Interactive comment on

"Emission of nitrous acid from soil and biological soil crusts represents a dominant source of HONO in the remote atmosphere in Cyprus"

by Hannah Meusel et al.

Anonymous Referee #1

Overview:
In this manuscript, the authors presented laboratory-determined emission rates of HONO and NO from soil and biological soil crust samples collected from arid and semi-arid environments in Cyprus, and extrapolated the results to the ambient conditions. The data and results presented are useful and are suitable for publication in Atmospheric Chemistry and Physics. However, the authors need to address the following comments before I could recommend the acceptance of this manuscript for publication:

Comment:
I am concerned about the validity of extrapolating the laboratory results to the ambient conditions in this study. The soil and biological soil crust samples were stored at room temperature for up to 15 weeks before some of the experiments were conducted. The samples might be deteriorated during the storage, and by the time of experiments in the laboratory, their chemical (nitrite) and biological (chlorophyll and microbial population) characteristics might be quite different from those under ambient condition.

Response:
This is a very good and valid comment. Some of the authors (Dianming Wu, Alexandra Tamm, Bettina Weber) have already investigated general storage properties of biological soil crust and soil samples and their measurements showed no significant loss of chlorophyll or nitrogen compounds during 4-month storage at room temperature as long as the samples were stored dry and in the dark. Also the storage temperature (-20°C, 4°C or room temperature) had no significant effect on nutrient/chlorophyll/fluxes. The respective study will be submitted soon.
A short note was added in the manuscript (chapter 2.1):
"Based on previous experiments in our laboratory, it can be anticipated that the sample's chemical (nutrient content) and biological (chlorophyll content) properties were not deteriorated during storage (a manuscript on this study will be submitted soon)."

Comment:
Furthermore, the laboratory experimental conditions were very different from those of the ambient, e.g., air and soil temperature, humidity, and their daily cycles. And finally, while the soil was always a HONO source in the laboratory dynamic chamber since dry zero air was flowing over the soil sample, it could be a net sink for HONO in the air under ambient conditions, for example, during the morning hours when RH is high and a significant level of HONO is present.

Response:
This is a good point. Of course, in the field soil temperature varies a lot following the solar radiation, ranging from 15° to 50°C. In the lab the average ambient temperature of 25°C was chosen and kept constant. Soil humidity probably also changes following diurnal cycles of ambient RH and temperature, but during the CYPHEX campaign soil humidity was very low caused by missing precipitation events.
As shown in Su et al. (2011) and VandenBoer et al. (2015), the soil could serve either as a source or as a sink depending on the difference between the equilibrium concentration at soil surface [HONO]* and the ambient [HONO]. Thus, instead of using the flux measured in the lab, we calculated [HONO]*, compared it to the ambient concentration, and then determined the flux ($F^* = v_T \cdot([HONO]^*-[HONO])$. The soil would act as a sink

when ambient concentrations were higher than [HONO]*. This was not the case, so the soil acted as a source (during daytime).
Please see also our comment below on diel patterns.

Comment:
While there is no doubt that HONO emission from soils could be an important source of atmospheric HONO under certain conditions, the results from this study should be considered as qualitative, and the actual contribution need to be verified and determined by field studies including flux measurements under ambient conditions. Two recent such measurements suggest that soil emission was not be a significant HONO source in boreal forest (Oswald et al., 2015) and at agricultural field site (Laufs et al., 2017).

Response:
We need to point out here, that in both studies mentioned above the ecosystems were very different to the one investigated in our study. While we studied samples from a Mediterranean dryland habitat, a boreal forest (Oswald et al., 2015) and an agricultural field (Laufs et al., 2017) were investigated in the other studies.
Oswald et al. (2015) measured HONO concentrations at two different heights, observed positive and negative gradients but fluxes were not determined. Laufs et al. (2017) also determined the flux and found positive fluxes during daytime. But both studies excluded soil emission to be a major source of HONO.
In dynamic chamber experiments Oswald et al. (2015) measured the HONO and NO flux and found emissions lower than or around the detection limit of 0.08 or 1 ng m^{-2} s^{-1}. But the forest soils from Finland had much lower nutrient contents compared to our study. Furthermore, a very low pH of 3 was found, at which a low diversity of soil bacteria was observed (Fierer and Jackson, 2006) and most bacteria won´t be active. It was shown that nitrification rates are very low at pH < 4 (Persson and Wiren, 1995; Ste-Marie and Pare, 1999) while it is not so clear for denitrification rates (Simek and Cooper, 2002).
Laufs et al. (2017) only indirectly excluded biological emission, as the soil in the field had higher soil water contents than the optimum soil water content found in Oswald et al. (2013). Furthermore, they didn´t find a significant correlation to temperature or humidity, what would be expected from biological soil emission. Instead they detected a positive correlation between the HONO flux and NO_2*J.
In our samples nutrient content was high and chamber studies showed a good correlation of HONO and NO fluxes to nutrient content. The soil humidity in the field can be assumed to be about 10% whc (as was observed for soils at high relative humidity; see Likos (2008) and Leelamanie (2010)). Thus, we consider our measurements, results and interpretations as being reasonable.

Moreover, Wong et al. (2013) also demonstrated that beside flux measurements, the $HONO/NO_2$ ratio can also be used to identify a surface source or to distinguish between surface and atmospheric source, respectively. A surface source results in a more pronounced diel pattern of $HONO/NO_2$ (with a peak around noon) while an atmospheric source (aerosol surface reactions) leads to a near constant $HONO/NO_2$. During the CYPHEX campaign a clear diel pattern of $HONO/NO_2$ was observed (Fig. R1; Meusel et al., 2016), indicating a surface source. As heterogeneous NO_2 conversion was supposed to play a minor role in HONO formation (NOx levels were too low) the soil emission is likely the major source of HONO in Cyprus.

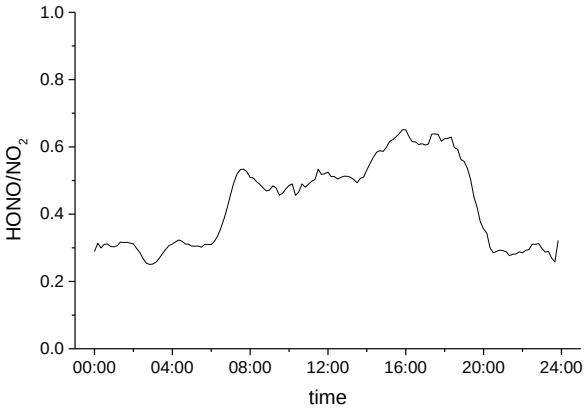

Fig R1: Mean diel course of HONO/NO2 during CYPHEX.

In the revised version of the manuscript (end of chapter 3.4) we now added: "While in Cyprus the observed soil emissions can explain high amounts of atmospheric HONO, other studies excluded soil emission to be a dominant source (Oswald et al., 2015; Laufs et al., 2017). Oswald et al. (2015) studied soil samples from a boreal forest in Finland and observed HONO emission below the detection limit. But those samples had very low nutrient contents and were highly acidic (pH ≈ 3) for which microbial activity is supposed to be low (Fierer and Jackson, 2006; Persson and Wiren, 1995; Ste-Marie and Pare, 1999; Simek and Cooper, 2002). Similarly, Laufs et al. (2017) didn´t find correlations between HONO fluxes and temperature or humidity measured in the field, and concluded that other HONO sources than biological soil emission must have been dominated. In contrast to the soil water content in Cyprus, the water contents at the field site studied by Laufs et al. (2017) were higher than the optimum soil water content presented by Oswald et al. (2013)."

Comment:

I would suggest the authors to add a figure to show diurnal plots of surface temperature and RH (from Figures 2C and 2D), extrapolated HONO and NO emission rates (from Figures 3 and 5, and RH information), and HONO and NO concentrations measured during the CYPHEX field study. Comparison of the diurnal variation patterns of extrapolated HONO flux and ambient HONO concentration should provide us with some insight into the potential importance of soil HONO emission as a HONO source over the day.

Response:

Following the reviewer's suggestion, we estimated a diel pattern of HONO fluxes and included a new figure.
When using the same correlation between HONO or NO flux and temperature as found by Oswald et al., (2013) and assuming a slight/linear diel change of soil water content at higher temperature we estimate the following diel pattern for the HONO and NO emission (Fig. R2). For a mean surface temperature ranging from 15-35°C we estimated a soil water content varying between 14 and 6 % whc (average 10% whc as described by Likos (2008) and Leelamanie (2010) for high ambient relative humidity) leading to emissions between 49 and 22% of the optimum flux. The HONO-N flux ranges from 0.5 to 7.5 ng m^{-2} s^{-1} (for the mean temperature; indicated by the orange area in the figure, left lower panel). With rising temperatures and a concurrent drop in swc, the flux increase, but has a small dip around noon. As already indicated in the original manuscript, we can convert the emission flux into a ground based source. Around noon, emissions explain about 70% of the missing HONO source. Similarly, NO emission and sources can be calculated. They are slightly lower than the HONO emission.

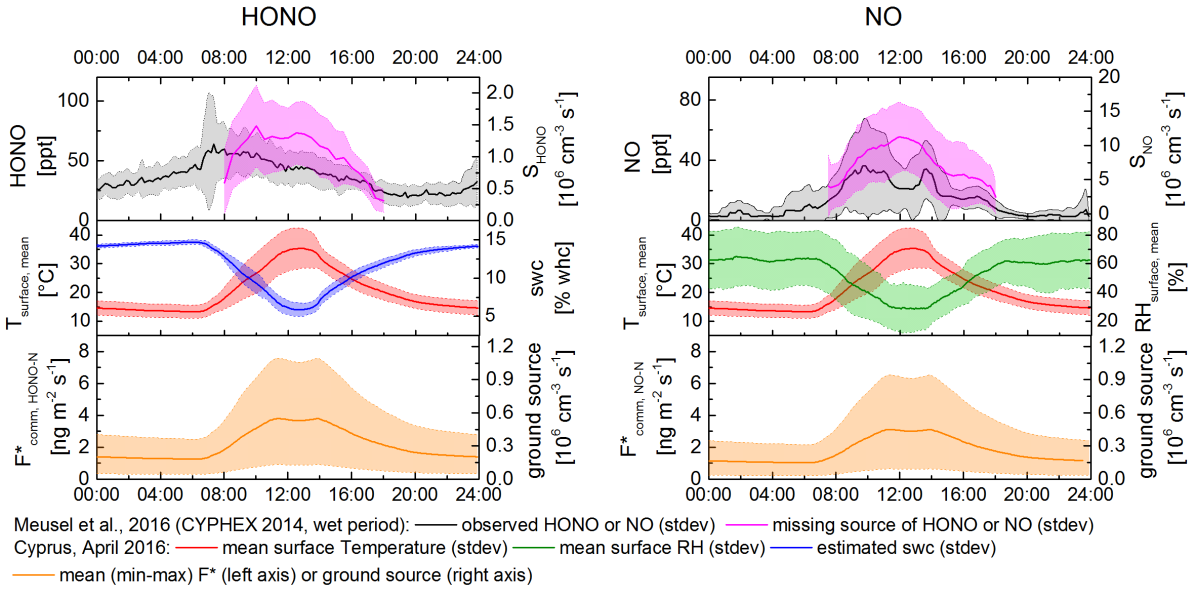

Fig. R2 (Fig. 8 in the revised manuscript): Diel pattern for HONO and NO emission in comparison with the observed HONO concentrations and missing source during the CYPHEX 2014 campaign. Upper panels: observed concentration of HONO and NO shown in black, missing source shown in pink. Middle panels: mean surface temperature and mean surface humidity measured in April 2016 in Cyprus and estimated soil water

content shown in red, green and blue, respectively. Lower panel: calculated mean F* (mean temperature) with the area indicating the lower and upper limit.

Instead of only showing the "one-point-study" in the manuscript, we changed the respective text section presenting the following thoughts and add the new figure into the manuscript (after Eq. 7):
"During the CYPHEX campaign in summer 2014 a mean boundary layer height of 300 m above ground layer was observed by means of a ceilometer. Due to missing precipitation during CYPHEX, but high relative humidity prevailing (CYPHEX 2014: 75-100%), a mean soil water content of 10% whc (at 25°C) can be estimated (Likos, 2008; Leelamanie, 2010), reducing the HONO source strength to 35% of the emission maximum at optimum swc. Integrating the lowermost versus the uppermost observed HONO emissions per soil/crust type, the emissions at 25°C and a swc of 10% whc would span a wide range between $1.1x10^5$ and $9.6x10^5$ cm^{-3} s^{-1}, covering 9 to 73% of the missing mean source of $1.3x10^6$ cm^{-3} s^{-1} observed in the field (Meusel et al., 2016). However, temperatures in the field have strong diel cycles, and a temperature increase from 25°C to 50°C has been shown to lead to 6-10 times higher emission at constant swc (Oswald et al., 2013; Mamtimin et al., 2016). On Cyprus the observed soil surface temperatures changed from 10 °C during night up to 45 °C during daytime (Fig. 8, red line, or Fig. S2). In the natural habitat the micrometeorological parameters change in concert, i.e., with increasing temperature the swc decreases, influencing the flux-enhancing effect of temperature. Based on the assumption of a linear change of swc with temperature a diel course of the swc between 6 and 14% of whc is simulated (Fig. 8, blue line), lowering the emission flux (22-49% of optimum). Applying the described swc dependence and the temperature dependence on flux rates as reported by Oswald et al. (2013), high daytime temperatures increase the simulated diel course of HONO-N flux up to daytime maximum of 7.5 ng m^{-2} s^{-1} (Fig. 8, lower panel), but with a notable dip at high noon, due to the opposing effect of decreasing swc at higher temperatures. The NO-N emissions show a similar pattern, with a slightly lower flux range (up to 6.4 ng m^{-2} s^{-1}). Converted into production rates (Eq. 7), the ground based soil and biocrust emissions at noon would be up to 1.1 x 10^6 cm^{-3} s^{-1} HONO-N and 0.9 x 10^6 cm^{-3} s^{-1} NO-N covering up to 85% and 8.5% of the missing HONO and NO source found during CYPHEX 2014 (Meusel et al., 2016)."

Specific comment:
Page 4, section 2.4 Trace gas exchange measurements: how was a sample placed into the chamber and what was the thickness the sample. The information would help readers in understanding the data presented.

Response:
The soil/biocrust samples were located in plastic petri dishes measuring 5.5 cm in diameter and about 1 cm in height. The sample to be measured was watered to full whc and the chamber was opened to place the sample in the center on the bottom of the chamber.
Besides the dimensions of the sample this was already described in the manuscript. Dimensions are now additionally described in the revised version of the manuscript.

Specific comment:
Page 7, section 3.3 NO and HONO flux measurements: Is the unit of ng m-2 s-1 based on the area that a sample (25-35 g) occupied in the field? Or is it based on the area of the sample occupied in the flow chamber? The authors need to explain how these parameters were derived from laboratory results, even if the method has been discussed in previous papers by the authors.

Response:
The samples were taken in the same petri dish that was placed into the chamber. So 25-35 g soil have a geometric surface of 23.8 cm^2 (petri dish). Fluxes were calculated for 1 m^2. Calculations are now explained in more detail in the supplement:
"Calculations of fluxes derived by dynamic chamber measurements:

$$[HONO] \cdot \frac{f}{A} \cdot \frac{p}{R \cdot T} \cdot M_N = F_{HONO-N} \qquad \text{(eq. S1)}$$

$$[NO] \cdot \frac{fr}{A} \cdot \frac{p}{R \cdot T} \cdot M_N = F_{NO-N} \qquad \text{(eq. S2)}$$

[HONO], [NO] measured mixing ratios in ppb
f = flow rate in $m^3\ s^{-1}$ (8 L min^{-1} = 1.33 x 10^{-4} $m^3\ s^{-1}$)
A = surface of sample in m^2 (0.00238 m^2)
p = pressure in Pa
R = ideal gas constant (8.31 J mol^{-1} K^{-1})
T = temperature in K (298 K)
M_N = molar weight of N (14 g mol^{-1})
F_{HONO-N}, F_{NO-N} = fluxes of HONO-N and NO-N in ng m^{-2} s^{-1} “

Specific comment:
Figure 5: Would the flux behavior be the same if the experiment is done reversely, i.e., flowing humid air over dry soil. This information may be important to understand if soil HONO emission is important HONO source in the evening and night.

Response:
We performed such an experiment and also observed HONO emission from dry soil flushed with humidified air (see Fig. R3). But we didn´t quantify HONO emissions over a wide range of humidity, yet. In near future we want to study this in more detail.

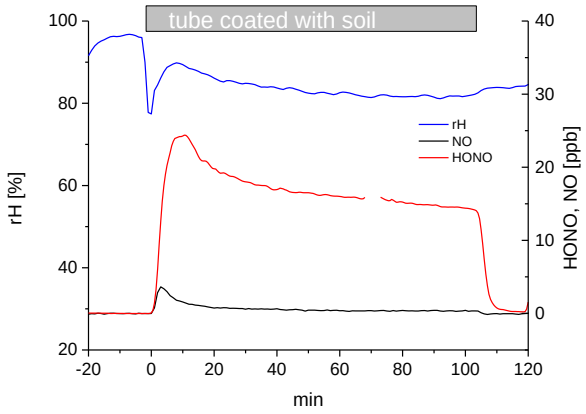

Fig. R3: HONO and NO emission from dry soil flushed with humidified air (rH ~85%). In this experiment soil from a local field around Mainz, Germany was taken, which was probably fertilized some time before sampling. The soil was coated on a glass tube (30 cm length, i.d. 0.9 cm, soil layer ~ 1 mm) according to Li et al., 2016. The gray bar indicates the time period when the coated flow tube introduced (at 0 min) and eliminated (at 105 min) from the gas exchange system.

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