

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 #2

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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 catego-

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size 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.

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

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can contribute to significant variability of certain soil measurements.

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.

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

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(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. 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 actually studied. It is very possible that the pie charts would look very different if other surface types were considered. So there is a large uncertainty here.

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

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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 NO_x 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.

Lastly, Figure 1 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 prominently 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.

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 NO_x 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.

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