Interactive comment on "Daytime formation of nitrous acid at a coastal remote site in Cyprus indicating a common ground source of atmospheric HONO and NO" by Hannah Meusel et al.

Anonymous Referee #2

General comments:

This paper uses measurements of HONO with a wide range of supporting data to assess sources of HONO in the remote coastal site in Cyprus. The findings are that there is a common source of HONO and NO and it is speculated that this is emission from microbial communities on soil surfaces. The work is important as HONO provides a route to OH radicals that is often not considered and sources of HONO in both urban and remote regions are uncertain. The authors have done a good job presenting their data and the conclusions they draw are reasonable. It undoubtedly adds to the sphere of knowledge surrounding atmospheric HONO. The paper is well presented with good clear figures and should be published in ACP subject to the authors addressing the following comments.

Response:

We thank the reviewer for the positive feedback. Please find our point-to-point responses listed below.

Specific comment:

The main conclusion of the paper is that there is a soil source of HONO and NO, which is arrived upon by looking at correlations between the 'missing' HONO source (i.e. the difference between HONO calculated using a steady state approximation including a series of known sources and the measured HONO) and a missing source of NO (based on NO deviations from the Leighton ratio). A strong correlation is given as evidence of a common source. Is this source thought to be photolytically driven? If not why are observations of NO at night seemingly zero (although it is quite difficult to see the exact levels on the plots), whereas HONO is shown to increase during the night. Maybe this is just a result of NO reacting with O_3 *before the measurement location but the authors should clarify this.*

Response:

True, the correlation analysis was based on daytime values only. For nighttime conditions, the chemistry is relatively slow and transport processes could strongly influence the budget of nitrogen-containing species, that's why we focus on the daytime chemistry.

The difference in nighttime accumulation of NO and HONO may be due to other reasons, like NO_2 heterogeneous conversion, being relevant for HONO accumulation within a shallow nocturnal boundary layer (here 0.4-1.6 %, in line with other literature, see chapter "5.1 nighttime HONO accumulation"), while there is no chemical source for NO. Also the nighttime reaction of NO + OH forming HONO would result in a preference in HONO accumulation, with nighttime OH concentration sometimes as high as 1×10^6 molecules cm^{-3} (see Fig. S3). As suggested by the referee, NO titration by the reaction with O_3 may also play a role for the absence of nighttime NO accumulation, with continuously high O_3 concentrations (60-90 ppb), while there is no major loss of HONO due to the lack of photolysis. Another option would be different temperature dependencies of NO and HONO emissions from soil (e.g., Oikawa et al., 2015; Mamtimin et al., 2016, which is now stated on page 12 line 31-35).

We modified one sentence of the "result" chapter, page 7, line 22). "In the absence of local NO sources low nighttime values are a result of the conversion of NO to NO_2 by O_3 which was continuously high (Beygi et al., 2011)"

Specific comment:

How far from the potential soil emission source in the measurement site? The authors should also comment on how this effects the validity of the steady state approximation, with reference to the Lee et al. 2013 study that gives caveats for the use of a steady state approximation to interpret HONO measurements.

Response:

Thanks to the comment. We are afraid that we may not have described our calculation properly and the using of $HONO_{PPS}$ was misleading. We actually followed the method in Su et al. (2008a) to calculate HONO missing source. With this method, we did not assume HONO to be at PSS, because the measured d[HONO]/dt has been accounted in the HONO missing source estimation and according to our measurement d[HONO]/dt was not equal to zero, which did mean that HONO was not at PPS.

$$\mathrm{S_{HONO}} = J_{HONO}[HONO] + k_2[OH][HONO] - k_1[OH][NO] - k_{het}[NO_2] + \frac{\Delta[HONO]}{\Delta t}$$

Lee et al. (2013) states that assuming HONO to be completely at PSS will likely overestimate the strength of any “unknown source”. In the Lee et al. (2013) case, the authors would come up with up to 1.1 ppb h^{-1} with the PSS approach. They argue that instead of presuming a PSS, they can explain the observed HONO from pure precursor chemistry by applying a simple chemical box model.

Lee et al. (2013) argue that the PSS assumption might not have been valid for their case study, because the transport time from nearby NO_x vehicle exhaust emission sources to the measurement site was likely less than the time required for HONO to reach PSS. Using a chemical box model, Lee et al. (2013) demonstrated that there is initially net HONO formation from assumed strong emissions (100 ppm for the sum of NO, NO_2, HONO), as high levels of NO in vehicle exhaust react with assumed entrainment of ambient OH. In the respective model daytime show-case, this HONO net production (d[HONO]/dt>0) , sustained for 2.5 min after precursor emission. Subsequently, net HONO loss dominated by photolysis led to a negative d[HONO]/dt in their calculations, which was sustained for several minutes until PSS is established after ca. 10 min (for mean daytime conditions) or up to several hours depending on time of day. This way, Lee et al. (2013) claim that “for all conditions, d[HONO]/dt is negative for a specific period of time, during which sampling vehicle exhaust can lead to overestimates of secondary HONO sources *if a photostationary state is inappropriately assumed*”, and hence “… there exists a window of time in which d[HONO]/dt is negative. Erroneously assuming the presence of PSS during this time period would lead to overestimates of secondary HONO sources.”

With respect to our analysis, first of all, we did not assume that HONO PSS is fully established at our measurement site (d[HONO]/dt was not equal to 0). However, even though for the Cyprus case, the mean upwind distance between the measurement site and the coast line is about 6 km. With a mean wind velocity of 3 m s^{-1} the respective air mass travel time over land/soil surface is about half an hour, i.e., several times the daytime lifetime of HONO. Moreover, and in strong contrast to Lee et al. (2013), at the Cyprus site the concentrations of HONO precursors were extremely low. In the Cyprus case, the observed atmospheric load of precursors (NO and OH) is by far too low to explain the observed HONO concentrations, or d[HONO]/dt, respectively (see Fig. 5). Even doubling the contribution of the chemical source (NO + OH) would not lead to a substantial reduction of the strength of the calculated un-identified HONO source.

To account for any caveats of any PSS assumptions, we now state in the text (page 10, line 14-30):

“Lee et al. (2013) argue that the HONO PSS assumption might overestimate the strength of any un-identified source, if the transport time from nearby NOx emission sources to the measurement site is less than the time required for HONO to reach PSS. In this study, the missing source was calculated according to Su et al., 2008a (eq.3), where PSS was not assumed. Also in our measurements, dHONO/dt was not equal to zero, as HONO was not at PSS.

$$S_{\mathrm{HONO}} = J_{HONO}[HONO] + k_2[OH][HONO] - k_1[OH][NO] - k_{het}[NO_2] + \frac{\Delta[HONO]}{\Delta t} \qquad \text{(Eq.3)}$$

with [HONO] being the measured HONO concentration and k_{het} the heterogeneous conversion rate of NO_2 to HONO, which was discussed above to be 1.6% h^{-1} during the wet period and 0.36% h^{-1} during the dry period. Δ[HONO]/Δt is the observed change of HONO concentration unequal to 0. The uncertainty of the calculated missing source S_{HONO} was estimated to be about 16% based on the Gaussian error propagation of instrument uncertainties of HONO, NO, NO_2, J and OH.

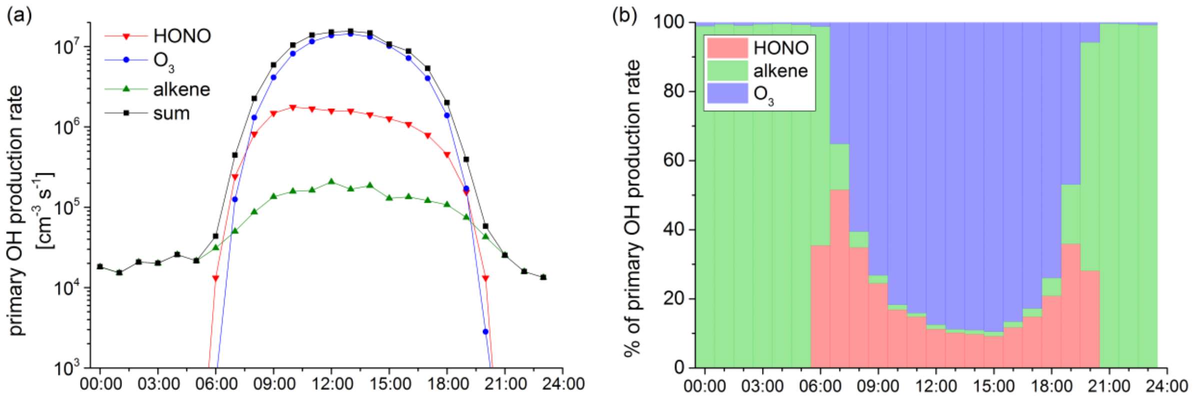
Nevertheless, at the study site of Cyprus, the mean upwind distance between the measurement site and the coast line was about 6 km, and the mean wind velocity was about 3 m s^{-1}. Accordingly, the respective air mass travel time over land is estimated to be about half an hour, which is somewhat longer than the daytime lifetime of HONO and might provide enough time for the equilibrium processes. Furthermore and in a strong contrast to Lee et al. (2013), at the Cyprus site the concentrations of HONO precursors (NO and OH) were extremely low, by far too low to explain the observed HONO concentrations.“

Specific Comment:

I find the analysis of OH production showing the importance of HONO confusing because it details production of OH from HCHO, which is indirect and requires conversion of the HO_2 produced with NO to form OH. I believe it would be better to just include HO_2 + NO as an OH source, regardless of where the HO_2 is coming from. Another option would be to have a total HOx radical budget analysis.

Response:

We thank the referee for disclosing this critical detail. OH budget analysis including photolysis of HCHO was done before e.g. by Alicke et al., 2002 but then also RO_2 primary production should be considered as it will also be converted in OH through cycling processes. HONO photolysis, ozonolysis of alkenes and photolysis of O_3 and subsequent reaction with water contribute to the primary OH production. HCHO photolysis firstly forms HO_2 which is in fast equilibrium with OH e.g. via the reaction of HO_2 and NO. Therefore it contributes to secondary OH production. In this study we focus on the evaluation of HONO sources and wanted to give a brief outlook on its importance on OH. To realize this we just show the primary OH production routes (and deleted the OH production via HCHO photolysis). Furthermore we changed the term “OH production” into “primary OH production”.
As written below, a complete detailed HOx budget analysis will be published from colleagues soon.



Revised fig. 9: Average diel pattern of primary OH production from HONO, O_3 and VOC, shown as a) production rate and b) percentage contributions to primary OH production.

Specific Comment:

The authors should also comment on the fact that the HONO source here is only important near to the surface (an estimate could be made of the vertical structure of HONO) and thus it is not relevant for the entire troposphere. This is important when considering HONO as an atmospheric 'oxidant'.

Response:

Indeed, many studies have shown decreasing HONO mixing ratios with altitude in the lowest few hundred meters of the troposphere (Vogel et al., 2003; Zhang et al., 2009; Young et al., 2012; Wong et al., 2012 and 2013; VandenBoer et al., 2013). According to the modelling results of Wong et al. 2013, we estimate that the ground HONO source could be important for up to 200–300 m a.g.l. According to the referee's suggestion we now state in the introduction (Page 3, line 9-13):

"Many studies have shown decreasing HONO mixing ratios with altitude in the lowest few hundred meters of the troposphere, due to respective short atmospheric lifetime compared to vertical transport time (Wong et al., 2012 and 2013; Vogel et al., 2003; VandenBoer et al., 2013; Zhang et al., 2009; Young et al., 2012;). According to the modelling results of Wong et al. 2013, we estimate that the ground HONO source could be important for up to 200–300 m a.g.l. This indicates that HONO is more relevant for the OH budget close to the surface than in high altitude air masses."

Comment:

The authors mention in the experimental description that OH was measured during the field campaign but there is then no further mention of it in the manuscript. Have the authors (or anyone else) examined the OH data to assess if the measured HONO is required to close the HOx budget? I realise this may be the subject of further publications but if it is stated that HOx was measured it seems odd that no mention is made of the results.

Response:

We thank the referee for this suggestion. In this study, we focused on HONO and its missing daytime source. OH data were used to calculate the HONO budget and HO_2 data were used to study the NO budget. The potential contribution of HONO photolysis to OH production is studied in a short chapter showing different OH production routes. A "total HO_x radical budget analysis" is not focus of this manuscript. A future CYPHEX paper of colleagues will deal with the HO_x budget closure study, including a detailed box modelling approach for the total HO_x budget and OH recycling. The manuscript will be submitted soon.

Comment:

The manuscript is generally well referenced however a recent study by Lee et al. 2016 in London contains a lot of detail about potential HONO sources in an urban area and should be referenced. There is also a recent study by Mamtimin et al. (2016) which discusses biogenic NO and HONO emissions that seems to be extremely relevant to this work. The authors should comment on how their results compare to this.

Response:

We greatly appreciate these reference suggestions. Both fit well into this study.

Mamtimin et al., 2016 is now cited in the introduction (page 3, line3), and twice in “common daytime source of HONO and NO” (page 12, line 28 and line 31-35) when comparing with other studies on HONO and NO emission.

“Mamtimin et al. (2016) investigated HONO and NO emissions of natural desert soil and with grapes or cotton cultivated soils in an oasis in the Taklamakan desert in the Xinjiang region in China. After irrigation they didn´t find direct emission, but when the soil had almost dried out (gravimetric soil water content 0.01-0.3) emissions up to 115 ng N m^{-2} s^{-1} were detected. In addition they observed soil-temperature dependent emission of reactive nitrogen.

Lee et al. (2016) is now cited once in the introduction (page 3, line 17) and in “daytime HONO budget” (page 11, line 15-16), discussing possible light induced HONO formation and comparing correlation factors:

“Lee et al. (2016) found even lower correlation with $[NO_2]$ ($R^2 = 0.0001$) but similar good correlation with $J_{NO2}*[NO_2]$ ($R^2=0.70$) at an urban background site in London.”

Minor comments:

The authors should make sure they clarify what the error bars on plots and in the text actually refer to (e.g. figures 4 and 7)

Correct. As also suggested by Referee #1, we now clarify what the error bars on plots and in the text actually refer to. Error bars in Fig. 4 and 7 (and ± values) indicate standard deviation (1 sigma).

P. 12 line 11: Use O_3 rather than ozone as has been done in the rest of the manuscript

Thanks for noticing. Is now changed accordingly in the text.

P. 7 line 7: there is a discrepancy between the detection limit stated here (2pptv) and that in the experimental section (5pptv) – please confirm.

Thanks for indicating. As also suggested by referee #1, a detection limit of 5 pptv is now stated in the revised versions of the manuscript.

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