



Large mixing ratios  
of HONO at  
Concordia in summer

M. Legrand et al.

# Large mixing ratios of atmospheric nitrous acid (HONO) at Concordia (East Antarctic plateau) in summer: a strong source from surface snow?

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Received: 1 April 2014 – Accepted: 27 April 2014 – Published: 12 May 2014

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Published by Copernicus Publications on behalf of the European Geosciences Union.

ACPD

14, 11749–11785, 2014

## Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

During the austral summer 2011/2012 atmospheric nitrous acid was investigated for the second time at the Concordia site (75°06' S, 123°33' E) located on the East Antarctic plateau by deploying a long path absorption photometer (LOPAP). Hourly mixing ratios of HONO measured in December 2011/January 2012 ( $35 \pm 5.0$  pptv) were similar to those measured in December 2010/January 2011 ( $30.4 \pm 3.5$  pptv). The large value of the HONO mixing ratio at the remote Concordia site suggests a local source of HONO in addition to weak production from oxidation of NO by the OH radical. Laboratory experiments demonstrate that surface snow removed from Concordia can produce gas phase HONO at mixing ratios half that of NO<sub>x</sub> mixing ratio produced in the same experiment at typical temperatures encountered at Concordia in summer. Using these lab data and the emission flux of NO<sub>x</sub> from snow estimated from the vertical gradient of atmospheric concentrations measured during the campaign, a mean diurnal HONO snow emission ranging between 0.5 and  $0.8 \times 10^9$  molecules cm<sup>-2</sup> s<sup>-1</sup> is calculated. Model calculations indicate that, in addition to around 1.2 pptv of HONO produced by the NO oxidation, these HONO snow emissions can only explain 6.5 to 10.5 pptv of HONO in the atmosphere at Concordia. To explain the difference between observed and simulated HONO mixing ratios, tests were done both in the field and at lab to explore the possibility that the presence of HNO<sub>4</sub> had biased the measurements of HONO.

## 1 Introduction

The existence of an oxidizing boundary layer over the Antarctic continent was first highlighted by measurements carried out at the South Pole, where a mean concentration of  $2.5 \times 10^6$  OH radicals cm<sup>-3</sup> was observed (Mauldin et al., 2001a), making the South Pole atmospheric boundary layer as oxidative as the remote tropical marine boundary layer (Mauldin et al., 2001b). Chen et al. (2001) and Davis et al. (2001) showed that the

ACPD

14, 11749–11785, 2014

## Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



---

**Large mixing ratios  
of HONO at  
Concordia in summer**M. Legrand et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

presence of high concentrations of  $\text{NO}_x$  produced by the photolysis of nitrate present in surface snow permits the required efficient recycling of  $\text{HO}_x$  into OH. Aside from snow photochemical emission of  $\text{NO}_x$  that acts as a secondary source of OH, the role of HONO as a primary source of OH remains unclear. Using a mist chamber followed by ion chromatography analysis of nitrite, Dibb et al. (2004) reported a median HONO mixing ratio close to 30 pptv at the South Pole. However, follow-up measurements by laser-induced fluorescence (LIF) indicated lower mixing ratios (6 pptv on average) and an interference with  $\text{HNO}_4$  has been suspected (Liao et al., 2006). Furthermore, as discussed by Chen et al. (2004) the consideration of 30 pptv of HONO in the lower atmosphere over the South Pole leads to an OH over-prediction by gas-phase photochemical models by a factor of 3 to 5. The authors questioned whether the discrepancy between observed and simulated concentrations of OH at the South Pole was due to measurements of HONO suffering from overestimation due to chemical interferences or if the mechanisms of the model missed  $\text{HO}_x$  and  $\text{NO}_x$  losses.

Even at the level of a few pptv, the presence of HONO requires a source other than the gas-phase reaction of NO with OH and many studies measuring HONO in atmospheres overlying snow covered regions suspected HONO to be emitted from the surface snow in addition to  $\text{NO}_x$  (see Grannas et al. (2007) for a review). It has to be emphasized that most of the studies of HONO have concerned high (Arctic, Greenland) and mid (Colorado and Alps) northern latitudes where, in relation to the chemical composition of snow, the involved HONO production processes would be very different compared to the case of Antarctica. Concerning Antarctic snow, following the pioneering shading experiment done by Jones et al. (2000) on snow from the coastal Antarctic site of Neumayer, numerous studies investigated the release of  $\text{NO}_x$  from the snow (see references in Frey et al., 2014), but only two studies reported on HONO snow emissions and none of them examined together HONO and  $\text{NO}_x$  emissions. Beine et al. (2006) reported small HONO fluxes ( $3 \times 10^7 \text{ molecule cm}^{-2} \text{ s}^{-1}$ ) above the Browning Pass (coastal Antarctic) snowpack. However, the snow chemical composition at that site is very atypical with a large presence of calcium (up to 4 ppm) attributed to



---

## Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

cordia in view to quantify a possible photochemical snow source of HONO. This was done by measuring simultaneously HONO with the LOPAP, NO and NO<sub>2</sub> with a 2-channel chemiluminescence detector. From these data we crudely estimate the amount of HONO released from snow within the lower atmosphere at Concordia on the basis of the NO<sub>x</sub> snow emissions derived from the vertical gradient of atmospheric concentrations measured during the campaign by Frey et al. (2014). The derived values of the HONO flux were used in 1-D modeling calculations to evaluate the contribution of this snow source to the large HONO mixing ratios observed at DC. Finally, to evaluate a suspected possible interference of HNO<sub>4</sub> on the HONO mixing ratio measured by the LOPAP, field experiments were conducted by heating sampled air prior to its introduction in the LOPAP device, heating being a convenient way to destroy HNO<sub>4</sub>. The selectivity to HNO<sub>4</sub> and the response of the LOPAP during the heating events was also investigated in laboratory by mass spectrometry at Paul Scherrer Institute (PSI).

## 2 Methods and site

### 2.1 HONO measurement method

HONO was measured using a long path absorption photometer (LOPAP) which has been described in detail elsewhere (Heland et al., 2001; Kleffmann et al., 2002). In brief, after being sampled into a temperature controlled stripping coil containing a mixture of sulfanilamide in a 1 N HCl solution, HONO is derivatized into a coloured azo dye. The light absorption by the azo dye is measured in a long path absorption tube by a spectrometer at 550 nm using an optical path length of 5 m. The LOPAP did not have long sampling lines or inlet. The stripping coil was placed directly in the atmosphere being sampled. The LOPAP has two stripping coils connected in series to correct interferences. In the first coil (channel 1), HONO is trapped quantitatively together with a small amount of the interfering substances. Assuming that these interfering species are trapped in a similar amount in the second coil (channel 2), the difference between

**Large mixing ratios  
of HONO at  
Concordia in summer**

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

the signals resulting from stripping in each coil provides an interference-free HONO signal (Heland et al., 2001). Air was sampled at a flow rate of  $1 \text{ L min}^{-1}$  and the flow rate of the stripping solution was of  $0.17 \text{ mL min}^{-1}$ . Calibrations were performed every five days. Relative deviations of the calibration signal were of 3% and 9% at  $3\sigma$  for channel 1 and 2, respectively. The quantification limit of the LOPAP instrument used in this study was as low as 1.5 pptv (taken as  $10\sigma$  of all zero measurements done by sampling pure  $\text{N}_2$ ) with a time resolution of 9 min. More details on the set up of the LOPAP device in the fields can be found in Kerbrat et al. (2012). Similarly to the first campaign, the amount of interferences in the second coil was on average  $9 \pm 7\%$  of total signal (instead of  $10 \pm 5\%$  found by Kerbrat et al., 2012, in 2010/2011). The LOPAP was tested for numerous possible interfering  $\text{NO}_x$  and  $\text{NO}_y$  species including alkyl nitrates. It was concluded that when significant the two channels approach was able to well correct the HONO data (Kleffmann and Wiesen, 2008). It has, however, to be emphasized that no tests have been conducted for  $\text{HNO}_4$ .

During the field campaign, HONO was occasionally sampled in the snow interstitial air by pumping air through a PFA tube (5 m long, 4 mm internal diameter) at a flow rate of  $1 \text{ L min}^{-1}$ . In addition, to evaluate a possible influence of  $\text{HNO}_4$  on HONO measurements, field experiments were undertaken by heating air sampled through a 9 m long PFA tube. Tests were performed to evaluate potential loss or formation of HONO in the PFA tubes by running the LOPAP for 30 min with and without a tube connected to the inlet of the LOPAP, sampling air at the same height. In order to account for possible fast natural change of HONO mixing ratios the test was repeated three times successively. The tests were carried out with ambient mixing ratios of 20 pptv as encountered at mid-day 23 December and 40 pptv in the morning 28 December. In the two cases losses of around 4 pptv and 7 pptv were observed when using the 5 m and 9 m long PFA tube, respectively. These losses will be considered in discussing HONO mixing ratios in interstitial air (see Sect. 3) or the interference of  $\text{HNO}_4$  (see Sect. 6).





**Large mixing ratios  
of HONO at  
Concordia in summer**

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

2013, 2014). The radicals (OH and RO<sub>2</sub>) were measured using chemical ionisation mass spectrometry (Kukui et al., 2012, 2014). During the campaign the photolysis rate of HONO was documented using a Met-Con 2π spectral radiometer equipped with a CCD detector and a spectral range from 285 to 700 nm (see details in Kukui et al., 2014).

Different surface snow samples were collected at DC and returned to the UK to be used in irradiation experiments (see Sects. 2.3 and 4). First, the upper 12 cm of snow were collected in December 2010. Second, the upper centimetre of snow corresponding to freshly drifted snow was collected 6 December 2011. The samples were characterized by their specific surface area (SSA). Measurements were performed using an Alpine Snowpack Specific Surface Area Profiler, an instrument similar to that one described by Arnaud et al. (2011) based on the infrared reflectance technique. Briefly, a laser diode at 1310 nm illuminates the snow sample at nadir incidence angle and the reflected hemispherical radiance is measured. The hemispherical reflectance at 1310 nm is related to the SSA using the analytical relationship proposed by Khokanovsky and Zege (2004). The SSA of the drifting snow is close to 26 m<sup>2</sup> kg<sup>-1</sup>, and the upper 12 cm is 17 m<sup>2</sup> kg<sup>-1</sup>. Such values appears to be close to typical Dome C values reported in the literature (Gallet et al., 2011), suggesting that lab experiments conducted on these snow samples (see Sect. 4) may be relevant to discuss at least qualitatively natural processes occurring at DC.

The upper surface snow (from 0 to 1 cm, and from 0 to 12 cm) at DC were also sampled and analysed for major anions and cations following working conditions reported in Legrand et al. (2013). For cations (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, and NH<sub>4</sub><sup>+</sup>), a Dionex 500 chromatograph equipped with a CS12 separator column was used. For anions, a Dionex 600 equipped with an AS11 separator column was run with a quaternary gradient of eluents (H<sub>2</sub>O, NaOH at 2.5 and 100 mM, and CH<sub>3</sub>OH) allowing the determination of inorganic species (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) as well as methanesulfonate (CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>). The acidity of samples can be evaluated by the ionic balance between anions and cations

with concentrations expressed in micro-equivalents per liter ( $\mu\text{eq. L}^{-1}$ ):

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

### 2.3 Snow irradiation experiments conducted at BAS

As discussed in Sect. 5, model simulations indicate that the production of HONO from the reaction of OH with NO is far too weak to explain observations at Dome C and that an additional light driven HONO source is needed. To quantify a possible photochemical snow source of HONO, lab experiments were conducted at BAS by irradiating snow collected at DC and measuring gas-phase evolution of NO and NO<sub>2</sub> with a 2-channel chemiluminescence detector (Bauguitte et al., 2012) as deployed at DC (Frey et al., 2013, 2014) and HONO with the LOPAP that ran at DC during the 2010/2011 and 2011/2012 campaigns. A 20 cm long cylinder (6 cm inner diameter) was filled with ~ 120 g of snow inside an airtight glass reaction chamber (total length of 40 cm, 6 cm inner diameter) and put in a freezer of which the temperature was varied between -5 to -35 °C. Further details on the characteristics of the reaction chamber can be found in Meusinger et al. (2014). The reaction chamber is maintained vertically in a freezer and a 1000 W Xenon-arc lamp was put above the freezer. The snow was irradiated by directing the light axially along the tube through a quartz window, which makes up the top surface of the chamber. Chemically pure air was supplied to the chamber from a pure air generator (Ecophysics, PAG003) in which air is dried at -15 °C. To match the relative humidity of the snow under investigation and limit metamorphism the chemically pure (humid) air was dried and passed through a cold trap at the temperature of the experiment. Note that with this system and for temperatures above -30 °C, no condensation trace was observed in the tubes outflow of the chamber. The flow rate of zero air was 4.3 L 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 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 check for potential leaks. While the inlet line between the reaction chamber and the NO<sub>x</sub> analyser was several m long, the length between the outlet

of the reaction chamber and the LOPAP inlet was kept as short as possible (i.e. 25 cm). To do so the inlet of the LOPAP was arranged in the freezer. The wavelength range of the 1000 W Xenon-arc lamp (Oriental Instruments) was 200–2500 nm, modulated using filters with various cut-on points.

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

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

The interference of the LOPAP device was examined at the PSI where a gas-phase 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 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>. The synthesis gas was fed into the sampling unit of the LOPAP and the resulting LOPAP signals in presence and absence of HNO<sub>4</sub> were compared. Heating the synthesis gas to a temperature of 100 °C prior to sampling by the LOPAP allowed selective removal of HNO<sub>4</sub> 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 synthesis gas were independently monitored with a chemical ionisation mass spectrometer (CIMS), which was calibrated by using several analysers as detailed in Ulrich et al. (2012). An example of the mix-

## Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



---

**Large mixing ratios  
of HONO at  
Concordia in summer**

M. Legrand et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

ing ratios of  $\text{HNO}_4$  and HONO measured by CIMS and of the corresponding LOPAP signals in channel 1 and 2 is shown in Fig. 2. The relative amount of HONO (780 pptv) and  $\text{HNO}_4$  (1000 pptv) observed in the synthesized mixture (prior heating) is typical for this synthesis (Bartels-Rausch et al., 2011). The experiment shows the response of the signals when the heating trap used to decompose  $\text{HNO}_4$  is applied. As seen in Fig. 2, the mixing ratios of HONO,  $\text{NO}_2$ ,  $\text{H}_2\text{O}_2$  or  $\text{O}_3$  that may influence the response of the LOPAP instrument did not change upon the thermal decomposition of  $\text{HNO}_4$ . A decrease of the LOPAP signal in channel 1 is observed during the heating event, indicating that 1 ppbv of  $\text{HNO}_4$  corresponds to a signal in the LOPAP of 150 pptv. Examination of the signals of the two LOPAP channels (Fig. 2) suggests that  $\text{HNO}_4$  has been efficiently sampled in the first channel. It is well known that  $\text{HNO}_4$  efficiently decomposes to  $\text{NO}_2^-$  in acidic solutions (Regimbal and Mozurkewich, 1997), just like HONO does in the LOPAP sample unit. Based on the identical hydrolysis products, one might thus expect a rather large interference. The high sampling efficiency of HONO and potentially  $\text{HNO}_4$ , both of which have similar partitioning coefficients to acidic solutions, is driven by the fast reaction of their hydrolysis product ( $\text{NO}_2^-$ ) with the reagents in the sampling solution of the LOPAP instrument. A full characterization of the interference by  $\text{HNO}_4$  (its behaviour and quantification over a large range of concentrations, in the presence or absence of other gases) is needed to improve the use of the LOPAP in very cold atmospheres. We suggest a detailed investigation of LOPAP instrument response to different compositions of test gas mixture (i.e. with larger mixing ratios of  $\text{H}_2\text{O}_2$ ), and with an investigation of the potentially complex (non-linear) chemistry of sampled gases. At this stage we can only exclude an oxidation of the dye used in the LOPAP instrument by  $\text{HNO}_4$ , as careful inspection of the absorption spectrum of the LOPAP dye reveals no significant change during heating. Assuming the interference of HONO signal by  $\text{HNO}_4$  to be linear, one would expect an interference of  $\sim 15$  pptv in the HONO signal due to a mixing ratio of 100 pptv of  $\text{HNO}_4$ . Given the absence of measurements of the mixing ratio of  $\text{HNO}_4$  at Concordia, further experiments were



---

## Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ing (around 5:00–7:00 LT) and evening (around 20:00 LT) maxima exceeding mid-day values by some 10 pptv. Therefore, in addition to an expected more efficient photolysis of HONO during the day, the increase of the daytime boundary layer may also accounts for the observed decreased HONO mixing ratios during the day in spite of a more active snow source (see discussions in Sect. 5). Such a diurnal variability characterized by noon minimum was also observed for NO<sub>x</sub> by Frey et al. (2013) and attributed to the interplay between photochemical snow source and boundary layer dynamics.

As shown in Fig. 3, the larger HONO mixing ratios calculated for 2011/2012 (diurnal mean of  $35 \pm 5.0$  pptv) with respect to the 2010/2011 ones (diurnal mean of  $30.5 \pm 3.5$  pptv) concern both the mid-day minimum and the morning/evening maxima. The difference between the two summers is however reduced when the first week of measurements undertaken December in 2011 is removed with a lower diurnal mean ( $31.7 \pm 4.3$  pptv instead of  $35 \pm 5$  pptv over the entire measurement period, see the blue points in Fig. 3). The case of beginning of December 2011 with respect to the rest of the summer 2011/2012 is highlighted in Fig. 3. It can be seen that the far thinner PBL height of early December (maximum of 145 m instead of 350 m over the entire period) may have lead to a more confined HONO production (see violet points in Fig. 3). Note also the relatively high ozone mixing ratios at that time ( $33 \pm 4$  ppbv in early December instead of  $26 \pm 1$  ppbv over the entire period). Conversely, at the end of the period the PBL became thicker (maximum of 570 m) and the mixing ratios of ozone ( $24 \pm 1$  ppbv) and nitrous acid ( $31 \pm 4$  pptv) were lower than on average (see red points in Fig. 3). Finally, early December 2011 the highest daily average mixing ratio of HONO was observed 7 and 8 December (56 pptv, Fig. 1) correspond not only to a thin PBL but also to lowest value of total ozone column (260 DU instead of  $296 \pm 20$  DDU on average) measured by the SAOZ at DC. Similarly, during the 2010/2011 campaign the highest values reported at the end of the campaign (44 pptv from 15 to 18 January) by Kerbrat et al. (2012) correspond to the lowest value of total ozone column (270 DU instead of  $303 \pm 17$  DDU on average). It therefore seems that HONO mixing ratios measured at 1 m at DC are also sensitive to the UV actinic flux reaching the surface. This link be-

tween stratospheric ozone and photochemistry of snow at the ground is discussed in more detail by Frey et al. (2014).

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

As already discussed by Kerbrat et al. (2012) (see also Sect. 5), the existence of a large photochemical source of HONO in the snow-pack is needed to explain these large mixing ratios of HONO measured above the snowpack. Measurements of the mixing ratio of HONO were therefore performed in snow interstitial air at different depths. From the top few cm of the snowpack down to 75 cm depth, mixing ratios of HONO in snowpack interstitial air tended to exceed those in the air above the snowpack, supporting the existence of a snow source of HONO (Fig. 4). However, given the interference of  $\text{HNO}_4$  on HONO mixing ratio data as discussed in Sect. 6, it is difficult to use the observed vertical gradient of HONO mixing ratio to derive an estimate of emission of HONO from the snowpack. Indeed, typical values of  $\text{HNO}_4$  mixing ratios are available in lower atmosphere of the Antarctic plateau (Sect. 6) but not yet in snow interstitial air. Also it remains difficult to accurately estimate the production rate of  $\text{HNO}_4$  in snow interstitial air from the reaction of  $\text{NO}_2$  with  $\text{HO}_2$  vs. its uptake on natural ice surface.

To confirm the snowpack as a source of HONO (and as detailed in the following section) we carried out a laboratory experiment to evaluate the ratio of HONO to  $\text{NO}_x$  released from natural surface snows collected at DC under controlled laboratory conditions (i.e. wavelength of light, temperature, snow specific area) to estimate the HONO snow emission flux relative to the snow emission flux of  $\text{NO}_x$  for the same snowpack

## Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



as derived from atmospheric concentration vertical gradient measured during the campaign by Frey et al. (2014).

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

Table 1 summarized the results of experiments conducted at BAS by irradiating surface snows collected at Dome C (see Sect. 2.3).  $\text{NO}_x$  and HONO are produced when snow is irradiated. Several laboratory experiments were conducted to investigate the wavelength, temperature and snow chemical composition dependence of HONO release from snow. Similar to previous laboratory experiments conducted by Cotter et al. (2003) on surface snows collected in coastal Antarctica, the  $\text{NO}_x$  release is found to halve when the optical filter in the front of the irradiation lamp (cut off for  $< 295 \text{ nm}$ ) is replaced by a cut off filter for illumination wavelength smaller than  $320 \text{ nm}$  (Table 1). Cotter et al. (2003) demonstrated no measurable emission of  $\text{NO}_x$  from the snow when illuminated with a lamp with wavelengths shaded below  $345 \text{ nm}$ , being consistent with  $\text{NO}_3^-$  photolysis. Figure 5 illustrates the wavelength dependence of HONO release showing the effect of insertion of a filter with different cut-on points. Similarly to the  $\text{NO}_x$ , the HONO release is decreased by a factor two when inserting the filter at  $320 \text{ nm}$  and become insignificant at  $385 \text{ nm}$  (Table 1).

While the observed wavelength dependency of the  $\text{NO}_x$  release supports the hypothesis that the photolysis of nitrate present in snow is the major source of released  $\text{NO}_x$  (via its major channel:  $\text{NO}_3^- + h\nu \rightarrow \text{NO}_2 + \text{O}^-$ ), for HONO it is still unclear if either the nitrate photolysis efficiently produces directly HONO from hydrolysis of  $\text{NO}_2^-$  produced by the second channel of the nitrate photolysis ( $\text{NO}_3^- + h\nu \rightarrow \text{NO}_2^- + \text{O}$ ) or HONO is secondary produced from  $\text{NO}_2$  (Villena et al., 2011). Indeed, lab experiments conducted on nitrate doped ice suggest that the first channel is a factor of 8–9 more efficient than the second one. It is suspected that the HONO production may be significantly higher than it is when considering this second channel since the  $\text{NO}_2$  produced by the first channel may subsequently acts as a precursor of HONO. The wavelength depen-

### Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





---

## Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

10 Among possible secondary productions it is generally accepted that the reduction of NO<sub>2</sub> on photo-sensitized organic material like humic acid (George et al., 2005; Bartels-Rausch et al., 2010) would proceed more efficiently than the disproportionation reaction of NO<sub>2</sub> (2NO<sub>2</sub> + H<sub>2</sub>O → HONO + HNO<sub>3</sub>) (Finlayson-Pitts et al., 2003).  
15 As discussed by Grannas et al. (2007), the relevance of this secondary production was supported even for Antarctica by the significant presence of dissolved fulvic acid reported for Antarctic snow (26–46 ppb C) by Calace et al. (2005). However, the previously assumed ubiquitous presence of organics in polar snow that is needed to reduce NO<sub>2</sub> into HONO was recently reviewed by Legrand et al. (2013) who found that organics (and humic acids) are far less abundant in Antarctica compared to Greenland or mid-latitude glaciers like the Alps. For instance, the typical dissolved organic content of summer surface snow is only 10–27 ppb C at Concordia (Legrand et al., 2013) against 110±45 ppb C at Summit and 300 ppb C in the Alps. Furthermore, recent HULIS measurements of surface snows collected at DC do not confirm the previously  
20 observed abundance (2 ppb C instead of 26–46 ppb C). From lab experiments conducted by irradiating ice films containing humic acid in the presence of NO<sub>2</sub>, Bartels-Rausch et al. (2010) derived production rates of HONO from NO<sub>2</sub>. From that the authors roughly estimated light driven HONO fluxes of 10<sup>13</sup> molecule m<sup>-2</sup> s<sup>-1</sup> from snow covered surface area assuming the presence of 100 pptv NO<sub>2</sub> in the snow interstitial air and a concentration of 10 ppb C of humic acid in snow. Keeping in mind uncertainties in  
25 extrapolating lab experiments to conditions relevant to the lower atmosphere at Dome C, with typical NO<sub>2</sub> mixing ratios of 1 to 10 ppbv in interstitial air at 10 cm below the surface at Dome C (Frey et al., 2014), the presence of 2 ppb C of HULIS in snow may still lead to a significant HONO production from NO<sub>2</sub> at the site.



---

## Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



state calculations indicate that under noon conditions encountered at DC (a  $J_{\text{HONO}}$  value of  $3.7 \times 10^{-3} \text{ s}^{-1}$ ,  $5 \times 10^6 \text{ OH rad. cm}^{-3}$  (Kukui et al., 2014), and 50 pptv of NO (Frey et al., 2014)), a HONO mixing ratio of 1 pptv is expected. Steady-state calculated diurnal HONO profile (Fig. 6) suggests a HONO maximum of 2.5 pptv at 19:00 LT due to the presence of a maximum of 120 pptv of NO (Frey et al., 2014). Nevertheless, an additional source of HONO is obviously required to account for observed mixing ratios of a few tens of pptv.

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

We used the MAR model with a horizontal resolution of 20 km centred at Concordia; a top level is at 1 hPa with 100 vertical levels. The vertical resolution is 0.9 m up to 23 m above the surface, and decreases upward. MAR  $K_z$  values are linearly interpolated to the vertical grid used in our 1-D simulation, spacing 0.1 m from the ground to 5 m, 0.2 m from 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 1200 m height, respectively. MAR data above a height of 1200 m were not used here since during investigated period the top of the PBL remained below this value. The MAR model uses primitive equations with the hydrostatic assumption. A description of the model that has been validated with respect to observations from Automatic Weather Station at DC, is given by Gallée and Gorodetskaya (2008) and references therein. Briefly the turbulence scheme is based on an E-e scheme and on

---

**Large mixing ratios  
of HONO at  
Concordia in summer**

M. Legrand et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

the Monin–Obukhov Similarity theory (MOST), outside and inside the lowest model layer of MAR, respectively. MAR simulations have been recently validated for winter with respect to observations from Automatic Weather Station at Concordia (Gallée and Gorodetskaya, 2008) and for summer (Gallée et al., 2014). The boundary layer (PBL) height was computed from MAR simulations by taking the height where the turbulent kinetic energy decreases below 5 % of the value of the lowest layer of the model.

In Fig. 6 we report the simulated diurnal cycle of HONO mixing ratio at 1 m above the ground at Concordia when a photochemical snow release of HONO is applied. The HONO flux used in these calculations was obtained by multiplying the values of the  $\text{NO}_x$  snow emission flux derived from field observations at Concordia (Frey et al., 2014) by the temperature dependent factor reported for surface snow in Table 1. Since, as discussed in Sect. 4, lab experiments indicate no significant change of the ratio of HONO/ $\text{NO}_x$  release when replacing the filter with a 295 nm cut-on point by the one at 320 nm (Table 1), and given a maximum of the aqueous absorption cross section for nitrate centered at 300 nm (Gaffney et al., 1992), we have assumed that the ratio is similar under the two wavelength conditions and used the temperature dependency found when the filter with a cut-off point at 295 nm was inserted (Table 1). In this way under temperature conditions encountered at Dome C we have assumed a HONO/ $\text{NO}_x$  ratio ranging from 0.57 during the day (at  $-25^\circ\text{C}$ ) and 0.3 at night (at  $-35^\circ\text{C}$ ). The derived HONO snow emission flux estimate would represent an upper limit since, as seen in Sect. 4, the upper 12 cm of snow emits less HONO than  $\text{NO}_x$  compared to the surface snow. As seen in Fig. 6, using this upper estimate of the HONO snow emission (mean diurnal value of  $0.8 \times 10^9 \text{ molecules cm}^{-2} \text{ s}^{-1}$ ) simulations show that, in addition to around 1.2 pptv of HONO produced by the NO oxidation, the HONO snow emissions can account for 10.5 pptv of HONO in the atmosphere at Concordia. Assuming a lower HONO to  $\text{NO}_x$  ratio of snow emissions as suggested by the experiment conducted with the upper 12 cm of snow collected at Concordia (Table 1), mean diurnal HONO emission of  $0.5 \times 10^9 \text{ molecules cm}^{-2} \text{ s}^{-1}$  is estimated leading to a related HONO mixing ratio of 6.5 pptv (total of 8 pptv together with NO oxidation). It has also to be empha-

sized that these estimated HONO snow emission fluxes were derived from values of the HONO/NO<sub>x</sub> photochemical production ratio observed in laboratory experiments carried out by flowing zero air through the snow instead of natural interstitial air of which the chemical composition may be very different.

5 An upper value of the ratio of HONO to NO<sub>x</sub> mixing ratios often serves as a reference value to discuss the consistency of HONO mixing ratios (Kleffmann and Wiesen, 2008; Villena et al., 2011). Steady-state calculations indicate that the HONO/NO<sub>x</sub> ratio reaches a maximum value equal to the ratio of HONO to NO<sub>x</sub> lifetimes ( $\tau_{\text{HONO}}/\tau_{\text{NO}_x}$ ),  
10 when it is assumed that HONO is the solely source of NO<sub>x</sub>. The measured HONO photolysis rate constants (see Sect. 2.2) indicate an atmospheric lifetime of HONO at Concordia ranging from 4.5 min to 24 min at 12:00 LT and 00:00 LT, respectively. Using OH and HO<sub>2</sub> concentrations observed by Kukui et al. (2014), an atmospheric lifetime of NO<sub>x</sub> ranging from 3 h at 12:00 LT to 7 h at 00:00 LT can be estimated. From that, the upper limit of the HONO/NO<sub>x</sub> ratio at Concordia would be close to 0.03 and 0.06  
15 at 12:00 LT and 00:00 LT, respectively. Using the HONO mixing ratios simulated when a mean diurnal HONO snow emission of  $0.8 \times 10^9 \text{ molecules cm}^{-2} \text{ s}^{-1}$  is considered (Fig. 6) and NO<sub>x</sub> mixing ratios observed at Concordia (around 200 pptv, Frey et al., 2014), we calculate a mean diurnal HONO/NO<sub>x</sub> ratio of 0.06. This value slightly exceeds the maximum steady state HONO/NO<sub>x</sub> ratio estimated from HONO and NO<sub>x</sub>  
20 photochemical lifetimes. Note, however, that more accurate estimation of the upper limit of the HONO/NO<sub>x</sub> ratio should take into account also HONO and NO<sub>x</sub> vertical distributions determined by the vertical diffusivity and the conversion of HONO to NO<sub>x</sub>, as well as by a possibility of non steady state conditions. As the consideration of these factors may lead to a higher HONO/NO<sub>x</sub> ratio, the higher HONO/NO<sub>x</sub> ratio of about 0.06  
25 cannot be considered as a strong indication of an error in the simulated HONO mixing ratios derived with an assumed HONO snow emission of  $0.8 \times 10^9 \text{ molecules cm}^{-2} \text{ s}^{-1}$ .

## Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





---

**Large mixing ratios  
of HONO at  
Concordia in summer**M. Legrand et al.

---

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

the absence of HNO<sub>4</sub> atmospheric data at Dome C hampers any accurate attempt to correct HONO data from the presence of HNO<sub>4</sub>. Instead, field experiments were conducted at Concordia heating the air sampled by the LOPAP to thermally decompose HNO<sub>4</sub>. This air was heated by sucking air through a 8 m long PFA tube covered with a temperature controlled heating tape and placed in an insulated box. When heating the tube, the air temperature in the PFA tube was of 37 °C leading to a lifetime of HNO<sub>4</sub> with respect to its thermal decomposition of 3.2 s (Sanders et al., 2011). The experiment was performed by running the LOPAP for ~ 20 min with and without heating the tube connected to the inlet of the LOPAP. In order to account for possible fast natural change of HONO mixing ratios the test was repeated three times successively. A systematic drop of HONO values was observed. Given the applied air sampling flow rate of 1.78 L min<sup>-1</sup> (1 L STP min<sup>-1</sup>), the residence time of the air in the tube is 3.3 s. If attributed to the thermal decomposition of HNO<sub>4</sub> during the heating (64 % under these working conditions), the mean observed drop of 5.5 pptv of HONO would correspond to an HNO<sub>4</sub> artefact of around 9 pptv.

This indirect estimation of an overestimation of HONO measurements due to the presence of HNO<sub>4</sub> is consistent with experiences conducted at PSI if the presence of 50–100 pptv of HNO<sub>4</sub> is assumed at Dome C. On the other hand, the difference between observed and simulated HONO mixing ratios presented in Sect. 5 suggests an overestimation close to 20 pptv. Finally, in their discussions of the observed levels of HO<sub>x</sub> radicals, Kukui et al., (2014) found that the consideration of 30 pptv of HONO is inconsistent with radical observations leading to about 2 times overestimation of RO<sub>2</sub> and OH concentrations. Conversely, neglecting the OH production from HONO leads to an underestimation of radical levels by a factor of 2. Kukui et al. (2014) showed that a quite fair agreement with OH measurements is achieved with HONO mixing ratios derived from the 1-D modelling with a HONO snow emission flux equal to about 30 % of that of NO<sub>x</sub>.

## 7 Conclusions

This second study of HONO conducted in the atmosphere of the East Antarctic plateau by deploying a LOPAP confirms unexpectedly high mixing ratios close to 30 pptv. A mixing ratio of 8–12 pptv can be rationalized based on emissions of HONO from snow of 0.5–0.8 × 10<sup>9</sup> molecules cm<sup>-2</sup> s<sup>-1</sup> derived from studies of the irradiation experiments surface snow collected from Concordia and scaled down to the NO<sub>x</sub> emissions derived from observations made at DC by Frey et al. (2014). Experiments conducted in the field and in the lab to identify the cause of such a discrepancy point to a possible overestimation of HONO in the range of 10 to 20 pptv due to the important presence of HNO<sub>4</sub> in this cold atmosphere. An accurate correction of the HONO data from the presence of HNO<sub>4</sub> is not yet possible. Further work, both in the lab to quantify the interference at different levels of HNO<sub>4</sub> and in the presence of various other species and in the field at Concordia to obtain mixing ratios of HONO and HNO<sub>4</sub> at the same time are needed.

*Acknowledgements.* The OPALE project was funded by the ANR (Agence National de Recherche) contract ANR-09-BLAN-0226. The measurement of the specific snow area was developed in the framework of the MONISNOW projet funded by the ANR-11-JS56-005-01contract. National financial support and field logistic supplies for the summer campaign were provided by Institut Polaire Français-Paul Emile Victor (IPEV) within programs No. 414, 903, and 1011. M. D. King was supported by NERC NE/F0004796/1 and NE/F010788, NERC FSF grants 555.0608 and 584.0609. Thanks to our Italian colleagues from Meteo-Climatological Observatory of PNRA for the meteorological data collected at Dome C.

## 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. Glaciol.*, 57, 17–29, 2011.

ACPD

14, 11749–11785, 2014

### Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





## Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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.

5 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, 989–1002, doi:10.5194/acp-12-989-2012, 2012.

Beine, H. J., Amoroso, A., Dominé, F., King, M. D., 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, doi:10.5194/acp-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, 441–446, doi:10.1016/0009-2614(76)85010-5, 1976.

20 Chen, G., Davis, D., Crawford, J., Nowak, J. B., Eisele, F., Mauldin, R. L., Tanner, D., Buhr, M., Shetter, R., Lefer, B., Arimoto, R., Hogan, A., and Blake, D.: An investigation of South Pole HO<sub>x</sub> chemistry: comparison of model results with ISCAT observations, *Geophys. Res. Lett.*, 28, 3633–3636, 2001.

25 Chen, G., Davis, D., Crawford, J., Mauldin III, R., Eisele, F., Huey, G., Slusher, D., Tanner, D., Dibb, J., Buhr, M., Hutterli, M., McConnell, J., Lefer, B., Shetter, R., Blake, D., Lombardi, K., and Arnoldy, J.: A reassessment of HO<sub>x</sub> South Pole chemistry based on observations recorded during ISCAT 2000, *Atmos. Environ.*, 38, 5451–5461, doi:10.1016/j.atmosenv.2003.07.018, 2004.

30 Cotter, E. S. N., Jones, A. E., Wolff, E. W., and Bauguitte, S. J.-B.: What controls photochemical NO and NO<sub>2</sub> production from Antarctic snow? Laboratory investigation as-

**Large mixing ratios  
of HONO at  
Concordia in summer**

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



sessing the wavelength and temperature dependence, *J. Geophys. Res.*, 108, D04147, doi:10.1029/2002JD002602, 2003.

Crowley, J. N., Ammann, M., Cox, R. A., Hynes, R. G., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume V – heterogeneous reactions on solid substrates, *Atmos. Chem. Phys.*, 10, 9059–9223, doi:10.5194/acp-10-9059-2010, 2010.

Davis, D., Nowak, J. B., Chen, G., Buhr, M., Arimoto, R., Hogan, A., Eisele, F., Mauldin, L., Tanner, D., Shetter, R., Lefer, B., and McMurry, P.: Unexpected high levels of NO observed at South Pole, *Geophys. Res. Lett.*, 28, 3625–3628, doi:10.1029/2000GL012584, 2001.

Dibb, J. E., Arsenault, M., Peterson, M. C., and Honrath, R. E.: Fast nitrogen oxide photochemistry in Summit, Greenland snow, *Atmos. Environ.*, 36, 2501–2511, doi:10.1016/S1352-2310(02)00130-9, 2002.

Dibb, J. E., Huey, L. G., Slusher, D. L., and Tanner, D. J.: Soluble reactive nitrogen oxides at South Pole during ISCAT 2000, *Atmos. Environ.*, 38, 5399–5409, 2004.

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

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

France, J. L., King, M. D., Frey, M. M., Erbland, J., Picard, G., Preunkert, S., MacArthur, A., and Savarino, J.: Snow optical properties at Dome C (Concordia), Antarctica; implications for snow emissions and snow chemistry of reactive nitrogen, *Atmos. Chem. Phys.*, 11, 9787–9801, doi:10.5194/acp-11-9787-2011, 2011.

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

Frey, M. M., Brough, N., Roscoe, H., Kukui, S., Savarino, J., Legrand, M., and Preunkert, S.: Drivers of atmospheric nitrogen oxide emissions from snow above the Antarctic Plateau in

---

**Large mixing ratios  
of HONO at  
Concordia in summer**

---

M. Legrand et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

summer: sensitivity to stratospheric ozone and impact on ozone production, *Atmos. Chem. Phys.*, this issue, 2014.

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

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

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

10 Gallée, H., Preunkert, S., Jourdain, B., Argentini, S., Frey, M., Genthon, C., and Legrand, M.: Characterization of the boundary layer at Dome C during OPALÉ, *Atmos. Chem. Phys.*, this issue, 2014.

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

Grannas, A. M., Jones, A. E., Dibb, J., Ammann, M., Anastasio, C., Beine, H. J., Bergin, M., Bottenheim, J., Boxe, C. S., Carver, G., Chen, G., Crawford, J. H., Dominé, F., Frey, M. M., Guzmán, M. I., Heard, D. E., Helmig, D., Hoffmann, M. R., Honrath, R. E., Huey, L. G., Hutterli, M., Jacobi, H. W., Klán, P., Lefer, B., McConnell, J., Plane, J., Sander, R., Savarino, J., Shepson, P. B., Simpson, W. R., Sodeau, J. R., von Glasow, R., Weller, R., Wolff, E. W., and Zhu, T.: An overview of snow photochemistry: evidence, mechanisms and impacts, *Atmos. Chem. Phys.*, 7, 4329–4373, doi:10.5194/acp-7-4329-2007, 2007.

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

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

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

---

**Large mixing ratios  
of HONO at  
Concordia in summer**

---

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- Jones, A. E., Weller, R., Wolff, E. W., and Jacobi, H.-W.: Speciation and rate of photochemical NO and NO<sub>2</sub> production in Antarctic snow, *Geophys. Res. Lett.*, 27, 345–348, 2000.
- Kerbrat, M., Legrand, M., Preunkert, S., Gallée, H., and Kleffmann, J.: Nitrous Acid at Concordia on the East Antarctic Plateau and its transport to the coastal site of Dumont d'Urville, *J. Geophys. Res.*, 117, D08303, doi:10.1029/2011JD017149, 2012.
- Kirchstetter, T. W., Harley, R. A., and Littlejohn, D.: Measurement of nitrous acid in motor vehicle exhaust, *Environ. Sci. Technol.*, 30, 2843–2849, doi:10.1021/es960135y, 1996.
- Kleffmann, J. and Wiesen, P.: Technical Note: Quantification of interferences of wet chemical HONO LOPAP measurements under simulated polar conditions, *Atmos. Chem. Phys.*, 8, 6813–6822, doi:10.5194/acp-8-6813-2008, 2008.
- Kleffmann, J., Heland, J., Kurtenbach, R., Lorzer, J., and Wiesen, P.: A new instrument (LOPAP) for the detection of nitrous acid (HONO), *Environ. Sci. Pollut. R.*, 4, 48–54, 2002.
- Kokhanovsky, A. A. and Zege, E. P.: Scattering optics of snow, *Appl. Optics*, 43, 1589–1602, 2004.
- Kukui, A., Legrand, M., Ancellet, G., Gros, V., Bekki, S., Sarda-Estève, R., Loisil, R., and Preunkert, S.: Measurements of OH and RO<sub>2</sub> radicals at the coastal Antarctic site of Dumont d'Urville (East Antarctica) in summer, *J. Geophys. Res.*, 117, D12310, doi:10.1029/2012JD017614, 2012.
- Kukui, A., Legrand, M., Preunkert, S., Frey, M., Loisil, R., Gil Roca, J., Jourdain, B., King, M., France, J., and Ancellet, G.: OH and RO<sub>2</sub> measurements at Dome C, East Antarctica, *Atmos. Chem. Phys.*, this issue, 2014.
- Kurtenbach, R., Becker, K. H., Gomes, J. A. G., Kleffmann, J., Lorzer, J. C., Spittler, M., Wiesen, P., Ackermann, R., Geyer, A., and Platt, U.: Investigations of emissions and heterogeneous formation of HONO in a road traffic tunnel, *Atmos. Environ.*, 35, 3385–3394, doi:10.1016/s1352-2310(01)00138-8, 2001.
- Legrand, M., Preunkert, S., Jourdain, B., Gallée, H., Goutail, F., Weller, R., and Savarino, J.: Year round record of surface ozone at coastal (Dumont d'Urville) and inland (Concordia) sites in East Antarctica, *J. Geophys. Res.*, 114, D20306, doi:10.1029/2008JD011667, 2009.
- Legrand, M., Preunkert, S., Jourdain, B., Guilhermet, J., Faïn, X., Alekhina, I., and Petit, J. R.: Water-soluble organic carbon in snow and ice deposited at Alpine, Greenland, and Antarctic sites: a critical review of available data and their atmospheric relevance, *Clim. Past*, 9, 2195–2211, doi:10.5194/cp-9-2195-2013, 2013.



**Large mixing ratios  
of HONO at  
Concordia in summer**

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

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

Mauldin III, R. L., Eisele, F. L., Cantrell, C. A., Kosciuch, E., Ridley, B. A., Lefer, B., Tanner, D. J., Nowak, J. B., Chen, G., Wang, L., and Davis, D.: Measurements of OH aboard the ASA P-3 during PEM-Tropics B, *J. Geophys. Res.*, 106, 32657–32666, 2001b.

Meusinger, C., Berhanu, T. A., Erbland, J., Savarino, J., and Johnson, M. S.: Laboratory study of nitrate photolysis in Antarctic snow, Part 1: Observed quantum yield, domain of photolysis and secondary chemistry, *J. Chem. Phys.*, submitted, 2014.

Preunkert, S., Ancellet, G., Legrand, M., Kukui, A., Kerbrat, M., Sarda-Estève, R., Gros, V., and Jourdain, B.: Oxidant Production over Antarctic Land and its Export (OPALE) project: an overview of the 2010–2011 summer campaign, *J. Geophys. Res.*, 117, D15307, doi:10.1029/2011JD017145, 2012.

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

Sander, S. P., Abbatt, J., Barker, J. R., Burkholder, J. B., Friedl, R. R., Golden, D. M., Huie, R. E., Kolb, C. E., Kurylo, M. J., Moortgat, G. K., Orkin, V. L., and Wine, P. H.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17, JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, available at: <http://jpldataeval.jpl.nasa.gov> (last access: 10 June 2011), 2011.

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

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

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

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

**Large mixing ratios  
of HONO at  
Concordia in summer**

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

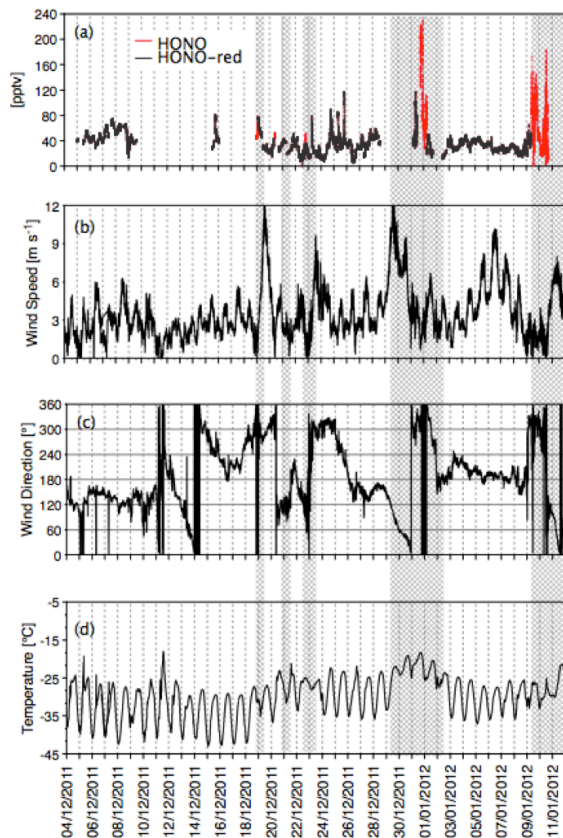
Printer-friendly Version

Interactive Discussion



**Table 1.** Results of irradiation experiments performed at the BAS laboratory on three different surface snows collected at Concordia. S1 and S2 are upper surface snows collected between 0 and 1 cm, S3 is the surface snow collected between 0 and 12 cm depth. The acidity is calculated by checking the balance between anions and cations (see Sect. 2.2). DL refers to detection limit and N.C. means non-calculated value.

Snow type	Date in 2013	Wavelengths $\lambda$ >	$T$ (°C)	HONO (pptv)	NO <sub>x</sub> (pptv)	HONO/NO <sub>x</sub>	NO <sub>3</sub> <sup>-</sup> (ppb)	H <sup>+</sup> (μeq. L <sup>-1</sup> )
S1	23 Jan	295 nm	-15	117 ± 5	137 ± 20	0.85 ± 0.1	1428	29.4
S1	24 Jan	295 nm	-15.5	120 ± 3	129 ± 16	0.93 ± 0.1	1428	29.4
S1	24 Jan	320 nm	-16	47 ± 1	67 ± 12	0.70 ± 0.1	1428	29.4
S1	24 Jan	385 nm	-16	< 3	< DL	N.C.	1428	29.4
S2	23 Apr	295 nm	-13	124 ± 1	162 ± 14	0.77 ± 0.1	1344	24.0
S2	23 Apr	295 nm	-22.5	86 ± 3	167 ± 40	0.52 ± 0.1	1344	24.0
S2	23 Apr	295 nm	-34	56 ± 1	210 ± 50	0.27 ± 0.2	1344	24.0
S3	25 Apr	295 nm	-21	15 ± 2	47 ± 27	0.32 ± 0.15	157	4.0



**Fig. 1.** Summer 2011/2012 time series of HONO mixing ratios (one minute average) **(a)**, wind conditions **(b and c)** and temperatures **(d)** at Concordia. Red points of the HONO record refer to time periods during which contamination from the station was possible with the wind was blowing from North (from 10° W to 60° E sector, see Sect. 2.2). Grey backgrounds indicate time period of overcast weather.

Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

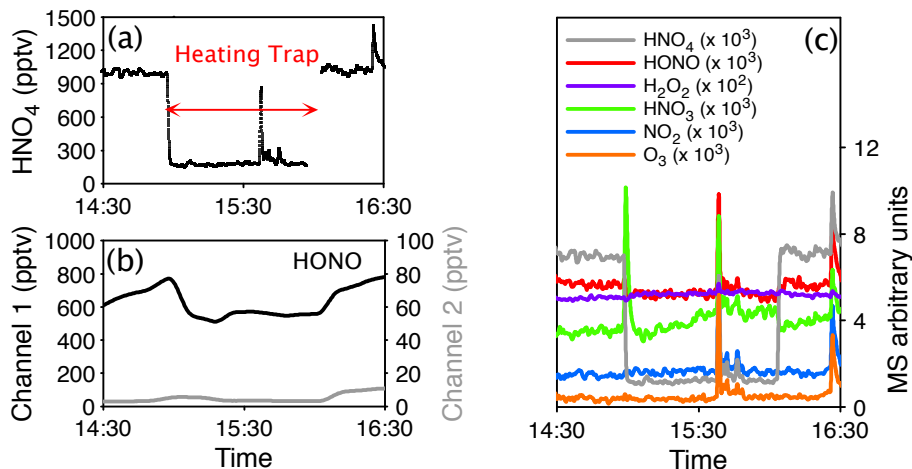
Interactive Discussion





## Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.



**Fig. 2.** The experiment carried out at the PSI laboratory in view to investigate the interference of  $\text{HNO}_4$  on HONO measurements made with the LOPAP deployed during the two Concordia campaigns. Left: time traces of  $\text{HNO}_4$  (top) and of the two LOPAP channels (bottom). Time at which the heating trap was activated is shown with a red horizontal arrow. Right: intensities of  $\text{NO}_2$ , HONO,  $\text{HNO}_3$ ,  $\text{HNO}_4$ ,  $\text{O}_3$ , and  $\text{H}_2\text{O}_2$  traces as detected by the mass spectrometer (see Sect. 2.4). Heating the gas mixture to  $100^\circ\text{C}$  leads to a sharp decrease in  $\text{HNO}_4$  and a small increase of  $\text{HNO}_3$  intensities.  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  remain stable whereas a very small decrease of HONO is detectable.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

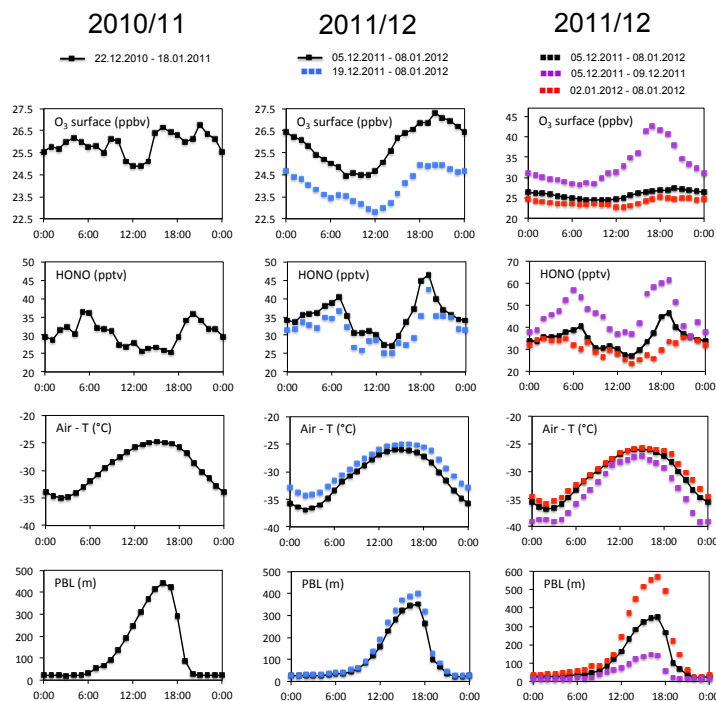
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

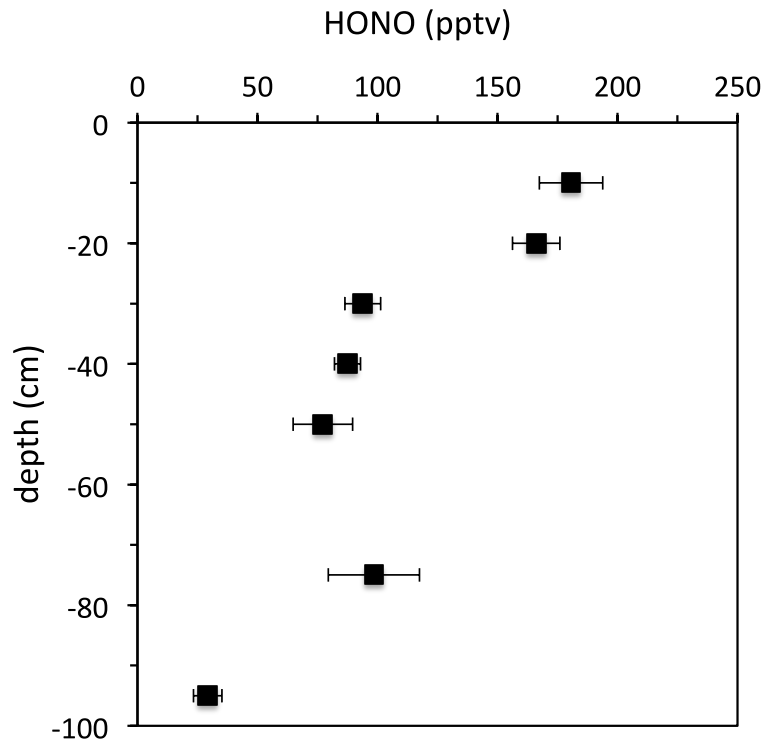
## Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.



**Fig. 3.** Left and central: from top to bottom, diurnal changes of surface ozone mixing ratio, HONO mixing ratio, air temperature and PBL height simulated by the MAR model (see Sect. 5) at Concordia over the entire period of measurements in 2010/2011 (left) and 2011/2012 central (black dots). The blue dots reported for the 2011/2012 summer correspond to the period between 19 December 2011 and 8 January 2012. Right: same as left and central but for the entire 2011/2012 period (black dots), at the beginning (early December, violet dots) and the end (red dots) of the period. Note the use of different vertical scales for right compared to left and central panels.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)



**Fig. 4.** Firn air mixing ratios of HONO down to 1 m depth measured at Concordia at 13 January 2012.

**Large mixing ratios of HONO at Concordia in summer**

M. Legrand et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

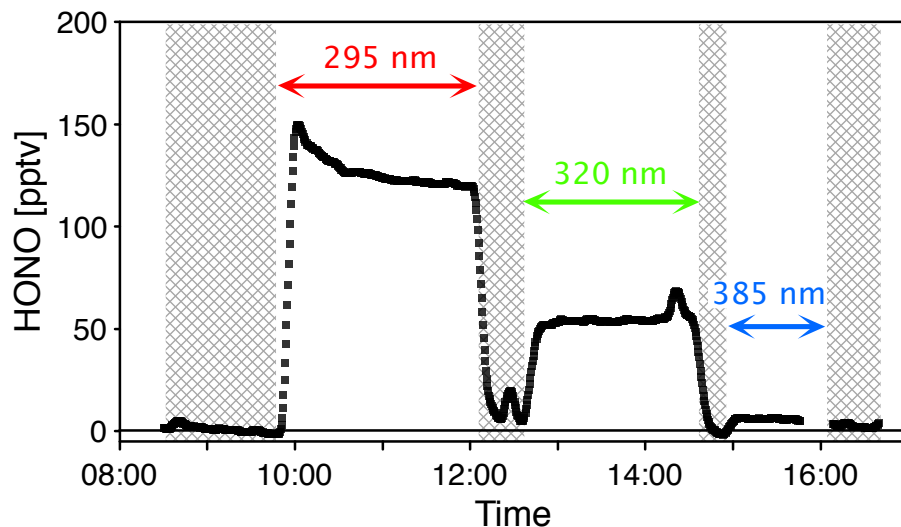
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Interactive Discussion



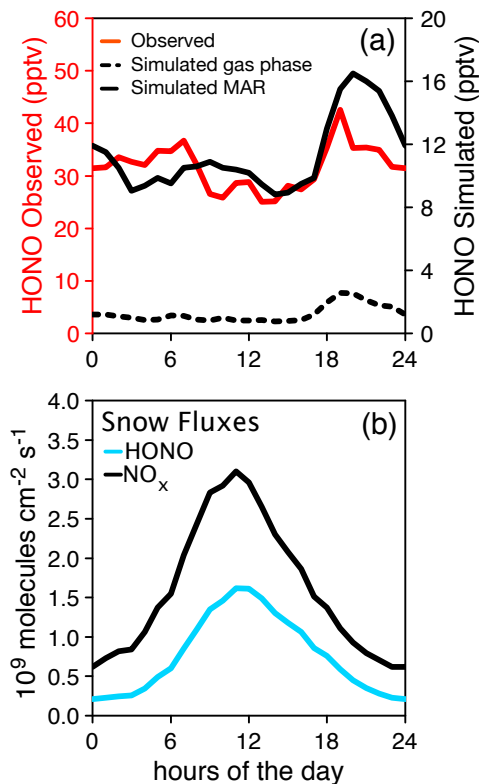
## Large mixing ratios of HONO at Concordia in summer

M. Legrand et al.



**Fig. 5.** Photochemical release of HONO from a surface snow collected at Concordia when irradiating it at a temperature of  $-16^{\circ}\text{C}$  (see Table 1) and inserting filters with cut-on points at 295 nm, 320 nm, and 385 nm on the Xenon-arc lamp (see Sect. 4). Vertical grey bands correspond to periods over which the lamp was switched off.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



**Fig. 6.** (a) Measured (red line) vs. simulated (black lines) (see Sect. 5) diurnal cycles of HONO mixing ratio at 1 m height. Note the use of a different vertical scale for observations (left) and simulations (right). The black dashed line is the simulation made when considering only the gas phase production of HONO from NO (without snow emissions). (b) Diurnal NO<sub>x</sub> snow source derived from field observations at Concordia (Frey et al., 2014) together with an estimated emission of HONO from snow based on laboratory snow irradiation experiments (see Sect. 4).