

***Interactive comment on* “Small HONO emissions from snow surfaces at Browning Pass, Antarctica” by H. J. Beine et al.**

Anonymous Referee #2

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General comments:

The paper describes first selective gas phase measurements of nitrous acid in Antarctica with a highly sensitive instrument. Gradient measurements show very low fluxes of HONO from the snow surface, although the conditions are favorable for the photochemical formation, based on the generally accepted photolysis of nitrate/HNO₃ in the snow. Thus, these gradient measurements clearly demonstrate that the mechanism of HONO formation from snow surfaces is clearly not at all properly understood, which should be the major outcome of the present study.

The authors try to explain the different observations (i.e. no HONO formation on aged

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and fresh snow, and some HONO production after the surface was windblown) by considerations of the state of nitrate in snow and by an alternative photochemical HONO formation pathway, which was proposed in a recent laboratory study. However, the discussion is all of a highly speculative nature. For example, it is not at all clear why HONO formation is not observed for fresh snow. The authors claim that nitric acid is adsorbed on fresh snow, however, especially for adsorbed nitric acid photochemical HONO formation would be expected based on the observations from laboratory studies. In addition, the different proposed states of nitrate in snow seem to be very speculative (see special comments). Thus, the discussion should mainly highlight the existing lack of knowledge in the formation mechanism.

Special comments:

Abstract, page 616, lines 10-12:

This sentence is not clear, see discussion above and results on HONO formation from recent laboratory studies on glass surfaces (Zhou et al., 2002, 2003, Ramazan et al., 2004).

Chapter 2.1, page 618, lines 1 + 5:

If the container is 20 m away from the measurement site, the sampling lines should be at least 20 m (here, 15 m given...).

Chapter 2.1, page 618, line 12:

Please specify the pH of the sampling solution, since interferences are known for instruments, which sample HONO under alkaline conditions (see for example: Spindler, et al., 2003, Atmos. Environ., 37, 2643-2662.).

Chapter 2.1, page 618, line 14:

Change UV-vis absorption to vis absorption, since the used dye absorbs light around 540 nm.

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Chapter 2.1, page 619, lines 2-8:

The calculation of the minimum detectable difference in the HONO concentration between the two different heights should be calculated individually, since this value can be significantly higher than the detection limit of the instrument of 0.5 ppt. For example, when the difference between two values around 3 ppt (see Figure 2a) is considered, the minimum detectable difference in the HONO concentration will be higher than 1 ppt. This will probably also affect the calculation of the minimum detectable fluxes (see Figure 2c).

Chapter 2.2, page 620, line 5:

It should be: King and Simpson, 2001 (see list of references).

Chapter 3.1, page 622, lines 1-2:

Can the authors estimate the relative importance of the sources of NO (nitrite photolysis vs. NO₂ photolysis)? In contrast to the statement by the authors, most of the NO might be formed by the photolysis of NO₂, because of the much higher quantum yield for the NO₂ channel (R1) compared to the nitrite channel (R2) in the photolysis of nitrate and the short photolytic lifetime of NO₂.

Chapter 3.1, page 622, lines 15-21:

In contrast to the statement by the authors, the estimated HONO production (using the quantum yield for (R2) from the study of Dubowski et al.) might not represent the upper limit, if mechanism 3) is significant. In this case, a significant fraction of the NO₂ formed by reaction (R1), might be converted into HONO.

Chapter 3.1, page 622, lines 8-9:

In the study of George et al., HONO formation on bulk substrates was studied (it was not an aerosol study).

Chapter 3.1, page 622, line 14: Mechanism 1) does not require nitrogen oxide, since

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HONO is formed by the direct photolysis of nitrate followed by the protonation of nitrite.

Chapter 3.2, page 623, line 10:

It should be: Chu and Anastasio (2003), see list of References.

Chapter 4, Figure 2:

In Figure 2, the total field campaign is shown and from Figure 2c, the nearly non-existing HONO fluxes become obvious. However, when looking at Figure 2a more closely, a clear diurnal variation of the HONO concentration is discernible (see for example days 325-330). Thus, it would be helpful to show the concentrations of HONO and the corresponding irradiation in more detail for a shorter period. From such a figure a correlation of HONO with the irradiation is expected (compare Figures 2 and 5). This would demonstrate the photochemical sources of HONO, which should be discussed in the paper. For example, could this diurnal variation be explained by a gas phase source, if no fluxes from the snow surface are observed?

Chapter 4.1, page 624, lines 8-9:

In the study of Dibb et al. mixing ratios of up to 70 ppt (not 30 ppt) were observed (probably caused by the non-selective sampling method, i.e. mist chamber).

Chapter 4.4, pages 626-627:

The discussion about the origin of nitrate in snow is not clear. For example, in Figure 4a an excellent correlation of NO_3^- and Na^+ with no significant intercept is observed for aged snow, which is explained by the reaction of nitric acid with existing sea salt in snow. However, this can only explain the excellent correlation, if the ratio of deposited sea salt to nitric acid is almost constant and independent of time, i.e. if sea salt and nitric acid have a common origin. Otherwise, there should be a significant lower correlation or a negative intercept in Figure 4a, since the concentration of Na^+ is much higher than that of nitrate (only a small portion of the existing sea salt is replaced by nitric acid in the snow). In addition, from the lower correlation of nitrate with Na^+ in

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Figure 4b the presence of adsorbed HNO_3 in fresh snow was proposed. However, the lower correlation is most probably simply caused by the lower ion concentration for fresh snow. The correlation would also be significantly lower for aged snow, if only the low concentration data were plotted in Figure 4a. In addition, since the slopes are very similar for aged and fresh snow (0.05 vs. 0.08) the state of nitrate is probably not as clear as proposed by the authors in this section.

Chapter 4.6, page 629, line 12:

$J(\text{NO}_3^-)$ was refined by the ratio of the modelled and measured irradiance at 350 nm. However, since nitrate photolysis is most important around 300 nm (see for example Burley and Johnson) and since the diurnal variation of the irradiance is different between 300 and 350 nm, a wavelength near 300 nm should be used for the calculations.

Chapter 5.2, page 631, line 25:

Details referred to in Figure 2 are hard to identify (see also below).

Technical corrections/suggestions

Figure 2:

No detail is discernible in Figure 2. Thus, the figure might be separated into two larger figures (for example Figure 2a separated from Figures 2b and c) leading to a more detailed presentation of the data.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 615, 2006.

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