurement of the absorption  
27 constants for nitrate in water between 270 and 335 nm, *Environ. Sci. Technol.*, 25, 207–209,  
28 1992.

29

30 Gallet, J.-C., Dominé, F., Arnaud, L., Picard, G., and Savarino, J.: Vertical profile of the  
31 specific surface area and density of the snow at Dome C and on a transect to Dumont  
32 D’Urville, Antarctica – albedo calculations and comparison to remote sensing products, *The*  
33 *Cryosphere*, 5, 631–649, doi:10.5194/tc-5-631-2011, 2011.

34

1 Gallée, H. and Gorodetskaya, I.: Validation of a limited area model over Dome C, Antarctic  
2 Plateau, during winter, 34, 61–72, *Clim. Dyn.*, doi:10.1007/s00382-008-0499-y, 2008.  
3

4 Gallée, H., Preunkert, S., Jourdain, B., Argentini, S., Frey, M., Genthon, C., Pietroni, I.,  
5 Casasanta, G., and Legrand, M. : Characterization of the boundary layer at Dome C during  
6 OPALE, *Atmos. Chem. Phys.*, this issue.  
7

8 George, C., Streckowski, R.S., Kleffmann, J., Stemmler, K., and Ammann, M.: Photoenhanced  
9 uptake of gaseous NO<sub>2</sub> on solid organic compounds: a photochemical source of HONO,  
10 *Faraday Discuss.*, 130, 195–211, 2005.  
11

12 Grannas, A.M., Jones, A.E., Dibb, J., Ammann, M., Anastasio, C., Beine, H.J., Bergin, M.,  
13 Bottenheim, J., Boxe, C.S., Carver, G., Chen, G., Crawford, J.H., Domine', F., Frey, M.M.,  
14 Guzmán, M.I., Heard, D.E., Helmig, D., Hoffmann, M.R., Honrath, R.E., Huey, L.G.,  
15 Hutterli, M., Jacobi, H.W., Klán, P., Lefer, B., McConnell, J., Plane, J., Sander, R., Savarino,  
16 J., Shepson, P.B., Simpson, W.R., Sodeau, J.R., von Glasow, R., Weller, R., Wolff, E.W., and  
17 Zhu, T.: An overview of snow photochemistry: evidence, mechanisms and impacts, *Atmos.*  
18 *Chem. Phys.*, 7, 4329–4373, <http://www.atmos-chem-phys.net/7/4329/2007/>, 2007.  
19

20 Gutzwiller, L., Arens, F., Baltensperger, U., Gäggeler, H.W., and Ammann, M.: Significance  
21 of semivolatile diesel exhaust organics for secondary HONO formation, *Environ. Sci.*  
22 *Technol.*, 36, 677-682, doi:10.1021/es015673b, 2002.  
23

24 Heland, J., Kleffmann, J., Kurtenbach, R., and Wiesen, P. : A new instrument to measure  
25 gaseous nitrous acid (HONO) in the atmosphere, *Environ. Sci. Technol.*, 35(15), 3207-3212,  
26 doi:10.1021/es000303t, 2001.  
27

28 Hudson, S.R., Warren, S.G., Brandt, R.E., Grenfell, T.C., and Six, D. : Spectral bidirectional  
29 reflectance of Antarctic snow: Measurements and parameterization, *J. Geophys. Res.*, 111,  
30 D18106, doi:10.1029/2006JD007290, 2006.  
31

32 Jones, A.E., Weller, R., Wolff, E.W., and Jacobi, H.-W.: Speciation and rate of  
33 photochemical NO and NO<sub>2</sub> production in Antarctic snow, *Geophys. Res. Lett.*, 27(3), 345–  
34 348, 2000.

1  
2 Kerbrat, M., Legrand, M., Preunkert, S., Gallée, H., and Kleffmann, J.: Nitrous Acid at  
3 Concordia on the East Antarctic Plateau and its transport to the coastal site of Dumont  
4 d'Urville, *J. Geophys. Res.*, 117, D08303, doi:10.1029/2011JD017149, 2012.  
5  
6 Kirchstetter, T.W., Harley, R.A., and Littlejohn, D.: Measurement of nitrous acid in motor  
7 vehicle exhaust, *Environ. Sci. Technol.*, 30, 2843-2849, 10.1021/es960135y, 1996.  
8  
9 Kleffmann, J., Heland, J., Kurtenbach, R., Lorzer, J., and Wiesen, P.: A new instrument  
10 (LOPAP) for the detection of nitrous acid (HONO), *Environ. Sci. Pollut. Res.*, (Sp. Iss. 4),  
11 48–54, 2002.  
12  
13 Kleffmann, J., and Wiesen, P.: Technical Note: Quantification of interferences of wet  
14 chemical HONO LOPAP measurements under simulated polar conditions, *Atmos. Chem.*  
15 *Phys.*, 8, 6813–6822, www.atmos-chem-phys.net/8/6813/2008/, 2008.  
16  
17 Kokhanovsky, A.A., and Zege, E.P.: Scattering optics of snow, *Appl. Optics*, 43, 1589–1602,  
18 2004.  
19  
20 Kukui, A., Legrand, M., Ancellet, G., Gros, V., Bekki, S., Sarda-Estève, R., Loisil, R., and  
21 Preunkert, S.: Measurements of OH and RO<sub>2</sub> radicals at the coastal Antarctic site of Dumont  
22 d'Urville (East Antarctica) in summer, *J. Geophys. Res.*, doi:10.1029/2012JD017614, 2012.  
23  
24 Kukui, A., Legrand, M., Preunkert, S., Frey, M., Loisil, R., Gil Roca, J., Jourdain, B., King,  
25 M., France, J., and Ancellet, G.: OH and RO<sub>2</sub> measurements at Dome C, East Antarctica,  
26 *Atmos. Chem. Phys.*, this issue.  
27  
28 Kurtenbach, R., Becker, K.H., Gomes, J.A.G., Kleffmann, J., Lorzer, J.C., Spittler, M.,  
29 Wiesen, P., Ackermann, R., Geyer, A., and Platt, U.: Investigations of emissions and  
30 heterogeneous formation of HONO in a road traffic tunnel, *Atmos. Environ.*, 35, 3385-3394,  
31 10.1016/s1352- 2310(01)00138-8, 2001.  
32

1 Legrand M., Preunkert, S., Jourdain, B., Gallée, H., Goutail, F., Weller, R., and Savarino, J.:  
2 Year round record of surface ozone at coastal (Dumont d'Urville) and inland (Concordia)  
3 sites in East Antarctica, *J. Geophys. Res.*, 114, D20306, doi:10.1029/2008JD011667, 2009.

4 Legrand, M., Preunkert, S., Jourdain, B., Guilhermet, J., Faïn, X., Alekhina, I., and Petit, J.R. :  
5 Water-soluble organic carbon in snow and ice deposited at Alpine, Greenland, and Antarctic  
6 sites: A critical review of available data and their atmospheric relevance, *Clim. Past*, 9, 2195-  
7 2211, doi:10.5194/cp-9-2195-2013, 2013.

8

9 **Li, X., Rohrer, F., Hofzumahaus, A., Brauers, T., Häsel, R., Bohn, B., Broch, S., Fuchs, H.,**  
10 **Gomm, S., Holland, F., Jäger, J., Kaiser, J., Keutsch, F. N., Lohse, I., Lu, K., Tillmann, R.,**  
11 **Wegener, R., Wolfe, G. M., Mentel, T. F., Kiendler-Scharr, A., and Wahner, A.: Missing**  
12 **Gas-Phase Source of HONO Inferred from Zeppelin Measurements in the Troposphere,**  
13 **Science, 344, 292-296, 2014.**

14

15 Liao, W., Case, A.T., Mastromarino, J., Tan, D., and Dibb, J.E. : Observations of HONO by  
16 laser-induced fluorescence at the South Pole during ANTCI 2003, *Geophys. Res. Lett.*, 33,  
17 L09810, doi:10.1029/2005GL025470, 2006.

18

19 Mauldin, R.L., Eisele, F.L., Tanner, D.J., Kosciuch, E., Shetter, R., Lefer, B., Hall, S.R.,  
20 Nowak, J.B., Buhr, M., Chen, G., Wang, P., and Davis, D. : Measurements of OH, H<sub>2</sub>SO<sub>4</sub>,  
21 and MSA at the South Pole during ISCAT, *Atmos. Environ.*, 28, 3629-3632, 2001a.

22

23 Mauldin III, R.L., Eisele, F.L., Cantrell, C.A., Kosciuch, E., Ridley, B.A., Lefer, B., Tanner,  
24 D.J., Nowak, J.B., Chen, G., Wang, L., and Davis, D. : Measurements of OH aboard the ASA  
25 P-3 during PEM-Tropics B., *J. Geophys. Res.*, 106, 32,657-32,666, 2001b.

26

27 Meusinger, C., Berhanu, T.A., Erbland, J., Savarino, J., and Johnson, M.S. : Laboratory Study  
28 of Nitrate Photolysis in Antarctic Snow, Part 1: Observed Quantum Yield, Domain of  
29 Photolysis and Secondary Chemistry, *J. Chem. Phys.*, **140, 244305, 2014.**

30

31 Preunkert S., Ancellet, G., Legrand, M., Kukui, A., Kerbrat, M., Sarda-Estève, R., Gros, V.,  
32 and Jourdain, B.: Oxidant Production over Antarctic Land and its Export (OPALE) project:  
33 An overview of the 2010-2011 summer campaign, *J. Geophys. Res.*,  
34 doi:10.1029/2011JD017145, 2012.

1  
2 Regimbal, J., and Mozurkewich, M.: Peroxynitric acid decay mechanisms and kinetics at low  
3 pH, *J. Phys. Chem. A*, 101, 8822–8829, 1997.

4 Sander, S.P., and Peterson, A.E.: Kinetics of the reaction  $\text{HO}_2+\text{NO}_2+\text{M}\rightarrow\text{HO}_2\text{NO}_2+\text{M}$ , *J.*  
5 *Phys. Chem.*, 88, 166-1571, 1984.

6

7 Sander, S.P., J. Abbatt, J.R. Barker, J.B. Burkholder, R.R. Friedl, D.M. Golden, R.E. Huie, C.  
8 E. Kolb, M.J. Kurylo, G.K. Moortgat, V.L. Orkin and P.H. Wine : "Chemical Kinetics and  
9 Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17," JPL Publication 10  
10 June 2011, Jet Propulsion Laboratory, Pasadena, <http://jpldataeval.jpl.nasa.gov>, 2011.

11

12 Slusher, D.L., Huey, L.G., Tanner, D.J., Chen, G., Davis, D.D., Buhr, M., Nowak, J.B.,  
13 Eisele, F., Kosciuch, E., Mauldin, R.L., Lefer, B.L., Shetter, R.E., and Dibb, J.E.:  
14 Measurements of pernitric acid at the South Pole during ISCAT 2000, *Geophys. Res. Lett.*,  
15 29, 2011, doi:10.1029/2002GL015703, 2002.

16

17 Slusher, D.L., Neff, W.D., Kim, S., Huey, L.G., Wang, Y., Zeng, T., Tanner, D.J., Blake, D.  
18 R., Beyersdorf, A., Lefer, B.L., Crawford, J.H., Eisele, F.L., Mauldin, R.L., Kosciuch, E.,  
19 Buhr, M.P., Wallace, H.W., and Davis, D.D.: Atmospheric chemistry results from the ANTCI  
20 2005 Antarctic plateau airborne study, *J. Geophys. Res. Atmos.*, 115, D07304,  
21 doi:10.1029/2009JD012605, 2010.

22

23 Ulrich, T., Ammann, M., Leutwyler, S., and Bartels-Rausch, T.: The adsorption of  
24 peroxyxynitric acid on ice between 230 K and 253 K, *Atmos. Chem. Phys.*, 12, 1833-1845,  
25 10.5194/acp-12-1833-2012, 2012.

26

27 Villena, G., Wiesen, P., Cantrell, C.A., Flocke, F., Fried, A., Hall, S.R., Hornbrook, R.S.,  
28 Knapp, D., Kosciuch, E., Mauldin III, R.L., McGrath, J.A., Montzka, D., Richter, D.,  
29 Ullmann, K., Walega, J., Weibring, P., Weinheimer, A., Staebler, R.M., Liao, J., Huey, L.G.,  
30 and Kleffmann, J. : Nitrous acid (HONO) during polar spring in Barrow, Alaska: A net source  
31 of OH radicals?, *J. Geophys. Res.*, 116, D00R07, doi:10.1029/2011JD016643, 2011.

32