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.

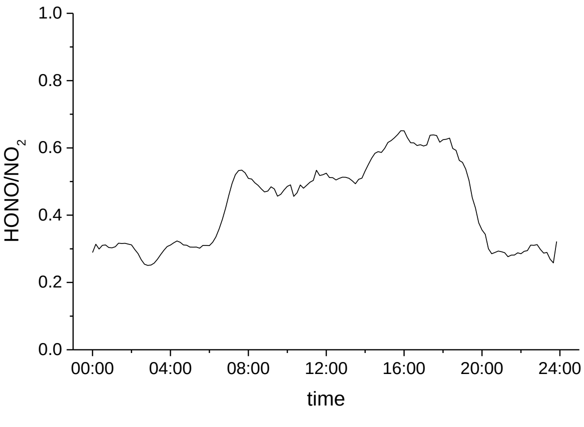

Fig R1: Mean diel course of HONO/NO2 during CYPHEX.

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 ($pH \approx 3$) 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.

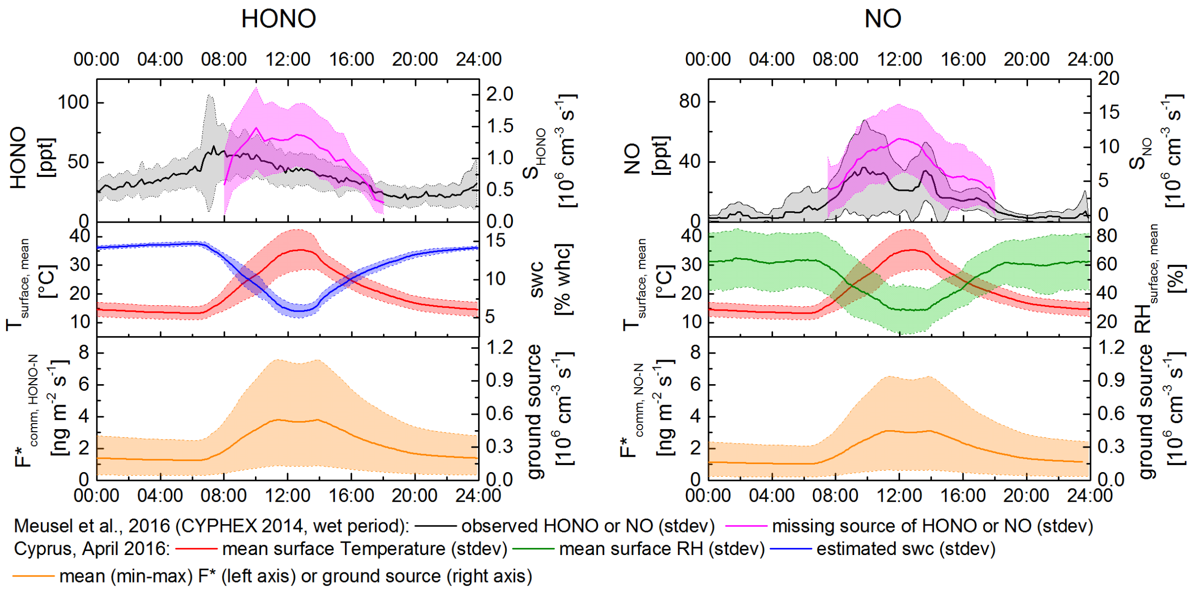

Fig. R2 (Fig. 8 in the revised manuscript): Diel pattern for HONO and NO emission in comparison with the observed HONO concentrations and missing source during the CYPHEX 2014 campaign. Upper panels: observed concentration of HONO and NO shown in black, missing source shown in pink. Middle panels: mean 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 cm² (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.

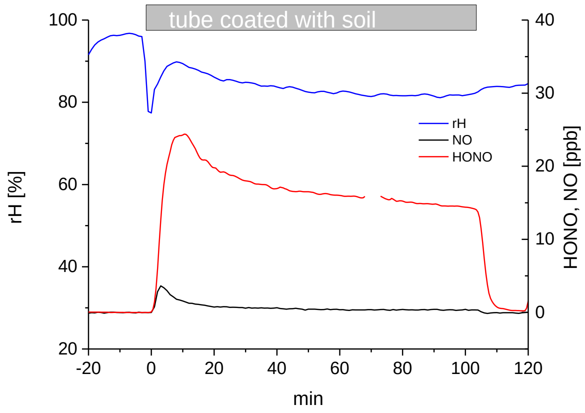

Fig. R3: HONO and NO emission from dry soil flushed with humidified air (rH ~85%). In this experiment soil from a local field around Mainz, Germany was taken, which was probably fertilized some time before sampling. The soil was coated on a glass tube (30 cm length, i.d. 0.9 cm, soil layer ~ 1 mm) according 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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Anonymous Referee #2

Overview:

The stated objective of this study is to characterize and quantify direct emissions of HONO and NO from soil samples collected from Cyprus. This is a follow-up paper to a study by the same group aimed at characterizing daytime formation of HONO during a larger field campaign (CYPHEX, summer 2014) in the same region of Cyprus. That study concluded that soil microbial source of HONO and NO may have contributed the measured mixing ratios of these gases. The present manuscript seeks to make that connection between those emissions and soil by carrying out chamber studies on soil collected at this site. The study site was characterized qualitatively using a gridded transect and visual identification to categorize nine types of ground cover (bare soil, light and dark cyanobacteria, chlorolichen, cyanolichen, moss-dominated, stone, litter, and vascular vegetation/shrub). Six of these soil coverage types were sampled and transported to lab to measure HONO and NO emissions using a dynamic chamber method. In addition, the chlorophyll and nutrient (ammonium, nitrate, and nitrite) levels of those samples were measured. Fluxes of gaseous HONO (measured via LOPAP) and NO (measured by chemluminescence) were found to be highest for bare soil, followed by light and dark biocrusts (Light and Dark BSC), which comprise a combined 2.5, 10, and 6 % of the total ground coverage, respectively. Emissions of HONO and NO were correlated to soil nitrite and nitrate levels (not ammonium or other parameters measured). Flux data along with surface coverage information was used to scale up fluxes in an attempt to estimate the contribution of biogenic soil emissions to the HONO and NO budget determined for the CYPHEX campaign. The conclusion of the paper is that biocrust emissions may close the Cyprus HONO budget.

The paper is clear, statistical methods are appropriate and the topic is of interest to the atmospheric science and biogeochemistry communities.
I have the following concerns about this manuscript regarding the study's approach, the appropriateness of the laboratory flux approach, and its conclusions.

Comment:

***Sampling methods**. Section 2.1 on sampling methods focuses on the procedure used to visually assign and quantify the surface coverage using the grid method, but lacks details on the sampling method used to collect* *samples for the laboratory chamber study. Details are limited to: "Each sample was collected in a plastic petri dish, sealed and stored in the dark at room temperature until further analysis (storage time less than 15 weeks)." What form did these samples have? What was their dimension and mass? How deep did the samples extend into the ground? Was the sample that was placed into the soil chamber a whole core or was it sieved and/or prepared in any way? The authors state that the storage time in laboratory was less than 15 weeks. Were samples around this long before the nutrient levels were measured, or were nutrient measurements made sooner. Much can happen 15 weeks, and nitrification can be taking place during storage that changes the nutrient pool and impact the lab measurements. This can contribute to significant variability of certain soil measurements.*

Response:
In order to take a sample in the field, the bottom part of a plastic petridish (diameter: 5.5 cm, height: 1 cm) was place upside down on the soil surface and pressed into the soil. A trowel was pushed below the base and together with the samples it was lifted from the ground and carefully turned around to remove surplus soil. The sample was closed with the upper lid of the perti dish, sealed with parafilm and tape and labelled. All samples were taken in dry state. If wet samples had been taken, these would have needed to be fully dried before sealing. The mass of those samples ranged between 25 and 35 g. The biocrust samples consist of a few mm of biocrust and the underlying soil (total height about 1 cm). For the chamber measurements the whole samples were used, so that the biocrust was intact/undamaged. The samples were measured in an untreated manner and only the samples for the nutrient and chlorophyll analysis were ground.
The storage (time) has a no significant impact on nutrient content and hence HONO and NO emissions, as co-authors of this study have investigated recently (see also comment to reviewer #1). Great care was taken that the biocrusts were stored in a dry state and in the dark to make sure that they are inactive.
The revised manuscript states:
Chapter 2.1: "Each sample was collected in dry state in a plastic petri dish (diameter 5.5. cm, height 1 cm), sealed and stored in the dark at room temperature until further analysis (storage time less than 15 weeks). 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)."
Chapter 2.4: "Intact soil and biocrust samples (25-35 g in a plastic petri dish with 5.5 cm diameter and about 1 cm height) were wetted with 8-13 g of pure water (18.2 MΩ) up to full water holding capacity and placed into a dynamic Teflon film chamber…Intact (biocrust) samples consist of a few mm of the biocrust and the underlying soil."
In the original manuscript (chapter 2.3) it was already stated, that the samples were ground for nutrient and chlorophyll analysis ("…the samples comprised of soil and its biocrust-cover were gently ground…", "Ground samples were extracted twice…")

Comment:
The sampling procedure and consistency/physical properties of the sample that was placed in the chambers is critical for this type of study. There has been a debate among researchers about how representative gas fluxes are for sieved or cored soil samples of environmental conditions. Previous studies suggest that such laboratory studies of soil cores give similar flux measurements as eddy covariance for grassland soils. In such soils, the surface porosity can be considered to be more similar to porosity of soil just below the surface and arguments could be made that gas exchange from soil in the field and in laboratory cores might be similar. However, biocrusts may present a particularly difficult biome to sample in this way since the intact soil and disturbed soil may have very different structural properties. The physical structure of these surfaces is defined by a network of filamentous growth and biomass that creates a hard crust that is often an impermeable layer that may impact gas exchange. These structural features are known to form hard crusts that prevent soil erosion in sensitive arid ecosystems. The soil exposed when soil is extracted as a core or sieved soil may provide a means to bypass surface structural properties that hinder gas exchange. Do the authors have any evidence to suggest that their method of sampling did not impact gas exchange from these samples? It is important to demonstrate that the results are close to reality and can be used for the type of scaled up estimation performed at the end of the manuscript.

Response:

In order to study the emissions from biocrusts, the samples must be intact as sieving would destroy the crust network/community which probably has an impact on exchange processes. To be as much representative as possible, we made sure that the whole core samples were not sieved or otherwise modified. Although the crust surface, especially with cyanobacteria, is quiet hard, it allows for exchange of nitrogen gases (please see Weber et al., 2015). Earlier studies have shown that NO emissions obtained by the dynamic chamber are consistent with flux measurements in the field (van Dijk et al., 2002; Rummel et al., 2002).

Added to the manuscript in chapter 2.4 (page 4, lines 34-35): "The dynamic chamber method…and in general showed good agreement with flux measurements in the field (van Dijk et al., 2002; Rummel et al., 2002)."

Comment:

While the physical appearance of biological soil crusts is a useful classification tool, it does not provide any information on the actual nitrification processes that occur in or below the biocrust and may be responsible for controlling soil emissions of HONO and NO. Much of the molecular biology that is important for atmosphere-land interactions is likely occurring just belowground (i.e., below the crust that is visible at the surface). It is also misleading to focus solely on the moss, lichen, actinobacteria, which are not the direct sources of these gases. Although biocrusts affect nutrient availability via N fixation, it is their possible associations with ammonia (and nitrite) oxidizing microbes (bacterial and archaea) that ultimately convert the fixed nitrogen to nitrite and nitrate. The current study does not consider the role of ammonia oxidizing microbes in association with biocrusts or the other surface types in the area. These microorganisms are not limited to living within or under biocrusts, but are present in most other soil types to differing degrees. It does make sense that such nitrifying organisms will thrive where their substrates are abundant. However, there are numerous other soil types where this may be the case. Further, there may be many other soil organisms that compete with nitrifiers for their substrates, that may reduce their abundance in soil that would seemingly favor nitrifier populations. The literature that does exist (e.g., Frontiers in Microbiology 2016, doi:10.3389/fmicb.2016.00505) on biocrust-nitrifier associations suggests that biocrusts do not necessarily host a greater abundance of ammonia oxidizing organisms compared to soil supporting trees, nitrogen fixing shrubs, etc. This is an important topic to address.

Response:

Thank you very much for that very good comment. The focus of the current study was to representatively quantify the HONO and NO emissions from the soil/biocrusts and to estimate their importance to the HONO budget by comparing these with the observed missing source. The underlying biological mechanisms were not focus of the current study and thus not discussed at greater detail.

It indeed is true that the dominating photoautotrophic compound doesn't tell us much about the microbial community below these, although, as suggested by the referee, these may have an effect on the belowground microbial community. A problem is, that different biocrust types could be distinguished in the field based on the dominating photoautotrophic compound, whereas microbial communities below the surface could not be determined by non-destructive methods. Within biocrusts, nitrification (and other nitrogen cycling processes) are expected to occur and the relevance of these processes is expected to be also substrate dependent (i.e. depending on the amount of ammonia present for nitrifiers to be used). We agree with the referee that these mechanisms are not restricted to biocrusts, but universally may also occur in non-crusted soils.

In the revised manuscript the following was added:

Chapter 1: "But much of the molecular biology/chemistry that is important for atmosphere-land interactions is likely occurring just below the crust (that is visible at the surface)."

Chapter 3.2: "The different biocrust types were distinguished in the field based on the dominating phototrophic compound but which provides no information about the microbial community below or about the magnitude of (de)nitrification processes. The microbial community couldn´t be determined by non-destructive methods."

Chapter 3.3: "Furthermore it was not possible to determine the microbial community below the biocrust or in bare soil. Although biocrusts increase nutrient availability via N fixation, it is their possible associations with ammonia oxidizing microbes (bacterial and archaea) that finally convert the fixed nitrogen to nitrite and nitrate. Nitrification and other nitrogen cycling processes are not restricted to biocrusts, but can also occur in non-crusted soils. The relevance of these processes is expected to depend on substrate richness (i.e. amount of ammonium available for nitrifiers)."

Comment:
Related to this, Figure 3 of the current manuscript demonstrates that there are other soil types throughout the landscape characterized by stones, litter, and vegetation cover that do not have associated flux values and were not included in the final conclusion regarding relative importance of biocrusts in HONO and NO emissions. The model only considered the approximately 45% of the surface types whose fluxes were characterized. It is possible that fluxes in the other soil types had as high or higher fluxes? If so, would this not make the estimate of contributions of soil emissions to overall atmospheric composition higher and possibly overshoot the Cyprus HONO budget determined in the field campaign? Indeed, Figure 8 is somewhat misleading since it must be noted that F only refers to the total HONO and NO flux associated with the 45% of surface types that were actual studied. It is very possible that the pie charts would look very different if other surfaces types were considered. So there is a large uncertainty here.*

Response:
To the best of our knowledge, there are no HONO and NO emissions from vascular vegetation, litter and stones. We also thoroughly searched the literature and did not find any publications showing emissions from these surface covers. This was also stated in the original manuscript "To the best of our knowledge, no data on reactive nitrogen emissions from vascular vegetation and plant litter have been published yet." (see original manuscript page 6, lines 14-15). Thus, we are very confident that F* (accounting for 45% of the total surface) represents the effective total emission from ground surface.

Comment:
In my opinion, a satisfying or conclusive connection between the soil emissions of NO and HONO and biocrusts has not been made. The most one can conclude from this study is that volatilization from soil bound nitrite could contribute to the NO and HONO measured in the air above the soil. Indeed, it may have been useful for the authors to include a better discussion of why they can rule out long range transport and atmospheric deposition of nitrate and NOx over time as the source of HONO and NO precursors to this soil. Even though this particular area of Cyprus may have a low population, is possible for it to accumulate anthropogenic inputs from population centers surrounding the Mediterranean basin over time? One is left wondering whether the results support the paper's title and the conclusions it suggests.

Response:
During the CYPHEX campaign (Meusel et al. 2016) very low NOx levels were detected (< 1ppb). Therefore deposition of NOx to the ground which could be converted into NO_2^-/NO_3^- and HONO was excluded as a relevant source. Also nitrate and ammonium concentrations in aerosol particles, ranging from 0.05-0.35 µg m^{-3} and 0.1-4 µg m^{-3}, respectively, (measured during CYPHEX) were too low to significantly account for HONO formation. It is not expected that the concentrations in this region are usually higher than found during CYPHEX. So deposition of reactive nitrogen species to the ground is low, and biologic processes (nitrification, denitrification) are the only reasonable explanations for HONO and NO emissions. The emissions were shown to be clearly linked to nutrient and particularly nitrite content Fig. 6), which in the current study seem to be driving HONO and NO emissions of crusted and non-crusted soils.
Please also check our response of referee #3 on [HONO]* calculations to answer the issue about simple volatilization from soil.
In the revised manuscript a short discussion was added:
"Nevertheless, a dominant contribution from microbial activity to the nutrient content is anticipated. Long range transport and atmospheric deposition of NOx and nitrate/nitrite/ammonium can be excluded to be a dominant source of HONO and NO precursors in local soil, as the observed concentrations in Cyprus ambient air were very low (Meusel et al., 2016; Kleanthous et al., 2014)."

Comment:

Lastly, Figure 2 presents a month of meteorological data (air and surface T, air and surface %RH, and precipitation) at the site for the month before samples were taken. The data features prominantly as Figure 2, yet is not used. So, it is unclear why an entire figure was devoted to this data when averages for these values during the time of sampling could have been provided in the text.

Response:

Agree, we now moved this figure to the supplement. Instead, we show a diel pattern of the mean surface temperature and RH with an estimated diel pattern for soil water content and simulated emissions (Fig. R2 or 8 in the revised manuscript; as suggested from referee #1).

Comment:

In conclusion, I feel that the strengths of this manuscript are that it is mostly well written and provides supporting evidence for the fact that soil emissions could have impacted the NOx and HONO budget during the CYPHEX 2014 field campaign. Weaknesses include: (i) there is minimal evidence from this study to support that the emissions are biological in nature (outside of the fact that the flux vs. soil moisture plot matches those of studies on pure cultures of ammonia oxidizing bacteria, Oswald et al.) and (ii) there is less evidence that the actual biocrusts are the dominant HONO and NO sources in this area since we have no data on emissions from 55% of the other surface types present in the study area. Care must be taken here to not draw too much information from these results. The approach described in this paper is not unique; its novelty is related to providing data on soil HONO and NO emissions from understudied region of the globe. Due to its limited scope, this study would have been better suited as supporting data to include in the field campaign paper by Meusel et al. 2016. It may be possible for this study to stand on its own if the above concerns are appropriately addressed in a revised manuscript.

Response:

The aim of this study was not to prove the biological role or to characterize the biological mechanisms of HONO and NO emissions, but to show that soil and biocrust-covered soil in a remote (low pollution) area are an important HONO source (not differentiating between biological or solely physical exchange processes). The residual 55% of the surface coverage which was not studied in detail are very unlikely to emit significant amounts of HONO or NO, and no single study has indicated such an emission, so that the calculated F* is considered to be representative for the whole (local) surface.

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Anonymous Referee #3

Summary:

Soil samples used in this work are from soils collected from the field, manipulated in a controlled lab environment, and then measured fluxes extrapolated to compare with the missing HONO source calculated for the CYPHEX field campaign in the same location. Soils were collected and categorized from a gridded sampling scheme. HONO and NO fluxes were measured from the soils in replicates in order to quantify which surface soil community members, if any, were responsible for the majority of the HONO fluxes observed. The authors performed nice controlled experiments in the lab and found some interesting conclusions, counter to previous findings in similar soils by this group. The manuscript may be acceptable for publication in Atmospheric Chemistry and Physics, subject to a number of concerns being addressed.

Comment:

There is no experimental control of soils devoid of microbial activity for each soil type. One would think it necessary to fumigate (or otherwise kill) soil samples of each type to control for biotic versus abiotic HONO and NO emissions, yet this is not presented. If possible, the authors should consider acquiring this data and adding it to the manuscript for comparison and correction of the dataset.

Response:

The main purpose of this study is to investigate if Cyprus soil and representative biocrust covers are indeed an important source for HONO, as was assumed from atmospheric observations in an earlier paper by Meusel et al. (2016). The role of biological activities versus physical emission was not focus of the present study, but was proven in earlier studies. As shown by Oswald et al. (2013), natural soils emit much more HONO and NO than sterilized samples, and also Weber et al. (2015) found strongly decreased emission upon sterilization, pointing to a biological emission process.

We add the following note into the introduction of the manuscript: "It was found that sterilized soil emit lower amounts of reactive nitrogen than natural soil (Oswald et al., 2013; Weber et al., 2015)."

Comment:

The consideration of the effects of the measured soil pH on HONO release using the method of the Su et al. (2011) work is not considered in the interpretation of the data. What proportion of the emissions measured in each case can be ascribed to simple partitioning? What effect does this have on comparisons between soil types considered in this work when abiotic exchange is estimated versus measured (see comment above) in the experimentally measured fluxes? A major concern is that if abiotic partitioning from dead soils is not favored by calculation from bulk pH measurements and nutrient loadings (i.e. soil pH » pKa HONO) then another emission mechanism is active and should be considered/discussed.

Response:

Following the suggestion by the referee, [HONO]* was calculated according to Su et al. (2011) for 2 different NO_2^- contents in the given range of observed NO_2^- content and their observed mean pH-value. In this calculation the absolute amount of nitrite was assumed to be constant, i.e., with lower soil water content the liquid phase nitrite concentration increases (please note that we did not find significant differences between nitrite concentrations before and after the chamber trace gas exchange experiments).

As expected, the calculated equilibrium concentration [HONO]* shows a positive dependence on nitrite concentration (compare dashed lines in Fig. R3) and pH (compare dashed red and orange lines in Fig. R3). At the optimum soil water content of 10-20 % (mass H_2O/mass soil) or 25-35% whc, respectively, the calculated [HONO]* (at pH = 7) is only about 5-10% of the one observed by chamber measurements. For slightly lower pH the calculated [HONO]* increase, and contribute about 17% to the measured.

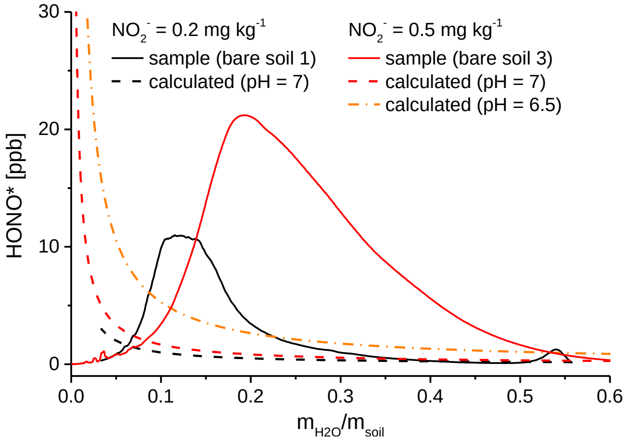


Fig. R4 (S3): Calculated [HONO]* for two different NO_2^- concentrations at pH 7 and pH 6.5 (dashed lines) in comparison with measured [HONO]* for two samples with similar NO_2^- content (solid lines) vs the gravimetric soil water content.

Indeed, as stated in Su et al. (2011) the calculated [HONO]* based on nitrite partitioning may deviate from the measured values due to the non-ideal solution behavior (adsorption, Kelvin and solute interaction effects on gas/liquid partitioning). Thus the agreement between simple models (based on ideal solution assumption) and measurements cannot be used to discriminate the physical and biological processes. We also want to clarify that the soil emission proposed by Su et al. (2011) is not an abiotic processes. Their conclusion is that biogenic nitrite in soil can be emitted to the atmosphere, of which the transport or partitioning is also subject to other physio-chemical processes like other nitrogen containing gases (e.g., NO, see fig. R4).

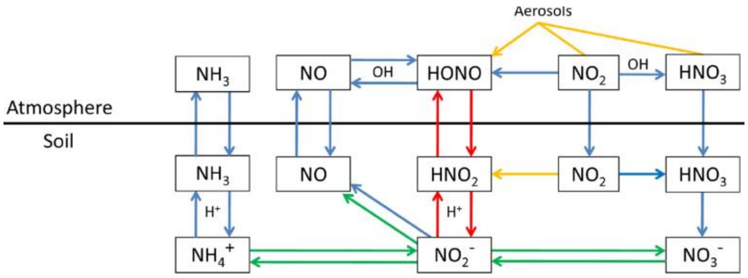


Fig. R5 (Fig 1 of Su et al., 2011): Coupling of atmospheric HONO with soil nitrite. Red arrows represent the multiphase processes linking gaseous HONO and soil nitrite (acid-base reaction and phase partitioning), green arrows represent biological processes, orange arrows represent heterogeneous chemical reactions converting NO_2 and HNO_3 into HONO, and blue arrows represent other related physicochemical processes in the N cycle.

This consideration is now also added to the revised version of the manuscript (end of chapter 3.3):
"Since most of the samples were slightly alkaline and only moss samples were slightly acidic, no effect of pH could be observed. But in general it is expected that with higher nutrient and lower pH values HONO emission is increased by simple partitioning processes (Su et al., 2011). The simulated equilibrium concentration at soil surface [HONO]* (equation see Su et al., 2011) is much lower than the measured one (see supplement Fig. S3). This deviation is probably based on the non-ideal behavior of the soil samples (adsorption, Kelvin and solute interaction effects on gas/liquid partitioning). But this method does not allow differentiation between physical or biological nitrite production processes."

Comment:

Scaling to atmospheric relevance for the field campaign is very interesting, but inappropriate to include in the title of the manuscript. The linkage between microbial activity and HONO and NO emissions is of growing importance to constrain and these lab-based measurements help to do so. However, the uncertainty in the extrapolation of the data to the field campaign observations of the missing daytime HONO source covers an order of magnitude range, which means at the low end of the estimate these processes account for < 10 % of the daytime HONO source. The authors do not discuss this limitation and should do so. The title of the manuscript should also remove the HONO budget closure implications due to this significant uncertainty. An important consideration here is one that has been reported and discussed much in the atmospheric community over the past 5 years and that is the vertical structure of HONO, and by proxy, the daytime HONO source strength near the ground surface. Using soil HONO emissions to scale to measurements made nearly 6 m above the ground may add additional error in the budget closure calculation as the perceived *missing source changes with height. This topic and the relevant references would be a worthwhile addition to this component of the discussion as there are several reports on vertical structure of HONO in arid agricultural and rural regions in the US.*

Response:

The title doesn´t really imply a HONO budget closure, it only indicates that soil emission can be a dominant source. Nevertheless, following the reviewer's suggestion, we now tuned the title reading "… represents an important source…".

Indeed, the range of HONO production given in the original manuscript had a high uncertainty, spanning an order of magnitude (based on the lowermost and uppermost fluxes observed in the lab). According to the suggestion of referee #1, we now give a more detailed best estimate, including more site-specific input variables (diel trend of temperature and soil water content). This confines the estimated source strength to $6x10^4$-$1.1x10^6$ cm^{-3} s^{-1}.

Anyhow, in agreement to the referee's objection we now better emphasize the uncertainty of the newly calculated HONO emissions in the discussion section of the revised version of the manuscript, like "… 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)…" (see also the response of referee #1).

It is true that there is a gradient in HONO concentration in the atmosphere with higher concentration near the ground. Our estimate does not include a respective chemistry-transport model (accounting for vertical gradients of atmospheric sinks and sources), nor accounts for the existence of a vertical profile of concentrations. The ground-based source was calculated for a boundary layer height of 300 m above ground level, found typical for Cyprus during the campaign 2014 (for details please see Meusel et al., 2016). The method is according to, e.g., Stemmler et al. (2006), who used homogeneous mixed air columns between 150 and 430 m for their calculations of a surface-based HONO source. A recent study calculated the height over a rural basin in Utah, USA, at which the influence of HONO surface fluxes on the total HONO column becomes negligible. At a height of 273 m the impact of the surface flux to the HONO budget was less than 1 ppt (Tsai et al., 2017).

We now discuss it in the manuscript:

"Field observations (VandenBoer et al., 2013; Zhang et al., 2009; Tsai et al. 2017) as well as model results (Wong et al., 2013) showed that HONO concentrations typically decrease exponentially from the surface upwards. Eq. 7 does not include a chemistry-transport model, nor accounts for the existence of a vertical profile of concentrations, which may bias the calculation on HONO source strength. But the method for predicting the ground source using homogeneous mixed air columns is consistent with other recent studies (Stemmler et al., 2006; Tsai et al., 2017). Tsai et al. (2017) clearly showed the presence of an important ground source of daytime HONO at a rural basin in Utah, during wintertime (no snow, low temperatures). They inferred that ground surface fluxes may account for 63±32% of the unidentified HONO daytime source throughout the day. HONO fluxes of up to 7.4 ng m^{-2} s^{-1} (Fig. 8, lower panel) determined in this study are comparable to HONO fluxes found in other regions, e.g., 2.7 ng m^{-2} s^{-1} reported for the northern Michigan forest canopy (Zhang et al., 2009; Zhou et al., 2011), the average daytime HONO flux of 7.0 ng m^{-2} s^{-1} measured over an agricultural field in Bakersfield (Ren et al., 2011), and the average HONO flux of about 11.6 ng m^{-2} s^{-1}) measured by Tsai et al. (2017). In contrast to the present study, the latter concluded that, under the prevailing high NOx conditions, the respective HONO formation was related to solar radiation and NO_2 mixing ratios, such as photo-enhanced conversion of NO_2 or nitrate photolysis on the ground. This can be ruled out in this study, as pure air (no NO_2) was used to purge the chambers and no light was applied. "

Comment:

The quality of the nutrient data cannot be determined as no accuracy, precision, or detection limit values are presented. The data table in the supplement reports measurements of zero, which should be represented by '< LOD' and the detection limits determined by the experimental runs calculated (do not use the instrument manufacturer's stated values). My concern is that some of the measurements made on the samples are near the detection limits and therefore highly uncertain, which may confound the comparisons made throughout the *manuscript. The authors should also be more cautious in their reported values from these measurements. Are these analytically certain to so many significant digits?*

Response:

Agreed, the reported data in the supplement table on nutrient levels close to 0 are now changed to "<LOD". The detection limits were checked again and were 0.012, 0.051, and 0.015 mg L^{-1} for NO_2^-, NO_3^- and NH_4^+, respectively. Transforming the unit to mg kg^{-1} results in detection limits of 0.014, 0.046 and 0.047 mg kg^{-1} for NO_2^- -N, NO_3^- - N, and NH_4^+ - N. Most of the nutrient levels are well above these levels, no concerns from your side.

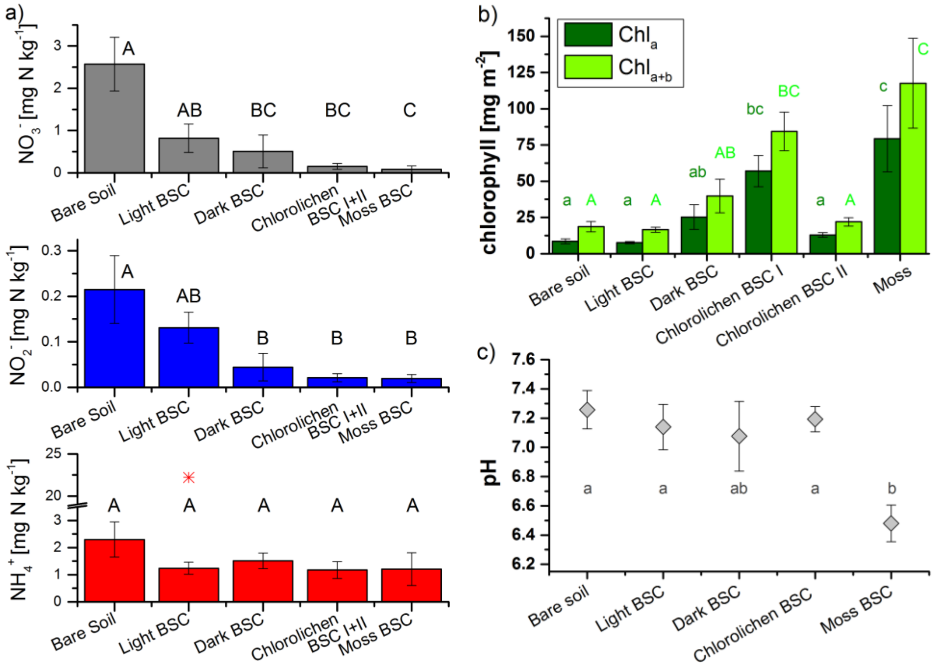
The detection limits are now added into the revised version of the manuscript: "The detection limits were 0.014, 0.046 and 0.047 mg kg-1 for NO_2^--N, NO_3^--N and NH_4^+-N."

Comment:

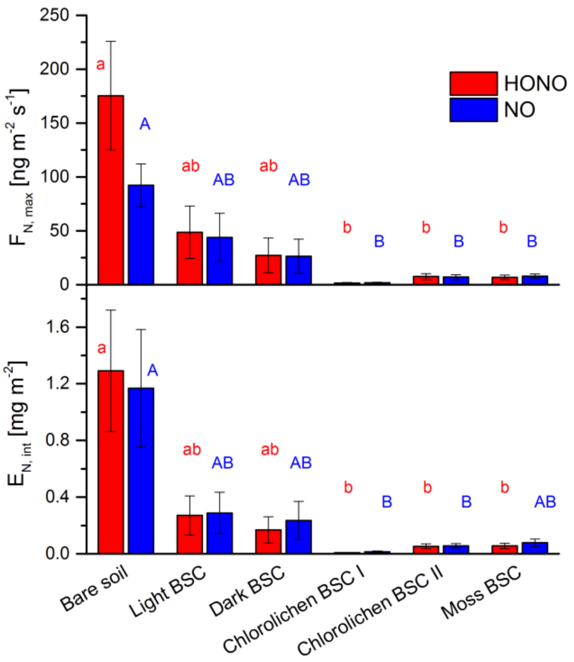
The experiments performed on nutrient content before and after experiments (Figure 4) is good to have performed, but this data does not need to be presented in the figure and would help make this a cleaner plot. The data can be replaced with one sentence in the manuscript stating that the nutrient levels were not different in the soils by performing the flux experiments. To that end, this suggests that the full set of measurements of these nutrients could be pooled and improve the statistical analyses performed, as it would reduce the standard error in the measurements. Further to this point, where replicate measurements have been made, the authors should be presenting the standard error of the mean and not the standard deviation as it aids in connecting the reader to the statistical results. The results and discussion surrounding the purpose, method selection, and outcomes of these statistical tests needs to be improved either through clarity in existing sections or expansion of the text.

Response:

Thanks for pointing out. The figures are modified accordingly. Figure 4a now shows the mean value of nutrient content of all samples and are not separated into samples without and after flux measurements. Error bars (in Fig 4a, b, c; 6) now indicate the standard error of the mean and not the standard deviation. Also in the text the standard deviation was changed to the standard error.



New Fig 4 (revised manuscript, fig.3): a: nutrient content *for all samples*, star indicate outlier in NH_4^+ content (for light BSC), for a-c error bar indicate *standard error of the mean*, letters indicate significant difference (p=0.05, of log data).



New Fig 6 (revised manuscript, fig. 5): …error bars indicate standard error of the mean…

Comment:

Details on linear regression in Figure 7 needs to be presented. There is presumably large uncertainty in both measurements being compared and the appropriate considerations must be included prior to assessing the relationship between them, along with the associated uncertainty in the result. Building on this, the direction of the trend and also its associated uncertainty from the regression fit may be more telling towards whether the strength of the coefficient is truly robust or being limited by the sample size available.

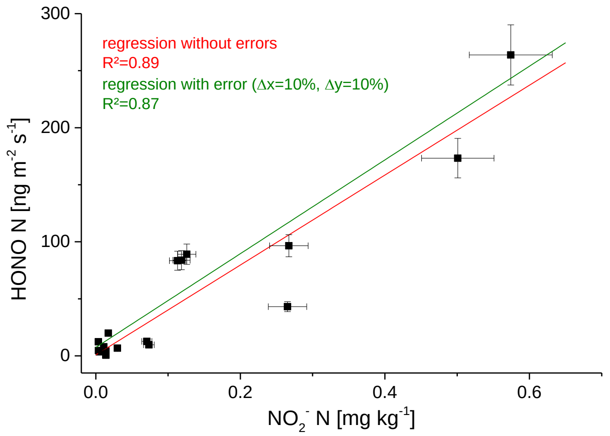
Response:

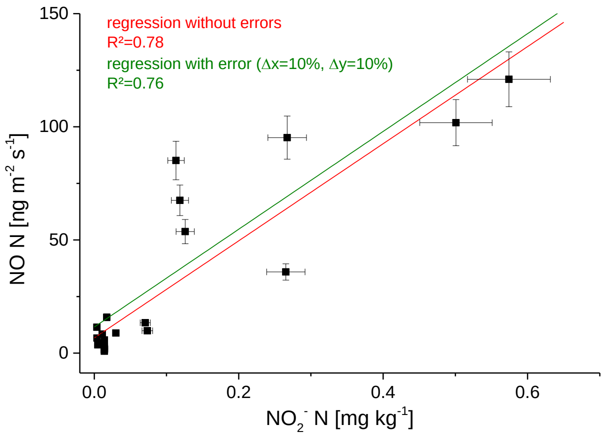
Regressions considering x-, and y- errors were performed as suggested by the referee. These were done by using the excel sheet for bivariate regressions provided by Cantrell, 2008. The errors were related to the uncertainties of the measurements (10%). In this method smaller values have smaller errors and therefore are weighted more. For nutrient levels < detection limit the value was set to the detection limit.

The coefficient of determination (R2) decreased slightly when errors are considered. But the correlation is still significant (see table below; error bars in the figures indicate the 10% uncertainty).

Table 1: Results of regressions performed by excel (Cantrell, 2008):

Nitrite – HONO (< LOD = LOD)		**Nitrite-NO** (< LOD = LOD)	
a) Errors (x , y) 10% of measured value		a) Errors (x , y) 10% of measured value	
Regression:	y = 410.9*x+7.4 (R^2 = 0.867) standard error m = 0.078, b = 6.52	Regression:	y = 216.1*x+11.5 (R^2 = 0.76) standard error m = 0.017, b = 5.04
b) Without errors		b) Without errors	
Regression:	y=394.14*x+0.804 (R^2=0.885) standard error m =30.4, b=5.5	Regression:	y=213.88.14*x+6.94 (R^2=0.776) standard error m =24.5, b=4.4





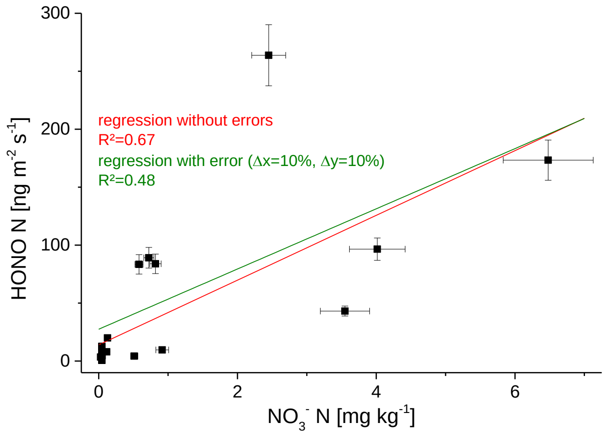
Nitrate – HONO
(< LOD = LOD)

a) Errors (x , y) 10% of measured value

Regression: $y = 25.97*x+27.46 (R^2 = 0.484)$
standard error m = 0.060, b = 11.3

b) Without errors

Regression: $y=22.68*x+10.74 (R^2=0.674)$
standard error m =3.46, b=6.19



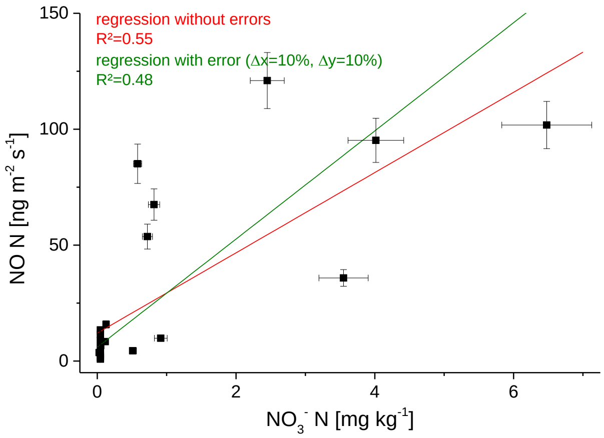
Nitrate-NO
(< LOD = LOD)

a) Errors (x , y) 10% of measured value

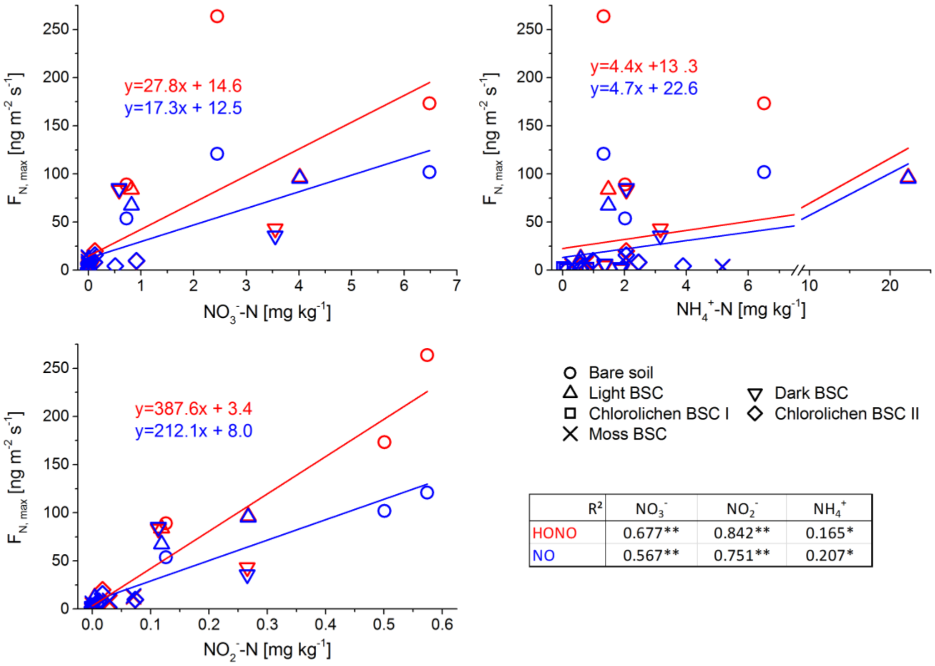
Regression: $y = 23.33*x+5.96 (R^2 = 0.475)$
standard error m = 0.074, b = 9.16

b) Without errors

Regression: $y=17.19*x+12.55 (R^2=0.547)$
standard error m =3.31, b=6.02



As the modified regressions are very similar to the original ones, we decided to keep the simple regressions, but added the regression details (lines and formula) into the plots of the revised manuscript.



R^2	NO_3^-	NO_2^-	NH_4^+
HONO	0.677**	0.842**	0.165*
NO	0.567**	0.751**	0.207*

(new Fig. 7, in the revised manuscript fig. 6)

Comment:

Figure 2 needs to be streamlined to present the relevant information for the contents of the manuscript. The level of detail here is not necessary.

Response:

Figure 2 was moved to the supplement and a diel pattern of soil or surface climate is shown now in Fig 8.

Minor Comments:

Fix tense and plurality issues throughout the manuscript.

Many sentences have issues with comma splicing, making them long and the purpose of the sentence difficult to follow.

Response:

We read through the manuscript again and carefully checked the tense and rewrote several sentences.

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Cantrell, C. A.: Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems, Atmos. Chem. Phys., 8, 5477-5487, 10.5194/acp-8-5477-2008, 2008.

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Emission of nitrous acid from soil and biological soil crusts represents an important~~dominant~~ source of HONO in the remote atmosphere in Cyprus

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Abstract. Soil and biological soil crusts can emit nitrous acid (HONO) and nitric oxide (NO). The terrestrial ground surface in arid and semi-arid regions is anticipated to play an important role in the local atmospheric HONO budget, deemed to represent one of the unaccounted HONO sources frequently observed in field studies. In this study HONO and NO emissions from a representative variety of soil and biological soil crust samples from the Mediterranean island Cyprus were investigated under controlled laboratory conditions. A wide range of fluxes was observed, ranging from 0.6 to 264 ng m^{-2} s^{-1} HONO-N at optimal soil water content (20-30% of water holding capacity, WHC). Maximum NO-N fluxes at this WHC ~~fluxes~~ were lower (0.8-121 ng m^{-2} s^{-1}). Highest emissions of both reactive nitrogen species were found from bare soil, followed by light and dark cyanobacteria-dominated biological soil crusts (biocrusts), correlating well with the sample nutrient levels (nitrite and nitrate). Extrapolations of lab-based HONO emission studies agree well with the unaccounted HONO source derived previously for the extensive CYPHEX field campaign, i.e., emissions from soil and biocrusts may essentially close the Cyprus HONO budget.

1 Introduction

Nitrous acid (HONO) plays an important role in tropospheric chemistry, as it is one of the major precursors of the hydroxyl (OH) radical which determines the oxidizing capacity of the atmosphere. In the early morning, HONO photolysis has been shown to contribute up to 30% to the local OH budget (Alicke et al., 2002; Kleffmann et al., 2005; Ren et al., 2003 and 2006; Meusel et al., 2016). Currently, the HONO formation processes, especially during daytime, are still not fully understood. Recent ground based field measurements showed unexpected high daytime concentrations of HONO, which could not be solely explained by atmospheric gas phase reactions (R1-R3) ~~only~~ (Kleffmann et al., 2003 and 2005; Su et al., 2008a; S~~oe~~örgel et al., 2011a; Su et al., 2011; Michoud et al., 2014; Czader et al., 2012; Wong et al., 2013; Tang et al., 2015; Oswald et al., 2015, Meusel et al., 2016).

$$\mathrm{OH} + \mathrm{NO} \rightarrow \mathrm{HONO} \qquad \text{(R1)}$$

$$\mathrm{HONO} \xrightarrow{\mathrm{hv}\ (300-405\ \mathrm{nm})} \mathrm{OH} + \mathrm{NO} \tag{R2}$$

$$\mathrm{HONO} + \mathrm{OH} \rightarrow \mathrm{NO_2} + \mathrm{H_2O} \tag{R3}$$

Several studies have shown that HONO can be heterogeneously formed from NO_2 on a variety of surfaces, e.g., soot, humic acid, minerals, proteins and organically coated particles (Ammann et al., 1998; Arens et al., 2001; Aubin et al., 2007; Bröske et al., 2003; Han et al., 2013; Kalberer et al., 1999; Kleffmann et al., 1999; Kleffmann and Wiesen, 2005; Lelievre et al., 2004; Kinugawa et al., 2011; Liu et al., 2015; Wang et al., 2003; Yabushita et al., 2009; Meusel et al., 2017). Light can activate some of these surfaces (humic acid, proteins and other organic compounds, titanium dioxide, soot), which enhances NO_2 uptake and HONO production (George et al., 2005; Langridge et al., 2009; Monge et al., 2010; Ndour et al., 2008; Ramazan et al., 2004; Stemmler et al., 2007; Kebede et al., 2013; Meusel et al., 2017). But NO_2 uptake coefficients and the ambient aerosol surface areas for heterogeneous reactions of NO_2 were nevertheless frequently found to be too low to account for the observed HONO production rates (Stemmler et al., 2007; Sarwar et al., 2008; Zhang et al., 2016). Besides the heterogeneous NO_2 reaction, Bejan et al. (2006) observed HONO formation during irradiation of nitrophenols. Photolysis of nitrate or nitric acid generates HONO as well (Baergen and Donaldson, 2013; Scharko et al., 2014; Zhou et al., 2003, 2011). Contrary to the detected missing HONO source near the ground, recent airborne measurements (500 – 1200 m above ground level) observed HONO concentrations, which could be explained by gas phase reactions only (Li et al., 2014; Neuman et al., 2016). However, vertical gradient studies showed higher HONO concentrations near the ground than in higher altitudes indicating a ground level source (Harrison and Kitto, 1994; Kleffmann et al., 2003; Ren et al., 2011; Stutz et al., 2002; VandenBoer et al., 2013; Villena et al., 2011; Zhou et al., 2011; Wong et al., 2012 and 2013; Vogel et al., 2003; Zhang et al., 2009; Young et al., 2012). This is supported by gas exchange studies showing that HONO and NO can be emitted from (natural) soil and biological soil crusts (biocrusts, BSC), even without applying atmospheric NO_2 (Su et al., 2011; Oswald et al., 2013; Mamtimin et al., 2016; Weber et al., 2015; Meixner and Yang, 2006). HONO and NO can be formed during biological processes (nitrification and denitrification; Pilegaard, 2013), in which NH_3 or NH_4^+ is oxidized stepwise or NO_3^- is reduced (Fig. 1). Depending on soil-pH and according to Henry´s law soil nitrite (NO_2^-) can be converted into gaseous HONO. It was found that sterilized soil emit lower amounts of reactive nitrogen than natural soil (Oswald et al., 2013; Weber et al., 2015).

Biocrusts grow within the uppermost millimeters to centimeters of soil in arid and semi-arid ecosystems. They are composed of photoautotrophic cyanobacteria, algae, lichens, and bryophytes, growing together with heterotrophic bacteria, fungi and archaea in varying proportions (Belnap et al., 2016). Depending on the dominating photoautotrophs,– cyanobacteria-dominated biocrusts with an initial thin light-colored and a well-developed dark type, cyanolichen- and chlorolichen-dominated biocrusts with lichens comprising cyanobacteria or green algae as photobionts, and bryophyte-dominated biocrusts are distinguished (Büdel et al., 2009). Many free living cyanobacteria but also those in symbiosis with fungi (forming lichens) and vascular plants can fix atmospheric nitrogen N_2 and convert it into ammonia (Cleveland et al., 1999; Belnap 2002; Herridge et al., 2008; Barger et al., 2016). Globally it ~~i~~has been estimated that 100-290 Tg (N) yr^{-1} is fixed biologically (Cleveland et al., 1999), of which 49 Tg yr^{-1} (17-49%) is fixed by cryptogamic covers, which comprise biocrusts, but also other microbially dominated biomes, like lichen and bryophyte communities occurring on soil, rocks and plants in boreal and tropical regions (Elbert et al., 2012). Studies have suggested, that nitrogen cycling in soil (N_2 fixation, nitrification, denitrification) and hence reactive nitrogen emission (NO, N_2O, HONO) is often enhanced by well-established biocrusts, especially by dark cyanobacteria (Cleveland et al., 1999; Elbert et al., 2012; Belnap, 2002; Barger et al., 2013; Johnson et al., 2005; Abed et al., 2013; Strauss et al., 2012; Weber et al., 2015). But much of the molecular biology/chemistry that is important for atmosphere-land interactions is likely occurring just below the crust (that is visible at the surface).

In Cyprus, an island in the semi-arid eastern Mediterranean area, biocrusts are ubiquitously covering ground surfaces and hence can be anticipated to play an important role in the local HONO budget. In the CYPHEX campaign 2014 (CYprus PHotochemical EXperiment) the observed diel cycles of HONO ambient air concentrations revealed strong unaccounted sources of HONO and NO, being well correlated with each other (Meusel et al., 2016). With low NO_2 concentrations and high HONO/NO_x ratios, respectively, direct emissions from combustion and heterogeneous reactions of NO_2 could be excluded as significant HONO sources, leaving emissions from soil and the respective surface cover to be the most plausible common source for both nitrogen species (Meusel et al., 2016).

In the present study we have measured HONO and NO fluxes from soil and biocrust samples from Cyprus by means of a dynamic chamber system. The aim of this study was to characterize and quantify direct trace gas emissions and demonstrate their impact on the atmospheric chemistry in the remote coastal environment of Cyprus.

2 Methods

2.1 Sampling

Bare soil and biocrust samples were collected on 27th April 2016 on the South/South-East side of the military station in Ineia, Cyprus (34.9638°N, 32.3778°E), where the CYPHEX campaign took place in 2014. It is a rural site about 600 m above sea level (asl), approximately 5-8 km from the coast and is surrounded by typical Mediterranean vegetation (olive and pine trees, small shrubs like *Pistacia lentiscus*, *Sacopoterium spinosum* and *Inula viscosa).* More details about the site can be found in Meusel et al. (2016).

In an area of about 8580 m² (South/South-East direction of the station) 50 grids (25x25 cm) were placed at randomly selected spots for systematic ground cover assessment. At each grid point occurrence of nine types of surface cover (i.e., light and dark cyanobacteria-, chlorolichen-, cyanolichen-, and moss-dominated biocrust, bare soil, stone, litter, vascular vegetation/shrub) were assigned and quantified. Spatially independent replicate samples were collected of light cyanobacteria-dominated biocrusts (light BSC), dark cyanobacteria-dominated biocrusts with cyanolichens (dark BSC), chlorolichen-dominated biocrusts (chlorolichen BSC I, chlorolichen BSC II), moss-dominated biocrusts (moss BSC) and of bare soil (Fig. S1 of the supplement). Each sample was collected in dry state in a plastic petri dish (diameter 5.5. cm, height 1 cm), sealed and stored in the dark at room temperature until further analysis (storage time less than 15 weeks). 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).

In total 43 samples were collected (Table 1) of which 18 samples, i.e., 3 replicates of each HONO emitting surface cover type were used directly (upfront) for nutrient analysis, while all others were first used for trace gas exchange measurements, prior to nutrient and chlorophyll content analysis.

2.2 Meteorological data

During CYPHEX the meteorological parameters were ~~even~~ measured at about 5 m above ground, considered not representative for the micro-habitat of the soil ground surface. Hence we placed three humidity (and temperature) sensors (HOBO Pro v2) just on top of the soil surface about 4 weeks prior to sample collection. Reference meteorological data (air temperature, humidity and precipitation) from Paphos airport (about 20 km south of the sample area, 12 m asl) and Prodromos (about 40 km east of the sampling area, 1380 m asl) during the sampling period as well as the precipitation data from the last 4 years (2013-2016) were provided by the Department of Meteorology, Cyprus (http://www.moa.gov.cy/moa/ms/ms.nsf/DMLmeteo_reports_en/MLmeteo_reports_en?opendocument; last access: Dec. 2016).

2.3 Soil characteristics: nutrient, chlorophyll and pH

Soil characteristics (nutrient, pH) have an effect on soil emission, e.g., higher nutrient level and lower pH would enhance emission according to Henry law (Su et al., 2011). Nutrient analysis was conducted on samples without gas exchange measurements (n = 3) and on replicate samples after gas exchange measurements in order to analyze potential effects of the applied 'wetting-drying' cycle. Nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+) were analyzed via flow injection analysis with photometric detection (FIAstar 5000, Foss, Denmark). Prior to that, the samples comprised of soil and its biocrust-cover were gently ground and an aliquot of 7 g was solved in 28 mL of 0.0125 M $CaCl_2$. After shaking for 1 hour the mixture was filtered on a N-free filter. The detection limits were 0.014, 0.046 and 0.047 mg kg^{-1} for NO_2^--N, NO_3^--N and NH_4^+-N, respectively.

Chlorophyll analysis, as an indicator of biomass of photo-autotrophic organisms, was done according to the dimethyl sulfoxide (DMSO) method (Ronen and Galun, 1984). Ground samples were extracted twice with $CaCO_3$ saturated DMSO (20 mL, 10 mL) at 65°C for 90 min. Both extracts were combined and centrifuged (3000 G) at 15°C for 10 min. The light absorption at 648, 665 and 700 nm was detected with a spectral photometer (Lambda 25 UV/VIS Spectrometer, Perkin Elmer, Rodgau). The amount of chlorophyll a (Chl_a) was calculated according to Arnon et al. (1974). Chlorophyll a+b (Chl_{a+b}) content was calculated according to Lange, Bilger and Pfanz (pers. comm. in Weber et al., 2013):

$$\mathrm{Chl_{a+b}}[\mu g] = \left(20.2 \cdot (E_{648} - E_{700}) + 8.02 \cdot (E_{665} - E_{700})\right) \cdot a \quad \text{(eq.1)}$$

$$\mathrm{Chl_a}[\mu g] = \left(12.19 \cdot (E_{665} - E_{700})\right) \cdot a \quad \text{(eq.2)}$$

where $Chl_{a+b}[\mu g]$, $Chl_a[\mu g]$ is the chlorophyll content of the sample, E_{648}, E_{665}, E_{700} are light absorption at the given wavelength, and a is the amount of DMSO used in mL.

The pH was determined for each surface cover type (n = 3-4) according to Weber et al. (2015, Suppl.). Here, 1.5 g of the ground sample was mixed with 3.75 mL of pure water and shaken for 15 min. Then the slurry was centrifuged (3000 G, 5 min) to separate the solid phase from the liquid solution. The latter was used for pH determination by means of a pH electrode (Inlab Export Pro-ISM, Mettler Toledo).

2.4 Trace gas exchange measurements

The dynamic chamber method for analyzing NO and HONO emissions from soil samples was already introduced before (Oswald et al., 2013; Weber et al., 2015; Wu et al., 2014) and in general showed good agreement with flux measurements in the field (van Dijk et al., 2002; Rummel et al., 2002). Intact s~~S~~oil and biocrust samples (25-35 g in a plastic petri dish with 5.5 cm diameter and about 1 cm height) were wetted with 8-13 g of pure water (18.2 MΩ) up to full water holding capacity and placed into a dynamic Teflon film chamber (≈47 L) flushed with 8 L min^{-1} dry pure air (PAG 03, Ecophysics, Switzerland). Intact (biocrust) samples consist of a few mm of the biocrust and the underlying soil. Typical drying cycles lasted between 6 and 8 hours. A Teflon coated internal fan ensured complete mixing of the chamber headspace volume. During the experiments the chamber was kept at constant temperature (25°C, the mean daytime air temperature during CYPHEX) and in darkness to avoid photochemical reactions. At the chamber outlet the emitted gases HONO, NO and water vapor were quantified. HONO was analyzed with a commercial long path absorption photometer (LOPAP, QUMA GmbH; Wuppertal, Germany), with a detection limit of ~4 ppt and 10% uncertainty (based on the uncertainties of liquid and gas flow, concentration of calibration standard and regression of calibration). To avoid any transformation of HONO in the tubing, the sampling unit including the stripping coil from LOPAP was directly connected to the chamber. NO_x ($NO + NO_2$) was detected with a commercial chemiluminescence detector (42i TL, Thermo Scientific; Watham, USA) modified with a photolytic converter with a detection limit of ~50 ppt (NO) and ~200 ppt (NO_2). An infrared CO_2 and H_2O analyzer (Li-840A, LICOR; Lincoln, USA) was used to log the drying and to calculate the soil water content (SWC) of the samples as follows:

$$SWC(WHC) = \frac{m_{H2O,t=n}}{m_{H2O,0}} * 100 \qquad \text{(eq. 3)}$$

$$m_{H2O,t=n} = m_{H2O,t=n-1} - \frac{S_{Licor,t=n}}{\sum_{t=0}^{t=N} S_{Licor}} * m_{H2O,0} \qquad \text{(eq. 4)}$$

with t=0 denoting the measurement start (wetted sample inserted into chamber), t=n: any time between 0 and N, t=N: time when sample had dried out and measurement was stopped, S_{Licor}: absolute H_2O signal at a given time, $m_{H2O,0}$: mass of water added to sample (water holding capacity, WHC), SWC: soil water content in % WHC.

2.5 Data analysis

Measured data of NO_2^-, NO_3^-, NH_4^+, Chl_{a+b}, Chl_a, NO and HONO optimum flux and NO and HONO integrated flux did not follow a normal distribution. Rather, log-transformed data were normally distributed (Shapiro-Wilk) and therefore used for statistical analysis (Pearson correlation, ANOVA including Tukey Test with significance level of $p = 0.05$) executed with OriginPro (version 9.0; OriginLab coporation, Northampton, Massachusetts, USA).

Precipitation data from the last 4 years (2013-2016), provided by the Department of Meteorology of Cyprus, indicat~~e~~ing about 30 rain events per year (precipitation > 1 mm with following one or more dry days) were used to estimate annual emissions of total nitrogen ~~by way~~in terms of HONO and NO.

3 Results and discussion

3.1 Meteorological conditions

One month before sampling, three sensors measuring temperature and relative humidity were installed directly above the soil surface ~~were installed~~ in the field to represent the micro-climate of the ground surface. Reference air temperature, humidity and precipitation measurements at Paphos airport and Prodromos showed one rain event on 11-12 April which is reflected by higher soil humidity (80-100%) and lower temperatures on these days (see Fig. S2~~2~~). As a consequence, the biological soil crusts were activated and went through one full wetting and drying cycle before sample collection. Temperature above the soil ranged from 10°C in the night to 50°C during the day when solar radiation was most intense. Air temperature was similar during the night but not as hot during the day ranging between 20° and 30°C. Humidity above the ground was low during daytime (<30% rH) and increased during the night up to 80%, while the atmospheric relative humidity (at Paphos airport) ranged between 47 and 73% (without rain event). Thus there were only little variations of humidity with height above the soil surface. Above the ground surface the relative humidity was somewhat lower during the day (mainly caused by higher temperatures) but somewhat higher during the night, compared to respective weather station data. During and shortly after the main rain event humidity at ground level was higher (80 and 100% rH) compared to ambient air humidity (70-85% rH). Ambient air temperatures were somewhat lower during sample collection of this study as compared to the CYPHEX field campaign in 2014. During CYPHEX, nighttime temperatures (3 m above ground level) did not drop below 18°C. Relative humidity (3 m above ground level) was mostly between 70 and 100% with only two short periods with humidity between 20-60% rH. Hence we can assume that soil surface temperatures were higher and ground rH in the same range during CYPHEX compared to sampling period.

3.2 Cyprus soil and biocrust characteristics

The different biocrust types were distinguished in the field based on the dominating phototrophic compound but which provides no information about the microbial community below or about the magnitude of (de)nitrification processes. The microbial community couldn´t be determined by non-destructive methods. Systematic mapping of surface covers revealed that moss-dominated biocrusts are the most frequent in the investigated Cyprus field site area (21.3%), followed by light (10.4%) and dark BSC (6.5%), whereas chlorolichen- (3.2%) and cyanolichen-dominated BSC (1.8%) only played a minor role (Fig. ~~3~~2, Fig. S1). The soil surface was partially covered by litter (26.3%), stones (19.5%) and vascular vegetation (8.5%), whereas open soil was rarely found (2.5%). It was previously established that soil and biocrusts emit HONO and NO (Weber et al., 2015; Oswald et al., 2013), jointly accounting for 45.6% of surface area in our studied region. To the best of our knowledge, no data on reactive nitrogen emissions from vascular vegetation and plant litter have been published yet.

Nutrient analysis revealed large variations in concentrations of nitrogen species ranging from 0 to 6.48, 0 to 0.57 and 0 to 22.2 mg (N) kg^{-1} of dry soil/crust mass for NO_3^-, NO_2^-, and NH_4^+, respectively (Fig. 3~~4~~a, Tab. S1 of the supplement). In general, no significant change in reactive nitrogen contents was found before and after the trace gas exchange experiments~~ (Fig. 4a)~~, indicating no significant impact of one wetting-drying cycle on the nutrient content. Bare soil samples had significantly higher levels of NO_3^- and NO_2^- content compared to dark, chlorolichen and moss BSC. Among the latter three, no significant differences in nutrient levels were observed. Light BSC had NO_2^- contents similar to bare soil. The NH_4^+ content was very similar in all samples, except for one outlier in the group of light BSC with strongly elevated NH_4^+. Higher nitrate and ammonium levels in bare soil compared to crust-covered samples were also reported recently for a warm desert site in South Africa (Weber et al., 2015), indicative of nutrient consumption/integration by the biocrusts. Nitrite, on the other hand, was lower for bare soil samples compared to biocrust samples. While NO_3^- was slightly higher, NH_4^+ and NO_2^- contents (especially of bare soil samples) were lower in the South African arid ecosystem compared to Cyprus.

Chlorophyll was only determined in the samples used for flux measurements. Chl_a ranged from 4.1 (bare soil) to 144.2 mg m^{-2} (moss BSC) and Chl_{a+b} from 9.3 (bare soil) to 211.3 mg m^{-2} (moss BSC), respectively (Fig. 43b, Tab. S1). From bare soil, via light BSC and chlorolichen BSC II, to dark BSC the chlorophyll content increased, but not significantly ($p > 0.2$). Nevertheless, Chl_a and Chl_{a+b} contents of chlorolichen BSC I and moss BSC were significantly higher than these of bare soil, light BSC and chlorolichen BSC II ($p<0.05$, Fig. 43~~b~~).. The range of chlorophyll contents is comparable to previous arid ecosystem studies (Weber et al., 2015).

The pH of soil and biocrusts ranged between slightly acidic (6.2) and slightly alkaline (7.6; Fig. 43c). The mean pH of 17 samples was 7.0, i.e., neutral. Only the pH of moss BSC samples was significantly lower than that of bare soil, light BSC and chlorolichen BSC samples ($p=0.05$). Soil and biocrust samples from South Africa were slightly more alkaline (7.1-8.2) with no significant difference among biocrust types (Weber et al., 2015).

3.3 NO and HONO flux measurements

All samples showed HONO and NO emissions during full wetting and drying cycles. The calculations of the emission or flux rates are shown in the supplement. Maximum emission rates of HONO were observed at about 17-33% WHC, and of NO at 20-36% with no significant differences between all soil cover types (Fig ~~5~~4). Emissions declined to zero at 0% WHC and to very small rates for >70%. Emission maxima strongly varied between soil cover types, but also between samples of the same cover type (see Fig. 4~~5~~ and ~~6~~5, and Table S1). Highest emissions of both HONO-N and NO-N were detected for bare soil (175 ± ~~87.3~~50.4 and 92.2 ± ~~34.7~~20.0 ng m^{-2} s^{-1}; values indicate mean ± standard error), followed by light (48.6 ± ~~48.5~~24.3 and 4~~3~~4.~~5~~0 ± ~~4~~22.~~1~~4 ng m^{-2} s^{-1}) and dark BSC (27.1 ± ~~35.9~~16.1 and ~~1~~26.~~7~~5 ± ~~18.3~~15.9 ng m^{-2} s^{-1}). Both types of chlorolichen- and moss-dominated biocrusts showed very low emission rates of reactive nitrogen (on average < 10 ng m^{-2} s^{-1}). Maximum HONO emissions were somewhat higher than maximum NO emissions, especially for bare soil. Integrating full wetting and drying cycles (6-8 hours), 0.04-1.9 mg m^{-2} HONO-N and 0.06-1.6 mg m^{-2} NO-N were released (Fig. ~~6~~5, lower panel). While the maximum fluxes of reactive nitrogen emission were higher for HONO than NO, especially from bare soil, the integrated emissions were similar or even larger for NO, which is released over a wider range of SWC.

In general, it is difficult to compare chamber flux measurements of different studies due to different experimental configurations, such as chamber dimension, flow rate, resident time and drying rate etc. Here, we compared our results to studies which applied the same method (with the same or very similar conditions). The emission rates ~~are~~were consistent with these studies where HONO-N or NO-N emissions from soil between 1-3000 ng m^{-2} s^{-1} were found (Su et al., 2011; Oswald et al., 2013; Mamtimin et al., 2016; Wu et al., 2014; Weber et al., 2015). Mamtimin et al. (2016) observed NO-N fluxes at 25°C of 57.5 ng m^{-2} s^{-1}, 18.9 ng m^{-2} s^{-1} and 4.1 ng m^{-2} s^{-1} for soil of grape and cotton fields and desert soil from an oasis in China, respectively. Oswald et al. (2013) found HONO-N and NO-N emissions between 2 and 280 ng m^{-2} s^{-1} (each) from different soil from all over the world covering a wide range of pH, nutrient content and organic matter. Biogenic NO emissions of 44 soil samples from arid and semi-arid regions were reviewed by Meixner and Yang (2006) with N-fluxes ranging from 0 to 142 ng m^{-2} s^{-1}.

In contrast to the results of the present study, where bare soil showed highest emissions, Weber et al. (2015) found lowest emission from bare soil in samples from South Africa. In that study, dark cyanobacteria-dominated biocrusts revealed highest emission rates (each HONO-N and NO-N up to 200 ng m^{-2} s^{-1}), followed by light cyanobacteria-dominated biocrusts (up to 120 ng m^{-2} s^{-1}), whereas in the present study, emissions of dark cyanobacteria-dominated biocrusts tended to be lower. No significant difference of HONO-N and NO-N emissions from light BSC between both sample origins were found. HONO-N and NO-N emissions of moss- and chlorolichen-dominated biocrusts were low in both studies (each <60 ng m^{-2} s^{-1}) but still significantly higher for samples from South Africa than from Cyprus. In the present study HONO maximum emissions were higher than for NO (while integrated emissions being comparable) while in the study of Weber et al. (2015) HONO maximum fluxes were somewhat lower than those of NO. The present results of nitrogen emissions correlated well with the nutrient contents (especially NO_2^- and NO_3^-, Fig. 6~~7~~). Bare soil, in which highest NO_3^- and NO_2^- levels were found, also showed highest HONO and NO emissions. A ~~very~~ good linear correlation was found between NO_2^- contents and emission of both nitrogen gas phase species for all samples ($R^2 = 0.84$ for HONO and 0.85 for NO; $p<0.001$). The level of correlation between NO_3^- and HONO and NO was lower, but still significant ($R^2 = 0.68$ and 0.67, respectively, $p<0.001$). ~~Only l~~Low correlations were found between HONO or NO emissions and NH_4^+-contents ($R^2 = 0.165$ and 0.232; $p=0.05$). Thus, in the present study it seems that reactive nitrogen emissions predominantly depend on NO_2^- and NO_3^- contents and not on surface cover types, although biocrusts (especially with cyanobacteria and cyanolichens) are able to fix atmospheric nitrogen (Belnap, 2002; Elbert et al., 2012; Barger et al., 2013; Patova et al., 2016). The results of a two-factorial ANOVA showed that HONO or NO emissions ~~are~~were not significantly related to soil cover type but rather with nitrite content, i.e., its direct aqueous precursor. For nitrate, the two-factorial ANOVA indicated dependencies of both cover type and nutrient content. Nevertheless, a dominant contribution from microbial activity to the nutrient content is anticipated. Long range transport and atmospheric deposition of NOx and nitrate/nitrite/ammonium can be excluded to be a dominant source of HONO and NO precursors in local soil, as the observed concentrations in Cyprus ambient air were very low (Meusel et al., 2016; Kleanthous et al., 2014). Furthermore it was not possible to determine the microbial community below the biocrust or in bare soil. Although biocrusts increase nutrient availability via N fixation, it is their possible associations with ammonia oxidizing microbes (bacterial and archaea) that finally convert the fixed nitrogen to nitrite and nitrate. Nitrification and other nitrogen cycling processes are not restricted to biocrusts, but can also occur in non-crusted soils. The relevance of these processes is expected to depend on substrate richness (i.e. amount of ammonium available for nitrifiers). ~~These~~Our results differ from those obtained by Weber et al. (2015) on South African samples, as there HONO and NO emissions were not correlated with bulk concentrations of ammonium, nitrite and nitrate. In their study nitrite content was lowest for bare soil compared to other biocrust types. Ammonium and nitrite~~s~~ levels were also lower than in the present study. Therefore Weber et al. (2015) indicated that biocrusts can enhance N-cycle and emission of reactive nitrogen.

Since most of the samples were slightly alkaline and only moss samples were slightly acidic, no effect of pH could be observed. But in general it is expected that with higher nutrient and lower pH values HONO emission is increased by simple partitioning processes (Su et al., 2011). The simulated equilibrium concentration at soil surface [HONO]* (equation see Su et al., 2011) is much lower than the measured one. This deviation is probably based on the non-ideal behavior of the soil samples (adsorption, Kelvin and solute interaction effects on gas/liquid partitioning). But this method does not allow argumentation on physical or biological processes.

3.4 Comparison of soil emission and observed missing source

To quantify the flux rate of HONO emissions from soil to the local atmosphere and to compare it to the unaccounted source found in Cyprus in 2014 (Meusel et al., 2016), we applied a standard formalism describing the atmosphere-soil exchange of trace gases as a function of the difference between the atmospheric concentration and the equilibrium concentration at the soil solution surface [HONO]* (Su et al., 2011):

$$F^{*} = \mathrm{v}_{T}\,([HONO]^{*} - [HONO]) \qquad \text{(eq.5)}$$

where [HONO] is the ambient HONO concentration measured on Cyprus (mean daytime average 60 ppt) and [HONO]* is the equilibrium concentration at soil surface. [HONO]* can be determined from measurements in a static chamber. In a dynamic chamber system, there is a concentration gradient of HONO between the headspace (where HONO was measured) and the soil surface. Here we used the measurements of water vapor to correct for the soil surface concentration and equilibrium concentration of HONO by assuming a similar gradient for the two species. A correction coefficient of 3.8 was determined, which is the ratio of the equilibrium rH of 100% over wet soil surface to the initial headspace rH of 25-30% after inserting the wet sample into the chamber. The transfer velocity, v_t, depends primarily on meteorological and soil conditions, and is typically on the order of ~1 cm s^{-1}. The flux rate of NO was calculated accordingly with mean daytime NO concentrations of 38 ppt. The calculated flux F* ~~i~~was about (67±3) % of the flux measured in the chamber.

The distribution of nine different surface cover types was mapped (Fig. 2), including stones, vascular vegetation and litter not being attributed to emit significant amounts of HONO and NO to the atmosphere. The residual HONO emitting surface covers comprised 45.6% of total surface in the investigated area. Combining the information on soil/biocrust population and the calculated flux F*, a site-specific community emission F_{comm} of HONO and NO can be estimated via following equation (eq. 6).

$$F_{comm,max} = \sum_{i}^{type} F_{max,i}^{*} * p_i/100 \qquad \text{or} \qquad F_{comm,int} = \sum_{i}^{type} F_{int,i}^{*} * p_i/100 \qquad \text{(eq. 6)}$$

where F_{comm} denotes the estimated community flux, $F_{max,i\ or\ int,i}^{*}$ the maximum or integrated emission rates of each individual surface cover type i [ng N m^{-2} s^{-1} or µg N m^{-2}] and p_i the fraction of population type i [%].

Under optimum soil water conditions (20-30% WHC) and constant temperatures of about 25°C, between 2.2 and 18.8 ng m^{-2} s^{-1} of total HONO-N and 1.6-16.2 ng m^{-2} s^{-1} of total NO-N are emitted from the different crust/soil population combinations derived from the vegetation cover assessment. In the lower range of total emissions the contribution from bare soil dominates~~d~~ with up to 69% (HONO) and 55% (NO), respectively, followed by moss BSC (HONO: 23%; NO: 32%). At high levels of total emission, the contribution from light BSC dominate~~d~~s (HONO: 43%, NO: 49%), decreasing the contribution of bare soil down to about 25% (HONO) and 13% (NO). Emissions from dark BSC contribute about 20% or 24% to the total HONO or NO flux while the contribution from moss BSC decreases~~d~~ to 10% or 12%, respectively. Emissions from chlorolichen BSC don´t~~didn´t~~ play a significant role (< 2.4%) in general (see Fig. ~~8~~7).

After heavy rainfalls moistening the soil to full water-holding capacity, 11-113 µg m^{-2} of HONO-N and 10-131 µg m^{-2} of NO-N can be calculated for one complete wetting-and-drying period. Assuming 30 rain events per year (based on the statistic of 4 years precipitation data), a wetting-drying cycle time of 7 days, and constant emissions in between them (at 10% WHC) up to 160 mg m^{-2} yr^{-1} of nitrogen can be emitted directly by the sum of HONO-N and NO-N from Cyprus natural ground surfaces, i.e., excluding heterogeneous conversion of NO_2 on ground surface.

The release of HONO from the ground surface to the atmosphere can be related to the atmospheric HONO production rate via eq. 7 (adapted from Su et al., 2011) and then compared to the missing source.

$$S_{\mathrm{ground}} = \frac{\cancel{0.35*}F*_{comm\cancel{;}\mathrm{max}(T,swc)}}{\mathrm{BLH}} * \mathrm{a} \qquad \text{(eq.7)}$$

with S_{ground}: HONO or NO emitted from ground surface; BLH: boundary layer height (mixed layer height) and a: factor to convert ng N in number of molecules (10^{-9}*6.022x10^{23}/14).

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 7.4 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). Note that during CYPHEX there were two periods with lower rH, in which even a NO sink was detected.

~~Based on the studies by Likos (2008) and Leelamanie (2010) and the meteorological conditions during CYPHEX (no rain event, but high rH, usually > 75%) a soil water content, slightly lower than the optimal water content for HONO and NO emissions, of 10% WHC was estimated, at which emissions of about 35% of the maximum was found.~~

~~In Cyprus during the summer of 2014 a mean boundary layer height of 300 m was observed by means of a ceilometer.~~. ~~The mean air temperature during the campaign was comparable to the lab based chamber studies (25°C) but soil temperatures at the Cyprus field site could largely vary during daytime and reach maximum temperatures of~~

~~up to 50°C (Fig. 4). At these high temperatures 6-10 fold higher emissions can be expected in general (Mamtimin et al., 2016), but also a quicker drying of the soil and biocrusts. At 25°C HONO emissions from the ground would equal a source strength of $1.1x10^5$-$9.8x10^5$ cm^{-3} s^{-1} and would cover up to 75% of the missing mean source of $1.3x10^6$ cm^{-3} s^{-1} (Meusel et al., 2016).~~ In some mornings of the campaign dew formation was expected causing an increase in soil humidity. Combined with rising temperatures after sun-rise these optimized meteorological conditions may have led to enhanced soil emissions and would confer a reasonable explanation for the strong HONO morning peaks observed during the campaign. ~~Similarly, the NO source strength from ground emission at 25°C is in the range from $8.3x10^4$ to $8.0x10^5$ cm^{-3} s^{-1}. As the observed unaccounted source of NO in Cyprus was of the order of 10^7 cm^{-3} s^{-1} soil emissions can only contribute up to 8% indicating other NO sources. Note that during CYPHEX there were two periods with lower rH, in which even a NO sink was detected.~~

Field observations (VandenBoer et al., 2013; Zhang et al., 2009; Tsai et al. 2017) as well as model results (Wong et al., 2013) showed that HONO concentrations typically decrease exponentially from the surface upwards. Eq. 7 does not include a chemistry-transport model, nor accounts for the existence of a vertical profile of concentrations, which may bias the calculation on HONO source strength. But the method for predicting the ground source using homogeneous mixed air columns is consistent with other recent studies (Stemmler et al., 2006; Tsai et al., 2017). Tsai et al. (2017) clearly showed the presence of an important ground source of daytime HONO at a rural basin in Utah, during wintertime (no snow, low temperatures). They inferred that ground surface fluxes may account for 63±32% of the unidentified HONO daytime source throughout the day. HONO-N fluxes of up to 7.4 ng m^{-2} s^{-1} (Fig. 8, lower panel) determined in this study are comparable to HONO-N fluxes found in other regions, e.g., 2.7 ng m^{-2} s^{-1} reported for the northern Michigan forest canopy (Zhang et al., 2009; Zhou et al., 2011), the average daytime HONO-N flux of 7.0 ng m^{-2} s^{-1} measured over an agricultural field in Bakersfield (Ren et al., 2011), and the average HONO-N flux of about 11.6 ng m^{-2} s^{-1}) measured by Tsai et al. (2017). In contrast to the present study, the latter concluded that, under the prevailing high NOx conditions, the respective HONO formation was related to solar radiation and NO_2 mixing ratios, such as photo-enhanced conversion of NO_2 or nitrate photolysis on the ground. This can be ruled out in this study, as pure air (no NO_2) was used to purge the chambers and no light was applied.

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. (2016) were higher than the optimum soil water content presented by Oswald et al. (2013).

4 Conclusions

HONO and NO emission rates from soil and biological soil crusts were derived by means of lab-based enclosure trace gas exchange measurements, and revealed quite similar ranges of reactive nitrogen source strengths. Emissions of both compounds strongly correlated with NO_2^- and NO_3^- content of the samples. Emissions from bare soil were highest, but bare soil surface spots were rarely found at the investigated CYPHEX field study site. The estimated total ground surface HONO flux in the natural habitat ~~i~~was consistent with the previously unaccounted source estimated for Cyprus, i.e., the unaccounted HONO source can essentially be explained by emissions from soil/biocrusts. For NO, the measured and simulated fluxes cannot account for the unaccounted NO source (during the humid periods of the CYPHEX campaign 2014), indicating that emission from soil was not the only missing source of NO.

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Table 1: Overview on the samples, distribution of replicates of soil/biocrust type and the different analysis:

Type	Only nutrient analysis	Flux measurements, followed by nutrient and chlorophyll analysis	Sum
Bare soil	3	3	6
Dark BSC	3	5	8
Light BSC	3	4	10
Light BSC + cyanolichen	3		
Chlorolichen BSC I	3	3	12
Chlorolichen BSC II		6	
Moss BSC	3	4	7
sum	18	25	43

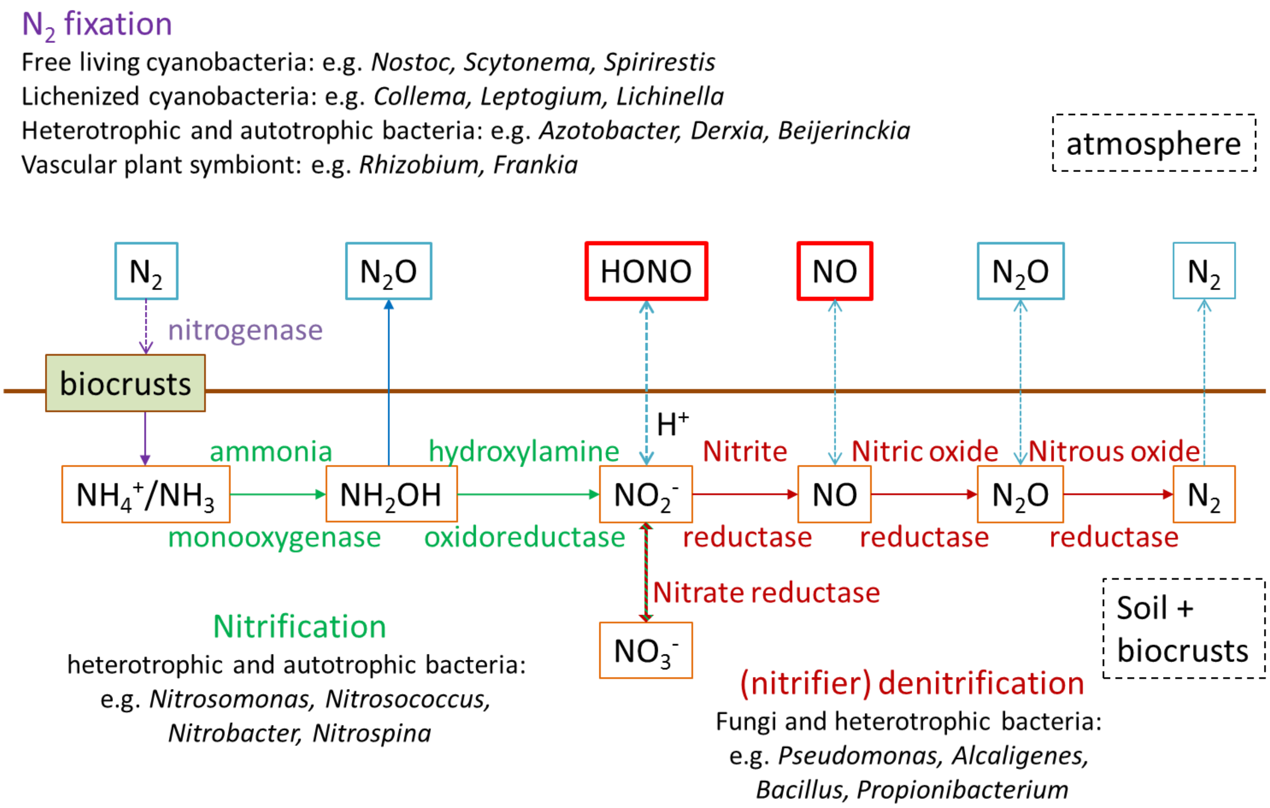
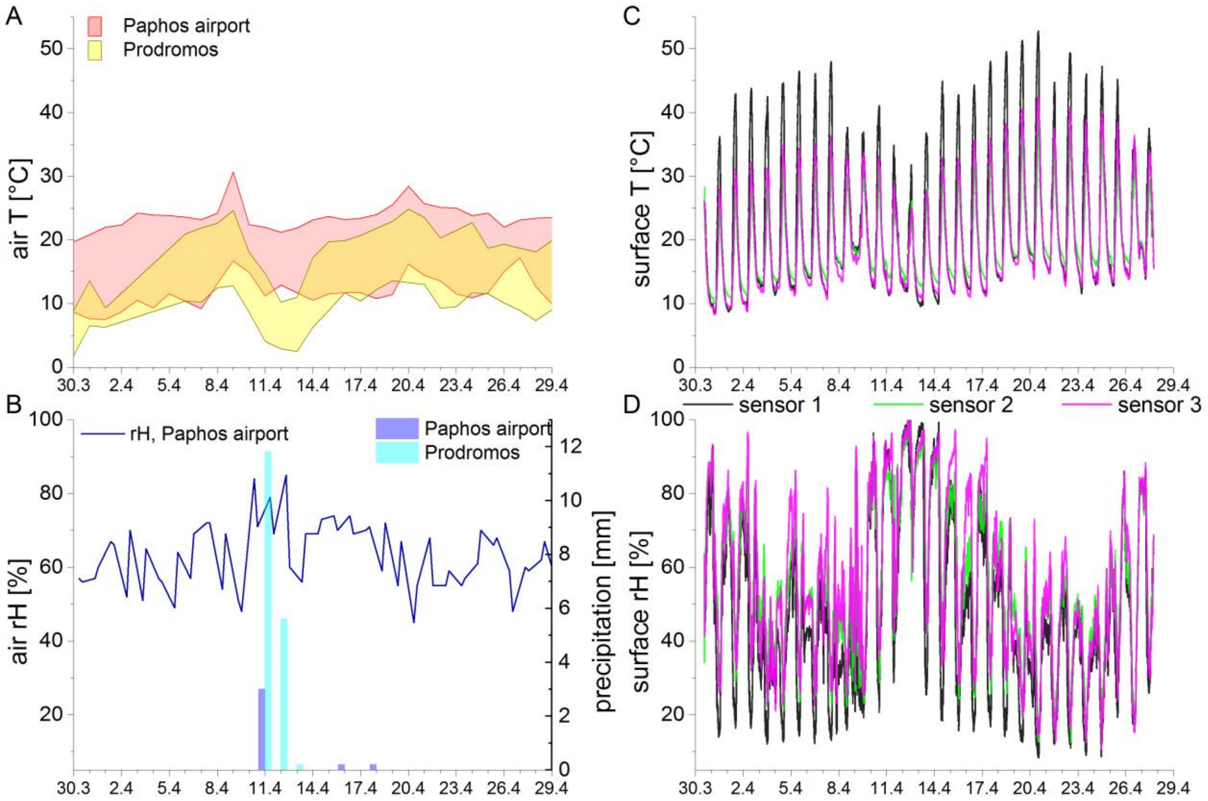


Fig. 1: Nitrogen cycle at the atmosphere and pedosphere/biosphere interface including nitrogen fixation, nitrification, denitrification and emission. Involved enzymes and organisms are specified.



~~Fig. 2: Climatic conditions of air and soil during April 2016, about one month before samples were taken. Atmospheric data was adopted from the Department of Meteorology, Cyprus. Minimum and maximum air temperatures (A) of one day at both sites are presented by red and yellow shaded areas. Air-rH data (B; dark blue line, left axis) were only available for Paphos airport, representing values at 8:00 and 13:00 local time. Precipitation data at Paphos airport and Prodromos (B; blue bars, right axis) show the daily rainfall. Surface temperature and rH are shown on the right side (C, D). The time resolution is 5 min. The variations between sensors arise from 3 different locations/surface (bare soil, next to rock, under shrubs). (http://www.moa.gov.cy/moa/ms/ms.nsf/DMLmeteo_reports_en/DMLmeteo_reports_en?OpenDocument)~~

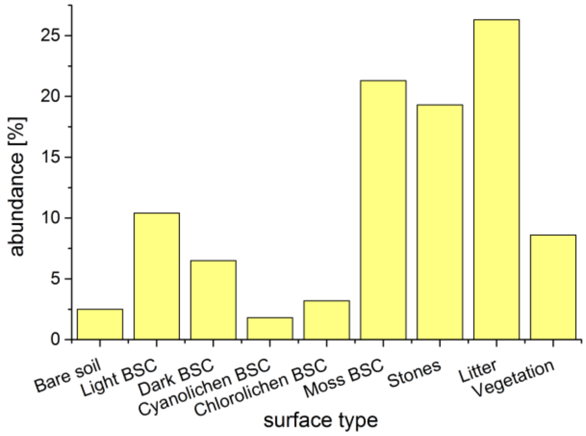
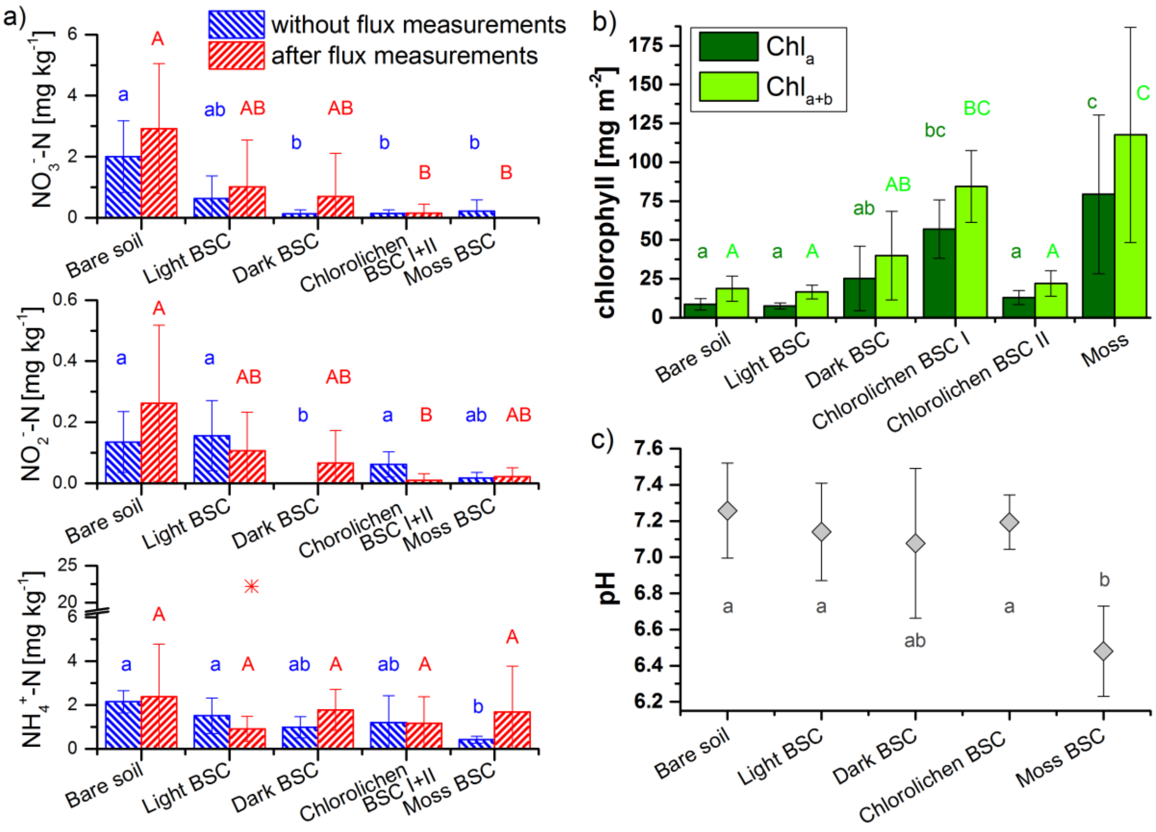


Fig. ~~3~~2: Distribution of different types of ground surfaces in the studied area. Information derived from 50 grids.


a)
without flux measurements
after flux measurements
NO$_3^-$-N [mg kg^{-1}]
0
2
4
6
A
a
ab
AB
AB
b
b
B
b
B
Bare soil
Light BSC
Dark BSC
Chlorolichen BSC I+II
Moss BSC
NO$_2^-$-N [mg kg^{-1}]
0.0
0.2
0.4
0.6
A
a
a
AB
AB
b
a
B
ab
AB
Bare soil
Light BSC
Dark BSC
Chorolichen BSC I+II
Moss BSC
NH$_4^+$-N [mg kg^{-1}]
0
2
4
6
20
25
*
A
a
a
A
ab
A
ab
A
b
A
Bare soil
Light BSC
Dark BSC
Chlorolichen BSC I+II
Moss BSC
b)
Chl$_a$
Chl$_{a+b}$
chlorophyll [mg m^{-2}]
0
25
50
75
100
125
150
175
a
A
a
A
ab
AB
bc
BC
a
A
c
C
Bare soil
Light BSC
Dark BSC
Chlorolichen BSC I
Chlorolichen BSC II
Moss
c)
pH
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
a
a
ab
a
b
Bare soil
Light BSC
Dark BSC
Chlorolichen BSC
Moss BSC

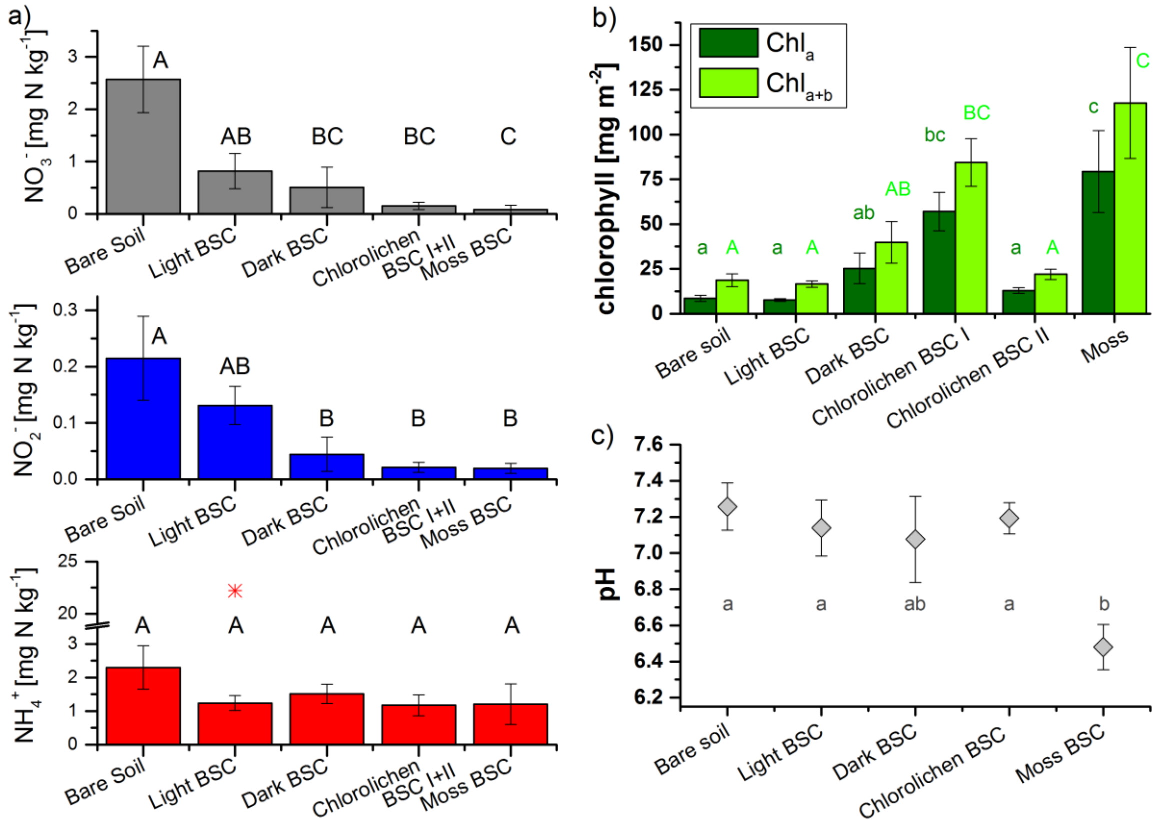

a)
NO$_3^-$ [mg N kg^{-1}]
0
1
2
3
A
AB
BC
BC
C
Bare Soil
Light BSC
Dark BSC
Chlorolichen BSC I+II
Moss BSC
NO$_2^-$ [mg N kg^{-1}]
0.0
0.1
0.2
0.3
A
AB
B
B
B
Bare Soil
Light BSC
Dark BSC
Chlorolichen BSC I+II
Moss BSC
NH$_4^+$ [mg N kg^{-1}]
0
1
2
3
20
25
*
A
A
A
A
A
Bare Soil
Light BSC
Dark BSC
Chlorolichen BSC I+II
Moss BSC
b)
Chl$_a$
Chl$_{a+b}$
chlorophyll [mg m^{-2}]
0
25
50
75
100
125
150
a
A
a
A
ab
AB
bc
BC
a
A
c
C
Bare soil
Light BSC
Dark BSC
Chlorolichen BSC I
Chlorolichen BSC II
Moss
c)
pH
6.2
6.4
6.6
6.8
7.0
7.2
7.4
7.6
a
a
ab
a
b
Bare soil
Light BSC
Dark BSC
Chlorolichen BSC
Moss BSC

Fig. 34: Nutrient- and chlorophyll contents as well as pH values of bare soil and biocrust samples of different types. a) Nitrate, nitrite and ammonium content~~s~~ of all replicates~~without and after flux measurements~~. The red star indicates an outlier, b) c~~C~~hlorophyll a and chlorophyll a+b contents of samples after flux measurements c) pH values of samples without and after flux measurements (bare soil and moss BSC: n = 4; light, dark and chlorolichen BSC: n = 3). Number of replicates for a and b see table 1. In all 3 plots error bars indicate ~~standard deviation~~ standard error of the mean and different letters indicate significant differences (of log-transformed data; p=0.05).

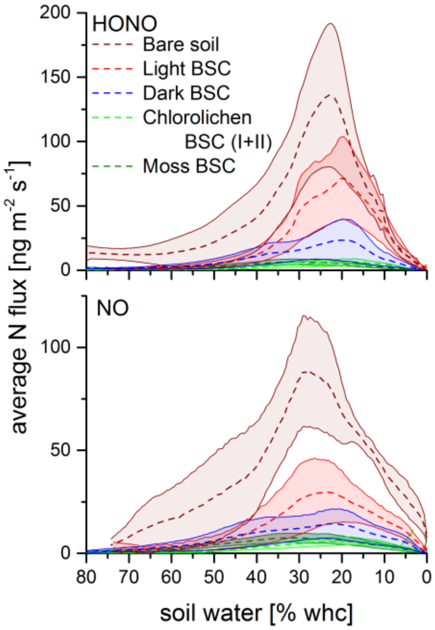
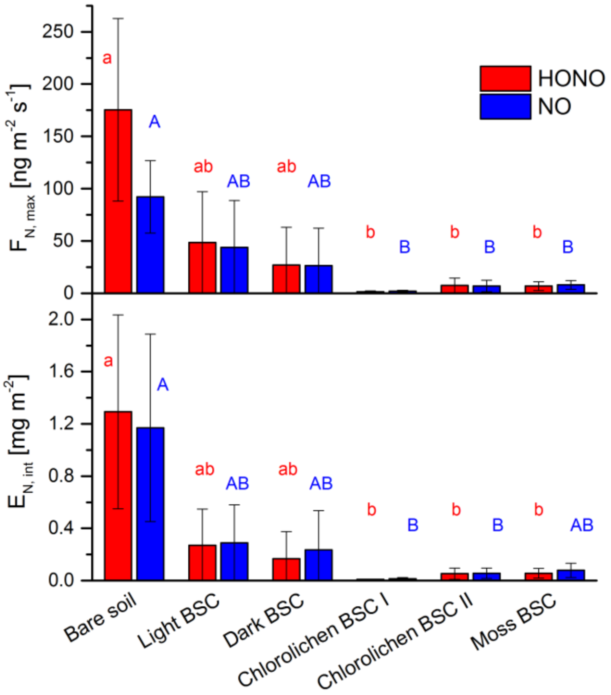


Fig. 4~~5~~: HONO and NO emission fluxes as a function of soil water content. Dotted lines are the mean fluxes. Shaded areas indicate the standard deviation.



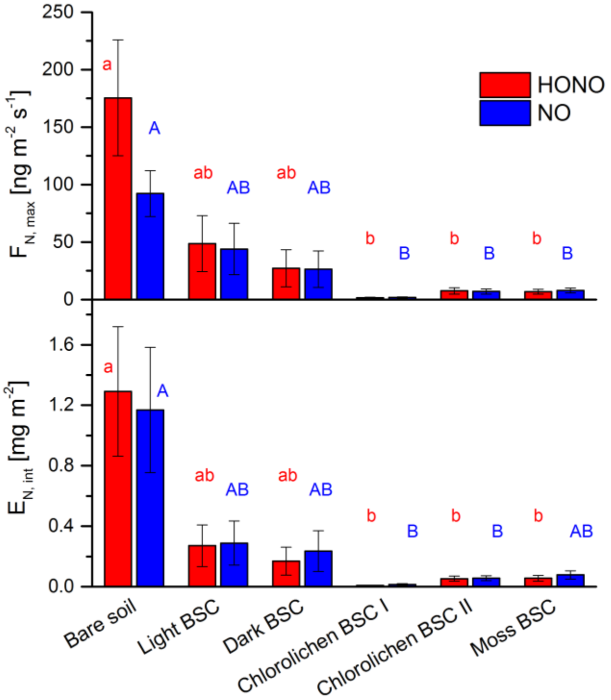
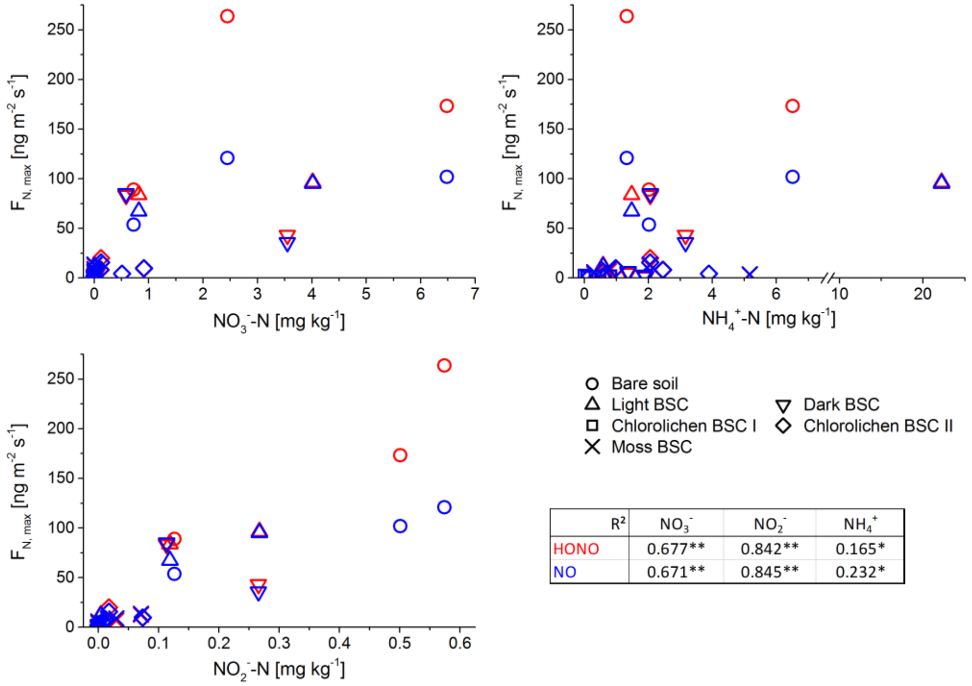
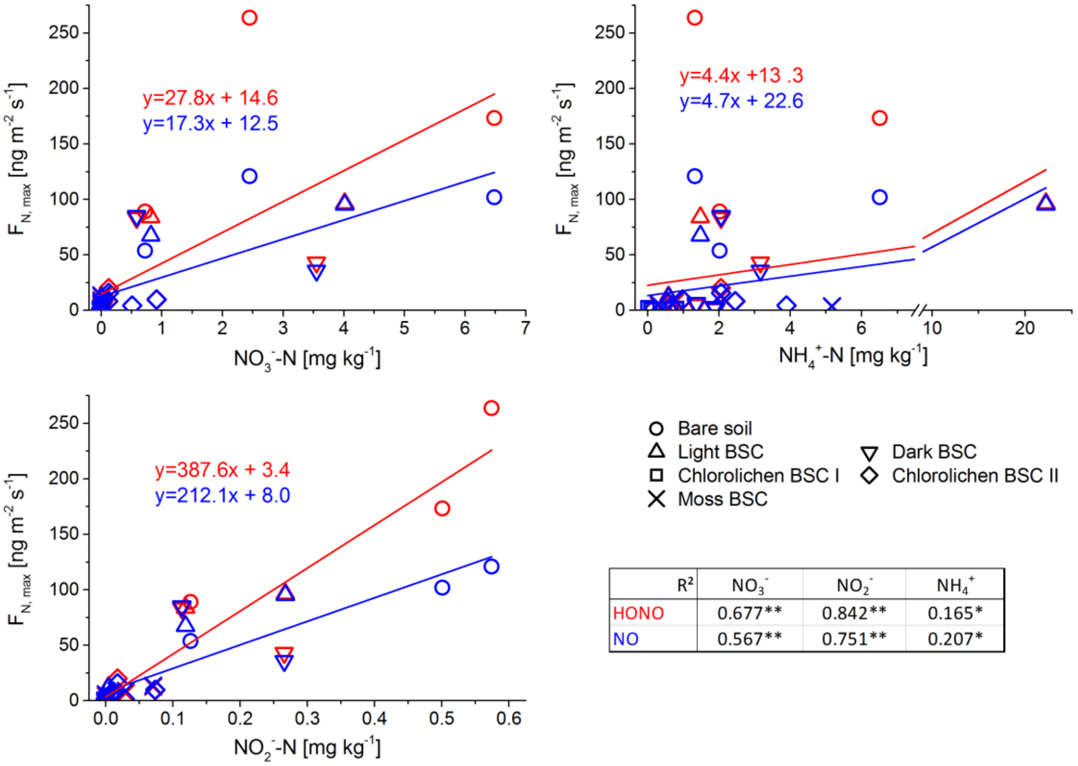


Fig. 5~~6~~: Emission of HONO and NO from bare soil and biocrusts. Upper panel: Maximum HONO-N and NO-N fluxes in ng m^{-2} s^{-1} at optimum water conditions; Lower panel: Emissions integrated over a whole wetting-and-drying cycle in mg (N) m^{-2}; letters show significant difference (p=0.05,of log-transformed data); error bars indicate standard ~~deviation~~error of the mean of replicates (bare soil n=3; light BSC n=4; dark BSC n=5; chlorolichen BSC I n=3; chlorolichen BSC II n=6; moss BSC n=4).



R²	NO_3^-	NO_2^-	NH_4^+
HONO	0.677**	0.842**	0.165*
NO	0.671**	0.845**	0.232*



R²	NO_3^-	NO_2^-	NH_4^+
HONO	0.677**	0.842**	0.165*
NO	0.567**	0.751**	0.207*

Fig. ~~6~~7: Correlation between maximum flux of HONO and NO and nutrient content of all Cyprus soil and biocrust samples with Pearson correlation factors (of log transformed data; **: $p < 0.001$; *: $p < 0.05$).

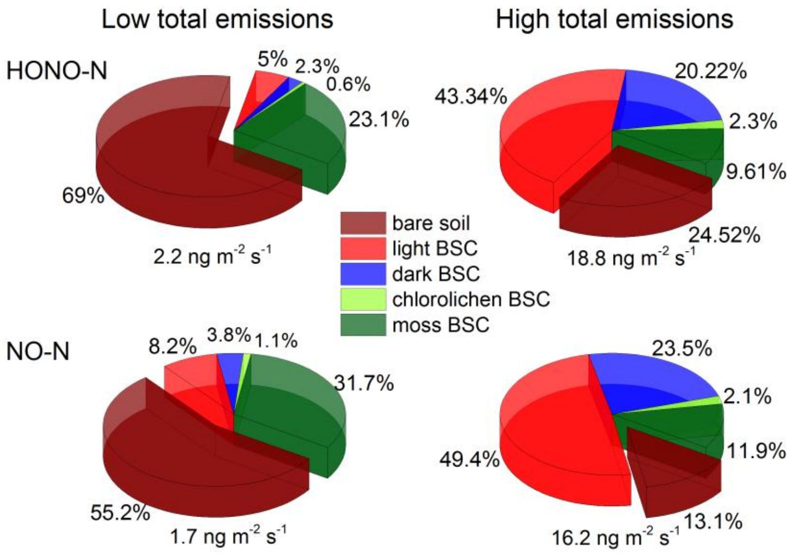


Fig. 78: Contributions of different ground surfaces to the total F*.

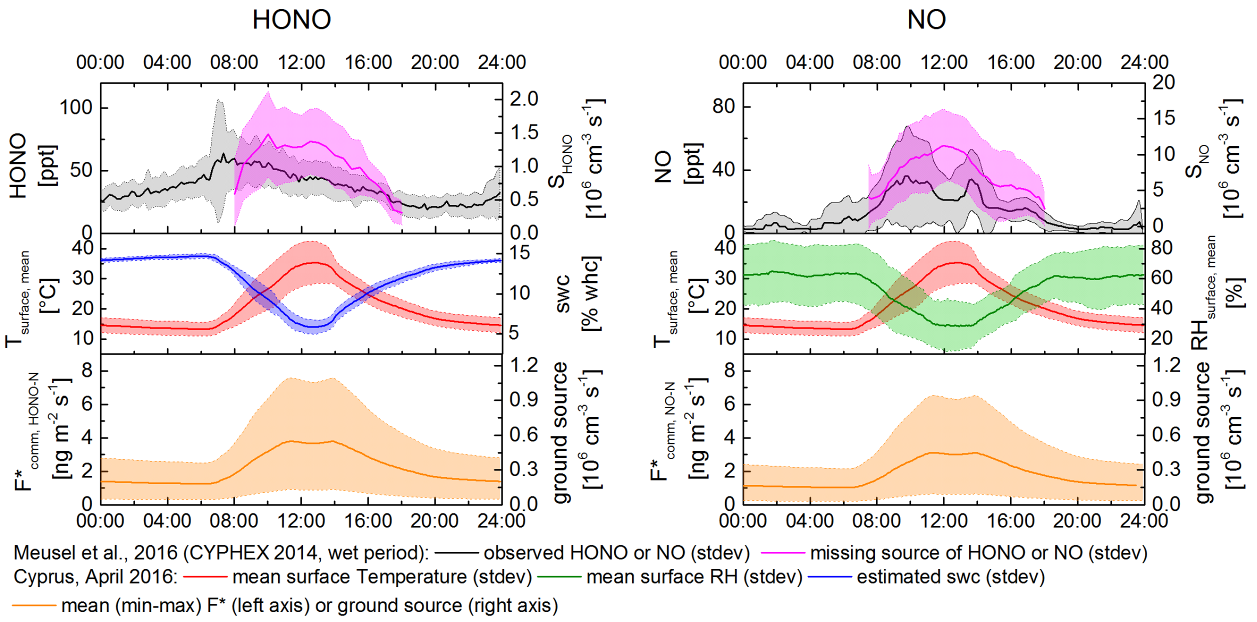


Fig. 8: Diel pattern for HONO and NO emission in comparison with the observed HONO concentrations and missing source during the CYPHEX 2014 campaign. Upper panels: observed concentration of HONO and NO shown in black, missing source shown in pink. Middle panels: mean surface temperature and mean surface 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.